PHYSICAL REVIEW B **67**, 024107 (2003)

Elasticity of carbon allotropes. I. Optimization, and subsequent modification, of an anharmonic Keating model for cubic diamond

C. S. G. Cousins
School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

(Received 10 May 2002; published 22 January 2003)

The inner elastic constants of single-crystal diamond at the second and third order characterize the response of the crystal to the internal displacement of its component sublattices, of which there are two, either alone or coupled to external strain. These constants feature in the decomposition of the macroscopic elastic constants at second and third order, and give rise to one linear and three quadratic independent internal strain parameters. All these constants have been obtained via the implementation of a Keating potential notionally restricted to two-body and three-body interactions between nearest neighbors. Four harmonic parameters have been optimized to reproduce the second-order elastic constants, the frequency of the (triply degenerate) optical mode at the zone center and the internal strain parameter. The resulting fit is excellent and also accounts very well for the frequencies of the TO modes at the *X* and *L* critical points. Excessively large frequencies predicted for the TA modes at these points are shown to be due to a particular four-body interaction that cannot be separated elastically from the three-body bond-bending interaction. The assignment of a fifth parameter allows all the critical point frequencies to be well fit, the largest discrepancies being 3% and 6% for the TA modes. One of six anharmonic parameters is shown to be statistically insignificant. The remaining five are fit to the pressure derivatives of the second-order elastic constants and to the various stress derivatives of the frequency of the zone-center modes. These parameters are used to predict the values of all the third-order elastic and inner elastic constants, and of the quadratic internal strain parameters. Finally the Keating strain is redefined so that the parameters of the model no longer depend on the dimensions of the unit cell chosen to describe the structure. New expressions are obtained for all elastic constants and the optimized parameters are appropriately modified.

DOI: 10.1103/PhysRevB.67.024107 PACS number(s): 62.20.Dc, 63.20.−e, 81.40.Jj

I. INTRODUCTION

A comprehensive treatment of general and specific aspects of the elasticity, through third order, of four carbon allotropes [cubic and hexagonal diamond (cD, hD), and hexagonal and rhombohedral graphite (rG, hG)], has recently been given.[1] The formal treatment of inner elastic constants and zone-center optic modes has been presented in Ref. 2 (hereafter C1) and of the anatomy of the macroscopic elastic constants and detailed protocols for their computation in Ref. 3 (hereafter C2). The four allotropes make an interesting group: the two with two atoms in the basis have the highest and the lowest symmetries, the two with four atoms in the basis have the same intermediate macroscopic symmetry but different microscopic symmetry; a different pairing contrasts the sp^3-bonded diamonds with the sp^2+p_z-bonded graphites and the remaining pairing comprises two stable structures on the one hand with a pair that consists of a structure rarely seen outside the high-pressure cell and a structure that has never been isolated on the other.

In this series of papers the elasticity of these allotropes is viewed in terms of a single model. Attention is focused initially on cD as it has the simplest structure and provides a natural starting point.

Over the years a number of valence-force-field approaches have been developed and (or) used to treat elasticity,[4–9] lattice dynamics,[10,11] and piezo-Raman spectroscopy,[12–15] in covalently bonded materials. These range from Keating's original two-parameter model[5] dealing with harmonic properties to the massive 21-term database of Vanderbilt *et al.*[8] that handles harmonic, third-order and fourth-order anharmonic properties of silicon.

In the desire to achieve a good description of both harmonic and third-order anharmonic properties of cubic diamond with the smallest number of parameters it was decided to develop and optimize the original Keating model[5,6] by including only such further interactions as were strictly necessary.

The elasticity of cD is detailed in C2 in a manner that explicitly reveals the contribution of inner elastic constants and internal strain. The key points are summarized in Sec. II. In C1 it is shown how zone-center mode frequencies and eigenvectors are related to the inner elastic constants, and how the definition of effective inner elastic constants leads to expressions for the pressure derivatives of the mode frequencies. Section III contains a summary of the essential results and also an extension of them to cover the uniaxial stress-dependence of the frequencies (phonon deformation potentials) so that a wealth of experimental data[12–15] can be considered.

Previous applications of the Keating model are reviewed in Sec. IV and the method is extended to include all three nearest-neighbor three-body interactions at the second order. The optimization of the four parameters of its harmonic part is carried out. It is shown that the bond-bending parameter obtained this way always contains implicitly a four-body contribution that cannot be separated from the normal three-body contribution by consideration of elasticity alone. Separation is achieved by fitting phonon frequencies at the *X* and

L points of the Brillouin zone.

Additionally six anharmonic terms have been considered at the third order.[6,15] In an exact fit of these to experimental values of the three pressure derivatives of the second-order elastic constants and of the three-phonon deformation potentials that describe the stress dependencies of the Raman frequency[14,15] it was found that one parameter was insignificant. For the optimized anharmonic potential the other five force constants were fit by least squares with almost no change in values. The full array of results is summarized in Sec. V. Finally in Sec. VI the elasticity of cD is expressed relative to rhombohedral axes. When compared with the standard cubic approach this reveals the drawback to the Keating model: namely that the model parameters depend on some lattice parameter. The situation is avoided by removing *explicit* references to the latter from the energy expressions. The resulting model parameters are then independent of the choice of unit cell.

TABLE I. The symmetry of the elastic constants and the inner elastic constants. The first column contains the sets of components of each that have been selected as independent and the second column contains the relationships (other than by legitimate permutation of subscripts, $C_{IJ}=C_{JI}$, $D_{iJK}=D_{iKJ}$, and $E_{ijK}=E_{jiK}$, for example) between the remaining nonzero components and the independent ones.

C_{11}	$C_{22}=C_{33}=C_{11}$
C_{12}	$C_{13}=C_{23}=C_{12}$
C_{44}	$C_{55}=C_{66}=C_{44}$
C_{111}	$C_{222}=C_{333}=C_{111}$
C_{112}	$C_{113}=C_{122}=C_{133}=C_{223}=C_{233}=C_{112}$
C_{123}	
C_{144}	$C_{255}=C_{366}=C_{144}$
C_{155}	$C_{166}=C_{244}=C_{266}=C_{344}=C_{355}=C_{155}$
C_{456}	
D_{14}	$D_{25}=D_{36}=D_{14}$
D_{114}	$D_{225}=D_{336}=D_{114}$
D_{124}	$D_{235}=D_{316}=D_{134}=D_{215}=D_{326}=D_{124}$
D_{156}	$D_{246}=D_{345}=D_{156}$
E_{11}	$E_{22}=E_{33}=E_{11}$
E_{111}	$E_{222}=E_{333}=E_{111}$
E_{112}	$E_{113}=E_{221}=E_{223}=E_{331}=E_{332}=E_{112}$
E_{126}	$E_{234}=E_{135}=E_{126}$
F_{123}	

II. ELASTICITY

The general formalism and symmetry analysis for the explicit development of elasticity in terms of partial, inner and total elastic constants is given in Refs. 16 and 17. Specific application to cD is given in C2.

As a crystal with a basis of only 2 atoms, neither of which occupies a site with inversion symmetry, cD requires a single inner displacement vector $\vec{\zeta}$ and 6 components of Lagrangian strain η to describe fully its elasticity. Symmetry analysis reveals the nonzero components of all the elastic and the inner elastic constants and these are shown in Table I.

The inner displacement vector $\vec{\zeta}$ is related to η by the components

$$\begin{aligned}
\zeta_1&=A_{14}\eta_4+A_{114}\eta_1\eta_4+A_{124}(\eta_2+\eta_3)\eta_4+A_{156}\eta_5\eta_6,\\
\zeta_2&=A_{14}\eta_5+A_{114}\eta_2\eta_5+A_{124}(\eta_1+\eta_3)\eta_5+A_{156}\eta_4\eta_6,\\
\zeta_3&=A_{14}\eta_6+A_{114}\eta_3\eta_6+A_{124}(\eta_1+\eta_2)\eta_6+A_{156}\eta_4\eta_5,
\end{aligned} \tag{1}$$

where A_{14} and A_{114} etc. are components of the internal strain tensors which are 3×6 and 3×6×6 arrays. Their values come from applying internal equilibrium conditions, see C2, and are given by

$$A_{14}=-D_{14}/E_{11} \tag{2}$$

and

$$\begin{aligned}
A_{114}&=-(D_{114}+A_{14}E_{111})/E_{11},\\
A_{124}&=-(D_{124}+A_{14}E_{112})/E_{11},\\
A_{156}&=-(D_{156}+2A_{14}E_{126}+A_{14}^2F_{123})/E_{11}.
\end{aligned} \tag{3}$$

Eliminating the $\vec{\zeta}$ from the elastic energy leads to the final expressions for the total elastic constants:

$$\begin{aligned}
C_{11}&=C_{11}^0,\\
C_{12}&=C_{12}^0,\\
C_{44}&=C_{44}^0-A_{14}^2E_{11},
\end{aligned} \tag{4}$$

at the second order and

$$\begin{aligned}
C_{111}&=C_{111}^0,\\
C_{112}&=C_{112}^0,\\
C_{123}&=C_{123}^0,\\
C_{144}&=C_{144}^0+2A_{14}D_{114}+A_{14}^2E_{111},\\
C_{155}&=C_{155}^0+2A_{14}D_{124}+A_{14}^2E_{112},\\
C_{456}&=C_{456}^0+3A_{14}D_{156}+3A_{14}^2E_{126}+A_{14}^3F_{123},
\end{aligned} \tag{5}$$

at the third.

A. Second- and third-order compliances

Second-order compliances S_{IJ} enter the general expressions for the effective elastic constants that are needed in the anharmonic parametrization. They are obtained from the stiffnesses C_{IJ} through the following relations,[18]

$$k \equiv S_{11}+2S_{12}=1/(C_{11}+2C_{12}),$$

$$k' \equiv S_{11}-S_{12}=1/(C_{11}-C_{12}),$$

$$k'' \equiv S_{44}=1/C_{44}. \tag{6}$$

The abbreviations k, k' and k'' serve to simplify the following expressions for the third-order compliances:[19]

$$K=S_{111}+6S_{112}+2S_{123}=-k^3(C_{111}+6C_{112}+2C_{123}),$$

$$S_{111}-3S_{112}+2S_{123}=-k'^3(C_{111}-3C_{112}+2C_{123}),$$

$$S_{111}-S_{123}=-kk'^2(C_{111}-C_{123}),$$

$$S_{144}+2S_{155}=-kk''^2(C_{144}+2C_{155}),$$

$$S_{144}-S_{155}=-k'k''^2(C_{144}-C_{155}),$$

$$S_{456}=-k''^3C_{456}. \tag{7}$$

where k and K are the harmonic and anharmonic linear compressibilities, respectively. The latter feature in the expressions that represent relative changes in lattice parameter a and unit cell volume Ω as a function of pressure, see C2:

$$\Delta a/a_0=-kp+\frac{1}{2}(K-k^2)p^2,$$

$$\Delta\Omega/\Omega_0=-3kp+\frac{3}{2}(K+k^2)p^2. \tag{8}$$

B. Pressure derivatives of the elastic constants

The hydrostatic pressure derivatives of the elastic constants are given by the following expressions:

$$C'_{11}=-k(C_{11}+C_{111}+2C_{112}),$$

$$C'_{12}=-k(C_{12}+2C_{112}+C_{123}),$$

$$C'_{44}=-k(C_{44}+C_{144}+2C_{244}), \tag{9}$$

and

$$B'=-\frac{1}{3}-\frac{k}{3}(C_{111}+6C_{112}+2C_{123}), \tag{10}$$

where the bulk modulus $B=(C_{11}+2C_{12})=1/3k$.

III. ZONE-CENTER OPTICAL MODES

The general results for optical mode frequencies and eigenvectors in this *semiclassical* approach are given in C1. Strictly speaking the frequencies should be directly related to the adiabatic tensors E^S_{ij}, the second derivatives of the *potential* energy U via the Hamiltonian in a quantum-mechanical formulation[20] or via the Lagrangian in a classical approach.[16,21] The E_{ij} used in the present development are isothermal tensors, second derivatives of the *free*-energy $F \equiv U-TS$ and thus only approximately correct. The discrepancies between E^S_{ij} and E_{ij} are extremely small because the vibrational energy is very much smaller than the potential energy for strongly bonded materials at modest temperatures.

The strain-dependence of the optic mode frequencies in terms of the E_{ijK} is subject to the same approximation but any discrepancies are expected to be very small for the same reason as before. A model that derives the strain-dependence of frequency from the difference of harmonic frequencies for strained and unstrained states is said to be *quasiharmonic*. A fully anharmonic model is a quantum-mechanical one that treats phonon-phonon interactions in terms of both third- and fourth-order anharmonicity.

A. The secular equation at equilibrium

For diamond the secular equation for the optical modes reduces to a 3×3 determinant with a triply degenerate root.[21]

$$\omega^2=\frac{4}{\rho_0}E_{11}=\frac{a^3}{2M}E_{11}, \tag{11}$$

where ρ_0 is the equilibrium density and M is the mass of a carbon atom.

B. The secular equation under stress

The procedure leading to the strain-dependence of the optic mode frequencies is cast in terms of third strain-derivatives of the free energy rather than of the potential energy. Any discrepancy is expected to be very small for the same reason as before.

The effective inner elastic constants $\overline{E}$ for arbitrary strain are shown in C1 to be

$$\overline{E}_{11}=E_{11}(1+\eta_1-\eta_2-\eta_3)+E_{111}\eta_1+E_{112}(\eta_2+\eta_3),$$

$$\overline{E}_{22}=E_{11}(1-\eta_1+\eta_2-\eta_3)+E_{111}\eta_2+E_{112}(\eta_1+\eta_3),$$

$$\overline{E}_{33}=E_{11}(1-\eta_1-\eta_2+\eta_3)+E_{111}\eta_3+E_{112}(\eta_1+\eta_2),$$

$$\overline{E}_{12}=(E_{11}+E_{126}+A_{14}F_{123})\eta_6,$$

$$\overline{E}_{13}=(E_{11}+E_{126}+A_{14}F_{123})\eta_5,$$

$$\overline{E}_{23}=(E_{11}+E_{126}+A_{14}F_{123})\eta_4. \tag{12}$$

The secular equation for the optical modes under a stress σ is

$$\left|\overline{E}_{ij}-\frac{\rho}{4}\omega^2\right|=0 \tag{13}$$

in which

$$\frac{\rho_0}{\rho}=1+k\sigma. \tag{14}$$

The phonon deformation potentials that describe the stress-dependence of the mode frequencies depend on the stress derivatives of both $\overline{E}_{ij}$ and ρ.

Under hydrostatic pressure p the effective constants are

$$\overline{E}_{11}=\overline{E}_{22}=\overline{E}_{33}=E_{11}(1+pk)-pk(E_{111}+2E_{112}) \tag{15}$$

and the eigenvalues remain triply degenerate with

$$\omega_H^2=\frac{4}{\rho}\overline{E}_{11}. \tag{16}$$

For a uniaxial stress σ in the direction $\vec{\ell}$ the stress components are given by $\sigma_J=\sigma\ell_i\ell_j$, where J is the conventional contraction of ij. Hooke's law, $\eta_I=S_{IJ}\sigma_J$, can now be used to eliminate η_I from the effective inner elastic constants in favor of $\sigma\ell_i\ell_j$ and derivatives with respect to stress found.

Three situations are relevant to the work described in this paper.

1. σ along [0 0 1]

This is a tetragonal deformation and the effective E tensor now has two different diagonal components

$$\overline{E}_{11}=\overline{E}_{22}=E_{11}(1-\sigma S_{11})+\sigma[S_{12}E_{111}+(S_{11}+S_{12})E_{112}],$$

$$\overline{E}_{33}=E_{11}(1-\sigma(2S_{12}-S_{11}))+\sigma(S_{11}E_{111}+2S_{12}E_{112}). \tag{17}$$

The eigenvalues consist of a doublet and a singlet given by

$$\omega_d^2=\frac{4}{\rho}\overline{E}_{11} \tag{18}$$

and

$$\omega_s^2=\frac{4}{\rho}\overline{E}_{33}. \tag{19}$$

2. σ along [1 1 1]

This is a trigonal deformation in which

$$\overline{E}_{11}=\overline{E}_{22}=\overline{E}_{33}=E_{11}\left[1-\frac{1}{3}\sigma(S_{11}+2S_{12})\right]+\frac{1}{3}\sigma(S_{11}+2S_{12})\times(E_{111}+2E_{112}),$$

$$\overline{E}_{12}=\overline{E}_{13}=\overline{E}_{23}=\frac{1}{3}\sigma S_{44}(E_{11}+E_{126}+A_{14}F_{123}). \tag{20}$$

The eigenvalues are

$$\omega_d^2=\frac{4}{\rho}(\overline{E}_{11}-\overline{E}_{12}) \tag{21}$$

and

$$\omega_s^2=\frac{4}{\rho}(\overline{E}_{11}+2\overline{E}_{12}). \tag{22}$$

3. σ along [1 1 0]

In this orthorhombic deformation an off-diagonal component is introduced

$$\overline{E}_{11}=\overline{E}_{22}=E_{11}(1-\sigma S_{12})+\frac{1}{2}\sigma[(S_{11}+S_{12})E_{111}+(S_{11}+3S_{12})E_{112}]$$

$$\overline{E}_{12}=\frac{1}{2}\sigma S_{44}(E_{11}+E_{126}+A_{14}F_{123})$$

$$\overline{E}_{33}=E_{11}(1-\sigma S_{11})+\sigma(S_{12}E_{111}+(S_{11}+S_{12})E_{112}). \tag{23}$$

Degeneracy has now been removed and three eigenvalues are obtained

$$\omega_\pm^2=\frac{4}{\rho}(\overline{E}_{11}\pm\overline{E}_{12}) \tag{24}$$

and

$$\omega_3^2=\frac{4}{\rho}\overline{E}_{33}. \tag{25}$$

C. Phonon deformation potentials

There are several different *ad hoc* definitions and notations used to describe the strain dependence of the optic mode frequencies at the zone center.[12,22] $K_{ij}\equiv\partial\omega^2/\partial\eta_{ij}$ and $\tilde{K}_{ij}\equiv\partial\ln\omega^2/\partial\eta_{ij}=(1/\omega_0^2)K_{ij}$ are general expressions whilst $p=K_{11}$, $q=K_{12}$ and $r=K_{44}$ are parameters specific to cubic symmetry. When the eigenvalue expressions in the previous sections are differentiated with respect to stress, relations precisely the same as those given in Ref. 12 are obtained with

$$\frac{p}{2\omega_0^2}=1+\frac{E_{111}}{2E_{11}},$$

$$\frac{q}{2\omega_0^2}=\frac{E_{112}}{2E_{11}},$$

$$\frac{r}{\omega_0^2}=1+\frac{E_{126}+A_{14}F_{123}}{E_{11}}, \tag{26}$$

together with the mode Grüneisen parameter

$$\gamma_G=-\frac{1}{3}\left(1+\frac{E_{111}+2E_{112}}{2E_{11}}\right). \tag{27}$$

A slighty different approach has been adopted by Nielsen[23] who defines a *phonoelastic* tensor Ω as the square root of the dynamical matrix. Elements of this tensor, expanded in powers of η, combine to give frequencies under strain. Certain of the linear coefficients then correspond to phonon deformation potentials: Ω_{11},Ω_{12}, and $2\Omega_{44}$ corresponding to the left-hand sides of the three members of Eq. (26) above.

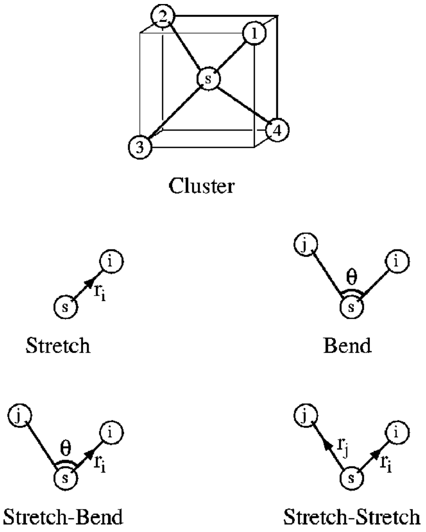

FIG. 1. Tetrahedral cluster and four basic interactions.

IV. THE KEATING MODEL

The Keating formalism[5] models the strain energy only and does not provide values for the cohesive energy or the lattice parameter a. The unit cell in diamond is defined by the vectors $\vec{a}_1=(a/2)[0,1,1]$, $\vec{a}_2=(a/2)[1,0,1]$ and $\vec{a}_3=(a/2)\times[1,1,0]$, where $a=3.567$ Å. The basis consists of two atoms with position coordinates (0,0,0) and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$.

The original strain variables are $(\vec{r}^{\,i}\cdot\vec{r}^{\,j}-\vec{r}^{\,i0}\cdot\vec{r}^{\,j0})/(a/2)\equiv\Delta_{ij}/(a/2)$, where i and j label atoms neighboring a particular reference atom, s, and $i0$ and $j0$ label the unstrained configuration. The connection between Δ_{ij}, the finite strain tensor η and the inner displacement vector $\vec{\zeta}$ follows from the definition of homogeneous deformation. If J is the deformation gradient matrix and $\vec{\delta}$ is the sublattice displacement then $I+2\eta=\tilde{J}J$ and $\vec{\zeta}=\tilde{J}\vec{\delta}$. From this we obtain $\vec{r}^{\,i}=J\vec{r}^{\,i0}\pm\tilde{J}^{-1}\vec{\zeta}$, where the sign depends on which sublattice the reference atom lies on,

$$\Delta_{ii}=2r_p^{i0}\eta_{pq}r_q^{i0}\pm2r_p^{i0}\zeta_p+\zeta_p\zeta_p \tag{28}$$

and

$$\Delta_{ij}=2r_p^{i0}\eta_{pq}r_q^{j0}\pm(r_p^{i0}+r_p^{j0})\zeta_p+\zeta_p\zeta_p, \tag{29}$$

where terms of order three and higher have been omitted.

A. Harmonic interactions

The tetrahedral cluster and the four basic interactions are shown in Fig. 1. The harmonic energy per cell stems from the nearest-neighbor two-body interaction (stretch), three nearest-neighbor three-body interactions (bend, stretch-bend and stretch-stretch) and a certain four-body interaction. It takes the form

$$E^{(2)}=\frac{1}{a^2}\sum_{s=1}^{2}\left[\sum_{i=1}^{4}\alpha\Delta_{ii}^2+\sum_{i=1}^{3}\sum_{j=i+1}^{4}[2\beta\Delta_{ij}^2+2\tau\Delta_{ii}\Delta_{jj}+\sigma(\Delta_{ii}+\Delta_{jj})\Delta_{ij}]+\sum_{i=1}^{4}\sum_{j=1}^{4}{}'\,\kappa\Delta_{ij}\Delta_{ik}\right]. \tag{30}$$

The κ term is related to the $f_{\phi\phi^*}$ valence force field parameter introduced by McMurry *et al.*[10] as an essential ingredient in the treatment of the flattening of the transverse acoustic dispersion curves towards the X and L points in the Brillouin zone. It relates to a chain of three bonds in a 180° dihedral-angle configuration. The prime on the final summation indicates that $j\neq i$ and the absence of a summation over k arises as follows. The bonds labeled j and k are attached to opposite ends of bond i and are parallel. Under homogeneous deformation the outer bonds are strained in the same way, forcing the two angles of the chain to change in the same way. This results in $\Delta_{ij}\Delta_{ik}=\Delta_{ij}^2$ and the interaction becomes formally indistinguishable from the simple three-body bond-bending interaction. Elastic constants and the zone-center frequency cannot be used to separate β from κ. However the expressions for some of the phonon frequencies at the zone boundary mix β and κ in different proportions thereby enabling the separation to be made.

The second-order elastic, inner elastic and internal strain parameters are given by the following, in which β^* denotes $\beta+\kappa$:

$$C_{11}=\frac{1}{a}(\alpha+3\beta^*-\sigma+3\tau),$$

$$C_{12}=\frac{1}{a}(\alpha-\beta^*-\sigma+3\tau),$$

$$B=\frac{1}{a}\left(\alpha+\frac{1}{3}\beta^*-\sigma+3\tau\right),$$

$$C_{44}^0=\frac{1}{a}(\alpha+\beta^*-\sigma-\tau),$$

$$D_{14}=\frac{4}{a^2}(\alpha-\beta^*-\tau),$$

$$E_{11}=\frac{16}{a^3}(\alpha+\beta^*+\sigma-\tau),$$

$$A_{14}=-\frac{a}{4}\left(\frac{\alpha-\beta^*-\tau}{\alpha+\beta^*+\sigma-\tau}\right),$$

$$\zeta_K=-\frac{4}{a}A_{14}, \tag{31}$$

where B is the bulk modulus, ζ_K is the Kleinman internal strain parameter and the remaining total second-order constant C_{44} is given by Eq. (4).

TABLE II. Parametrization of the harmonic part of the Keating model. As explained in the text all fits of β to experimental data are in fact fits of $\beta+\kappa$: this is indicated below by the use of β^*. Units are GPa for C_{IJ} and B, GPa Å^{-2} for E_{11}, and GPa Å for α etc.

	← α,β^* fittings →					α,β^*,τ	α,β^*,σ	Present work		
	← Exact →				LSq		Exact	Exact	LSq	Observed
C_{11}	Fit	Fit	756	433	990	1051	Fit	Fit	1072	1079(5) [a]
C_{12}	Fit	−199	Fit	447	69	100	Fit	Fit	131	124(5) [a]
E_{11}	756	Fit	Fit	Fit	666	770	Fit	Fit	562	553.4(8) [b]
C_{44}	576	350	567	−13	520	589	593	Fit	574	578(2) [a]
B	(Fit)	226	335	Fit	376	417	(Fit)	(Fit)	445	442(4) [a]
ζ_K	0.206	−0.45	0.28	1.02	0.131	0.20	0.12	0.074	0.093	0.125(20) [c]
α	1294	430	1006	1582	1068	1304	1056	987	1009	
β^*	852	1140	564	−12.2	821	848	852	852	840	
σ							−238	−250	−234	
τ						−33		19	21	

[a] Reference 24.

[b] Reference 25.

[c] Reference 26.

In addition, because Δ_{ii} and Δ_{ij} contain terms in ζ^2, the "harmonic" energy contains small anharmonic contributions via E_{111} and E_{112}. These are given by

$$E_{111}^{(2)}=E_{112}^{(2)}=\frac{16}{a^3}(\alpha-\beta^*+\sigma+3\tau). \tag{32}$$

Initially the model was limited to the α and β^* terms alone and applied to Group IV elements and III–V semiconductors.[5,7] The targets for fitting were C_{11}, C_{12}, and C_{44}.

Values of α and β^* deduced[24] from C_{11} and C_{12} gave C_{44} to more than 0.3%.[5] This very encouraging result hid a 37% error in E_{11} or a 17% error in the Raman frequency ω_0.[25] It also predicted a value of 0.21 for ζ_K. This was later measured and the much smaller value of 0.125 ± 0.020 was obtained.[26] With more experimental data available different fits can be made and these are listed in Table II. For columns 2 through 5 two data are used to determine α and β^* and the implications set out: at least one quantity is very poorly predicted each time and ζ_K in particular is bad. In column 6 a least-squares fit to four data by Anastassakis *et al.*[15] leads to $\alpha=1068$ GPa Å and $\beta^*=821$ GPa Å. This gives a value of ζ_K close to that measured, though ω_0 is still 10% too large and C_{12} is 44% too small.

The first extension of the Keating model to include an additional interaction was made by Bashenov *et al.*[27] who introduced (using γ) the term denoted here by τ. Column 7 lists the quoted values; the precise method of calculation remains unclear.

The case for the inclusion of the other three-body term was discussed by Rücker and Methfessel.[28] They pointed out that a good agreement for C_{11}, C_{12}, C_{44}, and ω_0 in diamond could be obtained using just α, β^*, and σ (γ in their paper) whereas it appeared important to introduce τ to improve the fit to the phonon dispersion in Si and Ge. Column 8 shows the result of this fitting. Each fit generates a unique relation for ζ_K in terms of the fitted parameters–in this case

$$1-2\zeta_K=\left(\frac{4a(C_{11}-3C_{12})}{M\omega_0^2}\right)^{1/2}. \tag{33}$$

This gives a value $\zeta_K=0.102$ that is close to a theoretical calculation[23] and reasonably close to the experiment.[26] The predicted value for C_{44} is now 593 GPa, much closer to the observed 578 GPa.

The inclusion of both extra terms will now be considered. Inversion of the earlier equations for C_{11}, C_{12}, E_{11}, and D_{14} (as $\zeta_K E_{11}$) yields

$$\alpha=\frac{a}{8}(C_{11}+C_{12})+\frac{a^3}{64}E_{11}(1+2\zeta_K),$$

$$\beta^*=\frac{a}{4}(C_{11}-C_{12}),$$

$$\sigma=-\frac{a}{2}(C_{11}-C_{12})+\frac{a^3}{16}E_{11}(1-\zeta_K),$$

$$\tau=-\frac{a}{8}(C_{11}-3C_{12})+\frac{a^3}{64}E_{11}(1-2\zeta_K). \tag{34}$$

These then imply

$$1-\zeta_K=\left(\frac{8a(C_{11}-C_{12}-C_{44})}{M\omega_0^2}\right)^{1/2} \tag{35}$$

giving $\zeta_K=0.074$, a value that is somewhat lower than either the measured value or theoretical predictions. If the tolerances on the experimental data are taken into account a range of values is obtained: $\zeta_K=0.074\pm0.009$. Although this is not quite enough to bracket the experimental range there are reasons, discussed in Sec. V, for supposing that the experimental

TABLE III. Phonon frequencies $f(\equiv\omega/2\pi)$ at the Γ, X, and L points. Units: THz for f, GPa Å for β^* etc.

Point	Mode	Exact fit		Least-sq. fit		Observed
Γ	LO,TO	39.93	39.93	40.23	40.23	39.93
X	LO,LA	37.09	35.36	37.09	35.45	35.80
	TO	31.36	31.36	31.68	31.68	32.39
	TA	29.41	24.78	29.20	24.78	24.04
L	LO	40.42	36.77	40.29	36.80	37.21
	LA	30.91	30.40	31.05	30.57	31.00
	TO	35.90	35.90	36.21	36.21	36.25
	TA	20.80	17.52	20.65	17.52	16.55
β^*		852		840		
β			605		605	
κ		0	247	0	235	

[a] Reference 25: errors are estimated at 2–3%

value may have been slightly overestimated. This four-parameter fit is listed in column 9. A least squares solution involving the observed value of ζ_K produces the fitting shown in column 10.

To check further the quality of the fits and to resolve the β/κ problem involves consideration of the zone-boundary phonons. At the X point these have frequencies given by

$$M\omega_{LO,LA}^2=4\alpha+8\beta+4\tau+4\kappa=4\alpha+8\beta^*+4\tau-4\kappa,$$

$$M\omega_{TO}^2=8\alpha-8\tau,$$

$$M\omega_{TA}^2=8\beta=8\beta^*-8\kappa, \tag{36}$$

and at the L point by

$$M\omega_{LO}^2=2\alpha+13\beta+\sigma+4\tau+4\kappa=2\alpha+13\beta^*+\sigma+4\tau-9\kappa,$$

$$M\omega_{LA}^2=6\alpha+\beta-3\sigma=6\alpha+\beta^*-3\sigma-\kappa,$$

$$M\omega_{TO}^2=8\alpha+4\beta+4\sigma-8\tau+4\kappa=8\alpha+4\beta^*+4\sigma-8\tau,$$

$$M\omega_{TA}^2=4\beta=4\beta^*-4\kappa. \tag{37}$$

Columns 3, 5, and 7 in Table III show the frequencies predicted using the four parameters α, β^*, σ, and τ (i.e., with no explicit κ term), in both exact and least-squares versions, and those observed. The least-squares fit appears to be very slightly better. The TO modes, which have no explicit κ component, are well predicted with errors of only -2% and

TABLE IV. Parametrization of the anharmonic part of the Keating model using pressure derivatives of the second-order elastic constants and the phonon deformation potentials. All input quantities are dimensionless. The units for γ etc. are GPa.

Input	Ref. 14	Ref. 15	Present work		Observed
C_{11}'	7.31		Fit	6.97	6.98(70) [a]
C_{12}'	3.23		Fit	2.09	2.06(70) [a]
C_{44}'	4.40	3.95	Fit	4.12	3.98(30) [a]
$(C_{11}'-C_{12}')/2$		2.45			2.46(10) [a]
$(C_{11}'+C_{12}'+2C_{44}')/2$		8.65			8.50(60) [a]
$(p+2q)/2\omega_0^2$	-3.35	-3.19	Fit	-3.18	$-3.18(24)$ [b]
$(p-q)/2\omega_0^2$	-0.50	-0.52	Fit	-0.52	$-0.52(8)$ [b]
r/ω_0^2	-1.2	-1.89	Fit	-1.89	$-1.9(2)$ [b]
γ	-1670	-1478	-1200	-1198	
δ	95	140	164	166	
ϵ	-499	-654	-567	-566	
η		-227	-139	-138	
θ		181	145	143	
ξ			0.55		

[a] Reference 24.

[b] Reference 14.

TABLE V. The inner elastic constants and internal strain parameters. Units are GPa Å^{-1} for D, GPa Å^{-2} for E, GPa Å^{-3} for F and Å for A.

D_{14}	46.6	E_{11}	561.9			A_{14}	-0.083	
						ζ_K	0.093	0.108 [a]
D_{114}	-259	E_{111}	-2705			A_{114}	0.06	1.39 [a]
D_{124}	-529	E_{112}	-998			A_{124}	0.79	1.11 [a]
D_{156}	-1028	E_{126}	-1860	F_{123}	-2879	A_{156}	1.32	1.96 [a]

[a] Reference 23.

-0.1%. Apart from one the remainder are overestimated: in particular the errors in the TA modes are 22% at X and 25% at L. This characteristic failure to pick up the flattening of the TA modes near the boundary is markedly reduced by setting $\kappa = 247$ GPa Å in the exact and $\kappa = 235$ GPa Å in the least-squares fittings to give the values listed in columns 4 and 6: the errors in the TA modes are now 3% and 6%, respectively and the separation of β^* has now been achieved with $\beta = 605$ GPa Å in each case.

With the simple model under consideration there is no way to improve all the zone-boundary frequencies. It can be shown[29] that the most general force constant fitting to nearest and next-nearest neighbor interactions imposes a condition on the calculated frequencies:

$$2(\omega_{LA}^2 - \omega_{LO}^2 + \omega_{TO}^2 - \omega_{TA}^2)_L = 3(\omega_{TO}^2 - \omega_{TA}^2)_X . \tag{38}$$

Observed values do not satisfy this equation: the left- and right-hand sides differ from their mean by 6%, a figure that suggests that the above fit is as good as it can be.

The inner elastic constants and internal strain parameters are collected together in summary Table V in Sec. V and the decomposition of the calculated constants and the associated compliances are shown in summary Table VI.

B. Anharmonic interactions

Keating extended his method to the anharmonic régime[6] by considering the γ, δ, and ϵ terms in the following expression for the anharmonic energy per cell

$$E^{(3)} = \frac{8}{3a^3} \sum_{s=1}^{2} \left[\sum_{i=1}^{4} \gamma \Delta_{ii}^3 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} [2\delta\Delta_{ij}^3 + 3\epsilon(\Delta_{ii} + \Delta_{jj})\Delta_{ij}^2 + 3\eta(\Delta_{ii}^2 + \Delta_{jj}^2)\Delta_{ij} + 6\theta\Delta_{ii}\Delta_{ij}\Delta_{jj} + 3\xi\Delta_{ii}\Delta_{jj}(\Delta_{ii} + \Delta_{jj})] \right], \tag{39}$$

where all nearest-neighbor two-body and three-body interactions have been written down. He successfully applied this model to fitting the third-order elastic constants of Si and Ge. The direct measurement of these constants for diamond would be extremely difficult for several reasons and has probably not been attempted. Nevertheless experimental data are available that relate to the third-order elastic constants, through pressure derivatives of second-order constants,[24] and to third-order inner elastic constants, in the form of stress derivatives of the Raman frequency.[14] The pattern of analysis used here is essentially the same as the one developed in Ref. 15. The latter work however involved only a two-parameter harmonic fitting and this affects, in principle, the fits to E_{111} and E_{112} and causes poorly fitted quantities (E_{11}, B, and perhaps, ζ_K) to distort the anharmonic fitting.

The third-order elastic and inner elastic constants are given by the following expressions:

$$C_{111} = \gamma - \delta + 9\epsilon - 3\eta - 3\theta + 9\xi,$$

$$C_{112} = \gamma - \delta + \epsilon - 3\eta - 3\theta + 9\xi,$$

$$C_{123} = \gamma + 3\delta - 3\epsilon - 3\eta - 3\theta + 9\xi,$$

TABLE VI. The elastic constants: stiffnesses are in GPa, compliances are in (TPa)$^{-1}$ at the second-order and in (TPa)$^{-2}$ at the third.

	Present work			Observed	γ,δ,ϵ fit	*Ab initio*				Observed
Stiffness	Partial	Internal	Total	Ref. 24	Ref. 14	Ref. 23	Ref. 28	Compliance	Total	via Ref. 24
C_{11}	1072.3		1072.3	1079(5)		1050(10)	1104.	S_{11}	0.958	0.949(5)
C_{12}	130.7		130.7	124(5)		127(4)	149.	S_{12}	-0.104	$-0.098(3)$
C_{44}	577.9	-3.9	574.0	578(2)		550(5)	581.	S_{44}	1.742	1.730(6)
C_{111}	$-6475.$		$-6475.$		-6260	$-6300(300)$		S_{111}	4.609	
C_{112}	$-1947.$		$-1947.$		-2260	$-800(100)$		S_{112}	0.936	
C_{123}	982.		982.		112	0(400)		S_{123}	-1.698	
C_{144}	91.	24.	115.		-674	0(300)		S_{144}	-2.230	
C_{155}	$-3079.$	81.	$-2998.$		-2860	$-2600(100)$		S_{155}	7.807	
C_{456}	$-355.$	219.	$-135.$		-823	$-1300(100)$		S_{456}	0.716	

$$C^0_{144}=\gamma+\delta-\epsilon-3\eta+\theta+\xi,$$

$$C^0_{155}=\gamma-\delta+3\epsilon-3\eta-3\theta+\xi,$$

$$C^0_{456}=\gamma-3\eta+3\theta-3\xi,$$

$$D_{114}=\frac{4}{a}(\gamma-\delta-\epsilon-\eta+3\theta+\xi),$$

$$D_{124}=\frac{4}{a}(\gamma+\delta-\epsilon-\eta+\theta+\xi),$$

$$D_{156}=\frac{4}{a}(\gamma-\eta+\theta-3\xi),$$

$$E^{(3)}_{111}=\frac{16}{a^2}(\gamma+\delta+3\epsilon+\eta+5\theta+\xi),$$

$$E^{(3)}_{112}=\frac{16}{a^2}(\gamma-\delta-\epsilon+\eta+\theta+\xi),$$

$$E_{126}=\frac{16}{a^2}(\gamma+\eta-\theta-3\xi),$$

$$F_{123}=\frac{64}{a^3}(\gamma+3\eta-3\theta-3\xi). \tag{40}$$

The full E_{111} and E_{112} are then given by

$$E_{111}=E^{(2)}_{111}+E^{(3)}_{111},$$

$$E_{112}=E^{(2)}_{112}+E^{(3)}_{112}, \tag{41}$$

and the remaining total third-order constants, C_{144}, C_{155}, and C_{456}, by expressions in Eq. (5).

The target quantities related to the pressure derivatives of the second-order constants are $C_{111}+2C_{112}$, $2C_{112}+C_{123}$, and $C_{144}+2C_{155}$, given by Eq. (9), where values of C'_{IJ} have been derived from Ref. 24. The latter work actually determines pressure derivatives of ultrasonic wave propagation coefficients and their C'_{11} and C'_{44} values must be increased by unity and C'_{12} decreased by unity for consistency with the definitions in Eq. (9). The targets related to the phonon deformation potentials are $E_{111}+2E_{112}$, $E_{111}-E_{112}$, and $E_{126}+A_{14}F_{123}$, given by Eq. (26), where values of *p*, *q*, and *r* have been deduced from Ref. 14 and E_{11} and A_{14} have been carried forward from the least-squares harmonic fit. The (equal) values of $E^{(2)}_{111}$ and $E^{(2)}_{112}$ arising from the fitting of the harmonic energy should be removed from the first of the above three targets. This quantity is, however, very small: for the exact fitting it is -20.6 GPa Å and a minute -0.4 GPa Å for the least-squares fitting.

With six targets and six force constants an exact fitting is possible. This gives a value for ξ (0.55 GPa) that is over 250 times smaller than the next smallest. It quantifies and confirms the observation in Ref. 15 that this term, which indicates anharmonic crosstalk between contiguous bonds, should probably be small. When ξ is neglected (on grounds of statistical insignificance) and the remaining five constants fit by least-squares the new values differ from the old by no more than 1.4%. The results of these fittings are displayed in Table IV together with the earlier fitting based on two harmonic terms and three anharmonic ones,[14] and that of Ref. 15. Differences between the present results and those in Ref. 15 are initially puzzling since the same basic approach and the same input data have been used in each case. Small differences are to be expected as a consequence of the use of different values of ζ_K, E_{11}, and *B*. The force constants derived in Ref. 15 are consistent with the values of the third-order constants and with the three-phonon deformation potentials but return values of 5.21, 3.32, and 11.33 for the three pressure derivatives on which they are supposed to be based. A clue is provided by Eqs. (7) in Ref. 15 where two of the three expressions contain twice the correct contribution of second-order constants: in fact all the three derivatives have been so used. The error arises from the inappropriate use of equations developed by Thurston and Brugger[30] to facilitate the determination of third-order elastic constants from ultrasonic measurements by including compensation for changes in specimen dimensions under stress.

One of the conclusions drawn in Ref. 15 was that the force constants η and θ made a relatively small contribution to the elastic constants but were crucial to fitting the phonon deformation potentials. The present results make this point even more strongly: the two constants almost completely cancel and provide less than 0.5% of the elastic constants.

All the calculated anharmonic constants have been entered in Tables V and VI in the following section.

V. SUMMARY OF RESULTS

The inner elastic constants and internal strain parameters are shown in Table V. Most of these are appearing for the first time. Only E_{11} and A_{14}/ζ_K are known experimentally (see Table II). The calculated value of E_{11} is just 1.5% too large whereas ζ_K at 0.093 is somewhat smaller than the 0.125 measured. The only other calculation of ζ_K is due to Nielsen[23] who used local-density functional theory with *ab initio* pseudopotentials. It is intriguing that the value he obtained in the course of fitting all the elastic constants to the local-density approximation output was 0.092(2), essentially the same as the present one. The value he actually reported, 0.108(1), was obtained by a quite separate, albeit more direct, calculation. The possibility that the experimental value is too large follows from the fact that the sample was subjected to a uniaxial stress of 6.2 GPa parallel to $[1,1,0]$. This is large enough to induce quadratic components in the inner displacement and leads to an effective parameter

$$\zeta_K=-\frac{4}{a}\{A_{14}+\sigma[S_{12}A_{114}+(S_{11}+S_{12})A_{124}]\}. \tag{42}$$

Inserting calculated values shows that the experiment probably yielded a value too high in the ratio 0.087 to 0.083. This would reduce ζ_K to 0.119, a shift of 5%, well within the already large experimental uncertainty. At the third order the present values are rather less than those obtained in Ref. 23.

TABLE VII. Calculated second-order partial and inner elastic constants of cubic diamond with respect to both cubic and rhombohedral axes. Units are GPa for C^0_{IJ}, GPa Å^{-1} for D_{iJ} and GPa Å^{-2} for E_{ij}.

Cubic		Rhombohedral		Cubic		Rhombohedral	
C^0_{11}	1072.3	C^0_{11}	1179.4	D_{14}	46.6	D_{16}	38.0
C^0_{12}	130.7	C^0_{12}	95.0			D_{15}	−26.9
C^0_{44}	577.9	C^0_{13}	59.3			D_{31}	−26.9
		C^0_{33}	1215.0			D_{33}	53.8
		C^0_{44}	506.5	E_{11}	561.9	E_{11}	561.9
		C^0_{14}	−50.5			E_{33}	561.9

The anatomy of the elastic constants is shown in Table VI where the difference between partial and total constants is illustrated. At the second-order additional *ab initio* calculations, in which the full-potential linear muffin-tin orbital method has been used, are available.[28] These are clearly of similar quality to those in Ref. 23. Inspite of its simplicity the four-parameter Keating model clearly matches the predictions of more sophisticated calculations with regard to elastic constants and the zone-center phonons.

At the third order the present results are quite similar to the previous three-parameter fit of Grimsditch *et al.*[14] This is expected as it is known that the extra two-parameters introduced in Ref. 15 and used here have their major impact on the phonon deformation potentials. Nielsen's calculations provide the only theoretical comparison. These have been included even though they are quoted to only two significant figures. The two largest constants, C_{111} and C_{155}, are in reasonable agreement with this work but C_{456} seems rather inflated, the present value is much more in keeping with the relative size of this constant in other diamond-structure materials.

The calculated compliances are essentially of the same quality as the stiffnesses. They can be used directly to give the linear compressibilities at second and third order: $k = 0.749$ TPa^{-1} and $K = 6.83$ TPa^{-2}. The corresponding volume compressibilities are $k_v = 3k = 2.25$ TPa^{-1} and $K_v = 3K = 20.5$ TPa^{-2}.

VI. A MODIFIED KEATING MODEL

There is a drawback to the use of the Keating model: its parameters are not independent of the unit cell. This fact appears to have passed unnoticed because the model has been applied exclusively to the diamond and zincblende structures. The problem arises from Keating's inclusion of the structure-specific lattice parameter a in his definition of strain.[5] It manifests itself most clearly in the attempt to account for the elasticity of hD which should be almost the same as that of cD insofar as the atoms in the two structures have precisely the same nearest neighbor configuration.

A. Cubic diamond referred to rhombohedral axes

The simplest way to illustrate the problem is to refer the elasticity of cD to rhombohedral axes. If these are taken to be $Ox_1 \| [1\bar{1}0]$, $Ox_2 \| [11\bar{2}]$ and $Ox_3 \| [111]$ the resulting sets of elastic and inner elastic constants have the forms appropriate to the rhombohedral Laue group RI. Each set divides into two subsets: the group of elements that corresponds to hexagonal symmetry and the group of elements that disappears if there is no rhombohedral symmetry. The transformed partial elastic and inner elastic constants are given in terms of the cubic constants by the expressions listed in Table 4 in C1 and Table 2 in C2. Total elastic constants transform in the same way as the partial constants because any inner elastic contributions to them transform compatibly.

The Keating parameters are not tensor components and there is no rule for their transformation. The Keating expressions for the partial and inner elastic constants can be transformed, however, and give rise, for example, to

$$C^0_{11} = \frac{2}{a}(\alpha + \beta^* - \sigma + \tau)$$

etc., where a is the lattice parameter of the cubic unit cell. The harmonic energy per cell in the cubic system is given by Eq. (30). This energy does not change when the axes are rotated, nor do the Δ_{ii} and Δ_{ij}, being differences of scalar products and thus independent of coordinate system. Yet we would not expect to find a appearing in the equation if we were starting directly from the rhombohedral description, which involves a unit cell containing six atoms and lattice parameters $a_h = a/\sqrt{2}$ and $c_h = \sqrt{3}a$, see Fig. 1 in C1. If Eq. (30) is used with a_h in place of a (explicitly in the initial factor and implicitly in Δ_{ii} and Δ_{ij}) it is necessary to halve the harmonic Keating parameters to regain acceptable second-order constants, the same bulk modulus for example. Similarly, for the anharmonic energy and third-order constants, division by $2\sqrt{2}$ is necessary. Using the parameters deduced earlier in this way generates the quasi-rhombohedral partial and inner elastic constants listed in Tables VII and VIII.

B. Recasting the energy expressions

The simplest satisfactory solution emerges if the a^{-2} and a^{-3} factors are removed from $E^{(2)}$ and $E^{(3)}$. Additionally a cosmetic alteration in the coefficients of individual terms in $E^{(2)}$ and $E^{(3)}$ will remove various powers of 2 whose presence is due to Keating's use of $a/2$ in place of a in his original definition of strain. The modified energies per cell become

TABLE VIII. Calculated third-order partial and inner elastic constants of cubic diamond with respect to both cubic and rhombohedral axes. Units are GPa for C^0_{IJK}, GPa Å^{-1} for D_{iJK}, GPa Å^{-2} for E_{ijK} and GPa Å^{-3} for F_{ijk}.

Cubic		Rhombohedral		Cubic		Rhombohedral		Cubic		Rhombohedral	
C^0_{111}	−6475	C^0_{111}	−12317	D_{114}	−259	D_{116}	−1161	E_{111}	−2705	E_{111}	−3712
C^0_{112}	−1947	C^0_{113}	−131	D_{124}	−529	D_{126}	−188	E_{112}	−998	E_{112}	−662
C^0_{123}	982	C^0_{133}	−1484	D_{156}	−1028	D_{136}	275	E_{126}	−1860	E_{113}	−326
C^0_{144}	91	C^0_{333}	−10520			D_{145}	−353			E_{126}	−1525
C^0_{155}	−3079	C^0_{144}	−304			D_{314}	−243			E_{135}	−1189
C^0_{456}	−355	C^0_{244}	−1371			D_{115}	821			E_{331}	−326
		C^0_{344}	−2833			D_{125}	−23			E_{333}	−4047
		C^0_{166}	−1610			D_{135}	−39			E_{114}	475
		C^0_{266}	−3482			D_{311}	610			E_{136}	475
		C^0_{366}	−196			D_{312}	−389				
		C^0_{114}	185			D_{313}	538	F_{123}	−2879	F_{112}	−2351
		C^0_{124}	164			D_{333}	−2596			F_{113}	1662
		C^0_{134}	754			D_{344}	94			F_{333}	−3325
		C^0_{444}	−908								

$$E^{(2)}=\sum_{s=1}^{2}\left[\sum_{i=1}^{4}\frac{1}{2}\alpha\Delta_{ii}^2+\sum_{i=1}^{3}\sum_{j=i+1}^{4}[\beta^*\Delta_{ij}^2+\sigma(\Delta_{ii}+\Delta_{jj})\Delta_{ij}+\tau\Delta_{ii}\Delta_{jj}]\right] \tag{43}$$

and

$$E^{(3)}=\sum_{s=1}^{2}\left[\sum_{i=1}^{4}\frac{1}{2}\gamma\Delta_{ii}^3+\sum_{i=1}^{3}\sum_{j=i+1}^{4}[\delta\Delta_{ij}^3+\epsilon(\Delta_{ii}+\Delta_{jj})\Delta_{ij}^2+\eta(\Delta_{ii}^2+\Delta_{jj}^2)\Delta_{ij}+\theta\Delta_{ii}\Delta_{ij}\Delta_{jj}+\xi\Delta_{ii}\Delta_{jj}(\Delta_{ii}+\Delta_{jj})]\right], \tag{44}$$

where factors of a half have been left in those interactions that are counted twice. The previous notation has been retained so that confusion is avoided: expressions for elastic constants will change (as shown below) but the conceptual foundation of the model remains the same.

C. Modified Keating parameters

Identification of the old and the new strain and energy expressions indicates how the parameters of the model must be modified: for example

$$\alpha_{\text{mod}}=\frac{2}{a^2}\alpha \tag{45}$$

and

$$\gamma_{\text{mod}}=\frac{16}{3a^3}\gamma. \tag{46}$$

The modified results for all the parameters deduced for cD by least squares fitting in Sec. IV are listed in Table IX.

D. Modified cubic diamond referred to cubic axes

All that remains is to collect together the modified expressions for the different categories of elastic constant. Powers of $4/a$ in the unmodified expressions for the inner elastic constants and the internal strain arose from components of the unstretched bond and are replaced here by powers of $\sqrt{3}/r_0$. At the second order

$$C_{11}=\frac{a}{2}(\alpha+3\beta^*-2\sigma+3\tau),$$

$$C_{12}=\frac{a}{2}(\alpha-\beta^*-2\sigma+3\tau),$$

$$B=\frac{a}{2}\left(\alpha+\frac{1}{3}\beta^*-2\sigma+3\tau\right),$$

$$C^0_{44}=\frac{a}{2}(\alpha+\beta^*-2\sigma-\tau),$$

$$D_{14}=\frac{a}{2}\frac{\sqrt{3}}{r_0}(\alpha-\beta^*-\tau),$$

TABLE IX. Modified Keating parameters.

	Previous	Modified	
α	1009 GPa Å	158.6 GPa Å^{-1}	0.9899 eV Å^{-4}
β^*	840	132.0	0.8238
σ	−234	−18.36	−0.1147
τ	21	3.31	0.0207
γ	−1198 GPa	−140.8 GPa Å^{-3}	−0.8788 eV Å^{-6}
δ	166	19.56	0.1221
ϵ	−566	−99.78	−0.6226
η	−138	−24.29	−0.1516
θ	143	50.55	0.3155

$$
\begin{aligned}
E_{11}&=\frac{a}{2}\,\frac{3}{r_0^2}(\alpha+\beta^*+2\sigma-\tau),\\
A_{14}&=-\frac{r_0}{\sqrt{3}}\left(\frac{\alpha-\beta^*-\tau}{\alpha+\beta^*+2\sigma-\tau}\right),\\
\zeta_K&=-\frac{\sqrt{3}}{r_0}A_{14},
\end{aligned}
\tag{47}
$$

where r_0 is the equilibrium bond length. Also

$$
E_{111}^{(2)}=E_{112}^{(2)}=\frac{2}{a}\,\frac{3}{r_0^2}(\alpha-\beta^*+2\sigma+3\tau)
\tag{48}
$$

represent the anharmonic contribution to the harmonic energy.

At the third order

$$
\begin{aligned}
C_{111}&=\frac{3a^3}{16}(\gamma-\delta+6\epsilon-2\eta-\theta+6\xi),\\
C_{112}&=\frac{a^3}{16}(3\gamma-3\delta+2\epsilon-6\eta-3\theta+18\xi),\\
C_{123}&=\frac{3a^3}{16}(\gamma+3\delta-2\epsilon-2\eta-\theta+6\xi),\\
C_{144}^0&=\frac{a^3}{16}(3\gamma+3\delta-2\epsilon-6\eta+\theta+2\xi),\\
C_{155}^0&=\frac{a^3}{16}(3\gamma-3\delta+6\epsilon-6\eta-3\theta+2\xi),\\
C_{456}^0&=\frac{3a^3}{16}(\gamma-2\eta+\theta-2\xi),\\
D_{114}&=\frac{a^3}{16}\,\frac{\sqrt{3}}{r_0}(3\gamma-3\delta-2\epsilon-2\eta+3\theta+2\xi),\\
D_{124}&=\frac{a^3}{16}\,\frac{\sqrt{3}}{r_0}(3\gamma+3\delta-2\epsilon-2\eta+\theta+2\xi),\\
D_{156}&=\frac{a^3}{16}\,\frac{\sqrt{3}}{r_0}(3\gamma-2\eta+\theta-6\xi),\\
E_{111}^{(3)}&=\frac{a^3}{16}\,\frac{3}{r_0^2}(3\gamma+3\delta+6\epsilon+2\eta+5\theta+2\xi),\\
E_{112}^{(3)}&=\frac{a^3}{16}\,\frac{3}{r_0^2}(3\gamma-3\delta-2\epsilon+2\eta+\theta+2\xi),\\
E_{126}&=\frac{a^3}{16}\,\frac{3}{r_0^2}(3\gamma+2\eta-\theta-6\xi),\\
F_{123}&=\frac{a^3}{16}\,\frac{3\sqrt{3}}{r_0^3}(3\gamma+6\eta-3\theta-6\xi).
\end{aligned}
\tag{49}
$$

The full E_{111} and E_{112} are then given by

$$
\begin{aligned}
E_{111}&=E_{111}^{(2)}+E_{111}^{(3)},\\
E_{112}&=E_{112}^{(2)}+E_{112}^{(3)}
\end{aligned}
\tag{50}
$$

as before.

VII. CONCLUSION

The original goal of finding a simple model to characterize both the harmonic and anharmonic aspects of the elasticity of diamond has been achieved: the four-parameter harmonic model provides an excellent fit to the second-order experimental data and the five-parameter anharmonic fitting predicts third-order elastic constants that are in reasonable agreement with both a previous three-parameter model and an *ab initio* calculation. Fewer parameters always lead to a poorer fit.

The single unexpected outcome has been the implication, supported by an earlier *ab initio* calculation, that the internal strain parameter ζ_K is possibly even smaller than observed, where it is already less than 25% of the values found for other group IV elements and III–V semiconductors.

Finally the Keating model has been recast in a form that makes the parameters characteristic of the bonds alone, and not dependent on the dimensions of the unit cell chosen to describe the structure. This means that the elasticity of cD can be referred to rhombohedral axes without altering the model parameters. In the following paper it is shown how these same parameters may be used to study hD.

---

[1] C.S.G. Cousins, Ph.D. thesis, Exeter, 2001.

[2] C.S.G. Cousins, J. Phys.: Condens. Matter **14**, 5091 (2002).

[3] C.S.G. Cousins, J. Phys.: Condens. Matter **14**, 5115 (2002).

[4] M.J.P. Musgrave and J.A. Pople, Proc. R. Soc. London, Ser. A **268**, 474 (1962).

[5] P.N. Keating, Phys. Rev. **145**, 637 (1966).

[6] P.N. Keating, Phys. Rev. **149**, 674 (1966).

[7] R.M. Martin, Phys. Rev. B **1**, 4005 (1970).

[8] D. Vanderbilt, S.H. Taole, and S. Narasimhan, Phys. Rev. B **40**, 5657 (1989).

[9] J.R. Guth, A.C. Hess, P.F. McMillan, and W.T. Petuskey, J. Phys.: Condens. Matter **2**, 8007 (1990).

[10] H.L. McMurry, A.W. Solbrig, Jr., J.K. Boyter, and C. Noble, J. Phys. Chem. Solids **28**, 2359 (1967).

[11] R. Tubino, L. Piseri, and G. Zerbi, J. Chem. Phys. **56**, 1022 (1972).

[12] F. Cerdeira, C.J. Buchenauer, F.H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).

[13] M.I. Bell, Phys. Status Solidi B **53**, 675 (1972).

[14] M.H. Grimsditch, E. Anastassakis, and M. Cardona, Phys. Rev. B **18**, 901 (1978).

[15] E. Anastassakis, A. Cantarero, and M. Cardona, Phys. Rev. B **41**, 7529 (1990).

[16] C.S.G. Cousins, J. Phys. C **11**, 4867 (1978).

[17] C.S.G. Cousins, J. Phys. C **11**, 4881 (1978).

[18] J.F. Nye, *The Physical Properties of Crystals* (Clarendon, Oxford, 1972).

[19] C.S.G. Cousins, J. Phys. C **1**, 835 (1968).

[20] G.P. Srivastava, *The Physics of Phonons* (Adam Hilger, Bristol, 1990).

[21] J.W. Martin, J. Phys. C **8**, 2858 (1975).

[22] A.K. Sood, E. Anastassakis, and M. Cardona, Phys. Status Solidi B **129**, 505 (1985).

[23] O.H. Nielsen, Physica B & C **139&140B**, 202 (1986); Phys. Rev. B **34**, 5808 (1986).

[24] H.J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **43**, 2944 (1972).

[25] J.L. Warren, R.G. Wenzel, and J.L. Yarnell, *Inelastic Scattering of Neutrons* (IAEA, Vienna, 1965), Vol. 1, p. 361.

[26] C.S.G. Cousins, L. Gerward, J. Staun Olsen, and B.J. Sheldon, J. Phys.: Condens. Matter **1**, 4511 (1989).

[27] V.K. Bashenov, D.I. Marvakov, and A.M. Mutal, Phys. Status Solidi B **86**, K7 (1978).

[28] H. Rücker and M. Methfessel, Phys. Rev. B **52**, 11 059 (1995).

[29] C.S.G. Cousins, J. Phys. C **15**, 1857 (1982).

[30] R.N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).