Elasticity of carbon allotropes. II. Modified anharmonic Keating model for hexagonal diamond

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The parameters of the modified Keating model deduced for cubic diamond are used to predict the elastic constants and zone-center optic mode frequencies of hexagonal diamond. A geometrical difference between the two structures at the third-neighbor level requires an adjustment to the β^* parameter that results in excellent agreement between the model and the three observed Raman frequencies. The lower symmetry and extra degree of freedom associated with the hexagonal unit cell permit exploration of three distinct régimes: quasi-cD (same bond lengths, atomic volume and c/a ratio), equal bondlengths with increased c/a ratio, and unequal bondlengths with unchanged c/a ratio. Numerically there is little difference between the predictions in each case. The quasi-cD case implies first an isotropic compressibility consistent with the observed constancy of the c/a ratio over a wide range of pressure and second no lifting of the triply degenerate Raman frequency which is consistent with experiment but slightly at variance with a first-principles calculation. All three cases yield a bulk modulus slightly smaller than the fitted value for the cubic allotrope, and similar values for the pressure derivatives of the elastic constants and of the optic mode frequencies.

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I. INTRODUCTION

The possibility of a hexagonal form of diamond was first suggested by Lonsdale in 1944.[1] When, twenty three years later, a mineral having the expected x-ray diffraction pattern was found to comprise over 30% of the diamonds in the Canyon Diablo and Goalpara meteorites it was named lonsdaleite[2] in her honor. It was suggested that the mineral formed from crystalline graphite inclusions by impact shock, either on collision with Earth or by earlier collisions in space.[3] More recently there has been a different suggestion: various laboratory simulations seem to favor its formation by vapor deposition, most probably in a presolar, circumstellar condensation process.[4] It has also been found, again accompanying cD, as an inclusion in Vietnamese rubies.[5] Less exotically hD is formed when hG is subjected to a pressure above 14 GPa. As will be seen in Ref. 6, this critical pressure is closely predicted by the modified Keating model to which the hG elasticity data has been fitted.

hD is more complex than cD, with more elastic constants at both second and third order, and with many more inner elastic constants. The formal details of the inner elastic constants and the zone-center optic modes were treated in Ref. 7 (hereafter C1) and the anatomy of the total second- and third-order elastic constants in Ref. 8 (C2).

As both cD and hD are sp^3 bonded, it is to be expected that total energies, bond lengths, and elastic constants will be very similar when compared in the appropriate manner. In fact some of the lattice properties of cD and hD have been calculated recently by Wu and Xu[9] using a total energy method. The small differences in total energies, bond lengths, and bulk moduli that they found reflect the fact that both structures have the same first- and second-neighbor environments, but different third-neighbor ones. The frequencies of zone-center optic phonons were also calculated: the triple-degeneracy of the cD Raman mode was partially lifted and the frequencies of the hD modes were about 2% smaller than their cubic counterpart.

II. THE HEXAGONAL DIAMOND STRUCTURE

Even though the Keating model is limited to first and second neighbors, small differences can still be accommodated as a result of the lower symmetry of hD. The extra degree of freedom, resulting from two lattice parameters in place of one, allows the equality of the four bond lengths to be relaxed: the axial bond may differ in length from the three nonaxial bonds. The structures of the two diamond allotropes are described in C1.

A. The quasi-cD case

This case, in which the atomic volume and all bond lengths are taken to be the same as those in cD, is depicted in Fig. 1. Taking $a_c = 3.567$ Å the lattice parameters in the quasi-cD case are $a = a_c/\sqrt{2} = 2.5222$ Å and $c = 2a_c/\sqrt{3} = 4.1188$ Å. The volume per atom $\Omega_0 = \sqrt{3}ca^2/8 = 5.6731$ Å^3. The common bond length is given by

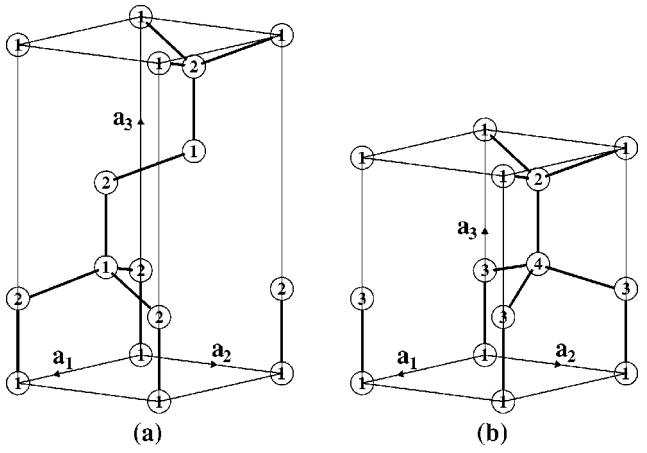

FIG. 1. (a) The triple-hexagonal cell for cD and (b) the primitive hexagonal cell of hD. The numbers indicate the distinct sublattices on which the atoms lie.

TABLE I. Modified Keating parameters.

	Harmonic			Anharmonic	
	GPa Å^{-1}	eV Å^{-4}		GPa Å^{-3}	eV Å^{-6}
α	158.6	0.9899	γ	−140.8	−0.8788
β^*	122.8	0.7663	δ	19.56	0.1221
σ	−18.36	−0.1147	ϵ	−99.78	−0.6226
τ	3.31	0.0207	η	−24.29	−0.1516
			θ	50.55	0.3155
			ξ	0.0	0.0

$$r_0=\frac{3}{8}c=\sqrt{\frac{3}{8}}a \tag{1}$$

and has the value 1.5446 Å.

B. The actual hD case

The detailed study of the hG to hD transformation undertaken by Yagi *et al.*[10] reveals a small departure from the quasi-cD case. The lattice parameters extrapolated to ambient pressure are $a=2.513(6)$ Å and $c=4.171(5)$ Å, indicating a slight decrease in the value of a but a 1.3% expansion in c. The c/a ratio goes up from the ideal 1.6330 to 1.66 and remains constant to at least 30 GPa pressure. In this case three bond lengths are given by

$$r_{0a}=\sqrt{\frac{1}{3}a^2+4z^2c^2} \tag{2}$$

and the fourth by

$$r_{0c}=\frac{1}{2}(1-4z)c, \tag{3}$$

where z is the structural coordinate that is equal to 1/16 in the quasi-cD case, see Table I in C1. The measurements of Yagi *et al.*[10] are not sufficient to give this parameter. If it is assumed that the structure retains equal bond lengths then $r_{0a}=r_{0c}=1.5474$ Å and z, which is given by $1-8z=4a^2/3c^2$, changes from 0.0625 to 0.0645. This scenario seems unlikely—it appears to take no advantage of the extra degree of freedom available. On the other hand the assumption that z remains at 1/16 produces a marked inequality of bond lengths: $r_{0a}=1.5417$ Å and $r_{0c}=1.5641$ Å, a difference of 1.5%. The actual behavior of hD probably lies somewhere in between. Calculations for both these extremes are presented below, together with those for the quasi-cD case.

III. MODIFIED KEATING MODEL

It is not in general possible to transfer force constants between different crystal structures of the same element. This is shown vividly by comparing the number and values of the parameters found for cD and hG in Refs. 11 and 6, respectively.

The Keating model for cD, however, is exceptionally simple in being focused solely on the tetrahedral configuration surrounding each atom. Every atom in hD has that same configuration in what is called the quasi-cD structure above. The difference in crystal structure between these two cases is completely invisible and it is inconceivable that different sets of Keating parameters would be required. Where a nonideal c/a ratio and(or) unequal bondlengths are present the system can be treated by associating unchanged Keating parameters with the perturbed geometry. The validity of this approach is supported by the results obtained.

TABLE II. The internal strain parameters. The final entry relates to cubic diamond. Units are Å.

Constant	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
A^1_{16}	0.153	0.152	0.152
A^1_{15}	0.069	0.070	0.087
A^1_{31}	0.069	0.068	0.069
A^1_{33}	−0.139	−0.140	−0.106
A_{14}	0.083		

A. The strain variables

The strains in the modified model for hD are

$$\Delta_{ii}=2r_p^{i0}\eta_{pq}r_q^{i0}+2r_p^{i0}z_p^{\pi}+z_p^{\pi}z_p^{\pi} \tag{4}$$

and

$$\Delta_{ij}=2r_p^{i0}\eta_{pq}r_q^{j0}+r_p^{i0}z_p^{\rho}+r_p^{j0}z_p^{\pi}+z_p^{\rho}z_p^{\pi}, \tag{5}$$

where terms of order three and higher have been omitted. The significance of $\vec{z}^{\pi}$ and $\vec{z}^{\rho}$ is as follows. Consider the reference atom belonging to sublattice 2 in Fig. 1(b). It has three bonds to atoms on sublattice 1 and one bond to an atom on sublattice 4. When i refers to sublattice 1 $\vec{z}^{\pi}=-\vec{\zeta}^1$ (minus because a positive value indicates 2 relative to 1, 3 relative to 2 or 1, or 4 relative to 3, 2 or 1). If i refers to sublattice 4 then $\vec{z}^{\pi}=\vec{\zeta}^2+\vec{\zeta}^3$ (because 4 relative to 2 is equivalent to 3 relative to 2 plus 4 relative to 3). Similarly for j and $\vec{z}^{\rho}$, and for the remaining reference atoms.

B. The energy

The expressions for the modified energies per cell are the same as those for cD, [Eqs. (43) and (44) in Ref. 11], except that the summations are now over four sublattices rather than two. The anharmonic term in ξ has been retained for the sake of formal completeness even though it was found to be insignificant *vis-à-vis* cD.

$$E^{(2)}=\frac{1}{2}\sum_{s=1}^{4}\sum_{i=1}^{4}\times\left(\alpha\Delta_{ii}^2+\sum_{j=1}^{4}{}'\ (\beta^*\Delta_{ij}^2+\sigma(\Delta_{ii}+\Delta_{jj})\Delta_{ij}+\tau\Delta_{ii}\Delta_{jj})\right) \tag{6}$$

TABLE III. The second- and third-order elastic constants, the bulk modulus and the pressure derivatives of the second-order constants. Constants are in GPa, derivatives are dimensionless.

Constant	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$	Constant	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
C_{11}	1133.5	1111.1	1111.1	C_{111}	−11912.0	−11592.0	−11586.0
C_{12}	113.8	111.5	111.5	C_{113}	−101.1	−101.6	−104.5
C_{13}	70.0	70.9	70.9	C_{133}	−1746.4	−1813.6	−1810.9
C_{33}	1177.3	1231.6	1231.7	C_{333}	−9662.8	−10367.0	−10380.0
C_{44}	476.5	482.6	482.6	C_{144}	−424.5	−426.7	−429.1
B	439.1	439.6	439.7	C_{244}	−1169.6	−1175.8	−1171.1
				C_{344}	−2831.0	−2940.0	−2942.0
C'_{11}	8.78	8.66	8.68	C_{166}	−1321.7	−1286.1	−1284.9
C'_{12}	1.54	1.53	1.52	C_{266}	−3432.5	−3340.1	−3338.9
C'_{13}	0.98	0.96	1.00	C_{366}	−214.7	−215.7	−217.3
C'_{33}	9.34	9.78	9.65				
C'_{44}	3.06	3.08	3.11				
B'	3.76	3.78	3.78				

and

$$E^{(3)}=\frac{1}{2}\sum_{s=1}^{4}\sum_{i=1}^{4}\Bigg(\gamma\Delta_{ii}^3+\sum_{j=1}^{4}{}'\,[\,\delta\Delta_{ij}^3+\epsilon(\Delta_{ii}+\Delta_{jj})\Delta_{ij}^2+\eta(\Delta_{ii}^2+\Delta_{jj}^2)\Delta_{ij}+\theta\Delta_{ii}\Delta_{ij}\Delta_{jj}+\xi\Delta_{ii}\Delta_{jj}(\Delta_{ii}+\Delta_{jj})]\Bigg). \tag{7}$$

There is one important detail relating to the transferable parameters that needs attention: the value of β^*. In the analysis of cD β^* was introduced as the combination $\beta+\kappa$, where κ represented the interactions of planar chains of three bonds, and the separation of β from κ was achieved by analysing phonon frequencies at the Brillouin zone boundary. In hD there are only nine chains per atom whereas cD has twelve. Thus where β^* was $132.0=95.1+36.9$ GPa Å^{-1} before it is replaced now by $95.1+\frac{3}{4}\times 36.9=122.8$ GPa Å^{-1}.

C. The partial and inner elastic constants

Expressions for the partial and inner elastic constants have been obtained by identifying the Keating energy density with the free energy per unit initial volume, ignoring first-order terms, and confirmed by using the generalized method of homogeneous deformation (detailed in C2) with a unit contribution from each of the model parameters in turn. As they are much more numerous than those of cD they are presented in tabular form in the Appendix. Also included in the Tables are the calculated values for each constant for each of the three régimes under consideration.

D. The internal strain parameters

Using the appropriate inner elastic constants in Eq. (11) in C1 yields the internal strain parameters that are shown in Table II. The accidental degeneracy displayed by the quasi-cD parameters is removed on passing to real hD. If A_{16}^1 is to be compared with the A_{14} of cD both parameters need to be scaled: the former by $a/2$, the latter by $a_c/4$, these being the projections of the bonds along the Ox_1 axes. This gives the values 0.121 and 0.093, respectively. Without the β^* adjustment $A_{16}^1=0.117$ which scales to 0.093 as is to be ex-

TABLE IV. The composition of the calculated elastic stiffnesses and the corresponding compliances and compressibilities for the "unequal bonds" régime. Stiffnesses are in GPa, second-order compliances in TPa^{-1} and third-order compliances in TPa^{-2}.

IJ	Partial	$\leftarrow C_{IJ}\rightarrow$ Internal	Total	S_{IJ} Total
11	1123.9	−12.8	1111.1	0.912
12	103.9	7.7	111.5	−0.089
13	65.6	5.3	70.9	−0.047
33	1242.5	−10.9	1231.6	0.817
44	485.2	−2.6	482.6	2.072
			k_a	0.776
			k_c	0.723
			k_v	2.275
111	−11985.3	393.6	−11591.7	8.8
113	−131.2	29.6	−101.6	−0.4
133	−1541.3	272.3	−1813.6	0.7
333	−11285.6	918.9	−10366.7	5.3
144	−306.0	−120.7	−426.7	0.6
244	−1378.0	202.3	−1175.8	3.8
344	−2942.0	2.0	−2940.0	10.0
166	−1566.4	280.3	−1286.1	3.5
266	−3388.3	48.2	−3340.1	11.7
366	−197.0	−18.7	−215.7	−0.2
			K_a	7.32
			K_c	6.63
			K_v	21.28

TABLE V. The zone-center optic modes. Experimental frequencies have been converted to THz. Comparative information for cD is given at the bottom.

			Calculated→		$r_{0a}\neq r_{0c}$	$r_{0a}=r_{0c}$
Mode	Eigenvector	Experiment	Ref. 9	Quasi-cD	$z=0.0625$	$z=0.0645$
E_{1g}	$z_1^1=-z_1^3=\frac{1}{\sqrt{2}}, z_1^2=0$	39.42–39.75 [a]	39.12	39.49	39.34	39.34
	$z_2^1=-z_2^3=\frac{1}{\sqrt{2}}, z_2^2=0$					
E_{2g}	$z_1^1=-z_1^2=z_1^3=\frac{1}{\sqrt{3}}$	35.08 [b]/35.22 [c]	35.77	35.80	35.67	35.67
	$z_2^1=-z_2^2=z_2^3=\frac{1}{\sqrt{3}}$					
E_{2u}	$z_1^2=1, z_1^1=z_1^3=0$		15.62	19.92	19.84	19.84
	$z_2^2=1, z_2^1=z_2^3=0$					
A_{1g}	$z_3^1=-z_3^3=\frac{1}{\sqrt{2}}, z_3^2=0$	39.42–39.75 [a]	39.39	39.49	39.99	40.00
B_{2g}	$z_3^1=-z_3^2=z_3^3=\frac{1}{\sqrt{3}}$		37.56	39.07	39.57	39.80
B_{1u}	$z_3^2=1, z_3^1=z_3^3=0$		33.55	30.93	31.32	31.19
T_{2g}		39.93 [d]	39.99	40.23		

[a]Reference 15.
[b]Reference 13.
[c]Reference 12.
[d]Reference 14.

pected. This shows that the β^* adjustment has a significant effect on the internal strain.

E. The total elastic constants and associated pressure derivatives

Armed with values of the internal strain and the inner elastic constants Eqs. (4), (5), (10), and (11) in C2 can be used to anatomize the macroscopic constants. In Table III the results for the total elastic constants at the second and third order, the bulk modulus, and the pressure derivatives of the second-order constants for the three régimes are shown. There does not appear to be any distinct trend in the changes from column to column. The bulk modulus is in all cases very close to the observed cD value of 442 GPa. The value of 445 GPa fit to cD drops to 439 GPa here as a result of the β^* adjustment. The calculations of Wu and Xu[9] give hD a bulk modulus 2.3% larger than that of cD, whilst the measurements of Yagi *et al.*[10] give 425 ± 25 GPa—equality within experimental error. The pressure derivative of the bulk modulus is about 2% more than the value 3.72 found for cD. Second the ''unequal bonds'' régime has been selected to show, in Table IV, the full decomposition of all constants into partial and internal contributions, together with the elastic compliances and the compressibilities. The inner elasticity contributes to every constant in hD, in marked contrast to the situation for cD. The internal share

TABLE VI. Pressure derivatives of optic-mode frequencies. The final entry relates to cubic diamond. Units are THz GPa^{-1}.

Mode	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$	Mode	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
E_{1g}	0.098	0.099	0.099	A_{1g}	0.098	0.099	0.100
E_{2g}	0.092	0.092	0.092	B_{2g}	0.093	0.095	0.096
E_{2u}	0.032	0.031	0.031	B_{1u}	0.101	0.102	0.101
T_{2g}	0.097			T_{2g}	0.097		

varies between 0.5% and 7.5% for the second-order constants and between 0.1% and 30% for the third-order ones.

The compressibilities are no longer isotropic as they are in cD and in the quasi-cD version of hD. For comparison the results for cD[11] were $k=0.749$ TPa^{-1}, $K=6.83$ TPa^{-2}, $k_v=2.25$ TPa^{-1}, and $K_v=20.5$ TPa^{-2}.

F. The zone-center optic modes

The frequencies and eigenvectors follow from the analysis in C1 and are presented in Table V. The calculated triply degenerate T_{2g} mode frequency of 40.23 THz in cD corresponds to the triple degeneracy of the two E_{1g} and the A_{1g} modes at 39.49 THz in the quasi-cD calculation. The 1.8% lower value is due entirely to the reduced value of β^* and falls nicely in the middle of the range of 0.5% to 2.8% reduction observed by Knight and White.[15] The E_{2g} frequency is well predicted, only exceeding the observed value by about 2%. For the Raman active modes the Keating model is in near-perfect agreement with the density functional calculations of Wu and Xu.[9] For the optically inactive modes, however, the agreement is poorer. Calculations for the real hD case reveal a slight reduction in the three doubly-degenerate frequencies and show the lifting of the triple degeneracy by an increase in frequency of the A_{1g} mode of about 650 GHz. This is rather larger than the 270 GHz found

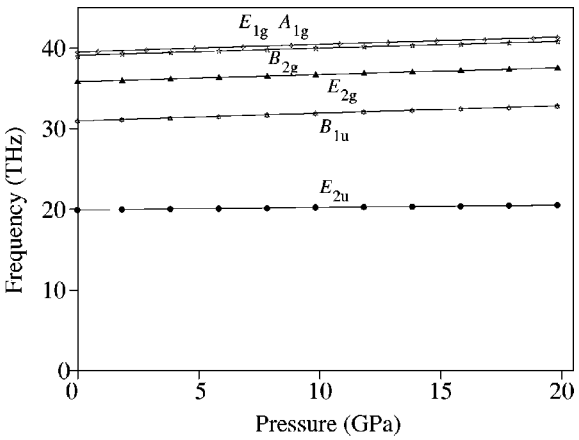

FIG. 2. Pressure dependence of the zone-center optic-mode frequencies.

TABLE VII. Coefficients of the modified Keating parameters in the second-order partial and inner elastic constants and evaluation of the constants under the three régimes described in the text. The lattice parameters are a and c, and t is an abbreviation for $\sqrt{3}$. The coefficients are valid only for the $z=1/16$ cases.

Constant	Factor	α	β^*	σ	τ	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
C_{11}^0	$4ta^2/3c$	1	1	−2	1	1147.0	1123.9	1124.0
C_{12}^0	$4ta^2/9c$	1	−1	−2	5	106.0	103.9	103.9
C_{13}^0	$tc/12$	1	−1	−2	11	64.8	65.6	66.9
C_{33}^0	$tc^3/32a^2$	7	5	−14	5	1188.0	1243.0	1238.0
C_{44}^0	$tc/12$	1	5	−2	−1	479.1	485.2	486.6
D_{16}^1	$2a/3c$	−2	2	1	2	−34.0	−33.5	−33.5
D_{15}^1	$t/3$	−1	1		1	−18.8	−18.8	−23.2
D_{31}^1	$t/3$	−1	1		1	−18.8	−18.8	−18.9
D_{33}^1	$tc^2/8a^2$	1	−1		−1	37.5	38.8	29.4
E_{11}^{11}	$4t/3c$	2	2	3	−2	280.9	277.4	277.4
E_{11}^{12}	$4t/3c$		1			68.8	68.0	68.0
E_{11}^{13}	$4t/3c$			−1		10.3	10.2	10.2
E_{33}^{11}	$tc/8a^2$	8	11	6	−2	350.8	357.8	358.8
E_{33}^{12}	$tc/8a^2$	6	1	−6		166.0	169.4	168.0
E_{33}^{13}	$tc/8a^2$		3	−10	6	80.2	81.8	82.6
$E_{111,112}^{11(2)}$	$4t/3c$	2	−2	3	6	20.4	20.3	20.3
$E_{111,112}^{12(2)}$	$4t/3c$				2	3.7	3.7	3.7
$E_{111,112}^{13(2)}$	$4t/3c$			−1		10.3	10.2	10.2
$E_{113}^{11(2)}$	$tc/8a^2$	4	−1	3	12	139.1	143.0	145.0
$E_{113}^{12(2)}$	$tc/8a^2$	3		−3	1	149.8	153.9	151.4
$E_{113}^{13(2)}$	$tc/8a^2$		3	−5		129.0	132.6	134.4
$E_{331}^{11(2)}$	$tc/2a^2$	2	−2	3	6	20.4	20.3	20.3
$E_{331}^{12(2)}$	$tc/2a^2$				2	3.7	3.7	3.7
$E_{331}^{13(2)}$	$tc/2a^2$			−1		10.3	10.2	10.2
$E_{333}^{11(2)}$	$3tc^3/64a^4$	4	−1	3	12	139.1	143.0	145.0
$E_{333}^{12(2)}$	$3tc^3/64a^4$	3		−3	1	149.8	153.9	151.4
$E_{333}^{13(2)}$	$3tc^3/64a^4$		3	−5		129.0	132.6	134.4

TABLE VIII. Coefficients of the modified Keating parameters in the third-order partial elastic constants and the D and F tensors.

Constant	Factor	γ	δ	ϵ	η	θ	ξ	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
C^0_{111}	$2ta^4/c$	1	−1	2	−2	−1	2	−12317.0	−11985.0	−11985.0
C^0_{113}	$tca^2/24$	3	3	−2	−6	−1	26	−130.5	−131.2	151.9
C_{133}	$tc^3/128$	1	−1	6	−2	−17	70	−1484.2	−1541.3	−1578.2
C_{333}	$3tc^5/1024a^2$	61	−13	46	−122	−13	46	−10519.0	−11286.0	−11026.0
C^0_{144}	$tca^2/24$	1	−1	1	−2	1	2	−304.4	−306.0	−305.5
C^0_{244}	$tca^2/24$	3		5	−6	1	−2	−1370.8	−1378.0	−1406.2
C_{344}	$tc^3/128$	1	−13	22	−2	−9	6	−2832.9	−2942.0	−2945.6
C^0_{166}	$2ta^4/9c$	3		2	−6	1	−2	−1609.7	−1566.4	−1566.4
C^0_{266}	$2ta^4/9c$	1	−4	6	−2	−3	2	−3482.0	−3388.3	−3488.3
C^0_{366}	$tca^2/24$	1	2		−2	−1	6	−196.0	−197.0	−213.9
D^1_{116}	$2a^3/3c$	−3		1	3	−1	2	517.4	511.0	511.0
D^1_{126}	$2a^3/3c$	−1	−2	1	1	1	−2	73.2	72.3	72.3
D^1_{136}	$ca/16$	−2	2	2	2	1	−12	80.0	80.7	88.7
D^1_{145}	$ca/32$	−4	1	−4	4	4	8	352.8	356.0	365.1
D^1_{314}	$ca/16$	−2	2	−1	2	1		274.3	276.8	280.6
D^1_{115}	$ta^2/6$	−3		1	2	−1	2	410.5	407.5	437.8
D^1_{125}	$ta^2/18$	−3	3	3	2	−2	−6	−11.3	−11.2	−5.8
D^1_{135}	$tc^2/96$	−3	−15	6	2	9	−18	−19.3	−19.8	3.7
D^1_{311}	$ta^2/6$	−3	−3	2	2	1	−2	305.2	303.0	318.3
D^1_{312}	$ta^2/18$	−3	3	6	2	−3	−18	−19.4	−19.3	−19.7
D^1_{313}	$tc^2/96$	−3	3	−6	2	−3	30	269.2	276.0	276.8
D^1_{333}	$tc^4/64a^2$	15	3	−6	−10	3	−6	−1298.0	−1375.0	−1220.0
D^1_{344}	$tc^2/96$	−18	12		2	−9	6	47.0	48.2	78.2
F^{111}_{112}	$2a/3c$	−4	1	1	−6	4	8	1018.0	1001.0	1001.0
F^{112}_{112}	$2a/3c$			−2				81.5	80.1	80.1
F^{113}_{112}	$2a/3c$			−1	2			20.9	20.6	20.6
F^{111}_{113}	$t/4$	−8	−3	−2	−12	4	8	708.9	708.5	738.2
F^{112}_{113}	$t/6$		−3	4		6		−1.6	−1.3	−0.8
F^{113}_{113}	$t/12$		−9	2	4		−24	−65.0	−65.0	−66.2
F^{121}_{113}	$t/12$		3	8		6		−4.2	−3.8	−2.5
F^{123}_{113}	$t/4$		−3			2		2.6	2.4	1.7
F^{131}_{113}	$t/6$			−2	2	−3		−28.6	−28.8	−29.8
F^{221}_{113}	$t/6$		6	4				−6.8	−6.2	−4.3
F^{111}_{333}	$3tc^2/64a^2$	32	9	−14	12	−20	−40	−1078.0	−1110.0	−1033.0
F^{112}_{333}	$tc^2/32a^2$	54	3	−10		6	−36	−740.8	−769.4	−729.7
F^{113}_{333}	$tc^2/64a^2$		9	−14	−52	12	24	194.8	202.6	194.2

by Wu and Xu.[9] The pressure derivatives of the frequencies are shown in Table VI. Apart from the E_{2u} modes they all have approximately the same value as that of cD. The unexciting variation of frequency with pressure up to 20 GPa is shown in Fig. 2.

IV. SUMMARY AND RESIDUAL PARADOX

It has been possible to provide a full and plausible picture of the elasticity of a material, about which very little is known, by transferring parameters from a well-characterized close relative. The adjustment of one of those parameters, β^*, in recognition of geometrical differences at the third-neighbor level, proved to be just what was required to give an accurate prediction of all three Raman frequencies.

There is no obvious significant difference between the three structure régimes considered but experiments have indicated[10] that the c/a ratio of hD remains constant under pressure at 1.66, slightly greater than the quasi-cD value of 1.633, up to at least 30 GPa. This result generates a paradox. It implies that $k_a > k_c$, making the hD crystal more compressible in the Ox_1 and Ox_2 directions than it is in the Ox_3

TABLE IX. Coefficients of the modified Keating parameters in the third-order E tensors.

Constant	Factor	γ	δ	ϵ	η	θ	ξ	Quasi-cD	$r_{0a}\neq r_{0c}$ $z=0.0625$	$r_{0a}=r_{0c}$ $z=0.0645$
$E_{111}^{11(3)}$	$4ta^2/3c$	3		1	1	1	−2	−1769.0	−1753.0	−1753.0
$E_{111}^{12(3)}$	$2ta^2/3c$			1				−177.9	−176.3	−176.3
$E_{111}^{13(3)}$	$4ta^2/3c$				−1			86.7	85.9	85.9
$E_{112}^{11(3)}$	$4ta^2/9c$	3	−3	−1	3	6		−301.9	−259.3	−259.3
$E_{112}^{12(3)}$	$2ta^2/9c$			1				−59.3	−58.8	−58.8
$E_{112}^{13(3)}$	$4ta^2/9c$				−1			28.9	28.7	28.7
$E_{113}^{11(3)}$	$tc/24$	6	−6	10	2	9	36	−461.7	−472.8	−501.4
$E_{113}^{12(3)}$	$tc/24$		−9	10				−348.9	−357.2	−354.5
$E_{113}^{13(3)}$	$tc/24$			6	−2	−9		−298.7	−305.9	−305.7
$E_{135}^{11(3)}$	$tc/96$	24	21	82	8	6	−24	−820.4	−840.0	−863.6
$E_{135}^{12(3)}$	$tc/48$		−9	20		−6		−367.8	−376.6	−374.3
$E_{135}^{13(3)}$	$tc/96$		−27	18	−8	−18	24	−225.9	−231.3	−230.8
$E_{331}^{11(3)}$	$tc/24$	6	−6	7	2	9	48	−372.7	−381.7	−398.7
$E_{331}^{12(3)}$	$tc/24$			1		−6	36	−119.8	−122.7	−126.6
$E_{331}^{13(3)}$	$tc/24$			3	−2	−9	12	−209.8	−214.7	−212.7
$E_{333}^{11(3)}$	$tc^3/256a^2$	168	−51	106	−52	−12	−24	−2561.0	−2717.0	−2651.0
$E_{333}^{12(3)}$	$tc^3/256a^2$	162	−9	46	−216	−6	36	−1682.0	−1779.0	−1723.0
$E_{333}^{13(3)}$	$tc^3/256a^2$		−27	90	−164	−36	120	−545.6	−577.2	−603.1
E_{114}^{11}	$a/12$	12	−3	−12	4	−12	−24	−263.8	−265.7	−282.3
E_{136}^{11}	$a/12$	12	−12	−15	4	−6	−12	−174.1	−175.4	−186.4
E_{136}^{13}	$a/4$			−1			4	62.9	63.4	62.7

direction, in which case the application of pressure must increase the c/a ratio! The only way in which the ratio can remain constant is if $k_a=k_c$, and that implies the quasi-cD scenario. It may well turn out that the original synthesizers of terrestrial hD, Bundy and Kasper,[16] were nearer the mark with their values of $a=2.52$ Å, $c=4.12$ Å, and $c/a=1.635$. More experimental work needs to be done to clarify this issue.

APPENDIX ELASTIC CONSTANTS IN THE MODIFIED KEATING MODEL

Each constant M_i is written as a linear combination of Keating parameters K_j with coefficients μ_j and a common factor F_i: $M_i=F_i\times\Sigma\mu_jK_j$. The second-order constants appear in Table VII and the third-order ones in Tables VIII and IX. The numerical coefficients relate only to the two cases where $z=1/16$.

[1] K. Lonsdale, Nature (London) **153**, 669 (1944).
[2] C. Frondel and U.B. Marvin, Nature (London) **214**, 587 (1967).
[3] R.E. Hanneman, H.M. Strong, and F.P. Bundy, Science **155**, 995 (1967).
[4] T.L. Daulton, D.D. Eisenhour, T.J. Bernatowicz, R.S. Lewis, and P.R. Buseck, Geochim. Cosmochim. Acta **60**, 4853 (1996).
[5] N.Q. Dao, V.X. Quang, N.Q. Huy, and J.P. Sylvestre, C. R. Acad. Sci., Ser. IIa: Sci. Terre Planetes **322**, 515 (1996).
[6] C.S.G. Cousins and M.I. Heggie, Phys. Rev. B **67**, 024109 (2003).
[7] C.S.G. Cousins, J. Phys.: Condens. Matter **14**, 5091 (2002).
[8] C.S.G. Cousins, J. Phys.: Condens. Matter **14**, 5115 (2002).
[9] B.R. Wu and J. Xu, Phys. Rev. B **57**, 13 355 (1998).
[10] T. Yagi, W. Utsumi, M. Yamakata, T. Kikegawa, and O. Shimomura, Phys. Rev. B **46**, 6031 (1992).
[11] C.S.G. Cousins, Phys. Rev. B **67**, 024107 (2003).
[12] R.J. Nemanich, J.T. Glass, G. Lucovsky, and R.E. Schroder, J. Vac. Sci. Technol. A **6**, 1783 (1988).
[13] S.R.P. Silva, G.A.J. Amaratunga, E.K.H. Salje, and K.M. Knowles, J. Mater. Sci. **29**, 4962 (1994).
[14] J.L. Warren, R.G. Wenzel, and J.L. Yarnell, *Inelastic Scattering of Neutrons* (IAEA, Vienna, 1965), Vol. 1, p. 361.
[15] D.S. Knight and W.B. White, J. Mater. Res. **4**, 385 (1989).
[16] F.P. Bundy and J.S. Kasper, J. Chem. Phys. **46**, 3437 (1967).