

1.10. Elastic constants.

The importance of the elastic constants for Earth sciences springs from the fact that most of the information about the deep Earth is obtained seismologically, by measuring the velocities of seismic waves passing through the Earth. Seismic wave velocities, in turn, are related to the bulk and shear moduli of the Earth-forming rocks and minerals. Acoustic anisotropy of the Earth, measurable seismologically, is related to the elastic anisotropy of the Earth-forming minerals and the degree of their alignment. A number of excellent books and reviews exist; I would emphasize Nye (1998), Sirotin & Shaskolskaya (1975), Wallace (1998), Alexandrov & Prodaivoda (1993), Born & Huang (1954), Belikov *et al.* (1970), Barron & Klein (1965), Fedorov (1968).

Elastic constants characterise the ability of a material to deform under any small stresses. They can be described by a fourth-rank tensor C_{ijkl} , relating the second-rank stress tensor σ_{ij} to the (also second-rank) strain tensor e_{kl} via the generalised Hooke's law:

$$\sigma_{ij} = C_{ijkl}e_{kl}, \quad \{1.10.1\}$$

where multiplication follows the rules of tensor multiplication (see Nye, 1998). Equation {1.10.1} can be simplified using the Voigt notation (Nye, 1998), which represents the fourth-rank tensor C_{ijkl} by a square 6*6 matrix C_{mn} . In these notations, indices '11', '22', '33', '12', '13', '23' are represented by only one symbol – 1, 2, 3, 6, 5, and 4, respectively. These notations significantly simplify all equations. So we write instead of {1.10.1}:

$$\sigma_i = C_{ij}e_j \quad \{1.10.2\}$$

Note that infinitesimal strains are being used; in this limit all definitions of strain (e.g., Eulerian, Lagrangian, Hencky, etc.) become equivalent. Under a small strain, the lattice vectors a_{ij}' of the strained crystal is obtained from the old lattice vectors a_{ij}^0 and the strain tensor e_{ij} using the relation:

$$a_{ij}' = (\delta_{ij} + e_{ij})a_{ij}^0. \quad \{1.10.3\}$$

In the original tensor notation and in the Voigt notation (Nye, 1998), the $(\delta_{ij} + e_{ij})$ matrix is represented as follows:

$$\begin{pmatrix} 1+e_{11} & e_{12} & e_{13} \\ e_{12} & 1+e_{22} & e_{23} \\ e_{13} & e_{23} & 1+e_{33} \end{pmatrix} = \begin{pmatrix} 1+e_1 & e_6/2 & e_5/2 \\ e_6/2 & 1+e_2 & e_4/2 \\ e_5/2 & e_4/2 & 1+e_3 \end{pmatrix} \quad \{1.10.4\}$$

The Voigt notation allows one to write elastic constants conveniently as a symmetric 6*6 matrix. Voigt notation is sufficient in most situations; only in rare situations such as a general transformation of the coordinate system the full fourth-rank tensor representation must be used to derive the transformed elastic constants.

The number of components of a fourth-rank tensor is 81; the Voigt notation reduces this to 36. The thermodynamic equality $C_{ij}=C_{ji}$ makes the 6*6 matrix of elastic constants symmetric, reducing the number of independent constants to the well-known maximum number of 21, possessed by triclinic crystals. Crystal symmetry results in further reductions of this number: 13 for monoclinic, 9 for orthorhombic, 6 or 7 (depending on the point group symmetry) for trigonal and tetragonal, 5 for hexagonal, and 3 for cubic crystals; for isotropic (amorphous) solids there are only 2 independent elastic constants. Elastic constants and their anisotropy are closely related to crystal structures.

One can define the inverse tensor S_{ijkl} (or, in Voigt notations, S_{ij}^{-1}), often called the elastic compliance tensor:

$$\{S_{ijkl}\} = \{C_{ijkl}\}^{-1} \text{ or } \{S_{ij}\} = \{C_{ij}\}^{-1} \quad \{1.10.5\}$$

For an orthorhombic crystal, this matrix inversion leads to the following explicit relations between C_{ij} and S_{ij} (Belikov *et al.*, 1970):

$$\begin{aligned} S_{11} &= (C_{22}C_{33} - C_{23}^2)/D \\ S_{22} &= (C_{11}C_{33} - C_{13}^2)/D \\ S_{33} &= (C_{11}C_{22} - C_{12}^2)/D \\ S_{44} &= 1/C_{44} \\ S_{55} &= 1/C_{55} \\ S_{66} &= 1/C_{66} \\ S_{12} &= -(C_{12}C_{33} - C_{13}C_{23})/D \\ S_{13} &= (C_{12}C_{23} - C_{13}C_{22})/D \\ S_{23} &= -(C_{11}C_{23} - C_{13}C_{12})/D, \end{aligned} \quad \{1.10.6\}$$

where $D = C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{23}^2C_{11} - C_{12}^2C_{33} - C_{13}^2C_{22}$. Relations {1.10.6} are automatically valid for tetragonal and cubic crystals.

The S_{ij} tensor can be defined via the generalised Hooke's law in its equivalent formulation:

$$e_i = S_{ij}\sigma_j \quad \{1.10.7\}$$

Linear compressibilities can be easily derived from the S_{ij} tensor. Full expressions for an arbitrary direction can be found in Nye (1998); along the coordinate axes the linear compressibilities are:

$$\begin{aligned} \beta_x &= -\frac{1}{l_x} \left(\frac{\partial l_x}{\partial P} \right)_T = \sum_{j=1}^3 S_{1j} = S_{11} + S_{12} + S_{13} \\ \beta_y &= -\frac{1}{l_y} \left(\frac{\partial l_y}{\partial P} \right)_T = \sum_{j=1}^3 S_{2j} = S_{12} + S_{22} + S_{23} \\ \beta_z &= -\frac{1}{l_z} \left(\frac{\partial l_z}{\partial P} \right)_T = \sum_{j=1}^3 S_{3j} = S_{13} + S_{23} + S_{33}, \end{aligned} \quad \{1.10.8\}$$

where l_x, l_y, l_z are linear dimensions along the axes of the coordinate system². For the bulk compressibility we have:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \beta_x + \beta_y + \beta_z = \sum_{i=1}^3 \sum_{j=1}^3 S_{ij} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23}) \quad \{1.10.9\}$$

The values of the elastic constants depend on the orientation of the coordinate system. There are two particularly important invariants of the elastic constants tensor – bulk modulus K and shear modulus G . These invariants are obtained by special averaging of the individual elastic constants. There are several different schemes of such averaging. Reuss averaging is based on the assumption of a homogeneous stress throughout the crystal, leading to the Reuss bulk modulus:

¹ Note that in Voigt notation $C_{ijkl} = C_{mn}$, but $S_{ijkl} = S_{mn}$ only when m and $n = 1, 2$, or 3 ; when either m or $n = 4, 5$, or 6 : $2S_{ijkl} = S_{mn}$; when both m and $n = 4, 5$, or 6 : $4S_{ijkl} = S_{mn}$ (Nye, 1998).

² These axes may not coincide with the lattice vectors for non-orthogonal crystal systems. Coordinate systems used in crystal physics are always orthogonal.

$$K_R = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})} = \frac{1}{\beta} \quad \{1.10.10\}$$

and shear modulus:

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})} \quad \{1.10.11\}$$

Expressions {1.10.7-1.10.11} are valid for crystals of any symmetry (Nye, 1998). It is important to realise that it is the Reuss bulk modulus, explicitly related to compressibility, that is used in constructing EOSs. This is also the modulus appearing in all thermodynamic equations involving the bulk modulus.

Another popular scheme of averaging is due to Voigt. It is based on the assumption of a spatially homogeneous strain, and leads to the following expressions for the Voigt bulk and shear moduli:

$$K_V = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})}{9} \quad \{1.10.12\}$$

$$G_V = \frac{C_{11} + C_{22} + C_{33} - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})}{15} \quad \{1.10.13\}$$

These equations are general, valid for crystals of any symmetry. For an isotropic polycrystalline aggregate the Voigt moduli give upper, and the Reuss moduli lower bounds for the corresponding moduli. More accurate estimates can be obtained from Voigt-Reuss-Hill averages:

$$K_{VRH} = \frac{K_V + K_R}{2}$$

$$G_{VRH} = \frac{G_V + G_R}{2} \quad \{1.10.14\}$$

The most accurate results (and tighter bounds) are given by Hashin-Shtrikman variational scheme, which is much more complicated, but leads to results similar to the Voigt-Reuss-Hill scheme (see Watt et al., 1976 for more details).

There are two groups of experimental methods of measuring the elastic constants: 1) static and low-frequency methods (based on determination of stress-strain relations for static stresses) and 2) high-frequency, or dynamic, methods (e.g., ultrasonic methods, Brillouin spectroscopy, etc.). High-frequency methods generally enable much higher accuracy. Static measurements yield isothermal elastic constants (timescale of the experiment allows thermal equilibrium to be attained within the sample), high-frequency measurements give adiabatic constants (Belikov *et al.*, 1970). The difference, which is entirely due to anharmonic effects (see below), vanishes at 0 K. Adiabatic C_{ij} are larger, usually by a few percent. The following thermodynamic equation gives the difference in terms of thermal pressure tensor b_{ij} (Wallace, 1998):

$$C_{ijkl}^S = C_{ijkl}^T + \frac{TV}{C_V} b_{ij} b_{kl} \quad , \quad \{1.10.15\}$$

where $b_{ij} = (\frac{\partial \sigma_{ij}}{\partial T})_V$ is related to the thermal expansion tensor. Equation {1.10.13} implies for the bulk moduli the already mentioned formula {1.2.25}:

$$K_S = K_T (1 + \alpha \gamma T) = K_T (1 + \frac{\alpha^2 K_T V}{C_V})$$

where α and γ are the thermal expansion and Grüneisen parameter, respectively. Adiabatic and isothermal shear moduli are strictly equal for cubic crystals and usually practically indistinguishable for crystals of other symmetries.

Acoustic wave velocities measured in seismological experiments and ultrasonic determinations of elastic constants are related to the adiabatic elastic constants. Isothermal constants, on the other hand, are related to the compressibility and EOS.

The general equation for the calculation of velocities of acoustic waves with an arbitrary propagation direction, the Christoffel equation (Sirotnin & Shaskolskaya, 1975), is:

$$C_{ijkl}^S m_j m_k p_l = \rho v^2 p_i \quad , \quad \{1.10.16\}$$

where p is the polarisation vector of the wave (of unit length), m unit vector parallel to the wave vector, and ρ the density of the crystal. It can be also represented in a form of a secular equation:

$$\det \| C_{ijkl}^S m_j m_k - \rho v^2 \delta_{il} \| = 0 \quad \{1.10.17\}$$

This equation has 3 solutions, one of which corresponds to a compressional, and the other two to shear waves. For example, one can obtain the following velocities for a cubic crystal along high-symmetry directions:

$$\text{a) } m \parallel [100]: v_1 = \sqrt{\frac{C_{11}}{\rho}} \quad (p=[100]), \quad v_2 = \sqrt{\frac{C_{44}}{\rho}} \quad (p=[010]), \quad v_3 = \sqrt{\frac{C_{44}}{\rho}} \quad (p=[001]),$$

$$\text{b) } m \parallel [110]: v_1 = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \quad (p=[110]), \quad v_2 = \sqrt{\frac{C_{44}}{\rho}} \quad (p=[001]), \quad v_3 = \sqrt{\frac{C_{11} - C_{12}}{\rho}}$$

$(p=[\bar{1}\bar{1}0]),$

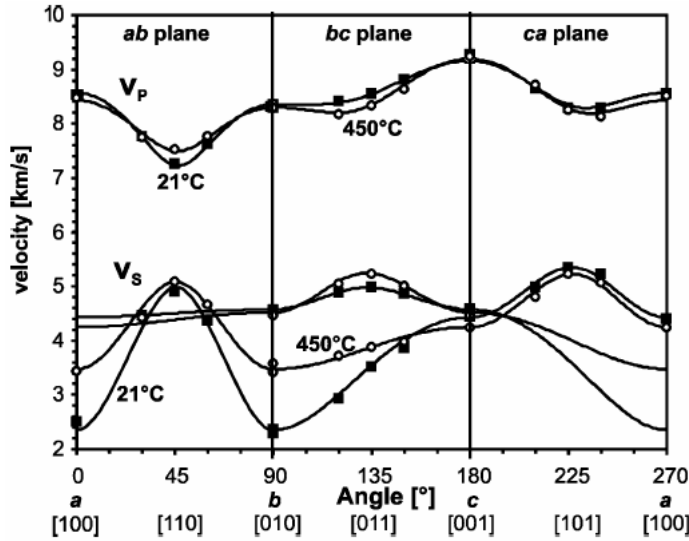


FIG. 1.10.1. Acoustic velocities as a function of the propagation direction in lawsonite $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$. [After Shilling et al., 2003.] Solid squares – at 21 °C, open circles – 450 °C.

The average velocities are given by famous equations (Belikov *et al.*, 1970):

$$v_p = \sqrt{\frac{3K + 4G}{3\rho}} \quad \{1.10.18\}$$

and

$$v_s = \sqrt{\frac{G}{\rho}}, \quad \{1.10.19\}$$

where the adiabatic Voigt-Reuss-Hill (or Hashin-Shtrikman) values are used for the bulk and shear moduli.

At constant P, T the elastic constants describing stress-strain relations {1.10.1} are given by:

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 G}{\partial e_{ij} \partial e_{kl}} \right)_T \quad \{1.10.20\}$$

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 H}{\partial e_{ij} \partial e_{kl}} \right)_T \quad \{1.10.21\}$$

Now let us derive from {1.10.20} an expression for the elastic constants in terms of the second derivatives of the internal energy; in this derivation we follow Ackland and Reed (2003). The unit cell of a crystal can be represented by a matrix $\vec{\mathbf{V}} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, and the volume of the equilibrium unit cell is then $V_0 = \det \vec{\mathbf{V}}$. Using {1.10.4}, for the volume V of a strained cell we obtain:

$$\frac{V}{V_0} = \frac{\det \vec{\mathbf{V}}}{\det \vec{\mathbf{V}}_0} = 1 + e_1 + e_2 + e_3 + e_1 e_2 + e_2 e_3 + e_1 e_3 - \frac{e_4^2}{4} - \frac{e_5^2}{4} - \frac{e_6^2}{4} + e_1 e_2 e_3 - \frac{e_1 e_4^2}{4} - \frac{e_2 e_5^2}{4} - \frac{e_3 e_6^2}{4} + \frac{e_4 e_5 e_6}{4} \quad \{1.10.22\}$$

Then one has in the standard tensor notation:

$$\frac{\Delta V}{V_0} = e_{ij} + \frac{1}{4} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) e_{ij} e_{kl} + O(e^3) \quad \{1.10.23\}$$

The change of the Gibbs free energy associated with strain is then to the second order:

$$\Delta G = \Delta F + P e_{ij} + \frac{PV}{4} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) e_{ij} e_{kl} \quad \{1.10.24\}$$

From this one has:

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial e_{ij} \partial e_{kl}} \right)_T + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \quad \{1.10.25a\}$$

and, by analogy,

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 E}{\partial e_{ij} \partial e_{kl}} \right)_T + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \quad \{1.10.25b\}$$

It is well known (Barron & Klein, 1965; Wallace, 1998) that under non-zero stresses there can be several different definitions of elastic constants. The constants C_{ijkl}^T and C_{ijkl}^S defined by equations {1.10.25ab} are those appearing in stress-strain relations and in the conditions of mechanical stability of crystals (see below), whereas the long-wavelength limit of lattice dynamics is controlled by $\frac{1}{V} \left(\frac{\partial^2 E}{\partial e_{ij} \partial e_{kl}} \right)_T$. These two definitions (via stress-strain relations and from long-wavelength lattice dynamics) become identical at zero pressure.

Calculating the second derivatives with respect to the finite Lagrangian strains η_{ij} , different equations are obtained (Wallace, 1998) for the case of hydrostatic pressure:

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S + P(\delta_{ij} \delta_{kl} - \delta_{il} \delta_{jk} - \delta_{jl} \delta_{ik}) \quad \{1.10.26a\}$$

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_T + P(\delta_{ij} \delta_{kl} - \delta_{il} \delta_{jk} - \delta_{jl} \delta_{ik}) \quad \{1.10.26b\}$$

For a general stress the analogous equations are:

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S - \frac{1}{2} (2\sigma_{ij} \delta_{kl} - \sigma_{ik} \delta_{jl} - \sigma_{il} \delta_{jk} - \sigma_{jl} \delta_{ik} - \sigma_{jk} \delta_{il}) \quad \{1.10.27a\}$$

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_T - \frac{1}{2} (2\sigma_{ij} \delta_{kl} - \sigma_{ik} \delta_{jl} - \sigma_{il} \delta_{jk} - \sigma_{jl} \delta_{ik} - \sigma_{jk} \delta_{il}) \quad \{1.10.27b\}$$

Cauchy relations, originally derived with the definition via the energy density, can be elegantly formulated in this definition as well (see below). Note, however, that the elastic constants C_{ijkl}^T , defined from stress-strain relations, have the full Voigt symmetry only at hydrostatic pressure. It is essential to distinguish between different definitions of elastic constants.