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Estimation of bond-bending force constants in tetrahedral semiconductors and their variation with pressure obtained from spectroscopic data

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The bond-bending force constant k_θ of the Keating-Martin (KM) model for the elastic constants of tetrahedral semiconductors is related to the optical spectrum according to $k_\theta r^2 = 4(1-f_i)\Delta E_m$, where r is the bond length, f_i is the Phillips fraction of ionic character, and ΔE_m is the reduction in single-particle energy per valence electron resulting from the over-all band gap. As the energy to bend a directed orbital is unrelated to the energy of competing phases, there is no d-core dehybridization or bottom of the band correction. The above formula is accurate to the limit of the KM model when $f_i \leq 0.5$. For more ionic compounds, it seems that $k_\theta r^2 = 2\Delta U_t$, where ΔU_t is the change in internal energy per atom pair upon transformation to the NaCl structure. The observed variation of k_θ with pressure is indeed equal to the value found by differentiation of the above formula. An approximate relation for Keating's third-order elastic parameter is derived: $\epsilon = -3k_\theta/2r$.

I. INTRODUCTION

It may be said that the s-p^3-hybridized covalently bonded solids, which occur in the diamond, zinc-blende, wurtzite, and chalcopyrite structures, are characterized by two properties. One would be the noncentral or bond-bending interatomic forces which are required to stabilize these loosely packed structures against shear.[1,2] The other would be the band gap around the Jones zone (the first four Brillouin zones, which exactly contain all the valence electrons) that accounts for the semiconducting properties and the interband optical spectra.[3] The purpose of this paper is to examine quantitatively the relation between these two properties.

In a valence-force-field model developed by Keating for the diamond structure[1] and extended by Martin to the zinc-blende structure,[2] the total distortion energy of each unit cell is

$$U = \frac{1}{2}\sum_{i=1}^{4} k_r(\Delta r_i)^2 + \sum_{s=1}^{2}\left[\frac{1}{2}\sum_{i,j>i} k_\theta^s (r\Delta\theta_{ij}^s)^2 + \sum_{i,j\neq i} k_{r\theta}^{\prime s}(\Delta r_i^s)(r\Delta\theta_{ij}^{s\prime}) + \sum_{i,j>i} k_{rr}^s(\Delta r_i^s)(\Delta r_j^s)\right]. \qquad (1)$$

In Eq. (1) we recognize that the bond-bending force constants k_θ^s may be different for the two atoms in the unit cell if these are not the same element. The two atoms are denoted by $s = 1, 2$, and the bonds about each atom are denoted by $i, j = 1, \ldots, 4$; r is the equilibrium bond length, Δr_i^s is the scalar change in length of bond i about atom s, and $\Delta\theta_{ij}^s$ is the change in angle formed by bonds i and j about atom s. Only the bonds about one atom are included in the first term of Eq. (1) in order to avoid double counting in the sum over unit cells.

In this paper only the bond-bending force constants k_θ of Eq. (1) will be considered. Moreover, when elastic constants are analyzed or when only long-wavelength acoustic or optic modes are considered, one can obtain only the sum of the force constants for the two atoms. Thus, Martin has determined the average bond-bending force constant

$$k_\theta = \tfrac{1}{2}(k_\theta^1 + k_\theta^2) \qquad (2)$$

for a number of diamond and zinc-blende structure semiconductors,[2] but the author is not aware of any determination of the difference $k_\theta^1 - k_\theta^2$. Martin found it convenient to tabulate his data in terms of two simplified parameters, a bond-stretching force constant α and a bond-bending force constant β. The relation between β and k_θ is[2]

$$k_\theta = \tfrac{2}{3}\beta. \qquad (3)$$

II. THEORY

Note that $k_\theta r^2$ is an energy; its value in Si is 3.16 eV according to Martin's evaluation. However, the Keating-Martin (KM) model is only approximate and an internal consistency check [see Table II and Eq. (16) of Ref. 2] indicates an uncertainty in such values of from 10 to 20%, depending upon the compound.

One may seek to relate the energy $k_\theta r^2$ to the covalent or directional part of the cohesive energy of the crystal. Let us denote this covalent energy per unit cell E_{cov}, and assume that the portion of the distortion energy due solely to bond bending

$$U(\Delta\theta_{ij}, \Delta r = 0) = E_{\text{cov}} \sum_{s=1}^{2} \sum_{i,j>i}^{4} [1 - \cos(\Delta\theta_{ij}^{s})]\,. \tag{4}$$

Keeping only the first term in the expansion of $1 - \cos(\Delta\theta)$ and comparing Eq. (4) with Eqs. (1) and (2), we find

$$k_\theta r^2 = \tfrac{1}{2} E_{\text{cov}}\,, \tag{5}$$

the covalent energy per atom.

Now it is important to determine what is the reference from which E_{cov} is measured. Readers with a chemical background will probably note that $k_\theta r^2 = 3.16$ eV in Si is of the general magnitude of the heat of atomization per atom,[4] $\Delta H_a = 4.68$ eV. However, this discrepancy is greater than could be ascribed to the uncertainties in the KM model. Moreover, as is illustrated in Table I, the chemical trends in E_{cov}, say in the series C, Si, Ge, and Sn, do not follow ΔH_a. It is also evident that the trends in E_{cov} do not follow the difference in total energy between the covalent phase of these materials and the competing metallic solid or metallic liquid phases. This author has previously denoted this difference in net energy per bond as E_b. E_{cov} in Ge is almost as great as in Si whereas $E_b(\text{Ge}) = 0.60 E_b(\text{Si})$, and E_{cov} in α-Sn is still fairly large whereas $E_b(\alpha\text{-Sn}) = 0$ above room temperature, where the metallic β-Sn phase is stable.

One must conclude that $k_\theta r^2$ and E_{cov} in the covalent solid are unrelated to the actual difference in energy of the competing metallic phases, or of the vapor phase. Indeed, these phases are separated by first-order transformations. But $k_\theta r^2$ and E_{cov} are proportional to the work done in bending the bonds in the covalent phase by a small angle. They must be related to that portion of the band gap around the Jones zone which results from the covalent or homopolar components of the crystal potential[6,7] because both characterize the s-p^3 covalent bond.

To resolve this paradox, we recall that the decrease in the single-particle energy of the covalent solid relative to a free-electron gas due solely to the opening of the band gap,[8] ΔE_m, is much larger than the net difference in total energy between the covalent solid and the actual competing metallic phase.[9,10] At least two factors are important in this regard. There is a difference in the "bottom of the band" energy which implies[9]

$$E_b = \tfrac{1}{8} \Delta E_m \tag{6}$$

if the second factor, d-core dehybridization,[10,11] is not operative. The d-core dehybridization effect results from the fact that atomic s and p orbitals must be hybridized, and thus made degenerate, by the crystal potential in order to form the s-p^3 hybridized covalent bonds, but the occupation of d-core states in the ion cores of ele-

TABLE I. Empirical values of $k_\theta r^2$ compared with theory [Eq. (10)] and with two alternate hypotheses, the heat of atomization ΔH_a and the internal energy of the covalent phase relative to the high-pressure metallic phase, E_b. The empirical value for α-Sn is from Ref. 13; all other values are taken from Ref. 2. The Phillips fraction of ionic characters f_i is given in the final column.

Crystal	$k_\theta r^2 \equiv \frac{1}{2}E_{\text{cov}}$ (eV)	$4(1-f_i)\Delta E_m$ (eV)	ΔH_a/atom (eV)	$16(1-f_i)E_b$ (eV)	f_i
C	8.45	9.47	7.37	9.47	0
Si	3.16	2.97	4.68	2.97	0
Ge	2.84	2.68	3.87	1.79	0
α-Sn	2.16	1.81	3.15	0.0	0
AlSb	1.98	1.84	3.48	1.63	0.45
GaP	2.42	2.71	3.58	2.34	0.33
GaAs	2.23	2.46	3.36	1.86	0.31
GaSb	2.11	2.00	3.00	1.32	0.26
InP	1.68	2.12	3.35	1.66	0.42
InAs	1.56	2.03	3.13	1.13	0.36
InSb	1.56	1.68	2.78	0.80	0.32
ZnS	1.09	2.44	3.18	2.12	0.62
ZnSe	1.06	2.14	2.70	1.85	0.63
ZnTe	1.29	1.78	2.46	1.53	0.61
CdTe	0.80	1.39	2.08	1.12	0.72
CuCl	0.23	2.24	3.08	2.11	0.75

ments occurring after Ca in the Periodic Table effects an increase in the energy difference between atomic s and p orbitals.[10-12] Thus, because the s-like wave functions penetrate the rather extended d-core states more effectively than do p-like wave functions, the s orbitals are reduced in energy relative to the p orbitals by the introduction of a d core. This decreases the net energy difference to the metallic phase by a factor D such that

$$E_b = \tfrac{1}{8}\,\Delta E_m D\,, \tag{7}$$

where D has been expressed in terms of the critical point structure of the optical spectra in previous publications.[5,11] $D=0$ for α-Sn under the condition that it is in equilibrium with metallic β-Sn.

Now the energy involved in distorting the s-p^3 covalent bond once it is formed ought not to depend upon the energy expended in hybridizing the atomic orbitals or in changing the "bottom of the band" energy between competing phases because these factors are not altered by small variations in bond angle. (Recall that no change in bond length is involved in the $k_\theta r^2$ term.) Therefore, $k_\theta r^2$ ought to be simply related to ΔE_m without the factors in Eqs. (6) and (7), which are required to determine the net energy difference between phases. Thus, $\Delta E_m \neq 0$ for α-Sn under the conditions that it is in equilibrium with metallic β-Sn and $k_\theta r^2$ is fairly large.[13]

In the case of diamond, Si, Ge, and α-Sn, for which the crystal potential is totally homopolar (covalent) so that the Phillips fraction of ionic character[7,14] $f_i=0$, we should expect

$$E_{\text{cov}} \equiv 2k_\theta r^2 = 8\Delta E_m\,, \tag{8}$$

where ΔE_m is the single-particle energy per electron, *because there are eight valence electrons per unit cell in the diamond structure*. The relation between ΔE_m and the *average* band gap E_g across the Jones zone,[5-9,14] which is determined from the optical dielectric constant of the solid,[6] has been shown to be[8]

$$\Delta E_m = -E_F\{3B^2[1+\ln(\tfrac{1}{2}B)] - 4B^3\}\,, \tag{9}$$

where $B = E_g/4E_F$ and E_F is the Fermi energy per electron of eight valence electrons per unit cell. This theoretical estimate, which is derived solely from knowledge of the optical dielectric constant, is compared with the elastic constant data in Table I. The agreement is within the limits of the KM model.

In the case of partially ionic crystals, such as those occurring in the zinc-blende structure, a fraction f_i of the total average band gap across the Jones zone results from the heteropolar (ionic) components of the crystal potential.[5-9,14] Both E_g and ΔE_m have larger values than would obtain if only the homopolar (covalent) components of the crystal potential were operative. But the ionic interaction will not contribute to $k_\theta r^2$ because it is electrostatic in nature and thus produces only central forces. Therefore it seems reasonable to extend Eq. (8) as

$$\tfrac{1}{2}E_{\text{cov}} \equiv k_\theta r^2 = 4(1-f_i)\,\Delta E_m \tag{10}$$

for zinc-blende crystals with a Phillips fraction of ionic character f_i. [Recall that Martin found the ratio β/α to be proportional to $(1-f_i)$.] This estimate is compared with experiment in Table I, where we find that the agreement is again within the limits of the KM model for the III-V compounds. The III-V compunods are primarily covalent and have values of f_i less than 0.5. In the case of the more ionic II-VI compounds and CuCl, Eq. (10) seriously overestimates the bond-bending force constants.

III. HYPOTHESIS FOR MOST IONIC CASES

When considering the soft bond-bending force constants among the more ionic compounds, one will note that there is a critical ionicity $F_i = 0.785$ which divides the compounds that occur in one of the tetrahedral structures at zero pressure from those which occur in the rocksalt structure.[7,15,16] Three compounds, MgS, MgSe, and HgS, have an ionicity $f_i = F_i$ within the limit of experimental error and occur in both a tetrahedral structure and the rocksalt structure or, in the case of HgS, a slight distortion of it.[11] Moreover, some covalent properties, including the violation of the Cauchy relation for the elastic constants of a solid having only central interatomic forces as well as the decrease in the optical dielectric constant with pressure, extend to the less ionic compounts, $0.79 < f_i < 0.92$, in the rocksalt structure.[6] (Recall that the rocksalt structure does not maximize either the Madelung constant or the packing efficiency and that the most ionic compounds occur in the CsCl structure.) Therefore, one should conclude that octahedral covalent forces[17] are still appreciable in the less ionic compounds of the rocksalt structure. If so, then they must be appreciable in the rocksalt phase of these II-VI and I-VI compounds, which is attained at high pressure.[18] The competition between tetrahedral and octahedral covalent bonding should influence this phase boundary.

Whereas we concluded that the energy difference between the s-p^3 covalent phase and the metallic or vapor phases was irrelevant to $k_\theta r^2$, it seems that competition between s-p^3 and octahedral covalent bonding should be relevant because this

TABLE II. Hypothesis that the competition between tetrahedral and octahedral covalent bonding determine the soft bond-bending force constants in the most ionic s-p^3 crystals [Eq. (11)] tested against experimental data.

Crystal	$k_\theta r^2$ (eV)	$2P_t\Delta V_t \approx 2\Delta U_I$ (eV)
ZnS	1.09	1.14
ZnSe	1.06	1.12
ZnTe	1.29	1.10
CdTe	0.80	0.34
CuCl	0.23	0.34

competition is obviously affected by distortion of the bond angles. Therefore, let us see if for the II-VI compounds and CuCl, $k_\theta r^2$ is proportional to the difference in internal energy between the tetrahedral phase of these compounds and the rocksalt phase attained under pressure. Phillips has shown how to estimate this energy difference quite successfully.[18] In Table II we compare against experiment the formula

$$\tfrac{1}{2}E_{\text{cov}} \equiv k_\theta r^2 = 2\Delta U_I \ , \tag{11}$$

where $\Delta U_I = P_t \Delta V_t$ is the observed energy difference between the zinc-blende and rocksalt phases per atom pair at the critical pressure P_t of the transformation. (It is assumed that this value approximately equals the internal energy difference between these phases at zero pressure.)

Obviously the form of Eq. (11) causes our estimate of k_θ to tend to zero as f_i goes to F_i rather than as f_i goes to 1.0 as impled by Eq. (10) and as assumed by Martin. This allows us to account for the very soft bond-bending force constants in the Cu halides and in AgI. The significance of the constant of proportionality required to fit ZnS, ZnSe, and ZnTe is not yet clear, and CdTe seems to disagree with the corresponding estimate.

IV. PRESSURE DEPENDENCE OF k_θ: THIRD-ORDER FORCE CONSTANT ϵ

The elastic constants of crystals are known to vary when subjected to static strain. Therefore, all the interatomic force constants of the KM model, Eq. (1), are functions of the interatomic spacing $\vec{x}_{ij} = \vec{R}_i - \vec{R}_j$ between atoms i and j. The derivatives of the elastic constants with respect to interatomic spacing are expressed as third-order elastic and force constants, respectively. The relations appropriate to the KM model are given by Keating.[19]

Here we shall only consider the derivative of k_θ or β, with hydrostatic strain, which Keating expressed as ϵ,

$$\epsilon = a_0 \frac{\partial \beta}{\partial u_r} = \tfrac{3}{2} a_0 \ \frac{\partial k_\theta}{\partial u_r} \ , \tag{12}$$

where $a_0 = \frac{1}{4}a = r/\sqrt{3}$ is the dimension of the unit cell (a is the usual lattice constant) and

$$u_r = x_{ij}^2 - 3a_0^2 \ . \tag{13}$$

As we consider only hydrostatic strain, we may equate $\vec{x}_{ij}$ with r and simplify Eq. (12) to

$$\epsilon = \frac{a_0}{2r}\frac{\partial \beta}{\partial r} = \frac{3a_0}{4r}\frac{\partial k_\theta}{\partial r} \ . \tag{14}$$

We may take the derivative of Eq. (9) by noting that the variation of the optical dielectric constant in these crystals with pressure fits a scaling law derived in Ref. 6 such that

$$B(r) \cong B(r = r_0)(r_0/r)^{1/2} \ , \tag{15}$$

and, of course, $E_F \propto r^{-2}$ so that

$$\frac{d\Delta E_m}{dr} = -(-2E_F\{3B^2[1 + \ln(\tfrac{1}{2}B)] - 4B^3\} - \tfrac{1}{2}E_F(7B^2 - 12B^3))/r \ . \tag{16}$$

TABLE III. Keating's third-order elastic parameter ϵ, a measure of the derivative of k_θ with compression, compared against the theory of Eq. (10) and against a convenient approximation to that theory [Eq. (18)].

Crystal	Reference	ϵ_{expt} (10^{12} dyn/cm^2)	ϵ_{calc} (10^{12} dyn/cm^2)	ϵ_{calc}, Eq. (18) (10^{12} dyn/cm^2)
Si	19	−0.47	−0.561	−0.553
Ge	19	−0.48	−0.449	−0.442
GaAs	20	−0.41	−0.411	−0.407
InSb	21	−0.15	−0.187	−0.185
GaSb	22	−0.26	−0.264	−0.261
C	...	...	−6.255	−6.198
AlSb	...	...	−0.240	−0.238
GaP	...	...	−0.506	−0.501
InP	...	...	−0.317	−0.314
InAs	...	...	−0.279	−0.276

The second term in the heavy parentheses of Eq. (16) is opposite in sign and less than the first term by a factor which is approximately 4 for Si (Ref. 8) and does not vary greatly from one crystal to another. Therefore, a convenient approximation with an accuracy of about ± 20% is

$$\frac{d\Delta E_m}{dr} \cong -1.5\Delta E_m/r\ . \tag{17}$$

It follows that

$$\frac{r}{k_\theta}\ \frac{\partial k_\theta}{\partial r} = \frac{r}{\beta}\ \frac{\partial \beta}{\partial r} \cong -3.5 \tag{18}$$

with an accuracy of 10% so that

$$\cong -1.01\beta/r = -1.52k_\theta/r \tag{19}$$

with an accuracy of 10%.

The values of ϵ calculated with the present theory for k_θ and with and without the approximation of Eq. (17) are compared with experiment[19-22] in Table III. Again the agreement is within the limits of the KM model for IV-IV and III-V crystals. Because Eq. (10) was not accurate in predicting k_θ for II-VI and I-VII compounds, it seems unlikely that Eq. (19) should be accurate in predicting ϵ for those cases and they are not included in Table III.

The observed negative sign of ϵ implies that the bond-bending force constants become stronger as the crystal is compressed. According to the theory of Sec. II, this corresponds to the fact that the optical dielectric constant decreases and the average band gap increases with pressure.[6,15,23] If the hypothesis for the softness of k_θ in II-VI and I-VII crystals given in Sec. III is correct, then one would expect

$$\epsilon r/\beta \approx 0,\quad f_i > 0.6 \tag{20}$$

for those compounds because the relative internal energy of the competing octahedral covalent bonds, and therefore the value of ΔU_I, does not change significantly with compression. It appears that measurements of the third-order elastic constants[24] in the wurtzite crystal CdS support this conclusion.[25,26]

V. COMPARISON WITH MARTIN'S ANALYSIS

Martin discovered[2] the remarkable linear variation with Phillips ionicity of the ratio of bond-bending to bond-stretching force constants β/α. This linear relation extended from the totally covalent elements Si and Ge through the II-VI compounds almost to the critical ionicity F_i beyond which a tetrahedral structure cannot be attained at any pressure. Here we have found a straightforward explanation for the absolute magnitude of β and of $k_\theta r^2$ in all four diamond-type elements and a reasonable extrapolation of this theory which is successful in the III-V compounds. Therefore, whatever the effect which causes this extrapolation [Eq. (10)] to fail in the more ionic II-VI and I-VII compounds must also affect the bond-stretching force constant α.

TABLE IV. Predicted values of the Keating-Martin elastic parameters for cases where experimental data are lacking.

Crystal	$k_\theta r^2$ (eV)	β (N/m)	ϵ (10^{12} dyn/cm^2)	f_i
SiC	5.28	35.7	−1.92	0.18
BN	8.57	84.1	−5.37	0.26
BP	4.87	20.4	−1.04	0.01
BAs	4.24	15.9	−0.77	0.00
AlN	4.75	21.3	−1.13	0.45
AlP	2.72	7.82	−0.33	0.31
AlAs	2.54	6.77	−0.28	0.27
GaN	4.26	18.1	−0.93	0.50
InN	3.17	10.9	−0.51	0.57

The elastic constants of diamond do not fit Martin's empirical relation[2]; the β/α ratio is radically larger for C than for Si or Ge. Here we were successful in accounting for the magnitude of β in C as well as in Si and Ge. Note that all the crystals studied in Table I except C have approximately the same atomic volume, while that for C is radically less. One may conclude that the variation with nearest-neighbor distance is different for β than for α.

VI. CONCLUSION

A simple quantitative relation between the noncentral or covalent interatomic forces and the average band gap around the Jones zone of diamond-type crystals has been hypothesized and demonstrated. The relation is as accurate as an analysis in terms of first- and second-neighbor interactions can test. The extrapolation of this relation to partially ionic s-p^3 crystals succeeds for III-V compounds but becomes inaccurate for II-VI and I-VII compounds. A competition between tetrahedral and octahedral covalent bonding is a suggested cause for the failure of this extrapolation to most ionic cases.

In the cases of SiC and the III-V compounds for which empirical values are not known to the author, predicted values of the Keating-Martin elastic parameters are presented in Table IV.

Note added in proof. Because Eq. (4) contains no odd powers of $\Delta\theta_{ij}^s$, the present theory predicts[27] a simple relation between ϵ and another third-order force constant δ defined by Keating[19] as

$$\delta \equiv \tfrac{3}{2} a_0 \frac{\partial \beta}{\partial u_s},$$

where

$$u_s \equiv \vec{x}_{ij} \cdot \vec{x}_{jk} + a_0^2 .$$

This relation follows from simple geometry and is

$$\beta = -\tfrac{1}{2}\sqrt{3}\,\epsilon .$$

This relation is well satisfied by available data.[25]

Note added in proof. Some time after this paper was submitted, a letter on the subject of the second-order bond-bending force constants in these same materials appeared [W. A. Harrison and J. Christopher Phillips, Phys. Rev. Lett. 33, 410 (1974)]. The role played here by the spectroscopic factor ΔE_m is there served by the introduction of two empirically adjusted parameters denoted λ and S.

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