

Semiempirical formulae for elastic moduli and brittleness of diamondlike and zinc-blende covalent crystals

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In the present work, semiempirical formulae for both bulk B and shear G moduli of diamondlike and zinc-blende covalent crystals are elaborated in terms of bond length and ionicity fraction of the bonding. The resulting expressions can be applied to a broad selection of covalent materials and their modulus predictions are in good agreement with the experimental data and those from *ab initio* calculations. Furthermore, the correlation between the ratio G/B and the aforementioned bonding parameters was investigated. The analysis of this relationship demonstrates that compared to the ionicity fraction, the bond length is the predominant parameter responsible for the brittle features of covalent materials.

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I. INTRODUCTION

In the past decades, numerous efforts have been made in establishing links between macroscopic properties of solids and their atomic-scale features. In particular, the elastic moduli, which are of importance in assessing the competition between the ductile and brittle failures, have been extensively investigated in relation to various microscopic characteristics of different sorts of materials, such as metals and covalently bonded crystals. Currently, most elastic modulus evaluations are carried out using the state-of-the-art *ab initio* calculation techniques; however, one has to keep in mind that the rationalization of these first-principles calculations often requires profound understanding of the nature of the chemical bonding and its attributes in various solid systems. As a result, analytical and semiempirical methods need to be elaborated in concert with computational approaches and estimations.

One of the earliest attempts at describing bulk modulus B in terms of electronic parameters¹ yielded a simple proportionality relation between B and the product of the electron concentration with Fermi energy. However, the resulting formula is of limited utility, since it usually gives values within a factor of 2 of the experimental values. Recently, Gilman² derived expressions for both bulk B and shear G moduli of metals based on simplified quantum-mechanical considerations. The derived expressions also suffer from notable deficiencies, as they ignore the effects induced by ionicity of the bonds and exchange-correlation interactions amongst others. Moreover, Gilman's formulae for B and G give a constant ratio $G/B=3/5$, which is close to the G/B ratio of some alkali metals such as sodium. Nonetheless, it remains an aberrant result, as one expects the G/B ratio, which is often used as a performance indicator to distinguish ductile and/or brittle transition of materials,^{3,4} to vary from one solid to another.

As for covalent materials, which constitute the subject matter of the present work, it was found by Cohen⁵ that their bulk modulus B (GPa) can be estimated by the following semiempirical expression:

$$B = \frac{N_c (1972 - 220\lambda)}{4 d^{3.5}}, \quad (1)$$

where N_c is the bulk coordination number, d is the bond length, and λ is an empirical ionicity parameter that takes the values of 0, 1, and 2 for IV, III-V, and II-VI group semiconductors, respectively. In this paper, we improved this formula by replacing the *ad hoc* empirical ionicity parameter with a more suitable ionicity factor. Additionally, a semiempirical formula for shear modulus of covalent crystals is developed. These results are then exploited to reveal the atomic-scale origins of the brittleness of covalently bonded solids through analysis of the dependence of the ratio G/B on the bond length and the ionicity fraction of the bonds.

II. THEORY AND RESULTS

Both bulk B and shear G moduli can be derived from the second derivative of the total energy E with respect to the appropriate deformation parameter at the equilibrium state as follows:^{6,7}

$$B = \Omega \left. \frac{\partial^2 E}{\partial \Omega^2} \right|_{\Omega=\Omega_0}, \quad (2)$$

$$G = \frac{1}{\Omega} \left. \frac{\partial^2 E}{\partial \delta^2} \right|_{\gamma=\gamma_0}, \quad (3)$$

where Ω and δ stand for volume and dimensionless deformation parameter, respectively. From Eqs. (2) and (3), it is evident that the first step in establishing the formulae for bulk and shear moduli is to approximate the energy derivatives in terms of chemical bonding parameters.

Due to their spherical symmetry and tight-binding character, the core electrons are nearly unresponsive to low-energy perturbations⁸ like those occurring under elastic deformation; while the valence electrons are completely affected by such phenomena. Consequently, the core electrons do not have a significant contribution to the elastic response of a material deforming within the limits of the elastic regime; whereas,

the valence electrons are fully involved in the distortion process. Since the involvement of core electrons in the elastic deformation is insignificant, the variation of their energy is also negligible. Therefore, within the limits of the elastic regime, the second derivative of the total energy can be approximated by the variation of the valence electrons' force. In the case of covalently bonded materials, as discussed by Philips,⁹ the band gap energy E_g provides an estimation of the valence bond strength and it results from homopolar and heteropolar or ionic contributions of the atoms to the bonds as follows:

$$E_g^2 = E_h^2 + C_i^2. \quad (4)$$

Here E_h refers to the homopolar or covalent contribution to the bonding, while C_i corresponds to the ionic contribution or the charge transfer to the bonds. In the case of purely covalent group IV crystals, such as diamond, silicon, or germanium, E_g is equal to E_h . Consequently, E_h characterizes the strength of the covalent bond. Cohen was the first to maintain⁶ that Philips' homopolar band gap energy is the dominant energy parameter in covalent solids. Recently, relationships connecting inherent traits such as thermal activation energies¹⁰ and hardness¹¹ to the homopolar band gap energy were elaborated in the case of covalent crystals. These works further confirm that the intrinsic properties of covalent materials are predominantly dictated by E_h . Using a scaling argument, E_h can be expressed in terms of d as follows:⁹

$$E_h = \frac{39.74}{d^{2.5}}, \quad (5)$$

where the units of E_h are in eV and d is in Å. Since for small amounts of deformation, the strain parameter is a linear function of the bond length, from Eq. (5), it follows that

$$\frac{\partial^2 E}{\partial \delta^2} \propto \frac{1}{d^{4.5}}. \quad (6)$$

The cylindrical-shaped charge volume of covalent crystals is a linear function of the bond length, $\Omega \approx \pi(2a_B)^2 d$ (a_B is Bohr radius) and it can be used in Eqs. (2) and (3), since it encloses the largest electron concentration.⁶ Thus Eqs. (2)–(6) yield

$$B \propto \frac{1}{d^{3.5}} \quad (7)$$

and

$$G \propto \frac{1}{d^{5.5}}. \quad (8)$$

The effects induced by the ionicity of the chemical bond in the case of binary compounds are described by the unitless ionicity fraction f_i , which is defined as:⁹

$$f_i = 1 - \frac{E_h^2}{E_g^2}. \quad (9)$$

It has been verified¹² that elastic moduli assume a decreasing linear trend with increasing ionicity. Therefore, based on

Eqs. (7) and (8) and the fact that B and G are linear functions of ionicity, these elastic moduli are expected to exhibit the following explicit dependences on d and f_i :

$$G_j = \frac{\alpha_j - \beta_j f_i}{d^{5.5}}, \quad (10)$$

$$B = \frac{\gamma - \eta f_i}{d^{3.5}}, \quad (11)$$

where α_j , β_j , γ , and η are constants, and the subscript j refers to the two covalent crystal groups discussed below. These constants can be extrapolated from a selection of experimental data of covalent materials. The resulting expressions are

$$G_a = \frac{5954.02 - 4538.404f_i}{d^{5.5}}, \quad (12a)$$

$$G_b = \frac{9058.22 - 6905.865f_i}{d^{5.5}}, \quad (12b)$$

$$B = \frac{1938.72 - 506.702f_i}{d^{3.5}}. \quad (13)$$

In Eqs. (12a), (12b), and (13), all elastic constants and moduli are in GPa and d is in Å as before. Sixteen data selected from the twenty-three experimental measurements in Table I were used to interpolate coefficients α_j and β_j in Eqs. (12a) and (12b) and the linear fitting curves together with selected data are shown in Fig. 1. In the case of bulk modulus B , nine experimental data plotted in Fig. 2 were employed to determine constants γ and η in Eq. (13). The calculated results from Eqs. (12a), (12b), and (13) are in a good agreement with the experimental observations in Table I. In the case of shear modulus G , our predictions for Si, Ge, Pb, SiC, HgSe, and HgTe, which were not included in fitting Eqs. (12a) and (12b), are within 16% of the experimental values. As for B , our calculations for the crystals unexploited in the extrapolation process generally fall within 19% of the experimental values. As regards the compounds BeS, BeSe, BeTe, MgS, BAs, and BSb, for which there exist no measurements known to the authors, the predictions are very close to the results of *ab initio* calculations, which give $B = 111$ GPa and $G = 81.2$ GPa for BeS,¹³ $B = 98$ GPa and $G = 66.6$ GPa for BeSe,¹³ $B = 70$ GPa and $G = 49.6$ GPa for BeTe,¹³ $B = 61.3$ GPa and $G = 34.8$ GPa for MgS,¹⁴ $B = 152$ GPa and $G = 149.6$ GPa for BAs,¹⁵ and $B = 116$ GPa and $G = 116.2$ GPa for BSb.¹⁵ In the case of β -HgS, our estimations are comparable to the results obtained from valence-force-field approach, which yields $B = 68.5$ GPa and $G = 19.6$ GPa.¹⁶ As for shear moduli of compounds AlP, AlAs, GaN, and InN whose experimental values are also unknown to the authors, the results assessed using Eq. (12b) agree with the outcomes of first-principles calculations testified in Ref. 17, which gives $G = 55.2$ GPa for AlP; Ref. 18, which gives $G = 46.4$ GPa for AlAs; and Ref. 19, which reports $G = 122.7$ GPa for GaN and $G = 83.3$ GPa for InN. Consequently, the reliability and accuracy of our formulae are

TABLE I. Experimental and calculated bulk modulus and shear modulus of diamondlike and zinc-blende covalent crystals and parameters related to the calculation of their elastic moduli.

Crystals	d (Å)	f_i	B_{expt} (GPa)	B_{calc} (GPa)	G_{expt} (GPa)	G_{calc} (GPa)	Group
C	1.55 ^a	0 ^b	442 ^c	418.2	535.7 ^c	534.5	a
α -Sn	2.81 ^a	0 ^b	53 ^a	52.1	...	20.3	a
Pb	3.17 ^d	0 ^d	41.7 ^c	34.2	10.1 ^c	10.4	a
BP	1.97 ^a	0.006 ^b	173 ^c	180.4	139 ^e	142.3	a
BN	1.57 ^a	0.256 ^b	369 ^f	373	414 ^g	400.9	a
AlN	1.90 ^h	0.449 ^b	201 ⁱ	180.9	114.8 ⁱ	114.7	a
SiC	1.88 ^d	0.177 ^b	211 ^a	202.9	175.8 ^j	160	a
BeS	2.10 ^d	0.312 ^b	...	132.7	...	76.7	a
BeSe	2.20 ^d	0.299 ^b	...	113.2	...	60.1	a
BeTe	2.40 ^d	0.169 ^b	...	86.5	...	42	a
MgS	2.43 ^d	0.639 ^k	...	72.2	...	23.1	a
ZnS	2.34 ^a	0.623 ^b	84.1 ^c	82.8	31.9 ^c	29.1	a
CdS	2.52 ^a	0.685 ^b	64.8 ^l	62.6	16.9 ^l	17.6	a
CdSe	2.62 ^a	0.699 ^b	55.7 ^m	54.4	13.6 ^m	13.9	a
CdTe	2.81 ^a	0.675 ^b	42.4 ^a	42.9	10.5 ⁿ	9.8	a
β -HgS	2.53 ^o	0.77 ^p	...	60.1	...	15	a
HgSe	2.63 ^o	0.62 ^q	48.5 ^q	55.1	16.5 ^q	15.4	a
HgTe	2.78 ^o	0.565 ^q	43.7 ^c	46.1	12.9 ^c	12.2	a
Si	2.35 ^a	0 ^b	100 ^c	97.4	70.8 ^c	82.4	b
Ge	2.45 ^a	0 ^b	77.8 ^c	84.2	56.6 ^c	65.5	b
BAs	2.07 ^d	0.002 ^b	...	151.8	...	165.4	b
BSb	2.24 ^f	0.03 ^s	...	114.3	...	104.8	b
AlP	2.36 ^a	0.307 ^b	86 ^a	88.3	...	61.7	b
AlAs	2.43 ^a	0.274 ^b	77 ^a	80.5	...	54.2	b
AlSb	2.66 ^a	0.426 ^b	59.3 ^c	56.1	31.1 ^c	28.2	b
ZnSe	2.45 ^a	0.676 ^b	62.4 ^a	69.3	32.9 ^c	31.7	b
ZnTe	2.64 ^a	0.546 ^b	51 ^c	55.6	24.8 ^c	25.4	b
GaP	2.36 ^a	0.374 ^b	88.8 ^c	86.6	58 ^c	57.6	b
GaAs	2.45 ^a	0.310 ^b	75.6 ^c	77.4	48.8 ^c	50.1	b
GaSb	2.65 ^a	0.261 ^b	57.4 ^c	59.6	35.4 ^c	34.1	b
GaN	1.94 ^o	0.5 ^b	190 ^t	164	...	144	b
InP	2.54 ^a	0.421 ^b	72.5 ^c	66.1	36.5 ^c	36.5	b
InAs	2.61 ^a	0.357 ^b	60 ^a	61.2	31.4 ^c	33.7	b
InSb	2.81 ^a	0.321 ^b	46.7 ^c	47.7	24.2 ^c	23.3	b
InN	2.16 ^o	0.578 ^b	137 ^p	111.1	...	73.3	b

^aReference 24.^bReference 9.^cReference 28.^dReference 25.^eReference 29.^fReference 30.^gReference 34.^hReference 11.ⁱReference 31.^jReference 35.^kReference 14.^lReference 32.^mReference 33.ⁿReference 36.^oReference 37.^pReference 16.^qReference 38.^rReference 26.^sReference 27.^tReference 39.

well verified. It is noteworthy that in most cases, the reported *ab initio* values of bulk and shear moduli were extrapolated from the elastic constants through the following relations:

$$B = 1/3(C_{11} + 2C_{12}), \quad (14)$$

$$G = 1/5(C_{11} - C_{12} + 3C_{44}). \quad (15)$$

Because of different bond-bending and bond-stretching features, the materials under study are split into two groups as far as their shear moduli are concerned (see Fig. 1). This is due to the fact that the compounds of the first-row elements

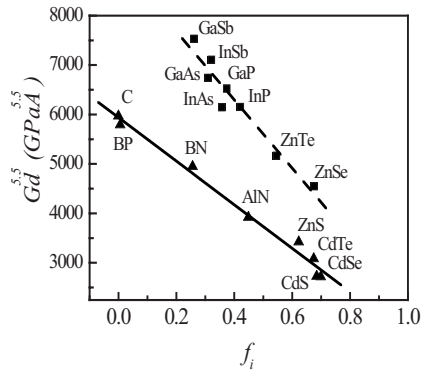


FIG. 1. $G_d^{5.5}$ as a function of ionicity fraction f_i ; the solid and dash lines are from Eqs. (12a) and (12b), respectively.

are not always directly comparable to those with heavier elements. This behavior stems from the differences in the bonding that are related to the s - p hybridization.¹² Thus, C, α -Sn, and Pb together with compounds formed of first-row elements (e.g., BP and BN) or elements of first and second rows such as SiC and AlN belong to group a; whereas Si, Ge, and compounds consisting of first-row elements and heavier ones such as BAs, BSb, GaN, and InN fit in group b. Furthermore, group a contains compounds of II-VI family (BeS, CdS, ZnS, HgTe, etc.), while all the III-V semiconductors without any first-row elements (e.g., GaP, AlSb, InAs etc.) constitute the rest of group b. The only exceptions to these general criteria of classification are ZnSe and ZnTe, which fall in group b as shown in Fig. 1. This reflects the existing difference between the band gaps of these crystals and that of ZnS.²⁰ In contrast to shear modulus, bulk modulus is not affected by the above mentioned angular properties of the chemical bond, and hence a universal linear relation between B and f_i can be obtained as displayed in Fig. 2. This results from the fact that bulk modulus quantifies the response of a crystal to a uniform volumetric tension. In this case, the solid suffers a symmetric deformation along the three main axes, and as a result no angular effects are created.

The developed G and B can be used to assess the brittle and/or ductile characteristics of covalent crystals. Pugh²¹ proposed that the resistance to plastic deformation is related to the product $G\mathbf{b}$, where \mathbf{b} is the Burgers vector, and that the

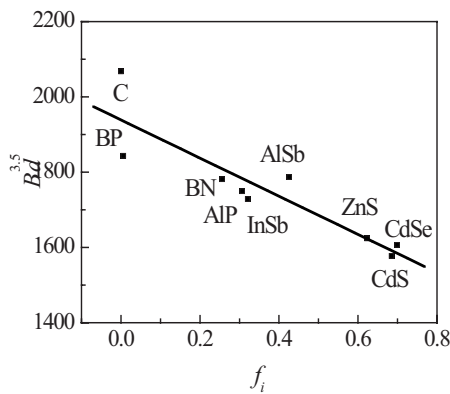


FIG. 2. $Bd^{3.5}$ as a function of ionicity fraction f_i ; the solid line is from Eqs. (13).

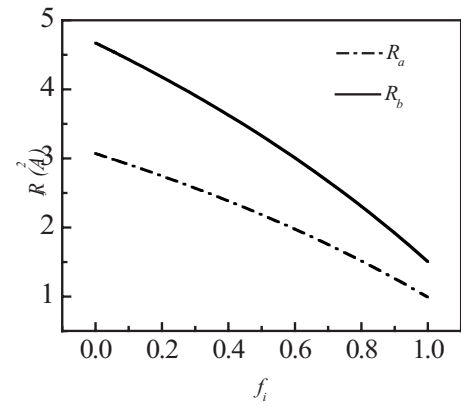


FIG. 3. R_j as a function of ionicity fraction f_i .

fracture strength is proportional to the product Ba , where a corresponds to the lattice parameter. If $G\mathbf{b}/Ba$ is high for a given material, the materials will behave in a brittle manner. Consequently, the $G\mathbf{b}/Ba$ reflects the competition between the shear and cohesive strengths at the crack tip of fracture. As \mathbf{b} and a are constants for specific materials, the $G\mathbf{b}/Ba$ can be simplified into G/B . This formula was recently exploited in the study of brittle versus ductile transition in intermetallic compounds from first-principles calculations.^{22,23} Using Eqs. (12a), (12b), and (13), we obtain the following expression for the G/B ratio for three groups of covalent crystals:

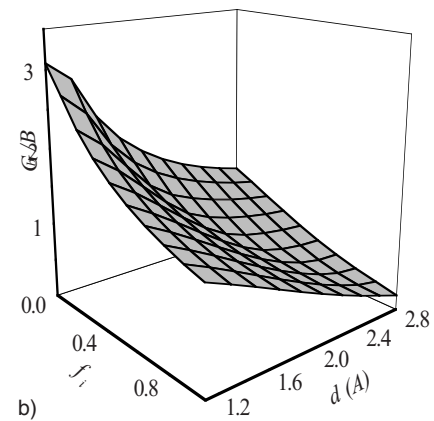
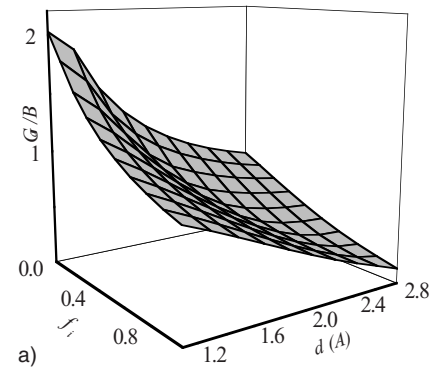


FIG. 4. (a) The ratio G_a/B as a function of ionicity and bond length. (b) The ratio G_b/B as a function of ionicity and bond length.

$$\frac{G_j}{B} = \frac{R_j(f_i)}{d^2}, \quad j = a, b, \quad (16)$$

where a and b represent two groups of covalent crystals. In Eq. (16), $R_j(f_i)$ is an ionicity-related function given by

$$R_j(f_i) = \frac{\alpha_j - \beta_j f_i}{1938.72 - 506.702 f_i}, \quad (17)$$

where α_j and β_j refer to the corresponding constants in expressions (12a) and (12b). From Fig. 3, it can be observed that as expected all the three R_j decrease with increasing ionicity and that they exhibit the same trend evinced by the corresponding curves in Fig. 1. Note that both curves display a nearly linear behavior, which suggests that the effects of ionicity are less significant than those induced by the bond lengths.⁴⁰ From expression (16), it is also evident that the ratio G/B assumes small values for large bond lengths. Three-dimensional surface plots displayed in Fig. 4 clearly demonstrate that the bond length plays a predominant role in the brittle behavior of covalent materials, since even for rela-

tively high ionicities, small values of d still yield G/B ratios larger or equal to 0.5, which is typical of brittle materials.^{3,4}

III. CONCLUSION

In summary, we developed a semiempirical formula for shear modulus of covalent materials and obtained an improved universal formula for their bulk modulus. The investigation of the ratio of these formulae, whose accuracy is comparable to that of the first-principles calculations, clearly demonstrated the predominance of the bond length in assessing brittle characteristics of covalent materials.

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