Chapter 2

SECOND, THIRD AND FOURTH ORDER ELASTIC CONSTANTS
AND THE FIRST AND SECOND ORDER PRESSURE DERIVATIVES
OF SECOND ORDER ELASTIC CONSTANTS IN HEXAGONAL
CRYSTALS

2.1 Introduction

Knowledge of higher order elastic constants like the third and fourth order elastic constants is essential for the study of the anharmonic properties of solids. The macroscopic theory of higher order elastic constants is given by Murnaghan [1]. The thermodynamic definition of higher order elastic constants is proposed by Brugger [2] and the theory of third order elastic constants is given by Birch [3]. The hexagonal system has 6 second order, 10 third order, 19 fourth order elastic constants. Third order elastic constants find applications in the effect of temperature [4,5] and pressure [6] on elastic constants, thermal expansion and Grüneisen gammas [7,8] in crystals, lattice parameter changes and phase transitions [9,10], Brillouin scattering [11] and piezo elasticity [12].

Elastic constants provide insight into the nature of the binding forces between atoms since they are represented by the derivatives of the internal energy (adiabatic constants) or of the free energy (isothermal constants). The higher order elastic constants are indispensable for the finite strain elasticity theory of Murnaghan [1] where the variation of elastic strain is non-linear with elastic stress.
Finite strain is in practice, limited to a finite hydrostatic strain plus superimposed infinitesimal strain of arbitrary type. The hydrostatic strain affects the response of the medium to the infinitesimal additional strain giving rise to effect of pressure upon the elastic constants. So the effective elastic constants determine the response of the compressed crystal to additional small strains.

In this chapter, the expressions for the second order, third order and fourth order elastic constants of a hexagonal crystal are derived using the sublattice displacements upto second degree in strains.

The expressions are also given for the effective second order elastic constants of hexagonal system based on finite strain elasticity theory in terms of the second order, third order and fourth order elastic constants. These expressions are used to obtain the first order pressure derivatives and second order pressure derivatives of the second order elastic constants of hexagonal crystals. First order pressure derivative is the first derivative of the second order elastic constants $C_{ij}$'s with respect to pressure $- [dC_{ij}/dp]$. The second order pressure derivative is the second derivative of the second order elastic constants $C_{ij}$'s with respect to pressure $- [d^2C_{ij}/dp^2]$.

### 2.2 Expressions for the Second, Third and Fourth order elastic constants of a hexagonal close packed (hcp) crystal

Many of the hexagonal metals have an axial ratio $p = c/a$ different from the ideal value $\sqrt{8}/3$. The basis vectors can now be written as

$$\hat{a}_1 = D \left( \frac{\sqrt{3}}{2}, \frac{1}{2}, 0 \right)$$
\( \hat{a}_2 = D(0, 1, 0) \)

\( \hat{a}_3 = D(0, 0, p) \) \hfill (2.2.1)

referred to a Cartesian system of axes. We have chosen here \( \hat{a}_2 \) as the y-axis.

In the present notation \((q_1, 0, 0)\) direction is normal to one of the sides of the hexagon. \((11\overline{2}0)\) is a direction joining the centre to one of the corners of the hexagon. In present notation this corresponds to \((q_1, -q_1, 0)\). Here \(D\) is the nearest neighbour distance in the basal plane. The position co-ordinates of the two non-equivalent atoms in the basis are

\[
R\begin{pmatrix} 0 \\ 1 \end{pmatrix} = D(0, 0, 0)
\]

\[
R\begin{pmatrix} 0 \\ 2 \end{pmatrix} = D\left(\frac{1}{2\sqrt{3}}, \frac{1}{2}, \frac{p}{2}\right) \hfill (2.2.2)
\]

Here, the interactions upto second neighbours are considered. The position co-ordinates of the neighbours of the atoms of the same type in the basal plane and non-equivalent type out of the basal plane of \(\begin{pmatrix} 0 \\ 1 \end{pmatrix} \) are given in Tables 2.2.1 and 2.2.2 respectively.
Table 2.2.1  Position co-ordinates of the nearest neighbours of the same type in the basal plane. These neighbours are denoted by I.

\[ \mathbf{R} \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix} = \mathbf{R} \begin{pmatrix} 0 & 1 \\ 2 & 2 \end{pmatrix} \text{ and } \left| \mathbf{R} \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix} \right| = D \]

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Considering interactions up to second neighbours, the potential energy per unit cell is

\[ \phi = \sum_{i=1}^{6} \phi R(I) + \sum_{j=1}^{6} \phi R(J) \]  \hspace{1cm} (2.2.3)

Here, \( I \) atoms are the six nearest neighbours of the same type in the basal plane and the \( J \) atoms are the six non-equivalent atoms which are out of the basal plane. The components of interatomic vector \( R \) after deformation is given by

\[ R'_i(I) = R_i(I) + \sum_{j} \epsilon_{ij} R_j(I) \]
Table 2.2.2  Nearest non-equivalent neighbours out of the basal plane. The neighbours above the basal plane are denoted by the index $J^1$ and those below the basal plane by $J^{11}$. All the six neighbours are collectively indicated by $J$.

\[
\mathbf{R} = \begin{pmatrix} 0 & 1 \\ 1 & 2 \end{pmatrix} = D \left( \frac{1}{3} + \frac{p^2}{4} \right)^{1/2}
\]

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$R'_i(J) = R_i(J) + \sum \varepsilon_{ij} R_j(J) + W_i$ \hspace{1cm} (2.2.4)

Here $\varepsilon_{ij}$ are the deformation parameters and are related to the macroscopic Lagrangian strain $\eta_{ij}$ by

$\eta_{ij} = \frac{1}{2} (\varepsilon_{ii} + \varepsilon_{jj} + \sum_k \varepsilon_{ki} \varepsilon_{kj})$ \hspace{1cm} (2.2.5)

$\bar{W}_i$ are the components of internal displacements of the lattice of particles of type $J$ relative to the lattice of particles of type $I$ and are given by

$\bar{W}_i = W_i + \sum_j \varepsilon_{ij} \bar{W}_j$ \hspace{1cm} (2.2.6)
The potential energy is expanded in powers of changes in the squares of vector distances $R(I)$ and $R(J)$ as [i.e., $\Delta R^2(K)$ where $K = I, J$]

$$\phi = \phi_o + K_2 \left[ \sum \Delta R^2(I)^2 + \sum \Delta R^2(J)^2 \right]$$

$$+ K_3 \left[ \sum \Delta R^2(I)^3 + \sum \Delta R^2(J)^3 \right]$$

$$+ K_4 \left[ \sum \Delta R^2(I)^4 + \sum \Delta R^2(J)^4 \right]$$

(2.2.7)

Here $K_2$ is the harmonic parameter. $K_3$ and $K_4$ are the third and fourth order anharmonic parameters which are defined as

$$K_2 = \frac{1}{2!} \left[ \frac{\partial^2 \phi(r)}{\partial r^2} \right]$$

$$K_3 = \frac{1}{3!} \left[ \frac{\partial^3 \phi(r)}{\partial r^3} \right]$$

$$K_4 = \frac{1}{4!} \left[ \frac{\partial^4 \phi(r)}{\partial r^4} \right]$$

(2.2.8)

The term $\left[ \frac{\partial \phi(r)}{\partial r^2} \right]$ does not exist as the derivatives are calculated in the equilibrium configuration. The Lennard-Jones potential is given by

$$\phi = \frac{-a}{r^m} + \frac{b}{r^n}$$

(2.2.9)
For this potential \( K_2, K_3 \) and \( K_4 \) are calculated as

\[
K_2 = \frac{1}{4} (\eta \, M/D^2) \quad (2.2.10)
\]

\[
K_3 = -K_2/6D^2 \, (m+n+6) \quad (2.2.11)
\]

\[
K_4 = K_2/48D^4[(m+n)(m+n+12)-mn+44] \quad (2.2.12)
\]

\[
\eta = nb(n-m)/2MD^{n+2} \quad (2.2.13)
\]

\( M \) – mass of the atom and \( D = a \) is the nearest neighbour distance in the basal plane.

Using equation (2.2.4)

\[
\Delta R^2(K) = 2\sum_{ij} \eta_{ii} R_i(K) R_j(K) + 2\sum R_i(K) \bar{W}_i
\]

\[
+ \sum_i \bar{W}_i^2 - 2\sum_{ij} \bar{W}_i \bar{W}_j \eta_{ij} \quad (2.2.14)
\]

The powers of \( \Delta R^2(K) \) from (2.2.14) are substituted into eqn. (2.2.7). The resulting equation is as follows:

\[
\Delta \phi = \phi - \phi_0
\]

\[
= K_2 \sum_K \left[ 4 \sum_{ijkl} \eta_{li} \eta_{kl} R_i(K) R_j(K) R_k(K) R_l(K) 
\right.
\]

\[
+ 4\sum_{ij} \bar{W}_i \bar{W}_j R_i(K) R_j(K) + 8 \sum_{ij} \eta_{ij} \bar{W}_i R_i(K)
\]

\[
R_j(K) R_l(K) + 4\sum_{ij} \bar{W}_i \bar{W}_j R_i(K) R_j(K)
\]

\[
+ 4\sum_i \bar{W}_i \bar{W}_i R_i(K) - 8 \sum_{ijkl} \eta_{li} \bar{W}_i \bar{W}_j \bar{W}_k R_i(K) R_j(K)
\]

\[
+ \sum_{ij} \bar{W}_i \bar{W}_j - 8 \sum_{ijkl} \bar{W}_i \bar{W}_j \bar{W}_k \eta_{kl} R_i(K) \right]
\]
Retaining the terms up to 4th degree in strain, we get the expression for the strain energy per unit volume of the unstrained lattice.

\[ + \sum_{i}^{k} \sum_{i}^{m} \sum_{j}^{l} \sum_{m}^{n} \sum_{o}^{p} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{op} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) \]

\[ + 24 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{m} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + 24 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{k} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + 12 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{m}^{2} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + 24 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{k}^{2} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + 12 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{j}^{2} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + K_{4} \sum_{ijklmnop}^{K} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{op} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) \]

\[ + 16 \sum_{ijkl} W_{i} W_{j} W_{k} W_{l} \]

\[ + R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) + 64 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{m} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) \]

\[ + 96 \sum_{ijklm} \eta_{ij} \eta_{kl} W_{n} R_{i}(K) R_{j}(K) R_{k}(K) R_{l}(K) R_{m}(K) R_{n}(K) \]

\[ (2.2.15) \]

Retaining the terms up to 4th degree in strain, we get the expression for the strain energy per unit volume of the unstrained lattice.
Ramanand et al. [13] had shown that in order to obtain the fourth order elastic constants of an hcp lattice, it is enough to obtain sublattice displacements up to second degree in strain. Considering only the terms giving rise to second degree strains in potential energy expansion, we get

$$\Delta \phi^{(2)} = K_2 \sum_K \left[ 4 \sum_{ij} \bar{W}_i \bar{W}_j R_i(K) R_j(K) + 8 \sum_{ijkl} \eta_{ij} \bar{W}_i \bar{W}_j R_i(K) R_j(K) \right]$$

$$- 8 \sum_{ijkl} \eta_{ij} \eta_{kl} \bar{W}_i \bar{W}_j R_i(K) R_j(K)$$

(2.2.16)

$$\Delta \phi^{(2)}$$ is evaluated taking into account interactions up to second neighbours. The internal displacements $$\bar{W}_i$$ can be obtained by minimising the strain energy with respect to $$\bar{W}_i$$, i.e.,

$$\bar{W}_x = [-D/2\sqrt{3}] [\eta_{yy} - \eta_{xx}] + [D/2\sqrt{3}] [\eta_{yy}^2 - \eta_{xx}^2] +$$

$$[\sqrt{3} p^2 D/4] [\eta_{zz} - \eta_{xx}]$$

$$\bar{W}_y = [-D/\sqrt{3}] \eta_{xy} + D/\sqrt{3} [\eta_{xy} (\eta_{yy} + \eta_{xx})] + [\sqrt{3} p^2 D/2] \eta_{xy} \eta_{zz}$$

$$\bar{W}_z = 0$$

(2.2.17)

Substituting the value of $$\bar{W}_i$$ in the expression for the strain energy per unit volume of the undeformed state and comparing the resulting expression with that of elastic energy density,

$$U = U_0 + \frac{1}{2!} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{3!} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn}$$

$$+ \frac{1}{4!} \sum_{ijklmnop} C_{ijklmnop} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{op} + \ldots$$

(2.2.18)
we get the expressions for the second, third and fourth order elastic constants

\[
\begin{align*}
C_{11} & = \{(167/8)D^4/V_a\} K_2 \\
C_{12} & = \{(41/8)D^4/V_a\} K_2 \\
C_{13} & = \{(5/3)D^4p^2/V_a\} K_2 \\
C_{33} & = \{3D^4p^4/V_a\} K_2 \\
C_{44} & = \{2D^4p^2/V_a\} K_2 \\
C_{66} & = \{(63/8)D^4/V_a\} K_2
\end{align*}
\]

(2.2.19)

\[
\begin{align*}
C_{111} & = \{(1099/10)D^6/V_a\} K_3 + \{(23/3)D^4/V_a\} K_2 \\
C_{112} & = \{(83/5)D^6/V_a\} K_3 - \{(7/5)D^4/V_a\} K_2 \\
C_{113} & = \{(5/3)D^6p^2/V_a\} K_3 + \{D^4p^2/V_a\} K_2 \\
C_{123} & = \{(7/5)D^6p^2/V_a\} K_3 - \{D^4p^2/V_a\} K_2 \\
C_{133} & = \{(16/5)D^6p^4/V_a\} K_3 \\
C_{344} & = \{3D^6p^4/V_a\} K_3 \\
C_{144} & = \{2D^6p^2/V_a\} K_3 \\
C_{155} & = \{(4/3)D^6p^2/V_a\} K_3 \\
C_{222} & = \{(175/2)D^6/V_a\} K_3 + \{(39/5)D^4/V_a\} K_2 \\
C_{333} & = \{(9/2)D^6p^6/V_a\} K_3
\end{align*}
\]

(2.2.20)

\[
\begin{align*}
C_{1111} & = \{(4390/9)D^8/V_a\} K_4 + \{(4D^6/V_a)\} K_3 - \{(143/6)D^4/V_a\} K_2 \\
C_{1112} & = \{(1474/9)D^8/V_a\} K_4 + \{(23/6)D^6/V_a\} K_3 \\
C_{1113} & = \{(24/9)D^8p^2/V_a\} K_4 + \{3D^6p^2/V_a\} K_3 - \{(12/6)D^4p^2/V_a\} K_2 \\
C_{1122} & = \{(502/9)D^8/V_a\} K_4 - \{(4/3)D^6/V_a\} K_3 - \{(11/2)D^4/V_a\} K_2 \\
C_{1123} & = \{(24/9)D^8p^2/V_a\} K_4 - \{D^6p^2/V_a\} K_3 + \{6D^4p^2/V_a\} K_2 \\
C_{1133} & = \{4D^8p^4/V_a\} K_4 + \{(3/2)D^6p^4/V_a\} K_3 - \{3D^4p^4/V_a\} K_2 \\
C_{1144} = C_{1244} = C_{1255} & = \{(24/9)D^8p^2/V_a\} K_4 - \{D^6p^2/V_a\} K_3
\end{align*}
\]
where $V_a$ is the volume of the unit cell, $D$ is the nearest neighbour distance and $p$ is the axial ratio $c/a$. The above expressions have been used in Chapter 3 and 4 to obtain the second, third and fourth order elastic constants of cadmium, zirconium, titanium, gadolinium, dysprosium and erbium.

### 2.3 Expressions for the First order pressure derivatives of the Second order elastic constants of hexagonal crystals

Let us consider a hexagonal lattice under a hydrostatic pressure $P$. Let $a_i$ be the co-ordinates of a material point in the natural state and $x_i$ the co-ordinates of the same material point after applying the pressure. The Jacobian after the application of the pressure

$$J = \begin{vmatrix} \frac{\partial x_i}{\partial a_j} \\ \frac{\partial x_i}{\partial a_j} \end{vmatrix} = \begin{vmatrix} (1-\alpha) & 0 & 0 \\ 0 & (1-\alpha) & 0 \\ 0 & 0 & (1-\beta) \end{vmatrix} \quad (2.3.1)$$

Every line element in the basal plane is reduced by a factor $\alpha$ and every line element parallel to the hexagonal axis is reduced by a factor $\beta$. 

| $C_{1155}$ | $= \left[ \frac{24}{9} D^8 p^2 / V_a \right] K_4 + \left[ 3 D^6 p^2 / V_a \right] K_3$ |
| $C_{1166}$ | $= \left[ \frac{1461}{9} D^8 / V_a \right] K_4 + \left[ \frac{2}{3} D^6 / V_a \right] K_3 + \left[ \frac{25}{18} D^4 / V_a \right] K_2$ |
| $C_{1233}$ | $= \left[ 4D^8 p^4 / V_a \right] K_4 - \left[ \frac{3}{2} D^6 p^4 / V_a \right] K_3 + \left[ 3D^4 p^4 / V_a \right] K_2$ |
| $C_{1333}$ | $= C_{3344} = \left[ 6D^6 p^6 / V_a \right] K_4$ |
| $C_{1344}$ | $= \left[ 4D^8 p^4 / V_a \right] K_4 - \left[ \frac{3}{2} D^6 p^4 / V_a \right] K_3$ |
| $C_{1355}$ | $= \left[ 4D^8 p^4 / V_a \right] K_4 + \left[ \frac{3}{2} D^6 p^4 / V_a \right] K_3$ |
| $C_{2222}$ | $= \left[ 9 D^8 p^2 / V_a \right] K_4 + \left[ 3D^6 p^2 / V_a \right] K_3 - \left[ 6 D^4 p^2 / V_a \right] K_2$ |
| $C_{3333}$ | $= \left[ 9D^8 p^4 / V_a \right] K_4$ |
| $C_{4444}$ | $= \left[ 6D^8 p^4 / V_a \right] K_4$ |

(2.2.21)
If \( \eta_{xx} = \eta_{yy} = \eta \) and \( \eta_{zz} = \xi \) are the Lagrangian strain parameters, then

\[
(1-\alpha)^2 = 1+2\eta \\
(1-\beta)^2 = 1+2\xi
\]

(2.3.2)

The density \( \rho \) in the deformed state is related to the density \( \rho_0 \) in the natural state by

\[
\frac{\rho}{\rho_0} = \frac{1}{|J|}
\]

(2.3.3)

Now if an infinitesimal strain is superimposed on the deformed state, the co-ordinates of the particle become

\[
x_i = X_i + \sum_j \beta_{ij} X_i
\]

(2.3.4)

where \( \beta_{ij} \) are the infinitesimal strain parameters. The Lagrangian strain parameters \( \eta_{ij} \) in the final state are obtained in terms of \( \eta, \xi \) and \( \beta_{ij} \) from the expression.

\[
\eta_{ij} = \frac{1}{2} \sum_p \left( \frac{\partial x_p}{\partial a_i} \frac{\partial x_p}{\partial a_j} - \delta_{ij} \right)
\]

(2.3.5)

The strain energy density \( U \) is expanded in powers of \( \eta_{ij} \) as

\[
U = U_0 + \frac{1}{2} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl}
\]

\[
+ \frac{1}{3!} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn}
\]

\[
+ \frac{1}{4!} \sum_{ijklmnop} C_{ijklmnop} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{op} + \ldots
\]

(2.3.6)

where \( C_{ijkl} \) and \( C_{ijklmn} \) are second and third order elastic constants in the natural state. The stress tensor \( T_{ij} \) is given by Murnaghan [1] as
Comparing this with the expression

\[ T_{ij} = -\rho \delta_{ij} + \sum_{pq} C'_{ij,pq} \beta_{pq} \] (2.3.8)

the effective SOE constants \( C'_{ij,pq} \) can be obtained to the first order in the strains \( \eta \) and \( \xi \) for hexagonal system

\[
C'_{11} = C_{11} + \eta \left( 4C_{11} + 2C_{12} + C_{111} + C_{112} \right) + \xi \left( -C_{11} + 2C_{13} + C_{113} \right)
\]

\[
C'_{12} = C_{12} + \eta \left( C_{111} + 2C_{122} + C_{222} + 2C_{12} \right) + \xi \left( -C_{12} + C_{123} \right)
\]

\[
C'_{13} = C_{13} + \eta \left( C_{113} + C_{123} \right) + \xi \left( C_{13} + C_{133} \right)
\]

\[
C'_{66} = C_{66} + \eta \left( C_{11} + C_{12} + 2C_{66} - \frac{1}{2} C_{112} + \frac{1}{2} C_{222} \right) + \xi \left( C_{13} - C_{66} + \frac{1}{2} C_{113} - \frac{1}{2} C_{123} \right)
\]

\[
C'_{33} = C_{33} + \eta \left( 4C_{13} - 2C_{33} + 2C_{133} \right) + \xi \left( 5C_{33} + C_{333} \right)
\]

\[
C'_{44} = C_{44} + \eta \left( \frac{1}{2} C_{11} + \frac{1}{2} C_{12} + C_{13} + C_{144} + C_{155} \right) + \xi \left( \frac{1}{2} C_{13} + \frac{1}{2} C_{33} + C_{44} + C_{344} \right)
\] (2.3.9)

To get the pressure derivatives, we substitute for \( \eta \) and \( \xi \) to the first order in \( p \).

\[
\eta = \frac{(C_{13} - C_{33})}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p = C_p \text{ and}
\]

\[
\xi = \frac{2C_{13} - C_{11} - C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p = D_p
\] (2.3.10)
The pressure derivatives \( \frac{\partial C'_y}{\partial p} \) are obtained by multiplying the coefficients of \( \eta \) and \( \xi \) in the expressions for \( C'_y \) in (2.3.9) by \( C \) and \( D \) respectively and adding the two terms we get the first order pressure derivatives as

\[
\frac{dC'_{11}}{dp} = (4C_{11} + 2C_{12} + C_{111} + C_{112}) \frac{d\eta}{dp} + \frac{d\xi}{dp} (-C_{11} + 2C_{13} + C_{113})
\]

\[
\frac{dC'_{12}}{dp} = (2C_{12} + C_{111} + 2C_{112} - C_{222}) \frac{d\eta}{dp} + \frac{d\xi}{dp} (-C_{12} + C_{123})
\]

\[
\frac{dC'_{13}}{dp} = (C_{113} + C_{123}) \frac{d\eta}{dp} + \frac{d\xi}{dp} (C_{13} + C_{133})
\]

\[
\frac{dC'_{33}}{dp} = (4C_{13} - 2C_{33} + 2C_{133}) \frac{d\eta}{dp} + (5C_{33} + C_{333}) \frac{d\xi}{dp}
\]

\[
\frac{dC'_{44}}{dp} = (\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{13} + C_{144} + C_{155}) \frac{d\eta}{dp} + \frac{d\xi}{dp}
\]

\[
\frac{d\xi}{dp} = (\frac{1}{2}C_{13} + \frac{1}{2}C_{33} + C_{44} + C_{344})
\]

\[
\frac{dC'_{66}}{dp} = (2C_{11} - \frac{1}{2}C_{112} + \frac{1}{2}C_{222}) \frac{d\eta}{dp} + (C_{13} - C_{56} + \frac{1}{2}C_{113} - \frac{1}{2}C_{12}) \frac{d\xi}{dp}
\]

(2.3.11)
2.4 Expressions for the Second Order pressure derivatives of the Second Order elastic constants of Hexagonal crystals

Comparing (2.3.7) and (2.3.8), the expressions for the effective second order elastic constants $C'_{\text{hexag}}$ can be obtained to the second order in the Lagrangian strains $\eta$ and $\xi$ for the hexagonal crystals as

\begin{align*}
C'_{11} &= C_{11} + \eta(4C_{11} + 2C_{12} + C_{111} + C_{112}) + \xi(-C_{11} + 2C_{13} + C_{113}) \\
&+ \eta^2(4C_{111} + 5C_{112} - C_{222} + \frac{1}{2}C_{1112} + \frac{1}{2}C_{1122}) \\
&+ \xi^2(\frac{3}{2}C_{11} - 2C_{13} - C_{113} + C_{133} + \frac{1}{2}C_{1133}) \\
&+ \eta\xi(-4C_{11} - 2C_{12} - C_{111} - C_{112} + 4C_{113} + 2C_{123} + C_{1113} + C_{1123}) \\
&+ \frac{1}{2}(3C_{11} - 2C_{12} - C_{13} - C_{133} + \frac{1}{2}C_{1333}) \\
&- \xi(2C_{11} - 2C_{12} - 4C_{113} - C_{133} - C_{1333}) \\
&+ \frac{1}{2}C_{11} \xi + \frac{1}{2}C_{13} \xi + \frac{1}{2}C_{133} \xi + \frac{1}{2}C_{1333} \xi
\end{align*}

\begin{align*}
C'_{12} &= C_{12} + \eta(2C_{12} + C_{111} + 2C_{122} - C_{112}) + \xi(-C_{12} + C_{113}) \\
&+ \eta^2(2C_{111} + 4C_{112} - 2C_{222} + \frac{1}{2}C_{1112} + \frac{1}{2}C_{1122}) \\
&+ \xi^2(\frac{3}{2}C_{11} - C_{123} + \frac{1}{2}C_{123}) + \eta\xi(-2C_{12} - C_{111} - 2C_{112} \\
&+ 2C_{123} + C_{222} + C_{1123} + C_{123})
\end{align*}

\begin{align*}
C'_{13} &= C_{13} + \eta(C_{113} + C_{123}) + \xi(C_{13} + C_{133}) + \eta^2(\frac{1}{2}C_{1113} + C_{1123}) \\
&+ \frac{1}{2}C_{1223}) + \xi^2(-\frac{1}{2}C_{13} + C_{133} + \frac{1}{2}C_{1333}) + \eta\xi(C_{113} + C_{123} + C_{1133} + C_{1233})
\end{align*}

\begin{align*}
C'_{33} &= C_{33} + \eta(4C_{13} - 2C_{33} + 2C_{133}) + \xi(5C_{33} + C_{333}) \\
&+ \eta^2(4C_{33} - 8C_{13} + 2C_{113} + 2C_{123} - 4C_{133} + C_{1133} + C_{1233}) \\
&+ \xi^2(\frac{1}{2}C_{33} + 4C_{333} + \frac{1}{2}C_{3333}) + \eta\xi(4C_{13} - 10C_{33}) \\
&+ 10C_{133} - 2C_{333} + 2C_{1333})
\end{align*}

\begin{align*}
C'_{44} &= C_{44} + \eta(\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{13} + C_{144} + C_{155}) \\
&+ \xi(\frac{1}{2}C_{13} + \frac{1}{2}C_{33} + C_{44} + C_{344}) + \eta^2(-2C_{13} + \frac{1}{2}C_{111}) \\
&+ \frac{1}{2}C_{113} + \frac{1}{2}C_{123} + \frac{3}{4}C_{112} - \frac{1}{4}C_{222} + \frac{1}{2}C_{1144} + \frac{1}{2}C_{1155}
\end{align*}
The Lagrangian strains $\eta$ and $\xi$ are given in eqn. (2.3.10). The second order pressure derivatives $\left(\frac{\partial^2 C}{\partial p^2}\right)$ are obtained by putting these $\eta$ and $\xi$ in expression (2.4.1) as C and D respectively. The expressions for the second order pressure derivatives are

$$\frac{d^2 C_{11}}{dp^2} = 2C^2(4C_{111} + 5C_{112} - C_{222} + \frac{1}{2}C_{1111} + \frac{1}{2}C_{1112} + \frac{1}{2}C_{1122})$$

$$+ 2D^2(\frac{3}{2}C_{11} - 2C_{13} + C_{133} + \frac{1}{2}C_{1333})$$

$$+ 2CD(-4C_{11} - 2C_{12} - C_{111} + C_{112} + C_{123} + C_{1113} + C_{1123})$$

$$\frac{d^2 C_{12}}{dp^2} = 2C^2(2C_{11} + 4C_{112} - 2C_{222} + \frac{1}{2}C_{1112} + C_{122} + \frac{1}{2}C_{1222})$$

$$+ 2D^2(\frac{3}{2}C_{12} + C_{13} + \frac{1}{2}C_{133} + \frac{1}{2}C_{1333})$$

$$+ 2CD(-2C_{12} + C_{11} - C_{112} + C_{113} + C_{1123} + C_{1133} + C_{1223})$$

$$\frac{d^2 C_{13}}{dp^2} = 2C^2(\frac{3}{2}C_{1113} + C_{1123} + \frac{1}{2}C_{1223}) + 2D^2(-\frac{1}{2}C_{13} + C_{133} + \frac{1}{2}C_{1333})$$

$$+ 2CD(C_{113} + C_{123} + C_{1133} + C_{1223})$$

(2.4.1)
These expressions (2.3.11) and (2.4.2) are used to calculate the first order and second order pressure derivatives of the second order elastic constants of the hexagonal metals cadmium, zirconium, titanium, gadolinium, dysprosium and erbium in Chapters 3 and 4.

\[
\frac{d^2 C'_{33}}{dp^2} = 2C^2(4C_{33} - 8C_{13} + 2C_{113} + 2C_{123} - 4C_{133} + C_{1133} + C_{1233}) \\
+ 2D^2 \left( \frac{7}{2}C_{33} + 4C_{3333} + \frac{1}{2}C_{333} \right) + 2CD \left( 4C_{13} - 10C_{33} \right) \\
+ 10C_{133} - 2C_{333} + 2C_{1333})
\]

\[
\frac{d^2 C'_{44}}{dp^2} = 2C^2(-2C_{13} + \frac{1}{2}C_{111} + \frac{1}{2}C_{113} + \frac{1}{2}C_{123} + \frac{3}{4}C_{112} - \frac{1}{4}C_{222} \\
+ \frac{1}{2}C_{1144} + \frac{1}{2}C_{1155} + \frac{1}{4}C_{1255} + \frac{3}{4}C_{1244}) \\
+ 2D^2 \left( \frac{1}{2}C_{33} - \frac{1}{2}C_{13} - \frac{1}{2}C_{44} + \frac{1}{4}C_{133} + \frac{1}{4}C_{333} + C_{344} + \frac{1}{2}C_{3344} \right) \\
+ 2CD \left( -\frac{1}{2}C_{11} - \frac{1}{2}C_{12} + C_{13} - C_{33} + \frac{1}{2}C_{113} + \frac{1}{2}C_{123} + C_{133} \\
+ C_{144} + C_{155} + C_{1344} + C_{1355} \right)
\]

\[
\frac{d^2 C'_{66}}{dp^2} = 2C^2(C_{111} + \frac{1}{2}C_{112} + \frac{1}{2}C_{222} + \frac{1}{4}C_{1111} + \frac{1}{4}C_{1112} - \frac{1}{4}C_{1122} - \frac{1}{4}C_{2222}) \\
+ 2D^2 \left( \frac{3}{2}C_{66} - C_{13} - \frac{1}{2}C_{113} + \frac{1}{2}C_{133} + \frac{1}{2}C_{123} + \frac{1}{4}C_{1135} - \frac{1}{4}C_{1233} \right) \\
+ 2CD \left( -2C_{11} + \frac{1}{2}C_{112} - \frac{1}{2}C_{222} + 2C_{113} + \frac{1}{2}C_{1113} + \frac{1}{2}C_{1223} \right)
\]

(2.4.2)
References


