

Michael J. Bucknum · Eduardo A. Castro

Anharmonic compression of the glitter lattice

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Abstract A previous report has described the crystal structure of glitter, which is a dense 3-,4-connected net composed of ethylenic columns that run parallel to the *c*-axis of the unit cell. Such a structure invites speculation as to its relative stiffness along that axis. A semiempirical expression due to Cohen was used in a previous communication to estimate its zero-pressure bulk modulus. This estimate exceeds that of any known material at 440 GPa. Further, by treating the ethylenic units as harmonic springs, a correction was computed for the elastic deformation of the carbon–carbon double bonds along the *c*-axis. This correction is on the order of 300 GPa for deformations of the double bonds of approximately 0.1 Å. The present communication treats the ethylenic units along the *c*-axis of glitter as anharmonic springs obeying a Morse potential and a Morse's law force. Within the anharmonic approximation, at modest bond length deformations, x' , the bulk modulus at pressure of the glitter lattice exceeds 1 TPa.

Keywords Glitter lattice · Anharmonic compression · Elastic modulus · Bulk modulus

Introduction

Earlier reports of the glitter structure have focused on its crystal structure and electronic band structure [1,2]. These reports have shown that glitter is a good metal with extensive π and π^* band dispersions about the Fermi level due to through-space p_σ and p_{spiro} interactions [2]. Band calculations on a CN_2 structure patterned on the glitter lattice indicate that this structure will be a

wide band gap ($\cong 4$ eV) insulator, it will therefore be transparent. There are obviously many other possible glitter phases containing B, C, N, Al, Si, P, and other elements that are candidate structures for study. The present report concentrates on the mechanical properties of the parent carbon glitter phase.

The bulk modulus, B , of the glitter lattice is first considered in terms of the zero-pressure bulk modulus, B_0 , which can be determined very accurately through a semiempirical expression developed by Cohen [3]. This analysis indicates that the zero-pressure bulk modulus of glitter is nearly the same as that in the diamond lattice. Next a correction is applied to B_0 for compression and consequent volume contraction in order to obtain B , the bulk modulus at pressure. This approximate correction is made in terms of the deformation of the stiffest bonds in the glitter unit cell, the two carbon–carbon double bonds. Bond-angle deformations and the deformation of the carbon–carbon single bonds within the unit cell are neglected in order to calculate the value of the bulk modulus at pressure, B .¹

In the first case, this correction term involves treating the carbon–carbon double bonds as harmonic springs. A simple expression is proposed based upon dimensional analysis for correcting the zero-pressure bulk modulus and the results are tabulated for deformations up to a 0.15 Å deformation of each carbon–carbon double

¹The carbon–carbon single bond is about half as stiff ($k = 450$ N/m) as the carbon–carbon double bond ($k = 960$ N/m), therefore the single bond will be expected to deform more easily under an applied force than the double bond. The compression of the carbon–carbon single bonds in the unit cell of glitter leads to a contraction of the lattice parameter a . Because of the contraction of the lattice parameter a , the force directed along the *c*-axis in glitter will be distributed over a smaller area, in the model described in this paper. This contraction will result in an increase in the correction stress–elastic modulus computed for the glitter lattice when taking into account the simultaneous compression of the carbon–carbon single and double bonds in the unit cell. A separate communication will consider the more complicated case of calculating the stress–elastic modulus on glitter from the simultaneous compression of the carbon–carbon single and double bonds in the unit cell

M. J. Bucknum
Georgia College and State University, CBX 82,
Milledgeville, GA, 31061 U.S.A

E. A. Castro (✉)
Theoretical Chemistry Division, INIFTA,
1900 La Plata, Argentina
E-mail: castro@quimica.unlp.edu.ar

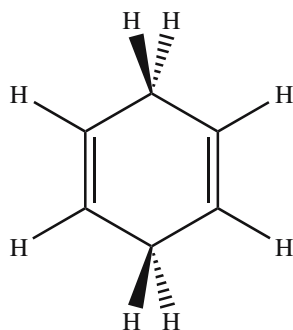


Fig. 1 The 1,4-cyclohexadiene molecule

bond. In the second case, all assumptions are identical, except that the carbon-carbon double bonds are treated as anharmonic springs obeying a Morse's law force [4]. In the next several sections, some preliminary features of the glitter structure will be addressed.

Crystal structure of glitter

The original report of the glitter structure described the crystal structure in terms of the molecular structure of the 1,4-cyclohexadiene molecule, as shown in Fig. 1 [5–7]. The crystal structure of the glitter lattice is shown in Fig. 2. Based upon the tetrahedral vertices being locally of D_{2d} symmetry, the lattice belongs to space group $P4_2/mmc$, # 131.

In 1,4-cyclohexadiene, the trigonal and tetrahedral carbon atoms are both distorted from ideality. The previous reports on glitter have been based upon a 1,4-cyclohexadiene model molecule with a C=C–C bond

angle of 123° and a trigonal C–C–C bond angle of 114° , a C–C bond length of 1.51 Å and a C=C bond length of 1.35 Å. From these parameters, all the unit cell contents of glitter can be computed, these unit cell contents were implied from the molecular parameters in the original report on glitter [1]. The tetrahedral C–C–C bond angle is approximately 107° . The fractional crystallographic coordinates of the carbon atoms in the unit cell of glitter, based upon the 1,4-cyclohexadiene molecular parameters, [5–7] are shown in Table 1. Also indicated in Table 1 are the fractional crystallographic coordinates for the hypothetical B_2C and CN_2 lattices that are isostructural with glitter [1,2]. The lattice parameters for glitter are given as, $a = 2.53$ Å and $c = 5.98$ Å, the density in this configuration is 3.12 g cm^{-3} .

A modified crystal structure in which all six tetrahedral C–C–C bond angles are set equal to the ideal tetrahedral angle of about 109.47° is possible, the trigonal C–C–C angles are thus forced to that ideal angle and the trigonal C=C–C angle is 125.25° . Such a lattice may exist based upon the probable structure of another hydrocarbon fragment that can be carved out of the glitter crystal structure, the molecule 1,3,5,7-tetramethylenecyclooctane. This molecule was first synthesized in 1959 by Benson and Lindsey [8]. The structure of the hydrocarbon is shown in Fig. 3.

1,3,5,7-Tetramethylenecyclooctane will likely exhibit the effect of endo-spiroconjugation described previously [2]. It is not clear that sites of endo-spiroconjugation should be exactly tetrahedral, but extended Hückel calculations show that they should be approximately in the shape of a tetrahedron for maximum electronic stability [2]. Therefore, an alternative lattice may be envisioned that may maximize the effect of endo-spiroconjugation, the tetrahedral glitter lattice. The lattice parameters of

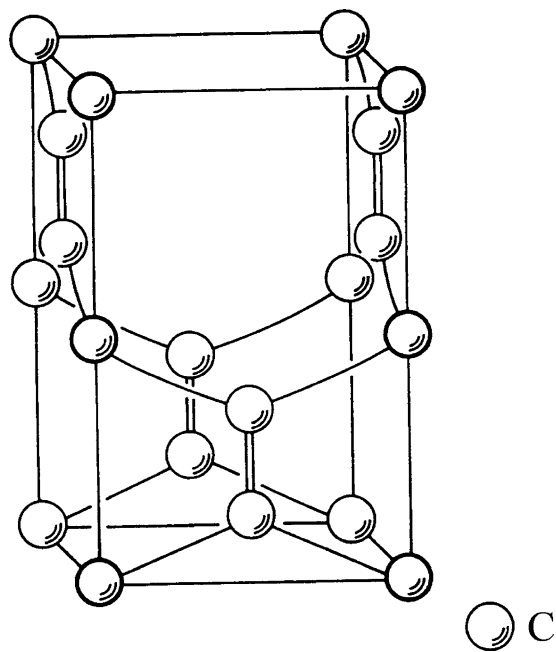


Fig. 2 Crystal structure of glitter lattice

Table 1 Fractional crystallographic coordinates of glitter based upon the 1, 4-Cyclohexadiene molecule, CN_2 and B_2C

Atom#	x/a	y/b	z/c	a (Å)	c (Å)
(a) 1, 4-Cyclohexadiene molecule					
1	0	0	0	2.532	5.988
2	$\frac{1}{2}$	0	0.1372		
3	$\frac{1}{2}$	0	0.3626		
4	0	0	$\frac{1}{2}$		
5	0	$\frac{1}{2}$	0.6374		
6	0	$\frac{1}{2}$	0.8629		
(b) CN_2					
1	0	0	0	2.470	6.102
2	$\frac{1}{2}$	0	0.1312		
3	$\frac{1}{2}$	0	0.3689		
4	0	0	$\frac{1}{2}$		
5	0	$\frac{1}{2}$	0.6314		
6	0	$\frac{1}{2}$	0.8691		
(c) B_2C					
1	0	0	0	2.616	6.840
2	$\frac{1}{2}$	0	0.1242		
3	$\frac{1}{2}$	0	0.3756		
4	0	0	$\frac{1}{2}$		
5	0	$\frac{1}{2}$	0.6240		
6	0	$\frac{1}{2}$	0.8754		

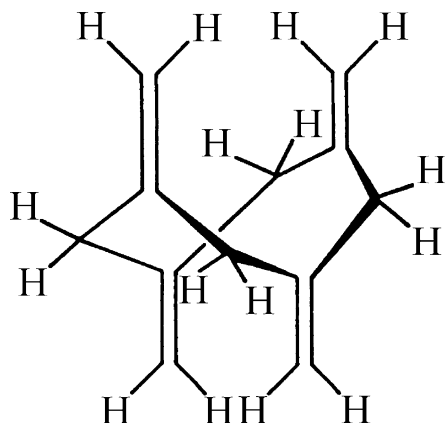


Fig. 3 The 1,3,5,7-tetramethylenecyclooctane molecule

this cell are, $a = 2.47 \text{ \AA}$ and $c = 6.19 \text{ \AA}$, its density is 3.20 g cm^{-3} . The fractional crystallographic coordinates are shown in Table 2. The calculations on the mechanical properties of glitter in the present report assume that the lattice is based upon the geometry of the 1,4-cyclohexadiene molecule, [5–7] as in the two previous reports [1,2].

Finally, it is instructive to point out the similarity of glitter to an actual mineral structure-type, that of Cooperite, PtS or PdO [9]. Figure 4 shows the structure of Cooperite, which has the space group $P4_2/mmc$, like glitter. In Fig. 5, glitter is shown in an alternative unit-cell setting that exemplifies the similarity of the two structures. One simply substitutes trigonal planar atom pairs for square planar vertices to generate the glitter structure from the Cooperite structure.

Topology of the glitter structure

As pointed out by Wells, crystal structures can be characterized not only by their symmetry (i.e., their space group), but they also can be characterized topologically by their Schläfli symbols (n, p) [10–23]. These symbols represent the average polygonality within the unit cell, n , and the average connectivity within the unit cell, p . In fact, because more than one given structure may have the same topology but different symmetry, it has been pointed out that the Schläfli symbols may have a deeper significance than that given by symmetry considerations alone.

Table 2 \AA Fractional crystallographic coordinates of glitter based upon the four-connected vertices being tetrahedral

Atom#	x/a	y/b	z/c	a (\AA)	c (\AA)
1	0	0	0	2.466	6.184
2	$\frac{1}{2}$	0	0.1407		
3	$\frac{1}{2}$	0	0.3588		
4	0	0	$\frac{1}{2}$		
5	0	$\frac{1}{2}$	0.6402		
6	0	$\frac{1}{2}$	0.8583		

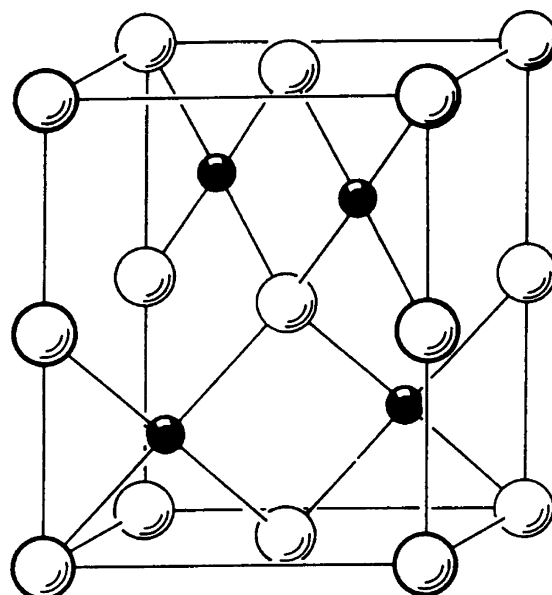


Fig. 4 Crystal structure of cooperite lattice

These topological characterizations are based upon Euler's equation relating the number of edges, E , to the number of faces, F , and the number of vertexes, V , in convex polyhedra, as shown in Eq. 1 [24]. By substituting the identities, $nF = 2E$ and $pV = 2E$ into Eq 1, we obtain Eq. 2. Equation 2 relates the secondary topological indexes, n and p , to the primary topological indexes E , F , and V [10–23]. This expression is completely sound for the convex polyhedra, and this provides the starting point for mapping out the topological space of structures for the crystalline materials. There are similar expressions relating n and p , to V and F [10–23].

$$V - E + F = 2 \quad (1)$$

$$\frac{1}{n} - \frac{1}{2} + \frac{1}{p} = \frac{1}{E} \quad (2)$$

For extended structures in 2- and 3-dimensions, like graphene (6, 3) and diamond (6, 4), although one can calculate the secondary topological indexes n and p , their solution in terms of an Euler equation gives infinity for the number of edges E in the 2-dimensional graphene sheet and a negative number for E in the 3-dimensional diamond structure. A modification of the classical Euler equation, one that is applicable to 2- and 3-dimensional extended structures, is evidently needed. Still n and p are rigorously determined in all crystalline structures where links between atoms in the unit cell can be identified unambiguously. The map shown in Fig. 6, due to Wells, can be used to determine the topological identity and location of all such crystalline structures [10–23].

Interestingly, all of the fullerenes can be characterized topologically as having connectivity of 3 and a varying fractional polygonality that runs between 5 and 6 [25].

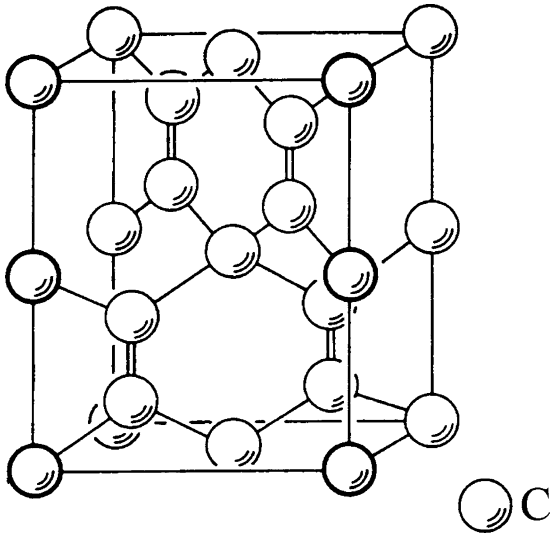
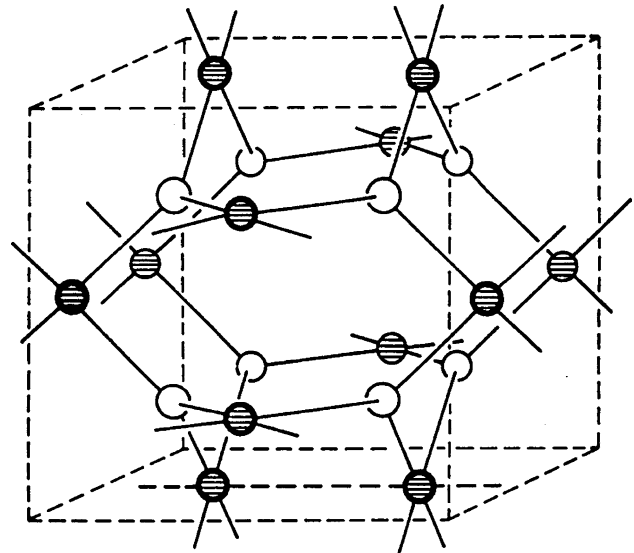


Fig. 5 Glitter lattice in alternative setting

Therefore n runs from just above 5 (where the Schläfli index (5, 3) is the classical Platonic structure, the pentagonal dodecahedron) to just below 6 (where the Schläfli symbol (6, 3) is the graphene net). Therefore, the fullerenes are a family of Archimedean polyhedra (meaning n is fractional). The most famous member of this family, Buckminsterfullerene, has 20 six-gons and 12 five-gons in each molecule. The Schläfli symbol for the buckyball is therefore $(5^{5/8}, 3)$.

The glitter lattice is part of the topological space of 3-,4-connected networks [10–23]. These structures were first described in connection with the crystal structures of Pt_3O_4 [26] shown in Fig. 7, and the mineral phenacite, Be_2SiO_4 , [27] shown in Fig. 8.

One can see in Fig. 7 the identities of n and p , all the shortest circuits in this Pt_3O_4 network are octagons, so $n=8$. In addition, there are 3 four-connected vertexes for every 4 three-connected vertexes (i.e., the Pt atoms are in square-planar coordination and the O atoms are in trigonal coordination). Therefore, the averaged index

Fig. 7 Crystal structure of Pt_3O_4 lattice

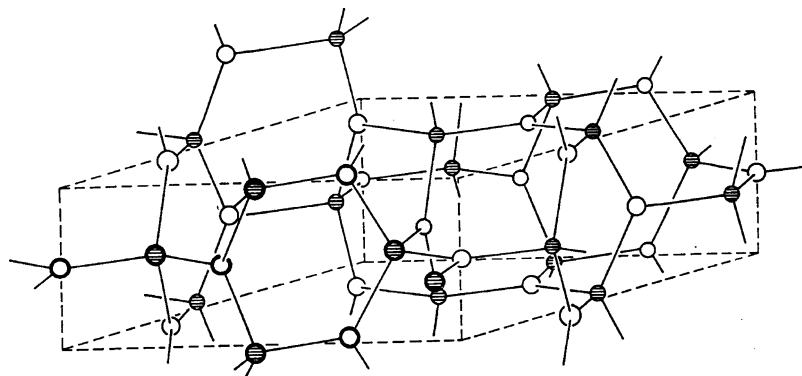
$p=3.4285\dots$ It is interesting here that the connectivity is a continued fraction, and because the polygonality is integer and the connectivity is fractional, the Schläfli symbol for the Pt_3O_4 network corresponds to that of the Catalan polyhedra. It is a Catalan structure.

Figure 8 indicates a more complex network, the phenacite structure-type. There are several isostructural systems based upon the phenacite network. The first to be identified was Be_2SiO_4 . There are apparently 3 six-gons for every 2 eight-gons in the unit of pattern, leading to a polygonality, n , equal to $6^{4/5}$. Thus the polygonality is a rational number. The connectivity, p , is 3.4285... the same continued fraction as was found in the connectivity of the Pt_3O_4 structure. They both have 4 three-connected vertexes and 3 four-connected vertexes in the unit of pattern. Because both the polygonality, n , and the connectivity, p , are fractional in the phenacite structure-type, it is classified topologically as “irregular,” or Wellsean [2].

Fig. 6 Topology map of regular structures

n	p						
	3	4	5	6	7	8	...
3	t	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

Fig. 8 Crystal structure of Be_2SiO_4 lattice



Evidently, glitter is one of virtually innumerable 3-,4-connected nets, many of which were first able to see the light of day through the enumerative work of Wells [10–23]. It was Wells who first identified the topological space of “irregular” structures. The “irregular” structures were discovered through his exploration of the space of 3-,4-connected nets. Such structures are therefore called Wellsean structures [2]. Inspection of Fig. 2 indicates that there is 1 six-gon for every 1 eight-gon in the unit of pattern of glitter. The polygonality is therefore 7 in this network. Similarly, there are 2 three-connected vertexes and 1 four-connected vertex in the unit of pattern, the connectivity is $3^{1/3}$. Glitter is therefore a Wellsean structure, with a Schläfli symbol $(7, 3^{1/3})$.

Finally, there are an infinite series of hypothetical 3-,4-connected networks, the graphite-diamond hybrids, which consist of fusing graphene sheets onto open-valence tetrahedral bonds in various crystallographic planes, (hkl) , of a diamond lattice. The electronic structure of these networks has been studied [28]. Topologically, these structures are Catalan with the connectivity, p , running between 3 and 4, and a uniform polygonality, n , given by 6^2 . It should be noted that glitter, with a polygonality of 7, is not a graphite–diamond hybrid. It is a topologically distinct structure containing eight-gons and six-gons.

Synthesis of glitter

In 1959, Benson and Lindsey investigated condensation reactions of the hydrocarbon allene and discovered several heretofore-unknown hydrocarbon oligomers of allene [8]. Of particular interest for the eventual synthesis of glitter was the identification of a tetramer of allene shown in Fig. 3. The reactions were carried out at 140°C using pure liquid allene with a divalent Ni catalyst present. Had the researchers used 1,1-dimethylallene

²Therefore the graphite-diamond hybrids, being Catalan networks composed of various ratios of three-connected and four-connected points, exclusively in six-gons, represent an interesting contrast to the fullerenes, these being Archimedean networks composed of various ratios of five-gons and six-gons and held together by three-connected points.

instead of allene, and the reaction proceeded in the identical way, they would have produced the tetramer molecule 9,9,10,10,11,11,12,12-octamethyl-1,3,5,7-tetramethylenecyclooctane instead. This latter molecule is precisely one unit cell of glitter, it is a hydrocarbon fragment of the unit cell of the glitter lattice.

In their work, Benson and Lindsey report that the tetramer is remarkably stable and does not decompose readily. In contrast, a trimer produced as a by-product in such reactions was remarkably unstable and reacted readily. No crystal structure was obtained for the tetramer, but a cycloaddition reaction occurred when the tetramer was mixed with tetracyanoethylene in tetrahydrofuran. This cycloaddition reaction indicated that there were through-space interactions of the adjacent double bonds. The reaction suggests that there is some degree of endo-spiroconjugation in the molecule, and may explain its great stability.

As glitter is a 3-,4-connected net, it is clear that it could likely be synthesized at conditions of pressure (P) and temperature (T) at which trigonal carbon and tetrahedral carbon atoms coexist. Such PT conditions exist in the neighborhood of the graphite–diamond phase boundary. It is not clear if an industrial scale, opposed anvil belt apparatus, like that used to make synthetic diamond, could be operated at the narrow range of temperatures and pressures along the phase boundary of graphite–diamond [29]. But evidently, from the synthesis of the remarkably stable tetramer, the allene condensation product 1,3,5,7-tetramethylenecyclooctane, there is a driving force for the tetramer to form and settle into a remarkably stable state. It is possible that a similar spontaneous self-assembly reaction could occur for the glitter lattice somewhere on the graphite–diamond phase boundary. One might therefore reasonably expect that there might be a thermodynamic stability field for glitter in the phase diagram of C. Table 3 indicates the theoretical diffraction pattern for glitter, based upon the parameters of the model molecule 1,4-cyclohexadiene. Also included in this table are the theoretical diffraction patterns for the B_2C and CN_2 lattices isostructural with glitter. All 3 theoretical diffraction patterns represent corrections to previously published data [1,2].

Elasticity theory: recent developments

Cohen has taken the lead of investigators dedicated to understanding the issues of strength of materials and their ultimate stiffness or hardness. In a series of papers written from the 1980's onward [30], he has made a successful attempt to simplify the mathematical language and principles through which elasticity and elastic properties of materials are understood by people working in the physical sciences. At the same time, Cohen has focused on providing a more intuitive basis through which people can understand elasticity and through which they can calculate elastic properties of various structures.

One of the most important contributions he has made in this area is the fitting of elasticity data on the volume modulus of elasticity of tetrahedral solids, the so-called diamond-like materials, to a semiempirical formula in the average bond distance in the unit cell, d , to the inverse $3^{1/2}$ power. In doing so, he simplified the problem of calculating the bulk modulus for cubic crystals from a formula involving 3 elastic constants to one based solely on the empirical parameter of average bond distance in the unit cell, d , and degree of ionicity, I , in the chemical bonds in the structure. Furthermore, by modifying this initial formula, which was applicable to tetrahedral solids, for application to solids with coordination numbers, N_c , different than 4, Cohen extended its applicability to other kinds of structures including non-cubic unit cells like his prototype superhard material β - C_3N_4 , which is a 3-,4-connected net lying in the hexagonal space group $P6_3/m$. [31–33]

The 21 elastic constants necessary to derive the elastic properties of anisotropic crystals, involving the stress–strain formalism, represent an important physical theory that may ultimately prove to be the most accurate formulation of elasticity theory that is possible. However, it can be seen that the calculation of 21 independent elastic parameters, even when considering simplifications due to symmetry, is quite a formidable and a decidedly counterintuitive way to view elasticity in materials.

As a considerable simplification of these ideas, we propose an intuitive model of the dynamic elasticity, in the spirit of the work of Cohen, which involves modeling covalent materials in terms of harmonic (or anharmonic) potentials between atom pairs, and the projection of the resultant elastic chemical bond deformation forces across a set of 3 mutually orthogonal pairs of lattice planes within the unit cell of the material. The fundamental and basic approximation of the model is to define the stress–elastic modulus as equivalent to a force - density integral, where the force is given by the sum of the elastic chemical bond deformations taking place inside the unit cell, and the volume parameter reflects the deformations taking place in the chemical bonds of the unit cell.

The formalism defined in this way generates a term in the zero-pressure bulk modulus, the static volume modulus of elasticity, as the constant of integration, and

Table 3 Calculated lattice spacings and relative intensities for diffraction from the glitter lattice, CN_2 lattice and B_2C lattice with Cu K_α radiation ($\lambda = 1.542 \text{ \AA}$) [47, 48]

$h k l$	$d(hkl) \text{ \AA}$	$\text{Sin } \theta(hkl)$	$\theta(hkl)^\circ$	$I(F \times F)$
(a) Glitter lattice				
1 0 0	2.530	0.3047	17.74	144
0 0 1	5.980	0.1289	7.41	0
1 1 0	1.788	0.4312	25.54	144
1 0 1	2.330	0.3309	19.32	332
1 1 1	1.713	0.4500	26.74	0
2 0 0	1.265	0.6095	37.55	1296
0 0 2	2.990	0.2578	14.94	69
2 1 0	1.131	0.6816	42.97	144
2 0 1	1.237	0.6232	38.55	0
1 0 2	1.931	0.3992	23.53	144
1 1 2	1.535	0.5022	30.15	246
1 2 1	1.111	0.6939	43.94	332
2 2 0	0.894	0.8624	59.59	1296
2 0 2	1.165	0.6618	41.44	69
2 1 2	1.058	0.7287	46.78	144
2 2 1	0.884	0.8721	60.70	0
2 2 2	0.857	0.8996	64.11	69
3 0 0	0.843	0.9145	66.13	144
0 0 3	1.993	0.3868	22.76	0
(b) CN_2 lattice				
1 0 0	2.470	0.3121	18.18	144
0 0 1	6.100	0.1263	7.25	0
1 1 0	1.747	0.4412	26.18	256
1 0 1	2.289	0.3367	19.67	422
1 1 1	1.679	0.4591	27.32	0
2 0 0	1.235	0.6242	38.62	1600
0 0 2	3.050	0.2527	14.63	97
2 1 0	1.105	0.6976	44.23	144
2 0 1	1.210	0.6371	39.57	0
1 0 2	1.919	0.4017	23.68	144
1 1 2	1.515	0.5088	30.58	200
1 2 1	1.087	0.7091	45.16	422
2 2 0	0.873	0.8830	62.00	1600
2 0 2	1.144	0.6738	42.36	97
2 1 2	1.038	0.7426	47.95	144
2 2 1	0.864	0.8922	63.15	0
2 2 2	0.839	0.9188	66.75	97
3 0 0	0.823	0.9366	69.48	144
0 0 3	2.033	0.3791	22.27	0
(c) B_2C lattice				
1 0 0	2.620	0.2942	17.10	144
0 0 1	6.840	0.1127	6.47	0
1 1 0	1.852	0.4162	24.59	64
1 0 1	2.446	0.3151	18.36	215
1 1 1	1.788	0.4311	25.53	0
2 0 0	1.310	0.5884	36.04	1024
0 0 2	3.420	0.2254	13.02	109
2 1 0	1.171	0.6583	41.17	144
2 0 1	1.286	0.5994	36.82	0
1 0 2	2.079	0.3708	21.76	144
1 1 2	1.628	0.4735	28.26	183
1 2 1	1.154	0.6680	41.91	215
2 2 0	0.926	0.8325	56.35	1024
2 0 2	1.223	0.6303	39.07	109
2 1 2	1.108	0.6957	44.08	144
2 2 1	0.917	0.8406	57.20	0
2 2 2	0.894	0.8623	59.57	109
3 0 0	0.873	0.8830	62.00	144
0 0 3	2.280	0.3381	19.76	0

Table 4 Corrections to the zero-pressure bulk modulus, B_0 , from harmonic compression of the double bonds in the glitter lattice [48]

Deformation, x' , in m	$\frac{2kx'}{a^2}$, in $\frac{N}{m^2}$; (Pa)	B in GPa
-0.010×10^{-10}	30.0×10^9	470
-0.020×10^{-10}	60.0×10^9	500
-0.030×10^{-10}	90.0×10^9	530
-0.040×10^{-10}	120.0×10^9	560
-0.050×10^{-10}	150.0×10^9	590
-0.060×10^{-10}	180.0×10^9	620
-0.070×10^{-10}	210.0×10^9	650
-0.080×10^{-10}	240.0×10^9	680
-0.090×10^{-10}	270.0×10^9	710
-0.100×10^{-10}	300.0×10^9	740
-0.110×10^{-10}	330.0×10^9	770
-0.120×10^{-10}	360.0×10^9	800
-0.130×10^{-10}	390.0×10^9	830
-0.140×10^{-10}	420.0×10^9	860

a power series in the attendant strain on the unit cell in each of the three mutually orthogonal crystallographic directions. Physically, the zero-pressure bulk modulus can be represented as a function of “ k/a ” where k is the force constant of the bonds in the unit cell, and a is the corresponding lattice parameter. The identification of the ratio “ k/a ” as being related to the zero-pressure bulk modulus, draws a connection with the work of Feynman on elasticity of materials [34]. Furthermore, the terms to 1st order, given by “ kx'/a^2 ” (where x' is the elastic chemical bond deformation parameter and a^2 is the area of the crystalline plane normal to that chemical bond deformation) take account, explicitly, of the contribution to the elasticity of crystalline materials from the deformations of the bonds that take place as a result of applied stresses. The formalism therefore leads to 2 lateral dynamic components and an axial component of the elasticity. In this formalism, one assumes a particular orientation of the unit cell in Cartesian space. This reduces the complexity of calculating 21 independent elastic constants for a given anisotropic crystalline material, to the problem of writing down 3 independent dynamic elastic parameters for the unit cell, in addition to the term in the zero-pressure elasticity, the constant in the strain integration.

Overall, the theory presented in this paper extends the intuitive ideas of Cohen and Feynman on elasticity, as proposed for simplifying the computation of static zero-pressure elasticity [30], into the realm of the dynamic elasticity, and the corresponding elastic deformations of the unit cell of a material. The theory presented in this paper describes computation of the elasticity given along only 1 of 3 possible independent, mutually orthogonal crystallographic directions. Ultimately, it is the intention of the authors to extend these ideas to all three crystallographic axes of a unit cell of a material. With this introduction, the next several sections present the basic ideas of our elasticity model, in 1 dimension, with both harmonic and anharmonic axial pair potentials assumed for the chemical bonds in the computation of the elastic properties of glitter.

Harmonic compression

As described above, the present communication focuses on the mechanical properties of glitter, specifically the volume modulus of elasticity (the bulk modulus). The first indication of the stiffness of glitter was provided by analysis with the semiempirical equation developed by Cohen for the zero-pressure bulk modulus of materials [3]. This semiempirical equation was obtained by a judicious fit of available experimental data on bulk moduli of structures adopting the diamond lattice (tetrahedral solids). It is shown as Eq. 3 below:

$$B_0 = \frac{1972 - 220I \langle N_c \rangle}{\langle d \rangle^{3.5} 4} \quad (3)$$

In Eq. 3, d is the weighted average bond length in the unit cell, N_c is the weighted average coordination number (the connectivity, p) in the unit cell, and I is the ionicity in the structure (a parameter dependent on the weighted average difference in electronegativity of the elements in the unit cell). One can see immediately that the zero-pressure bulk modulus is strongly dependent on the weighted average bond length in the unit cell. The shorter the chemical bonds, the higher the zero-pressure bulk modulus.

From the perspective of a relation developed from spectroscopic research on diatomic molecules, Badger’s rule, shown as Eq. 4, the Cohen formula is physically reasonable [35, 36]. Badger’s rule states that the force constant for a given chemical bond, k in Nm^{-1} , is proportional to the inverse cube of the corresponding internuclear distance, d in m.

$$k(d - C_1)^3 = C_2 \quad (4)$$

The constants in the equation, C_1 and C_2 , make the relation exact and dimensionally consistent, and they differ depending on the row of the Periodic Table from which the atoms are taken to be bonded. Therefore, Cohen’s formula may be thought of as approximately relating the mean force constant of the chemical bonds in a unit cell of a given structure, to the zero-pressure bulk modulus, B_0 , of that structure. For smaller values of d , to a power of approximately 3, the force constant becomes correspondingly larger and the chemical bonds in the unit cell are stiffer. Interestingly, empirical relations of B_0 for various structures, based upon the force constants of the bonds in the unit cell of these structures, were first analyzed by Waser and Pauling in 1950 [37].

If the parameters of the diamond structure, most importantly the bond length of 1.54 Å, are inserted into Eq. 3, a zero-pressure bulk modulus of 435 GPa is obtained. This represented the zenith in volume stiffness of crystalline materials until the publication of the glitter structure. [1, 38] The major parameter affecting the computed bulk modulus for the glitter lattice is the weighted average bond length of 1.46 Å, 0.08 Å shorter

than the C–C single bonds in diamond. Equation 3 predicts that glitter will have a zero-pressure bulk modulus of 440 Gpa. This is about 1 percent larger than the zero-pressure bulk modulus in diamond.

Beyond zero-pressure, the question naturally arises as to the corrections to B_0 with compression of the unit cell volume. In an earlier communication, a preliminary assessment of the volume stiffness to compression of the unit cell of glitter was made by approximating the correction to B_0 with what was probably the largest contribution to the bulk modulus at pressure, the elastic compression of the carbon–carbon double bonds [2]. This approximation was made under the assumption of a harmonic potential for the carbon–carbon double bond. Such compression would occur along virtually any axis $[hkl]$ of the unit cell, but the component of force of that deformation, normal to a given crystallographic plane of the unit cell (hkl) , divided by the area of that given crystallographic plane (hkl) , here (001), which would be a correction to B_0 , would approximately be given by Eq. 14 shown below

A rigorous, and exact, derivation of the correction term in Eq. 5 is provided by defining the volume stress–elastic modulus, associated with the elastic deformation of the chemical bonds in a unit cell, by the following integral:

$$\text{Elastic modulus} = \int \frac{F(x')}{V(x')} dx' \quad (5)$$

Here we are specifying the case of uniaxial compression, where only one deformation variable, x' , is considered as contributing to the volume stress–elastic modulus. The other components of the volume stress–elastic modulus, the bond angles and y' and z' , are assumed to stay fixed in this model. $F(x')$ represents the force exerted in elastic deformation. In this approximation, it is a Hooke's law force given by $2kx' \cos \theta$. $V(x')$ represents the dependence of the volume of the unit cell on the elastic deformation parameter, x' . From these specifications, we get the following expression for the volume stress in glitter based upon the exclusive deformations of the carbon–carbon double bonds, through compression in the unit cell along the \mathbf{c} -axis:

$$\text{Elastic modulus} = \int \frac{2kx'}{a^2(c-2x')} \cos \theta dx' \quad (6)$$

$$\text{Elastic modulus} = \frac{2k}{a^2} \cos \theta \int \frac{x'}{(c-2x')} dx' \quad (7)$$

$$\text{Elastic modulus} = \frac{2k}{a^2} \cos \theta \left\{ \frac{x'}{2} - \frac{c}{2^2} \ln |c-2x'| \right\} \quad (8)$$

$$\text{Elastic modulus} = \frac{kx'}{a^2} \cos \theta - \left\{ \frac{2k}{a^2} \cos \theta \left(\frac{c}{4} \ln |c-2x'| \right) \right\} \quad (9)$$

However, $|\mathbf{c}-2x'| = (\mathbf{c}-2x')$ for compression, where x' corresponds to compression, so:

$$\text{Elastic modulus} = \frac{kx'}{a^2} \cos \theta - \left\{ \frac{2k}{a^2} \cos \theta \left(\frac{c}{4} \ln (c-2x') \right) \right\} \quad (10)$$

Upon expanding the logarithm, we obtain the following power series:

$$\text{e.m.} = \frac{kx'}{a^2} \cos \theta - \left\{ \frac{2k}{a^2} \cos \theta \left(\frac{c}{4} \left(-\left(\frac{2x'}{c}\right)^1 - \frac{1}{2} \left(\frac{2x'}{c}\right)^2 - \frac{1}{3} \left(\frac{2x'}{c}\right)^3 - \dots \right) \right) \right\} \quad (11)$$

Which reduces, essentially, to the correction factor in Eq. 14:

$$\text{e.m.} = \frac{2kx'}{a^2} \cos \theta \left(\frac{x'}{c} \right)^0 + \frac{kx'}{a^2} \cos \theta \left(\frac{x'}{c} \right) + \frac{kx'}{a^2} \cos \theta \left(\frac{4}{3} \right) \left(\frac{x'}{c} \right)^2 + \dots \quad (12)$$

The terms in the power series at $(x'/c)_1$ and higher, represent negligible corrections to the zeroth-order term, at the bond length deformations, x' , presented in this paper. Thus, the dynamic stress is given by Eq. 13:

$$\text{Elastic modulus} = \frac{2kx'}{a^2} \cos \theta \quad (13)$$

$$\mathbf{B} = \mathbf{B}_0 + \left[\frac{2kx'}{a^2} \right] \cos \theta \quad (14)$$

Here k is the force constant of the double bond in Nm^{-1} , x' is the deformation of the chemical bond in m; where the deformation of the bond is given by $x' = (x - x_e)$, here x_e is the equilibrium internuclear distance of the bond, in m; and \mathbf{a} is the basal plane lattice parameter, in m. The quotient is adjusted for the cosine of the angle between the chemical bond (in this case, the ethylenic bonds in the unit cell of glitter) and the crystallographic axis $[hkl]$ along which is applied the compressive force, this angle is given by θ .

Inspection shows that such a quotient has the dimensions of a pressure (i.e., a force divided by an area). Therefore, it is dimensionally consistent with a correction term to the zero-pressure bulk modulus, B_0 . The term has its maximum when $\theta = 0^\circ$ (or 0 radians), this corresponds to compression along the \mathbf{c} -axis. In the previous communication of the ideas in this model, $\theta = 0^\circ$ was just the case that was considered [2]. Under these assumptions, the correction to the zero-pressure bulk modulus, B_0 , for the elastic deformation of the ethylenic bonds in the unit

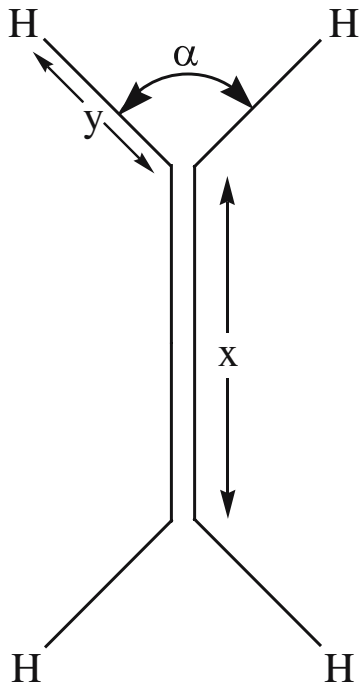


Fig. 9 Principal parameters affecting B_0 in glitter

cell of glitter, is calculated to be of the order of 300 GPa (about 68% of B_0) for deformations of the double bonds of approximately 0.1 Å.

Along the lines of the relation proposed in Eq. 14, Feynman derived expressions for the elasticity moduli of a prototype crystal structure in a static model [34]. These elastic moduli were derived by treating the chemical bonds in the unit of pattern of the structure as possessing harmonic potentials, similar to the assumptions adopted in Eq. 14. From Feynman's derivation within this static model, he obtained expressions for the elastic moduli of the prototype structure, a cubic rocksalt structure-type, in terms of the ratios of the force constants, k in Nm^{-1} , of the chemical bonds in the unit cell, to the lattice parameters, a in m, of the unit cell. The archetypal expression of the elastic moduli that Feynman obtained in this analysis is shown in Eq. 15.

$$\text{Elastic modulus} \propto \frac{k}{a} \quad (15)$$

Such expressions of the elasticity moduli of a crystal structure, in a static model, are entirely analogous to expressions like that shown in Eq. 14, where a modulus of elasticity of a prototype crystal structure is being calculated in a dynamic model. In the dynamic model treated in Eq. 14, a strain is produced by deformations of only a single set of symmetry-equivalent chemical bonds in the unit of pattern. This strain yields a corresponding dynamic correction stress-elastic modulus, analogous to the static expressions given in the Feynman analysis, to the given elasticity modulus.

A derivation of Eq. 14 is provided above. This derivation is based upon defining the correction stress-elastic modulus to the zero-pressure bulk modulus, B_0 , in terms of a function that is the ratio of the forces in the unit cell produced by chemical bond deformations, to the corresponding volume deformation of the unit cell (i.e., F/V). Such a function has the dimensions of a force density, i.e., Nm^{-3} , and when this quantity is integrated, it formally produces a dynamic correction term with the dimensions of a stress, Nm^{-2} . A separate communication will discuss this derivation more fully, including its generalization to chemical-bond deformations with dynamic strain-stress components along all three Cartesian axes of a unit cell.

The basic physical assumptions involved in the proposed expression shown in Eq. 14 for the computation of the bulk modulus of glitter at pressure, B , are outlined in the remainder of this section. Figure 9 shows the three principal parameters that would contribute to corrections to B_0 from strains to the volume of the unit cell of glitter from their deformations.

Bond-angle deformations, distortions of the unit cell parameter α in Fig. 9, imply the operation of non-central forces [37]. There is some evidence that bond angles are preserved to high pressure, up to a phase transition [39]. In this paper, it is assumed that the bond angles, including the tetrahedral angle not shown in Fig. 9, are preserved to high pressures.

The carbon-carbon single bonds, shown as the molecular parameter y in Fig. 9, will deform elastically under pressure just like the carbon-carbon double bonds. There will be a component of force, along the crystallographic axis of interest $[hkl]$, associated with the deformation of the carbon-carbon single bonds, but this analysis is more complicated as it involves a continuous change in the dimensions of the a and c lattice parameters of the unit cell simultaneously. Therefore it will be treated in a separate communication.

Neglecting the above-mentioned contributions to the correction of the zero-pressure bulk modulus, we focus on the carbon-carbon double bonds in the unit cell of glitter. The potential for these bonds will be approximated by Eq. 16, a harmonic potential [40].

$$U(x') = \frac{1}{2}kx'^2 \quad (16)$$

Here k is the force constant for the double bond, in Nm^{-1} , and x' is the deformation from the equilibrium state, in m, where $x' = (x - x_0)$. A plot of such a potential is shown in Fig. 10, the steeper the parabolic curve the larger the force constant. Also note that $(kx'^2/2)$ has the dimensions of energy, i.e., Nm or J.

Upon taking the derivative with respect to deformation, x' , the Hooke's law force expression is obtained through the elementary identity shown in Eq. 17:

$$\frac{\partial U}{\partial x'} = kx' \quad (17)$$

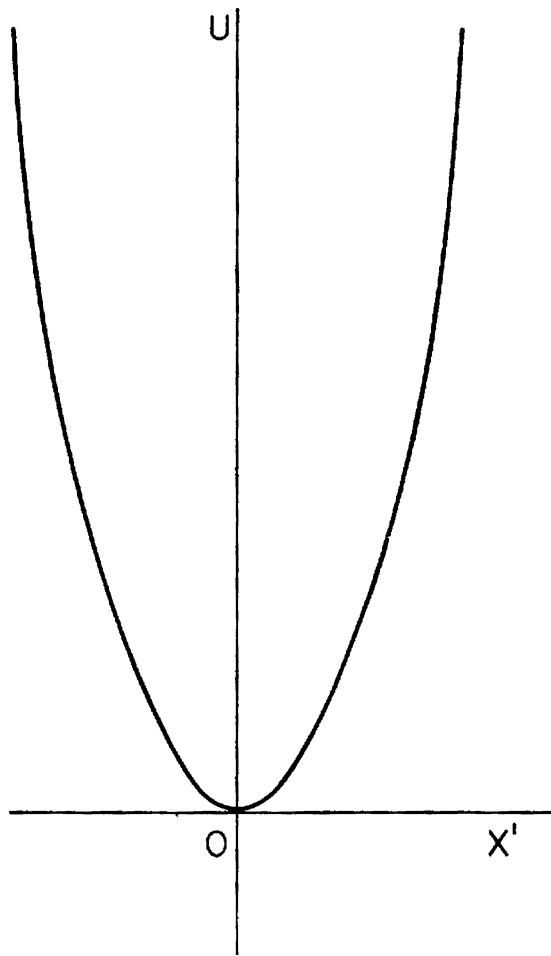


Fig. 10 Harmonic potential function

This formula differs from the more familiar expression of Hooke's law given by $F = -kx'$, in which the Hooke's law force is said to be the restoring force of a spring. In Eq. 16, the Hooke's law force is written as $F = kx'$. When x' is less than zero (i.e., corresponding to compression) the force is negative, or opposite in direction to the applied force. Therefore, the sign of the Hooke's law force merely represents a chosen reference frame (i.e., set of axes) for the Hooke's spring system under consideration.

Note kx' has the dimensions of a force, N , and that this force is produced in compression or tension (in tension, $x' = (x - x_c)$, is positive) and is linear with deformation. This linearity is an important characteristic of a harmonic potential³. When the harmonic spring or bond is in compression, this corresponds to excursions up the left side of Fig. 10 and the deformation, $x' = (x - x_c)$ is negative, and vice versa for the spring or

³Strictly speaking, the Hooke's potential is termed harmonic because upon solving for the equation of motion involving the Hooke's potential (i.e., a mass attached to a Hooke's law spring), a second order differential equation is obtained, $x'' + \omega^2 x = 0$, which on solution results in a sinusoidal equation of motion, $x(t)$

bond in tension. Figure 11 shows a plot of $\frac{\partial U}{\partial x'}$ versus x' . The plot shows the linearity of the force explicitly.

What is required in order to analyze the correction to the zero-pressure bulk modulus for elastic deformation, is the sum of the forces for deformation through a distance x' . Taking the second derivative with respect to deformation will yield the force constant. When this latter expression is integrated through the deformation distance, the sum of the forces will result; we show this elementary operation in order to illustrate the principle here to anticipate the non-linear, anharmonic integration described in the following section. Thus, we will obtain the elementary identity shown in Eq. 18.

$$\int_{x'=0}^{x'=x-x_c} \left(\frac{\partial^2 U}{\partial x'^2} \right) dx' = kx' \Big|_{x'=0}^{x'=x-x_c} \quad (18)$$

Assuming that compression occurs along the c -axis of the unit cell of glitter, dimensional analysis suggests that a force divided by an area can be obtained by adding together the forces on each of the 2 carbon-carbon double bonds in compression, and dividing by the area of the (001) plane, which is normal to the compression force⁴. Such a correction term, as originally proposed in Eq. 14, is shown in Eq. 19 for the case of a compression force directed parallel to the c -axis. This is the correction term for harmonic compression. The angle between the compression force and the axes of the carbon-carbon double bonds in the unit cell of glitter, is 0 radians.

$$B = B_0 + \frac{2kx'}{a^2} \cos 0^\circ \quad (19)$$

With k equal to 960 Nm^{-1} , [41] and a equal to $2.53 \times 10^{-10} \text{ m}$, [1] it is straightforward to calculate B for the elastically deformed glitter lattice. The corrections are tabulated below. One can see from such tabulation that the dynamic stresses associated with the deformation of the double bonds in glitter are considerable in this model, approaching the magnitude of the zero-pressure bulk modulus, B_0 .

⁴Dimensional analysis has been used extensively by scientists (a leading reference would be given by, Bridgman PW (1949) The physics of high pressure, 1st edn. Bell G Sons, Boston; and the references therein) to estimate the bulk moduli of crystalline materials, including inert-gas solids, alkali halide crystals, metals and covalent solids. Typically, the bulk modulus of a given material is estimated from the ratio of the internal energy of the unit cell of the material to the unit cell volume, U/V . Such a ratio has the dimensions of a pressure, so it is consistent with a measure of the bulk modulus. In the present paper, an alternative dimensionally consistent ratio to the ratio U/V , one that reflects the mechanism by which the bulk modulus is increased by elastic deformation of the unit cell, is proposed. Like U/V , this latter ratio, which is in terms of F/A ; where F is the force produced in elastic deformation and A is the area of a given crystallographic plane (hkl) normal to that force, is dimensionally consistent with a factor in the computation of the total bulk modulus of a material.

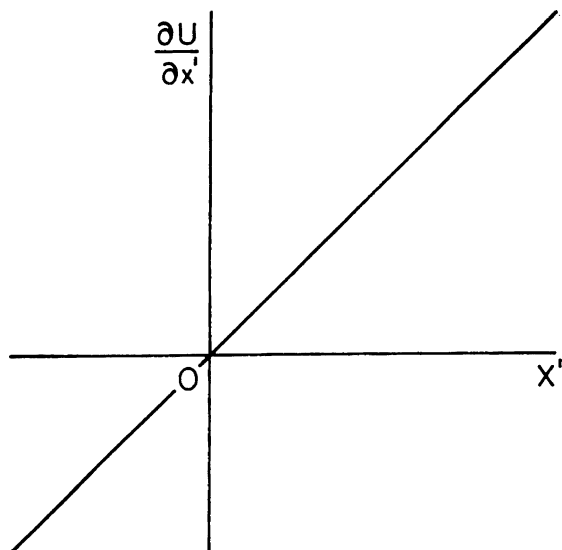


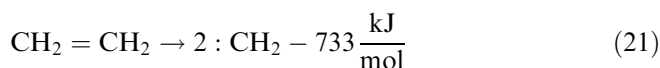
Fig. 11 $\partial U/\partial x'$ versus x' for harmonic potential

Anharmonic compression

Based upon the foregoing analysis of the correction to the zero-pressure bulk modulus of glitter, B_0 , due to harmonic compression of the ethylenic bonds in the unit cell, a similar analysis is presented in this section by treating the ethylenic bonds as anharmonic springs. Figure 9 shows the relevant unit cell parameters which could contribute to volume strain in the glitter structure. As in the harmonic approximation, the parameters α and y are assumed to stay fixed under compression parallel to the c -axis of the unit cell within the anharmonic approximation. The reasons for these assumptions have been described in Sect. 6.

Morse introduced an anharmonic potential-energy function to describe the vibrational characteristics of chemical bonds between atom pairs in a molecule in 1929 [42, 43]. This potential function is shown in Eq. 20, where D_e is the dissociation energy of the atom pair considered, in Nm (or J), and, a , is an empirical-fitting parameter which is, $\sqrt{\frac{k}{2D_e}}$, where k is the force constant of the atom pair in Nm^{-1} . For the carbon-carbon double bonds considered in the unit cell of glitter, the dissociation energy is approximated by Eq. 21 from experimental data on an ethylene fragment [44].

$$U(x') = D_e(1 - e^{-ax'})^2 \quad (20)$$



With such a potential-energy function, Morse was able to solve the diatomic molecular Schrödinger equation exactly, and the vibrational levels for a given electronic state were found to agree quite closely with empirical measurements.

Dimensional analysis indicates that the fitting parameter, a , has the dimensions of m^{-1} . It can be thought of as a characteristic reciprocal length associated with a chemical bond. Upon expanding the quadratic, it is clear that as a becomes arbitrarily larger, the value of the exponential diminishes rapidly and the potential approaches a constant value of D_e . The potential energy curve becomes extremely shallow. Conversely, when the dissociation energy is large compared to the force constant, a approaches arbitrarily smaller values and the potential function becomes arbitrarily steep, even for small deformations x' .

Fortunately, the parameter, a , is of the order 10^{10} m^{-1} for typical chemical bonds. Therefore, this parameter is of the inverse magnitude as that of typical deformations of chemical bonds, x' , in m. For instance, the value of the characteristic reciprocal length for the carbon-carbon single bond is, $a = 8.26 \times 10^{10} \text{ m}^{-1}$, and that for the carbon-carbon double bond is, $a = 1.98 \times 10^{10} \text{ m}^{-1}$ [45, 46]. Therefore, it is clear that the force constant, k , becomes larger simultaneously as $2D_e$ increases, which is physically reasonable. With characteristic reciprocal lengths of approximately $a = 10^{10} \text{ m}^{-1}$, the Morse potential takes on the appearance of the curve in Fig. 12.

In this diagram, the harmonic potential energy function, shown in Fig. 10, is superimposed upon the anharmonic potential energy function [40]. It is assumed in this diagram that the force constants, k , for the harmonic and anharmonic potentials, are identical, so their characteristics can be compared.

For small deformations about the ground vibrational state of the ground electronic state, deformations from

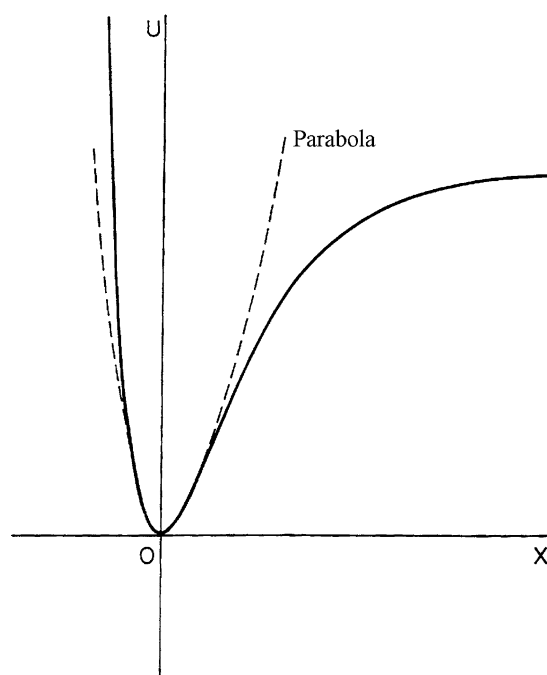


Fig. 12 The Morse potential

Table 5 Corrections to the zero-pressure bulk modulus, B_0 , from anharmonic compression of the double bonds in the glitter lattice

deformation, x' , in m	$(e^{-ax'} - e^{-2ax'})$	$1506(e^{-ax'} - e^{-2ax'})$ $\cos \pi$, ($B-440$) in GPa
-0.010×10^{-10}	-0.0203926	30.711
-0.020×10^{-10}	-0.0420300	63.297
-0.030×10^{-10}	-0.0649546	97.820
-0.040×10^{-10}	-0.0892147	134.35
-0.050×10^{-10}	-0.1149023	173.04
-0.060×10^{-10}	-0.1420618	213.94
-0.070×10^{-10}	-0.1707702	257.18
-0.080×10^{-10}	-0.2010979	302.85
-0.090×10^{-10}	-0.2331187	351.07
-0.100×10^{-10}	-0.2669093	401.96
-0.110×10^{-10}	-0.3025603	455.65
-0.120×10^{-10}	-0.3401358	512.24
-0.130×10^{-10}	-0.3797438	571.89
-0.140×10^{-10}	-0.4214661	634.72
-0.150×10^{-10}	-0.4654088	700.90

the equilibrium internuclear distance, x_e , the two curves correspond to each other, both being parabolic with a potential energy close to its minimum value. At relatively reasonable deformations of the given atom pair, on the order of 0.05×10^{-10} m, it is clear the two curves separate. For an atom pair in tension, the right side of Fig. 12, the potential for the anharmonic spring is smaller than that of the harmonic spring; and in fact, the anharmonic spring converges to a value, $U(x') = D_e$, at large deformations in tension of the order of the bond length of the atom pair.

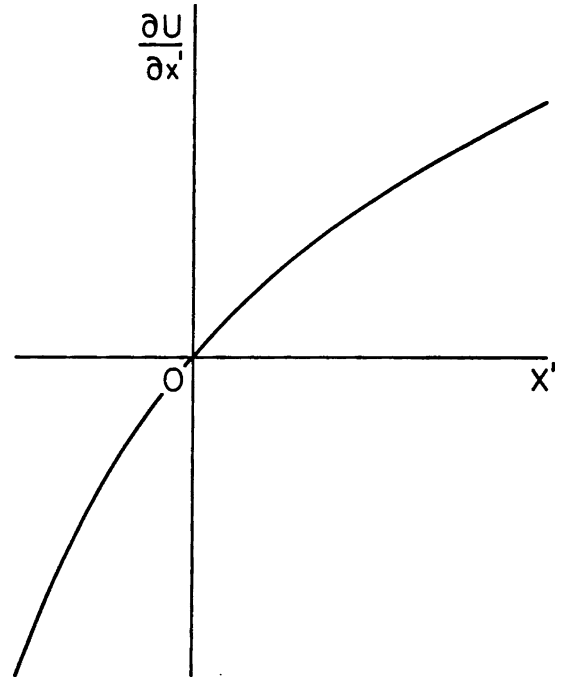
For an atom pair in compression, the left side of Fig. 12, it is clear that both curves diverge to infinity at large deformations x' , but it is also clear that the instantaneous slope (i.e., the value of $\partial U / \partial x'$) of the anharmonic potential is increasingly much steeper than that of the harmonic potential, for larger and larger compressions of the given atom pair. In fact, the instantaneous slope of the harmonic potential, $\partial \frac{kx'^2}{2} / \partial x'$, has been shown in the previous section to be linear in x' , while the instantaneous slope of the Morse potential, shown in Fig. 13, is non-linear in x' . Note that $\frac{\partial U}{\partial x'}$ in Eq. 22 has the dimensions of a force, N.

$$\frac{\partial U}{\partial x'} = 2D_e a (e^{-ax'} - e^{-2ax'}) \quad (22)$$

From Fig. 12 and Eq. 22, it is obvious that under the assumptions given in the previous section for corrections to the zero-pressure bulk modulus for compression of the carbon-carbon double bonds along the c -axis in the unit cell of glitter, the Morse's force law will give larger corrections than the Hooke's force law.

It can be seen from the Morse's force law function, $\frac{\partial U(x')}{\partial x'}$, that the two inverse exponential functions, $e^{-ax'}$ and $e^{-2ax'}$, control the magnitude of the force. Both of these functions are plotted in Fig. 14.

The functions have the same asymptotic behavior. For negative x' , they diverge to infinity and for positive

**Fig. 13** The Morse's force law

x' they converge to 0. All this is consistent with Fig. 13. It can be seen that the difference function in the Morse's force law, $(e^{-ax'} - e^{-2ax'})$, diverges under compression much more rapidly than the simple deformation, x' , that occurs in the linear Hooke's law force. And unlike the Hooke's law force, in the Morse's force law the difference term $(e^{-ax'} - e^{-2ax'})$ converges to zero for positive x' (i.e., for tension). This latter feature of the Morse's force law ensures that dissociation occurs for the given chemically bonded atom pair at tensions of the order of the bond length of the atom pair.

We may obtain an expression that has the dimensions of a force constant (i.e., Nm^{-1}) for a Morse's law force by differentiating the Morse potential twice (i.e., $\frac{\partial^2 U}{\partial x'^2}$).

$$\frac{\partial}{\partial x'} \left(\frac{\partial U}{\partial x'} \right) = k (2e^{-2ax'} - e^{-ax'}) \quad (23)$$

This expression indicates the change of the Morse's law force constant with bond length deformation x' . In the harmonic approximation, the force constant is a constant characteristic of the chemical bond, k .

Ultimately, it is desired that the sum of the forces produced by anharmonic compression of the two ethylenic bonds (modeled here as anharmonic springs) in the unit cell of glitter, under the assumptions outlined in the previous section, be divided by the basal plane area (i.e., a^2 , where a is the lattice parameter of glitter), to obtain the dynamic correction term to B_0 . Therefore, if we integrate Eq. 23, we will calculate the sum of the non-linear, anharmonic compression forces acting along a given deformation x' . This is shown by the elementary identity in Eq. 24 below:

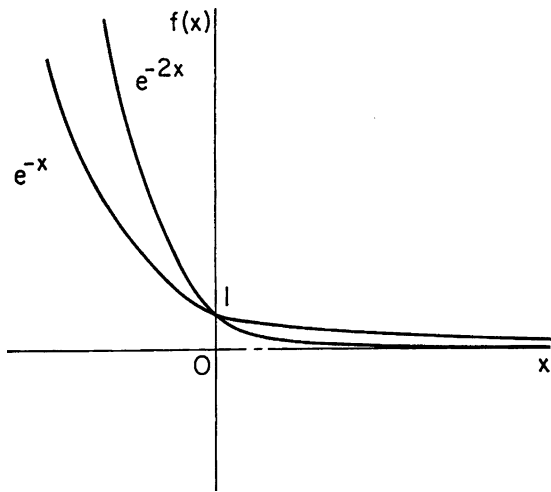


Fig. 14 Exponential functions of the Morse's force law

$$\int_{x'=0}^{x'=x-x_e} \left(\frac{\partial^2 U}{\partial x'^2} \right) dx' = 2D_e a \left(e^{-ax'} - e^{-2ax'} \right) \Big|_{x'=0}^{x'=x-x_e} \quad (24)$$

Finally, in order to obtain the corrections to B_0 , we evaluate the quotient that occurs in the expression for B below in Eq. 25a. This quotient resembles that first introduced in the previous Section, except the Hooke's law force, $F = kx'$, is replaced with the non-linear Morse's law force, given by the relation $F = 2D_e a(e^{-ax'} - e^{-2ax'})$.

$$B = B_0 + \frac{2 \int_{x'=0}^{x'=x-x_e} \left(\frac{\partial^2 U}{\partial x'^2} \right) dx'}{a^2} \cos 0^\circ \quad (25a)$$

$$B = B_0 + \frac{2(2D_e a (e^{-ax'} - e^{-2ax'})) \Big|_{x'=0}^{x'=x-x_e}}{a^2} \cos 0^\circ \quad (25b)$$

Table 5 lists the relevant parameters for evaluating the dynamic correction stress–elastic modulus to the zero-pressure bulk modulus in the anharmonic approximation.

Conclusions

The elastically deformed glitter lattice may undergo an increase in stiffness of between 300 GPa and 400 GPa for a 3% decrease in $\Delta V/V$, if compression is applied parallel to the \mathbf{c} -axis of the unit cell and applied exclusively to the elastic deformation of the carbon–carbon double bonds in the unit cell. For a volume deformation corresponding to a 5% decrease in $\Delta V/V$, if compression is applied parallel to the \mathbf{c} -axis under these assumptions, the corresponding increase in stiffness is between

450 GPa and 700 GPa. In the anharmonic approximation, this brings the bulk modulus at pressure, B , to a total value of 1.14 TPa, almost an order of magnitude beyond the zero-pressure bulk modulus of glitter⁵

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⁵In order to access a bulk modulus in glitter in the 10 TPa regime, under the assumptions outlined in this paper, one would need to deform the \mathbf{c} -axis by about 20%. This formidable elastic deformation would result in the carbon–carbon double bonds being compressed to about 0.80 Å from their zero-pressure state at 1.35 Å. It's possible that with the simultaneous deformation of the single and double bonds in glitter, one may yield more modest \mathbf{c} -axis reductions in order to attain the 10 TPa regime.

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