

## Calculation of the Optical Transitions for PbS, PbSe, PbTe, SnTe and GeTe Using a 3-Parameter Model Potential\*

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The energy levels of the semiconductors PbS, PbSe, PbTe, SnTe, and GeTe are calculated by an empirical pseudo-potential method at the points of highest symmetry of the Brillouin zone. A 3-parameter effective-potential model employing "square wells" around the atoms and repulsive delta functions at the sites of the nuclei is used in the calculation. The pseudo-wave-functions are expanded in a series of symmetrized plane waves. The potential parameters are fitted to obtain energy differences which are equivalent to the experimentally obtained optical transitions of the five semiconductors. The purpose of the present work is to show the effectiveness of a new method for parametrizing the pseudo-potential which is analogous to the Kronig-Penney model.

Os níveis de energia dos semicondutores PbS, PbSe, PbTe, SnTe e GeTe são calculados, nos pontos de maior simetria da zona de Brillouin, pelo método do pseudo-potencial empírico. É usado no cálculo um modelo de potencial efetivo a três parâmetros com "poços quadrados" em **tórno** dos átomos e funções delta repulsivas nas posições dos núcleos. As pseudo-funções de onda são expandidas em série de ondas planas **simetrizadas**. Os parâmetros do potencial são ajustados de modo a se obter diferenças de energia que são equivalentes as transições ópticas, obtidas experimentalmente, dos cinco semicondutores. O objetivo do presente trabalho é mostrar a eficácia de um **nôvo** método de parametrização do pseudo-potencial que é análogo ao modelo de Kronig-Penney.

### 1. Introduction

The Kronig-Penney potential was the first used in energy-band calculations because of its simplicity<sup>1</sup>. Improved results were obtained later by the pseudo-potential method<sup>2</sup>, which leads to Phillips cancel-

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lation theorem<sup>3</sup>. A disadvantage of the latter method, however, is the necessity of constructing the effective potential by fitting three to five coefficients of its Fourier transform to the experimental data available. This procedure results in a loss of the physical picture of the crystal potential. A method that uses a modified Kronig-Penney model to construct the effective potential is here described. The essential idea, suggested by an analysis of Phillips' cancellation theorem, is the addition of a repulsive Dirac delta function to each "square-well" for each type of atom in the crystal. This effective potential has been used<sup>4</sup> for a number of semiconductors and showed that the abrupt changes due to the "square-wells" makes the convergence of the secular equation rather slower for empty lattices, such as those of *ZnS* type.

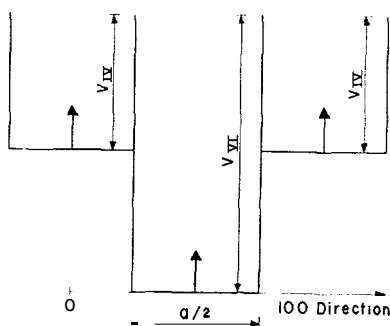


Fig. 1 - Potential wells with Dirac delta in the [100] direction

The IV-VI compounds *PbS*, *PbSe*, *PbTe*, *SnTe*, *GeTe* are semiconductors which have the *NaCl* structure. The fundamental gap occurs at the L point of the Brillouin zone or close to it. From experimental and theoretical results<sup>5,6,7</sup> we can assert that these semiconductors show similar properties. For example, the optical transitions are related to the lattice parameters in a simple manner. Therefore, these semiconductors can be assumed to have similar band structures. The purpose of the present work is to obtain the optical transitions for these five semiconductors with the empirical pseudo-potential method applied to the  $\Gamma$ , L and X points of the Brillouin zone. An expansion of the pseudo-wave function in symmetrized plane waves and a 3-parameter effective potential are used. The latter is obtained by surrounding each atom with a constant-potential sphere and considering a Dirac delta pulse of repulsive potential at the center of each sphere.

The effective potential model is defined and the matrix of the effective Hamiltonian for the points of highest symmetry of the Brillouin zone is

calculated in Section 2, using symmetrized plane waves. In Section 3 we explain the calculation procedure for the energy levels and the method used in the search for effective potential parameters able to reproduce the optical transitions of each compound.

## 2. The Effective Potential

The pseudo-potential method permits us to write the Schrodinger equation for an electron in a crystal

$$[-\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1)$$

as

$$[-\nabla^2 + V_{ef}(\mathbf{r})]\phi(\mathbf{r}) = E\phi(\mathbf{r}). \quad (2)$$

Thus, the energy levels can be determined using smooth pseudo-functions  $\phi(\mathbf{r})$ . These can be expanded in a series of symmetrized plane waves, after factoring the secular equation.

We define

$$\mathbf{k}_m = \mathbf{k} + \mathbf{K}_m, \quad (3)$$

where  $\mathbf{k}$  refers to the Brillouin zone or to its boundaries and  $\mathbf{K}_m$  is a reciprocal-lattice vector.

The pseudo-function  $\phi_{ij,\mathbf{k}}^z(\mathbf{r})$  can be written as

$$\phi_{ij,\mathbf{k}}^z(\mathbf{r}) = \sum_m c_{im} |\mathbf{k}_m, j\rangle, \quad (4)$$

where the normalized symmetrized plane waves are given by

$$|\mathbf{k}_m, \mathbf{j}\rangle = a^{-3/2} (C_{\mathbf{k}_m, j}^z)^{1/2} (d/h) \sum_{\lambda} \Gamma_{\alpha}(R_{\lambda})_{ij}^* R_{\lambda} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (5)$$

$a$  is the lattice parameter,  $C_{\mathbf{k}_m, j}^z$  is a normalization constant,  $d$  is the dimension of the irreducible representation  $\Gamma_{\alpha}$  of the group of the vector  $\mathbf{k}$ ,  $h$  is its dimension and  $\Gamma_{\alpha}(R_{\lambda})_{ij}^*$  is the complex conjugate of the  $(ij)$  element of the matrix for the  $R_{\lambda}$  operation of the group.

## 2.1. Criterion for Choosing the Orthogonal Symmetrized Plane Waves

Let us consider

$$I_{ij} = (d/h) \Gamma_{\alpha}(R_{\lambda})_{ij}^* \int_{cell} \exp [i(R_{\lambda} \mathbf{k}_m - \mathbf{k}) \cdot \mathbf{r}] d\mathbf{r} \quad (6)$$

which is proportional to the matrix element  $\langle \mathbf{k}_m, i | \mathbf{k}_n, j \rangle$ . Let

$$\mathbf{R} = \mathbf{A}\mathbf{X}, \quad (7)$$

where  $\mathbf{X}$  belongs to the  $\{\mathbf{X}\}$  sub-group for which  $\mathbf{X}\mathbf{k} = \mathbf{k}$ , and  $\mathbf{A}\mathbf{k} = \mathbf{k}$ . Then

$$I_{ij} = (d/h) \sum_{\mathbf{X}} \Gamma_{\alpha}(\mathbf{X})_{ij}^*. \quad (8)$$

If  $\mathbf{k}_m$  gives rise to  $l$  four-vectors ( $1 < l < \mathbf{d}$ ), we can choose for the  $O_h$  group and its sub-groups the four-vectors in such a way that

$$I_{ij} \propto \delta_{ij}. \quad (9)$$

In the case  $l = \mathbf{d}$  it is easy to show that the four-vectors are orthogonal, so that we can write

$$\langle \mathbf{k}_m, i | \mathbf{k}_n, j \rangle = \delta(|\mathbf{k}_m, i\rangle, |\mathbf{k}_n, j\rangle), \quad (10)$$

a fact which simplifies the calculations.

## 2.2. The 3-Parameter Effective Potential

We define an effective potential for the IV-VI semiconductors by considering "square-wells" surrounding the atoms inside spheres  $E$  which just touch one another, plus a positive potential pulse at each nucleus (see Figure 1). Since these semiconductors have a  $NaCl$  structure, and assuming atom IV to be at the origin, then

$$\text{in atom IV: } V(\mathbf{r}) = V_{IV} + v_{IV} a^3 \delta(\mathbf{r}), \quad r \leq a/4, \quad (11a)$$

$$\text{in atom VI: } V(\mathbf{r}) = V_{VI} + v_{VI} a^3 \delta[\mathbf{r} - (a/2)(\mathbf{i} + \mathbf{j} + \mathbf{k})], \quad a/4 \leq r \leq a/2, \quad (11b)$$

$$\text{and } V(r) = 0, \text{ in the rest of the cell.} \quad (11c)$$

To reduce these four parameters to three, we define the dimensionless average radius as

$$\bar{\rho} = \bar{r}/a = (1/a) \frac{\int_{\epsilon} r V(\mathbf{r}) d\mathbf{r}}{\int_{\epsilon} V(\mathbf{r}) d\mathbf{r}} \quad (12)$$

and impose the condition of equal average radii on the two atoms in the cell:

$$\bar{\rho}_{IV} = \bar{\rho}_{VI}. \quad (13)$$

For convenience, we introduce

$$V_0 = (V_{IV} + V_{VI})/2, \quad (14)$$

$$b = (V_{IV} - V_{VI})/2V_0, \quad (15)$$

the parameters being now  $V_0$ ,  $b$ ,  $\bar{\rho}$ .  $V_0$  is the "intensity" of the effective potential given in Rydbergs and  $b$  is the "ionicity" of the crystal and is dimensionless.

If atom IV is at the origin, atom VI is at position  $\mathbf{r}$ ,  $= (a/2)(\mathbf{i} + \mathbf{j} + \mathbf{k})$ . We can write the matrix element of the effective Hamiltonian between four-vectors  $\mathbf{r}$  and  $\mathbf{s}$  as

$$\begin{aligned} H_{rs} = & k_n^2 \delta(|\mathbf{k}_n, i\rangle, |\mathbf{k}_m, j\rangle) + (C_{\mathbf{k}_n, i}^* \cdot C_{\mathbf{k}_m, j})^{1/2} (d/h) V_0 \times \\ & \times \sum_{\lambda} \Gamma_{\alpha}(R_{\lambda})_{ij}^* \{ [1 + \exp(i\mathbf{Q} \cdot \mathbf{r}_0)] - b [1 - \exp(i\mathbf{Q} \cdot \mathbf{r}_0)] \} \times \\ & \times \{ (\pi/3 \times 4^4)(3/\bar{\rho} - 16) + (\pi/16)j_1(Qa/4)/(Qa/4) \}, \end{aligned} \quad (16)$$

where  $j_1(x)$  is the spherical Bessel function and

$$\mathbf{Q} = \mathbf{k}_n - R_{\lambda} \mathbf{k}_m. \quad (17)$$

In order to show the dependence on  $a$  (lattice parameter), we use the reduced potential parameter

$$V_0^{red} = (a/a_0)^2 V_0, \quad (18)$$

where  $a_0 = 10$  atomic units. Then, the reduced energy eigenvalues given by

$$\Delta E^{red} = (a/a_0)^2 \Delta E_{exp} \quad (19)$$

are obtained.

### 3. Discussion and Results

The convergence of the eigenvalues has been tested by considering, for a given set of parameters, matrices with dimensions 5, 10, 15 and 20. For the lowest energy eigenvalues, a satisfactory convergence has been obtained.

In the calculations we only considered the following irreducible representations:

$$L_1, L'_2, L_3, L'_3, \Gamma_1, \Gamma_{15}, \Gamma'_{25}, X_1, X_3, X'_4 \text{ and } X'_5.$$

The others are irrelevant because the wave vector of their four-vectors have relatively large moduli giving rise to very high energy levels, far beyond the region of interest.

All theoretical and experimental results on these compounds indicate that the gap  $E_0$  between the valence and the conduction bands is direct and occurs at the L point of the Brillouin zone, or near to it<sup>5,7,8</sup>.

For *PbS*, *PbSe* and *PbTe*, the top of the valence band is generally attributed to  $L_2(2)$ , that is, to the second lowest level of the irreducible representation<sup>5,6,9</sup>  $L_2$ . The bottom of the conduction band is generally attributed to  $L'_2(2)$ <sup>6,9,10</sup> or to  $L'_3(1)$ . These three levels are very close in energy.

For *SnTe* and *GeTe* the top of the valence band is almost always attributed to  $L'_2(2)$  and the bottom of the conduction band to  $L_2(2)$ <sup>7,10,11,12</sup>. This establishes a scheme for band inversion between (*PbS*, *PbSe*, *PbTe*) and (*SnTe*, *GeTe*). Again, the levels  $L_1(2)$ ,  $L_2(2)$  and  $L_3(1)$  are close together.

The experimental data upon which we have based our calculations are those of Ref. 5. For the experimental value of the gap we have used the data of Refs. 7, 10, 11, 13.

Table I shows the parameter values which successfully simulated the semiconductors under study.

Semiconductor	$a(\text{\AA})$	$V_{0(Ry)}^{red}$	$V_{0(Ry)}$	$b$	$\bar{\rho}$	$V_{IV(Ry)}$	$V_{VI(Ry)}$
<i>PbS</i>	5.94	-2.250	-1.786	0.121	0.1945	-2.002	-1.570
<i>PbSe</i>	6.12	-2.150	-1.608	0.120	0.1932	-1.801	-1.415
<i>PbTe</i>	6.34	-2.140	-1.491	0.100	0.1900	-1.640	-1.342
<i>SnTe</i>	6.32	-2.025	-1.420	0.095	0.1887	-1.555	-1.285
<i>GeTe</i>	6.00	-1.850	-1.441	0.102	0.1893	-1.588	-1.294

**Table 1** - Values of the parameters for the semiconductors

In Tables II and III we compare our theoretical results with the experimental values.

From Tables II and III one can see that the transitions for *PbS*, *PbSe*, *PbTe* are of the same kind. For *SnTe* the only difference occurs in transition  $E_6$ , and in *GeTe* it was not possible to determine the transition responsible for the experimental value  $E_6$ . It is probable that this transition occurs at a point of lower symmetry. We have found no experimental value for the  $E_6$  transition of *GeTe* in the literature. Nevertheless, assuming that it exists (approximately equal to the  $E_6$  transition for *SnTe*), it could be simulated by the difference  $L'_2(2) - L_1(2)$ . Transitions  $E_6$  and  $E_7$  of *GeTe* are of the same kind as the transitions  $E_6$  and  $E_7$  of the other semiconductors.

The agreement with experimental data is satisfactory, especially for the lower gaps. The  $E_6$  and  $E_7$  gaps for *PbS*, *PbSe*, *PbTe* and *GeTe*, as well as the  $E_6$  gap for the *SnTe*, are very sensitive to small variations in the

gap	PbS		PbSe		PbTe		Transitions
	exp.	theor.	exp.	theor.	exp.	theor.	
$E_0$	0.022 a to 0.027 a	0.023	0.013 a to 0.019 a	0.019	0.015 a to 0.021 a	0.021	$L'_3(1) - L_1(2)$
$E_1$	0.135 a to 0.143 a	0.134	0.113 a to 0.117 a	0.112	0.091 a to 0.093 a	0.091	$L'_2(2) - L_1(2)$
$E_2$	0.235 a to 0.270 a	0.245	0.185 a to 0.229 a	0.216	0.145 a to 0.180 a	0.167	$L'_3(1) - L_3(1)$
$E_3$	0.368 a to 0.390 a	0.356	0.323 a to 0.342 a	0.309	0.245 a to 0.257 a	0.238	$L'_2(2) - L_3(1)$
$E_4$	0.595 a	0.570	0.522 a	0.516	0.463 a	0.473	$X_3(1) - X'_5(1)$
$E_5$	0.720 a	0.672	0.669 a	0.609	0.573 a	0.556	$\Gamma'_{25}(1) - \Gamma_{15}(1)$
$E_6$	1.022 a	0.919	0.919 a	0.852	0.823 a	0.788	$L'_3(2) - L_3(1)$

a) see Ref. 5.

**Table II** - Theoretical and experimental values of the transitions (Energies in Rydbergs).

$\rho$  parameter. If we increase  $\bar{\rho}$ ,  $E_c$  decreases and  $E_v$  increases, thus improving  $E_g$  and worsening  $E_{\text{eff}}$ . As higher gaps are less reliable, we preferred to fit  $E_{\text{eff}}$ , keeping also in mind that the semiconductor properties are directly related to the nature of the fundamental gap.

gap	SnTe		Transitions	GeTe		Transitions
	exp.	theor.		exp.	theor.	
$E_g$	0.022 c	0.119	$L'_3(1) - L_1(2)$	0.015 b	0.007	$L'_3(1) - L_1(2)$
$E_1$	0.066 a to 0.071 a	0.074	$L'_2(2) - L_1(2)$	—	0.064	$L'_2(2) - L_1(2)$
$E_2$	0.134 a to 0.152 a	0.149	$L'_3(1) - L_3(1)$	0.146 a	0.157	$L'_3(1) - L_3(1)$
$E_3$	0.223 a to 0.235 a	0.204	$L'_2(2) - L_3(1)$	0.235 a	0.214	$L'_2(2) - L_3(1)$
$E_4$	0.448 a	0.452	$X_3(1) - X'_5(1)$	0.397 a	—	—
$E_5$	0.544 a	0.532	$\Gamma_{25}(1) - \Gamma_{15}(1)$	0.456 a	0.464	$X_3(1) - X'_5(1)$
$E_6$	0.669 a	0.546	$L'_3(2) - L_1(2)$	0.573 a	0.548	$\Gamma_{25}(1) - \Gamma_{15}(1)$

a) see Ref. 5; b) see Ref. 7; c) see Refs. 11,9, 13

**Table III** - Theoretical and experimental values of the transitions (Energies in Rydbergs).

The principal result of this work is the reproduction, with a simple effective-potential model, of the optical transitions of five semiconductors.

Energy band calculations based on this simple effective potential developed in Fourier series for seventeen semiconductors are now in progress.

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