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Towards a microscopic theory of the modulus of elasticity in crystalline covalent materials and a survey of potential superhard materials

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The present report is an account of the generalization of the dynamic elasticity theory earlier proposed by Bucknum et al. and applied to the cubic diamond and tetragonal glitter lattices. It describes a theory of elasticity in which the elasticity moduli are based upon the microscopic constants of the various structure-types. Such microscopic constants include the force constants of the chemical bonds in the unit of pattern of the material, its associated lattice parameters, and the elastic chemical bond deformation parameters of the material. In developing the outward features of the dynamic elasticity model, it is shown that an integral over the force density in the unit cell of a given material; where the force is modeled based upon the elastic deformation forces of the chemical bonds in the unit of pattern of the material, and the volume is written as a function of the deformations taking place inside the unit cell of the material; generates the terms for calculating its modulus of elasticity at pressure, in components, that are directed along the principal axes of the unit cell. Several potential solutions to the problem of superhardness are discussed and illustrated.

1. Introduction

Bucknum et al. previously reported the calculated bulk modulus at pressure of the tetragonal glitter [1] and cubic diamond [2] structure types by applying a dynamic elasticity theory to these structures. In this work, the bulk modulus at pressure of a given material, B, was calculated starting from the zero-pressure

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bulk modulus, B_0, which can be approximated for crystalline covalent materials according to a formula due to Cohen [3]. Corrections to the zero-pressure bulk modulus were subsequently calculated on the basis of the potential elastic chemical bond deformations taking place inside the given unit cell in response to an applied stress. In particular, the theory relied upon the projections of these elastic chemical bond deformation forces, inside the unit cell, as stresses across the principal crystallographic planes of the given lattice. From this analysis, it was shown that tetragonal glitter attains a higher bulk modulus at pressure than does cubic diamond, along its **c**-axis, and therefore tetragonal glitter appears to be a superior material to cubic diamond, in terms of the axial stresses tolerated against its basal plane in response to an applied mechanical stress [1, 2].

In what follows, an attempt is made to generalize the results of these two earlier studies on cubic diamond and tetragonal glitter, by assuming a generic force density integral to model stress in a material. By carrying out the machinations of the integration of such a force density function, it results in the generation of a power series in the attendant strain on the unit cell. The terms of the power series can be identified with physically realistic corrections to the zero-pressure, static bulk modulus. These are the result of the manifestation of the elastic chemical bond deformation forces existent in the elastically deformed unit cell of the covalent material studied, as stresses inside the unit cell.

2. History of elasticity

Historically, the field of elasticity has been focused on the elastic properties of bulk materials, without reference to any crystalline structure [4]. One of the first such phenomenological moduli of elasticity discovered was that of a modulus of elasticity with respect to length deformation [5]. The well-known Young's modulus, Y, is defined in equation (1):

$$\text{stress} = Y\left(\frac{\Delta l}{l}\right). \tag{1}$$

In this expression, the stress applied as a force-per-unit-area of the material studied, is measured against the strain produced in the material, where the strain is measured as the incremental deformation, $\Delta l/l$, of the length of the specimen.

A curve relating stress to strain, in the bulk material, is plotted, and from the slope of this curve one obtains the Young's modulus for the material. A typical plot for obtaining the Young's modulus is shown in figure 1.

Notice in figure 1 the regions of elastic deformation and plastic deformation. In order to determine the modulus of elasticity one must make measurements in the region of elastic deformation of the material. The study of plastic deformation is an important field in its own right and will not be discussed further here.

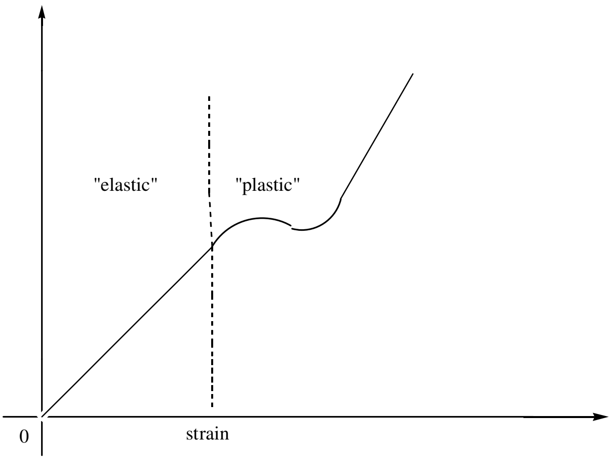

Figure 1. Stress–strain curve for determining moduli of elasticity.

Some typical values of the Young's modulus are shown in table 1. Note the Young's modulus represents the slope of the stress–strain curve for elastic length deformation of a bulk material. This modulus of elasticity, as can be seen from table 1, can be considerable, reaching a value in excess of 1.8 TPa for carbon nanotubes [6]:

An important point should be addressed here with regard to the Young's modulus, Y, of a bulk material. It together with a measure of the ratio of the longitudinal strain to the lateral strain in a stressed bulk material, the so-called Poisson's ratio, σ, can be used to calculate, in principle, all the elastic constants of a bulk material, including the bulk modulus, B, to be discussed below [7].

The idea of modulus of elasticity was generalized to three dimensions, later on, with the introduction of the notion of the bulk modulus, B [8]. The bulk modulus is also known as the volume modulus of elasticity, it is defined in equation (2):

Table 1
Selected values of the Young's modulus in various materials.

Material	Young's modulus, Y, GPa	Reference
Carbon nanotube	1800	[6]
Steel	200	[8]
Aluminum	70	[8]
Glass	65	[8]
Concrete	30	[8]
Wood	13	[8]
Polystyrene	3	[8]

$$\text{stress} = B\left(\frac{\Delta V}{V}\right). \tag{2}$$

In this expression, the stress applied over the volume of the material is measured against the strain produced in the material. This is incremental deformation, $\Delta V/V$, of the volume of the specimen. An analogous stress–strain curve for the bulk material, similar to figure 1, but based upon incremental volume deformation, $\Delta V/V$, is used to determine the bulk modulus of the material under consideration.

B is defined in equation (2) with respect to the incremental change of volume of the material, $\Delta V/V$. In contrast, the bulk modulus of elasticity can be identified with respect to a bulk sample of an ideal gas. This can be accomplished by defining the bulk modulus in terms of the volume derivative of the internal pressure of a material, as shown in equation (3):

$$B = -V\left(\frac{\partial P}{\partial V}\right) \tag{3i}$$

$$B = -V\frac{\partial}{\partial \mathrm{V}}\left(\frac{nRT}{V}\right) = P. \tag{3ii}$$

From equation (3ii), we see that the bulk modulus of an ideal gas, B, is just equal to the pressure of the ideal gas, P. This gives some perspective on what the physical meaning of the bulk modulus is, and suggests its central importance among the various moduli of elasticity in determining properties like the relative strength of materials with respect to volume deformation. It can also be thought of as a measurement of the internal energy of a material divided by its respective volume, U/V, or an energy density [9]. Some typical values of the bulk modulus of materials are shown in table 2. One can see that the bulk modulus of cubic diamond, at 435 GPa, represents the zenith in B_0 among real materials.

Table 2
Selected values of the Bulk modulus in various materials.

Material	Bulk Modulus, B, GPa	Reference
Cubic diamond	435	[1]
Steel	160	[8]
Mercury	27	[8]
Glycerine	4.8	[8]
Water	2.2	[8]
Ethanol	0.90	[8]

3. The crystalline modulus of elasticity

In what follows here, an alternative definition of elastic modulus, applicable to crystalline materials (as opposed to macroscopic, bulk samples of material), is given in terms of a coefficient which has the dimensions of a force density, multiplied by an integral in the strain over the unit cell of the crystalline material, the strain being generated by elastic chemical bond deformation forces created by an applied mechanical stress. The generalized expression is shown in equation (4):

$$\text{elastic modulus} = \int \frac{F(r')}{V(r')}\mathrm{d}r' \tag{4i}$$

elastic modulus

$$= \sum_{i=1}^{N} \left\{ \int \frac{N_i k_i x_i'}{\mathbf{bc}(\mathbf{a} + d_i x_i')}\mathrm{d}x_i' + \int \frac{N_i k_i y_i'}{\mathbf{ac}(\mathbf{b} + d_i y_i')}\mathrm{d}y_i' + \int \frac{N_i k_i z_i'}{\mathbf{ab}(\mathbf{c} + d_i z_i')}\mathrm{d}z_i' \right\}. \tag{4ii}$$

Equation (4i) is the generic statement of the new elasticity law [1]. It states that elastic modulus is equal to an integral over the force density of a material undergoing elastic chemical bond deformations inside the unit of pattern of the material, in response to an applied stress.

Equation (4ii) recasts the relation in terms of a crystalline material with orthogonal axes **a**, **b** and **c**, N bonds per unit cell, the length decrement along the crystallographic axes from elastic chemical bond deformation, given by, $(\mathbf{a} + \mathrm{d}x')$, $(\mathbf{b} + \mathrm{d}y')$ and $(\mathbf{c} + \mathrm{d}z')$, and the assumption of a harmonic potential for chemical bonds. Here x', y' and z' are the elastic chemical bond deformations represented by $r'\cos\alpha$, $r'\cos\beta$, and $r'\cos\chi$, respectively (where $r' = (r - r_\mathrm{e})$ is the actual deformation of the chemical bond considered from its equilibrium value, r_e). The given angular factors refer to the projections of those elastic chemical bond deformations with respect to the three orthogonal crystallographic axes **a**, **b** and **c** [10]. The factor k is just the force constant of the chemical bond considered, assuming a harmonic potential energy function between atom pairs in the crystal. Finally, the factor d refers to the number of elastic chemical bond deformations connected with the compressions of the respective crystallographic axes (and concomitantly the unit cell volume) **a**, **b** and **c**. This latter factor can be obtained from elementary trigonometric analysis applied to the lattice under consideration.

As an example of such a crystalline material, consider the cubic diamond lattice shown in figure 2 [11].

Here **a**, **b** and **c** are the three orthogonal unit cell vectors of cubic diamond, N is the number of bonds per unit cell, which is given by 16, the force constant for the carbon–carbon single bonds in cubic diamond is given by 450 N/m [12], and the length decrements are given by the expressions $(\mathbf{a} + 4x')$, $(\mathbf{b} + 4y')$ and $(\mathbf{c} + 4z')$, which can easily be justified on the basis of elementary trigonometric

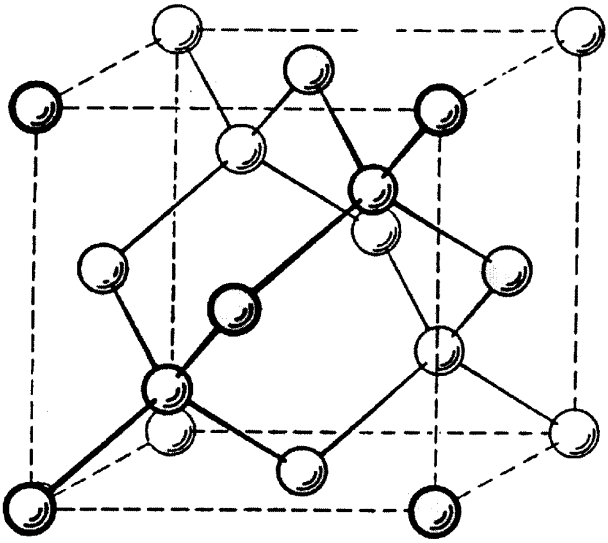

Figure 2. Cubic diamond lattice, Space Group Fd3m.

analysis [13]. Cubic diamond is a particularly simple lattice because of its high symmetry and the presence of only one type of chemical bond in the unit cell.

One can see in equation (4ii), that the elastic modulus of the material is expressed in terms of the dimensions and microscopic parameters of the unit cell of the material. The terms in equation (4ii) correspond to the compressions along each of its axes **a**, **b** and **c**. Therefore, it is broken up into 3 component Young's-like moduli of elasticity. Nonetheless, the 3 component length deformation moduli of elasticity have a composite value that is a measure of the bulk modulus, B, of the crystalline material at pressure, or the volume modulus of elasticity over the unit cell volume at pressure.

The motivation for the use of a force density integral to model elastic modulus has been given previously [1] in the form of Feynman's analysis of static elasticity in crystalline materials [7]. In the Feynman analysis, the NaCl lattice is treated and the chemical bonds are equated to harmonic springs having a force constant of k. Using strain parameters taken over the entire unit cell, and harmonic potential energy functions based upon these strain parameters of the NaCl crystal lattice, Feynman expanded out and collected the resulting harmonic potential energy terms, and divided by the static volume of the crystal, given by $\mathbf{a}^3$ (where **a** is the lattice parameter of the NaCl unit cell). From this analysis, term-by-term he equated the calculated coefficients in the energy density, U/V, with the given elastic constants of the lattice. Finally, by taking advantage of the high symmetry of the cubic NaCl structure-type, in space group Fm–3m, he determined the following general relation between the moduli of elasticity of the cubic crystal and its corresponding microscopic constants.

$$\text{elastic modulus} \propto \frac{k}{\mathbf{a}}. \tag{5}$$

Here k is the force constant of the chemical bonds in the NaCl lattice, with the dimensions of N/m, and **a** is the respective lattice parameter in m. Note the ratio of these microscopic constants has the dimensions of N/m^2, or the dimensions of a pressure, therefore it is consistent with an elasticity modulus for a material [14].

Taking this result as a theoretical basis, it was conjectured by the author in [1] that a dynamic elasticity term for a material, analogous to the static elastic constants of the Feynman analysis, could be gotten in the form of the elasticity expression shown in equation (6):

$$\text{elastic modulus} \propto \frac{kr'}{\mathbf{a}^2}. \tag{6}$$

where r' represents an elastic chemical bond deformation, and $\mathbf{a}^2$ is the area of a crystalline plane normal to that elastic chemical bond deformation.

It was discovered in this work [1] that a methodology of generating such dynamic elasticity terms, in their exact formulation on the basis of the unit of pattern of the respective crystalline material, was by defining the elastic modulus of a unit cell as an integral over the force density in the material. The force density is defined as the total force of elastic chemical bond deformations within the unit of pattern, divided by the corresponding volume function of the unit cell, as that unit cell volume is distorted from the initial volume by the elastic chemical bond deformations. This is generally accomplished by taking distortions of the unit cell along the 3 component axes, **a**, **b** and **c**, in 1 dimension at a time.

4. The strain integral

From equation (4ii), one can see the elasticity expressions for crystalline materials take the generic form shown below:

$$\text{elastic modulus} = \frac{Nk}{\mathbf{ab}} \int \frac{z'}{\mathbf{c} + \mathrm{d}z'} \mathrm{d}z', \tag{7}$$

where the collection of constants, given by $Nk/\mathbf{ab}$, has the dimensions of a force density, and the integral over the strain parameters (unlike the strain, $\Delta l/l$, in equation (1) has the dimensions of a length when it is integrated.

Clearly equation (1), as it is written for the Young's modulus, Y, has a close, one might say analogous, relationship to the elastic modulus relationship shown in equation (7). One could, in fact, rearrange equation (1) to make the connection more concrete, as is shown in equation (8):

$$\text{stress} = \left(\frac{Y}{l}\right)\Delta l. \tag{8}$$

In such an expression, the term Y/l is derived from a set of constants characteristic of the bulk material. The term Y/l has the dimensions of a force density, while the strain parameter is modified to have the dimensions of a length, Δl. This is analogous to the term shown in equation (7), which is alternatively written down on the basis of the consideration of the microscopic constants of a crystalline material.

Therefore, in equation (7), a collection of crystallographic-molecular constants over the unit cell of the material considered, defines a characteristic microscopic force density constant for the unit cell of the material. This is multiplied by an integral over the strain of the unit cell, which nonetheless, upon integration, yields an infinite series of terms, each of which has the dimensions of a length. The product of the force density constant, and the strain integral over the unit cell, is therefore a measure of the dynamic elastic modulus in the material.

Starting from equation (7), we can derive the elastic modulus expression on the unit cell of a material in the following manner (where we treat only one dimension, z', for clarity):

$$\text{elastic modulus} = \int \frac{Nkz'}{\mathbf{ab}(\mathbf{c} + \mathrm{d}z')}\mathrm{d}z' \tag{9i}$$

$$\text{elastic modulus} = \frac{Nk}{\mathbf{ab}} \int \frac{z'}{(\mathbf{c} + \mathrm{d}z')}\mathrm{d}z' \tag{9ii}$$

$$\text{elastic modulus} = B_0 + \frac{Nk}{\mathbf{ab}}\left\{\frac{z'}{\mathrm{d}} + \frac{\mathbf{c}}{\mathrm{d}^2}\ln|\mathbf{c} + \mathrm{d}z'|\right\}. \tag{9iii}$$

Upon expanding the logarithm, we obtain:

$$\text{elastic modulus} = B_0 + \frac{N}{d}\frac{kz'}{\mathbf{ab}} + \left\{\frac{Nk}{\mathbf{ab}}\frac{\mathbf{c}}{d^2}\left(\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^1 + \frac{1}{2}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^2 + \frac{1}{3}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^3 + \cdots\right)\right\} \tag{9iv}$$

which reduces to the following power series in the attendant strain, $z'/\mathbf{c}$.

$$\text{elastic modulus} = \mathrm{B}_0 + \frac{2N}{d}\frac{kz'}{\mathbf{ab}}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^0 + \frac{1}{2}\frac{N}{d}\frac{kz'}{\mathbf{ab}}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^1 + \frac{1}{3}\frac{N}{d}\frac{kz'}{\mathbf{ab}}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^2 + \cdots. \tag{9v}$$

From the derivation given in equation (9) one can see, term-by-term, the moduli of elasticity of crystalline materials emerge, generated from the kernel function in the form of a strain integral multiplied by a force density constant. One can see that the constant of integration, B_0, can be equated to the static elastic constant of zero-pressure bulk modulus of the material. However, it is cast as a function of the crystallographic-molecular parameters of the crystal, k the force constant of the chemical bonds inside the unit cell, and the lattice parameter $\mathbf{a}$ of the unit cell. This is analogous to the case of the Feynman analysis of the static elastic constants of the rocksalt lattice, where the ratio $k/\mathbf{a}$ properly has the dimensions of a stress: [15]

$$B_0 = f(k/\mathbf{a}). \tag{10}$$

The 1st-order term in the power series is given by the elastic chemical bond deformation force, modeled as a harmonic, Hooke's law force, kz', divided by the area of the crystalline plane (hkl) normal to that deformation force. It is a term in force-divided-by-area, F/A, and represents the first dynamic contribution to the bulk modulus at pressure, B. Note that other chemical bond potentials, including a Morse potential [1], can be substituted for a harmonic potential in order to arrive at a more accurate elastic modulus expression.

$$\text{elastic modulus} \propto \frac{2N}{d}\left(\frac{kz'}{\mathbf{ab}}\right). \tag{11}$$

The 2nd-order term in the power series is given in terms of the energies of elastic chemical bond deformations, modeled as Hooke's law springs, divided by the corresponding volume of the unit cell, U/V. Such higher order terms may be important at high degrees of strain associated with plastic deformation.

$$\text{elastic modulus} \propto \frac{1}{2}\frac{N}{d}\frac{kz'}{\mathbf{ab}}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right). \tag{12}$$

The 3rd-order term, and higher terms in the power series, correspond to harmonic potential energy densities, U/V, multiplied successively by strain parameters, $z'/\mathbf{c}$, ($y'/\mathbf{b}$ and $x'/\mathbf{a}$), to higher and higher powers.

$$\text{elastic modulus} \propto \frac{1}{3}\frac{N}{d}\frac{kz'}{\mathbf{ab}}\left(\frac{\mathrm{d}z'}{\mathbf{c}}\right)^2. \tag{13}$$

It is clear from the magnitudes of $x' = r'\cos\alpha$ ($y' = r'\cos\beta$ and $z' = r'\cos\chi$), the elastic chemical bond deformation parameters, and $\mathbf{a}$ ($\mathbf{b}$ and $\mathbf{c}$), the lattice parameters of the unit cell of the material, that major contributions to the stress on a crystalline material generally cut off at the term in the harmonic energy density, U/V. The 2nd-order term in the power series. Therefore, the major contributions to the bulk modulus at pressure in crystalline materials, under conditions of elastic deformation, occur from the zeroth-order term, the static elastic modulus (given by $B_0 = f(k/\mathbf{a})$) and the 1st-order term in the strain integration, the force-over-area term ($F/A \propto kz'/\mathbf{ab}$). The higher terms in the power series ($U/V \propto kz'^2/2\mathbf{abc}$ and higher terms) all converge to 0 as the strain parameter, $x'/\mathbf{a}$ ($y'/\mathbf{b}$ and $z'/\mathbf{c}$), is successively raised to higher and higher powers. At high degrees of strain of the chemical bonds, as in the situation in plastic deformation, such higher order terms may become important.

5. Review of dynamic elasticity theory

The formulation of elasticity in covalent crystalline materials, according to the relation given in equation (4), provides a generalized approach to defining and describing the elasticity of these materials on a microscopic scale using microscopic constants of the structure.

The terms of 1st-order, in the strain integration power series, taking the form of force-over-area stresses, F/A, may be considered to be analogous to the Young's moduli in bulk materials, as defined by equation (8). Nonetheless, the sum of such 1st-order terms, in the physically meaningful form of stresses against each principal crystallographic face of the unit cell of the material (i.e. the (100), (010) and (001) faces), constitute, in composite, a measure of the dynamic bulk modulus of a crystalline material, B. Under elastic deformation, higher order terms in the strain integration power series all vanish, as the strain parameter, $x'/\mathbf{a}$ ($y'/\mathbf{b}$ and $z'/\mathbf{c}$), approaches 0.

As all crystal systems (cubic, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic and triclinic) can be modeled in terms of orthogonal axes, **a**, **b** and **c**. Even if this means lowering the symmetry of the unit cell. It thus becomes possible to calculate elastic moduli in any crystal system undergoing elastic deformation, from the formulation provided in equation (4) of this paper, with some modification for different types of chemical bonds (with pair potentials which may differ from harmonic, Hooke's law potentials) and for different orientations of those chemical bonds with respect to the crystallographic axes **a**, **b** and **c** as needed. One can model the dynamic elastic moduli of such materials exactly in terms of the elastic chemical bond deformation forces attendant on each of the three orthogonal crystallographic planes (100), (010) and (001).

The problem of the constant of integration in this analysis, the static zero-pressure bulk modulus of a crystalline material, becomes increasingly difficult to evaluate as the bonds in a crystal structure are distorted from orthogonality [7]. The prescription of dynamic elasticity does not provide a guide as to how one can get at the exact expressions for this constant of integration, as it comes up in each such elastic modulus analysis. Some important guiding principles for the formulation of B_0 have been provided by the lead of investigators such as Pauling et al. [16], Feynman [7], and Cohen [3], who have proposed approximations to the static moduli of elasticity, generally based upon

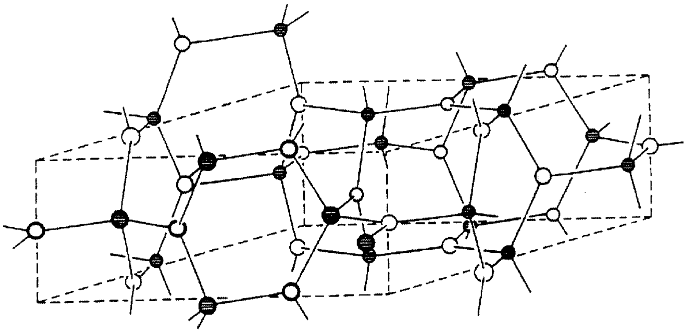

Figure 3. Hexagonal β-C_3N_4 lattice, Space Group P6_3/m.

considerations of the force constants in the unit cell of a material and the lattice parameters [17].

As an indication of the uniformity of the problem of identifying a modulus of elasticity in arbitrary crystalline materials, one can consider the work of Pauling and Waser [16] who identify the following Badger-like relation [18] between the force constant k of the bonds in the elements in their solid states, and the respective bond distances, d, in the elements:

$$k \propto d^{-3}. \tag{14}$$

An attempt at calculating an explicit covalent–ionic B_0 from semi-empiric considerations, based upon calculations of electronic energy density, U/V, of the corresponding covalent-ionic chemical bonding in the materials, is that given by Cohen [3] below:

$$B_0 = \left(\frac{1972 - 220(\mathrm{I})}{\langle d\rangle^{3.5}}\right)\left(\frac{\langle N_c\rangle}{4}\right). \tag{15}$$

Here I is the ionicity in the material, N_c is the averaged coordination number, and d is the averaged bong length, inside the unit cell. Fortunately, the Cohen formula extends its accuracy to all covalent-ionic materials studied so far with tetrahedral bond structures (the so-called diamond-like solids) and is generalized to substances with coordination numbers different from 4. So one can use the formula to accurately model the zero-pressure elasticity of the diamond lattice in space group Fd3m, and related covalent-ionic materials like hexagonal β-C_3N_4 in space group P6_3/m, shown in figure 3 [19], and tetragonal glitter in space group P4_2/mmc, shown in figure 4 [1].

6. Potential and real superhard materials

From equation (15) we can identify those covalent–ionic materials that lie at the zenith of hardness, according to the identification of the zero-pressure

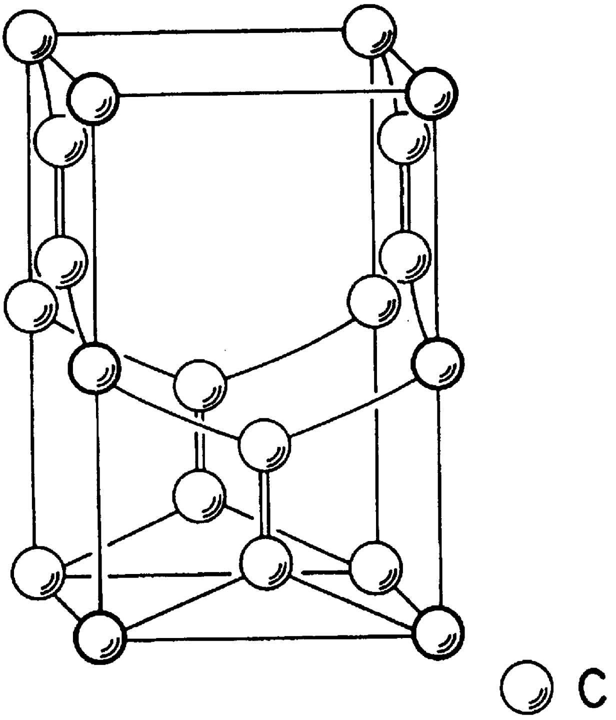

Figure 4. Tetragonal glitter lattice, Space Group $P4_2/mmc$.

bulk modulus, B_0, as a measure of a material's hardness. Table 3 summarizes the calculations of B_0 by equation (15) for candidate covalent–ionic crystalline materials including, cubic diamond, hexagonal diamond in space group $P6_3/mmc$, hexagonal β-C_3N_4 [19], hexagonal hexagonite in space group P6/mmm, shown in figure 5 [20], and tetragonal glitter [1].

The constant of the strain integration, the zero-pressure bulk modulus, seems to reach a barrier at about 440 GPa, with all the calculated zero-pressure

Table 3
Calculated zero-pressure Bulk moduli of superhard materials according to the Cohen prescription.

Material	B_0 in GPa	Reference
Cubic diamond	435	[1]
Hexagonal diamond	435	[3]
β-C_3N_4	427	[9]
Hexagonite	427	[20]
Glitter	440	[1]

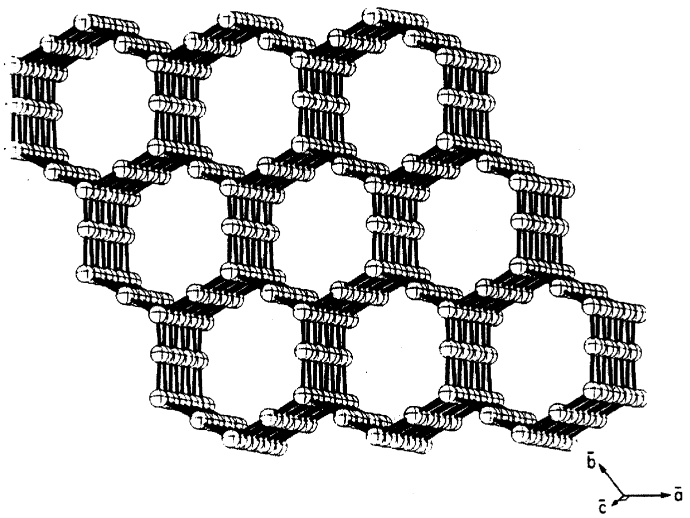

Figure 5. Hexagonal hexagonite lattice, Space Group P6/mmm.

bulk moduli clustered not far from this value, with glitter being at the top ($B_0 =$ 440 GPa).

Carbon allotropes, whether real, as in the case of cubic and hexagonal diamond, or hypothetical, as in the case of hexagonal hexagonite and tetragonal glitter, comprise many of the hardest possible materials. Even hexagonal β-C_3N_4 is in large degree comprised of C. Earlier on, it has been seen that carbon nanotubes have the very highest values of the Young's modulus of materials [6], Y, another measure of stiffness. Judging from these results, it is clear that one should be looking in the direction of carbon when trying to discover novel superhard materials [21].

Beyond the zero of pressure, we have some preliminary results of the dynamic elasticity of some of these materials [1, 2]. When factoring in the zero-pressure bulk modulus, B_0, assuming harmonic potential energy functions between atom pairs [1] and with modest bond length deformations of about 0.1 Å, on the carbon–carbon single, and double bonds respectively, we have identified the dynamic lateral and axial elastic moduli in tetragonal glitter and cubic diamond shown in equations (16) and (17), respectively:

$$\begin{aligned} B_{\text{glitter}} = B_0 &+ \left(\frac{2k_2 r_2' \cos 0^\circ}{\mathbf{a}^2} + \frac{4k_1 r_1' \cos 57^\circ}{\mathbf{a}^2} \right)_{\text{axial}} \\ &+ \left(\frac{4k_1 r_1' \cos 33^\circ}{\mathbf{ac}} + \frac{4k_1 r_1' \cos 33^\circ}{\mathbf{ab}} \right)_{\text{lateral}} \end{aligned} \tag{16}$$

$$B_{\text{diamond}} = B_0 + \left(\frac{8kr'\cos 54.73^\circ}{\mathbf{bc}} + \frac{8kr'\cos 54.73^\circ}{\mathbf{ac}}\right)_{\text{lateral}} + \left(\frac{8kr'\cos 54.73^\circ}{\mathbf{ab}}\right)_{\text{axial}}. \tag{17}$$

The results of the calculations on these lattices are shown in table 4.

From the data in table 4, it can be seen that tetragonal glitter has a 33% higher bulk modulus at pressure, directed along its **c**-axis, B_c, at 893 GPa [1], than does cubic diamond at 600 GPa [2].

7. Conclusion

Evidently, the solution of the integral over the force density, shown earlier in equation (4), provides the key to solving the problem of the ultimate strength of materials, as measured from their elastic moduli. Solution of equation (4) shows that maximizing parameters such as the force constant of the chemical bonds in the unit of pattern of the given material, or alternatively minimizing the lattice parameters for a given material, are both directions one could go in to maximize the dynamic bulk modulus, B. The cubic diamond, hexagonal diamond, hexagonal β-C_3N_4, hexagonal hexagonite and tetragonal glitter structure-types, clearly provide some of the most obvious solutions to the problem of the ultimate hardness of materials.

Cubic diamond is a dense material ($\rho = 3.56\,\text{g/cm}^3$) with strong, covalent carbon–carbon single bonds with an associated force constant, k, of 450 N/m [12] and a relatively small lattice parameter of 3.55 Å [11]. Cubic diamond is the very hardest material known. As an alternative, one can consider tetragonal glitter ($\rho = 3.15\,\text{g/cm}^3$) with its stronger, covalent carbon–carbon double bonds with their associated force constant, k, of 960 N/m [12] and smaller basal plane lattice parameters of 2.53 Å [1]. Because of the geometry of the tetragonal glitter structure, the Hooke's law forces, attendant on all the carbon–carbon bonds in glitter, will have components directed across the structure's basal plane. Such a

Table 4
Axial correction stresses and total Bulk moduli parallel to the **c**-axis for cubic diamond and tetragonal glitter at a 0.1 Å chemical bond deformation.

Material	Axial correction stress	B_c, GPa
Diamond	$B_c \alpha B_0 + \left(\frac{8kr' \cos 54.73^\circ}{\mathbf{ab}}\right)_{\text{axial}}$	600
Glitter	$B_c \alpha B_0 + \left(\frac{2k_2 r'_2 \cos 0^\circ}{\mathbf{a}^2} + \frac{4k_1 r'_1 \cos 57^\circ}{\mathbf{a}^2}\right)_{\text{axial}}$	893

situation leads to a maximization of the 1st-order term in the strain integration power series, shown in equation (9), compared to the situation in the other structures like cubic diamond.

It therefore appears that tetragonal glitter, although of a comparable stiffness to cubic diamond in the lateral **bc**- and **ac**-planes (with an approximate modulus of 540 GPa along [100] and [010] directions), will be considerably stiffer than cubic diamond across the basal plane of the lattice (i.e. along the [001] lattice direction in tetragonal glitter the modulus of elasticity is 893 GPa). When one considers the constraints associated with creating an extended 3D structure, that has nominal structural stability along all three Cartesian directions (i.e. **a**, **b** and **c)**, with stronger, multiple covalent bonds directed across a relatively small crystallographic face (like (001) in glitter), and that is a chemically intuitive structure, it appears that tetragonal glitter is perhaps a unique structure-type with the potential for achieving the absolute zenith in dynamic bulk modulus, B, of any such conceivable structure drawn from the Periodic Table of the elements. Certainly it appears that tetragonal glitter is the hardest potential covalent material from this analysis. It is not clear whether a structure drawn from the metallic elements in the Periodic Table could ever achieve a greater dynamic bulk modulus, B, than carbon-based glitter. The metallic potential is different from the Hooke's law (or Morse's law) potential of covalent bonding. It appears to be the case, from experience, that the metallic potential has lateral contributions to it in addition to the usual axial pair potential of the Hooke's law force. The metallic bonds tend to be slippery and appear not to be good candidates for maximizing out the dynamic bulk modulus, B, as it has been worked out here from solution of equation (4).

If one can roughly equate the bulk modulus of a material (especially its bulk modulus of elasticity with respect to the crystallographic faces, of a well-oriented single crystal, in contact with a sample in a high pressure anvil device like the diamond anvil cell (DAC) [22]) to the maximum accessible static pressure, it can attain, on a sample of material. One could then boldly state that the glitter lattice, which is evidently Nature's hardest material, seems to put a limit on the highest accessible static pressures attainable in the laboratory at somewhere between 900 to 1100 GPa (in the neighborhood of 10 Mb). The higher figure is obtained from analysis of the carbon–carbon bonds in glitter as Morse's law springs [1]. The 10 Mb regime represents a doubling of the record set at near 5 Mb by Mao et al. in studies of metallic hydrogen [22]. It would appear that difficult issues, such as the potential high pressure metallization of hydrogen, could possibly be resolved by an opposed anvil device comprised of carefully oriented tetragonal glitter single crystals. This is in addition to the phenomenal amount of scientific information that could be obtained on phase transitions and structures at pressures approaching the 10 Mb limit by such a device, and the general study of physical phenomena, like electrical resistance, at such tremendous pressures approaching 10 Mb.

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$$\cos\theta = \frac{(hkl)(xyz)^T}{||hkl|| \cdot ||xyz||} \tag{i}$$

where, in the case shown in Equation (i), we are calculating the projection factor for the chemical bond vector with components (x, y, z) onto the hklth crystallographic plane.

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