Chapter 2

Computational design of materials with extreme mechanical properties

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2.1 *Ab initio* elasticity of single-crystal solids

For a strained crystal, the most general linear relationship which connects stress to strain is provided by the generalized version of the well-known Hooke's law

$$\sigma_{mn} = C_{mnij}\varepsilon_{ij}$$

The strained crystal possesses an elastic energy density of

$$e_{tot} = E_{tot}/V = \frac{1}{2}C_{mnij}\varepsilon_{mn}\varepsilon_{ij} = \frac{1}{2}C_{\alpha\beta}\varepsilon_{\alpha}\varepsilon_{\beta}$$

For a cubic lattice, only three independent elastic constants remain,

$$C_{\alpha\beta}(cubic) = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}$$

whereas for a tetragonal lattice contains six elastic constants

$$C_{\alpha\beta}(tetragonal) = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix}$$

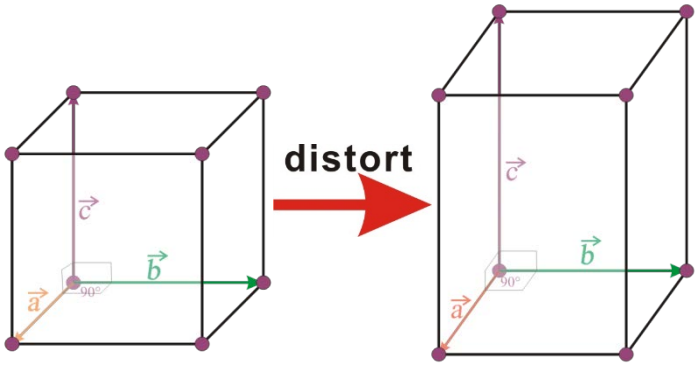
ab initio methods for computing single crystal elastic constants

The energy-strain approach:

The energy-strain approach is based on the computed total energies of properly strained crystal. For each strain type, several magnitudes of strains are applied and the corresponding total energies are computed with an ab initio approach. The stiffness is then derived from the curvature of the energy-strain relation by means of a least-squares fit.

As an example, the deformations used for the calculation of the elastic constants in a cubic crystal are discussed. The elastic energy density for a cubic crystal can be expressed as

$$e_{tot} = \frac{1}{2}c_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + \frac{1}{2}c_{44}(\varepsilon_{23}^2 + \varepsilon_{31}^2 + \varepsilon_{12}^2) + c_{12}(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{33}\varepsilon_{22} + \varepsilon_{11}\varepsilon_{33})$$



$$\varepsilon_1 = \varepsilon_2 = da/a\,,\ \varepsilon_3 = dc/c\,,$$
$$\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$$

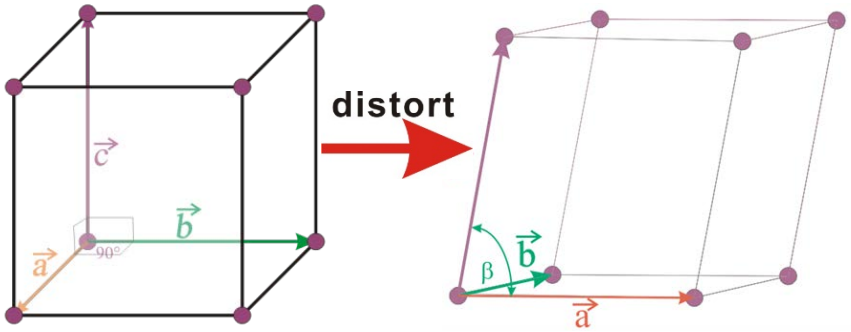
$$e_{tot} = (c_{11} + c_{12})\varepsilon_{11}^2 + 2c_{12}\varepsilon_{11}\varepsilon_{33} + \frac{c_{11}}{2}\varepsilon_{33}^2$$
$$= \frac{c_{11} + 2c_{12}}{6}\left(\frac{dV}{V}\right)^2 + \frac{2(c_{11} - c_{12})}{6}\left(\frac{d(c/a)}{c/a}\right)^2$$

c11 and c12 can be determined from the energy-strain relationship with different magnitudes of tetragonal distortion.

A trigonal lattice can also be produced by distorting a cubic crystal along its [111] direction to yield a crystal structure of

$a = b = c$, and $\alpha = \beta = \gamma \neq 90°$

$$e_{tot} = \frac{1}{2}c_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + \frac{1}{2}c_{44}(\varepsilon_{23}^2 + \varepsilon_{31}^2 + \varepsilon_{12}^2) + c_{12}(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{33}\varepsilon_{22} + \varepsilon_{11}\varepsilon_{33})$$



$a = b = c$, and $\alpha = \beta = \gamma = 90°$

$a = b = c$, and $\alpha = \beta = \gamma \neq 90°$

$$e_{tot} = \frac{c_{11} + 2c_{12}}{6}\left(\frac{dV}{V}\right)^2 + \frac{2c_{44}}{3}\left(\frac{d(c/a)}{c/a}\right)^2$$

The shear constant G=c44 can then be determined from the energy-strain relationship with different magnitudes of triangle deformation

Bulk modulus *B* of a crystal

- To determine the bulk modulus *B* of a crystal, we assume the crystal is subjected to hydrostatic isotropic compression. By calculating the curvature at the equilibrium volume V0

$$B = V \left. \frac{\partial^2 E}{\partial V^2} \right|_{V_0} = \frac{1}{3}(c_{11} + 2c_{12})$$

The stress-strain approach

Assuming cubic symmetry, the elastic constants can be expressed in terms of the stress tensor by

$$c_{44} = \frac{1}{2}\frac{\partial \sigma_{12}}{\partial \varepsilon_{12}}$$

$$\frac{1}{2}(c_{11} - c_{12}) = -\frac{1}{2}\frac{\partial \sigma_{33}}{\partial \varepsilon_{33}}$$

$$B = \frac{1}{3}(c_{11} + 2c_{12}) = \frac{\partial \sigma_{11}}{\partial \varepsilon_{11}}$$

Whereas within the *energy-strain* approach several magnitudes of strain have to be evaluated in order to obtain the elastic constant from an analytic fit to the total energy data, within the *stress-strain* approach just one evaluation is sufficient to obtain the same information.

Elastic Constants of a Polycrystalline Material

- Elastic moduli of polycrystalline materials can be derived by macroscopic averaging from its single crystal elastic constants.
- **The averaging encumbers all possible orientations of the crystal**, and there is a well-defined lower and upper limit for the elastic moduli.
- Based on the averaging procedures, the *ab initio* treatment for single crystals can be extended to polycrystalline samples.

Case study: *ab initio* calculation of elastic properties of BN.

- Create the crystal structure of cubic BN
- Optimize the structure
- Calculate the elastic constants of BN
- Description of the elastic constants of the crystal