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Formal elasticity of four carbon allotropes: II. The anatomy of the macroscopic elastic constants, compliances, and pressure derivatives and a generalized method of homogeneous deformation

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Abstract

The formal contributions of inner elastic constants to the macroscopic second- and third-order elastic constants of four diamond and graphite allotropes of carbon are analysed. Second- and third-order compliances and compressibilities, effective elastic constants, and pressure derivatives of the second-order constants are also presented. A generalized method of homogeneous deformation is developed to relate the computationally friendly infinitesimal strain approach to the thermodynamically rigorous finite-strain formalism. Computational protocols, involving up to nine distinct shape-changing deformations, are developed to facilitate the determination of all second- and third-order elastic and inner elastic constants, and hence of all derived quantities.

1. Introduction

This and the preceding paper [1] (hereafter C1) are formal studies in which the elasticity of the diamond and graphite allotropes of carbon are treated through the third order. They have been written to pave the way for a number of individual studies in which the various models that have been proposed from time to time will be evaluated, and possibly improved upon. Such studies benefit from the investigation of as many related properties as possible and motivate the detailed attention that is being paid to the microscopic aspects arising from the relative motion of sublattices, characterized by inner elastic constants and internal strain tensors. Apart from cubic diamond (cD), which though treated before [2] is included here for completeness, there has not to my knowledge been any analysis of the composition of the elastic constants of the more complex hexagonal allotropes (hD and hG) or of the simple but low-symmetry rhombohedral graphite (rG), all of which possess a rich complement of inner elastic constants [1].

The rotationally invariant finite-strain approach is set out in section 2 following the general principles laid out in [3] and [4]. The treatment of crystal equilibrium leads to expressions for the total elastic constants in terms of partial and inner elastic constants, and internal strain tensors—the *anatomy* in the title.

The complementary constants, the elastic compliances, are treated in section 3 together with the linear and quadratic compressibilities. The effective elastic constants and their pressure derivatives are presented in section 4.

Complex treatments of elasticity, via total-energy calculations for example, or models in which many-body terms are introduced to represent bond order, are not easily handled analytically and usually require the energy to be calculated for a sufficiently large set of deformations and the results processed by numerical differentiation. Such computations are most readily handled through the computationally friendly method of homogeneous deformation and the resulting Fuchs constants [5] converted subsequently to Brugger constants [6], their thermodynamically rigorous, finite-strain counterparts. This procedure, which is particularly intricate for the inner elastic constants, is detailed extensively in section 5. The section concludes with an exposition of computational procedures of sufficient scope to enable all constants to be computed.

2. Elasticity

The expression for a contribution to the free energy per unit initial volume is written in contracted notation as follows:

$$\begin{aligned} \rho_0 F(\zeta^\lambda, \eta) = & \rho_0 F(0, 0) + C_I^0 \eta_I + D_i^\lambda \zeta_i^\lambda + \frac{1}{2} C_{IJ}^0 \eta_I \eta_J + D_{iJ}^\lambda \zeta_i^\lambda \eta_J + \frac{1}{2} E_{ij}^{\lambda\mu} \zeta_i^\lambda \zeta_j^\mu \\ & + \frac{1}{6} C_{IJK}^0 \eta_I \eta_J \eta_K + \frac{1}{2} D_{iJK}^\lambda \zeta_i^\lambda \eta_J \eta_K + \frac{1}{2} E_{ijk}^{\lambda\mu} \zeta_i^\lambda \zeta_j^\mu \eta_K + \frac{1}{6} F_{ijk}^{\lambda\mu\nu} \zeta_i^\lambda \zeta_j^\mu \zeta_k^\nu, \end{aligned} \quad (1)$$

where Greek superscripts run from 1 to 3 in the cases of hD and hG. For rG and cD the superscripts are all unity and may thus be omitted for clarity. The coefficients C_I^0 , C_{IJ}^0 , and C_{IJK}^0 are contributions to the *partial* elastic constants which are themselves the contributions to the *total* elastic constants C_I , C_{IJ} , and C_{IJK} that are independent of inner displacement. A full description of the structure and symmetry of the four allotropes is given in C1. Symmetry analysis [7] reveals which elastic constants may be non-zero and what relations exist between them. Some constants may be selected as independent and these constitute the set that must be evaluated in order to get a full description of the elasticity. They are presented for cD and rG in tables 1 and 2. Also shown in the latter are the elastic constants of cD transformed to a rhombohedral system of axes, a form suitable for considering the cD-to-rG solid-state transition. The elastic constants of the hexagonal allotropes are displayed in table 3.

The *inner* elastic constants were treated comprehensively in C1. The D_{iJ}^λ -elements express the strength of the coupling between internal and external strain and the $E_{ij}^{\lambda\mu}$, closely related to the lattice-dynamical coupling constants, determine the frequencies, and for the hexagonal allotropes the eigenvectors, of the optic modes at the zone centre. The remaining third-order constants, D_{iJK}^λ , $E_{ijk}^{\lambda\mu}$, and $F_{ijk}^{\lambda\mu\nu}$, are involved in the strain dependence of various parameters that would be constant in the harmonic approximation. The constants defined in this context are generally called Brugger constants [6]. When all contributions α to the free energy have been included in equation (1), equilibrium conditions require that the sums of the first-order terms should be zero: $\sum_\alpha (C_I^0)_\alpha \equiv 0$ and $\sum_\alpha (D_i^\lambda)_\alpha \equiv 0$. The final expressions for C_I , C_{IJ} , and C_{IJK} as sums of partial and inner elastic constants are then obtained by eliminating ζ^λ from the free energy using

$$\zeta_i^\lambda = A_{iJ}^\lambda \eta_J \quad (2)$$

Table 1. The symmetry of the elastic constants of cubic diamond. The left-hand column contains the sets of components of each constant that have been selected as independent and the right-hand column contains the relationships between the remaining non-zero components and the independent ones. Equality of constants that differ only in the order of their subscripts is understood.

C_1	$C_2 = C_3 = C_1$
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}	

(there is no need for a term quadratic in η below the fourth order) and then D_{IJ}^λ using

$$D_{IJ}^\lambda + E_{ij}^{\lambda\mu} A_{jJ}^\mu = 0. \quad (3)$$

The final expressions for the total elastic constants are thus

$$C_{IJ} = C_{IJ}^0 - A_{iI}^\lambda A_{jJ}^\mu E_{ij}^{\lambda\mu} = C_{IJ}^0 - \Delta_{IJ} \quad (4)$$

and

$$C_{IJK} = C_{IJK}^0 + A_{iI}^\lambda D_{iJK}^\lambda + A_{iJ}^\lambda D_{iIK}^\lambda + A_{iK}^\lambda D_{iIJ}^\lambda + A_{iI}^\lambda A_{jJ}^\mu E_{ijK}^{\lambda\mu} + A_{iI}^\lambda A_{jK}^\mu E_{ijj}^{\lambda\mu} \\ + A_{iJ}^\lambda A_{jK}^\mu E_{ijI}^{\lambda\mu} + A_{iI}^\lambda A_{jJ}^\mu A_{kK}^\nu F_{ijk}^{\lambda\mu\nu} = C_{IJK}^0 + \Delta_{IJK}. \quad (5)$$

The expressions for the non-zero components Δ_{IJ} and Δ_{IJK} for the different allotropes are obtained by taking appropriate sets of independent non-zero inner elastic constants and internal strain tensor components from tables 4, 6, and 7 in C1. The considerable differences between the two hexagonal allotropes are a direct consequence of the different site symmetries in the two structures: the two distinct pairs of equivalent sites in hG each have $\bar{6}m2$ symmetry whereas the four equivalent sites in hD have the lower $3m$ symmetry.

2.1. Cubic diamond

At the second order,

$$\Delta_{44} = (A_{14})^2 E_{11} \quad (6)$$

and at the third,

$$\Delta_{144} = 2A_{14}D_{114} + (A_{14})^2 E_{111} \\ \Delta_{155} = 2A_{14}D_{124} + (A_{14})^2 E_{112} \\ \Delta_{456} = 3A_{14}D_{156} + 3(A_{14})^2 E_{126} + (A_{14})^3 F_{123}. \quad (7)$$

Table 2. The symmetry of the elastic constants of rhombohedral graphite. The left-hand column contains the sets of components of each constant that have been selected as independent and the centre column contains the relationships between the remaining non-zero components and the independent ones. Equality of constants that differ only in the order of their subscripts is understood. The right-hand column contains the elastic constants of diamond referred to rhombohedral axes in terms of the cubic constants. Upper signs refer to the reverse setting, lower to the obverse.

Rhombohedral graphite	Rhombohedral diamond
C_1 $C_2 = C_1$	C_1
C_3	C_1
C_{11} $C_{22} = C_{11}$	$(C_{11} + C_{12} + 2C_{44})/2$
C_{12} $C_{66} = (C_{11} - C_{12})/2$	$(C_{11} + 5C_{12} - 2C_{44})/6$
C_{13} $C_{23} = C_{13}$	$(C_{11} + 2C_{12} - 2C_{44})/3$
C_{33}	$(C_{11} + 2C_{12} + 4C_{44})/3$
C_{44} $C_{55} = C_{44}$	$(C_{11} - C_{12} + C_{44})/3$
C_{14} $C_{24} - C_{56} = -C_{14}$	$\pm(C_{11} - C_{12} - 2C_{44})/3\sqrt{2}$
C_{111} $C_{112} = C_{111} - C_{166} - 3C_{266}$	$(C_{111} + 3C_{112} + 12C_{155})/4$
C_{113} $C_{122} = C_{111} - 2C_{166} - 2C_{266}$	$(C_{111} + 4C_{112} + C_{123} + 2C_{144} - 4C_{155})/6$
C_{133} $C_{222} = C_{111} + C_{166} - C_{266}$	$(C_{111} + 6C_{112} + 2C_{123} - 8C_{456})/9$
C_{333} $C_{123} = C_{113} - 2C_{366}$	$(C_{111} + 6C_{112} + 2C_{123} + 12C_{144} + 24C_{155} + 16C_{456})/9$
C_{144} $C_{223} = C_{113}$	$(C_{111} + 3C_{112} - 4C_{123} + 9C_{144} - 3C_{155} - 2C_{456})/18$
C_{244} $C_{233} = C_{133}$	$(C_{111} - C_{112} + C_{144} + C_{155} + 2C_{456})/6$
C_{344} $C_{155} = C_{244}$	$(C_{111} - C_{123} - 3C_{144} + 6C_{155} - 2C_{456})/9$
C_{166} $C_{255} = C_{144}$	$(C_{111} - C_{112} + 4C_{144} + 4C_{155} + 8C_{456})/12$
C_{266} $C_{355} = C_{344}$	$(C_{111} + 3C_{112} - 4C_{123} - 12C_{144} + 36C_{155} - 8C_{456})/36$
C_{366} $C_{456} = (C_{244} - C_{144})/2$	$(C_{111} - C_{123} + 12C_{144} - 8C_{456})/18$
C_{114} $C_{224} = -(C_{114} + 2C_{124})$	$\pm(C_{111} + C_{112} - 2C_{123} - 4C_{144} - 4C_{155})/6\sqrt{2}$
C_{124} $C_{156} = (C_{114} + 3C_{124})/2$	$\pm(C_{111} - 3C_{112} + 2C_{123} - 8C_{456})/18\sqrt{2}$
C_{134} $C_{256} = (C_{114} - C_{124})/2$	$\pm(C_{111} - C_{123} - 6C_{155} + 4C_{456})/9\sqrt{2}$
C_{444} $C_{234} = -C_{356} = -C_{134}$	$\mp(C_{111} - 3C_{112} + 2C_{123} + 3C_{144} - 3C_{155} - 2C_{456})/9\sqrt{2}$
$C_{446} = C_{124}$	
$C_{455} = -C_{444}$	

2.2. Rhombohedral graphite

At the second order,

$$\begin{aligned}
 \Delta_{11} &= (A_{31})^2 E_{33} + (A_{16})^2 E_{11} \\
 \Delta_{12} &= (A_{31})^2 E_{33} - (A_{16})^2 E_{11} \\
 \Delta_{13} &= A_{31} A_{33} E_{33} \\
 \Delta_{33} &= (A_{33})^2 E_{33} \\
 \Delta_{44} &= (A_{15})^2 E_{11} \\
 \Delta_{14} &= A_{15} A_{16} E_{11}.
 \end{aligned} \tag{8}$$

Table 3. The symmetry of the elastic constants of hexagonal diamond and hexagonal graphite. The left-hand column contains the sets of components of each constant that have been selected as independent and the right-hand column contains the relationships between the remaining non-zero components and the independent ones. Equality of constants that differ only in the order of their subscripts is understood.

C_1	$C_2 = C_1$
C_3	
C_{11}	$C_{22} = C_{11}$
C_{12}	$C_{23} = C_{13}$
C_{13}	$C_{55} = C_{44}$
C_{33}	$C_{66} = \frac{1}{2}(C_{11} - C_{12})$
C_{44}	
C_{111}	$C_{112} = C_{111} - C_{166} - 3C_{266}$
C_{113}	$C_{122} = C_{111} - 2C_{166} - 2C_{266}$
C_{133}	$C_{222} = C_{111} + C_{166} - C_{266}$
C_{333}	$C_{123} = C_{113} - 2C_{366}$
C_{144}	$C_{223} = C_{113}$
C_{244}	$C_{233} = C_{133}$
C_{344}	$C_{155} = C_{244}$
C_{166}	$C_{255} = C_{144}$
C_{266}	$C_{355} = C_{344}$
C_{366}	$C_{456} = \frac{1}{2}(C_{244} - C_{144})$

At the third order,

$$\begin{aligned}
 \Delta_{111} &= 3A_{16}D_{211} + 3A_{31}D_{311} + 3(A_{16})^2E_{112} + 6A_{16}A_{31}E_{136} + 3(A_{31})^2E_{331} \\
 &\quad - (A_{16})^3F_{112} + 3(A_{16})^2A_{15}F_{113} + (A_{31})^3F_{333} \\
 \Delta_{113} &= 2A_{16}D_{136} + A_{33}D_{311} + 2A_{31}D_{313} + (A_{16})^2E_{113} + 2A_{16}A_{33}E_{136} + 2A_{31}A_{33}E_{331} \\
 &\quad + (A_{31})^2E_{333} + (A_{16})^2A_{33}F_{113} + (A_{31})^2A_{33}F_{333} \\
 \Delta_{133} &= 2A_{33}D_{313} + A_{31}D_{333} + (A_{33})^2E_{331} + 2A_{31}A_{33}E_{333} + A_{31}(A_{33})^2F_{333} \\
 \Delta_{333} &= 3A_{33}D_{333} + 3(A_{33})^2E_{333} + (A_{33})^3F_{333} \\
 \Delta_{144} &= -A_{16}D_{145} + 2A_{15}D_{125} + A_{31}D_{344} \\
 &\quad + 2A_{31}A_{15}E_{315} + (A_{15})^2E_{112} - A_{16}(A_{15})^2F_{112} + A_{31}(A_{15})^2F_{113} \\
 \Delta_{244} &= A_{16}D_{145} + 2A_{15}D_{115} + A_{31}D_{344} + 2A_{31}A_{15}E_{315} + (A_{15})^2E_{111} \\
 &\quad + A_{16}(A_{15})^2F_{112} + A_{31}(A_{15})^2F_{113} \\
 \Delta_{344} &= 2A_{15}D_{135} + A_{33}D_{344} + 2A_{33}A_{15}E_{315} + (A_{15})^2E_{113} + A_{33}(A_{15})^2F_{113} \\
 \Delta_{166} &= -A_{16}(D_{211} + 2D_{222}) + \frac{1}{2}A_{31}(D_{311} - D_{312}) + (A_{16})^2(2E_{111} - E_{112}) \\
 &\quad + 2A_{31}A_{16}E_{136} + (A_{16})^3F_{112} + A_{31}(A_{16})^2F_{113} \\
 \Delta_{266} &= A_{16}(2D_{211} + D_{222}) + \frac{1}{2}A_{31}(D_{311} - D_{312}) - (A_{16})^2(E_{111} - 2E_{112}) \\
 &\quad + 2A_{31}A_{16}E_{136} - (A_{16})^3F_{112} + A_{31}(A_{16})^2F_{113} \\
 \Delta_{366} &= 2A_{16}D_{136} + \frac{1}{2}A_{33}(D_{311} - D_{312}) + (A_{16})^2E_{113} + 2A_{33}A_{16}E_{136} + A_{33}(A_{16})^2F_{113} \\
 \Delta_{114} &= 2A_{16}D_{125} + A_{15}D_{211} + 2A_{16}A_{15}E_{112} + 2A_{31}A_{15}E_{136} \\
 &\quad - (A_{16})^2A_{15}F_{112} + 2A_{16}A_{15}A_{31}F_{113} \\
 \Delta_{124} &= -A_{16}D_{125} + A_{15}D_{212} + A_{31}D_{314} + A_{16}A_{15}(E_{111} - E_{112}) + (A_{16})^2A_{15}F_{112} \\
 \Delta_{134} &= A_{16}D_{135} + A_{15}D_{136} + A_{33}D_{314} + A_{16}A_{15}(E_{113} + E_{135}) + A_{33}A_{15}E_{136} + A_{16}A_{15}A_{33}F_{113} \\
 \Delta_{444} &= -3A_{15}D_{145} - (A_{15})^3F_{112}.
 \end{aligned} \tag{9}$$

2.3. Hexagonal diamond

In C1 it was useful to define some composite constants in order to simplify expressions for the pressure derivatives of the optic mode frequencies. A similar need arises here. The composite constants are

$$\begin{aligned}
 E_{ij}^{aa} &\equiv E_{ij}^{11} - E_{ij}^{12} + E_{ij}^{13} \\
 E_{ij}^{bb} &\equiv E_{ij}^{11} - E_{ij}^{13} \\
 F_{112}^{11a} &\equiv F_{112}^{111} - 3F_{112}^{112} + 3F_{112}^{113} \\
 F_{113}^{1bb} &\equiv F_{113}^{111} - F_{113}^{113} - 2F_{113}^{121} + 2F_{113}^{123} + 2F_{113}^{131} + F_{113}^{221} \\
 F_{113}^{1cc} &\equiv F_{113}^{111} - 2F_{113}^{131} - F_{113}^{113}.
 \end{aligned}$$

At the second order,

$$\begin{aligned}
 \Delta_{11} &= 2(A_{31}^1)^2 E_{33}^{bb} + 2(A_{16}^1)^2 E_{11}^{aa} \\
 \Delta_{12} &= 2(A_{31}^1)^2 E_{33}^{bb} - 2(A_{16}^1)^2 E_{11}^{aa} \\
 \Delta_{13} &= 2A_{31}^1 A_{33}^1 E_{33}^{bb} \\
 \Delta_{33} &= 2(A_{33}^1)^2 E_{33}^{bb} \\
 \Delta_{44} &= 2(A_{15}^1)^2 E_{11}^{bb}.
 \end{aligned} \tag{10}$$

At the third order,

$$\begin{aligned}
 \Delta_{111} &= 6A_{16}^1 D_{211}^1 + 6A_{31}^1 D_{311}^1 + 6(A_{16}^1)^2 E_{112}^{aa} + 12A_{16} A_{31} E_{136}^{bb} + 6(A_{31}^1)^2 E_{331}^{bb} \\
 &\quad - 2(A_{16}^1)^3 F_{112}^{11a} + 6(A_{16}^1)^2 A_{31}^1 F_{113}^{1bb} + 2(A_{31}^1)^3 (F_{333}^{111} - 3F_{333}^{113}) \\
 \Delta_{113} &= 4A_{16}^1 D_{136}^1 + 2A_{33}^1 D_{311}^1 + 4A_{31}^1 D_{313}^1 + 2(A_{16}^1)^2 E_{113}^{aa} + 4A_{16} A_{33} E_{136}^{bb} + 4A_{31}^1 A_{33}^1 E_{331}^{bb} \\
 &\quad + 2(A_{31}^1)^2 E_{333}^{bb} + 2(A_{16}^1)^2 A_{33}^1 F_{113}^{1bb} + 2(A_{31}^1)^2 A_{33}^1 (F_{333}^{111} - 3F_{333}^{113}) \\
 \Delta_{133} &= 4A_{33}^1 D_{313}^1 + 2A_{31}^1 D_{333}^1 + 2(A_{33}^1)^2 E_{331}^{bb} + 4A_{31}^1 A_{33}^1 E_{333}^{bb} + 2A_{31}^1 (A_{33}^1)^2 (F_{333}^{111} - 3F_{333}^{113}) \\
 \Delta_{333} &= 6A_{33}^1 D_{333}^1 + 6(A_{33}^1)^2 E_{333}^{bb} + 2(A_{33}^1)^3 (F_{333}^{111} - 3F_{333}^{113}) \\
 \Delta_{144} &= -2A_{16}^1 D_{145}^1 + 4A_{15}^1 D_{125}^1 + 2A_{31}^1 D_{344}^1 + 4A_{31}^1 A_{15}^1 E_{315}^{bb} + 2(A_{15}^1)^2 E_{112}^{bb} \\
 &\quad - 2A_{16}^1 (A_{15}^1)^2 (F_{112}^{111} - F_{112}^{113}) + 2A_{31}^1 (A_{15}^1)^2 F_{113}^{1cc} \\
 \Delta_{244} &= 2A_{16}^1 D_{145}^1 + 4A_{15}^1 D_{115}^1 + 2A_{31}^1 D_{344}^1 + 4A_{31}^1 A_{15}^1 E_{315}^{bb} + 2(A_{15}^1)^2 E_{111}^{bb} \\
 &\quad + 2A_{16}^1 (A_{15}^1)^2 (F_{112}^{111} - F_{112}^{113}) + 2A_{31}^1 (A_{15}^1)^2 F_{113}^{1cc} \\
 \Delta_{344} &= 4A_{15}^1 D_{135}^1 + 2A_{33}^1 D_{344}^1 + 4A_{33}^1 A_{15}^1 E_{315}^{bb} + 2(A_{15}^1)^2 E_{113}^{bb} + 2A_{33}^1 (A_{15}^1)^2 F_{113}^{1cc} \\
 \Delta_{166} &= -2A_{16}^1 (D_{211}^1 + 2D_{222}^1) + A_{31}^1 (D_{311}^1 - D_{312}^1) + 2(A_{16}^1)^2 (2E_{111}^{aa} - E_{112}^{aa}) + 4A_{31}^1 A_{16}^1 E_{136}^{bb} \\
 &\quad + 2(A_{16}^1)^3 F_{112}^{11a} + 2A_{31}^1 (A_{16}^1)^2 F_{113}^{1bb} \\
 \Delta_{266} &= 2A_{16}^1 (2D_{211}^1 + D_{222}^1) + A_{31}^1 (D_{311}^1 - D_{312}^1) - 2(A_{16}^1)^2 (E_{111}^{aa} - 2E_{112}^{aa}) + 4A_{31}^1 A_{16}^1 E_{136}^{bb} \\
 &\quad - 2(A_{16}^1)^3 F_{112}^{11a} + 2A_{31}^1 (A_{16}^1)^2 F_{113}^{1bb} \\
 \Delta_{366} &= 4A_{16}^1 D_{136}^1 + A_{33}^1 (D_{311}^1 - D_{312}^1) + 2(A_{16}^1)^2 E_{113}^{aa} + 4A_{33}^1 A_{16}^1 E_{136}^{bb} + 2A_{33}^1 (A_{16}^1)^2 F_{113}^{1bb}.
 \end{aligned} \tag{11}$$

2.4. Hexagonal graphite

The following composite constants are useful:

$$\begin{aligned} E_{11}^{1c} &\equiv E_{11}^{11} - \frac{1}{2}E_{11}^{12} \\ E_{11}^{3c} &\equiv E_{11}^{33} - \frac{1}{2}E_{11}^{12} \\ F_{112}^{1cc} &\equiv \frac{1}{4}F_{112}^{112} - F_{112}^{123} + F_{112}^{133}. \end{aligned}$$

At the second order, after using $E_{11}^{22} = 2E_{11}^{12} = 2E_{11}^{23}$ and $A_{16}^2 = -\frac{1}{2}(A_{16}^1 + A_{16}^3)$ (see C1), we obtain

$$\begin{aligned} \Delta_{11} &= (A_{16}^1)^2 E_{11}^{1c} + (A_{16}^3)^2 E_{11}^{3c} + 2A_{16}^1 A_{16}^3 (E_{11}^{13} - \frac{1}{2}E_{11}^{12}) \\ \Delta_{12} &= -\Delta_{11}. \end{aligned} \quad (12)$$

At the third order,

$$\begin{aligned} \Delta_{111} &= 3A_{16}^1 D_{211}^1 + 3A_{16}^3 D_{211}^3 + 3(A_{16}^1)^2 E_{112}^{1c} + 3(A_{16}^3)^2 E_{112}^{3c} + 6A_{16}^1 A_{16}^3 (E_{112}^{13} - \frac{1}{2}E_{112}^{12}) \\ &\quad - (A_{16}^1)^3 (F_{112}^{111} - \frac{3}{4}F_{112}^{112}) - \frac{3}{4}(A_{16}^1)^2 A_{16}^3 F_{112}^{223} \\ &\quad - 3A_{16}^1 (A_{16}^3)^2 F_{112}^{1cc} - (A_{16}^3)^3 (F_{112}^{333} - \frac{3}{4}F_{112}^{223}) \\ \Delta_{113} &= 2A_{16}^1 D_{136}^1 + 2A_{16}^3 D_{136}^3 + (A_{16}^1)^2 E_{113}^{1c} + (A_{16}^3)^2 E_{113}^{3c} + 2A_{16}^1 A_{16}^3 (E_{113}^{13} - \frac{1}{2}E_{113}^{12}) \\ \Delta_{144} &= -A_{16}^1 D_{145}^1 - A_{16}^3 D_{145}^3 \\ \Delta_{244} &= -\Delta_{144} \\ \Delta_{166} &= -A_{16}^1 (D_{211}^1 + 2D_{222}^1) - A_{16}^3 (D_{211}^3 + 2D_{222}^3) + (A_{16}^1)^2 (2E_{111}^{1c} - E_{112}^{1c}) \\ &\quad + (A_{16}^3)^2 (2E_{111}^{3c} - E_{112}^{3c}) + 2A_{16}^1 A_{16}^3 (2E_{111}^{13} - E_{112}^{13} - E_{111}^{12} + \frac{1}{2}E_{112}^{12}) \\ &\quad + (A_{16}^1)^3 (F_{112}^{111} - \frac{3}{4}F_{112}^{112}) + (A_{16}^3)^3 (F_{112}^{333} - \frac{3}{4}F_{112}^{223}) \\ &\quad + \frac{3}{4}(A_{16}^1)^2 A_{16}^3 F_{112}^{223} + 3A_{16}^1 (A_{16}^3)^2 F_{112}^{1cc} \\ \Delta_{266} &= A_{16}^1 (2D_{211}^1 + D_{222}^1) + A_{16}^3 (2D_{211}^3 + D_{222}^3) + (A_{16}^1)^2 (2E_{112}^{1c} - E_{111}^{1c}) \\ &\quad + (A_{16}^3)^2 (2E_{112}^{3c} - E_{111}^{3c}) + 2A_{16}^1 A_{16}^3 (2E_{112}^{13} - E_{111}^{13} - E_{112}^{12} + \frac{1}{2}E_{111}^{12}) \\ &\quad - (A_{16}^1)^3 (F_{112}^{111} - \frac{3}{4}F_{112}^{112}) - (A_{16}^3)^3 (F_{112}^{333} - \frac{3}{4}F_{112}^{223}) \\ &\quad - \frac{3}{4}(A_{16}^1)^2 A_{16}^3 F_{112}^{223} - 3A_{16}^1 (A_{16}^3)^2 F_{112}^{1cc} \\ \Delta_{366} &= \Delta_{113}. \end{aligned} \quad (13)$$

3. Compliances and compressibilities

Measurements of lattice parameter and volume change under pressure by means of x-ray or neutron diffraction may be used to extract elasticity information from crystals too small to subject to more conventional techniques, such as ultrasonics. The primary quantities obtained are compressibilities.

The compatibility of Hooke's law extended to terms quadratic in the strain

$$\sigma_I = C_{IJ}\eta_J + \frac{1}{2}C_{IJK}\eta_J\eta_K \quad (14)$$

with its inverse form

$$\eta_I = S_{IJ}\sigma_J + \frac{1}{2}S_{IJK}\sigma_J\sigma_K \quad (15)$$

defines implicitly both second- and third-order elastic compliances. The second-order ones are given by standard matrix inversion whilst the third-order ones are given by [8, 9]

$$S_{IJK} = -S_{IP}S_{JQ}S_{KR}C_{PQR}. \quad (16)$$

Under hydrostatic pressure $\sigma_J = -p\delta_J$, where $\delta_J = 1$ if $J = 1, 2$, or 3 and zero otherwise, whence

$$\eta_I = -pS_{IJ}\delta_J + \frac{1}{2}p^2S_{IJK}\delta_J\delta_K = -k_I p + \frac{1}{2}K_I p^2 \quad (17)$$

implicitly defining harmonic and anharmonic linear compressibilities.

3.1. Cubic diamond

When $\eta_1 = \eta_2 = \eta_3$ we have (dropping subscripts)

$$k = S_{11} + 2S_{12} \quad (18)$$

and

$$K = S_{111} + 6S_{112} + 2S_{123}. \quad (19)$$

On setting $2\eta_1 = 2\eta_2 = 2\eta_3 = \Delta a^2/a_0^2$ we obtain

$$\Delta a/a_0 = -kp + \frac{1}{2}(K - k^2)p^2 \quad (20)$$

for lattice parameter change.

The exact expression for the volume V of a finitely strained crystal is

$$(V/V_0)^2 = \det(I + 2\eta) \quad (21)$$

and leads to volume change given by

$$\Delta V/V_0 = -3kp + \frac{3}{2}(K + k^2)p^2. \quad (22)$$

3.2. Hexagonal diamond, hexagonal graphite and rhombohedral graphite

For the axial allotropes, in which $2\eta_1 = 2\eta_2 = \Delta a^2/a_0^2$ and $2\eta_3 = \Delta c^2/c_0^2$, there are two compressibilities of each kind:

$$\begin{aligned} k_a &= S_{11} + S_{12} + S_{13} \\ k_c &= 2S_{13} + S_{33} \\ K_a &= S_{111} + 2S_{112} + 2S_{113} + S_{122} + 2S_{123} + S_{133} \\ K_c &= 2S_{113} + 2S_{123} + 4S_{133} + S_{333}. \end{aligned} \quad (23)$$

The lattice parameters change as

$$\begin{aligned} \Delta a/a_0 &= -k_a p + \frac{1}{2}(K_a - k_a^2)p^2 \\ \Delta c/c_0 &= -k_c p + \frac{1}{2}(K_c - k_c^2)p^2 \end{aligned} \quad (24)$$

and the volume as

$$\Delta V/V_0 = -k_v p + \frac{1}{2}(K_v + 4k_a k_c - k_c^2)p^2 \quad (25)$$

where $k_v = 2k_a + k_c$ and $K_v = 2K_a + K_c$.

4. Effective elastic constants and their pressure derivatives

Ultrasonic velocity measurements made on an initially stressed crystal yield effective elastic constants. When such a crystal is further deformed its energy can be expressed either in terms of the additional deformation and the effective elastic constants or in terms of the overall deformation and the elastic constants of the crystal in the unstrained state. The procedure is described fully for arbitrary strain in [10, section 8]. The expressions so obtained are differentiated to give the pressure derivatives of the second-order constants.

4.1. Cubic diamond

The effective constants are

$$\begin{aligned}\bar{C}_{11} &= C_{11}(1 + 3\eta_1 - \eta_2 - \eta_3) + C_{111}\eta_1 + C_{112}(\eta_2 + \eta_3) \\ \bar{C}_{12} &= C_{12}(1 + \eta_1 + \eta_2 - \eta_3) + C_{112}(\eta_1 + \eta_2) + C_{123}\eta_3 \\ \bar{C}_{44} &= C_{44}(1 - \eta_1 + \eta_2 + \eta_3) + C_{144}\eta_1 + C_{155}(\eta_2 + \eta_3).\end{aligned}\quad (26)$$

Differentiation of the above, after setting $\eta_1 = \eta_2 = \eta_3 = -kp$, gives the following pressure derivatives:

$$\begin{aligned}-C'_{11} &= k(C_{11} + C_{111} + 2C_{112}) \\ -C'_{12} &= k(C_{12} + 2C_{112} + C_{123}) \\ -C'_{44} &= k(C_{44} + C_{144} + 2C_{155}).\end{aligned}\quad (27)$$

4.2. Hexagonal diamond and hexagonal graphite

For both allotropes, the effective constants are

$$\begin{aligned}\bar{C}_{11} &= C_{11}(1 + 3\eta_1 - \eta_2 - \eta_3) + C_{111}\eta_1 + C_{112}\eta_2 + C_{113}\eta_3 \\ \bar{C}_{12} &= C_{12}(1 + \eta_1 + \eta_2 - \eta_3) + C_{112}\eta_1 + C_{122}\eta_2 + C_{123}\eta_3 \\ \bar{C}_{13} &= C_{13}(1 + \eta_1 - \eta_2 + \eta_3) + C_{113}\eta_1 + C_{123}\eta_2 + C_{133}\eta_3 \\ \bar{C}_{33} &= C_{33}(1 - \eta_1 - \eta_2 + 3\eta_3) + C_{133}(\eta_1 + \eta_2) + C_{333}\eta_3 \\ \bar{C}_{44} &= C_{44}(1 - \eta_1 + \eta_2 + \eta_3) + C_{144}\eta_1 + C_{244}\eta_2 + C_{344}\eta_3.\end{aligned}\quad (28)$$

Differentiation, after setting $\eta_1 = \eta_2 = -k_a p$ and $\eta_3 = -k_c p$, then gives the following pressure derivatives:

$$\begin{aligned}-C'_{11} &= k_a(2C_{11} + C_{111} + C_{112}) + k_c(-C_{11} + C_{113}) \\ -C'_{12} &= k_a(2C_{12} + C_{112} + C_{122}) + k_c(-C_{12} + C_{123}) \\ -C'_{13} &= k_a(C_{113} + C_{123}) + k_c(C_{13} + C_{133}) \\ -C'_{33} &= 2k_a(-C_{33} + C_{133}) + k_c(3C_{33} + C_{333}) \\ -C'_{44} &= k_a(C_{144} + C_{244}) + k_c(C_{44} + C_{344}).\end{aligned}\quad (29)$$

It was not possible, using the above procedure, to reproduce the expressions for the effective elastic constants of hexagonal crystals under isotropic pressure given in [11].

4.3. Rhombohedral graphite

The effective constants are

$$\begin{aligned}\bar{C}_{11} &= C_{11}(1 + 3\eta_1 - \eta_2 - \eta_3) + C_{111}\eta_1 + C_{112}\eta_2 + C_{113}\eta_3 + C_{114}\eta_4 \\ \bar{C}_{12} &= C_{12}(1 + \eta_1 + \eta_2 - \eta_3) + C_{14}\eta_4 + C_{112}\eta_1 + C_{122}\eta_2 + C_{123}\eta_3 + C_{124}\eta_4 \\ \bar{C}_{13} &= C_{13}(1 + \eta_1 - \eta_2 + \eta_3) + C_{14}\eta_4 + C_{113}\eta_1 + C_{123}\eta_2 + C_{133}\eta_3 + C_{134}\eta_4 \\ \bar{C}_{33} &= C_{33}(1 - \eta_1 - \eta_2 + 3\eta_3) + C_{133}(\eta_1 + \eta_2) + C_{333}\eta_3 + C_{334}\eta_4 \\ \bar{C}_{44} &= C_{44}(1 - \eta_1 + \eta_2 + \eta_3) - C_{14}\eta_4 + C_{144}\eta_1 + C_{244}\eta_2 + C_{344}\eta_3 + C_{444}\eta_4 \\ \bar{C}_{14} &= C_{14}(1 + \eta_1) + \frac{1}{2}(C_{12} + C_{13})\eta_4 + C_{114}\eta_1 + C_{124}\eta_2 + C_{134}\eta_3 + C_{144}\eta_4.\end{aligned}\quad (30)$$

As $\eta_4 = 0$ under hydrostatic pressure, their pressure derivatives are simply the same as those of hD and hG augmented by

$$-C'_{14} = k_a(C_{14} + C_{114} + C_{124}) + k_c C_{134}.\quad (31)$$

5. Generalized homogeneous deformation

The elastic constants of finite-strain theory can only be computed directly when the contributions to the energy of the system are simple analytical functions of the interatomic separations or of the unit-cell volume. The favoured alternative is to use infinitesimal strain theory with suitably tailored homogeneous deformations. In the traditional approach two such *ad hoc* deformations were sufficient to determine the two second-order elastic shear constants of FCC metals, such as copper [5] and aluminium [12], in which there is no inner elasticity. In the latter work the deformation was not defined in terms of a parameter that tended to zero in the unstrained state and in neither case was the volume conserved to better than first order. If the method is to be applied to higher-order elastic constants and to hexagonal and rhombohedral material, where there are at least five second-order, ten third-order, and numerous inner elastic constants, a rigorous formal procedure is necessary.

Homogeneous deformations are represented by deformation gradient matrices and may operate on the crystal structure with or without sublattice displacements. They may be defined in a generalized way in terms of a uniform volume-changing part and a shape-changing part. The latter is represented by

$$J(x) = S(x)[I + xP] \quad (32)$$

where P is a 3×3 matrix of small integers or zeros that determines a particular deformation of shape, I is the unit 3×3 matrix, and x is a measure of the strain. $S(x)$ is a scaling function used to ensure that the determinant of $J(x)$ is unity, so that the volume of the crystal is undisturbed by the shape-changing part. It is given in terms of the trace and determinant of P (t_p and d_p) and the trace of the matrix of the cofactors of the elements of P (c_p) by

$$[S(x)]^{-3} = 1 + t_p x + c_p x^2 + d_p x^3. \quad (33)$$

The uniform volume-changing part is a factor $(1 + v)^{1/3}$, where v is the relative change of volume of the unit cell under strain, giving

$$H(x, v) = (1 + v)^{1/3} J(x) \quad (34)$$

for the net deformation gradient matrix.

The displacement of sublattice α is defined by a small vector \vec{u}^α such that the position vector \vec{r}_0^α of a particular atom on the sublattice in the unstrained crystal becomes \vec{r}^α after strain where

$$\vec{r}^\alpha = H(x, v)\vec{r}_0^\alpha + \vec{u}^\alpha. \quad (35)$$

An individual contribution to the free energy per unit initial volume in this approach may be written as

$$\begin{aligned} \rho_0 F(u^\alpha, v, x) = & \rho_0 F(0, 0, 0) + c_v^0 v + c_x^0 x + d_i^\alpha u_i^\alpha + \frac{1}{2} c_{vv}^0 v^2 + c_{vx}^0 vx + \frac{1}{2} c_{xx}^0 x^2 \\ & + d_{iv}^\alpha u_i^\alpha v + d_{ix}^\alpha u_i^\alpha x + \frac{1}{2} e_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{6} c_{vvv}^0 v^3 + \frac{1}{2} c_{vvx}^0 v^2 x \\ & + \frac{1}{2} c_{vxx}^0 vx^2 + \frac{1}{6} c_{xxx}^0 x^3 + \frac{1}{2} d_{ivv}^\alpha u_i^\alpha v^2 + d_{ivx}^\alpha u_i^\alpha vx \\ & + \frac{1}{2} d_{ixx}^\alpha u_i^\alpha x^2 + \frac{1}{2} e_{ijv}^{\alpha\beta} u_i^\alpha u_j^\beta v + \frac{1}{2} e_{ijx}^{\alpha\beta} u_i^\alpha u_j^\beta x + \frac{1}{6} f_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma, \end{aligned} \quad (36)$$

for a specific choice of P . Summation over repeated subscripts i , j , and k and over the superscripts α , β , and γ is implied: the former run from 1 to 3 and the latter from 1 to 2 (cD and rG) or 1 to 4 (hD and hG). The coefficients labelled with vs and/or xs are linear combinations; e.g., d_{ivx}^α is a combination of several of the d_{iJK}^α . Lower-case symbols c , d , e , and f have been used for the different tensors to indicate their kinship with the upper-case

versions used in the finite-strain approach. Coefficients defined in the above way are called Fuchs constants following their introduction in [5].

The Lagrangian strain is given by

$$2\eta(x, v) + I = \tilde{H}(x, v)H(x, v) \tag{37}$$

where the tilde denotes matrix transposition. The rotationally invariant measures of inner displacement $\vec{\zeta}^\lambda$ are defined from the relative displacements of atoms on two sublattices by

$$\vec{\zeta}^\lambda(x, v) = \tilde{H}(x, v)(\vec{u}^{\lambda+1} - \vec{u}^\lambda) \tag{38}$$

or

$$\vec{\zeta}^\lambda(x, v) = \tilde{H}(x, v)\Lambda^{\lambda\alpha}\vec{u}^\alpha \tag{39}$$

where

$$\Lambda = \begin{bmatrix} -1 & 1 & \cdot & \cdots & \cdot & \cdot \\ \cdot & -1 & 1 & \cdots & \cdot & \cdot \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ \cdot & \cdot & \cdot & \cdots & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdots & -1 & 1 \end{bmatrix}.$$

No generality is lost if P is taken to be symmetric and thus finally we have

$$2\eta(x, v) + I = (1 + v)^{2/3}[S(x)]^2[I + 2xP + x^2P^2] \tag{40}$$

and

$$\vec{\zeta}^\lambda(x, v) = (1 + v)^{1/3}S(x)(I + xP)\Lambda^{\lambda\alpha}\vec{u}^\alpha. \tag{41}$$

The constants calculated directly from equation (36) are related to those appearing in equation (1) through chain rule differentiation with the operators

$$\begin{aligned} \frac{\partial}{\partial x} &= \left(\frac{\partial \eta_I}{\partial x}\right) \frac{\partial}{\partial \eta_I} \\ \frac{\partial}{\partial v} &= \left(\frac{\partial \eta_I}{\partial v}\right) \frac{\partial}{\partial \eta_I} \\ \frac{\partial}{\partial u_i^\alpha} &= \left(\frac{\partial \zeta_j^\lambda}{\partial u_i^\alpha}\right) \frac{\partial}{\partial \zeta_j^\lambda} = H_{ij}(x, v)\tilde{\Lambda}^{\alpha\lambda} \frac{\partial}{\partial \zeta_j^\lambda}. \end{aligned} \tag{42}$$

Coefficients are evaluated at zero strain when differentiation is complete.

The completely general relationships between Fuchs and Brugger constants are given by the expressions below in which summation over repeated subscripts is assumed. The convention $\delta_I = 1$ when $I = 1, 2,$ or 3 and is zero otherwise is used. The coefficients t_i are related to those in equation (33) by $t_1 = -t_p, t_2 = 5t_p^2 - 6c_p,$ and $t_3 = -(20t_p^3 - 45t_p c_p + 27d_p).$ P and Q each appear in two guises: as 3×3 matrices with elements $P_{ij}, Q_{ij},$ and as 6×1 matrices with elements $P_I, Q_I.$ The latter relate to the former in the same way as η_I relates to $\eta_{ij}.$

Under volume strain alone:

$$\begin{aligned} 3c_v^0 &= \delta_I C_I^0 \\ 9c_{vv}^0 &= -\delta_I C_I^0 + \delta_I \delta_J C_{IJ}^0 \\ 27c_{vvv}^0 &= 4\delta_I C_I^0 - 3\delta_I \delta_J C_{IJ}^0 + \delta_I \delta_J \delta_K C_{IJK}^0. \end{aligned} \tag{43}$$

Under shape strain alone:

$$\begin{aligned}
3c_x^0 &= (t_1\delta_I + 3P_I)C_I^0 \\
9c_{xx}^0 &= (t_2\delta_I + 12t_1P_I + 9Q_I)C_I^0 + (t_1^2\delta_I\delta_J + 3t_1(\delta_I P_J + \delta_J P_I) + 9P_I P_J)C_{IJ}^0 \\
54c_{xxx}^0 &= 4(t_3\delta_I + 9t_2P_I + 27t_1Q_I)C_I^0 + 3(2t_1t_2\delta_I\delta_J + 3(t_2 + 4t_1^2)(\delta_I P_J + \delta_J P_I) \\
&\quad + 72t_1P_I P_J + 9t_1(\delta_I Q_J + \delta_J Q_I) + 27(P_I Q_J + P_J Q_I))C_{IJ}^0 + 2(t_1^3\delta_I\delta_J\delta_K \\
&\quad + 3t_1^2(\delta_I\delta_J P_K + \delta_I\delta_K P_J + \delta_J\delta_K P_I) + 9t_1(\delta_I P_J P_K + \delta_J P_I P_K + \delta_K P_I P_J) \\
&\quad + 27P_I P_J P_K)C_{IJK}^0.
\end{aligned} \tag{44}$$

Under volume and shape strain together:

$$\begin{aligned}
18c_{ux}^0 &= 4(t_1\delta_I + 3P_I)C_I^0 + (2t_1\delta_I\delta_J + 3(\delta_I P_J + \delta_J P_I))C_{IJ}^0 \\
54c_{vux}^0 &= -4(t_1\delta_I + 3P_I)C_I^0 + 3(2t_1\delta_I\delta_J + 3(\delta_I P_J + \delta_J P_I))C_{IJ}^0 \\
&\quad + 2(t_1\delta_I\delta_J\delta_K + (\delta_I\delta_J P_K + \delta_I\delta_K P_J + \delta_J\delta_K P_I))C_{IJK}^0 \\
54c_{vxx}^0 &= 4(t_2\delta_I + 12t_1P_I + 9Q_I)C_I^0 + (2(t_2 + 4t_1^2)\delta_I\delta_J + 36t_1(\delta_I P_J + \delta_J P_I) \\
&\quad + 72P_I P_J + 9(\delta_I Q_J + \delta_J Q_I))C_{IJ}^0 + 2(t_1^2\delta_I\delta_J\delta_K \\
&\quad + 2t_1(\delta_I\delta_J P_K + \delta_I\delta_K P_J + \delta_J\delta_K P_I) \\
&\quad + 3(\delta_I P_J P_K + \delta_J P_I P_K + \delta_K P_I P_J))C_{IJK}^0.
\end{aligned} \tag{45}$$

Under sublattice displacement(s) alone:

$$\begin{aligned}
d_p^\alpha &= \tilde{\Lambda}^{\alpha\lambda} D_p^\lambda \\
e_{pq}^{\alpha\beta} &= \tilde{\Lambda}^{\alpha\lambda} \tilde{\Lambda}^{\beta\mu} E_{pq}^{\lambda\mu} \\
f_{pqr}^{\alpha\beta\gamma} &= \tilde{\Lambda}^{\alpha\lambda} \tilde{\Lambda}^{\beta\mu} \tilde{\Lambda}^{\gamma\nu} F_{pqr}^{\lambda\mu\nu}.
\end{aligned} \tag{46}$$

Under volume strain and sublattice displacement(s) together:

$$\begin{aligned}
3d_{pv}^\alpha &= \tilde{\Lambda}^{\alpha\lambda} (D_p^\lambda + \delta_J D_{pJ}^\lambda) \\
9d_{pvv}^\alpha &= \tilde{\Lambda}^{\alpha\lambda} (-2D_p^\lambda + \delta_J D_{pJ}^\lambda + \delta_J\delta_K D_{pJK}^\lambda) \\
3e_{pqv}^{\alpha\beta} &= \tilde{\Lambda}^{\alpha\lambda} \tilde{\Lambda}^{\beta\mu} (2E_{pq}^{\lambda\mu} + \delta_K E_{pqK}^{\lambda\mu}).
\end{aligned} \tag{47}$$

Under shape strain and sublattice displacement(s) together:

$$\begin{aligned}
3d_{px}^\alpha &= \tilde{\Lambda}^{\alpha\lambda} (t_1 D_p^\lambda + 3P_{Ip} D_i^\lambda + (t_1\delta_J + 3P_J) D_{pJ}^\lambda) \\
9d_{pxx}^\alpha &= \tilde{\Lambda}^{\alpha\lambda} ((t_2 - t_1^2) D_p^\lambda + 6t_1 P_{Ip} D_i^\lambda + ((t_2 + 2t_1^2)\delta_J + 18t_1 P_J + 9Q_J) D_{pJ}^\lambda \\
&\quad + 6P_{Ip} (t_1\delta_J + 3P_J) D_{iJ}^\lambda + (t_1^2\delta_J\delta_K + 3t_1(\delta_J P_K + \delta_K P_J) + 9P_J P_K) D_{pJK}^\lambda) \\
3e_{pqx}^{\alpha\beta} &= \tilde{\Lambda}^{\alpha\lambda} \tilde{\Lambda}^{\beta\mu} ((2t_1 E_{pq}^{\lambda\mu} + 3P_{jq} E_{pj}^{\lambda\mu} + 3P_{ip} E_{iq}^{\lambda\mu}) + (t_1\delta_K + 3P_K) E_{pqK}^{\lambda\mu}).
\end{aligned} \tag{48}$$

Under volume and shape strain, together with sublattice displacement:

$$\begin{aligned}
18d_{pvx}^\alpha &= \tilde{\Lambda}^{\alpha\lambda} (2t_1 D_p^\lambda + 6P_{ip} D_i^\lambda + 2(4t_1\delta_J + 9P_J) D_{pJ}^\lambda + 6\delta_J P_{ip} D_{iJ}^\lambda \\
&\quad + (2t_1\delta_J\delta_K + 3(\delta_J P_K + \delta_K P_J)) D_{pJK}^\lambda).
\end{aligned} \tag{49}$$

5.1. Computational procedures

A sufficient variety of deformations must be selected to ensure that all the independent elastic and inner elastic constants can be uniquely determined. Several dozen distinct ones are used. These involve

Table 4. Specification of the shape-changing matrices P and the corresponding scaling functions. $P_{ij} = P_{ji}$ in each case.

Number	P_{11}	P_{22}	P_{33}	P_{12}	P_{13}	P_{23}	$S(x)^{-3}$
Cubic diamond							
1	1	0	0	0	0	0	$1+x$
2	0	0	0	1	1	1	$1-3x^2+2x^3$
3	0	1	-1	1	1	0	$1-3x^2-x^3$
Hexagonal graphite (1-5), hexagonal diamond (1-7), rhombohedral graphite (1-9)							
1	0	0	3	0	0	0	$1+3x$
2	0	0	3	0	0	1	$1+3x-x^2$
3	0	0	3	1	0	0	$1+3x-x^2-3x^3$
4	1	-1	0	0	0	0	$1-x^2$
5	0	0	0	1	1	1	$1-3x^2+2x^3$
6	0	0	3	0	0	-1	$1+3x-x^2$
7	0	0	0	-1	1	1	$1-3x^2+2x^3$
8	1	1	0	1	1	0	$1+2x-x^2-x^3$
9	1	1	0	-1	1	0	$1+2x-x^2-x^3$

- (i) uniform volume change on its own,
- (ii) a set of different shape-changing matrices P , detailed for the four carbon allotropes under discussion in table 4, each to be used both with and without volume change,
- (iii) one of the components of sublattice displacement u_i^α , or one of the pairs u_i^α, u_j^β , or one of the triplets $u_i^\alpha, u_j^\beta, u_k^\gamma$, either alone or combined with the previous items.

Each deformation is used with a grid of seven equally spaced values of x , v , and/or each u_i^α as appropriate. The energy is determined at each point in the grid and partial energy derivatives are calculated by numerical differentiation, using least-squares fitting of a polynomial (a cubic is completely satisfactory) to seven equally spaced points.

5.2. Formal checks

There are numerous opportunities for errors to arise in a complex calculation. To test the accuracy of the calculations that have been made on the individual allotropes (papers in preparation), the extravagance of calculating all possible components of the d -, e -, and f -tensors was indulged. This showed explicitly that all expected crystal symmetry relations were satisfied. In this test there may be more than a million applications of the energy algorithm and several hundred applications of the least-squares fitting subroutine. Where components should have been zero, small values arising from statistical noise were found, though in all cases these were a million or more times smaller than the smallest non-zero components of the same tensor.

The accuracy of the subsequent conversion of the Fuchs constants to Brugger constants was tested in two ways. In the first the energy algorithm was replaced by the summation of a simple pair potential $\phi(r) = 1/r^6$ over a cluster of more than 8000 atoms. The results of this were compared with the direct calculation of Brugger constants for this potential using the modified Ewald method described in [5]. In the second test the energy algorithm was replaced by equation (1) with the previously computed values of all the elastic constants. Self-consistency was total.

6. Summary

Building on the foundation of the preceding paper the composition of the second- and third-order elastic constants of four carbon allotropes in terms of their inner elastic constants and internal strain tensors has been presented. Certain properties derived from these constants, such as compliances, compressibilities, and pressure derivatives, are closely related to parameters that can be obtained directly by x-ray or neutron diffraction or from ultrasonic velocity measurements. These have also been exposed explicitly.

The generalized method of homogeneous deformation provides a coherent way of calculating every partial and inner elastic constant belonging to a specified crystal structure. The route that proceeds from infinitesimal strains to elastic energies, to Fuchs constants, to Brugger constants is the only viable one when the interaction potentials involved are more complex than inverse powers of interatomic separation. It is particularly suitable for total-energy methods.

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