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Elastic properties of semiconductors studied by extended Hückel theory

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For thirty diamond- and zinc-blende-structure semiconductors, the elastic shear constant $(c_{11}-c_{12})/2$, polarity α_p, effective atomic charge Z^*, transfer parameter β, and transverse charge e_T^* are calculated from band-structure calculations based on the extended Hückel tight-binding method. The results are compared with previous theoretical calculations and experiment. It is found that improved agreement with experiment is obtained for $(c_{11}-c_{12})/2$ in comparison to a calculation based upon universal tight-binding parameters, which was already in rather good accord. For the effective charges, inclusion of nonorthogonalities in the Hückel theory increases their estimated values considerably and brings them into good agreement with experiment.

I. INTRODUCTION

Theoretical studies for the elastic properties of semiconductors have been made by many researchers, using, for example, a bond-orbital model (BOM),[1] band-structure calculations, and the "special-points" method,[2] a first-principles linear-combination-of-atomic-orbitals method,[3] pseudopotential methods within the local-density approximation,[4-6] the linear muffin-tin orbitals method,[7,8] and the extended Hückel tight-binding (XHTB) method.[9]

Very recently, Kitamura and Harrison[10] studied the elastic properties of semiconductors by calculating their band structures on the basis of a universal tight-binding parameters (UTBP) method. In this method, the effect of nonorthogonality between atomic basis states is included approximately in the energy calculations through the inclusion of the overlap repulsion. They found satisfactory agreement between experiment and the calculated results for the elastic stiffness constants and Kleinman internal displacement parameter, but good agreement was not obtained for the properties related to effective charges. They suspected that some of the discrepancies may have arisen from their failure to include nonorthogonality of the atomic basis states in the analysis.

As far as we know, the only study of the elastic properties by the XHTB band-structure calculation was for diamond by Watkins and Messmer.[9] In the present paper, we use the XHTB method, which was developed by Kitamura and Muramatsu to calculate band structures of complicated materials such as perovskite-type compounds KMF_3 (M=Mn, Fe, Co, Ni, Cu, and Zn)[11] and K_2PdCl_6,[12] to systematically study elastic properties for a large number of semiconductors. In principle, this XHTB method can be carried out if the crystal structure and lattice constant for a given material are known. One uses atomic calculations for obtaining numerical atomic basis states.

The purpose of the present work is not only to check the reliability of the XHTB method, but also to discuss the effect of nonorthogonality between atomic basis states in the XHTB method. In order to address the problem which arose in the UTBP method,[10] we could reformulate the UTBP method to include the effect of nonorthogonality between the atomic basis states. Here we use instead the XHTB method in which nonorthogonality between the atomic states is already taken into account.

In the present paper, we calculate the elastic shear constant $(c_{11}-c_{12})/2$, polarity α_p, effective atomic charge Z^*, transfer parameter β, and transverse charge e_T^* for thirty diamond- and zinc-blende-structure semiconductors, and make a comparison of these calculations with experiment for $(c_{11}-c_{12})/2$, transverse charge and the value of polarity with the ionicity defined by Phillips.[13,14] In the BOM proposed by Harrison,[1] which describes the electronic structures of semiconductors, there is a relation between the $(c_{11}-c_{12})/2$ and the bond length d, covalency α_c, and quantities λ and V_2^h defined in the BOM. Starting from this relation, we express the bulk modulus B in terms of d, λ, and V_2^h, and also the ratio of c_{12}/c_{11} in terms of α_c alone. These parameters are evaluated within the framework of the XHTB method. These semiempirical expressions prove reasonable; particularly for the bulk modulus B, good agreement between experiment and prediction is found, and the expression for c_{12}/c_{11} accounts for its experimental trends with respect to a variation of α_c.

Before proceeding to Sec. II, we note two differences between the BOM, XHTB, and UTBP methods. One is the basis state chosen. In the BOM, sp^3 orbitals for cation and anion are selected as the basis states, while in the XHTB and UTBP methods atomic orbitals are used as the basis states. A second is that the BOM and UTBP methods include only the first nearest-neighbor interaction for which universal parameters are optimized, whereas in the XHTB method interactions are taken into account up to a sufficiently large distance that the interactions become negligibly small.[11,12]

II. CALCULATIONAL PROCEDURE

Theoretical details for the band-structure calculations based on the method are given in our previous paper.[11] The point to be emphasized in our band-structure calculation based on this method is that no empirical atomic data are used; our calculations are entirely from first principles. Atomic states are obtained from a self-consistent-field (SCF) calculation based on the Herman and Skillman prescription[15] and the Schwarz exchange-correlation parameters.[16] Hamiltonian matrix elements are evaluated in the Wolfsberg-Helmholtz approximation[17] as follows:

$$\langle \phi^{\mu}_{L}(\mathbf{r})|H|\phi^{\nu}_{L'}(\mathbf{r}-\mathbf{r}_{\nu})\rangle=(G/2)(\varepsilon^{\mu}_{L}+\varepsilon^{\nu}_{L'}) \times\langle \phi^{\mu}_{L}(\mathbf{r})|\phi^{\nu}_{L'}(\mathbf{r}-\mathbf{r}_{\nu})\rangle \;, \qquad (1)$$

where G is an adjustable parameter and $\phi^{\mu}_{L}(\mathbf{r}-\mathbf{r}_{\mu})$ is the atomic orbital with a quantum state denoted by the collective index $L=(l,m)$ for the μth atom located at $\mathbf{r}_{\mu}$. The atomic energy ε^{μ}_{L} is for the L state of the μth atom and G is taken to be 1.75 (Ref. 1). The overlap integral

$$\langle \phi^{\mu}_{L}(\mathbf{r})|\phi^{\nu}_{L'}(\mathbf{r}-\mathbf{r}_{\nu})\rangle \;,$$

which is necessary to evaluate the Hamiltonian matrix elements, can be transformed into basic overlap integrals using the direction cosines (ξ,η,ζ) of $\mathbf{r}_{\nu}$, as shown in the table of Slater and Koster.[18] These basic overlap integrals are numerically calculated using the atomic states obtained from the SCF calculations and elliptic coordinates.[19] For example, the Hamiltonian matrix element

$$\langle \phi^{\mu}_{p_x}(\mathbf{r})|H|\phi^{\nu}_{p_y}(\mathbf{r}-\mathbf{r}_{\nu})\rangle$$

is given by $\xi\eta V^{\mu,\nu}_{pp\sigma}-\xi\eta V^{\mu,\nu}_{pp\pi}$, where $V^{\mu,\nu}_{l,l',m}$ is the basic Hamiltonian matrix element between the l (s or p) orbital of the μth atom located at (0,0,0) and the l' (s or p) orbital of the νth atom located at $(0,0,r_{\nu})$ for m (σ or π) states.

The essential steps in the calculation of strain energy are described in Ref. 10. Bands are calculated and averaged over a grid of points within the first Brillouin zone (BZ). A total of 6912 points are used for a tetragonal phase generated by a [001] uniaxial strain. The band energy defined by Eq. (3) in Ref. 10 is directly calculated by averaging the energy eigenvalues over the grid points in the irreducible segment of the first BZ following the same procedures as in Ref. 10.

The transverse charge e^{*}_{T} is given as $Z^{*}+4\beta/3$, using the effective atomic charge Z^{*} and transfer parameter β, which are defined by $Z^{*}=4\alpha_{p}-\Delta Z$ and $\beta=(d/4)\partial Z^{*}/\partial d$, respectively.[10] Here, d is the bond length, the value of ΔZ is 1, 2, and 3 for III-V, II-VI, and I-VII semiconductor compounds, respectively. The polarity α_{p} is calculated as follows:

$$\alpha_{p}=\sum_{\mathbf{k}}^{\Omega'} g(\mathbf{k})\alpha_{p}(\mathbf{k})\Big/\sum_{\mathbf{k}}^{\Omega'} g(\mathbf{k}) \;, \qquad (2a)$$

$$\alpha_{p}(\mathbf{k})=(\tfrac{1}{4})\sum_{n}^{E_{\mathbf{k},n}\le E_F}\left[\{\langle \Psi^{a}_{\mathbf{k},n}|\Psi^{a}_{\mathbf{k},n}\rangle-\langle \Psi^{c}_{\mathbf{k},n}|\Psi^{c}_{\mathbf{k},n}\rangle\}/\langle \Psi_{\mathbf{k},n}|\Psi_{\mathbf{k},n}\rangle\right] \;, \qquad (2b)$$

where E_F is the Fermi level of semiconductors. The wave function $\Psi_{\mathbf{k},n}(\mathbf{r})$ is a solution of the Schrödinger equation

$$\underline{H}\Psi_{\mathbf{k},n}(\mathbf{r})=E_{\mathbf{k},n}\Psi_{\mathbf{k},n}(\mathbf{r}) \;.$$

It is written as a linear combination of basis functions with the coefficient $u^{\mu}_{L}(\mathbf{k},n)$. The coefficient $u^{\mu}_{L}(\mathbf{k},n)$ is determined from the secular equation

$$\underline{H}(\mathbf{k})\mathbf{u}(\mathbf{k})=E_{\mathbf{k}}\underline{S}(\mathbf{k})\mathbf{u}(\mathbf{k}) \;,$$

where $\underline{S}(\mathbf{k})$ is not a unit matrix in the XHTB band-

TABLE I. The number of $g(\mathbf{k})$ of $\mathbf{k}$ vectors in the stars for the wave number $\mathbf{k}$ defined within the volume surrounded by symmetry points Γ, X, W, K, Z, W_1, W_2, and U_1 shown in Fig. 1 of Ref. 10.

Points

$\mathbf{k}$	Γ	X	W	K	Z	W_1	W_2	U_1	otherwise
$g(\mathbf{k})$	1	2	2	$\frac{4}{3}$	1	2	2	$\frac{8}{3}$	16

Lines

$\mathbf{k}$	ΓX	XW	WK	$K\Gamma$	ZW_2	W_2U_1	U_1Z	WW_1	W_1X	ΓZ	W_1W_2	KU_1
$g(\mathbf{k})$	4	4	$\frac{8}{3}$	4	4	$\frac{16}{3}$	4	$\frac{16}{3}$	4	2	$\frac{8}{3}$	4

Surfaces

$\mathbf{k}$	ΓXWK	ZW_2U_1	XWW_1	ΓZW_2W_1X	ΓKU_1Z	$WKU_1W_2W_1$
$g(\mathbf{k})$	8	8	8	8	8	8

structure calculation because of the nonorthogonality between the basis functions. Moreover, the $\Psi_{\mathbf{k},n}(\mathbf{r})$ can be expressed as the sum of the wave function at cation $[\Psi^{c}_{\mathbf{k},n}(\mathbf{r})]$ and anion $[\Psi^{a}_{\mathbf{k},n}(\mathbf{r})]$ sites. The wave number $\mathbf{k}$ specifying the $\Psi_{\mathbf{k},n}(\mathbf{r})$ is defined within the irreducible segment Ω' surrounded by symmetry points Γ, X, W, K, Z, W_1, W_2, and U_1 of the first BZ shown in Fig. 1 of Ref. 10, and n is the index for the branch of bands. $g(\mathbf{k})$ denotes the number of the so-called "star of $\mathbf{k}$" and is tabulated in Table I.

We note that this polarity [Eq. (2)] reduces to that of bond orbital theory when $\underline{S}$ is taken as the unit matrix (orthogonality is assumed). From Eq. (2) we may also see the $ed\alpha_p$ corresponds to the bond dipole moment.

III. RESULTS AND DISCUSSION

The calculated results for the elastic shear constant $(c_{11}-c_{12})/2$ in 10^{11} (ergs/cm^3), polarity α_p, effective charge Z^*, transfer parameter β and transverse charge e_T^* for diamond-structure semiconductors C, Si, Ge, and Sn and zinc-blende-structure semiconductors BeS, BeSe, BeTe, BN, BP, BAs, AlP, AlAs, AlSb, SiC, CuF, CuCl, CuBr, CuI, ZnS, ZnSe, ZnTe, GaP, GaAs, GaSb, AgI, CdS, CdTe, InP, InAs, and InSb are tabulated in Table II, together with the experimental values[1] of the bond length d in Å, $(c_{11}-c_{12})/2$ and e_T^* and with a polarity α_p deduced from the ionicity f_i of Phillips as $f_i^{1/2}$. From Table II, we see that the calculated α_p corresponds well with the square root of Phillips's ionicity. A comparison of the calculated values for $(c_{11}-c_{12})/2$ and e_T^* with the experimental ones indicates that the values obtained from the XHTB method are closer to experiment than those obtained from the UTBP method.[10] The significant improvement for the e_T^* may be related to the fact that the calculated polarity is larger, as is the Phillips's polarity for all the semiconductors investigated.

In order to see the role of nonorthogonality between the atomic basis states, we have recalculated the polarity in the so-called "Hückel approximation," in which the same secular equation

$$\underline{H}(\mathbf{k})\mathbf{u}(\mathbf{k})=E_{\mathbf{k}}\underline{S}(\mathbf{k})\mathbf{u}(\mathbf{k})$$

TABLE II. Results for the shear constant $(c_{11}-c_{12})/2$ in 10^{11} (ergs/cm^3), polarity α_p, effective atomic charge Z^*, transfer parameter β, and transverse charge e_T^* obtained for diamond- and zinc-blende-structure semiconductors from XHTB band-structure calculations. Bond length d and the experimental values of $(c_1-c_{12})/2$ and e_T^* were taken from Ref. 1 and the polarity of Phillips was deduced from Phillips's ionicity f_i (Ref. 14) as $\alpha_p=f_i^{1/2}$. The results of the $(c_{11}-c_{12})/2$ and e_T^* taken from Ref. 10, which are calculated from UTBP method, are also given for comparison.

		$(c_{11}-c_{12})/2$			polarity α_p		e_T^*				
Crystal	d (Å)	XHTB	UTBP	Expt.	XHTB	Phillips	Z^*	β	XHTB	UTBP	Expt.
BeS	2.10	4.58			0.792	0.534	1.17	0.253	1.507		
BeSe	2.20	4.93			0.741	0.511	0.964	0.241	1.285		
BeTe	2.40	4.83			0.611	0.411	0.444	0.128	0.615		
BN	1.57	16.5			0.689	0.507	1.75	0.122	1.913		2.47
BP	1.97	14.2		10.8	0.211	0.241	−0.158	−0.219	−0.450		
BAs	2.07	11.6			0.117	0.161	−0.533	−0.272	−0.896		
C	1.54	35.0	34.2	47.55	0.0	0.0	0.0				
AlP	2.36	3.55			0.629	0.623	1.51	0.355	1.983		2.28
AlAs	2.43	3.77			0.574	0.657	1.30	0.353	1.771		2.3
AlSb	2.66	3.36		2.255	0.425	0.658	0.702	0.219	0.994		1.93
SiC	1.88	9.60			0.522	0.421	2.09	0.370	2.583		2.57
Si	2.35	7.14	3.56	5.09	0.0	0.0	0.0				
CuF	1.84	0.695			0.993	0.875	0.974	0.119	1.133		
CuCl	2.34	0.645		0.455	0.934	0.864	0.736	0.248	1.067		1.12
CuBr	2.49	0.781			0.903	0.857	0.613	0.301	1.014		1.49
CuI	2.62	1.20			0.854	0.832	0.417	0.385	0.930		2.40
ZnS	2.34	1.41	1.675	1.950	0.856	0.789	1.42	0.393	1.944	1.251	2.15
ZnSe	2.45	1.56	1.36	1.610	0.819	0.789	1.28	0.432	1.856	1.150	2.03
ZnTe	2.64	1.80	0.97	1.530	0.734	0.774	0.936	0.445	1.529	0.980	2.00
GaP	2.36	3.55	2.635	3.935	0.589	0.573	1.35	0.368	1.841	0.886	2.04
GaAs	2.45	3.25	2.05	3.245	0.529	0.557	1.12	0.365	1.607	0.710	2.16
GaSb	2.65	3.28	1.485	2.405	0.382	0.510	0.529	0.236	0.844	0.398	2.15
Ge	2.44	5.49	2.70	4.030	0.0	0.0	0.0				
AgI	2.80	0.700			0.877	0.879	0.510	0.353	0.981		1.40
CdS	2.53	0.707			0.873	0.824	1.49	0.353	1.961		2.77
CdTe	2.81	1.12	0.665	0.835	0.772	0.822	1.09	0.438	1.674	1.240	2.35
InP	2.54	2.01	1.675	2.230	0.659	0.649	1.64	0.417	2.196	1.261	2.55
InAs	2.61	2.16	1.435	1.900	0.612	0.599	1.45	0.426	2.018	1.071	2.53
InSb	2.81	2.14	1.07	1.510	0.485	0.572	0.940	0.344	1.399	0.746	2.42
Sn	2.80	3.43			0.0	0.0	0.0				

TABLE III. Results for polarity α_p obtained from the band-structure calculations based on the UTBP, Hückel tight-binding (HTB), and XHTB methods. Those values are denoted as α_p(UTBP), α_p(HTB), and α_p(XHTB), respectively. The values of the α_p(UTBP) were deduced from those of Z^* listed in Table II of Ref. 10. For comparison, the values of Phillips's polarity α_p(Phillips) tabulated in Table II in the present paper and of polarity α_p(BOM), obtained from the bond-orbital model are also listed. The α_p(BOM) is calculated from $V_3^h(\text{BOM})/[V_2^h(\text{BOM})^2+V_3^h(\text{BOM})^2]^{1/2}$ using the values of hybrid covalent energy V_2^h(BOM) tabulated in Table IV in the present paper and of hybrid polar energy V_3^h(BOM) given by hybrid energies ε_h^c and ε_h^a of cation and anion as $(\varepsilon_h^c-\varepsilon_h^a)/2$. The parameters, which were necessary in order to evaluate the V_2^h(BOM) and V_3^h(BOM), were taken from Ref. 20.

Crystal	α_p(UTBP)	α_p(HTB)	α_p(XHTB)	α_p(Phillips)	α_p(BOM)
GaP	0.351	0.415	0.589	0.573	0.480
GaAs	0.331	0.368	0.529	0.557	0.467
GaSb	0.274	0.262	0.382	0.510	0.392
InP	0.427	0.457	0.659	0.649	0.578
InAs	0.403	0.421	0.612	0.599	0.562
InSb	0.347	0.329	0.485	0.572	0.497
ZnS	0.611	0.617	0.856	0.789	0.734
ZnSe	0.597	0.582	0.819	0.789	0.729
ZnTe	0.565	0.509	0.734	0.774	0.702
CdTe	0.625	0.535	0.772	0.822	0.754

as in XHTB is solved, but with $\underline{S}(\mathbf{k})=\underline{1}$; that is, nonorthogonality is neglected. The results are tabulated in Table III, together with those for the UTBP method [α_p(UTBP)] and for the XHTB method [α_p(XHTB)]. The value of α_p(HTB) for the Hückel approximation is close to that of α_p(UTBP). From a comparison of α_p(HTB) and α_p(XHTB), we see that the effect of nonorthogonality is to enhance the value of polarity, and thus bond dipoles. Therefore, we can say that at least within the framework of the XHTB method, nonorthogonality between the atomic basis states plays an important role in determining any physical quantity which is calculated by use of the wave functions $\Psi_{\mathbf{k},n}(\mathbf{r})$. We may expect that if the UTBP method is reformulated to include the effect of nonorthogonality between the atomic basis states, it will give a good value to α_p and, therefore, also to e_T^*.

According to the BOM proposed by Harrison,[1] the elastic shear constant $(c_{11}-c_{12})/2$ is given as

$$(c_{11}-c_{12})/2=\sqrt{3}\lambda V_2^h\alpha_c^3/2d^3\ , \tag{3}$$

where covalency α_c is defined by $(1-\alpha_p^2)^{1/2}$, λ is a dimensionless parameter, and V_2^h is a hybrid covalent energy. Let us apply Eq. (3) using α_c, λ, and V_2^h obtained from the XHTB band-structure calculations. The dimensionless parameter λ and the hybrid covalent energy V_2^h are defined in direct analogy with Ref. 1 as follows:

TABLE IV. Values of λ defined by Eq. (4a) and of V_2^h in eV defined by Eq. (4b) obtained for diamond- and zinc-blende-structure semiconductors by using the XHTB method. The value of V_2^h obtained for BOM using universal tight-binding parameters taken from Ref. 20 is also tabulated as V_2^h(BOM) for comparison. It is noted that the value of λ in the BOM is 0.854 for all the diamond- and zinc-blende-structure semiconductors (Ref. 10).

Crystal	d (Å)	λ	V_2^h	V_2^h(BOM)	Crystal	d (Å)	λ	V_2^h	V_2^h(BOM)
BeS	2.10	0.757	9.16	5.57	CuI	2.62	0.757	7.61	3.58
BeSe	2.20	0.765	9.11	5.07	ZnS	2.34	0.737	7.96	4.49
BeTe	2.40	0.785	8.58	4.26	ZnSe	2.45	0.753	7.95	4.09
BN	1.57	0.728	11.5	9.96	ZnTe	2.64	0.779	7.66	3.52
BP	1.97	0.771	10.2	6.33	GaP	2.36	0.779	8.59	4.41
BAs	2.07	0.773	9.87	5.73	GaAs	2.45	0.786	8.47	4.09
C	1.54	0.741	12.1	10.36	GaSb	2.65	0.803	8.02	3.50
AlP	2.36	0.779	8.49	4.41	Ge	2.44	0.795	8.71	4.13
AlAs	2.43	0.784	8.46	4.16	AgI	2.80	0.751	7.00	3.13
AlSb	2.66	0.802	7.94	3.47	CdS	2.53	0.735	7.33	3.84
SiC	1.88	0.754	10.2	6.95	CdTe	2.81	0.776	7.18	3.11
Si	2.35	0.792	8.91	4.45	InP	2.54	0.781	7.97	3.81
CuF	1.84	0.615	7.55	7.25	InAs	2.61	0.786	7.96	3.61
CuCl	2.34	0.709	7.75	4.49	InSb	2.81	0.804	7.59	3.11
CuBr	2.49	0.731	7.76	3.96	Sn	2.80	0.815	7.74	3.13

$$\lambda=\frac{\sqrt{3}}{2}\frac{|V_{pp\sigma}^{c,a}|+|V_{sp\sigma}^{a,c}|+2\sqrt{3}(|V_{pp\sigma}^{c,a}|+|V_{pp\pi}^{c,a}|)}{|V_{ss\sigma}^{c,a}|+\sqrt{3}(|V_{sp\sigma}^{c,a}|+|V_{sp\sigma}^{a,c}|)+3|V_{pp\sigma}^{c,a}|}\,, \tag{4a}$$

and

$$V_2^h=\langle h_c|H|h_a\rangle$$
$$=\tfrac{1}{4}[|V_{ss\sigma}^{c,a}|+\sqrt{3}(|V_{sp\sigma}^{c,a}|+|V_{sp\sigma}^{a,c}|)+3|V_{pp\sigma}^{c,a}|]\,, \tag{4b}$$

which characterizes a bond constructed from sp^3 hybrid orbitals $|h_c\rangle$ and $|h_a\rangle$ on the cation and anion. In the BOM, λ takes a constant value of 0.854 (Ref. 10). The values of the dimensionless parameter λ and hybrid covalent energy V_2^h, which were obtained by calculating the basic Hamiltonian matrix elements in the XHTB method, are tabulated in Table IV, together with the values of V_2^h obtained from the BOM denoted as V_2^h(BOM). Here, it should be noted that the values of λ calculated from the XHTB method are almost the same for all the crystals and somewhat smaller than the value of the BOM (0.854 for all the diamond- and zinc-blende-structure semiconductors). Using these values listed in Table IV, we have checked the covalency dependence of the value of $[(c_{11}-c_{12})/2]d^3/\lambda V_2^h$, which we will hereafter denote by κ. The result is tabulated in Table V, and its α_c dependence is shown in Fig. 1. In Fig. 1, the straight-line fit to the calculated points is

$$\kappa\equiv[(c_{11}-c_{12})/2]d^3/\lambda V_2^h=0.75\alpha_c^2\ . \tag{5}$$

We note that within the framework of the BOM, the value of κ is equal to $(\sqrt{3}/2)\alpha_c^3$.

TABLE V. Results for the value of κ defined by $[(c_{11}-c_{12})/2]d^3/\lambda V_2^h$, covalency α_c defined by $(1-\alpha_p^2)^{1/2}$, and the value of $\lambda V_2^h/d^3$ in 10^{11} ergs/cm^3 obtained for diamond- and zinc-blende-structure semiconductors using the XHTB method. For comparison, the values of $\lambda V_2^h/d^3$ obtained from BOM and the experimental bulk modulus B_{expt} are also tabulated in units of 10^{11} ergs/cm^3 together with $b_0 a^{-m}(1-g_0 f_i)$ [Neumann's relation (Ref. 21) for evaluating the bulk modulus], where $b_0=1.102$, $m=3.56$, and $g_0=0.27$; a is a lattice constant in nm and f_i is Phillips's ionicity. Note that $\lambda V_2^h/d^3$ gives the bulk modulus in the XHTB and $2\lambda V_2^h/d^3$ does so in the BOM.

Crystal	d (Å)	κ	α_c	$\lambda V_2^h/d^3$ XHTB	BOM	B_{expt}	Neumann
BeS	2.10	0.382	0.611	12.0	8.22		13.4
BeSe	2.20	0.470	0.672	10.5	6.51		11.4
BeTe	2.40	0.618	0.792	7.80	4.21		8.59
BN	1.57	0.476	0.725	34.6	35.2	36.9[a]	37.9
BP	1.97	0.865	0.977	16.5	11.3	17.2[b]	17.9
BAs	2.07	0.841	0.993	13.8	8.83		15.1
C	1.54	0.893	1.0	39.3	38.8	44.2[c]	43.7
AlP	2.36	0.441	0.777	8.05	4.58	8.60[d]	8.56
AlAs	2.43	0.509	0.819	7.40	3.96	7.73[d]	7.61
AlSb	2.66	0.620	0.905	5.41	2.52	5.93[c]	5.51
SiC	1.88	0.519	0.853	18.5	14.3	22.8[e]	20.4
Si	2.35	0.819	1.0	8.70	4.69	9.78[c]	9.70
CuF	1.84	0.0581	0.118	11.9	15.9		18.4
CuCl	2.34	0.0938	0.357	6.86	4.79	3.93[c]	7.87
CuBr	2.49	0.133	0.430	5.88	3.50		6.33
CuI	2.62	0.234	0.520	5.13	2.72		5.36
ZnS	2.34	0.192	0.517	7.33	4.79	7.80[c]	8.20
ZnSe	2.45	0.239	0.574	6.51	3.80	5.95[c]	6.96
ZnTe	2.64	0.346	0.679	5.19	2.61	5.09[c]	5.38
GaP	2.36	0.435	0.808	8.15	4.58	8.87[c]	8.72
GaAs	2.45	0.448	0.849	7.24	3.80	7.48[c]	7.66
GaSb	2.65	0.592	0.924	5.54	2.57	5.63[c]	5.88
Ge	2.44	0.718	1.0	7.63	3.88	7.52[c]	8.50
AgI	2.80	0.182	0.480	3.83	1.95		4.12
CdS	2.53	0.133	0.488	5.32	3.24	6.44[d]	6.10
CdTe	2.81	0.278	0.636	4.02	1.92	4.24[c]	4.20
InP	2.54	0.330	0.752	6.08	3.18	7.25[c]	6.52
InAs	2.61	0.383	0.791	5.63	2.77	5.80[c]	6.03
InSb	2.81	0.486	0.875	4.40	1.92	4.66[c]	4.68
Sn	2.80	0.744	1.0	4.60	1.95	5.31[d]	5.20

[a] Reference 22.
[b] Reference 23.
[c] Reference 1.
[d] Reference 24.
[e] Reference 25.

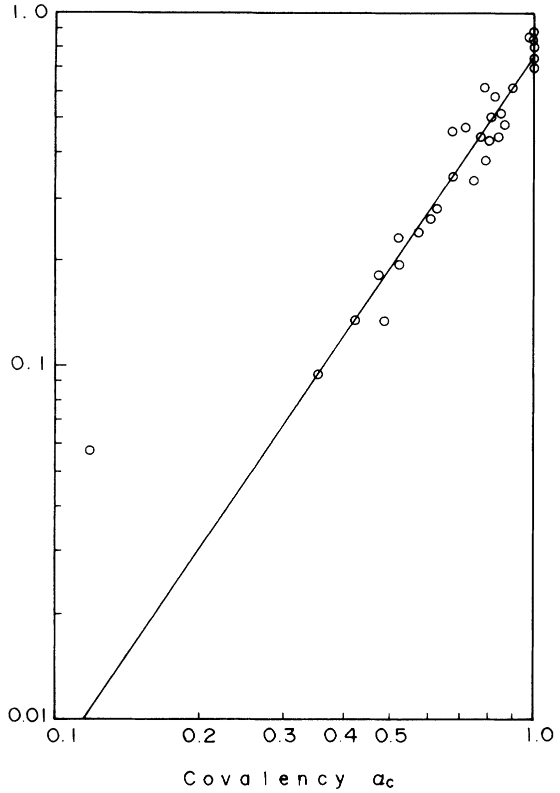

FIG. 1. Plot of $[(c_{11}-c_{12})/2]d^3/\lambda V_2^h$ ($\equiv\kappa$) vs covalency α_c for diamond- and zinc-blende-structure semiconductors listed in Table V. The values of the κ and α_c were obtained from the XHTB band-structure calculations. The line represents $\kappa=0.75\alpha_c^2$.

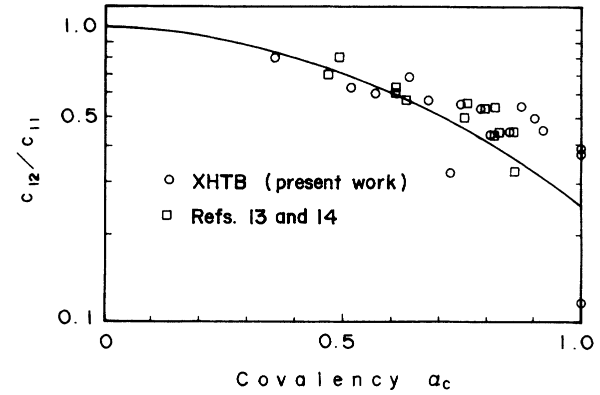

FIG. 2. Curve of Eq. (6c) for the ratio c_{12}/c_{11} as a function of covalency α_c, together with the experimental values of c_{12}/c_{11}. The experimental values indicated by a circle (○) and a square (□) are, respectively, plotted against the values of the covalency calculated from the band-structure calculations and from Phillips's ionicities.

Equation (5) leads us to a very interesting result if we use the empirical relation given by Martin[26] that the ratio of the bond-bending force constant [$\propto(c_{11}-c_{12})d^3$] relative to the bond-stretching force constant [$\propto Bd^3$] varies linearly with ionicity f_i ($=1-\alpha_c^2$) for diamond- and zinc-blende-structure semiconductors. Figure 5 of Ref. 26 or Fig. 3 on p. 266 of Ref. 14 indicates, in fact, that the ratio is proportional to $1-f_i=\alpha_c^2$. Since we see from Eq. (5) that the bond-bending force is proportional to α_c^2, we expect the bond-stretching force to be independent of polarity and the bulk modulus B to be proportional to $\lambda V_2^h/d^3$. We see that, in fact, the experimental bulk modulus is very nearly *equal to* $\lambda V_2^h/d^3$. In the BOM the values of V_2^h are generally smaller by a factor of 2 and the bulk modulus is more nearly given by

$$2\lambda V_2^h(\mathrm{BOM})/d^3=6.712\times10^{13}/d\ [\text{Å}]^5\ ,$$

which may be useful because it is so simple to evaluate.

Also listed in Table V are values obtained from Neumann's empirical relation.[21] Table V indicates that the $\lambda V_2^h/d^3$ obtained by using the XHTB method is in excellent agreement with the experimental bulk modulus. For the compounds for which there are no available experimental data of elastic stiffness constants, our results can be compared with the results obtained from Neumann's relation; very good agreement is found.

Finally, from Eq. (5) and

$$B=\lambda V_2^h/d^3=(c_{11}+2c_{12})/3\ ,$$

we can write the expressions for c_{11}, c_{12} and c_{12}/c_{11} as follows:

$$c_{11}=B(1+\alpha_c^2)\ , \tag{6a}$$

$$c_{12}=B[1-(\alpha_c^2/2)]\ , \tag{6b}$$

$$c_{12}/c_{11}=[1-(\alpha_c^2/2)]/(1+\alpha_c^2)\ . \tag{6c}$$

The curve of c_{12}/c_{11} obtained from Eq. (6c) is shown in Fig. 2, together with the experimental values as a function of the covalency α_c. We see that there is a considerable deviation from the curve, although it describes approximately the experimental trend. We strongly hope that elastic stiffness constants will be measured for crystals for which there are no available experimental data and compared with our predictions. A particular interest is the dependence of c_{12}/c_{11} on α_c in the region of the low covalency ($\alpha_c\lesssim0.5$).

IV. SUMMARY

We have calculated the elastic shear constant $(c_{11}-c_{12})/2$, polarity α_p, effective atomic charge Z^*, transfer parameter β, and transverse charge e_T^* for thirty diamond- and zinc-blende-structure semiconductors from band-structure calculations based on the XHTB method. This explicitly includes the effect of nonorthogonality between atomic basis states. We found that (1) polarity α_p calculated by the XHTB method is close to the counterpart obtained from Phillips's ionicity, and (2) the values of $(c_{11}-c_{12})/2$ and e_T^* obtained from the XHTB band-structure calculations are improved as compared with those obtained from the band-structure calculations based on the universal tight-binding parameters method.[10]

From an expression for the elastic shear constant $(c_{11}-c_{12})/2$ in the BOM and the empirical fact that the ratio of a bond-bending force constant to a bond-stretching one is proportional to the square of covalency α_c, we deduced forms for the bulk modulus B and elastic stiffness constants c_{11} and c_{12} with a single empirical adjustment. We found that the expression for the bulk modulus B gives the values quite close to the experimental ones and for the elastic stiffness constants predicts fairly well the experimental trends of c_{12}/c_{11}.

In the present paper, we have not treated the BOM, but performed the band-structure calculations based on the XHTB method. Although both the BOM and XHTB methods are based on the tight-binding approximation, their practical treatments are different from each other in detail. Therefore, it is difficult to discuss these two methods on the same footing. However, some features should be common to these two methods. We think that λ may be one such feature. In the BOM, the value of λ is a constant value of 0.854 for all the diamond- and zinc-blende-structure semiconductors, while its value in the XHTB method varies from 0.615 to 0.815 for the crystals investigated in the present work, for an average value of 0.764.

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[1] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, New York, 1980) (reprinted by Dover, New York, 1988).

[2] D. J. Chadi and R. M. Martin, Solid State Commun. **19**, 643 (1976).

[3] B. N. Harmon, W. Weber, and D. R. Hamann, Phys. Rev. B **25**, 1109 (1982).

[4] O. H. Nielsen and R. M. Martin, Phys. Rev. Lett. **50**, 697 (1983).

[5] S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[6] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3792 (1985).

[7] N. E. Christensen, Solid State Commun. **50**, 177 (1984).

[8] M. Methfessel, C. O. Rodriguez, and O. K. Andersen, Phys. Rev. B **40**, 2009 (1989).

[9] G. D. Watkins and R. P. Messmer, in *Computational Methods for Large Molecules and Localized States in Solids,* edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1973).

[10] M. Kitamura and W. A. Harrison, Phys. Rev. B **44**, 7941 (1991).

[11] M. Kitamura and S. Muramatsu, Phys. Rev. B **41**, 1158 (1990).

[12] M. Kitamura and S. Muramatsu, Phys. Rev. B **42**, 1417 (1990).

[13] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[14] J. C. Phillips, in *Chemical Models of Energy Bands, Handbook on Semiconductors,* edited by W. Paul (North-Holland, Amsterdam, 1982), Vol. 1.

[15] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[16] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[17] M. Wolfsberg and L. Helmholtz, J. Chem. Phys. **20**, 837 (1962).

[18] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[19] M. Kitamura, S. Muramatsu, and C. Sugiura, Phys. Rev. A **35**, 2838 (1987).

[20] W. A. Harrison, Phys. Rev. B **24**, 5835 (1981).

[21] H. Neumann, Cryst. Res. Technol. **22**, 99 (1987).

[22] E. Knittle, R. M. Wentzcovitch, R. Jeanloz, and M. L. Cohen, Nature **337**, 349 (1989).

[23] W. Wettling and J. Windscheif, Solid State Commun. **50**, 33 (1984).

[24] F. Bechstedt and W. A. Harrison, Phys. Rev. B **39**, 5041 (1989).

[25] J. A. Majewski and P. Vogl, Phys. Rev. B **35**, 9666 (1987).

[26] R. M. Martin, Phys. Rev. B **1**, 4005 (1970).