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Semiconductor properties based upon universal tight-binding parameters

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The bond-orbital model for calculating properties of semiconductors utilizes nearest-neighbor universal matrix elements in a minimal-basis tight-binding formulation. It also neglects the coupling between bond orbitals and neighboring antibonding orbitals. The accuracy of these two approximations is tested by making only the first and calculating the bands, densities of states, and dielectric susceptibilities without further approximation. $\chi_1(0)$ is calculated for 30 semiconductors and $\chi_2(\omega)$ is calculated for silicon. Errors in the conduction bands shift the E_1 and E_2 peaks (seen to be associated with *sp* and *pp* coupling, respectively) to higher energy and cause an underestimate in $\chi_1(0)$ by a factor of about 2 for all semiconductors. The calculations described were based upon the Gilat-Raubenheimer scheme with tetrahedral decomposition for both zinc-blende and wurtzite structures. The calculation for zinc blende was greatly simplified, at some cost in efficiency, by use of hexagonal or quadrangular Brillouin zones. This also allowed a direct calculation of the photoelastic tensors, carried out for 30 cubic semiconductors and apparently the first values, theoretical or experimental, for most of these.

I. INTRODUCTION

Tight-binding theory was utilized many years ago in the study of the properties of covalent solids by Coulson, Redei, and Stocker[1] and by Leman and Friedel.[2] More recently a bond orbital model (BOM) based upon this approach was introduced by Harrison[3] and by Harrison and Ciraci[4] and a similar approach was used by Lannoo and Decarpigny.[5] These simplified approaches made the *bond orbital approximation* of neglecting the coupling between bonding and antibonding orbitals and gave very crude energy bands, but they allowed elementary calculations of a range of properties.

Use of a similar simplified tight-binding approximation, but without the bond orbital approximation by Chadi and Cohen,[6] gave greatly improved valence bands and even meaningful conduction bands. The largest errors had been removed by the elimination of the bond orbital approximation. Similarly, full tight-binding calculations of elastic constants in semiconductors by Chadi and Martin[7] gave significant improvement over those obtained with the bond orbital approximation. The present study makes a similar comparison for dielectric properties. A second aspect of the problem is the origin of the matrix elements which enter the calculation. They can be calculated from first principles,[8] but the studies cited above all obtained them by fits to band structures known either from experiment or more complete theories. More recently a universal set was obtained by Harrison[9] by examining the systematics of fitted values. This set has been utilized in the calculation of a wide range of bonding and dielectric properties of insulators as well as semiconductors.[10] Most of these calculations utilized the bond orbital approximation and it is of interest to know what part of the errors arise from these simplest parameters and what part from the bond orbital approximation. By carrying out the calculation of the dielectric properties with and without the bond orbital approximation and then comparing with experiment we can find the errors introduced by each approximation.

In Sec. II we present universal parameters and outline the method of calculation. In Sec. III we give the bands for ZnS in both the zinc-blende and wurtzite structures obtained with these matrix elements. In Sec. IV we give the method for calculation of densities of states and the results for silicon. In Sec. V the matrix elements of the gradient are evaluated and the susceptibility calculated. In Sec. VI we introduce lattice strains and evaluate the photoelastic constants, both in full calculation and in the bond orbital approximation.

II. THE FORMULATION

We follow Harrison[10] in assuming that the electronic states can be represented by linear combinations of valence orbitals alone, that is to say, the corresponding *s* orbitals and *p* orbitals in covalent semiconductors. Next, only the nearest-neighbor matrix elements are included. There are then four independent matrix elements: $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, and $V_{pp\pi}$. Harrison found empirically that these matrix elements were approximately given by

$$V_{\alpha\beta}=\eta_{\alpha\beta}\hbar^2/md^2 . \tag{1}$$

Here d is the distance between the nearest-neighbor atoms, and the dimensionless coefficients are

$$\eta_{ss\sigma} = -1.40, \quad \eta_{pp\sigma} = 3.24, \qquad (2)$$
$$\eta_{sp\sigma} = 1.84, \quad \eta_{pp\pi} = -0.81 .$$

Finally the diagonal matrix elements of the Hamiltonian are approximated by the calculated orbital energies, that is, the calculated atomic term values. It has been found more recently that the form, Eq. (1), and the coefficients, Eq. (2), can be approximately derived by matching the free-electron energy bands to the tight-binding energy bands.[11]

From these universal matrix elements we can construct and diagonalize the Hamiltonian matrix of any covalent semiconductor. From the diagonalization we obtain approximate energy bands and the electronic states expressed as linear combinations of the atomic orbitals. Most properties of solids are determined by the electronic structure, so the introduction of the universal parameters makes it possible to study properties systematically and, in some sense, from first principles. Here we undertake a few such studies and can thereby obtain a measure of the validity of this simple approximate description of the electronic structure.

III. THE ENERGY BANDS

The calculation of energy bands is almost immediate once the matrix elements are given. For the zinc-blende structure, for example, there are two atoms per primitive cell and four orbitals per atom, thus one Bloch sum for each orbital

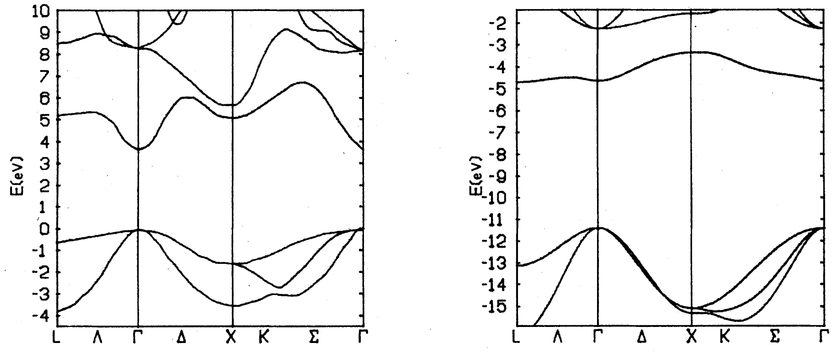
$$|\chi_{\vec{k}}^{\alpha}\rangle = \sum_{\vec{R}_n} \frac{1}{\sqrt{N_p}} e^{i\vec{k}\cdot\vec{R}_n} |\alpha, n\rangle, \qquad (3)$$

where $|\alpha, n\rangle$ is the orbital of type α on the atom at $\vec{R}_n$. The eight-by-eight Hamiltonian matrix based upon these Bloch sums is readily constructed[6] in terms of the nearest-neighbor matrix elements given in Eqs. (1) and (2) and atomic term values.[10] The corresponding bands for ZnS in the zinc-blende structure are shown in Fig. 1, where they are compared with the empirical pseudopotential method (EPM) calculation by Bergstresser and Cohen.[12] These two calculations are completely independent. Note that we used no parameters from ZnS but the bond length. Ours is unquestionably less accurate but vastly simpler in the sense that no experimental information about zinc sulfide is required and that the use of a computer of power greater than a hand-held calculator is completely inessential. For the same reason the calculation of a variety of other properties in terms of this electronic structure becomes elementary and requires no empirical input.

The largest discrepancy between the two sets of bands is seen in the conduction band from Γ to X. The tight-binding bands are seen to rise along this line while the EPM bands are seen to drop, running approximately parallel to the topmost valence bands along this line. The behavior of the EPM bands is correct in this regard and this error in the tight-binding bands will cause errors in all of our calculations, in addition to any errors we introduce by further approximations.

Although our main purpose is not to calculate the energy-band structure of semiconductors, the electronic structure calculated as the present approximation is considerably improved over that of BOM. In Table I we listed the energy gaps of several semiconductors using BOM and the present calculation. Furthermore, the upper valence bands and conduction bands of cubic semiconductors in BOM are flat;[10] however, in the present approximation reasonable valence bands and meaningful conduction bands are obtained. The improvement in calculated electronic structure would affect the calculations of other related physical quantities.

The calculation of bands for the wurtzite struc-



(a) (b)

FIG. 1. Energy bands for cubic ZnS. Part (a) shows the bands as determined by Bergstresser and Cohen (Ref. 12); part (b) shows the tight-binding bands obtained with universal parameters.

TABLE I. Energy gap in bond orbital model and in present approximation in eV. E_g^{BOM}: Band gap in bond orbital model. E_g^{TB}: Band gap in present tight-binding approximation. E_g^{expt}: Experimental band gap from Ref. 10, p. 253.

Material	E_g^{BOM}	E_g^{TB}	E_g^{expt}
C	20.55	13.88	5.5
Si	5.42	3.68	1.13
Ge	3.53	1.91	0.76
GaAs	4.34	2.89	1.52
ZnSe	6.65	5.49	2.82
ZnS	8.03	6.76	3.8

ture is only slightly more complicated than that for the zinc-blende bands. There are four atoms per primitive cell and the tight-binding band calculation requires diagonalization of a 16×16 matrix. The Brillouin zone for this structure is a hexagonal prism. Bands for ZnS in the wurtzite structure are shown in Fig. 2(a).

IV. INTEGRALS OVER THE BRILLOUIN ZONE

In order to calculate properties of a solid in terms of its electronic structure, we frequently need to calculate integrals over the Brillouin zone. For example, the electronic density of states is obtained from the following integral:

$$D(E)=\frac{2\Omega}{(2\pi)^3}\int_{E(\vec{k})=E}\frac{dS}{\nabla_k E\,|_n}, \tag{4}$$

where Ω is the volume of this system and the integral is over the surface S in wave-number space at which the band energy is E and $\nabla_k E\,|_n$ is the component of the gradient normal to S. There are many different methods for calculating such integrals. We use the Gilat-Raubenheimer method, but based upon tetrahedral cells, as done by Rath and Freeman[13] and by Jepsen and Andersen.[14] This method is especially convenient for the wurtzite structure because the Brillouin zone in this case is a prism. For semiconductors in the zinc-blende or diamond structure, the customary Brillouin zone is a truncated octahedron, which shows the full symmetry of the crystal. The corresponding irreducible Brillouin zone is $\frac{1}{48}$ of the entire Brillouin zone. There are two pyramids in one irreducible Brillouin zone, and the tetrahedral decomposition is more complicated. For wurtzite, because of the lower symmetry, the irreducible Brillouin zone is $\frac{1}{24}$ of the Brillouin zone, but it is a prism, and application of the Gilat-Raubenheimer method is simpler. The irreducible Brillouin zone is divided into identical triangular prisms and each is divided into three tetrahedra.

Several authors have given the formulas for calculating the densities of states using the tetrahedron method[13,14] in terms of the energies at the four corners, assuming them all unequal, $E_1 < E_2 < E_3 < E_4$. We have generalized these to the case $E_1 \leq E_2 \leq E_3 \leq E_4$ and obtained

$$\begin{aligned}
&D(E)=0 \quad \text{if } E\leq E_1 \text{ or } E\geq E_4,\\
&D(E)=3\frac{v(E-E_4)^2}{(E_4-E_1)(E_4-E_2)(E_4-E_3)} \quad \text{if } E>E_3,\\
&D(E)=3\frac{v(E-E_1)^2}{(E_4-E_1)(E_3-E_1)(E_2-E_1)} \quad \text{if } E<E_2,\\
&D(E)=\frac{3v(E-E_1)^2}{(E_2-E_1)(E_3-E_1)(E_4-E_1)}-\frac{3v(E-E_2)^2}{(E_2-E_1)(E_3-E_2)(E_4-E_2)}\\
&\qquad \text{if } E_2\leq E\leq E_3 \text{ and } E_1\neq E_2,\\
&D(E)=\frac{3v(E-E_1)}{(E_3-E_1)(E_4-E_1)}\left(\frac{E_3-E}{E_3-E_1}+\frac{E_4-E}{E_4-E_1}\right)\\
&\qquad \text{if } E_2\leq E\leq E_3 \text{ and } E_1=E_2.
\end{aligned} \tag{5}$$

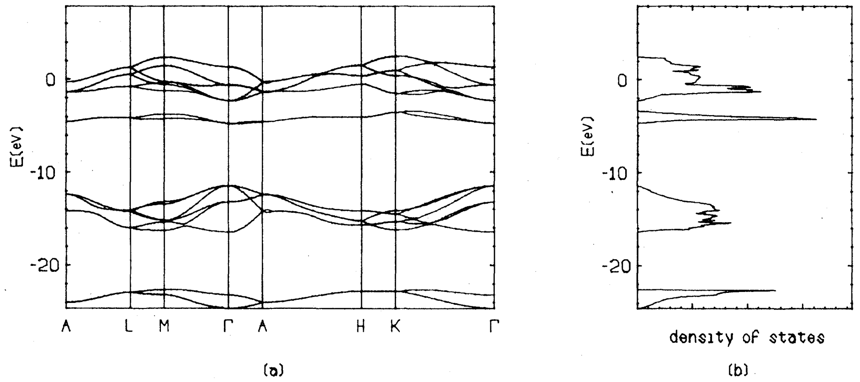


FIG. 2. (a) Tight-binding bands for wurtzite ZnS obtained using universal parameters. (b) The density of states for wurtzite ZnS, obtained using universal parameters.

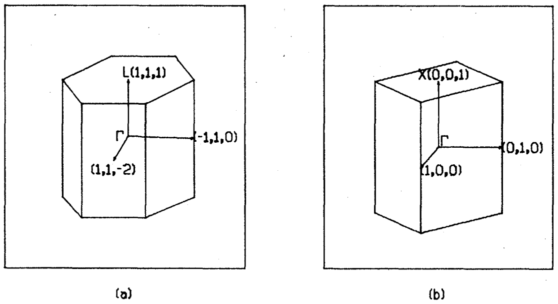


FIG. 3. (a) Hexagonal Brillouin zone for the zinc-blende structure. (b) Quadrangular Brillouin zone for the zinc-blende structure.

Here v is the volume of the small tetrahedron. The density of states obtained for the wurtzite ZnS is shown in Fig. 2(b). (294 tetrahedra in the irreducible zone were used but there is little change if only 75 are used.) Note that the same program can be used for zinc-blende–structure semiconductors. That is, we can construct a hexagonal Brillouin zone, oriented along [111] as shown in Fig. 3(a). Each is displaced from the other by a lattice wave number and they fill all of the wave-number space so they may be used for integration over the bands. However, we must integrate over $\frac{1}{12}$ of the full Brillouin zone because the [111] direction here is an axis of three fold rather than sixfold symmetry. We have also another choice, a quadrangular Brillouin zone shown in Fig. 3(b) and with it we need to calculate integrals over $\frac{1}{16}$ of this Brillouin zone. Neither of these two Brillouin zones takes full advantage of the symmetry of the crystal, so more computer time is required in calculating integrals to the same accuracy. The advantage of choosing them is that only a slight modification of the simple program for the hexagonal Brillouin zone is required. In addition it is possible to study the variations of physical properties under uniaxial strain because the symmetry of these Brillouin zones is not changed under uniaxial strain. Figures 4(a) and 4(b) are the electronic densities of states in silicon calculated by using the hexagonal and quadrangular Brillouin zone with the matrix elements of Chadi and Cohen.[6] Both of them give essentially the same results as those obtained by Chadi and Cohen. The electronic densities of states in zinc blende ZnS with universal parameters is also shown in Fig. 4(c). It differs little from that shown in Fig. 2(b) for the wurtzite structure.

It is also of interest to obtain integrals over the bands with an appropriate weighting factor $F(\vec{k})$, such as oscillator strength. Gilat and Bharatiya[16] have given formulas for these which we rewrite. We define $F(E)$ as the average of $F(\vec{k})$ over a constant energy surface in the tetrahedron, and F_1, F_2, F_3, and F_4 as values of $F(\vec{k})$ at the corners 1, 2, 3, and 4; when generalized from $E_1 < E_2 < E_3 < E_4$ to $E_1 \leqslant E_2 \leqslant E_3 \leqslant E_4$, the formulas of Gilat and Bharatiya become

$$\begin{aligned}
&F(E)D(E) = 0 \quad \text{if } E \leqslant E_1 \text{ or } E \geqslant E_4\,,\\
&F(E)D(E) = F_1 D(E) + \left(\frac{F_{41}}{E_{41}} + \frac{F_{42}}{E_{42}} + \frac{F_{43}}{E_{43}}\right)\frac{v(E-E_4)^3}{E_{41}E_{42}E_{43}} + \frac{3F_{41}(E-E_4)^2 v}{E_{41}E_{42}E_{43}} \quad \text{if } E \geqslant E_3\,,\\
&F(E)D(E) = F_1 D(E) + \left(\frac{F_{41}}{E_{41}} + \frac{F_{31}}{E_{31}} + \frac{F_{21}}{E_{21}}\right)\frac{v(E-E_1)^3}{E_{42}E_{32}E_{21}} \quad \text{if } E \leqslant E_2\,,\\
&F(E)D(E) = F_1 D(E) + \left(\frac{F_{41}}{E_{41}} + \frac{F_{31}}{E_{31}} + \frac{F_{21}}{E_{21}}\right)\frac{v(E-E_1)^3}{E_{21}E_{31}E_{41}} - \left(\frac{F_{42}}{E_{42}} + \frac{F_{32}}{E_{32}} + \frac{F_{21}}{E_{21}}\right)\frac{v(E-E_2)^3}{E_{21}E_{32}E_{42}} - \frac{3F_{21}(E-E_2)^2 v}{E_{21}E_{32}E_{42}}\\
&\qquad \text{if } E_2 < E < E_3 \text{ and } E_2 \neq E_1\,,\\
&F(E)D(E) = F_1 D(E) + \frac{(E-E_1)v}{E_{31}E_{41}}\left[-(E-E_1)^2\left(\frac{F_{32}+F_{31}}{E_{31}^2} + \frac{F_{42}+F_{31}}{E_{31}E_{41}} + \frac{F_{42}+F_{41}}{E_{41}^2}\right)\right.\\
&\qquad\qquad \left. + 3(E-E_1)\left(\frac{F_{42}}{E_{41}} - \frac{F_{32}}{E_{31}}\right) + 3F_{21}\right] \quad \text{if } E_2 < E < E_3 \text{ and } E_2 = E_1\,.
\end{aligned} \tag{6}$$

Here $F_{ij} = F_i - F_j$, $E_{ij} = E_i - E_j$. This then provides all the parameters and formulas needed to calculate properties in the tight-binding context and to test various approximations which have been used.

V. MATRIX ELEMENTS OF THE GRADIENT AND THE SUSCEPTIBILITY

In terms of one-electron wave functions, the susceptibility can be expressed as[10]

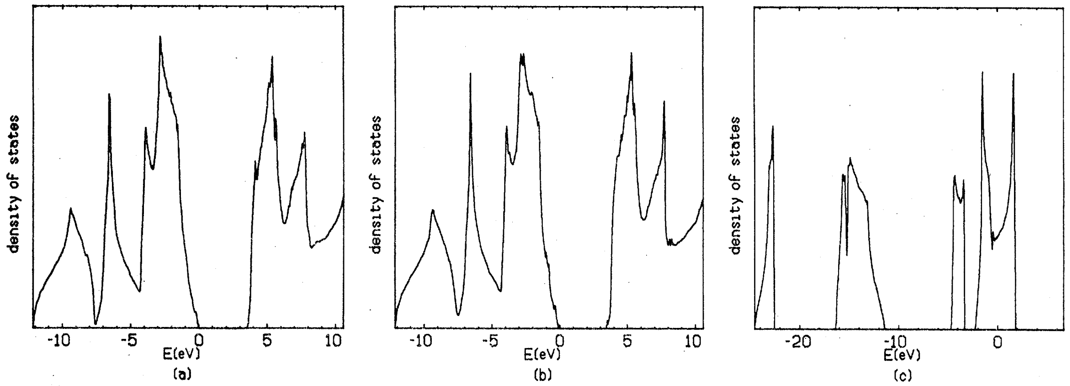


FIG. 4. (a) Density of states for silicon, using the hexagonal Brillouin zone and the Chadi and Cohen (Ref. 6) tight-binding parameters. (b) Density of states for silicon, using the quadrangular Brillouin zone and Chadi and Cohen (Ref. 6) tight-binding parameters. (c) Density of states for cubic ZnS using the hexagonal Brillouin zone and universal parameters.

$$\chi_1(0)=\frac{2\hbar^4e^2}{m^2\Omega}\sum_{\vec{k}\,(\mathrm{full}),\ \vec{k}'\,(\mathrm{empty})}\left|\left\langle\psi_{\vec{k}'}\left|\frac{\partial}{\partial x}\right|\psi_{\vec{k}}\right\rangle\right|^2\Big/(E_{\vec{k}'}-E_{\vec{k}})^3\,,$$

$$\chi_2(\omega)=\frac{\pi}{\Omega}\sum_{\vec{k}\,(\mathrm{full}),\ \vec{k}'\,(\mathrm{empty})}\left|\left\langle\psi_{\vec{k}'}\left|\frac{e\hbar}{m\omega}\frac{\partial}{\partial x}\right|\psi_{\vec{k}}\right\rangle\right|^2 \qquad (7)$$

$$\times\,\delta(E_{\vec{k}'}-E_{\vec{k}}-\hbar\omega)\,.$$

Here the summation is over different conduction bands, valence bands, and the wave vectors of the entire Brillouin zone.

In our calculations, the electron wave function for the ith band is written as linear combination of atomic orbitals:

$$\psi_{\vec{k}}^{i}(r)=\sum_{n,\alpha}A(\vec{k},i,\alpha)e^{i\vec{k}\cdot\vec{R}_n}|\alpha,n\rangle\,. \qquad (8)$$

The $A(\vec{k},i,\alpha)$ can be obtained by solving the corresponding eigenequation of the Hamiltonian. We also need the matrix elements of the gradient between the atomic states. The fact that the polarization per atom in a given field is so much higher in a semiconductor than in the free atom suggests that the matrix elements between the wave functions at the same atom are much less important than the interatomic matrix elements. Harrison[17] has obtained an expression for the matrix elements of the gradient, assuming the forms, Eqs. (1) and (2), for the matrix elements of the Hamiltonian; that result is

$$\nabla_{\alpha\beta}=\langle\alpha|\vec{\nabla}|\beta\rangle=\eta_{\alpha\beta}\frac{\vec{d}}{d^2}\,. \qquad (9)$$

Here $\vec{d}$ is the position vector from the atom with the state $|\alpha\rangle$ to that with the state $|\beta\rangle$ and $\eta_{ss\sigma}$, $\eta_{sp\sigma}$, $\eta_{pp\sigma}$, $\eta_{pp\pi}$ are given by Eq. (2) as before.

The susceptibilities of cubic covalent semiconductors calculated using (7), (8), and (9) are shown in Table II and compared with the known experimental values. There is a difference of a factor of order 2 between the calculated results and experimental results, and in fact, scaling the predicted values by exactly 2 gives estimates with an rms error of only 14%. Thus the universal parameters describe very well the variation from material to material though they do not give good absolute values. It is reasonable to estimate the susceptibilities of materials, for which we do not have experimental values, by simply multiplying our results by 2. These values are also shown in Table II.

The error factor of 2–3 comes at least partly from the inaccuracy of the band structure in the nearest-neighbor-interaction approximation. For silicon the $\epsilon_2(\omega)$ vs ω curve calculated using Eqs. (7)–(9) is shown in Fig. 5, in comparison with the experimental curve. Because of the inaccuracy of the conduction bands, the peak E_1 has disappeared and E_2 is shifted from the observed 4.4 eV to a higher frequency near 6 eV. Shifting E_2 to a higher frequency makes the calculated $\chi_1(0)$ smaller.

The bond orbital model[10] replaces the electronic structure by a two-level system with an energy difference equal to E_2. This may be thought of as an approximation to the calculations carried out here. In that model also it was necessary to introduce a scale factor (γ^2) of order 2; however, that scale factor varied from 1.2 to 3.0 from the carbon row to the tin row. It now appears that the variation comes principally from the shift of the E_1 peak relative to the E_2 peak, an effect at least approximately included in our calculation here.

TABLE II. Susceptibility of covalent semiconductors.

Material	Experimental values	Values calculated with universal parameters	Estimated value, scaled by 2
C	0.37	0.19	0.37
BN	0.28	0.18	0.35
Si	0.87	0.38	0.76
AlP	0.56	0.30	0.59
Ge	1.19	0.51	1.01
GaAs	0.79	0.39	0.77
ZnSe	0.39	0.22	0.44
CuBr	0.27	0.13	0.26
Sn	1.83	0.69	1.38
InSb	1.17	0.48	0.95
CdTe	0.49	0.24	0.48
AgI	0.31	0.14	0.27
SiC	0.45	0.24	0.48
BP		0.25	0.51
BeS		0.19	0.39
BAs		0.29	0.57
BeSe		0.21	0.43
CuF		0.09	0.19
BeTe		0.24	0.50
AlAs	0.64	0.33	0.66
GaP	0.64	0.33	0.66
ZnS	0.33	0.19	0.38
CuCl	0.37	0.12	0.23
AlSb	0.73	0.41	0.81
InP	0.68	0.33	0.60
CdS	0.33	0.18	0.36
GaSb	1.07	0.48	0.96
InAs	0.90	0.38	0.76
ZnTe	0.50	0.26	0.51
CuI	0.36	0.15	0.31

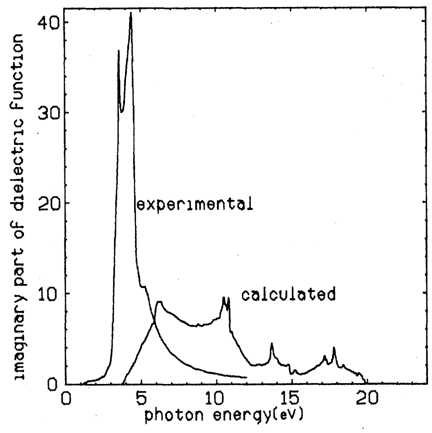


FIG. 5. Experimental and calculated frequency dependence of the imaginary part of the dielectric function for silicon. The experimental one was from Phillipp and Ehrenreich (Ref. 18). The calculated one was obtained using the hexagonal Brillouin zone and universal parameters.

A detailed analysis of the spectrum confirmed the expected result that the E_2 peak is dominated by transitions from the p-like valence bands to the p-like conduction bands, at an energy near the $\Gamma_{15}^c - \Gamma_{25}^v$ energy difference. It also suggested that the E_1 peak is dominated by transitions from the p-like valence bands to the s-like conduction bands, though at an energy higher than the $\Gamma_2^c - \Gamma_{25}^v$ difference which is to be associated with the E_0 threshold. Then the shift of the s-like bands, and therefore of the E_1 peak, to lower energy for the heavier semiconductors arises directly from the fact that the *sp* splitting does *not* vary from element to element as d^{-2} while the interatomic matrix elements do. These trends, which are most clearly seen in the bands given by Froyen and Harrison,[11] explain why the bond orbital approximation underestimates the increase in susceptibility with increasing atomic number.

We may also note that even in calculations of the susceptibility based upon more accurate bands, there is disagreement with the experiment by as much as a factor of 1.4.[19] It has been pointed

TABLE III. Photoelastic tensors: BOM values were calculated from Eq. (15) or (16) using experimental values for $4\pi\chi_{11}$. Tight-binding values were calculated by integrating Eq. (7) over the Brillouin zone before and after uniaxial strain is applied. All experimental values except *b*, *c*, were derived from p_{11} and p_{12} according to the following equations: $\frac{1}{3}(q_{1111}+2q_{1122})=-\frac{1}{3}\epsilon^2(p_{11}+p_{12})$, and $\frac{1}{2}(q_{1111}-2q_{1122})=\frac{1}{2}\epsilon^2(p_{11}-p_{12})$.

Material	$\left(\frac{q_{1111}+2q_{1122}}{3}\right)_{\text{BOM}}$	$\left(\frac{q_{1111}+2q_{1122}}{3}\right)_{\text{TB}}$	$\left(\frac{q_{1111}+2q_{1122}}{3}\right)_{\text{expt}}$	$\left(\frac{q_{1111}-q_{1122}}{2}\right)_{\text{BOM}}$	$\left(\frac{q_{1111}-q_{1122}}{2}\right)_{\text{TB}}$	$\left(\frac{q_{1111}-q_{1122}}{2}\right)_{\text{expt}}$
C	1.6	2.0	0.54[a] 4.0[a]	4.7	5.5	10[a] 4.5[a]
BN	0.4	1.1		3.5	4.2	
Si	3.7	10	4.3[b] 2.7[c]	11	8.7	8.6[b] 7.7[c]
AlP	−1.3	3.4		7.0	6.4	
Ge	5.0	30	63[d] 36[e]	15	−0.5	9.0[d] 3.3[e]
GaAs	−1.2	9.7	11.8[f] 18[g]	9.9	5.5	3.9[f] 1.5[g]
ZnSe	−3.9	0.3	2.0[h]	4.9	4.5	1.7–5.1[f]
CuBr	−4.0	−1.3	−3.8[f]	3.4	3.2	1.4[f]
Sn	7.7	110		23	55	
InSb	−3.3	18		14.7	5.5	
CdTe	−6.5	0.5		6.2	5.4	
AgI	−4.8	−1.6		3.9	3.6	
SiC	1.4	2.7		5.7	6.2	
BP	1.6	3.1		6.4	6.7	
BeS	−2.2	1.0		4.9	4.5	
BAs	2.0	4.0		7.1	6.7	
BeSe	−2.3	0.6		5.4	5.3	
CuF	−2.6	−1.0		2.4	2.3	
BeTe	−2.6	0.8		6.2	5.9	
AlAs	−1.0	5.1		8.1	6.7	
GaP	−1.5	5.7	26[f]	8.1	3.6	5.7[f]
ZnS	−3.3	0	−0.64[f]	4.2	4	1.4[f]
CuCl	−5.5	−1.9	−8.9[i]	4.7	4.4	2.2[i]
AlSb	−0.8	8.1		9.2	5.9	
InP	−3.0	5.3		8.6	6.6	
CdS	−4.0	−0.6		4.2	3.9	
GaSb	−1.1	19		13	3.6	
InAs	−3.3	9.1		11	6.7	
ZnTe	−4.8	1.4		6.3	5.4	
CdI	−5.2	−1.25	−4.6[i]	4.5	4.1	2.1[i]

[a] Reference 22, $\lambda = 0.59\mu$.

[b] Reference 21, $\lambda = 1.152\mu$.

[c] Reference 21, $\lambda = 3.391\mu$.

[d] Reference 22, $\lambda = 10.6\mu$. Values for Ge were changed in sign from Ref. 22 to accord with our prediction and with Ref. e since the original Ref. 24 gave no signs.

[e] Reference 22, $\lambda = 0.34\mu$.

[f] Reference 23, $\lambda = \infty$.

[g] Reference 23, $\lambda = 0.115\mu$.

[h] Reference 23, $\lambda = 0.0633\mu$.

[i] Reference 22, $\lambda = 0.63\mu$.

out[20] that the electron-hole interaction which is not included in one-electron calculations may play an important role.

VI. PHOTOELASTIC TENSOR

Since the calculation of susceptibility can be carried out for crystals under uniaxial strain, we can directly calculate the photoelastic tensor. This tensor is defined by[21]

$$\delta\epsilon_{ij}=\sum_{kl} q_{ijkl}e_{kl}\,, \tag{10}$$

where $\delta\epsilon_{ij}$ is the change in the dielectric tensor due to the strain e_{kl}.

In the cubic semiconductors, there are two independent nonvanishing coefficients, q_{1111} and q_{1122}. Because we can use the quadrangular Brillouin zone even for the cubic semiconductors in which a uniaxial strain is applied, it is straightforward to calculate the q_{1111} and q_{1122} by calculating the susceptibility tensor before and after such a strain is applied; we used a strain of $e_{33}=0.05$. It would seem that a calculation of $\delta\chi_{ij}/\chi_{ij}$ is more reliable than $\delta\chi_{ij}$ directly. Correspondingly, we scaled each calculated $\delta\epsilon_{ij}=4\pi\delta\chi_{ij}$ by the ratio of the experimental to the calculated susceptibility. The calculated results for $\frac{1}{3}(q_{1111}+2q_{1122})$ and $\frac{1}{2}(q_{1111}-q_{1122})$ appropriate to isotropic and volume-conserving strains are listed in Table III, along with the available experimental values.

There are not very extensive data for comparison and not so consistent values where more than one measurement exists. One might say that our predictions of an experimental value are about as close as the value of an earlier measurement.

We have also estimated the photoelastic constant using the more approximate bond orbital model. In that model the susceptibility may be expressed for a cubic semiconductor as the function of distance d between nearest-neighbor atoms as indicated in Sec. V,[10,25]

$$\chi=Ne^2\gamma^2d^2\alpha_c^3/(12V_2)\,. \tag{11}$$

Here N is the electron density, $V_2=2.16\hbar^2/md^2$ is the covalent energy, and α_c is the covalency

$$\alpha_c=V_2/(V_2^2+V_3^2)^{1/2} \tag{12}$$

with the polar energy $V_3=(\epsilon_p^c-\epsilon_p^a)/2$ independent of d. Under a uniform compression, the nearest-neighbor distance d changes, and along with it N and V_2. By differentiation we obtain

$$\frac{d}{\chi}\frac{\partial\chi}{\partial d}=6\alpha_c^2-5 \tag{13}$$

but also

$$\frac{\Delta\chi}{\chi}=\frac{\Delta\epsilon_{11}}{4\pi\chi}=\frac{1}{4\pi\chi}(q_{1111}+2q_{1122})\frac{\Delta d}{d}\,. \tag{14}$$

We obtain immediately

$$\frac{q_{1111}+2q_{1122}}{3\times 4\pi\chi_1}=\tfrac{1}{3}(6\alpha_c^2-5)\,. \tag{15}$$

Under a strain $e_{11}=-e_{22}$, and other strains zero, d is not changed to first order in the strain, nor are therefore V_2, α_c, or N. However, $d^2/3$ in Eq. (11) becomes d_x^2 for fields and polarization in the x direction. Thus

$$\Delta\chi_{11}/\chi_{11}=2e_{11}$$

and since $\Delta\chi_{11}/\chi_{11}=(1/4\pi\chi_{11})(q_{1111}-q_{1122})e_{11}$, we have

$$\frac{q_{1111}-q_{1122}}{4\pi\chi_{11}\times 2}=1\,. \tag{16}$$

These bond-orbital-model results, Eqs. (15) and (16), are also listed in Table III.

As predictions they are less accurate than the full theory but the simple formulas predict the principal trends. The volume-dependent coefficient given in Eq. (15) suggests that $(q_{1111}+2q_{1122})/12\pi\chi_1$ should equal $\frac{1}{3}$ for the homopolar semiconductor; the average of the experimental values for C, Si, and Ge are 0.48, 0.31, and 3.3, a significant discrepancy only for Ge. Equation (15) suggests that the coefficient should drop as the covalency decreases and indeed the averages of the experimental values for Ge, GaAs, ZnSe, and CuBr are 3.3, 1.5, 0.41, and −1.1. However, the formulas overestimate the trend; they would suggest negative values for almost all compound semiconductors. The volume-conserving coefficient is suggested to be unity, independent of both covalency and of row in the Periodic Table. The experimental values for Ge, GaAs, ZnSe, and CuBr are 0.41, 0.27, 0.69, and 0.41, respectively. For C, Si, and Ge they are 1.5, 0.75, and 0.41. As for many properties most trends and general magnitudes are correctly given by the simple theory with universal parameters. However, significant improvement comes from the full calculation, even if universal parameters are again used.

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