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Formal elasticity of four carbon allotropes: I. The inner elastic constants, internal strain tensors, and zone-centre optic mode frequencies and their pressure dependences

C S G Cousins

School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK

E-mail: CCousins@exeter.ac.uk

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Abstract

The symmetry structure of the six families of inner elastic constants (derivatives of the free energy with respect to one, two, or three components of the relative sublattice displacement) that enter the elasticity, through the third order, of the cubic and hexagonal diamond allotropes and of the hexagonal and rhombohedral graphite allotropes is analysed in detail. This is followed by derivations (i) of the forms of the linear and quadratic internal strain tensors, (ii) of the expressions for the zone-centre optic mode frequencies and eigenvectors, and (iii) of the effective inner elastic constants that determine these frequencies in arbitrarily strained crystals together with (iv) the derived pressure dependences of those frequencies.

1. Introduction

This and the following paper [1] contain a full, formal treatment of the elasticity, through the third order, of four diamond and graphite allotropes of carbon. They have been written to pave the way for individual studies of the elasticity of each allotrope. In order to be fully comprehensive it is necessary to look at as many related properties as possible: not solely macroscopic elastic constants, but optic mode frequencies, their stress and/or pressure dependence, and internal strain. In other words it is necessary to focus on microscopic aspects—the consequences of the relative movements of sublattices.

In section 2 parallel definitions of two families of microscopic tensors are introduced (following the general principles laid out earlier in [2] and [3]). A full symmetry analysis of these inner elastic constants is given, for each structure, in section 3. The analysis is more intricate than that employed for macroscopic tensors, such as the ordinary elastic constants, because the translations associated with screw and glide operations can no longer be ignored.

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Thus although hexagonal diamond (hD) and hexagonal graphite (hG) belong to the same space group there are significant differences in the make-up of their inner elastic constants due to the different symmetry characteristics of the atomic sites. Some of the results for cubic diamond (cD) have been obtained before [4, 5] but are repeated here for completeness. In addition they have been put into a non-conventional form, by transformation of axes, to facilitate comparison with rhombohedral graphite (rG) and with intermediate structures along possible solid-state transformation paths from rG to cD; see [6] and [7].

General expressions for the linear and quadratic internal strain tensors are given in section 4. The independent components of the linear tensors are presented for all four allotropes. Those of the quadratic tensor are given for cD alone.

The frequencies of optic modes at the zone centre and their eigenvectors are treated in section 5 via a secular equation that relates to the optic modes alone. Explicit solutions for each allotrope are given. The variation of frequency with strain can be followed if the secular equation for the strained crystal can be obtained. This is possible in terms of effective inner elastic constants that are defined in a way similar to that used for the macroscopic elastic constants. Results are listed for each allotrope in section 6. Finally, expressions for the pressure dependence of the optic mode frequencies have been deduced and presented in section 7.

2. Sublattice tensors and inner elastic constants

The microscopic tensors considered here are partial derivatives of contributions to the free energy per unit initial volume with respect to sublattice displacements under strain. They are *microscopic* because they refer to energy associated with parts of the basis—the energy of covalent bonds sited on the atoms occupying a single sublattice, for example—and they occur only in those structures where some or all of the atomic sites lack inversion symmetry.

There are two approaches to the definition of elastic constants. The first is in terms of the infinitesimal-strain matrix ϵ, derived from the deformation gradient matrix $H = I + \epsilon$, and the displacements $\vec{u}^\alpha$ of the sublattices from their equilibrium positions. Atomic coordinates are given by $\vec{r}^\alpha = H\vec{r}_0^\alpha + \vec{u}^\alpha$ and α runs from 1 to n, the number of atoms in the basis, with $\vec{u}^\alpha \equiv 0$ for sites with inversion symmetry. The second is in terms of the finite-, or Lagrangian, strain matrix η, given by $2\eta + I = \tilde{H}H$, where the tilde denotes transposition, and $\vec{w}^\alpha = H\vec{u}^\alpha$: constants defined this way are usually referred to as Brugger constants [8]. The two forms coexist because strains in the first case are more computationally friendly when contributions to the energy are not simple analytical functions of interatomic distances or atomic volume whilst strains and sublattice displacements in the second case are rotationally invariant and therefore rigorous thermodynamically. It is the finite-strain approach that is followed in the remainder of this paper. As η is symmetric, the usual Voigt contraction of suffixes will be implemented: the strain represented by η_I where I runs from 1 to 6.

The $\vec{w}^\alpha$ are not all independent because homogeneous deformation does not shift the centre of mass. Thus $\sum_1^n \vec{w}^\alpha = 0$, assuming that all atoms in the basis have the same mass, as is the case in this study. This redundancy is removed by defining $n-1$ independent inner displacements $\vec{\zeta}^\lambda$ through the prescription $\vec{\zeta}^\lambda = \vec{w}^{\lambda+1} - \vec{w}^\lambda$ or $\vec{\zeta}^\lambda = \Lambda^{\lambda\alpha}\vec{w}^\alpha$ on introducing the rectangular matrix

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

Two sets of microscopic constants may be defined: the first consists of three families of *sublattice tensors* relating to *sublattice displacement*:

$$d_i^\alpha = \rho_0(\partial F/\partial w_i^\alpha)_0$$
$$e_{ij}^{\alpha\beta} = \rho_0(\partial^2 F/\partial w_i^\alpha\,\partial w_j^\beta)_0$$
$$f_{ijk}^{\alpha\beta\gamma} = \rho_0(\partial^3 F/\partial w_i^\alpha\,\partial w_j^\beta\,\partial w_k^\gamma)_0;$$

the second of three parallel families of *inner elastic constants* relating to *inner displacement*:

$$D_i^\lambda = \rho_0(\partial F/\partial \zeta_i^\lambda)_0$$
$$E_{ij}^{\lambda\mu} = \rho_0(\partial^2 F/\partial \zeta_i^\lambda\,\partial \zeta_j^\mu)_0$$
$$F_{ijk}^{\lambda\mu\nu} = \rho_0(\partial^3 F/\partial \zeta_i^\lambda\,\partial \zeta_j^\mu\,\partial \zeta_k^\nu)_0$$

where ρ_0 is the equilibrium density, F is the free energy per unit mass, and the subscripts i, j, and k take values from 1 to 3. Whereas a single letter, C, is used for ordinary elastic constants of different orders, the sequences d, e, f and D, E, F are used here in mnemonic spirit to distinguish at a glance between first, second, and third derivatives with respect to displacements. The constants in the upper set are related to those in the lower via chain rule differentiation with the operator

$$\frac{\partial}{\partial w_i^\alpha} = \left(\frac{\partial \zeta_i^\lambda}{\partial w_i^\alpha}\right)\frac{\partial}{\partial \zeta_i^\lambda} = \tilde{\Lambda}^{\alpha\lambda}\,\frac{\partial}{\partial \zeta_i^\lambda} \tag{1}$$

where $\tilde{\Lambda}$ is the transpose of the matrix defined above.

The three remaining families couple internal and external strain and comprise the following sets:

$$d_{iJ}^\alpha = \rho_0(\partial^2 F/\partial w_i^\alpha\,\partial \eta_J)_0$$
$$d_{iJK}^\alpha = \rho_0(\partial^3 F/\partial w_i^\alpha\,\partial \eta_J\,\partial \eta_K)_0$$
$$e_{ijK}^{\alpha\beta} = \rho_0(\partial^3 F/\partial w_i^\alpha\,\partial w_j^\beta\,\partial \eta_K)_0$$

and

$$D_{iJ}^\lambda = \rho_0(\partial^2 F/\partial \zeta_i^\lambda\,\partial \eta_J)_0$$
$$D_{iJK}^\lambda = \rho_0(\partial^3 F/\partial \zeta_i^\lambda\,\partial \eta_J\,\partial \eta_K)_0$$
$$E_{ijK}^{\lambda\mu} = \rho_0(\partial^3 F/\partial \zeta_i^\lambda\,\partial \zeta_j^\mu\,\partial \eta_K)_0$$

in which the subscripts J and K may have values from 1 to 6. The constants involving inner displacement are given in terms of the those involving sublattice displacement by

$$D_{\cdots}^\lambda = -\sum_{p=1}^{\lambda} d_{\cdots}^p$$
$$E_{\cdots}^{\lambda\mu} = \sum_{p=1}^{\lambda}\sum_{q=1}^{\mu} e_{\cdots}^{pq} \tag{2}$$
$$F_{\cdots}^{\lambda\mu\nu} = -\sum_{p=1}^{\lambda}\sum_{q=1}^{\mu}\sum_{r=1}^{\nu} f_{\cdots}^{pqr}$$

for all valid subscript sequences i, iJ, or iJK on d and D; all ij or ijK on e and E; and all ijk on f and F.

As the n sublattice displacements $\vec{w}^{\alpha}$ are not independent it follows from application of (1) that

$$\begin{aligned}
&\sum_{p=1}^{n} d^{p}_{\cdots} = 0 \\
&\sum_{p=1}^{n} e^{\alpha p}_{\cdots} = \sum_{p=1}^{n} e^{p\beta}_{\cdots} = 0 \\
&\sum_{p=1}^{n} f^{\alpha\beta p}_{\cdots} = \sum_{p=1}^{n} f^{\alpha p\gamma}_{\cdots} = \sum_{p=1}^{n} f^{p\beta\gamma}_{\cdots} = 0
\end{aligned} \tag{3}$$

for any values of α, β, or γ. The results are true *a fortiori* for double or triple summations.

It is easily seen that as λ, μ, and ν increase the number of terms on the right of (2) escalates. Smaller numbers can be retrieved by combining (2) and (3) to give alternative, equivalent, definitions. For example, combining the summations involving λ in corresponding tensors gives

$$\begin{aligned}
D^{\lambda}_{\cdots} &= + \sum_{p=\lambda+1}^{n} d^{p}_{\cdots} \\
E^{\lambda\mu}_{\cdots} &= - \sum_{p=\lambda+1}^{n} \sum_{q=1}^{\mu} e^{pq}_{\cdots} \\
F^{\lambda\mu\nu}_{\cdots} &= + \sum_{p=\lambda+1}^{n} \sum_{q=1}^{\mu} \sum_{r=1}^{\nu} f^{pqr}_{\cdots},
\end{aligned} \tag{4}$$

where the signs on the right are the opposite of those in (2). If the limits on a second superscript are modified the sign will be reversed again, and so on.

3. Symmetry

The essential geometry of the structures—the space groups, primitive unit-cell vectors, atomic coordinates, and the allocation of sublattice indices—is summarized in table 1. To make comparison easy the four structures are show in figure 1 in relation to hexagonal cells: triple cells for cD and rG and primitive ones for hD and hG.

Although the inner elastic constants are free of redundancy, a certain arbitrariness has been introduced: a relabelling of the sublattices will lead to a shuffling of values of the components of the tensors. For this reason it is much simpler to treat the symmetry of the sublattice tensors d, e, and f and subsequently to deduce that of the inner elastic constants D, E, and F. The simpler part has already been done. The forms of the individual tensors of the d^{α}, $e^{\alpha\beta}$, and $f^{\alpha\beta\gamma}$ families, their non-zero components, and any interdependences, have been extracted from tables 10 to 14 in [3] at the appropriate point group ($\bar{4}3m$ for cD, $3m$ for rG and hD, and $\bar{6}m2$ for hG), and are presented in tables 2 and 3. Some additional simplification follows from the commutative nature of differentiation: $e^{\alpha\beta}_{ij\cdot} = e^{\alpha\beta}_{ji\cdot}$ when $\alpha = \beta$, $d^{\alpha}_{iJK} = d^{\alpha}_{iKJ}$, and several similar relations for $f^{\alpha\beta\gamma}_{ijk}$.

3.1. Cubic diamond and rhombohedral graphite

A major simplification occurs for structures in which the basis comprises two atoms only, so $n = 2$. Then λ, μ, and ν take only the value 1 and the superscripts on D, E, and F become redundant. It also follows that the summations in (2) disappear, leaving only single terms on

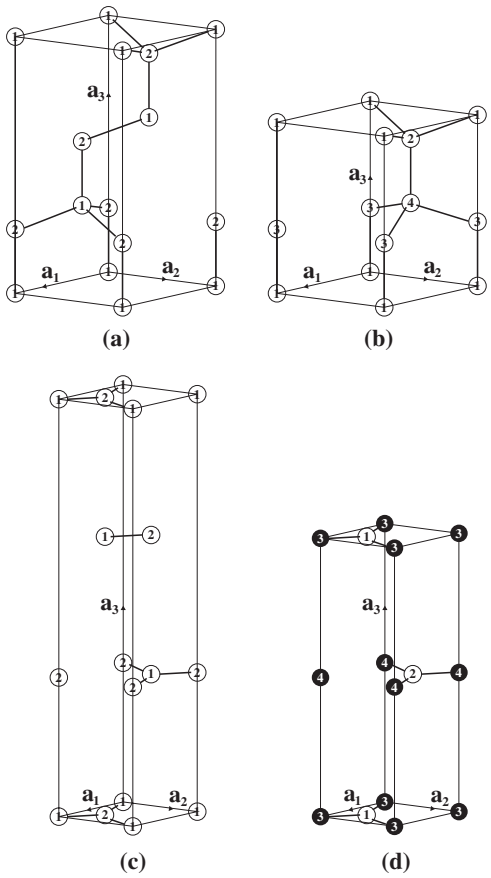

Figure 1. In (a) a triple hexagonal cell is used for cD to facilitate comparison with hD in (b). In (c) a triple cell is used similarly for rG to contrast its layer structure (ABCA) with that of hG (ABA) in (d). In hG the distinction between non-equivalent pairs of atoms is made by depth of shading. sp^3 or sp^2 bonds entirely within a cell have been emphasized.

the right involving $p = q = r = 1$ and giving the simplest possible general set of independent components:

$$D_{i..} = -d^{1}_{i..}$$
$$E_{ij.} = e^{11}_{ij.}$$
$$F_{ijk} = -f^{111}_{ijk}.$$

A full collection of specific independent components is shown in table 4 and the complete collection of all non-zero components is obtained by collating the entries in this table with those in tables 2 and 3.

The alternative description of the inner elasticity of cD that will facilitate comparison with the intermediate structures along the cD-to-rG transformation path is produced by a rotation of axes. The matrix

$$a = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{bmatrix}$$

Table 1. Essential geometry and the assignment of sublattice indices to the atomic sites in the various structures. In cD a is the lattice parameter of the cubic cell; in rG a and c are the lattice parameters of the non-primitive triple hexagonal cell and $\gamma = c/a$ is the axial ratio. Ideal rG has $u = 1/6$ and ideal hD has $z = 1/16$.

		cD	rG	hD	hG
Space group		$Fd\bar{3}m$	$R\bar{3}m$	$P6_3/mmc$	
Unit-cell vectors	$\vec{a}_1$	$\frac{a}{2}[0, 1, 1]$	$\frac{a}{6}[3, \sqrt{3}, 2\gamma]$	$a[1, 0, 0]$	
	$\vec{a}_2$	$\frac{a}{2}[1, 0, 1]$	$\frac{a}{6}[-3, \sqrt{3}, 2\gamma]$	$a\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right]$	
	$\vec{a}_3$	$\frac{a}{2}[1, 1, 0]$	$\frac{a}{3}[0, -\sqrt{3}, \gamma]$	$a[0, 0, \gamma]$	
Wyckoff sites		a	c	f	d : b
Site symmetry		$\bar{4}3m$	$3m$	$3m$	$\bar{6}m2$
Sublattice indices	1	$-(\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8})$	$-(u\ u\ u)$	$(\frac{1}{3}\ \frac{2}{3}\ z)$	$(\frac{1}{3}\ \frac{2}{3}\ \frac{3}{4})$:
	2	$(\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8})$	$(u\ u\ u)$	$(\frac{2}{3}\ \frac{1}{3}\ 1-z)$	$(\frac{2}{3}\ \frac{1}{3}\ \frac{1}{4})$:
	3			$(\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2}-z)$	$:(0\ 0\ \frac{3}{4})$
	4			$(\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}+z)$	$:(0\ 0\ \frac{1}{4})$

Table 2. The symmetry of the individual sublattice tensors in cD: the non-zero components of each and the relationships between them. α, β, and γ equal 1 or 2.

$d^{\alpha}_{14} = d^{\alpha}_{25} = d^{\alpha}_{36}$
$e^{\alpha\beta}_{11} = e^{\alpha\beta}_{22} = e^{\alpha\beta}_{33}$
$d^{\alpha}_{114} = d^{\alpha}_{225} = d^{\alpha}_{336}$
$d^{\alpha}_{124} = d^{\alpha}_{134} = d^{\alpha}_{215} = d^{\alpha}_{235} = d^{\alpha}_{316} = d^{\alpha}_{326}$
$d^{\alpha}_{156} = d^{\alpha}_{246} = d^{\alpha}_{345}$
$e^{\alpha\beta}_{111} = e^{\alpha\beta}_{222} = e^{\alpha\beta}_{333}$
$e^{\alpha\beta}_{112} = e^{\alpha\beta}_{113} = e^{\alpha\beta}_{221} = e^{\alpha\beta}_{223} = e^{\alpha\beta}_{331} = e^{\alpha\beta}_{332}$
$e^{\alpha\beta}_{126} = e^{\alpha\beta}_{135} = e^{\alpha\beta}_{216} = e^{\alpha\beta}_{234} = e^{\alpha\beta}_{315} = e^{\alpha\beta}_{324}$
$f^{\alpha\beta\gamma}_{123} = f^{\alpha\beta\gamma}_{132} = f^{\alpha\beta\gamma}_{213} = f^{\alpha\beta\gamma}_{231} = f^{\alpha\beta\gamma}_{312} = f^{\alpha\beta\gamma}_{321}$

transforms the usual cD coordinate system ($0x_1$, $0x_2$, and $0x_3$ along [100], [010], and [001] respectively) to one in which $0x'_1$ lies along $[1\bar{1}0]$, $0x'_2$ along $[11\bar{2}]$, and $0x'_3$ along [111]. Tensors in the new system are related to those in the old by the transformation law [9]

$$T'_{ijk\ldots} = a_{ip}a_{jq}a_{kr}\cdots T_{pqr\ldots}.$$

The tensors that are in contracted form must first be uncontracted, then transformed, then recontracted. These results have been added to table 4. Rotation of axes cannot increase the actual number of independent components of any tensor. The apparent increase conceals numerous relations between the members of the modified set.

3.2. Hexagonal diamond and hexagonal graphite

When structures have a basis of four atoms the analysis becomes more intricate and depends on space group symmetry arguments. Both hD and hG belong to the space group $P6_3/mmc$, (No 194 in the International Tables for Crystallography [10]), which is non-symmorphic.

Table 3. The symmetry of the individual sublattice tensors in hG (left-hand column only), rG, and hD (both columns): the non-zero components of each and the relationships between them. The point groups behind these relations are indicated. α, β, and γ equal 1 or 2 in rG; 1, 2, 3, or 4 in hD and hG.

$\bar{6}m2$	$6mm$
	d^α_3
$d^\alpha_{16} = d^\alpha_{21} = -d^\alpha_{22}$	$d^\alpha_{15} = d^\alpha_{24}$
	$d^\alpha_{31} = d^\alpha_{32}$
	d^α_{33}
$d^\alpha_{116} = -\frac{1}{4}(d^\alpha_{211} + 3d^\alpha_{222})$	$d^\alpha_{115} = d^\alpha_{224}$
$d^\alpha_{126} = \frac{1}{4}(3d^\alpha_{211} + d^\alpha_{222})$	$d^\alpha_{125} = d^\alpha_{214}$
$d^\alpha_{136} = d^\alpha_{213} = -d^\alpha_{223}$	$d^\alpha_{135} = d^\alpha_{234}$
$d^\alpha_{145} = -d^\alpha_{244} = d^\alpha_{255}$	$d^\alpha_{146} = d^\alpha_{256} = \frac{1}{2}(d^\alpha_{115} - d^\alpha_{125})$
$d^\alpha_{212} = d^\alpha_{266} = \frac{1}{2}(d^\alpha_{116} - d^\alpha_{126})$	$d^\alpha_{311} = d^\alpha_{322} = d^\alpha_{312} + 2d^\alpha_{366}$
$d^\alpha_{314} = -d^\alpha_{324} = d^\alpha_{356}$	$d^\alpha_{313} = d^\alpha_{323}$
	d^α_{333}
	$d^\alpha_{344} = d^\alpha_{355}$
$f^{\alpha\beta\gamma}_{112} = f^{\alpha\beta\gamma}_{121} = f^{\alpha\beta\gamma}_{211} = -f^{\alpha\beta\gamma}_{222}$	$f^{\alpha\beta\gamma}_{113} = f^{\alpha\beta\gamma}_{223}$
	$f^{\alpha\beta\gamma}_{131} = f^{\alpha\beta\gamma}_{232}$
	$f^{\alpha\beta\gamma}_{311} = f^{\alpha\beta\gamma}_{322}$
	$f^{\alpha\beta\gamma}_{333}$
$\bar{6}m2$, $6mm$, part of $3m$ $\cdots$	$\cdots$ rest of $3m$
$e^{\alpha\beta}_{11} = e^{\alpha\beta}_{22}$	
$e^{\alpha\beta}_{33}$	
$e^{\alpha\beta}_{111} = e^{\alpha\beta}_{222}$	
$e^{\alpha\beta}_{112} = e^{\alpha\beta}_{221}$	
$e^{\alpha\beta}_{113} = e^{\alpha\beta}_{223}$	
$e^{\alpha\beta}_{126} = e^{\alpha\beta}_{216} = \frac{1}{2}(e^{\alpha\beta}_{111} - e^{\alpha\beta}_{112})$	$e^{\alpha\beta}_{114} = e^{\alpha\beta}_{125} = e^{\alpha\beta}_{215} = -e^{\alpha\beta}_{214}$
$e^{\alpha\beta}_{135} = e^{\alpha\beta}_{234}$	$e^{\alpha\beta}_{136} = e^{\alpha\beta}_{231} = -e^{\alpha\beta}_{232}$
$e^{\alpha\beta}_{315} = e^{\alpha\beta}_{324}$	$e^{\alpha\beta}_{316} = e^{\alpha\beta}_{321} = -e^{\alpha\beta}_{322}$
$e^{\alpha\beta}_{331} = e^{\alpha\beta}_{332}$	
$e^{\alpha\beta}_{333}$	

This indicates the presence of screw and glide symmetry elements. The 24 symmetry elements are represented by augmented 4×4 partitioned matrices:

$$\{R_i|\vec{t}\,\} = \begin{bmatrix} R_i & \vec{t} \\ 0 & 1 \end{bmatrix}$$

where the R_i are 3×3 point symmetry operations and $\vec{t}$ is a 3×1 column vector representing the fractional translation associated with R_i. Half the operations have $\vec{t} = [0/0/0]$ and half have $\vec{t} = [0/0/\frac{1}{2}]$.

The position coordinates and the indices assigned to the sublattices are shown in table 1. In table 5 are shown the permutations of the sublattice indices induced by the 24 operations

Table 4. Independent components of the inner elastic constants: cD in columns 1 and 4, and rG in columns 2 and 5. In columns 3 and 6 cD is referred to the rhombohedral system in reverse setting ($0x'_1$ along $[1\bar{1}0]$, $0x'_2$ along $[11\bar{2}]$, and $0x'_3$ along $[111]$) (upper signs) and, with a further rotation of 90° about $0x'_3$, in obverse setting (lower signs): linear combinations of elements from columns 1 or 4 are equivalent to the element in columns 2 or 5. The full sets of non-zero components are obtained by reading columns 1 and 2, and 4 and 5 in conjunction with the relations in tables 2 and 3.

	D_3	$\equiv 0$	D_{114}	D_{116}	$\pm\frac{1}{\sqrt{6}}(D_{114}+D_{124}+2D_{156})$
D_{14}	D_{16}	$\pm\frac{2}{\sqrt{3}}D_{14}$	D_{124}	D_{126}	$\mp\frac{1}{3\sqrt{6}}(D_{114}-7D_{124}+2D_{156})$
	D_{15}	$-\frac{1}{\sqrt{3}}D_{14}$	D_{156}	D_{136}	$\pm\frac{2}{3\sqrt{6}}(2D_{114}+D_{124}-2D_{156})$
	D_{31}	$-\frac{1}{\sqrt{3}}D_{14}$		D_{145}	$\mp\frac{2}{3\sqrt{6}}(D_{114}-D_{124}-D_{156})$
	D_{33}	$\frac{2}{\sqrt{3}}D_{14}$		D_{314}	$\pm\frac{1}{3\sqrt{6}}(D_{114}-D_{124}+2D_{156})$
				D_{115}	$-\frac{1}{2\sqrt{3}}(D_{114}+D_{124}+2D_{156})$
				D_{125}	$-\frac{1}{6\sqrt{3}}(5D_{114}+D_{124}-2D_{156})$
				D_{135}	$\frac{1}{3\sqrt{3}}(D_{114}-4D_{124}+2D_{156})$
				D_{311}	$-\frac{2}{\sqrt{3}}D_{124}$
				D_{312}	$-\frac{2}{3\sqrt{3}}(2D_{114}+D_{124}-2D_{156})$
				D_{313}	$\frac{1}{3\sqrt{3}}(D_{114}+2D_{124}-4D_{156})$
				D_{333}	$\frac{4}{3\sqrt{3}}(D_{114}+2D_{124}+2D_{156})$
				D_{344}	$-\frac{1}{3\sqrt{3}}(2D_{114}-2D_{124}+D_{156})$
E_{11}	E_{11}	E_{11}	E_{111}	E_{111}	$\frac{1}{2}(E_{111}+E_{112}+2E_{126})$
	E_{33}	E_{11}	E_{112}	E_{112}	$\frac{1}{6}(E_{111}+5E_{112}-2E_{126})$
			E_{126}	E_{113}	$\frac{1}{3}(E_{111}+2E_{112}-2E_{126})$
				E_{126}	$\frac{1}{6}(E_{111}-E_{112}+4E_{126})$
				E_{135}	$\frac{1}{3}(E_{111}-E_{112}+E_{126})$
				E_{331}	$\frac{1}{3}(E_{111}+2E_{112}-2E_{126})$
				E_{333}	$\frac{1}{3}(E_{111}+2E_{112}+4E_{126})$
				E_{114}	$\pm\frac{1}{3\sqrt{2}}(E_{111}-E_{112}-2E_{126})$
				E_{136}	$\pm\frac{1}{3\sqrt{2}}(E_{111}-E_{112}-2E_{126})$
F_{123}	F_{112}	$\pm\frac{2}{\sqrt{6}}F_{123}$			
	F_{113}	$-\frac{1}{\sqrt{3}}F_{123}$			
	F_{333}	$\frac{2}{\sqrt{3}}F_{123}$			

Table 5. Permutations of sublattice indices corresponding to space group symmetry operations for the hexagonal structures. $\vec{t}$ is the fractional translation column vector $[0/0/\frac{1}{2}]$. The spaced colon separates the non-equivalent pairs in hG.

Symmetry operations in space group $P6_3/mmc$						Subgroup formed with row 1	Permutations hD	Permutations hG
$\{1\|0\}$	$\{3^+\|0\}$	$\{3^-\|0\}$	$\{m\|0\}$	$\{m'\|0\}$	$\{m''\|0\}$	$R3m$	(1)(2)(3)(4)	(1)(2) : (3)(4)
$\{i\|0\}$	$\{\bar{3}^+\|0\}$	$\{\bar{3}^-\|0\}$	$\{2\|0\}$	$\{2'\|0\}$	$\{2''\|0\}$	$P\bar{3}m1$	(12)(34)	(12) : (34)
$\{2_z\|\vec{t}\,\}$	$\{6^+\|\vec{t}\,\}$	$\{6^-\|\vec{t}\,\}$	$\{c\|\vec{t}\,\}$	$\{c'\|\vec{t}\,\}$	$\{c''\|\vec{t}\,\}$	$P6_3mc$	(14)(23)	(12) : (34)
$\{m_z\|\vec{t}\,\}$	$\{\bar{6}^+\|\vec{t}\,\}$	$\{\bar{6}^-\|\vec{t}\,\}$	$\{2_\circ\|\vec{t}\,\}$	$\{2_\prime\|\vec{t}\,\}$	$\{2_\prime\|\vec{t}\,\}$	$P\bar{6}m2$	(13)(24)	(1)(2) : (3)(4)

of the space group. The latter divide into four subsets of six operations. Those in the first row form a subgroup of point symmetry $3m$ and leave the sublattice indices in hD unchanged. Those in the first and fourth rows together form a subgroup of point symmetry $\bar{6}m2$ and leave the hG indices unchanged. This determines the fundamental form of the individual sublattice tensors and indicates that those in hD will have more non-zero components than those in hG. The two structures therefore require individual treatment.

3.2.1. Hexagonal diamond. The components of the d- and f-tensors in hD are divided conveniently into mutually exclusive $\bar{6}m2$ and $6mm$ sets, as shown in table 3. The operations in rows 1 and 2 of the table 5 together constitute the subgroup $P\bar{3}m1$. Because half the operations interchange the sublattice indices $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ simultaneously the point group $\bar{3}m$ determines the non-zero elements of sum tensors such as $d^1_{i..} + d^2_{i..}$. Since $\bar{3}m$ is centrosymmetric *all* elements of sum tensors bearing an odd number of superscripts vanish. Thus

$$d^1_{i..} + d^2_{i..} = 0$$
$$d^3_{i..} + d^4_{i..} = 0.$$

The operations in rows 1 and 3 similarly comprise the subgroup $P6_3mc$, with row 3 operations producing the interchanges $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$. The point group $6mm$ now determines the non-zero elements of sum tensors such as $d^1_{i..} + d^4_{i..}$. Finally operations in rows 1 and 4 together constitute the subgroup $P\bar{6}m2$, with row 4 operations producing the interchanges $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$. The point group $\bar{6}m2$ now determines the non-zero elements of sum tensors such as $d^1_{i..} + d^3_{i..}$. Thus the following deductions can be made:

$$d^1_{i..} + d^3_{i..} = -(d^2_{i..} + d^4_{i..}) \neq 0 \qquad \bar{6}m2 \text{ elements}$$
$$= 0 \qquad 6mm \text{ elements}$$
$$d^1_{i..} + d^4_{i..} = -(d^2_{i..} + d^3_{i..}) \neq 0 \qquad 6mm \text{ elements}$$
$$= 0 \qquad \bar{6}m2 \text{ elements.}$$

In summary,

$$d^1_{i..} = -d^2_{i..} = \pm d^3_{i..} = \mp d^4_{i..}$$

with the upper (lower) signs applicable to $\bar{6}m2$ ($6mm$) elements. In conjunction with (2) or (4) and (3), these give independent, zero, and dependent components as follows:

$$D^1_{i..} = -d^1_{i..}$$
$$D^2_{i..} = 0$$
$$D^3_{i..} = \pm D^1_{i..},$$

with the same interpretation of signs.

Similarly it is possible to use the above arguments to generate sixteen relations that are satisfied by the f-tensors:

$$\begin{array}{ccccccc} f_{ijk}^{111} & = & -f_{ijk}^{222} & = & \pm f_{ijk}^{333} & = & \mp f_{ijk}^{444} \\ f_{ijk}^{112} & = & -f_{ijk}^{221} & = & \pm f_{ijk}^{334} & = & \mp f_{ijk}^{443} \\ \vdots & & \vdots & & \vdots & & \\ f_{ijk}^{144} & = & -f_{ijk}^{233} & = & \pm f_{ijk}^{322} & = & \mp f_{ijk}^{411}. \end{array}$$

Equations (2)–(4) are then invoked many times to establish a preliminary *maximum* number of independent components (13) and a minimum number of dependent components (also 13):

$$\begin{aligned} F_{ijk}^{\lambda\mu\nu} &= -\sum_{p=1}^{\lambda}\sum_{q=1}^{\mu}\sum_{r=1}^{\nu} f_{ijk}^{pqr} \qquad && \lambda\mu\nu < 222 \\ F_{ijk}^{222} &= 0 \\ F_{ijk}^{\lambda\mu\nu} &= \pm F_{ijk}^{4-\lambda,4-\mu,4-\nu} \qquad && \lambda\mu\nu > 222, \end{aligned}$$

reading $\lambda\mu\nu$ as a three-digit number and with the same interpretation of $\pm$ as before. There is only a single independent sublattice tensor component in the $\bar{6}m2$ set, which may be taken as $f_{222}^{\alpha\beta\gamma}$. As the three subscripts are equal, the commutative property of differentiation implies that all components with permuted superscripts are equal. This property carries over to the inner elastic constants $F_{ijk}^{\lambda\mu\nu}$ and reduces the number of independent constants to three and renders six more zero. For the $6mm$ set the component $f_{333}^{\alpha\beta\gamma}$ gives the same result. The remaining three independent components each permit the interchange of a different pair of superscripts. The net result is that six $F_{113}^{\lambda\mu\nu}$ may be chosen as independent and the remaining components $F_{131}^{\lambda\mu\nu}$ and $F_{311}^{\lambda\mu\nu}$ related to them. All these results are embodied in table 6.

All the components of the second-order e-tensors and most of those of the third order belong in common to $3m$, $\bar{3}m$, $\bar{6}m2$, and $6mm$ symmetry, the remainder to $\bar{3}m$ and $3m$ only. The difference between these sets lies in the effect of the symmetry operations on the signs of individual components: in the main set the (uncontracted) subscript sequences have the form ii, $iiii$, $iijj$, or $ijij$ and the components do not change sign under any operation; in the residual set the sequences are $iijk$, $ijik$, $ijii$, or $ijkk$ (one 3 and an odd number of 2s, in fact) and the components change sign under operations in rows 3 and 4 of table 5. In the main set attention therefore focuses on difference tensors, such as $e_{ij.}^{11} - e_{ij.}^{22}$, whose signs are reversed by operations in rows 2, 3, and 4 of the table. This shows that all such difference tensors are null and thus that

$$\begin{aligned} e_{ij.}^{11} &= e_{ij.}^{22} = \pm e_{ij.}^{33} = \pm e_{ij.}^{44} \\ e_{ij.}^{12} &= e_{ij.}^{21} = \pm e_{ij.}^{34} = \pm e_{ij.}^{43} \\ e_{ij.}^{13} &= e_{ij.}^{24} = \pm e_{ij.}^{31} = \pm e_{ij.}^{42} \\ e_{ij.}^{14} &= e_{ij.}^{23} = \pm e_{ij.}^{32} = \pm e_{ij.}^{41} \end{aligned}$$

where the plus signs are taken throughout. The residual set of third-order terms gives rise to the minus signs via the nullification of sum tensors, such as $e_{ij.}^{11} + e_{ij.}^{33}$ and $e_{ij.}^{23} + e_{ij.}^{32}$, by the operations of rows 3 and 4 in table 5.

The inner elastic constants follow from (2) or (4) and (3). Independent and dependent constants for the main set are

$$E_{ij.}^{11} = e_{ij.}^{11}$$

Table 6. Interrelation of components of the inner elastic constants of hD. The left-hand elements in column 1 and the lower part of column 2, associated with the subscript sequence in column 2 if any, may be taken as an independent set. The full sets of non-zero components are obtained by reading columns 1 and 2 in conjunction with the appropriate relations in table 3. All components D^2_{iJ}, D^2_{iJK} and F^{222}_{ijk} are zero.

$D^1_3 = -D^3_3$	
$D^1_{16} = D^3_{16}$	
$D^1_{iJ} = -D^3_{iJ}$	$iJ = 15, 31, 33$
$E^{11}_{ii} = E^{33}_{ii}$	$ii = 11, 33$
$E^{12}_{ii} = E^{21}_{ii} = \frac{1}{2}E^{22}_{ii} = E^{23}_{ii} = E^{32}_{ii}$	$ii = 11, 33$
$E^{13}_{ii} = E^{31}_{ii}$	$ii = 11, 33$
$D^1_{iJK} = D^1_{iKJ} = D^3_{iJK} = D^3_{iKJ}$	$iJK = 116, 126, 136, 145, 314$
$D^1_{iJK} = D^1_{iKJ} = -D^3_{iJK} = -D^3_{iKJ}$	$iJK = 115, 125, 135, 311, 312, 313, 333, 344$
$E^{11}_{ijK} = E^{33}_{ijK}$	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
$E^{12}_{ijK} = E^{21}_{ijK} = \frac{1}{2}E^{22}_{ijK} = E^{23}_{ijK} = E^{32}_{ijK}$	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
$E^{13}_{ijK} = E^{31}_{ijK}$	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
$E^{11}_{ijK} = -E^{33}_{ijK}$	$ijK = 114, 136, 316$
$E^{13}_{ijK} = -E^{31}_{ijK}$	$ijK = 114, 136, 316$
$F^{111}_{112} = F^{333}_{112}$	
$F^{112}_{112} = F^{121}_{112} = F^{122}_{112} = F^{211}_{112} = F^{212}_{112} = F^{221}_{112}$	
$= F^{123}_{112} = F^{132}_{112} = F^{213}_{112} = F^{231}_{112} = F^{312}_{112} = F^{321}_{112}$	
$= F^{223}_{112} = F^{232}_{112} = F^{233}_{112} = F^{322}_{112} = F^{323}_{112} = F^{332}_{112}$	
$F^{113}_{112} = F^{131}_{112} = F^{133}_{112} = F^{311}_{112} = F^{313}_{112} = F^{331}_{112}$	
$F^{111}_{113} = -F^{333}_{113}$	
$F^{112}_{113} = F^{122}_{113} = F^{212}_{113} = -F^{232}_{113} = -F^{322}_{113} = -F^{332}_{113}$	
$F^{113}_{113} = -F^{331}_{113}$	
$F^{121}_{113} = F^{211}_{113} = -F^{233}_{113} = -F^{323}_{113}$	
$F^{123}_{113} = F^{213}_{113} = -F^{231}_{113} = -F^{321}_{113}$	
$F^{131}_{113} = -F^{133}_{113} = F^{311}_{113} = -F^{313}_{113}$	
$F^{221}_{113} = -F^{223}_{113}$	
$F^{111}_{333} = -F^{333}_{333}$	
$F^{112}_{333} = F^{121}_{333} = F^{122}_{333} = F^{211}_{333} = F^{212}_{333} = F^{221}_{333}$	
$= -F^{223}_{333} = -F^{232}_{333} = -F^{233}_{333} = -F^{322}_{333} = -F^{323}_{333} = -F^{332}_{333}$	
$F^{113}_{333} = F^{131}_{333} = -F^{133}_{333} = F^{311}_{333} = -F^{313}_{333} = -F^{331}_{333}$	

$$
\begin{aligned}
E^{12}_{ij.} &= e^{11}_{ij.} + e^{12}_{ij.} \\
E^{13}_{ij.} &= -e^{14}_{ij.} \\
E^{22}_{ij.} &= 2E^{12}_{ij.} \\
E^{21}_{ij.} &= E^{23}_{ij.} = E^{32}_{ij.} = E^{12}_{ij.} \\
E^{31}_{ij.} &= E^{13}_{ij.} \\
E^{33}_{ij.} &= E^{11}_{ij.}
\end{aligned}
$$

and for the residual set are

$$
\begin{aligned}
E^{11}_{ij.} &= e^{11}_{ij.} \\
E^{13}_{ij.} &= -e^{14}_{ij.} \\
E^{12}_{ij.} &= E^{21}_{ij.} = E^{22}_{ij.} = E^{23}_{ij.} = E^{32}_{ij.} = 0 \\
E^{31}_{ij.} &= -E^{13}_{ij.} \\
E^{33}_{ij.} &= -E^{11}_{ij.}.
\end{aligned}
$$

This completes the analysis for hD.

3.2.2. Hexagonal graphite. The arguments for hG are largely a repeat of those above but with outcomes that differ because the basis consists of two non-equivalent pairs rather than a single quartet. All the individual d-, e-, and f-tensors have $\bar{6}m2$ symmetry. Operations in rows 1 to 4 combined constitute $P6_3/mmc$ and all elements of sum tensors, such as $d^1_{i..} + d^2_{i..}$, vanish as the associated point group $6/mmm$ is centrosymmetric. Thus

$$
\begin{aligned}
d^1_{i..} + d^2_{i..} &= 0 \\
d^3_{i..} + d^4_{i..} &= 0
\end{aligned}
$$

with no further interrelations. Thus, using (2) and (3),

$$
\begin{aligned}
D^1_{i..} &= -d^1_{i..} \\
D^2_{i..} &= 0 \\
D^3_{i..} &= +d^4_{i..}
\end{aligned}
$$

giving two independent inner elastic constants where hD had one.

For the f-tensors there are sixteen pairs of relations:

$$
\begin{array}{lcllcl}
f^{111}_{ijk} & = & -f^{222}_{ijk} & f^{333}_{ijk} & = & -f^{444}_{ijk} \\
f^{112}_{ijk} & = & -f^{221}_{ijk} & f^{334}_{ijk} & = & -f^{443}_{ijk} \\
\vdots & & & \vdots & & \\
f^{144}_{ijk} & = & -f^{233}_{ijk} & f^{322}_{ijk} & = & -f^{411}_{ijk}.
\end{array}
$$

In conjunction with (2)–(4) it is found that the independent and zero elements are

$$
\begin{aligned}
F^{111}_{ijk} &= -f^{111}_{ijk} \\
F^{112}_{ijk} &= -(f^{111}_{ijk} + f^{112}_{ijk}) \\
F^{113}_{ijk} &= +f^{114}_{ijk} \\
F^{123}_{ijk} &= +(f^{114}_{ijk} + f^{124}_{ijk}) \\
F^{133}_{ijk} &= -f^{144}_{ijk} \\
F^{223}_{ijk} &= -(f^{144}_{ijk} + f^{244}_{ijk}) \\
F^{333}_{ijk} &= +f^{444}_{ijk} \\
F^{222}_{ijk} &= 0.
\end{aligned}
$$

The numerous dependent elements, related by permutation of superscripts for the reason given above for hD, are displayed in table 6.

The analysis of the e- and E-tensors follows that of the main group in hD though with a slightly different outcome:

$$\begin{aligned}
E^{11}_{ij.} &= e^{11}_{ij.} \\
E^{12}_{ij.} &= e^{11}_{ij.} + e^{12}_{ij.} \\
E^{13}_{ij.} &= -e^{14}_{ij.} \\
E^{22}_{ij.} &= 2E^{12}_{ij.} \\
E^{21}_{ij.} &= E^{23}_{ij.} = E^{32}_{ij.} = E^{12}_{ij.} \\
E^{31}_{ij.} &= -e^{41}_{ij.} \\
E^{33}_{ij.} &= e^{44}_{ij.}.
\end{aligned}$$

This concludes the analysis for hG.

4. Internal strain tensors

The inner displacement vectors ζ^λ are related to the finite strain η by

$$\zeta^\lambda_i = A^\lambda_{iJ}\eta_J + \tfrac{1}{2}A^\lambda_{iJK}\eta_J\eta_K \tag{5}$$

where the *internal strain tensors* A^λ_{iJ} and A^λ_{iJK} are 3×6 and $3 \times 6 \times 6$ arrays respectively. The symmetry of these tensors is the same as that of the D^λ-tensors and the elements that are non-zero for the structures under discussion can be read from tables 4, 6, or 7 as appropriate (except that the condition $A^2_{iJ} = 0$ does not always apply, as shown below). In principle these tensors may be determined experimentally by analysing x-ray diffraction from stressed single crystals. In practice the measurements are either difficult because the effect is very small, as in cD [11], or impossible because a sufficiently large single crystal cannot be obtained, as in hG, rG, and hD. Theoretically their values may be obtained from internal equilibrium conditions, which have the form [2]

$$D^\lambda_{iJ} + E^{\lambda\mu}_{ij}A^\mu_{jJ} = 0 \tag{6}$$

at the second order and

$$D^\lambda_{iJK} + E^{\lambda\mu}_{ijJ}A^\mu_{jK} + E^{\lambda\mu}_{ijK}A^\mu_{jJ} + F^{\lambda\mu\nu}_{ijk}A^\mu_{jJ}A^\nu_{kK} + E^{\lambda\mu}_{ij}A^\mu_{jJK} = 0 \tag{7}$$

at the third. If a composite inner elastic constant is defined through

$$G^\lambda_{iJK} \equiv D^\lambda_{iJK} + E^{\lambda\mu}_{ijJ}A^\mu_{jK} + E^{\lambda\mu}_{ijK}A^\mu_{jJ} + F^{\lambda\mu\nu}_{ijk}A^\mu_{jJ}A^\nu_{kK},$$

then (7) takes the form

$$G^\lambda_{iJK} + E^{\lambda\mu}_{ij}A^\mu_{jJK} = 0$$

and its solution parallels that of (6). Apart from the case of cD, only the independent linear tensor components will be given in the following lists.

4.1. Cubic diamond

Equation (6) yields a single linear component given by

$$A_{14} = -D_{14}/E_{11} \tag{8}$$

and (7) gives three quadratic components

$$\begin{aligned}
A_{114} &= -G_{114}/E_{11} \\
A_{124} &= -G_{124}/E_{11} \\
A_{156} &= -G_{156}/E_{11}
\end{aligned} \tag{9}$$

Table 7. Interrelation of components of the inner elastic constants of hG. The left-hand elements in column 1, associated with the subscript sequence in column 2 if any, may be taken as an independent set. The full sets of non-zero components are obtained by reading columns 1 and 2 in conjunction with the appropriate relations in table 3. All components D^2_{iJ}, D^2_{iJK}, and F^{222}_{ijk} are zero.

D^1_{16}	
D^3_{16}	
E^{11}_{ii}	$ii = 11, 33$
$E^{12}_{ii} = E^{21}_{ii} = \frac{1}{2}E^{22}_{ii} = E^{23}_{ii} = E^{32}_{ii}$	$ii = 11, 33$
$E^{13}_{ii} = E^{31}_{ii}$	$ii = 11, 33$
E^{33}_{ii}	$ii = 11, 33$
$D^1_{iJK} = D^1_{iKJ}$	$iJK = 116, 126, 136, 145, 212, 314$
$D^3_{iJK} = D^3_{iKJ}$	$iJK = 116, 126, 136, 145, 212, 314$
E^{11}_{ijK}	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
$E^{12}_{ijK} = E^{21}_{ijK} = \frac{1}{2}E^{22}_{ijK} = E^{23}_{ijK} = E^{32}_{ijK}$	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
$E^{13}_{ijK} = E^{31}_{ijK}$	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
E^{33}_{ijK}	$ijK = 111, 112, 113, 126, 135, 315, 331, 333$
F^{111}_{112}	
$F^{112}_{112} = F^{121}_{112} = F^{122}_{112} = F^{211}_{112} = F^{212}_{112} = F^{221}_{112}$	
$F^{113}_{112} = F^{131}_{112} = F^{311}_{112}$	
$F^{123}_{112} = F^{132}_{112} = F^{213}_{112} = F^{231}_{112} = F^{312}_{112} = F^{321}_{112}$	
$F^{133}_{112} = F^{313}_{112} = F^{331}_{112}$	
$F^{223}_{112} = F^{232}_{112} = F^{322}_{112} = F^{233}_{112} = F^{323}_{112} = F^{332}_{112}$	
F^{333}_{112}	

in which

$$G_{114} = D_{114} + A_{14}E_{111}$$
$$G_{124} = D_{124} + A_{14}E_{112}$$
$$G_{156} = D_{156} + 2A_{14}E_{126} + (A_{14})^2 F_{123}.$$

4.2. Rhombohedral graphite

The four independent linear tensor components are

$$\begin{aligned} A_{16} &= -D_{16}/E_{11} \\ A_{15} &= -D_{15}/E_{11} \\ A_{31} &= -D_{31}/E_{33} \\ A_{33} &= -D_{33}/E_{33}. \end{aligned} \tag{10}$$

4.3. Hexagonal diamond

The solutions of (6) for hD, invoking the dependences to be found in table 6, lead to

$$\begin{aligned} A^1_{16} &= A^3_{16} = -D^1_{16}/(E^{11}_{11} - E^{12}_{11} + E^{13}_{11}) \\ A^1_{15} &= -A^3_{15} = -D^1_{15}/(E^{11}_{11} - E^{13}_{11}) \\ A^1_{31} &= -A^3_{31} = -D^1_{31}/(E^{11}_{33} - E^{13}_{33}) \\ A^1_{33} &= -A^3_{33} = -D^1_{33}/(E^{11}_{33} - E^{13}_{33}) \end{aligned} \tag{11}$$

with

$$A^2_{iJ} = -\tfrac{1}{2}(A^1_{iJ} + A^3_{iJ}). \tag{12}$$

4.4. Hexagonal graphite

The solutions of (6) for hG, invoking the dependences to be found in table 7, lead to

$$A^2_{iJ} = -\tfrac{1}{2}(A^1_{iJ} + A^3_{iJ})$$

in this case also. The independence of D^1 and D^3, however, leads to similarly independent A^1 and A^3 given by

$$A^1_{16} = \frac{(E^{33}_{11} - \frac{1}{2}E^{12}_{11})D^1_{16} - (E^{13}_{11} - \frac{1}{2}E^{12}_{11})D^3_{16}}{(E^{13}_{11} - \frac{1}{2}E^{12}_{11})^2 - (E^{11}_{11} - \frac{1}{2}E^{12}_{11})(E^{33}_{11} - \frac{1}{2}E^{12}_{11})} \tag{13}$$

and

$$A^3_{16} = \frac{(E^{11}_{11} - \frac{1}{2}E^{12}_{11})D^3_{16} - (E^{13}_{11} - \frac{1}{2}E^{12}_{11})D^1_{16}}{(E^{13}_{11} - \frac{1}{2}E^{12}_{11})^2 - (E^{11}_{11} - \frac{1}{2}E^{12}_{11})(E^{33}_{11} - \frac{1}{2}E^{12}_{11})}. \tag{14}$$

The inner displacement is confined to the basal plane in hG.

5. Zone-centre optic modes

The frequencies of the optical modes at the zone centre may be obtained from the $E^{\lambda\mu}$-tensors. The relationship between these tensors and the more familiar coupling constants $\Phi^{\alpha\beta}$ was demonstrated in [2, section 5]:

$$E^{\lambda\mu}_{ij} = \tilde{Q}^{\lambda\alpha}\Phi^{\alpha\beta}_{ij}Q^{\beta\mu}$$

where

$$Q = \begin{bmatrix} \mu_1 - 1 & \mu_2 - 1 & \cdots & \mu_{n-1} - 1 \\ \mu_1 & \mu_2 - 1 & \cdots & \mu_{n-1} - 1 \\ \vdots & \vdots & \vdots & \vdots \\ \mu_1 & \mu_2 & \cdots & \mu_{n-1} - 1 \\ \mu_1 & \mu_2 & \cdots & \mu_{n-1} \end{bmatrix}$$

is an $n \times (n-1)$ rectangular matrix in which $\mu_k = (\sum_{p=1}^{k} m_p)/(\sum_{p=1}^{n} m_p)$, m_p being the mass of the atom on sublattice p and n the number of sublattices. In the present context all the masses are equal and $\mu_k = k/n$.

The secular equation of lattice dynamics transforms into a determinant relating to optical modes alone:

$$|E^{\lambda\mu}_{ij} - \omega^2 K^{\lambda\mu}\delta_{ij}| = 0 \tag{15}$$

where $K^{\lambda\mu} = \tilde{Q}^{\lambda\alpha}\rho^{\alpha\beta}Q^{\beta\mu}$ is an element of an $(n-1) \times (n-1)$ density matrix and ρ is a diagonal $n \times n$ matrix given by

$$\rho = \rho_0 \begin{bmatrix} \mu_1 & \cdot & \cdots & \cdot & \cdot \\ \cdot & \mu_2 - \mu_1 & \cdots & \cdot & \cdot \\ \vdots & \vdots & \vdots\vdots\vdots & \vdots & \vdots \\ \cdot & \cdot & \cdots & \mu_{n-1} - \mu_{n-2} & \cdot \\ \cdot & \cdot & \cdots & \cdot & 1 - \mu_{n-1} \end{bmatrix}.$$

Again the condition of equal masses brings simplification: every element is equal to $1/n$ and $\rho = (\rho_0/n)I_n$, where I_n is the $n \times n$ unit matrix.

In general, to each value of ω^2 there corresponds an eigenvector given by

$$E_{ij}^{\lambda\mu} z_j^{\mu} = \omega^2 K^{\lambda\mu} z_i^{\mu}. \tag{16}$$

For cD and rG it is taken as a normalized relative sublattice displacement vector $\vec{z}$ whilst for hD and hG it is Z, a triad of such vectors: $Z = [\vec{z}^1, \vec{z}^2, \vec{z}^3]$.

Where relevant the mode frequencies have been labelled with subscripts R or I to indicate Raman or infra-red activity.

5.1. Cubic diamond and rhombohedral graphite

For both cD and rG, Q is the column vector $[-\frac{1}{2}/\frac{1}{2}]$ and K reduces to the scalar $\rho_0/4$. As E is diagonal, the secular equation for optic modes reduces to

$$|E_{11} - \tfrac{1}{4}\rho_0\omega^2|^3 = 0$$

for cD, giving the triply degenerate frequency

$$\omega_R^2(\mathrm{T_{2g}}) = \frac{4}{\rho_0} E_{11}. \tag{17}$$

The eigenvectors are indeterminate: a set such as $\vec{z} = [1, 0, 0]$, $\vec{z} = [0, 1, 0]$, and $\vec{z} = [0, 0, 1]$ could be chosen to represent an LO mode and two TO modes in the limit $\vec{k} \to 0$ along one of the cubic axes. For rG the equation reduces to

$$|E_{11} - \tfrac{1}{4}\rho_0\omega^2|^2 \, |E_{33} - \tfrac{1}{4}\rho_0\omega^2| = 0$$

giving a doubly degenerate frequency

$$\omega_R^2(\mathrm{E_g}) = \frac{4}{\rho_0} E_{11} \tag{18}$$

with eigenvectors $\vec{z} = [\cos\theta, \sin\theta, 0]$ with arbitrary θ and a non-degenerate one

$$\omega_R^2(\mathrm{A_{1g}}) = \frac{4}{\rho_0} E_{33} \tag{19}$$

whose eigenvector is $\vec{z} = [0, 0, 1]$. This and two values of θ differing by $\pi/2$ will then represent an LO mode and two TO modes in the limit $\vec{k} \to 0$ along the unique axis or any direction perpendicular to it. All other directions see a mixing of longitudinal and transverse character.

5.2. Hexagonal diamond

When $n = 4$, Q and K are given by

$$Q = \frac{1}{4}\begin{bmatrix} -3 & -2 & -1 \\ 1 & -2 & -1 \\ 1 & 2 & -1 \\ 1 & 2 & 3 \end{bmatrix}$$

and

$$K = \frac{\rho_0}{16}\begin{bmatrix} 3 & 2 & 1 \\ 2 & 4 & 2 \\ 1 & 2 & 3 \end{bmatrix}.$$

The resulting secular equation is a product of three 3×3 subdeterminants

$$|\Delta_1| \, |\Delta_2| \, |\Delta_3| = 0$$

where the matrix Δ_i is

$$\Delta_i = \begin{bmatrix} E_{ii}^{11} - \frac{3}{16}\rho_0\omega^2 & E_{ii}^{12} - \frac{1}{8}\rho_0\omega^2 & E_{ii}^{13} - \frac{1}{16}\rho_0\omega^2 \\ E_{ii}^{12} - \frac{1}{8}\rho_0\omega^2 & 2(E_{ii}^{12} - \frac{1}{8}\rho_0\omega^2) & E_{ii}^{12} - \frac{1}{8}\rho_0\omega^2 \\ E_{ii}^{13} - \frac{1}{16}\rho_0\omega^2 & E_{ii}^{12} - \frac{1}{8}\rho_0\omega^2 & E_{ii}^{33} - \frac{3}{16}\rho_0\omega^2 \end{bmatrix}$$

and symmetry imposes $\Delta_1 = \Delta_2$. Each of the subdeterminants factorizes into a linear and quadratic part: the repeated determinant has the roots

$$\begin{aligned} \omega^2(\mathrm{E_{2u}}) &= \frac{8}{\rho_0}E_{11}^{12} \\ \omega_R^2(\mathrm{E_{1g}}) &= \frac{8}{\rho_0}(E_{11}^{11} - E_{11}^{13}) \\ \omega_R^2(\mathrm{E_{2g}}) &= \frac{8}{\rho_0}(E_{11}^{11} - E_{11}^{12} + E_{11}^{13}) \end{aligned} \tag{20}$$

resulting in three degenerate pairs of frequencies. The third determinant has the same form and gives

$$\begin{aligned} \omega^2(\mathrm{B_{1u}}) &= \frac{8}{\rho_0}E_{33}^{12} \\ \omega_R^2(\mathrm{A_{1g}}) &= \frac{8}{\rho_0}(E_{33}^{11} - E_{33}^{13}) \\ \omega^2(\mathrm{B_{2g}}) &= \frac{8}{\rho_0}(E_{33}^{11} - E_{33}^{12} + E_{33}^{13}) \end{aligned} \tag{21}$$

for the remaining frequencies.

The ith components of the $\vec{z}^{\lambda}$ for a specific mode are the solutions of $|\Delta_i[z_i^1, z_i^2, z_i^3]| = 0$ when ω^2 in Δ_i has been replaced by its eigenvalue. The results for the above modes are

$$Z(\mathrm{E_{2u}}) = [[0,0,0],[\cos\theta,\sin\theta,0],[0,0,0]]$$

$$Z(\mathrm{E_{1g}}) = \left[\left[\frac{1}{\sqrt{2}}\cos\theta, \frac{1}{\sqrt{2}}\sin\theta, 0\right], [0,0,0], \left[-\frac{1}{\sqrt{2}}\cos\theta, -\frac{1}{\sqrt{2}}\sin\theta, 0\right]\right]$$

$$Z(\mathrm{E_{2g}}) = \left[\left[\frac{1}{\sqrt{3}}\cos\theta, \frac{1}{\sqrt{3}}\sin\theta, 0\right], \left[-\frac{1}{\sqrt{3}}\cos\theta, -\frac{1}{\sqrt{3}}\sin\theta, 0\right], \left[\frac{1}{\sqrt{3}}\cos\theta, \frac{1}{\sqrt{3}}\sin\theta, 0\right]\right]$$

$$Z(\mathrm{B_{1u}}) = [[0,0,0],[0,0,1],[0,0,0]]$$

$$Z(\mathrm{A_{1g}}) = \left[\left[0,0,\frac{1}{\sqrt{2}}\right], [0,0,0], \left[0,0,-\frac{1}{\sqrt{2}}\right]\right]$$

$$Z(\mathrm{B_{2g}}) = \left[\left[0,0,\frac{1}{\sqrt{3}}\right], \left[0,0,-\frac{1}{\sqrt{3}}\right], \left[0,0,\frac{1}{\sqrt{3}}\right]\right].$$

Vibrational patterns corresponding to these eigenvectors are shown in figure 2.

5.3. Hexagonal graphite

The hexagonal allotropes have identical complements of components $E_{ii}^{\lambda\mu}$ and thus the same secular equation. The only difference arises from the dependency $E_{ii}^{11} = E_{ii}^{33}$ that holds for hD

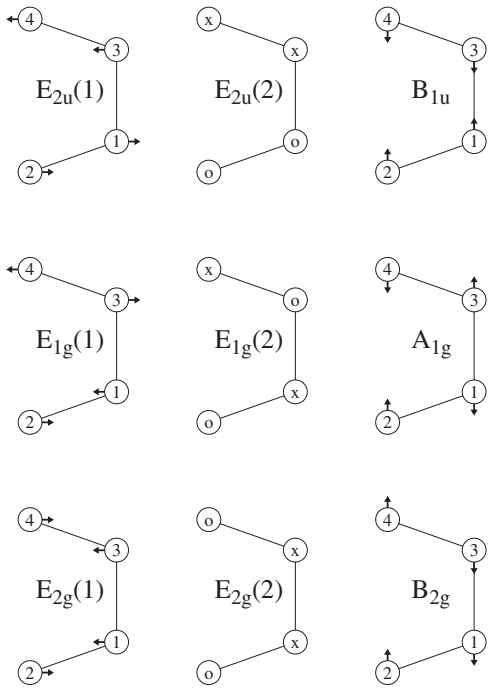

Figure 2. A representative set of vibration patterns for hD. 'x' and 'o' indicate motions into and out of the page.

but not for hG. This is responsible for the slightly more complicated expressions that follow. The three degenerate pairs of frequencies are given by

$$\begin{aligned}\omega_I^2(\mathrm{E_{1u}}) &= \frac{8}{\rho_0}E_{11}^{12}\\ \omega_R^2(\mathrm{E_{2g2}}) &= \frac{4}{\rho_0}[E_{11}^{11} - E_{11}^{12} + E_{11}^{33} + E_{11}^{\dagger}]\\ \omega_R^2(\mathrm{E_{2g1}}) &= \frac{4}{\rho_0}[E_{11}^{11} - E_{11}^{12} + E_{11}^{33} - E_{11}^{\dagger}]\end{aligned} \tag{22}$$

where

$$(E_{11}^{\dagger})^2 = (E_{11}^{12} - 2E_{11}^{13})^2 + (E_{11}^{11} - E_{11}^{33})^2$$

and the three non-degenerate frequencies by

$$\begin{aligned}\omega_I^2(\mathrm{A_{2u}}) &= \frac{8}{\rho_0}E_{33}^{12}\\ \omega_R^2(\mathrm{B_{1g2}}) &= \frac{4}{\rho_0}[E_{33}^{11} - E_{33}^{12} + E_{33}^{33} + E_{33}^{\dagger}]\\ \omega_R^2(\mathrm{B_{1g1}}) &= \frac{4}{\rho_0}[E_{33}^{11} - E_{33}^{12} + E_{33}^{33} - E_{33}^{\dagger}]\end{aligned} \tag{23}$$

where

$$(E_{33}^{\dagger})^2 = (E_{33}^{12} - 2E_{33}^{13})^2 + (E_{33}^{11} - E_{33}^{33})^2.$$

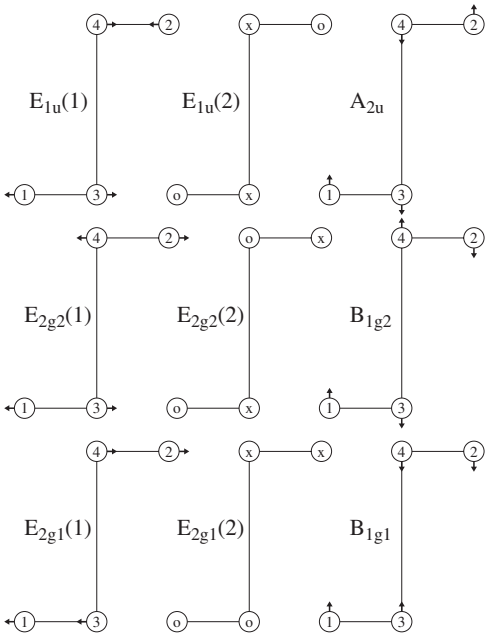

Figure 3. A representative set of vibration patterns for hG. 'x' and 'o' indicate motions into and out of the page.

The eigenvectors for the E_{1u} and A_{2u} modes have the same form as their hD counterparts. The remainder are slightly less constrained: the parameters a and b are, in every case, arbitrary;

$Z(E_{1u}) = [[0, 0, 0], [\cos\theta, \sin\theta, 0], [0, 0, 0]]$

$Z(E_{2g2}) = [[a\cos\theta, a\sin\theta, 0], [\frac{1}{2}(b-a)\cos\theta, \frac{1}{2}(b-a)\sin\theta, 0], [-b\cos\theta, -b\sin\theta, 0]]$

$Z(E_{2g1}) = [[a\cos\theta, a\sin\theta, 0], [-\frac{1}{2}(a+b)\cos\theta, -\frac{1}{2}(a+b)\sin\theta, 0], [b\cos\theta, b\sin\theta, 0]]$

$Z(A_{2u}) = [[0, 0, 0], [0, 0, 1], [0, 0, 0]]$

$Z(B_{1g2}) = [[0, 0, a], [0, 0, \frac{1}{2}(b-a)], [0, 0, -b]]$

$Z(B_{1g1}) = [[0, 0, a], [0, 0, -\frac{1}{2}(a+b)], [0, 0, b]].$

Vibrational patterns corresponding to these eigenvectors are shown in figure 3.

The present approach has been checked against the traditional lattice dynamical treatment of hG by Maradudin [12]. After allowing for a different labelling of sublattices, agreement is total.

6. Effective inner elastic constants

When an initially strained crystal is further deformed, its energy can be expressed in two ways: either in terms of the additional deformation and 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, in the context of the macroscopic elastic constants, by Wallace in [13, section 8] and is readily extended to cover the microscopic constants.

The effective E-tensors, denoted by $\bar{E}_{ij}^{\lambda\mu}$, may be used in the secular equation (with the appropriate density ρ) to obtain the optic mode frequencies in stressed crystals. Strains can be chosen to introduce off-diagonal elements and remove degeneracies. Phonon deformation

parameters, which characterize the strain dependence of the frequency [14, 15], are easily derived from the $\bar{E}$-tensors below. It will be seen that these expressions can be very lengthy. The results for the simplest case, that of hydrostatic pressure, are presented in section 7.

6.1. Cubic diamond

$$\begin{aligned}
\bar{E}_{11} &= E_{11}(1+\eta_1-\eta_2-\eta_3)+E_{111}\eta_1+E_{112}(\eta_2+\eta_3)\\
\bar{E}_{22} &= E_{11}(1-\eta_1+\eta_2-\eta_3)+E_{111}\eta_2+E_{112}(\eta_1+\eta_3)\\
\bar{E}_{33} &= E_{11}(1-\eta_1-\eta_2+\eta_3)+E_{111}\eta_3+E_{112}(\eta_1+\eta_2)\\
\bar{E}_{12} &= (E_{11}+E_{126}+A_{14}F_{123})\eta_6\\
\bar{E}_{13} &= (E_{11}+E_{126}+A_{14}F_{123})\eta_5\\
\bar{E}_{23} &= (E_{11}+E_{126}+A_{14}F_{123})\eta_4.
\end{aligned} \tag{24}$$

6.2. Rhombohedral graphite

$$\begin{aligned}
\bar{E}_{11} &= E_{11}(1+\eta_1-\eta_2-\eta_3)+E_{111}\eta_1+E_{112}\eta_2+E_{113}\eta_3+E_{114}\eta_4\\
&\quad +F_{112}A_{16}(\eta_1-\eta_2)+F_{113}(A_{31}(\eta_1+\eta_2)+A_{33}\eta_3)\\
\bar{E}_{12} &= \bar{E}_{21}=E_{11}\eta_6+E_{114}\eta_5+E_{126}\eta_6+F_{112}A_{16}\eta_6\\
\bar{E}_{13} &= \tfrac{1}{2}(E_{11}+E_{33})\eta_5+E_{135}\eta_5+E_{136}\eta_6+F_{113}A_{16}\eta_6\\
\bar{E}_{22} &= E_{11}(1-\eta_1+\eta_2-\eta_3)+E_{111}\eta_2+E_{112}\eta_1+E_{113}\eta_3-E_{114}\eta_4\\
&\quad -F_{112}A_{16}(\eta_1-\eta_2)+F_{113}(A_{31}(\eta_1+\eta_2)+A_{33}\eta_3)\\
\bar{E}_{23} &= \tfrac{1}{2}(E_{11}+E_{33})\eta_4+E_{135}\eta_4+E_{136}(\eta_1+\eta_2)+F_{113}A_{16}(\eta_1-\eta_2)\\
\bar{E}_{31} &= \tfrac{1}{2}(E_{11}+E_{33})\eta_5+E_{315}\eta_5+E_{316}\eta_6+F_{113}A_{16}\eta_6\\
\bar{E}_{32} &= \tfrac{1}{2}(E_{11}+E_{33})\eta_4+E_{315}\eta_4+E_{316}(\eta_1+\eta_2)+F_{113}A_{16}(\eta_1-\eta_2)\\
\bar{E}_{33} &= E_{33}(1-\eta_1-\eta_2+\eta_3)+E_{331}(\eta_1+\eta_2)+E_{333}\eta_3+F_{333}(A_{31}(\eta_1+\eta_2)+A_{33}\eta_3).
\end{aligned} \tag{25}$$

6.3. Hexagonal diamond

$$\begin{aligned}
\bar{E}^{\lambda\mu}_{11} &= E^{\lambda\mu}_{11}(1+\eta_1-\eta_2-\eta_3)+E^{\lambda\mu}_{111}\eta_1+E^{\lambda\mu}_{112}\eta_2+E^{\lambda\mu}_{113}\eta_3+E^{\lambda\mu}_{114}\eta_4\\
&\quad +F^{\lambda\mu\nu}_{112}A^{\nu}_{16}(\eta_1-\eta_2)+F^{\lambda\mu\nu}_{113}(A^{\nu}_{31}(\eta_1+\eta_2)+A^{\nu}_{33}\eta_3)\\
\bar{E}^{\lambda\mu}_{12} &= \bar{E}^{\lambda\mu}_{21}=E^{\lambda\mu}_{11}\eta_6+E^{\lambda\mu}_{114}\eta_5+E^{\lambda\mu}_{126}\eta_6+F^{\lambda\mu\nu}_{112}A^{\nu}_{16}\eta_6\\
\bar{E}^{\lambda\mu}_{13} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_5+E^{\lambda\mu}_{135}\eta_5+E^{\lambda\mu}_{136}\eta_6+F^{\lambda\mu\nu}_{131}A^{\nu}_{16}\eta_6\\
\bar{E}^{\lambda\mu}_{22} &= E^{\lambda\mu}_{11}(1-\eta_1+\eta_2-\eta_3)+E^{\lambda\mu}_{111}\eta_2+E^{\lambda\mu}_{112}\eta_1+E^{\lambda\mu}_{113}\eta_3-E^{\lambda\mu}_{114}\eta_4\\
&\quad -F^{\lambda\mu\nu}_{112}A^{\nu}_{16}(\eta_1-\eta_2)+F^{\lambda\mu\nu}_{113}(A^{\nu}_{31}(\eta_1+\eta_2)+A^{\nu}_{33}\eta_3)\\
\bar{E}^{\lambda\mu}_{23} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_4+E^{\lambda\mu}_{135}\eta_4+E^{\lambda\mu}_{136}(\eta_1+\eta_2)+F^{\lambda\mu\nu}_{131}A^{\nu}_{16}(\eta_1-\eta_2)\\
\bar{E}^{\lambda\mu}_{31} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_5+E^{\lambda\mu}_{315}\eta_5+E^{\lambda\mu}_{316}\eta_6+F^{\lambda\mu\nu}_{311}A^{\nu}_{16}\eta_6\\
\bar{E}^{\lambda\mu}_{32} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_4+E^{\lambda\mu}_{315}\eta_4+E^{\lambda\mu}_{316}(\eta_1+\eta_2)+F^{\lambda\mu\nu}_{311}A^{\nu}_{16}(\eta_1-\eta_2)\\
\bar{E}^{\lambda\mu}_{33} &= E^{\lambda\mu}_{33}(1-\eta_1-\eta_2+\eta_3)+E^{\lambda\mu}_{331}(\eta_1+\eta_2)+E^{\lambda\mu}_{333}\eta_3+F^{\lambda\mu\nu}_{333}(A^{\nu}_{31}(\eta_1+\eta_2)+A^{\nu}_{33}\eta_3).
\end{aligned} \tag{26}$$

6.4. Hexagonal graphite

$$\begin{aligned}
\bar{E}^{\lambda\mu}_{11} &= E^{\lambda\mu}_{11}(1+\eta_1-\eta_2-\eta_3)+E^{\lambda\mu}_{111}\eta_1+E^{\lambda\mu}_{112}\eta_2+E^{\lambda\mu}_{113}\eta_3+F^{\lambda\mu\nu}_{112}A^{\nu}_{16}(\eta_1-\eta_2)\\
\bar{E}^{\lambda\mu}_{12} &= \bar{E}^{\lambda\mu}_{21}=E^{\lambda\mu}_{11}\eta_6+E^{\lambda\mu}_{126}\eta_6+F^{\lambda\mu\nu}_{112}A^{\nu}_{16}\eta_6\\
\bar{E}^{\lambda\mu}_{13} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_5+E^{\lambda\mu}_{135}\eta_5\\
\bar{E}^{\lambda\mu}_{22} &= E^{\lambda\mu}_{11}(1-\eta_1+\eta_2-\eta_3)+E^{\lambda\mu}_{111}\eta_2+E^{\lambda\mu}_{112}\eta_1+E^{\lambda\mu}_{113}\eta_3-F^{\lambda\mu\nu}_{112}A^{\nu}_{16}(\eta_1-\eta_2)\\
\bar{E}^{\lambda\mu}_{23} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_4+E^{\lambda\mu}_{135}\eta_4\\
\bar{E}^{\lambda\mu}_{31} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_5+E^{\lambda\mu}_{315}\eta_5\\
\bar{E}^{\lambda\mu}_{32} &= \tfrac{1}{2}(E^{\lambda\mu}_{11}+E^{\lambda\mu}_{33})\eta_4+E^{\lambda\mu}_{315}\eta_4\\
\bar{E}^{\lambda\mu}_{33} &= E^{\lambda\mu}_{33}(1-\eta_1-\eta_2+\eta_3)+E^{\lambda\mu}_{331}(\eta_1+\eta_2)+E^{\lambda\mu}_{333}\eta_3.
\end{aligned} \tag{27}$$

7. The pressure dependence of the optic mode frequencies

Under hydrostatic pressure, $\eta_4=\eta_5=\eta_6=0$, $\eta_1=\eta_2=\eta_3=-kp$ for cD and $\eta_1=\eta_2=-k_a p$, $\eta_3=-k_c p$ in the remaining three cases, where k, k_a, and k_c are linear compressibilities. These strains are inserted into the effective constants above, the effective constants into the appropriate eigenvalue equations (again with the appropriate density, which is also pressure dependent), and the latter differentiated with respect to p. No degeneracies are lifted by hydrostatic pressure.

Some composite constants are defined below in order to shorten the lengths of some of the expressions for hG and hD.

7.1. Cubic diamond

$$\frac{\mathrm{d}\omega^2_R(\mathrm{T_{2g}})}{\mathrm{d}p}=-\frac{4k}{\rho_0}(2E_{11}+E_{111}+2E_{112}). \tag{28}$$

7.2. Rhombohedral graphite

$$\begin{aligned}
\frac{\mathrm{d}\omega^2_R(\mathrm{E_g})}{\mathrm{d}p} &= -\frac{4}{\rho_0}(2k_aE_{11}+k_a(E_{111}+E_{112}+2F_{113}A_{31})+k_c(E_{113}+F_{113}A_{33}))\\
\frac{\mathrm{d}\omega^2_R(\mathrm{A_{1g}})}{\mathrm{d}p} &= -\frac{4}{\rho_0}(2k_cE_{33}+2k_a(E_{331}+F_{333}A_{31})+k_c(E_{333}+F_{333}A_{33})).
\end{aligned} \tag{29}$$

7.3. Hexagonal diamond

The composite constants are

$$\begin{aligned}
E^{aa}_{ii.} &\equiv E^{11}_{ii.}-E^{12}_{ii.}+E^{13}_{ii.}\\
E^{bb}_{ii.} &\equiv E^{11}_{ii.}-E^{13}_{ii.}\\
F^{aa\nu}_{ii3} &\equiv F^{11\nu}_{ii3}-F^{12\nu}_{ii3}+F^{13\nu}_{ii3}\\
F^{bb\nu}_{ii3} &\equiv F^{11\nu}_{ii3}-F^{13\nu}_{ii3}
\end{aligned}$$

and the pressure derivatives are

$$\begin{aligned}
\frac{\mathrm{d}\omega^2(\mathrm{E_{2u}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_a E^{12}_{11} + k_a(E^{12}_{111} + E^{12}_{112} + 2F^{12v}_{113}A^{v}_{31}) + k_c(E^{12}_{113} + F^{12v}_{113}A^{v}_{33})) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{E_{1g}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_a E^{aa}_{11} + k_a(E^{aa}_{111} + E^{aa}_{112} + 2F^{aav}_{113}A^{v}_{31}) + k_c(E^{aa}_{113} + F^{aav}_{113}A^{v}_{33})) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{E_{2g}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_a E^{bb}_{11} + k_a(E^{bb}_{111} + E^{bb}_{112} + 2F^{bbv}_{113}A^{v}_{31}) + k_c(E^{bb}_{113} + F^{bbv}_{113}A^{v}_{33}))
\end{aligned} \tag{30}$$

and

$$\begin{aligned}
\frac{\mathrm{d}\omega^2(\mathrm{B_{1u}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_c E^{12}_{33} + 2k_a(E^{12}_{331} + F^{12v}_{333}A^{v}_{31}) + k_c(E^{12}_{333} + F^{12v}_{333}A^{v}_{33})) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{A_{1g}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_c E^{aa}_{33} + 2k_a(E^{aa}_{331} + F^{aav}_{333}A^{v}_{31}) + k_c(E^{aa}_{333} + F^{aav}_{333}A^{v}_{33})) \\
\frac{\mathrm{d}\omega^2(\mathrm{B_{2g}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_c E^{bb}_{33} + 2k_a(E^{bb}_{331} + F^{bbv}_{333}A^{v}_{31}) + k_c(E^{bb}_{333} + A^{v}_{33}F^{bbv}_{333})).
\end{aligned} \tag{31}$$

7.4. Hexagonal graphite

The composite constant is

$$E^{cc}_{ii.} \equiv E^{11}_{ii.} - E^{12}_{ii.} + E^{33}_{ii.}$$

and the pressure derivatives are

$$\begin{aligned}
\frac{\mathrm{d}\omega^2_I(\mathrm{E_{1u}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_a E^{12}_{11} + k_a(E^{12}_{111} + E^{12}_{112}) + k_c E^{12}_{113}) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{E_{2g2}})}{\mathrm{d}p} &= -\frac{4}{\rho_0}\left(2k_a(E^{cc}_{11} + E^{\dagger}_{11}) + k_a(E^{cc}_{111} + E^{cc}_{112}) + k_c E^{cc}_{113} + \frac{\mathrm{d}\bar{E}^{\dagger}_{11}}{\mathrm{d}p}\right) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{E_{2g1}})}{\mathrm{d}p} &= -\frac{4}{\rho_0}\left(2k_a(E^{cc}_{11} - E^{\dagger}_{11}) + k_a(E^{cc}_{111} + E^{cc}_{112}) + k_c E^{cc}_{113} - \frac{\mathrm{d}\bar{E}^{\dagger}_{11}}{\mathrm{d}p}\right)
\end{aligned} \tag{32}$$

where

$$\begin{aligned}
\frac{\mathrm{d}\bar{E}^{\dagger}_{11}}{\mathrm{d}p} &= \frac{E^{12}_{11} - 2E^{13}_{11}}{E^{\dagger}_{11}}(k_a(E^{12}_{111} - 2E^{13}_{111} + E^{12}_{112} - 2E^{13}_{112}) + k_c(E^{12}_{113} - 2E^{13}_{113})) \\
&\quad + \frac{E^{11}_{11} - E^{33}_{11}}{E^{\dagger}_{11}}(k_a(E^{11}_{111} - E^{33}_{111} + E^{11}_{112} - E^{33}_{112}) + k_c(E^{11}_{113} - E^{33}_{113}))
\end{aligned}$$

and

$$\begin{aligned}
\frac{\mathrm{d}\omega^2_I(\mathrm{A_{2u}})}{\mathrm{d}p} &= -\frac{8}{\rho_0}(2k_c E^{12}_{33} + 2k_a E^{12}_{331} + k_c E^{12}_{333}) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{B_{1g2}})}{\mathrm{d}p} &= -\frac{4}{\rho_0}\left(2k_c(E^{cc}_{33} + E^{\dagger}_{33}) + 2k_a E^{cc}_{331} + k_c E^{cc}_{333} + \frac{\mathrm{d}\bar{E}^{\dagger}_{33}}{\mathrm{d}p}\right) \\
\frac{\mathrm{d}\omega^2_R(\mathrm{B_{1g1}})}{\mathrm{d}p} &= -\frac{4}{\rho_0}\left(2k_c(E^{cc}_{33} - E^{\dagger}_{33}) + 2k_a E^{cc}_{331} + k_c E^{cc}_{333} - \frac{\mathrm{d}\bar{E}^{\dagger}_{33}}{\mathrm{d}p}\right)
\end{aligned} \tag{33}$$

where

$$\begin{aligned}
\frac{\mathrm{d}\bar{E}^{\dagger}_{33}}{\mathrm{d}p} &= \frac{E^{12}_{33} - 2E^{13}_{33}}{E^{\dagger}_{33}}(2k_a(E^{12}_{331} - 2E^{13}_{331}) + k_c(E^{12}_{333} - 2E^{13}_{333})) \\
&\quad + \frac{E^{11}_{33} - E^{33}_{33}}{E^{\dagger}_{33}}(2k_a(E^{11}_{331} - E^{33}_{331}) + k_c(E^{11}_{333} - E^{33}_{333})).
\end{aligned}$$

8. Summary

The different microscopic tensors that arise in connection with the elasticity and with the frequencies and eigenvectors of the zone-centre optic modes in four carbon allotropes have been analysed in detail for the first time. Expressions for the internal strain tensor components have also been derived and may be seen to relate to the frequencies of the Raman-active modes. This illustrates a general symmetry requirement, first given by Miller and Axe [16], that only Raman-active modes contribute to the internal strain part of the elastic constants. These results are carried forward to the companion paper in which the macroscopic elasticity through the third order is subjected to similar detailed scrutiny. Finally the effective inner elastic constants under arbitrary strain have been determined and used to obtain the pressure derivatives of the optic mode frequencies.

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