

Dynamic elasticity of cubic diamond

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Previously, the structure of the carbon allotrope glitter has been disclosed, and a theory accompanying the structural report as to its bulk modulus at pressure predicted it would be among the hardest materials possible. The dynamic elasticity theory developed in that paper, involving the forces generated in elastic chemical bond deformations resulting from applied mechanical forces, is here applied to the cubic diamond lattice. Stresses, both lateral and axial, contribute to the bulk modulus of cubic diamond at pressure. The ultimate strength of the cubic diamond lattice, in the approximations of the dynamic elasticity theory presented in this paper, is estimated to be in excess of 1 TPa, at modest bond length deformations of about 0.1 Å, and when including the zero pressure bulk modulus B_0 in the computation. In particular, the dynamic elasticity model predicts the hardest direction of cubic diamond will be for an isotropic mechanical force applied along $\langle 111 \rangle$ directions of the structural unit cell.

KEY WORDS: cubic diamond, elasticity, crystal structure, force density

AMS subject classification: elasticity, crystallography

1. Introduction

Cubic diamond is the ultimate hard material, with a zero-pressure bulk modulus estimated to be in excess of 442 GPa [1]. Borazon, the synthetic abrasive with the stoichiometric composition BN developed by Wentorf et al. at General Electric, is the only other material patterned on the cubic diamond structure-type, that achieves a zero-pressure bulk modulus approaching that of cubic diamond, at 367 GPa [1]. The other materials patterned on the cubic diamond structure-type possess zero-pressure bulk moduli significantly lower than that of C-based cubic diamond or the analogous BN material called Borazon [2].

On the basis of the design of the original WC Bridgman anvils in the early 20th century, the diamond anvil cell (DAC) was introduced, in 1959, as a device for achieving the highest possible pressures in the laboratory [3]. The novel design exploited the transparency of C-based diamond across the electromagnetic

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spectrum, in studies of IR spectra of materials at pressure, X-ray diffraction structure determinations at pressure, and other high pressure studies [1].

It is the purpose of the present report, to estimate the ultimate strength of the cubic diamond lattice, by developing and applying a dynamic elasticity theory to the structure to extend current estimations of its strength in a static approximation. This dynamic elasticity theory has been introduced previously with application to the glitter lattice, another superhard material under development now [4]. The theory enables one to calculate corrections to the zero-pressure bulk modulus, B_0 , from stresses introduced to the unit of structure of the material from elastic chemical bond deformation forces attendant on the principal crystallographic planes of the lattice, given in an orthogonal crystallographic setting as the planes (100), (010) and (001). Such elastic chemical bond deformation forces are generated in response to applied mechanical forces on the structure.

After introducing the dynamic elasticity theory in section 2, the actual stress equations for the cubic diamond structure-type will be developed in section 3, and the results of the calculations for the dynamic elastic moduli corrections to the zero-pressure static elasticity, given by the zero-pressure bulk modulus B_0 , for cubic diamond, will be tabulated. The paper concludes with a discussion of the bearing the current results have on the use of cubic diamond in high-pressure equipment, including predictions of the theory that may be useful to investigators in the field. Besides predicting the ultimate strength–elasticity expressions for the C-based cubic diamond structure-type, the present theory describes how specific axes of the cubic diamond lattice, i.e. the $\langle 111 \rangle$ axes, are the stiffest directions in which to apply mechanical forces, in order to translate the greatest amount of applied force into an applied stress.

2. Dynamic elasticity theory

Feynman has analyzed the problem of elasticity, in a static model, for the cubic rocksalt structure-type [5]. From this analysis, in a harmonic potential approximation, he obtained elasticity moduli of the form shown in equation (1) below:

$$\text{elastic modulus} \propto \frac{k}{\mathbf{a}}. \quad (1)$$

The elasticity moduli were derived and characterized in terms of fundamental parameters of the crystal, including the force constant, k , of the constituent bonds in the rocksalt structure-type, and the given lattice parameter of the cubic rocksalt lattice, \mathbf{a} . Note that the ratio Feynman derived for the elastic moduli, given by k/\mathbf{a} , in which k , the force constant of the chemical bond in the lattice, has the units of N/m, and the lattice parameter of the rocksalt unit cell, \mathbf{a} , has the units of m, properly has the dimensions of a stress or alternatively

an elastic modulus, therefore the analysis is internally consistent from a physical perspective [5].

It has been conjectured previously by the authors [4], that a ratio that is also dimensionally a stress or an elastic modulus for a crystalline material, can be gotten in terms of the fundamental parameters of the crystalline substance as given by the force constant of the constituent bonds in the unit cell, k in N/m, the corresponding lattice parameter given by \mathbf{a} in m, and finally, the elastic chemical bond deformation parameter, $r' = (r - r_e)$, in m. This type of expression, shown in equation (2), is representative of a dynamic stress or a dynamic elastic modulus. Physically, this prototypical dynamic elastic modulus expression, shown in (2), represents a force generated in elastic chemical bond deformation, divided by the area of a crystallographic plane, (hkl) , normal to that elastic chemical bond deformation force:

$$\text{elastic modulus} = \frac{kr'}{\mathbf{a}^2}. \quad (2)$$

Such expressions as those shown in (2) are the basis for the dynamic elasticity model presented in this paper. These ratios, in terms of a force over an area, F/A , are, from a dimensional analysis perspective, entirely consistent with the elastic constant ratios, given by k/\mathbf{a} , as derived for the rocksalt lattice by Feynman earlier [5] and shown in equation (1). Such dynamic elastic constant ratios as shown in equation (2), are also entirely consistent, from the perspective of dimensional analysis, with the more familiar ratios of U/V employed in the 1st principles calculations of bulk modulus of crystalline materials, where U is the internal energy of the unit cell, and V is the corresponding unit cell volume. Such elasticity analyses have been used extensively in the estimation of the zero-pressure bulk moduli, B_0 , of various crystalline lattices by Cohen and others [6].

Furthermore, it has been discovered previously by the authors [4], that defining these dynamic elastic moduli, as shown prototypically in (2), of a unit cell of a crystalline material, whose chemical bonds are undergoing elastic deformations due to an applied stress, through the use of a force density integral, as shown generically in equation (3), results in the generation of dynamic elasticity correction terms to the zero-pressure, static bulk modulus, like the prototype term shown in equation (2):

$$\text{elastic modulus} = \int \frac{F(r')}{V(r')} dr'. \quad (3)$$

In the force density integral shown in equation (3), F represents the sum of the elastic chemical bond deformation forces inside the unit cell, in response to an applied mechanical force of deformation (i.e. a mechanical stress). Components of these forces are seen to be normal to given crystallographic planes, (hkl) 's, and can therefore be equated to specific corrections of the zero-pressure elastic constants of a crystalline material. The specific bond forces are modeled

here, in this paper on C-based cubic diamond, as Hooke's law forces, as shown below in equation (4):

$$\frac{\partial U}{\partial r'} = kr'. \quad (4)$$

The volume denominator in equation (3), $V(r')$, is written as a function of the elastic chemical bond deformation parameter, r' , as well. This function describes the simultaneous change in the unit cell volume, with the generation of the elastic chemical bond deformation forces, $F(r')$, inside the unit cell.

Upon integrating equation (3) with respect to the chemical bond deformation parameter r' , which has the dimensions of a length, a term with the dimensions of a stress (or elastic modulus), is formally produced, in the physical sense of dimensional analysis. This elastic modulus correction term is expressed in the form of equation (2), as an elastic chemical bond deformation force divided by the area of the principal crystallographic plane, (hkl) , to which the deformation force is normal. The result, then, of this integration is the generation of dynamic corrections terms to the zero-pressure elasticity of a given crystalline material in a theoretical framework that is internally consistent both dimensionally and physically [4].

By writing down the components of the elastic chemical bond deformation, the components of r' directed along the Cartesian axes (i.e. orthogonal axes x , y and z), inside the unit of pattern of a material, one obtains a sum of force density integral expressions which describe the dynamic elasticity of the crystalline material considered. The integration of such expressions generates the terms for calculating the dynamic correction elastic moduli over the unit of pattern of the material [4].

3. Dynamic elasticity of diamond

Cubic diamond, the unit of pattern of which is pictured in figure 1, is a highly symmetrical material, belonging to the cubic symmetry space group Fd3m, (i.e. space group #227). It has a lattice parameter, \mathbf{a} , of 3.56 Å. Elementary vector analysis, shows the carbon-carbon single bonds are oriented parallel to the $\langle 111 \rangle$ axes of the cubic unit cell.

One can write down an expression for the sum of the components of the elastic chemical bond deformation forces attendant on all the C-C single bonds within the unit of pattern shown in figure 1. Such an expression is shown as equation (5), assuming an isotropic application of a mechanical stress:

$$\sum_{i=1}^{16} F_i = 16 \{ kr' \cos \alpha + kr' \cos \beta + kr' \cos \chi \}. \quad (5)$$

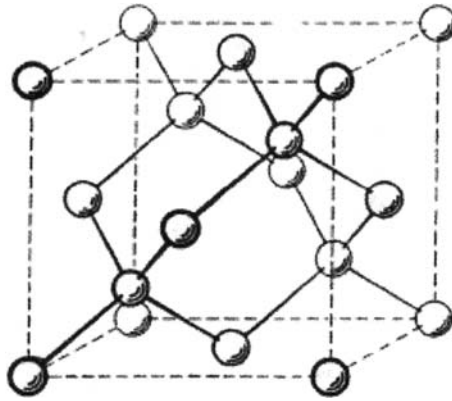


Figure 1. Cubic diamond unit cell.

In this expression, the factor of 16 represents the number of bonds within the C-based, cubic diamond unit of pattern shown in figure 1. The constant k is just the force constant of the C–C single bonds, it has the value of 450 N/m [7], and r' is the deformation parameter for the chemical bonds, in units of m (i.e. meter). Here we are assuming the potential energy function between the C–C single bonds is harmonic [4].

The factors $\cos \alpha$, $\cos \beta$ and $\cos \chi$ represent the projections of the elastic chemical bond deformation forces, kr' , onto the crystallographic planes (100), (010) and (001), respectively, which are normal to these forces. We can therefore simply rewrite equation (5) in terms of the orthogonalized deformation parameters x' , y' and z' , as follows:

$$\sum_{i=1}^{16} F_i = 16\{kx' + ky' + kz'\}. \quad (6)$$

In equation (6), the components of the deformation forces along the principal crystallographic directions; [100], [010] and [001]; are represented by x' , y' and z' , respectively.¹

According to the prescription introduced in equation (3), of the previous section, we next write down the corresponding force density integral for cubic diamond, in which the forces generated in elastic chemical bond deformations, are divided by the corresponding change in unit cell volume:

¹A note about $\cos \alpha$, $\cos \beta$ and $\cos \chi$. One can easily obtain these values from elementary vector analysis by forming the ratios of the type shown in equation (i): $\cos \theta = \frac{(hkl)(x y z)^T}{\|hkl\| \cdot \|x y z\|}$ 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 hkl th crystallographic plane.

$$\text{elastic mod.} = \int \frac{16kx'}{\mathbf{bc}(\mathbf{a} + 4x')} dx' + \int \frac{16ky'}{\mathbf{ac}(\mathbf{b} + 4y')} dy' + \int \frac{16kz'}{\mathbf{ab}(\mathbf{c} + 4z')} dz'. \quad (7)$$

Indicated in the denominator are the volume functions, $V(r')$, in which the lattice parameters are given, for clarity, as \mathbf{a} , \mathbf{b} and \mathbf{c} . The occurrence of the number 4 in these functions, reflects the fact that a net factor of 4 bond deformations, in total, contribute to the actual compressions along the \mathbf{a} , \mathbf{b} and \mathbf{c} axes of cubic diamond, from the respective chemical bond deformations taking place inside the unit cell, in response to the isotropic mechanical stress applied.

One can simplify the expressions in equation (7), as a result, the integrals are seen to take the following generic form:

$$\text{elastic modulus} = \frac{Nk}{\mathbf{ab}} \int \frac{z'}{(\mathbf{c} + dz')} dz'. \quad (8)$$

Such integrals have been evaluated previously by the authors [4], and it has been shown that they reduce the terms shown in equation (7) to the following forms (where B_0 is the constant of the integration):²

$$\text{elastic modulus} = B_0 + \frac{8kx'}{\mathbf{bc}} + \frac{8ky'}{\mathbf{ac}} + \frac{8kz'}{\mathbf{ab}} \quad (9)$$

equation (9) reflects the mechanism of dynamic elasticity that corrects the zero-pressure bulk modulus of cubic diamond (given by B_0), for an applied isotropic mechanical force, F , as a stress on the crystalline unit cell.

Finally, we insert a projection factor, $\cos\theta$, for the component of the applied force, F , directed along crystallographic axes $\langle hkl \rangle$, onto the chemical bond vectors (x, y, z) . It can be seen from this perspective, and from examination of figure 1, that the factor $\cos\theta$, shown below in equation (10), will have its maximum for isotropic forces directed along $\langle 111 \rangle$ axes of cubic diamond.

$$\text{elastic modulus} = B_0 + \frac{8kx'}{\mathbf{bc}} \cos\theta + \frac{8ky'}{\mathbf{ac}} \cos\theta + \frac{8kz'}{\mathbf{ab}} \cos\theta. \quad (10)$$

Table 1 indicates the respective axial and lateral correction moduli to the zero-pressure bulk modulus, B_0 , of the cubic diamond unit cell, for isotropic

²Solution of the generic integral shown in equation (8): (i), elastic modulus = $\int \frac{F(z')}{V(z')} dz'$, (ii), elastic modulus = $\int \frac{Nkz'}{\mathbf{ab}(\mathbf{c} + dz')} dz'$, (iii), elastic modulus = $\frac{Nk}{\mathbf{ab}} \int \frac{z'}{(\mathbf{c} + dz')} dz'$, (iv), elastic modulus = $\frac{Nk}{\mathbf{ab}} \left\{ \frac{z'}{d} + \frac{\mathbf{c}}{d^2} \ln|\mathbf{c} + dz'| \right\}$, (v), elastic modulus = $\frac{N}{d} \frac{kz'}{\mathbf{ab}} + \left\{ \frac{Nk}{\mathbf{ab}} \left\{ \frac{\mathbf{c}}{d^2} \ln|\mathbf{c} + dz'| \right\} \right\}$. Upon expanding the logarithm, we obtain: (vi), elastic modulus = $\frac{N}{d} \frac{kz'}{\mathbf{ab}} + \left\{ \frac{Nk}{\mathbf{ab}} \frac{\mathbf{c}}{d^2} \left(\left(\frac{dz'}{\mathbf{c}} \right)^1 + \frac{1}{2} \left(\frac{dz'}{\mathbf{c}} \right)^2 + \frac{1}{3} \left(\frac{dz'}{\mathbf{c}} \right)^3 + \dots \right) \right\}$ which reduces to the correction term: (vii), elastic modulus = $\frac{2N}{d} \frac{kz'}{\mathbf{ab}} \left(\frac{dz'}{\mathbf{c}} \right)^0 + \frac{N}{d} \frac{kz'}{\mathbf{ab}} \left(\frac{dz'}{\mathbf{c}} \right)^1 + \dots$ where, because z'/\mathbf{c} is negligible, the 0th order term, only, survives: (viii), elastic modulus = $\frac{2N}{d} \frac{kz'}{\mathbf{ab}} \left(\frac{dz'}{\mathbf{c}} \right)^0$ (ix), elastic modulus = $\frac{2N}{d} \frac{kz'}{\mathbf{ab}}$.

Table 1
Dynamic elastic moduli corrections to zero-pressure bulk modulus, B_0 , of cubic diamond.

Bond length deformation, x' , in Å	Axial e.m. correction along [001]	Lateral e.m. corrections along [100] & [010]
-0.010	28.565 GPa	28.565 GPa
-0.020	57.131 GPa	57.131 GPa
-0.040	114.26 GPa	114.26 GPa
-0.060	171.40 GPa	171.40 GPa
-0.080	228.52 GPa	228.52 GPa
-0.100	285.65 GPa	285.65 GPa

forces directed along the $\langle 111 \rangle$ axes of the unit of structure. The unit of pattern is assumed to be oriented in a right-handed system of Cartesian axes.

It is apparent from the data in Table 1 that elastic chemical bond deformations in excess of $x' = 0.0600 \text{ \AA}$ (when considering the tetrahedral angle in the cubic diamond lattice of 109.47° , $r' = 0.0600 \text{ \AA} / \cos 54.73^\circ = 0.104 \text{ \AA}$), on the C–C single bonds, will lead to axial stresses in excess of 171 GPa along each orthogonal, crystallographic axis. Previous calculations on the glitter unit of pattern indicate a unit cell in glitter with dynamic bulk moduli comparable to diamond at comparable bond length deformations [4].

When factoring in lateral and axial stresses, and the zero-pressure bulk modulus of cubic diamond (i.e. $B_0 = 442 \text{ GPa}$) together, cubic diamond has a dynamic bulk modulus of nearly 1 TPa, beyond a 0.104 \AA elastic chemical bond deformation limit on the C–C single bonds in the C-based unit of pattern.

References

- [1] R.M. Hazen, *The New Alchemists* (Times Books-Random House, New York, 1994).
- [2] M.L. Cohen, *Science* 261 (1993) 307.
- [3] (a) C.E. Weir, E.R. Lippincott, A. Van Valkenburg and E.N. Bunting, *J. Res. Nat. Bur. Stand.* 63A (1959) 55. (b) J.C. Jamieson, A.W. Larson and N.D. Nachtrieb, *Rev. Sci. Instrum.* 30 (1959) 1016.
- [4] M.J. Bucknum, and E.A. Castro, *J. Math. Chem.* 38(1) (2005) 27.
- [5] R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, 1st ed. (Addison-Wesley, Reading, MA, 1964).
- [6] A.Y. Liu, and M.L. Cohen, *Phys. Rev. B*, 41 (1990) 10727.
- [7] G. Herzberg, *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand Co. Inc., Princeton, 1950).