degenerate quickly into phonons $\hbar\omega \leq 2\Delta$ and only then are they long enough lived to be emitted into the Ge. This indicates that we have succeeded in generating milliwatts of phonon power over a very restricted spectrum and have detected only a small portion (the upper cutoff region) of the distribution which makes the system effectively a monochromatic source of phonons. We have observed scattering of these modes by the hydrogenic-like levels of Sb in Ge and the coupling obeys the symmetry restrictions. We believe that we have seen two types of scattering: (1) a resonance absorption indicated by the resonance peak, and (2) inelastic scattering manifested by a step in the background of the absorption curve, both structures occurring at a stress equivalent to a splitting of 2Δ.

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Calculation of Energy-Band Pressure Coefficients from the Dielectric Theory of the Chemical Bond*

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The dielectric theory of the chemical bond has been extended to calculate pressure coefficients of interband energy differences in acceptable agreement with experiment. Some improvements in Van Vechten's prescriptions are suggested by these new, more stringent tests. An approximate empirical rule for pressure coefficients is confirmed, and deviations from it predicted.

Van Vechten has recently proposed[1] a general model for tetrahedrally coordinated A^NB^{8-N} compounds which is based on Phillips's[2] spectroscopic theory of electronegativity differences and appears to yield good agreement between predicted energy-band separations and experimental results. In this Letter we extend this model to calculate the expected pressure dependences of three direct and two indirect energy gaps in nineteen group IV, group III-V, and group II-VI semiconductors. With a few exceptions which will be discussed in detail, we have adopted Van Vechten's prescriptions for these energy gaps and have avoided adjusting his numerical values for parameters, so that our comparison of calculated with measured pressure coefficients may provide a new test for his model.

A brief summary of Van Vechten's prescriptions follows:

(1) A direct interband energy separation E_i in a compound neither of whose elements possesses core states (in practice, d states) close in energy to the valence-band energies is given by

$$E_i = E_{h,i}[1+(C/E_{h,i})^2]^{1/2}, \qquad (1)$$

where $E_{h,i}$, the homopolar gap, is assumed to be a function of nearest-neighbor distance d only and to be given by[3]

$$E_{h,i} \propto d^{s_i}. \qquad (2)$$

Indeed, the homopolar part of any energy separation is assumed to scale with distance in this way. C represents the change in gap produced by the antisymmetric potential in a binary compound, and is assumed to be independent of the direct gap under consideration.

In calculations, experimental determinations of $E_{h,i}$ for two group-IV elements ($C=0$) give s_i and therefore $E_{h,i}$ for the other materials. C is obtained from the real, static, electronic dielectric constant of the compound under consideration from

$$\epsilon_0 = 1 + DA(\hbar\omega_p)^2/(E_h{}^2 + C^2). \tag{3}$$

In this formula, $\omega_p{}^2 = 4\pi N e^2/m$ with $N = 4\times$ (atomic density). E_h is the isotropic homopolar gap of the Penn model,[4] which is assumed to scale[3] as d^s. The factor A is equal to $1-(E_g/4E_\mathrm{F}) + \frac{1}{3}(E_g/4E_\mathrm{F})^2$, where $E_g{}^2 = E_h{}^2 + C^2$ and E_F is the free-electron Fermi energy for 4 electrons per atomic volume. Generally, A is about 0.9. The factor D is a correction for d-core effects[1] which will be discussed below.

(2) The effect of core states (here d states), near in energy to the valence-band bonding states, on interband energy differences is introduced through the expression

$$E_i = [E_{h,i} - (D_\mathrm{av} - 1)\Delta E_i][1 + (C/E_{h,i})^2]^{1/2}. \tag{4}$$

For our purposes, only the direct gaps E_0 and E_1 are considered; E_0 $[\Gamma_{25'}(\Gamma_{15}) \rightarrow \Gamma_{2'}(\Gamma_1)]$ and E_1 $[L_{3'}(L_3) \rightarrow L_1]$ involve s-like conduction-band states which are the ones assumed to be most affected by the d states. In expression (4), ΔE_0 and ΔE_1 scale only as the nearest-neighbor distance and are determined by fit to experiment on group-IV elements. D_av is a weighted average of factors D for skew compounds[16] and is equal to D for atoms from the same row. The values of D are determined in principle from the ratio of the effective plasma frequency to the free-electron value and are tabulated in Table IV of Ref. 1(a).

(3) The absolute value of the energy of the top of the valence band at $\vec{k}=0$ ($\Gamma_{25'}$ or Γ_{15}) is given by the negative of the ionization potential I:

$$I = I_h[1 + (C/L_h)^2]^{1/2}, \tag{5}$$

where I_h is the homopolar contribution to I.

(4) The splitting of the X_1-X_3 conduction-band states in heteropolar crystals is assumed to be a linear function of C only, viz. $2\Delta X = 0.142C$.

(5) The absolute value of the maximum valence-band energy at the X point X_4 (X_5) is argued to be a property of the rows only, and specifically, independent of the value of the "antisymmetric gap" C. Thus

$$E_{X_4} = E_{X_4}(\mathrm{Si})[(d_A d_B)^{1/2}/d_\mathrm{Si}]^{s_j}, \tag{6}$$

where $j = X_4$ and d_A, d_B, and d_Si are the covalent radii[1] for the two elements of the compound and for silicon, respectively. We prefer to modify the model and describe E_{X_4} by an expression similar to that in Eq. (1). Thus

$$E_{X_4} = E_{X_4,h}[1 + (C/E_{X_4,h})^2]^{1/2}, \tag{7}$$

where

$$E_{X_4,h} \propto d^{s_j}, \tag{8}$$

since this postulate[3] is more consistent with the overall model than is Eq. (6). In principle, atmospheric pressure band structures might be supposed to differentiate between prescriptions (6) and (7). The result is that prescription (7) rather than (6) leads to somewhat better agreement with experiment at atmospheric pressure; however, since $(C/E_{X_4,h})$ is roughly $\frac{1}{3}$ in the crystals tested, this comparison is not very good for differentiating between them. We shall see later that a comparison with experiment of calculated pressure coefficients, which involves making a choice between Eqs. (6) and (7), leads to a more critical test.

(6) The energy of the $L_{3'}$ (L_3) valence-band state below $\Gamma_{25'}$ (Γ_{15}) is set equal to a constant fraction t of the energy separating $\Gamma_{25'}$ and X_4. Van Vechten arbitrarily set $t=0.5$. However, we shall set $t=0.4$ since Zallen and Paul found that under pressure the relative shifts of $L_{3'}$ and X_4 with respect to $\Gamma_{25'}$ were in this ratio.[5] This somewhat less arbitrary assumption actually leads to better indirect gaps at atmospheric pressure. Thus the pressure dependence of $E_{L_{3'}}$ is fixed by Eq. (5) plus Eq. (7). The choice of t only affects the calculated coefficients for Γ to L transitions.

The pressure coefficients of the ionization potential, the absolute energy of the X_4 valence-band level, and the direct and indirect gaps are simply derived from Eqs. (5), (7), and (4). The direct-gap pressure coefficients are given, from

(4), by

$$\frac{dE_i}{dP}=[1+(C/E_{h,i})^2]^{1/2}\left[\frac{dE_{h,i}}{dP}-\Delta E_i\frac{d(D_{\rm av}-1)}{dP}-(D_{\rm av}-1)\frac{d\Delta E_i}{dP}\right]+\left[\frac{E_i}{1+(E_{h,i}/C)^2}\right]\left[\frac{1}{C}\frac{dC}{dP}-\frac{1}{E_{h,i}}\frac{dE_{h,i}}{dP}\right]. \tag{9}$$

The pressure coefficients of the indirect gaps follow by a suitable combination of the pressure coefficients of the direct gaps and of the absolute energies of the $\Gamma_{25'}$ (Γ_{15}) and X_4 levels. In Eq. (9), the atmospheric pressure values of C, E_i, $E_{h,i}$, ΔE_i, and $D_{\rm av}$ for each crystal are taken from Van Vechten's prescriptions as described by Eq. (1)-(5). E_{X_4} is taken from Eq. (7). The Van Vechten model, however, does not include the variation with nearest-neighbor distance of $D_{\rm av}$, and for III-V and II-VI compounds, it is not possible to extract the variation with distance of C in the manner described for materials in the NaCl structure.[1]

Van Vechten introduced the correction term $(D_{\rm av}-1)\Delta E_i$ into Eq. (4) to take account of the effect of d-core states on valence-conduction-band transition energies. His arguments are based on an increase in the oscillator strengths for valence-conduction-band transitions, caused by the negative terms in the f-sum rule associated with valence-band–d-core transitions. It is evident that the valence-conduction interband energies will be affected by the presence of d-core states not too distant in energy from the valence band, and therefore with a charge distribution overlapping that of the valence states to some extent. Such an effect may be differentiated from the changes in interband energies produced by differences among compounds of $E_{h,i}$ and C [see Eqs. (1), (2), and (4)]. Thus we shall write as the correction term for the compound $A^N B^{8-N}$, $N \leqslant 4$,

$$(D_{\rm av}-1)\Delta E_i \propto \Delta E_i d^y[\varphi_A R_A(1-f)^x+\varphi_B R_B(1+f)^x], \tag{10}$$

where f is the ionicity.[2] The factor ΔE_i recognizes that the correction will depend on the transition considered. The factor d^y recognizes that there will very likely be a dependence on lattice constant, assumed to be a simple power law on a par with Eqs. (2) and (8). The factors R_A and R_B recognize that the effect will depend on the atomic d core involved. The factors $(1-f)^x$ and $(1+f)^x$ recognize that any such effect should depend on the redistribution of charge, $4f$ per atom, away from the ideal covalent distribution $f=0$. Finally, φ_A and φ_B are unity for atoms with d cores, and zero otherwise.

The perturbative effect of the d core will depend in some inverse way on the ionization potential of the outermost d electron, which increases sharply from left to right across the periodic table. Thus provided $\varphi_A=\varphi_B=1$, $A\neq B$, we have $R_A \gg R_B$ and for this case,

$$(D_{\rm av}-1)\Delta E_i \rightarrow \Delta E_i d^y R_A(1-f)^x. \tag{11}$$

R_A and R_B are assumed volume independent, and the pressure dependence of $D_{\rm av}-1$ is finally determined from that of f, which follows from the discussion of C in the next section. The parameters x and y are regarded as adjustable to fit the pressure coefficients. Van Vechten's expression for D can be reduced to a form very similar to (11), and indeed, since it does not involve f, we use it to determine D at atmospheric pressure.[6] However, we consider Eq. (11) a better point of departure for a consideration of volume coefficients.

Van Vechten pointed out that in ionic materials (i.e., $E_h=0$), $(r/C)dC/dr\approx 0$. This implies that the condition that the total energy be a minimum, which determines the equilibrium lattice constant, is equivalent to the condition that the mean ionic potential C be a maximum.[1a] We shall first assume $dC/dP=0$ as the simplest extrapolation, and then compare the resultant pressure coefficients, especially for the dielectric constants, with the available experimental values.

From fitting the pressure coefficient dE_0/dP of Ge, we obtain $y=13$, and this assumption, along with $dC/dP=0$ and the other assumptions regarding atmospheric pressure values of parameters, suggests that $x\approx 2.4$. However, values of x and y close to these give an adequate description of the experimental results, and we have not carried out an extensive optimization procedure.

The pressure coefficients of the direct and indirect gaps and of the refractive indices determined with these assumptions for $D_{\rm av}$ and C are shown in Table I. The agreement with experiment is good. Included in the right-hand columns

Table I. Ionicity, pressure coefficients, and compressibilities of several zinc-blende and wurtzite compounds.

Compounds	f	dE_o/dP 10^{-6}eVbar^{-1}		dE_1/dP 10^{-6}eVbar^{-1}		dE_2/dP 10^{-6}eVbar^{-1}		$dE_{\Gamma L}/dP$ 10^{-6}eVbar^{-1}		$dE_{\Gamma X}/dP$ 10^{-6}eVbar^{-1}		$d(\ln n)/dP$ 10^{-6}bar^{-1}		dI/dP 10^{-6}eVbar^{-}	K 10^{-6}bar^{-1}
		Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.		
Si	0	3.7	5.0$(E')_o$	2.7		3.6	3	1.2		-0.1	-1.5	-0.3±0.05	-0.3	2.3	1.02
Ge	0	14.3	14.2	7.1	7.5	4.4	5.5	5.4	5	-0.1	-1.5	-1.0±0.2	-0.7(-1.0)	2.9	1.33
GaSb	0.261	14.7	14.7	6.6	7.5	4.0	6	4.8	5	-0.6	-	-0.8 "		3.1	1.77
GaAs	0.310	11.0	10.7-11.7	4.5	5.0	3.6		2.8		-0.8		-0.5±0.2	-0.7±0.1	2.5	1.34
InSb	0.321	15.8	15.5-17.6	7.6	8.5	4.3	6	5.5		-0.9		-1.1 "		3.3	2.20
GaP	0.328	9.2	10.5±1.6	4.6	5.8	3.2		2.8		-0.8	-1.1	-0.3 "		2.1	1.13
InAs	0.357	12.2	9.6-10.8	7.5	7.0	3.8		6.0		-0.1		-0.7 "		2.9	1.72
InP	0.421	9.5	8.5	4.8		3.0		3.4		-1.0		-0.4 "		2.3	1.38
AlSb	0.426	13.5	10 ±2[a]	7.0		3.4		2.5		-1.0	-1.5	-0.5 "		2.8	1.69
GaN	0.43	5.3	4.2	2.3		2.1		1.2		-0.7		-0.05±0.1		1.0	0.5
ZnTe	0.610	8.1	7	3.7		3.3		1.7		-1.7		0.01 "		2.7	2.00
ZnS	0.623	7.2	6.5±1	3.5		3.0		1.7		-1.7		0.05±0.1	-0.1	2.2	1.39
ZnSe	0.630	7.1	7	4.0		3.3		2.0		-1.8	-2.0	0.07 "		2.3	1.70
CdTe	0.668	8.1	8	3.9		3.1		1.9		-1.9		0.1 "		2.9	2.36
CdS	0.69	6.1	4.5-5	3.0		1.8		1.8		-2.3		0.05 "		2.0	1.53
CdSe	0.70	6.9		3.2		2.7		1.9		-1.7		0.05 "		2.3	1.86
HgTe	0.65	12.0	14 ± 1.5	5.4		3.4									2.40
HgSe	0.68	13.0		5.9		3.9									2.54
HgS	0.79	10.4		3.2		3.8									2.67
Error Estimate		±1		±1		±1		±1.5		±1.5				±1	

[a] Uniaxial stress measurement.

are the theoretical variations of the ionization potentials with pressure and of the compressibilities, which allow the reader to find the deformation potential of any of the band edges. Several details may be noted.

(a) At least for the conduction band of Ge, the deduced volume deformation potential is reasonable. From Table I, the calculated absolute shift of L_1 is $+2.5\times10^{-6}$ eV bar^{-1}, which leads to a deformation potential $E_1 = -1.9$ eV $= \Xi_d + \frac{1}{3}\Xi_u$. From piezoresistance measurements, $\Xi_u = 18$ eV whence $\Xi_d = -7.9$ eV $= -0.44\Xi_u$. Paige[7] has suggested that the best estimate of Ξ_d at 77°K is $\Xi_d = -0.38\Xi_u$, so that our calculations give acceptable values for the deformation of the band edges. We hasten to add that the test is not a very sensitive one, since Paige's best estimate of Ξ_d/Ξ_u with = 18 eV corresponds to an absolute shift of L_1 of $+1.1\times10^{-6}$ eV bar^{-1}.

(b) The pressure coefficients of the $\Gamma_{25'} \rightarrow X_1$ transition are notable. Experimentally, these are usually close to -1.5×10^{-6} eV bar^{-1}. Using the Van Vechten prescription for E_{X_4}, we can derive values of typically $+2\times10^{-6}$ eV bar^{-1}. On the other hand, redefining E_{X_4} as we have done [Eq. (7)] results in the improved agreement with experiment as illustrated.

(c) Where a test is possible, the agreement between calculated and measured pressure coefficients of the refractive index is good. It is notable, however, that the agreement is much worsened if the effect of changes in $D_{\rm av}$ is omitted from Eq. (3). For example, Eq. (3) yields for $d(\ln n)/dP$ of GaAs, with the $D_{\rm av}$ variation omitted, a coefficient of -0.095 bar^{-1}, considerably different from the experimental value of -0.7 bar^{-1}.[8]

(d) The overall agreement of calculated with experimental coefficients would appear to justify the assumption that $dC/dP = 0$. This point may be further scrutinized in the following two ways. (i) It is found that the coefficients for the direct interband transitions are quite insensitive to dC/dP. However, a relatively small variation of C with P, for example, $(1/C)dC/dP = K/3$—which corresponds to setting $C \propto d^{-1}$—would eliminate the difference between calculation and experiment for the $d(\ln n)/dP$ of GaAs and ZnSe, but would produce changes in dI/dP, dE_2/dP, and dE_{X_4}/dP leading to a positive, rather than the experimentally determined negative, coefficient for $X_1 - \Gamma_{15}$. We conclude that either the variation of C with P is close to zero, or that something is wrong with the original assumptions regarding the prescriptions for E_{X_4} and I. (ii) We saw earlier that the conduction-band splitting X_3-X_1 or $2\Delta X$ is 0.14 C. An infrared absorption peak in n-type GaP has been identified as due to transitions X_1 to X_3, and the pressure coefficient of the separation $2\Delta X$ measured as less than 1×10^{-6}

eV bar^{-1}. This yields $(1/C)dC/dP \approx 2.2\times 10^{-5}$ $\text{bar}^{-1} \approx 6(K/3)$. Such a variation of C would destroy the overall agreement shown in Table I. We conclude that the experimental error on the pressure coefficient of the GaP absorption was sufficient to be consistent with a much smaller variation of C, and/or that the assumption in Sec. (4) that the splitting $2\Delta X$ depends only on C is inaccurate.

(e) In order to calculate a pressure dependence for $D_{\text{av}}-1$, we were forced to use an expression for it somewhat changed from that of Van Vechten. In particular, this expression takes account of shifts in valence charge between ions and suggests quite different pressure coefficients (of say E_0) for compounds of nearly the same f but different d-core ionization energies; thus the predicted pressure dependences of E_0 for InP ($f = 0.421$) and AlSb ($f = 0.426$) are significantly different. Comparison of such predictions for the pressure coefficients with their experimental values may be useful in indicating the best form for such d-core corrections.

(f) A comment is in order on an empirical rule[9] for pressure coefficients, viz., that they be nearly equal for the same pair of states in all members of the germanium family. In practice this rule has been applied with good success to elucidate properties of the group IV and group III-V compounds, but it has often been an uncertain guide for II-VI compounds. From the table we see that, with the exception of Si, which has no d core, and GaN, the values of dE_0/dP for the group IV and group III-V compounds are all near to 12×10^{-6} eV bar^{-1}. On the other hand, the coefficients for the II-VI compounds, other than those of mercury, cluster around 8×10^{-6} eV bar^{-1} while the coefficients for the mercury chalcogenides are about 12×10^{-6} eV bar^{-1}. Similar remarks apply to E_1. There seems to be no monotonic trend of either pressure coefficients or deformation potentials with increasing f as has been sometimes asserted.[10] The present observations rationalize deviations which had been noted to be superimposed on the empirical rule, but which can be seen from Table I not to impair its usefulness in predicting band-structure distortions under pressure.

As we pointed out at the beginning, we have tinkered as little as possible with Van Vechten's prescriptions and numerical values for parameters, so that our comparison of calculated with experimental pressure coefficients might be a fair test of his model for tetrahedrally bonded compounds. Specifically, we have changed his prescription for E_{X_4} to a form more consistent with his prescriptions for other energies; we have altered the energy of $L_{3'}$ relative to those of Γ_{15} and X_4 to give a better fit to somewhat meager experimental advice; and we have developed a correction for the effect of d cores on interband transitions which permits the results of volume changes to be estimated. At the cost of adding only two new parameters to Van Vechten's theory we have been enabled to calculate any number (here 120) of pressure coefficients. The resultant overall agreement of calculation with experiment is sufficiently good to allow judicious extrapolation to hitherto unmeasured transitions and compounds. The demand of a fit to experimental pressure coefficients clarifies the necessity for a d-core correction term and suggests a preferred form for it which may be tested. The calculations raise questions regarding the volume dependence of the antisymmetric potential C and prescriptions for interband energies and splittings involving C. Finally, the results confirm the approximate validity of an empirical rule for pressure coefficients and rationalize deviations from it. However, useful as this extension of Van Vechten's model may be, both in affording an additional test of it and in providing extrapolation of calculated pressure coefficients to new transitions or new compounds, it is not construed by us to be necessarily the unique way of systematizing and extrapolating these coefficients.

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