Elastic constants.
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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:

$$\sigma_{ij} = C_{ijkl}\eta_{kl}\ , \qquad \{1\}$$

where multiplication follows the rules of tensor multiplication (see Nye, 1998). Equation {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}:

$$\sigma_i = C_{ij}\eta_j \qquad \{2\}$$

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:

$$a_{ij}' = (\delta_{ij}+\eta_{ij})a_{ij}^0\ . \qquad \{3\}$$

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

$$\begin{pmatrix} 1+\eta_{11} & \eta_{12} & \eta_{13} \\ \eta_{12} & 1+\eta_{22} & \eta_{23} \\ \eta_{13} & \eta_{23} & 1+\eta_{33} \end{pmatrix} = \begin{pmatrix} 1+\eta_1 & \eta_6/2 & \eta_5/2 \\ \eta_6/2 & 1+\eta_2 & \eta_4/2 \\ \eta_5/2 & \eta_4/2 & 1+\eta_3 \end{pmatrix} \qquad \{4\}$$

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.

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

$$\{S_{ijkl}\} = \{C_{ijkl}\}^{-1} \text{ or } \{S_{ij}\} = \{C_{ij}\}^{-1} \qquad \{5\}$$

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

$$\eta_i = S_{ij}\sigma_j \qquad \{6\}$$

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,

[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).

usually by a few percent. The following thermodynamic equation gives the difference in terms of thermal pressure tensor b_{ij} (Wallace, 1998):

$$C^S_{ijkl} = C^T_{ijkl} + \frac{TV}{C_V} b_{ij} b_{kl} \ , \qquad \{7\}$$

where $b_{ij} = (\frac{\partial \sigma_{ij}}{\partial T})_V$ is related to the thermal expansion tensor. For the bulk modulus:

$$K_S = K_T(1+\alpha\gamma T) = K_T(1+\frac{\alpha^2 K_T V}{C_V}) \qquad \{8\}$$

where α and γ are the thermal expansion and Grüneisen parameter, respectively.

At constant *P,T* the elastic constants describing stress-strain relations {1} are given by:

$$C^T_{ijkl} = \frac{1}{V}(\frac{\partial^2 G}{\partial \eta_{ij} \partial \eta_{kl}})_T \qquad \{9\}$$

while at constant P,S they are given by

$$C^S_{ijkl} = \frac{1}{V}(\frac{\partial^2 H}{\partial \eta_{ij} \partial \eta_{kl}})_S \qquad \{10\}$$

Now let us derive from {9} 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 $\overleftrightarrow{\mathbf{V}} = (\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3})$, and the volume of the equilibrium unit cell is then $V_0 = \det \overleftrightarrow{\mathbf{V}}$. Using {4}, for the volume V of a strained cell we obtain:

$$\frac{V}{V_0} = \frac{\det \overleftrightarrow{\mathbf{V}}}{\det \overleftrightarrow{\mathbf{V}}_0} = 1 + \eta_1 + \eta_2 + \eta_3 + \eta_1\eta_2 + \eta_2\eta_3 + \eta_1\eta_3 - \frac{\eta_4^2}{4} - \frac{\eta_5^2}{4} - \frac{\eta_6^2}{4} + \eta_1\eta_2\eta_3 - \frac{\eta_1\eta_4^2}{4} - \frac{\eta_2\eta_5^2}{4} - \frac{\eta_3\eta_6^2}{4} + \frac{\eta_4\eta_5\eta_6}{4} \qquad \{11\}$$

Then one has in the standard tensor notation:

$$\frac{\Delta V}{V_0} = \eta_{ii} + \frac{1}{4}(2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\eta_{ij}\eta_{kl} + O(e^3) \qquad \{12\}$$

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

$$\Delta G = \Delta F + Pe_{ii} + \frac{PV}{4}(2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\eta_{ij}\eta_{kl} \qquad \{13\}$$

From this one has:

$$C^T_{ijkl} = \frac{1}{V}(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}})_T + \frac{P}{2}(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \qquad \{14a\}$$

and, by analogy,

$$C^S_{ijkl} = \frac{1}{V}(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}})_S + \frac{P}{2}(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \qquad \{14b\}$$

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 B^T_{ijkl} and B^S_{ijkl} defined by equations {14ab} 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 $\frac{1}{V}(\frac{\partial^2 E}{\partial\eta_{ij}\partial\eta_{kl}})_S$. These two definitions (via stress-strain relations and from long-wavelength lattice dynamics) become idential at zero pressure. Calculating the second derivatives with respect to the finite Lagrangian strains, different equations are obtained (Wallace, 1998).

ABINIT implementation. In ABINIT, the so-called "proper" elastic constants are calculated as follows:

$$C_{ijkl}^{proper} = \frac{1}{V_0}\frac{d}{d\eta_{kl}}(V\sigma_{ij}) \quad , \qquad \{15\}$$

where V_0 is the volume of the undeformed crystal at given pressure (stress), and V is the volume changed by strain η_{kl}. Here we have only the first derivative, so only first-order changes of V are important (to first order, $\frac{V}{V_0} = \frac{\det\overleftrightarrow{\mathbf{V}}}{\det\overleftrightarrow{\mathbf{V}}_0} = 1+\eta_1+\eta_2+\eta_3$). These "proper" elastic constants do not correspond to the stress-strain definition {1}.

$$C_{ijkl}^{proper} = \frac{1}{V_0}\frac{d}{d\eta_{kl}}(V\sigma_{ij}) = \frac{1}{V_0}\frac{d}{d\eta_{kl}}[V_0(1+\eta_{kl}\delta_{kl})(\sigma_{ij}^0 + C_{ijkl}\eta_{kl})] = \frac{d}{d\eta_{kl}}[\sigma_{ij}^0 + \sigma_{ij}^0\eta_{kl}\delta_{kl} + O(\eta^2)] =$$

$$= C_{ijkl+}\frac{d}{d\eta_{kl}}(\sigma_{ij}^0\eta_{kl}\delta_{kl}) = C_{ijkl} + \sigma_{ij}^0\delta_{kl} \quad , \qquad \{16\}$$

where σ_{ij}^0 is the stress in the reference structure (for which the elastic constants are being calculated). From {16} the stress-strain defined elastic constants are:

$$C_{ijkl} = C_{ijkl}^{proper} - \sigma_{ij}^0\delta_{kl} \qquad \{17\}$$

In case of hydrostatic pressure ($P = -\sigma_{11} = -\sigma_{22} = -\sigma_{33}$) we obtain corrections only for C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, e.g.: $C_{11} = C_{11}^{proper} + P$, $C_{12} = C_{12}^{proper} + P$.

At non-hydrostatic conditions, the situation becomes more complicated, in particular the Voigt symmetry (C_{ij}=C_{ji}) will be kept only by the "proper" constants – while for stress-strain constants it will be broken, as originally noted by Barron and Klein (1965). For example, from {17} C_{41} will involve a stress correction, while C_{14} will not.

For a systematic treatment of the strain, stress, electrical field and polarisation, see related document "vanderbilt-anaddb-notes.pdf".

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