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DIELECTRICALLY DEFINED ELECTRONEGATIVITY AND INTERBAND ENERGY GAPS OF COVALENT SOLIDS

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(Reçu le 1er août 1973)

Résumé. — Un certain nombre de contradictions contenues dans un article (1969) de Van Vechten sur les énergies interbandes des solides covalents est discuté. En particulier nous montrons que les énergies correspondant à E₀, E₁ et E₂ ne peuvent être exprimées par une formule du type \( E_{g}^2 = E_{h}^2 + C^2 \), indépendamment de la présence du niveau d interne.

Abstract. — Several inconsistencies contained in a paper (1969) by Van Vechten on interband energy calculation of covalent solids are discussed. In particular it is shown that energy gaps corresponding to \( E_0 \), \( E_1 \) and \( E_2 \) can not be fitted to an expression of type \( E_{g}^2 = E_{h}^2 + C^2 \), whether there is a d-core or not.

The quantum dielectric model of electronegativity proposed by Phillips [1]-[3] is very successful in explaining a series of related properties of partially ionic covalent solids. At the basis of this model lie two approximations. The first is the single band gap model for the electronic dielectric constant, which is equivalent to a single Sellmeier oscillator of the well-known form [4]. The actual energy bands are replaced by a pair of bonding and antibonding bands, separated by an average energy gap.

The second draws its origin from ideas proposed by Herman [5] and Callaway [6] in 1955, namely that the zinc-blende type energy bands can be considered as perturbed diamond-type energy bands, the difference of potential of the two atoms in a unit cell being the perturbation term.

Combining these two approximations, Phillips [1] proposed that the average band gap \( E_{g} \) in the single oscillator model of the electronic dielectric constant of a heteropolar (partially ionic) crystal be related to the homopolar (completely covalent) band gap \( E_{h} \) by

\[
E_{g}^2 = E_{h}^2 + C^2
\]

where \( C \) represents the contribution of the heteropolar potential to the band gap. \( E_{g} \) and \( E_{h} \) are determined from experimental values of the dielectric constant, and the parameter \( C \) is determined from the eq. (1).

The fractional covalency and ionicity are then defined as the ratio of \( E_{g}^2 \) and \( C^2 \) to \( E_{g}^2 \). Though this definition of ionicity is entirely arbitrary, this is certainly a useful scaling parameter and its application to such over-all properties as cohesive energy proved very successful [2], [3].

In the present paper we are mainly concerned with one particular aspect of these applications, namely that of calculation of interband energies of tetrahedrally coordinated partially ionic solids, recently published by Van Vechten [7], [8]. We believe that \( C \) is an averaged-out parameter which is certainly valid for the study of physical quantities of statistical character, but too crude a parameter to be relied on in such calculations as interband energy gaps.

We will first re-examine some of the aspects of the original model of Phillips in the light of its subsequent use in the band structure study, and then discuss several of the basic assumptions of Van Vechten’s model. Finally we will comment on some of the results obtained by Van Vechten [8].

The electronic dielectric constant \( e(\omega, q) \) at \( q = 0 \) contains in the quantum mechanical definition [4] an energy denominator. This energy is the band gap between a pair of valence and conduction bands for which an optical transition is allowed. The average band gap \( E_{g} \) in the two band model is thus some sort of average (taken with the \( f \)-factor as the weighting factor) value taken throughout the Brillouin zone. On the other hand, the anti-symmetric potential \( V_{a} \) mixes the bonding and anti-bonding states of a diamond-type crystal at each point of the Brillouin zone. Which (optically allowed) band gaps actually interact directly via the anti-symmetric potential is...
given by group theory. It is well known [9] that for such cases as
\[ \Gamma_{25} \to \Gamma_{15} \quad (k = 0) \quad \text{or} \quad \text{L}_3 \to \text{L}_3 \left( k = \frac{\pi}{a} \left( \frac{1}{2} \frac{1}{2} \frac{1}{2} \right) \right), \]
where the two bands interact directly through \( V_a \) (they are actually pairs of bonding and anti-bonding orbitals) one can neglect interactions with other bands (bands originating from orbitals other than the outermost sp\(^3\) shells) and solve the resulting 2 x 2 secular determinant to obtain an equation analogous to (1), where \( C \) is to be replaced by 2 \( \langle V_a \rangle \).
\( \langle V_a \rangle \) is the matrix element of the anti-symmetric potential between the interacting conduction and valence states.) On the other hand for \( \Gamma_{25} \to \Gamma_{25} \), \( \text{L}_3 \to \text{L}_1 \) and \( \text{X}_4 \to \text{X}_1 \left( k = \frac{\pi}{a} (100) \right) \), where there is no direct interaction between the conduction and valence states via \( V_a \) one must either solve a large secular determinant containing states which interact with either of the two states, or obtain the changes of band gap in 2nd-order perturbation theory [10].

This treatment leads to the famous linear variation in \( \Delta \) of these interband gaps [5], [9] within an isoelectronic sequence, while the first group of peaks shows a curvature when plotted in \( \Delta \). \( \Delta \) is the phenomenological parameter introduced by Herman [5] which is assumed to be proportional to \( V_a \). In reality, however, for \( E_0 \) (\( \Gamma_{25} \to \Gamma_{25} \)) and \( E_1 \) (\( \text{L}_3 \to \text{L}_1 \)) peaks, the valence band interact with the nearby second conduction band via \( V_a \), and the variation of energy gaps in terms of \( \Delta \) has a hybrid character. It is of basic importance to recognize that the different types of behaviour of the energy gaps are due to considerations of symmetry. Now in Phillips' model all band gaps are replaced by the same expression (1).

We now examine some of the assumptions made in Van Vechten's paper on interband energy gaps. The point we are most concerned with is the way in which the different behaviours of interband energy gaps are handled. Van Vechten does not recognize considerations of symmetry; instead he attributes this difference to the presence of a filled d-band, and proposes two different schemes according to whether a given semi-conductor has a filled d-band or not.

First we discuss the case where there is no filled d-band in the core, which corresponds to second and third row compounds. For this case Van Vechten [8] proposes that all band gaps be represented by:

\[ E_{g,i} = \text{E}_i n_c(1 + C^2/E^2_{h})^{1/2} \quad (2) \]

(where is a generalization of Phillips' model). \( E_{g,i} \) is the actual energy gap corresponding to the peak \( E_i \) (we follow the usual nomenclature for the absorption peaks [11]) and \( E_{h} \) is the corresponding homopolar component of the energy gap suitably scaled from those of diamond and silicon, according to the lattice parameter. \( C \) is the heteropolar component of energy gap deduced from the electronic dielectric constant according to (1). One can immediately say, from the symmetry arguments presented above, that this formula should give acceptable values of the energy gap corresponding to peaks \( E_0 \) and \( E_1 \). From the same arguments, however, one does not see how the other energy gaps can be put in the above form, in particular with the same value of \( C \). Actually the situation for the peak \( E_2 \) (\( \text{X}_4 \to \text{X}_1 \)) is special. For all of the diamond or zinc-blende type semi-conductors studied, the energy of this peak lies very near (this is the strongest of the five peaks) the average energy gap \( E_0 \) (see Table I). It is then obvious that

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( E_0 ) (eV)</th>
<th>( E_2 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>13.6</td>
<td>12.2</td>
</tr>
<tr>
<td>Si</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td>Ge</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Sn</td>
<td>3.1</td>
<td>3.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>ZnSe</td>
<td>7.1</td>
<td>6.8</td>
</tr>
<tr>
<td>InSb</td>
<td>3.7</td>
<td>3.6</td>
</tr>
<tr>
<td>CdTe</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>7.8</td>
<td>8.2</td>
</tr>
<tr>
<td>CdS</td>
<td>7.1</td>
<td>&lt;7.8</td>
</tr>
</tbody>
</table>

(*) In zinc-blende type solids (\( \text{X}_4 \to \text{X}_1 \)) splits into (\( \text{X}_5 \to \text{X}_1 + \text{X}_3 \)) \( E_2 \) is taken as the centre of gravity of the two peaks for such cases.

Where there is only one peak observed (like CdS) it is indicated by inequality signs.

We should, however, expect no agreement between the experimental data and the formula (2) for \( E_0 \) and \( E_1 \). Unfortunately there are only two cases studied by Van Vechten [8], namely BP and SiC, to check this point. Even for these, the data is not complete (no data for \( E_0 \) of BP). For \( E_0 \) of SiC,
however, the discrepancy is fairly serious (7.75 eV against 8.48 eV from (2)).

We now discuss the cases where one or both of the constituent atoms produce a filled d-band; this is the case for most of the solids considered. Van Vechten proposes that for \( E_0 \) (\( \Gamma_{25} \rightarrow \Gamma_{15} \)), \( E_1 \) (\( L_3 \rightarrow L_1 \)) and \( E_2 \) (\( X_4 \rightarrow X_1 \)) the same scheme as (2) be used. For \( E_0 \) (\( \Gamma_{25} \rightarrow \Gamma_2 \)) and \( E_1 \) (\( L_1 \rightarrow L_2 \)) the formula (2) is replaced by the following one:

\[
E_{g,1} = \varepsilon_{n,1} \left( 1 + \frac{C^2}{\varepsilon_{n,1}^2} \right)^{1/2}
\]

where

\[
\varepsilon_{n,1} = \varepsilon_{n,1} - (D_{av} - 1) \Delta E_1
\]

(3)

\( E_{g,1} \) and \( E_{n,1} \) are as before. \( D_{av} \) is some average value (this again is an obscure point which is not easy to understand [8]) of the parameter \( D \), which is the square of the ratio of the effective plasma frequency to the free electron value calculated assuming 4 valence electrons per atom [7]. \( \Delta E_1 \) is an adjustable parameter, of which the nature is not explained.

Van Vechten explains the reason for the differentiation between the two groups of band gaps in the following way: when free atomic energies of 4s and 4p states of Ge are compared with 3s and 3p levels of Si, it is found that 4s level of Ge is lowered by about 3.9 % (= 1.8 eV) relative to 4p level, due to the presence of 3d charge density around the core. And, he continues, as the conduction bands for \( E_0 \) (\( \Gamma_{25} \rightarrow \Gamma_2 \)) and \( E_1 \) (\( L_1 \rightarrow L_2 \)) the formula (2) is replaced by the following one:

\[
E_{g,1} = \varepsilon_{n,1} \left( 1 + \frac{C^2}{\varepsilon_{n,1}^2} \right)^{1/2}
\]

(4)

\( L_{av} \) is some average value (this again is an obscure point which is not easy to understand [8]) of the parameter \( D \), which is the square of the ratio of the effective plasma frequency to the free electron value calculated assuming 4 valence electrons per atom [7]. \( \Delta E_1 \) is an adjustable parameter, of which the nature is not explained.

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\[
E_{g,1} = \varepsilon_{n,1} \left( 1 + \frac{C^2}{\varepsilon_{n,1}^2} \right)^{1/2}
\]

(5)

and not by

\[
E_1 = \varepsilon_{n,1}(1 + \frac{C^2}{\varepsilon_{n,1}^2})^{1/2}
\]

However, as table II shows for several randomly chosen examples, (5) gives completely unacceptable values for these gaps. The reason for this difficulty is, as pointed out above, that these energy gaps can not be described by an expression of the type, eq. (2) to begin with.

**TABLE II**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( E_0 ) (eV)</th>
<th>( E_0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>1.55</td>
<td>3.15</td>
</tr>
<tr>
<td>ZnSe</td>
<td>3.38</td>
<td>5.90</td>
</tr>
<tr>
<td>InSb</td>
<td>0.38</td>
<td>2.12</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.89</td>
<td>4.99</td>
</tr>
<tr>
<td>ZnS</td>
<td>4.37</td>
<td>6.66</td>
</tr>
<tr>
<td>CdS</td>
<td>2.73</td>
<td>6.05</td>
</tr>
</tbody>
</table>

It might be argued at this point that eq. (3) is conform to the Phillips’ model (eq. (2)) in which \( C \) is now corrected for the d-effect as follows:

\[
E_{g,1} = \varepsilon_{n,1} \left( 1 + \frac{C^2}{\varepsilon_{n,1}^2} \right)^{1/2}
\]

with

\[
C_i^2 = C^2(\varepsilon_{i,1}/\varepsilon_{n,1})^2
\]

It is not clear at all why the d-correction on \( C \) should be of the above form. \( C \) is a parameter determined by the crystal as a whole, just as the electronic dielectric constant \( \varepsilon \) is. One of the most noteworthy claims in Van Vechten's work is precisely that all the energy gaps can be described by the parameter \( C \) which is unique for a given crystal.

The situation can be summarized as follows.

1) It is reasonable to represent the dielectrically determined average energy gap of the heteropolar semi-conductor by \( E_i^d = E_i^a + C^2 \). This is because...
the dielectric constant, from which $C$ is determined, is a bulk property of a crystal which is determined primarily by contributions from general points in the BZ. There is only one irreducible representation at a general point of the BZ and a gap can approximately be determined by the above expression.

ii) Of the five main peaks in the optical spectra, two ($E_0$ and $E_1$) are between states directly connected by $V_a$, just as it is at a general point of the BZ. It is then justified to employ an expression of the type given by eq. (1) and the results are expected to be reasonably good.

iii) Unfortunately, however, the remaining peaks $E_0$, $E_1$, and $E_2$ are of different categories, as the states across the gap are not interacting directly via $V_a$. It is not surprising then that the same scheme does not apply for these peaks, whether or not a d-core is present. The proposed formula, eq. (3)-(4), is obviously inconsistent with the basic idea of Phillips which Van Vechten claims is fundamental to his work.

We discuss briefly the apparent good agreement of calculated values with experimental data, which according to Van Vechten is better than the pseudo-potential calculation of Cohen and Bergstresser [13]. First we remark that any band gap $E_i$ can be put into the form $E_i^2 = E_i^2 + C_i^2$, provided that the $C_i$ are determined individually (which then amounts to defining $C_i$). The point is that $C$ is deduced from the dielectric constant and assumed to have the same value for $E_0$, $E_1$, and $E_2$ in Van Vechten’s model. By taking the logarithmic derivative of (2), we obtain the following relation:

$$\frac{\Delta E_i}{E_i} = \left[C^2 + C_i^2\right] \frac{\Delta C}{C}.$$  \hspace{1cm} (6)

This shows that as far as $C < E_i^2$, the relative error $\Delta E_i/E_i$ is only a fraction of the relative uncertainty of $C$. This is actually the case for most of the 15 zinc-blende type semi-conductors studied by Van Vechten [8]. $C_i$ can be expressed in terms of the form factors of pseudo-potential. Cohen and Bergstresser [13] employed $V_a(3)$, $V_a(4)$ and $V_a(11)$ in their study of 14 semi-conductors. $C_i$’s for $E_0$ and $E_1$ are then seen to be certain linear combinations of $V_a(4)$ and $V_a(3) - V_a(11)$, the coefficients being obtained from the secular determinant. It is more straightforward to fit the experimental gaps $E_0$ and $E_1$ to eq. (2) and compare the obtained $C_i$’s, to the parameter $C$ as determined by Phillips and used in Van Vechten’s work. Table III is a collection of these values obtained for $E_0$ and $E_1$. It is seen from this table that effectively $\Delta E_i/E_i$ is only a small fraction of $\Delta C/C$ for the III-V compounds and less so for II-VI compounds. This is also seen in [8] where $E_1$ gaps are recalculated with 20% larger values of $C$ to improve the agreement with experimental data. For this change of 20% in values of $C$, the corresponding change in $E_1$ is remarkably small: 0.3% ~ 11%. On the average $\Delta E_1/E_1$ is about 5%, except for II-VI compounds for which $C$ becomes larger. One particular remark we would make about energy gaps calculated by Van Vechten concerns the cuprous halides, CuCl, CuBr and CuI. The experimental studies [14], [15] as well as the first principles energy bands calculations [16], [17] show that the highest valence band is from the 3d orbitals of Cu, with some hybridization of halide p-orbitals. In this condition, it is not clear at all what the effective number of valence electrons should be; this is represented by the parameter $D$ in the Phillips model of two bands. It is perhaps not surprising then that the energy gaps calculated by Van Vechten show no correlation with either the first principles calculated values or spectroscopic data. It is also clear that the $C$ parameter should be reviewed for these compounds by taking the d-band critically into account [18], [19].

**Acknowledgement.** — The author wishes to thank P. Lenglart and M. Lannoo for their comments on the initial manuscript.

**TABLE III**

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta C_0/C$</th>
<th>$\Delta C_1/C$</th>
<th>$\Delta E_0/E_0'$</th>
<th>$\Delta E_1/E_1'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>0.12</td>
<td>0.13</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>SiC</td>
<td>0.07</td>
<td>0.11</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>GaP</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>AlSb</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>InP</td>
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<td>0.01</td>
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<td>0.00</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
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</tr>
<tr>
<td>InAs</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>InSb</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CdS</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Deviation of $C_i$ for $E_0$ and $E_1$ from the « average anti-symmetric energy gap » $C$ of Phillips-Van Vechten.**

$$\Delta C_i = C_i - C \quad \text{where} \quad E_i^2 = E_{ni}^2 + C_i^2$$

$E_{ni}$ is the value calculated by Van Vechten using $C$. The calculated $\Delta C_i/C$, $\Delta E_0/E_0'$ and $\Delta E_1/E_1'$ are compared with the experimental values shown in the table.
References

[10] Though this is a second-order treatment in perturbation, it must be noted that the energy denominators in the 2nd-order energy term are not the unperturbed energy gap of the transition in question, as is erroneously written (formula (1.8) in ref. [8]).