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Oscillator strengths in tetrahedral semiconductors*

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Values of the optical matrix elements are estimated from experimental values of the dielectric constant and the energy of the optical reflectivity peak. The matrix elements of the momentum operator are found independent of polarity, as in studies by Lawaetz and by Cohen. This is found to be consistent with the expectations of the Penn model of the dielectric constant and with linear-combination-of-atomic-orbitals models. It is also found to differ from but not nullify the assumptions of the Phillips–Van Vechten ionicity model. The matrix elements of momentum also vary significantly with bond length (or metallicity), but in such a way that both the bond-orbital and the pseudopotential descriptions simultaneously retain essential validity. Significant corrections to the γ values of the bond-orbital model for the heavier elements are suggested by the study.

I. INTRODUCTION

The optical dielectric constant in simple tetrahedral solids (measured at frequencies below interband absorption, but above the absorption associated with vibrational modes) has gained particular significance since Phillips[1] used it to define an ionicity scale for these sytems. Similarly a recent attempt at a linear-combination-of-atomic-orbitals (LCAO) theory relating the electronic structure to the bonding properties of these systems used optical properties to obtain values for the parameters of the theory.[2,3] Recently, attention has been brought[4,5] to the fact that the two approaches arrive at different results about the trends in isoelectronic series of compounds with varying polarity. The purpose of this paper is to present an analysis of the assumptions of the two theories and of the relevant experimental data which will allow us to conclude that the two approaches are not in fact inconsistent, but represent different definitions of parameters, such as average energy gaps. We will also, however, show that the trends in parameters predicted by the tight-binding model are in agreement with the trends obtained by other workers in unrelated ways.

II. DIELECTRIC CONSTANT

It is convenient at the outset to write the dielectric constant in three equivalent forms, in all cases based upon the two types of levels which both analyses contemplated; we label these levels a and b for antibonding and bonding, or equivalently for conduction band and valence band, respectively. One form, which is derivable immediately for localized states by calculating the energy to second order in a perturbing Hamiltonian $-e\mathcal{E}x$, is

$$\epsilon_0 = 1 + 8\pi N e^2 \sum_a \frac{\langle b|x|a\rangle\langle a|x|b\rangle}{E_{ab}}. \tag{1}$$

Here the sum over bonding states has been replaced by N, the density of valence electrons, and E_{ab} is the magnitude of the energy difference between the two types of levels.

A familiar relation[6] between the matrix elements of the coordinate and of the momentum

$$\langle a|x|b\rangle = -i\hbar\langle a|p_x|b\rangle / mE_{ab}, \tag{2}$$

allows this to be written in the equivalent form

$$\epsilon_0 = 1 + \frac{8\pi N e^2\hbar^2}{m^2} \sum_a \frac{\langle b|p_x|a\rangle\langle a|p_x|b\rangle}{E_{ab}^3}, \tag{3}$$

which remains applicable when the states $|b\rangle$ and $|a\rangle$ become Bloch states in the solid.

A third convenient form is in terms of the dimensionless oscillator strength

$$f_{ab} = 2\langle b|p_x|a\rangle\langle a|p_x|b\rangle/(mE_{ab}).$$

Writing the result in terms of the plasma frequency $\omega_p^2 = 4\pi N e^2/m$ gives

$$\epsilon_0 = 1 + \sum_a \left(\frac{\hbar\omega_p}{E_{ab}}\right)^2 f_{ab}. \tag{4}$$

These dimensionless oscillator strengths are of particular significance since they satisfy a rigorous sum rule

$$\sum_a f_{ab} = 1, \tag{5}$$

where the sum is over *all* states, occupied as well as unoccupied.

These three expressions for the dielectric constant are equivalent but provide quite different guides to the intuition. The form in Eq. (1) is particularly useful in discussions of LCAO models. Equation (3) is most useful in discussions of the dielectric constant in terms of pseudopotentials and Jones zones, and Eq. (4) is most appropriate to discussions of the Phillips ionicity state.

Let us now assume that one of the excitation energies E_{ab} dominates the sum over a in (1), (3), or (4). The result may be written

$$\epsilon_0 = 1 + (\hbar\omega_p/E_{ab})^2 \bar{f}\,, \tag{6}$$

where

$$\bar{f} = \sum_a{}' f_{ab}; \tag{7}$$

or as

$$\epsilon_0 = 1 + (\hbar\omega_p/E_{ab})^2\, 2\bar{p}_x^2/E_{ab}\,, \tag{8}$$

where

$$\bar{p}_x^2 = \sum_a{}' |\langle b|p_x|a\rangle|^2; \tag{9}$$

or finally as

$$\epsilon_0 = 1 + (\hbar\omega_p/E_{ab})^2 (2m/\hbar^2) E_{ab}\bar{x}^2\,, \tag{10}$$

where

$$\bar{x}^2 = \sum_a{}' |\langle b|x|a\rangle|^2. \tag{11}$$

In Eqs. (7), (9), and (11) the prime on the summation indicates that only *empty* states a are to be included.

We will later make use of all of these various expressions, but at this point we find it convenient to discuss both the ionicity model and the bond-orbital model in terms of Eq. (6). In the simplest version of the ionicity model (see, e.g., the discussion by Phillips in Ref. 4), the basic equation for ϵ_0, namely,

$$\epsilon_0 = 1 + (\hbar\omega_p/E_{ab})^2 \tag{12}$$

is obtained from (6) by invoking the sum rule (5) whereby $\bar{f}=1$. In Ref. 4 the satisfaction of the sum rule is presented as a theoretical necessity. Comparison of Eq. (5) with Eq. (7), however, reveals that $\bar{f}=1$ only if there are no occupied states contributing to the sum in (5). Since all crystals of interest do have occupied core states lying below the valence bands, we conclude that $\bar{f}=1$ is always an approximation. In fact, this had been recognized by Van Vechten,[7] who set $\bar{f}=D>1$ for materials having occupied d levels immediately below the valence bands.[8]

In view of the above remarks, the two models in question may be described in a systematic way as follows: The ionicity model starts with Eq. (6). It then prescribes that $\bar{f}=1$ for C and Si and in all compounds isoelectronic with them. [Combined with Eq. (6) and experiment this provides a *definition* of E_{ab} in this model.] It further prescribes that $\bar{f}=D>1$ for materials containing at least one element from the Ge, Sn, and Pb rows, which have high-lying occupied d levels. An empirical prescription is postulated to fix D for each material; that prescription yields an $\bar{f}$ which decreases only very slowly in an isoelectronic series. Having fixed $\bar{f}$, the experimental value of ϵ_0 is then used, from which a value for the energy gap $E_{ab}=E_g$ is immediately obtained. Chemical trends and the definition of ionicity are then based solely on these energy gaps by breaking them up into two terms:

$$E_g^2 = E_h^2 + C^2. \tag{13}$$

This is a prescription defining C, not a result derived from a detailed theory. An additional prescription to fix E_h for each material[1,7] is supplied. The entire procedure is legitimate, but we wish to point out an important observation regarding the meaning of the gap E_g, namely, that E_g is an average gap which simulates the entire excitation spectrum of the crystal, not only those excitations which may be viewed as bonding-antibonding in nature. One should therefore be cautious about identifying E_g as the bonding-antibonding gap or as the Jones-zone gap of pseudopotential theory,[10] or in identifying the prescription (13) with either theory.

We have just seen that the ionicity model starts with Eq. (6), makes an assumption about $\bar{f}$, and extracts energy gaps from the experimental value for ϵ_0. The approach used in the bond-orbital model is quite different. There, a detailed, though approximate, model was specified and various properties, including the dielectric constant, were calculated in terms of the parameters of the model. A form for the gap, analogous to Eq. (13), followed from the model rather than appearing as a separate postulate. The gap itself, the bonding-antibonding splitting, was identified with the principal peak in the reflectivity spectrum, usually denoted by E_2. With E_{ab} fixed at E_2, Eq. (6) can be used to extract experimental values for $\bar{f}$ from the observed values of ϵ_0. One can then study the trends of $\bar{f}$ and, equivalently, from Eqs. (8) and (10), the trends of the momentum and position matrix elements in an isoelectronic series. We will do this in the remainder of the paper. Note that similar results are not obtainable from the ionicity model, which postulates a prescription for $\bar{f}$, with an energy gap chosen to be consistent with that prescription.

Before we proceed, a word of caution is necessary. The choice of the reflectivity peak for E_{ab} is not the only possibility. It is, however, a natural one both from the point of view of LCAO theory and the bond-orbital model[3] and from the point of view of pseudopotential theory[10] and the Penn model,[9] in which the energy denominator may be associated with the Jones-zone gap. Furthermore, it is known for a number of tetrahedral semiconductors and provides a consistent standard. Finally, we will find trends which are the same as for matrix elements obtained in unrelated ways. The two trends of interest are variations with increasing atomic number (increasing metallicity) and with increasing polarity. It is convenient therefore to consider the series C, Si, Ge, Sn and the compounds isoelectronic with them. Table I lists the appropriate experimental values for these systems, which comprise about a third of the elemental and binary tetrahedral compounds.

TABLE I. Experimental optical constants for the homopolar semiconductors and the isoelectronic compounds.

Material	d (Å)	ϵ_0	E_2 (eV)	$d^2E_2m/\hbar^2$
C	1.54	5.7 [a]	12.2 [g]	4.0
Si	2.35	12.0 [a]	4.5 [h,i]	3.4
Ge	2.44	16.0 [a]	4.4 [h]	3.6
Sn	2.80	24 [b]	3.7 [h]	4.0
AlP	2.34	8 [c]	5.5 [c]	
GaAs	2.45	10.0 [d,e]	5.0 [h]	
InSb	2.81	15.7 [d,e]	4.1 [h]	
ZnSe	2.45	5.9 [f]	6.4 [j]	
CdTe	2.81	7.2 [f]	5.0 [j]	

[a] N. A. Goryunova, *Chemistry of Diamond-Like Semiconductors* (Chapman and Hall, London, 1965).

[b] R. E. Lindquist and A. W. Ewald, Phys. Rev. 135, A191 (1964).

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[h] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[i] The peak, observed in footnote h, shifted between 4.3 and 4.5, depending on the polarization of the light. We select the value which lies between the C and Ge values.

[j] F. H. Pollak, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967,* edited by D. G. Thomas (Benjamin, New York, 1968), p. 552.

The remaining compounds are "skew," containing atoms from different rows of the periodic table. The data for these systems are scattered, but they follow similar trends. An adequate analysis is possible by studying only the materials listed.

III. DIMENSIONLESS OSCILLATOR STRENGTHS

We look first at the dimensionless oscillator strengths $\bar{f}$, which are obtainable immediately from Eq. (6) and Table I. The results are shown in Table II. Looking first at the variation with increasing metallicity, we see that there is a steady increase as we move downward in the table. We note values less than unity, indicating that oscillator strength exists at high-energy excitations which do not participate[11] significantly in the determination of ϵ_0. For the materials of the Ge and Sn rows we note values greater than unity, which are possible, as discussed earlier, because of the presence of the occupied d levels just below the valence bands.

It is important to note that the need for explicitly including a d-state correction[7] is a result of the use of the sum rule; the additional terms in the dielectric constant due to the matrix elements between d states and conduction-band states (these correspond physically to the polarization of the d states by the field) are small, particularly for Ge, Sn, and the group-III–V compounds. Thus, although it was correct and necessary to make these corrections in Van Vechten's[7] study, we now believe that they should not have been made in the analysis by Harrison and Ciraci[3] in which the sum rule was not used. We will return to this question shortly and see that this has the effect of modifying the values of the parameter γ (for the heavy elements) which they introduced, but otherwise does not affect the analysis.

We see also from Table II that there is a conspicuous decrease in the dimensionless oscillator strength with increasing polarity in each isoelectronic series. We will see that this decrease in the dimensionless oscillator strength with polarity

TABLE II. Dimensionless oscillator strengths for the semiconductors listed on the left-hand side as determined in the present work by the bond-orbital model (BOM) and in the Phillips-Van Vechten (PV) ionicity model.

			$\bar{f}$ (BOM)			$\bar{f}$ (PV)		
C			0.71			1.00		
Si	AlP		0.81	0.75		1.00	1.00	
Ge	GaAS	ZnSe	1.17	1.01	0.82	1.26	1.24	1.17
Sn	InSb	CdTe	1.92	1.53	0.95	1.46	1.43	1.30

is just what is expected, on the basis both of LCAO and of pseudopotential theory. This is an important point but does not nullify the assumptions of the ionicity model in which $\bar{f}$ is taken to be only slowly decreasing with polarity in an isoelectronic series (see Table I). The difference is that $\bar{f}$ in the ionicity is the totality of oscillator strength for the valence electrons, whereas $\bar{f}$ in the present discussion is the amount of oscillator strength contained in the bonding-antibonding excitations, which are assumed to determine ϵ_0 completely.

IV. POLARITY DEPENDENCE

We turn next to the matrix elements of x and of p_x. It is convenient to give them in dimensionless form. In the case of the matrix elements of x we note that if $|a\rangle$ and $|b\rangle$ were simple symmetric and antisymmetric combinations of δ-function-like localized states separated by bond length d, the matrix element would be $\frac{1}{2}d$ if x was measured along the bond. The angular average which enters the calculation of the dielectric constant reduces the *rms* matrix element by a factor of $3^{-1/2}$, so we divide the experimental matrix elements by $d/2\sqrt{3}$ before tabulating. Similarly for the matrix elements of p_x, if $|b\rangle$ and $|a\rangle$ were a simple sine and cosine with wave number equal to that at the center of a Jones-zone face $[\vec{k}=(110)(2\pi/a)]$, the matrix element of p along that wave number would be $2^{3/2}\pi/a=(\frac{3}{2})^{1/2}\pi/d$. The angular factor $3^{-1/2}$ arises again and we tabulate the matrix element normalized to the ideal value; the two sets of matrix elements are given in Tables III and IV.

We look first at the variation of the matrix elements with polarity; this comparison is unaffected by our normalization of the matrix elements, since the bond lengths do not vary appreciably in an isoelectronic series. We see that it is the matrix elements of p_x which are independent of polarity. This independence would be immediately predicted on the basis of simple pseudopotential theory, such as the Penn[9] model of the dielectric constant. The states above and below the Jones-zone gap (or any other gap) are sinelike and cosinelike; they may shift in *phase* with polarity but cannot shift in relative phase (they must remain orthogonal), and so the matrix element is not expected to change. Also the calculation of the matrix element of x is found[2,3] in the LCAO theory to vary with polarity as $(1-\alpha_p^2)^{1/2}=V_2/(V_2^2+V_3^2)^{1/2}$, or inversely with the band gap. This, combined with Eq. (2), similarly predicts the matrix elements of p_x to be independent of polarity.

TABLE III. "Normalized" matrix elements of x, namely $2\sqrt{3}\langle a|x|b\rangle/d$, as determined in the present work. Compounds are arranged as in Table II.

1.06		
1.22	1.07	
1.43	1.24	0.99
1.74	1.47	1.05

TABLE IV. "Normalized" matrix elements of p, namely $\sqrt{2}d\langle a|p_x|b\rangle/(\pi\hbar)$, as determined in the present work. Compounds are arranged as in Table II.

0.52		
0.52	0.55	
0.64	0.64	0.65
0.86	0.81	0.71

A similar conclusion was reached by Lawaetz,[12] who determined momentum matrix elements in connection with a study of the conduction-band effective masses in terms of the $\vec{k}\cdot\vec{p}$ formula. The same matrix element enters, but between different states, so the absolute values differ. However, the trends in his values, given in Table V, are seen to be the same. Similarly, Cohen[13] has calculated such matrix elements for the series Ge, GaAs, and ZnSe using empirical nonlocal pseudopotentials. He obtained for our normalized momentum matrix elements 1.07, 1.03, and 0.99, respectively, for one point on the Jones zone and 1.54, 1.53, and 1.50 for another. It is striking that all of these different approaches lead to the same qualitative conclusion: The matrix elements of p_x, and *not* the dimensionless oscillator strengths, are independent of polarity.

V. METALLICITY DEPENDENCE

We next turn to the absolute values of the matrix elements and the trends with metallicity or bond length. For this we need consider only the homopolar semiconductors. Note first that since the band gaps vary inversely with the square of bond length (this was noted by Harrison and Ciraci[3] and is demonstrated in the final column of Table I here), Eq. (2) suggests that the matrix elements of x will have the same variation as the matrix elements of p_x. The simplest Penn model,[9] assuming pure sinelike and cosinelike states and all states contributing equally, would suggest a universal value of unity for the normalized matrix ele-

TABLE V. Normalized momentum matrix elements obtained by Lawaetz, Ref. 12, using $\sqrt{2}d\langle X|p_x|\Gamma_2'\rangle/\pi\hbar$. Compounds are arranged as in Table II.

1.25		
1.26	1.14	
1.44	1.43	1.39
1.58	1.56	1.48

ments of p_x. This is, in fact, not too far from the truth, but misses the trend with increasing metallicity. Similarly, the simplest LCAO model based upon hybrids localized at the ends of the bonds would suggest a universal value of unity for the homopolar semiconductors for the normalized matrix elements of x. This again is semiquantitatively correct, but misses the trend. It is remarkable that if we take both of these models to be simultaneously correct, the two matrix elements may be inserted into Eq. (2) to give a prediction that the band gaps would be inversely proportional to d^2 and that the product $md^2E_{ab}/\hbar^2$ would have the universal value $6^{1/2}\pi \approx 7.7$, a prediction with no quantitative experimental input. The values listed in the final column in Table I indicate that this is not far from the truth either. This suggests that the stable semiconductors are such that *both* of these extreme views of the electronic structure have essential validity. In particular, the extreme tight-binding limit is best for C (for which the normalized matrix element of x is closest to 1) and must be refined as we move down the column, whereas the extreme plane-wave limit is best for Sn (for which the normalized momentum matrix element is closest to 1) and must be refined as we move up the column.

The trend with metallicity arises, as does the difference in the Table I values from the predicted $6^{1/2}\pi$, from the deviations in the wave functions from pure plane waves and from the deviations of the bond orbitals from the idealized form. From the pseudopotential point of view, it could well be that the orthogonality to d states is responsible for the trend in the heavy elements, consistent with the d-state corrections used by Van Vechten.[7] The values in Tables IV and V suggest this more than the values in Table III. (The difference in the two sets would not occur if the final values in Table I were exactly constant.) However, if the sum rule is not used, this becomes inconsequential. If we are to incorporate this trend in the description of the electronic structure, we must include a parameter which varies with metallicity. The parameter used by Harrison and Ciraci was defined such that the matrix element of x, with x measured along the bond, was $\langle a|x|b\rangle = \frac{1}{2}\gamma d$. Its value should be taken as 1.06, 1.22, 1.43, and 1.74 for the four rows in the Periodic Table, the four values from the first column in Table III. Similarly, matrix elements of p_x could be scaled from their ideal values using the first column of Table IV; however, Table V would suggest that different scaling factors may be appropriate for different properties.

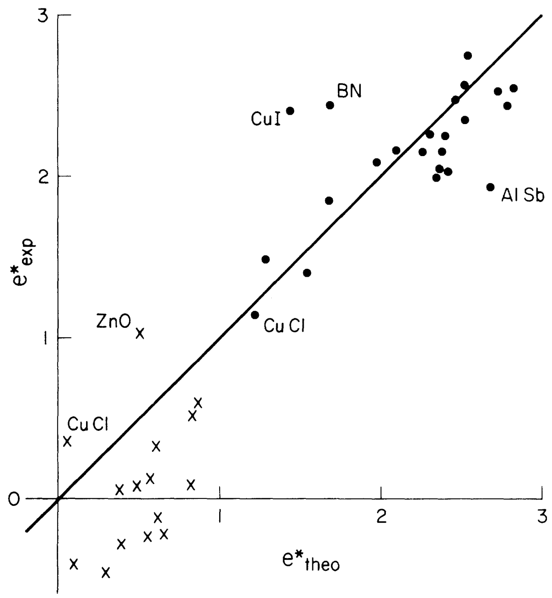

FIG. 1. Experimental macroscopic transverse charges [compiled by G. Lucovsky, R. M. Martin, and E. Burstein, Phys. Rev. B 4, 1367 (1971)] (points) and experimental piezoelectric charges [compiled by R. M. Martin, Phys. Rev. B 5, 1607 (1972)] (crosses) plotted against the values predicted by the bond-orbital model, using new values for γ.

VI. EFFECTS OF MODIFYING

We note again that the use of values of 1.43 and 1.74 for γ for Ge and Sn corrects what we believe was an error in the Harrison-Ciraci treatment. We should check to see how this affects the correlations which they found. The parameter γ did not enter many properties, but did enter the effective transverse and piezoelectric charges. We have recalculated those charges (using the formulas of Ref. 3) with values of γ corresponding to the first column in Table III, using again geometric means for skew compounds. We also became aware that for some 30% of the 38 tetrahedral semiconductors which were studied with the LCAO theory as well as with ionicity theory, there were no published experimental values for the dielectric constants; values for most of these had been chosen by Van Vechten[7] to fit chemical trends. These, of course, do not add information about chemical trends reflected in either theory, so we have eliminated them. The resulting plot, shown in Fig. 1, shows a slightly better accord with experiment that the earlier study,[3] but not significantly so. Since only γ is affected, the other correlations are unchanged.

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[2] W. A. Harrison, Phys. Rev. B 8, 4487 (1973).

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[8] We should also note that in the detailed development of the ionicity model (see, e.g., Refs. 1 and 7), use was made of the full Penn (Ref. 9) formula for ϵ_0. That formula may be viewed as a special case of Eq. (12), with E_{ab} given by $E_{ab}=E_g(1-B+\frac{1}{3}B^2)^{-1/2}$, where $B=E_g/E_F$ and E_F is the free-electron Fermi energy. Physically, Eq. (12) corresponds to a single-gap spectrum, whereas the Penn model corresponds to excitation energies distributed about E_g by a fraction B of the occupied bandwidth. In both cases, the formulas for ϵ_0 correspond to ignoring core states and setting $\bar{f}=1$. The discussion in the main part of this paper would apply equally well whether E_{ab} is viewed as a single gap or a distributed Penn gap.

[9] D. R. Penn, Phys. Rev. 128, 2093 (1962); discussed also in Ref. 1, p. 105.

[10] V. Heine and R. O. Jones, J. Phys. C 2, 719 (1969).

[11] This can arise because of the additional factor of E_{ab}^{-2} entering the formula for ϵ_0. Compare Eqs. (4) and (5).

[12] P. Lawaetz, Phys. Rev. B 4, 3460 (1971).

[13] M. L. Cohen, quoted by Phillips, Ref. 4.