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Calculation of bulk moduli of diamond and zinc-blende solids

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Theoretical arguments on the role of covalency in determining the bulk moduli of diamond and zinc-blende semiconductors and insulators are shown to yield a surprisingly simple and accurate expression for determining the bulk moduli B of these materials. One resulting formula for compounds in the center of the Periodic Table depends only on the nearest-neighbor separation d. It has the form $B=1761d^{-3.5}$ for B in GPa and d in Å.

I. INTRODUCTION

In the past few years, it has become possible[1] to compute lattice constants, bulk moduli, cohesive energies, phonon spectra, and other static properties knowing only the atomic numbers and masses of the atoms composing the materials. Although applications of these total-energy approaches have been limited to simple solids and solid surfaces; in principle, extensions to more complicated structures appear to be limited only by the availability of computer resources.

Because the *ab initio* calculations are complex and require significant effort, more empirical approaches have been developed[2,3] to compute properties of materials. In many cases, the empirical methods offer the advantage of applicability to a broad class of materials and illustrate trends. In many applications, these empirical approaches do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of these approaches allows a broader class of researchers to calculate useful properties, and often trends become more evident.

In this paper, an empirical calculation of the bulk modulus B for a specific class of materials is presented. The theory yields a formula with three attractive features. Only the nearest-neighbor distance is required as input, the computation of B itself is trivial, and the accuracy of the results rivals that of *ab initio* calculations.

II. THE BULK MODULUS AND COVALENCY

At zero temperature,

$$B=-\frac{Vdp}{dV}=\frac{Vd^2u}{dV^2}, \tag{1}$$

where V, p, and u are the volume, pressure, and energy. For specific models of the attractive and repulsive potentials, Eq. (1) can be used to give reasonable estimates of B for systems such as inert-gas solids[4] and alkali-halide crystals.[4,5] In turn, experimental measurements of B can be used to fix the parameters of the models.

For metals, a free-electron gas model[4,6] yields a simple expression for u and hence B. Dimensional analysis alone gives a reasonable estimate since it suggests that B should scale as the Fermi energy E_F divided by the volume per electron. The direct calculation using Eq. (1) and the free-electron gas energy of $\frac{3}{5}E_F$ per electron gives

$$B=\tfrac{2}{3}nE_F=\left[\frac{6.13}{r_s}\right]^3 \text{ GPa}, \tag{2}$$

where n is the electron concentration and r_s is the electron gas parameter. Although Eq. (2) often gives values within a factor of 2 of the measured results, it is clearly far from complete since the effects of exchange, correlation, and the ionic potential are ignored. Full *ab initio* calculations for specific metals[1,7] which include these terms give excellent results, and expressions[8] for *s-p* metals based on model potentials have had some success.

In contrast, a similar situation does not exist for covalent materials. Neither a simple free-electron gas approach nor a "6-12" potential model is appropriate for a covalent system. It can be argued that this class of materials is the most interesting to study since the largest bulk moduli (lowest compressibilities) are found in this group.

To achieve a scaling relation for B similar to Eq. (2) for metals, it is convenient to use the Phillips—Van Vechten scheme[2] for determining a suitable energy scale. In the Phillips—Van Vechten approach, tetrahedral compounds sharing eight valence electrons per atom pair are characterized by a covalent or homopolar gap E_h and an ionic gap C. These are related to the electronic dielectric function and the plasma energy E_p,

$$\epsilon=1+\frac{E_p^2}{E_h^2+C^2}. \tag{3}$$

A convenient series of solids to examine using this model is Ge, GaAs, and ZnSe. For all three, $E_p\sim 15.6$ eV and $E_h\sim 4.3$ eV. The dielectric constant change results from the charge transfer in going from a group-IV to III-V to II-VI material. According to Phillips,[2] $C=0$, 2.9, and 5.6 eV for Ge, GaAs, and ZnSe. Similarly, other III-V and II-VI compound semiconductor dielectric constants can be obtained from their homopolar counterparts. An important observation for studying B is that the lattice constants of Ge, GaAs, and ZnSe are approximately the same, i.e., the nearest-neighbor distance $d \sim 2.45$ Å. Hence, the lattice constant is roughly independent of C for this row, and d depends predominantly on E_h. Extending this argument to B, it is expected that B will not depend strongly on C.

The above considerations and the expectation that covalency will dominate B suggest that E_h should be chosen as the energy variable for covalent systems in analogy with E_F for the free-electron gas case. Since the electronic charge is concentrated in the covalent bond, a reasonable estimate of this volume completes the scaling for B. Investigations of charge-density plots[9] for covalent bonds reveal bond geometries of roughly cylindrical shape with volumes $\sim \pi(2a_B)^2 d$, where a_B is the Bohr radius. Using these values, the above argument gives

$$B = 45.6 E_h d^{-1} \tag{4}$$

for B in GPa, E_h in eV, and d in Å. If the Phillips[2] values for E_h are used, excellent estimates of B are obtained.

Phillips[2] used a scaling argument based on the group-IV elements to find the dependence of E_h on d for the whole class of tetrahedral compounds sharing eight valence electrons per atom pair. He chooses E_h proportional to $d^{-2.5}$. Using this scaling and Eq. (4), we obtain

$$B = 1761 d^{-3.5} , \tag{5}$$

where the nearest-neighbor distance d is in Å and B is in GPa. This expression is expected to be appropriate for group-IV, III-V, and II-VI materials in the diamond and zinc-blende structure in the center of the Periodic Table. The effects of ionicity are not included explicitly; however, the Phillips values for E_h and his scaling relation average the ionicity contributions.

III. COMPARISON WITH EXPERIMENT

It is instructive first to examine Eq. (4) and the dependence of B on E_h for the group-IV materials C, Si and Ge. Since the ionic gap $C=0$ in these cases, E_h is uniquely determined from ϵ and d (which fixes E_p); hence, we denote E_h determined in this way as $E_h(\epsilon)$. The resulting values for C, Si and Ge are $E_h(\epsilon) = 14.7$, 5.07, and 4.06 eV. These differ from the Phillips[2] values of 13.5, 4.77, and 4.31 eV because the latter were chosen to optimize the results for the broader group of materials, to force the $d^{-2.5}$ scaling of E_h, and to characterize E_h as an average optical gap. However, for the group-IV elements, $E_h(\epsilon)$ gives very accurate values for B when used in Eq. (4). It is also useful for a given row such as the first row of the Periodic Table where E_h is expected to be dominant. The results for C, Si, and Ge using $E_h(\epsilon)$ in Eq. (4) are given in Table I. This table illustrates that for the purely covalent materials, B is just a function of ϵ and d, and it can be estimated to better than 2%. Almost all the experimental values used in this paper are obtained from the Landolt-Börnstein tables.[10] To obtain B from the elastic constants, the expression $3B = C_{11} + 2C_{12}$ is used.

Two other materials in the group-IV class are α-Sn and cubic SiC. Although SiC is partially ionic and in the zinc-blende structure, this material is often considered to be part way between a group-IV covalent and a III-V ionic semiconductor. For both α-Sn and SiC, many electronic and structural properties are less well determined than for C, Si, and Ge. Using the results for Table I for $E_h(\epsilon)$ and the $d^{-2.5}$ scaling, we can estimate $E_h(\epsilon)$ and B using only the values of d (2.81 Å for α-Sn and 1.89 Å for SiC). The results for B are 53 GPa for α-Sn and 211 GPa for SiC which agree exactly with the standard measured values.[7] If this approach is used for all of the group IV's, then $E_h \sim 43 d^{-2.5}$ and $B = 1972 d^{-3.5}$. The results for B differ from experiment by C—2%, Si—0%, Ge—9%, α-Sn—0%, and SiC—0%. Clearly, Ge is anomalous in this series for this type of scaling. One expects C, Si, and SiC to scale consistently, and it can be argued that Ge is more metallic, but then α-Sn should have a lower measured value of B. To form a consistent series from this point of view, B for α-Sn should be in the 45-GPa range. If this were the case, it would be appropriate to include a metallization factor and to analyze the group-IV materials within a covalent and metallic bonding scheme.

To extend the calculation to all the zinc blendes, it is advantageous to adopt Phillip's view that C and Si are the purest covalent systems since there are no ionic and little d-like or metallic contributions to the bonding. In this sense, they form a small subset, and his values of E_h are more universal than the $E_h(\epsilon)$ used above. Using these values or his scaling of E_h with d, Eq. (4) or Eq. (5) give B for a broad range of materials. It is possible to change the coefficient 1761 to 1961 in Eq. (5) to represent $E_h(\epsilon)$ as shown above or to consider it a fitting parameter. Here we rely on the bond-volume argument given previously and the $d^{-2.5}$ scaling of E_h to obtain Eq. (5). The B values for the zinc-blende compounds in the center of the Periodic Table are given in Table II for the III-V compound semiconductors and in Table III for the II-VI compounds.

TABLE I. Calculated bulk moduli for group-IV materials using Eq. (4). The covalent gap $E_h(\epsilon)$ is determined from ϵ and E_h.

	d (Å)	E_p (eV)	ϵ	$E_h(\epsilon)$ (eV)	B(calc) (GPa)	B(expt) (GPa)	Diff. (%)
C	1.54	31.2	5.5	14.7	435	442	1.6
Si	2.35	16.6	11.7	5.07	98	98	0
Ge	2.45	15.6	15.8	4.06	76	77.2	1.6

TABLE II. Comparison of calculated [using Eq. (5)] and measured values of the bulk moduli of III-V zinc-blende semiconductors.

	d (Å)	B(expt) (GPa)	B(calc) (GPa)	Diff. (%)
AlP[a]	2.36	86	87	1.1
AlAs[a]	2.43	77	79	2.5
AlSb	2.66	58	57	1.7
GaP	2.36	89	87	2.2
GaAs	2.45	75	77	2.6
GaSb	2.65	57	58	1.7
InP	2.54	71	67	5.6
InAs	2.61	60	61	1.6
InSb	2.81	47	47	0

[a] B(expt) estimated from an incomplete set of elastic data.

TABLE III. Comparison of calculated [using Eq. (5)] and measured values of the bulk moduli of II-VI zinc-blende semiconductors.

	d (Å)	B(expt) (GPa)	B(calc) (GPa)	Diff. (%)
ZnS	2.34	77	90	14.4
ZnSe	2.46	62	75	17.3
ZnTe	2.64	51	59	13.6
CdS	2.52	62	69	10.1
CdSe	2.62	53	60	11.7
CdTe	2.81	42	47	10.6

Some systematic behavior is observed in the results of Tables I and II. For the III-V compounds, the differences between experiment and theory are less than 3% except for InP. The discrepancies are five times as large for the II-VI compound semiconductors. The theoretical estimates are all larger than the measured values for the II-VI compounds, and the tendency is similar for the III-V compounds. Although it can be argued that for many of these compounds the theoretical-experimental differences are of the same order as differences between reported measured values, it is expected that these trends are real.

A likely origin for the above result is the increase of ionicity and loss of covalency in going from the group-IV to III-VI and II-VI semiconductors. Because of the larger contribution of covalency to B, it is probably the loss of covalent bond charge which reduces B. The extra contribution of the ionic character of the bond to bonding and B is about half of its covalent counterpart. This can be estimated by examining the I-VII rocksalt compounds[4,5] which are almost completely ionic. Analysis of the results gives an approximate scaling for these materials

$$B=550d^{-3}\,, \tag{6}$$

where B and d are given in GPa and Å, respectively. Hence, for the values of d considered, the ionic contribution to B is of the order of 40 to 50% smaller. A more detailed analysis of the ionic contribution to B will be given elsewhere.[11] The empirical result $B=(1971-220\lambda)d^{-3.5}$ is appropriate for the group-IV ($\lambda=0$), III-V ($\lambda=1$), and II-VI ($\lambda=2$) semiconductors.

IV. DISCUSSION

From the comparison of the results of Eq. (5) with the measured values of B, two improvements in the approach appear possible. One is to account for the increasing covalency in going to the upper rows of the Periodic Table, and the other is to include the effects of ionicity explicitly. The first effect was discussed earlier and accounted for through the use of a larger constant in Eq. (5) (i.e., 1972 replaces 1761). With this modification, it should be possible to investigate the elements in the first two rows. Materials made from these elements have the largest bulk moduli and therefore are likely to be the hardest materials.

Starting with the elements B, C, N, Si, and P, the expression $B=1972d^{-3.5}$ and Eq. (5) give the following values for the known diamond and zinc-blende compounds in this group (in GPa); diamond (435), silicon (99), SiC (212), BN (367), and BP (166). To estimate B for hypothetical or "proposed" compounds or alloys, the ionic or covalent radii[2,4] can be used to give an estimate of the nearest-neighbor distance. For example, if a tetrahedral compound could be formed between C and N, an estimate of d would be 1.47 to 1.49 Å depending on which reported values of the radii are taken. The corresponding estimate of the bulk modulus would be 461 to 483 GPa, which is significantly larger than diamond.

Alloys and more complex structures with tetrahedral bonding may be understood in an approximate way by taking average nearest-neighbor distances. Interesting cases are C—BN and C—BP. It should be noted that in all of the above considerations and estimates ionicity has been ignored. Including this effect[11] will weaken the bond. It is also interesting to note that some researchers have speculated that the intraplane stiffness (or hardness) of graphite may be larger than diamond. Since the nearest-neighbor distance in a layer is shorter in graphite than in diamond, the expressions used here are to some extent consistent with this picture. However, the two-dimensional geometry and the sp^2 bonding make a direct comparison difficult.

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