Equations of State

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Why EoS ?

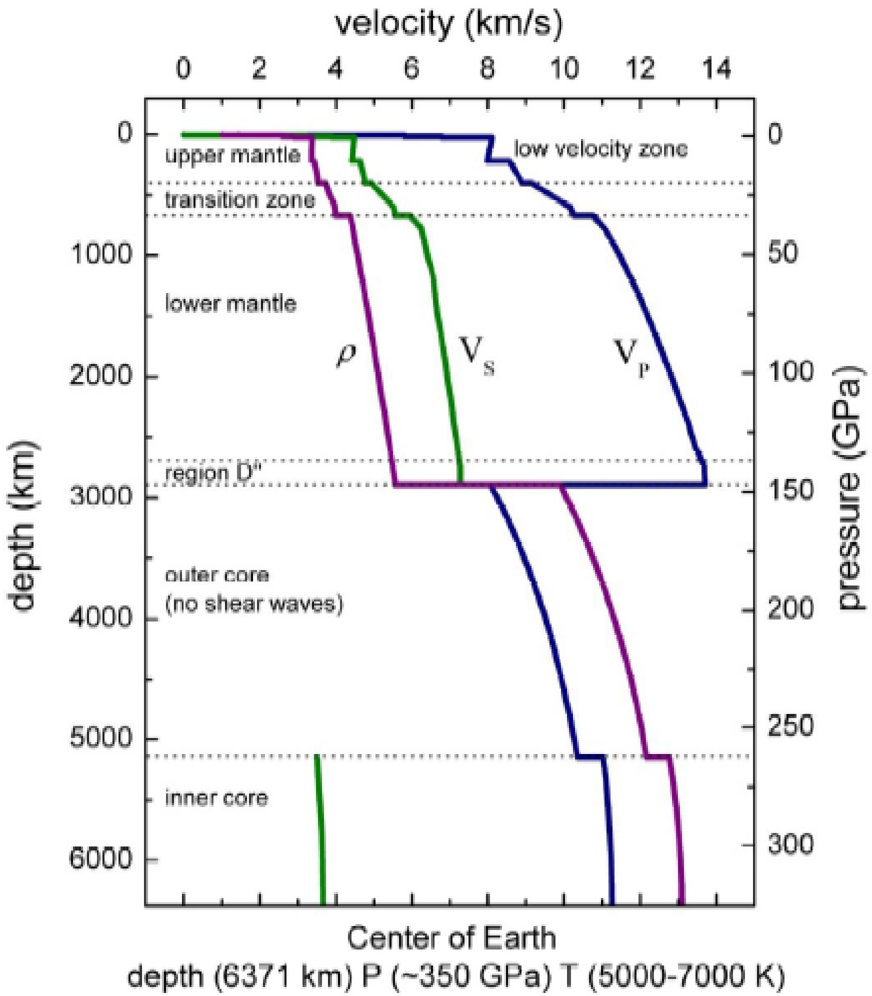
The Earth's interior is divided globally into layers having distinct seismic properties

Speed with which body waves travel through the Earth's interior are simply related to the density and elastic moduli of the constituent materials

$$v_P^2 = \left(K_S + \frac{4}{3}G_S\right)\Big/\rho$$

$$v_S^2 = G_S/\rho$$

$$v_\Phi = \sqrt{\Phi} = \sqrt{K/\rho}$$



Dziewonski and Anderson 1981

Outline

❶ **Overview of few equations of state: Principles and assumptions**

❷ **Hydrostaticity and pressure scales**

❸ **Working example**

Helmholtz free energy

$$A(V,T) = A_c(V) + A_{vib}(V,T) + A_{el}(V,T)$$

compression curve

vibrational contribution

electronic contribution

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$P(V,T) = P_c(V) + P_{vib}(V,T) + P_{el}(V,T)$$

reference curve

thermal pressure

Higher order derivatives of the energy function

$K_T = -V(\partial P/\partial V)_T$ $\quad$ $K'_T = (\partial K_T/\partial P)_T$ $\quad$ etc...

Finite strain theory

Infinitesimal elasticity:

❶ strains are determined by stresses and are reversible

❷ strains are small and their squares and products are negligible

Reference state:

❶ unstrained state (Lagrangian)

❷ deformed state, i.e. volume at final compression (Eulerian)

❸ incremental strain (Hencky)

These EoS are empirical !

Birch-Murnaghan EoS

Stacey et al. (1981)

Helmholtz free energy: $A = A_2 f^2 + A_3 f^3 + A_4 f^4 + \ldots$

$$f = -\varepsilon = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right] \qquad \left\{ \text{Lagrangian} \quad f = -\varepsilon = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{2/3}\right] \right\}$$

Determination of the A coefficients at $P = 0$ with $V = V_0$, $K = K_0$ and $K' = K_0'$

$$P = -\frac{dA}{df}\frac{df}{dV} = 3K_0 f (1 + 2f)^{5/2} \left(1 + \frac{3}{2}(K_0' - 4) f + \frac{3}{2}\left(K_0 K_0'' + (K_0' - 4)(K_0' - 3) + \frac{35}{9}\right) f^2 \right)$$

IV order Birch-Murnaghan EoS

Birch-Murnaghan EoS

Assumptions:

❶ Eulerian strains under hydrostatic compression

❷ strictly derived only for isotropic or cubic materials

❸ solid under compression is homogeneously strained

❹ EoS are continuously differentiable

❺ higher order terms of the Taylor expansion are negligible

Birch-Murnaghan EoS

The behaviour of K' is a valuable test of the plausibility of a EoS

$$P = \left(-\frac{dA}{dV}\right)_{T=0} = 3K_0 f(1+2f)^{5/2}\left(1+\frac{3}{2}(K_0'-4)f+\frac{3}{2}\left(K_0K_0''+(K_0'-4)(K_0'-3)+\frac{35}{9}\right)f^2\right)$$

Plausibility in the limit of large compression: $\frac{V_0}{V} \rightarrow \infty$

K' negative

$$K' = K_0' + \frac{3}{2}K_0K_0''\left(\left(\frac{V}{V_0}\right)^{-2/3} - 1\right)$$

$$\frac{V_0}{V} = \left[1 + \frac{2K_0'}{-3K_0K_0''}\right]^{3/2}$$

Logarithmic EoS

Hencky strain:

$$\varepsilon = \int_{l_0}^{l} d\varepsilon = \ln \frac{l}{l_0}$$

The integration is possible only if the principal axes do not rotate during deformation

Hydrostatic compression

Poirier and Tarantola 1998

$$\varepsilon_H = \frac{1}{3} \ln \frac{V}{V_0}$$

Logarithmic EoS

$$A = A_2 f^2 + A_3 f^3 + A_4 f^4 + \ldots$$ with $$f = -\varepsilon_H = \frac{1}{3}\ln\frac{V_0}{V}$$

Poirier and Tarantola 1998

$$P = -\frac{dA}{df}\frac{df}{dV} = \frac{1}{3V}\frac{dA}{df} = \frac{1}{V_0}\frac{V_0}{V}\sum_{n=2}^{N}\frac{n a_n}{3^n}\left(\ln\frac{V_0}{V}\right)$$

Determination of the *a* coefficients at $P = 0$ with $V = V_0$, $K = K_0$ and $K' = K_0'$

$$P = K_0\frac{\rho}{\rho_0}\ln\frac{\rho}{\rho_0}\left[1 + \left(\frac{K_0' - 2}{2}\right)\ln\frac{\rho}{\rho_0}\right]$$

III order

Interatomic potential

Forces between atoms in the crystal are defined with

assumed interatomic potential

↓

calculation of density as a function of pressure

EoS

Empirical approach as for strain EoS

Born-Mie potential

$$E(r) = -\frac{a}{r^m} + \frac{b}{r^n}$$

attractive forces

repulsive forces

Poirier 2000

$$P = \frac{3K_0}{n-m}\left[\left(\frac{V_0}{V}\right)^{1+n/3} - \left(\frac{V_0}{V}\right)^{1+m/3}\right]$$

Born-Mie potential

$$P = \frac{3K_0}{n-m}\left[\left(\frac{V_0}{V}\right)^{1+n/3} - \left(\frac{V_0}{V}\right)^{1+m/3}\right]$$

Different values of *m* and *n* have been used in the literature (Stacey et al. 1981)

Special case: $m = 2$ and $n = 4$

Plausibility: $$K' = K_0' + K_0 K_0'' \frac{P}{K}$$

$$P = \frac{3}{2}K_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]$$

II order Birch-Murnaghan EoS

Vinet EoS

Empirical potential: $A(1+ar)e^{-br}$

A, a, b constants depending on the material

Vinet et al. 1987, Poirier 2000

$$P = 3K_0\left(\frac{V}{V_0}\right)^{-2/3}\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\exp\left\{\frac{3}{2}(K_0'-1)\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\right\}$$

Good for very high compression of metals and ionic solids

Thermal pressure

$$P(V,T) = P_c(V) + P_{vib}(V,T)$$

P-V-T Birch-Murnaghan EoS

298 K V_0, K_0, K_0' … **Isotherm at room temperature**

***T* (K)** V_{T0}, K_{T0}, K_{T0}' … **Isotherm at any given temperature**

$$V(T) = V_0(T_0)\exp\int_{T_0}^{T}\alpha(T)dT$$ with $$\alpha(T) = a + bT$$

and

$$K(T) = K_0(T_0) + \left(\frac{\partial K}{\partial T}\right)_P (T - T_0)$$ linear variation with *T*

Usual assumption: *K'* is the same at all T

Thermal pressure

(Jackson and Ridge, 1996)

(Anderson et al., 1989)

$$P(V,T) = P_c(V) + P_{th}(V,T)$$

$$\left(\frac{\partial P}{\partial T}\right)_V$$

$$\Delta P_{th} = P_{th}(V,T) - P_{th}(V,T_0) = \int_{T_0}^{T} [\alpha K_T]_V \, dT$$

More general: $\Delta P_{th} = \int_{T_0}^{T} [\alpha K_T](P_0,T)\,\delta T + \left(\frac{\partial K_T}{\partial T}\right)_V \left\{ -\ln\left(\frac{V}{V_0}\right)(T - T_0) + \int_{T_0}^{T}\int_{T_0}^{T} \alpha \, dT\,dt \right\}$

Simplest case: $\Delta P_{th} = \alpha K_T \Delta T$

αK_T independent of temperature and volume

$$\Delta P_{th}(V,T) = a_1(T - T_0) + a_2 \ln\left(V/V_0\right)(T - T_0) + a_3(T - T_0)^2 + a_4(T - T_0)^3$$

„Thermodynamic“ EoS

➊ **Thermal expansion at atmospheric pressure: *$V(T,P_0)$***

➋ **Compression at 300 K: *$V(T_0,P)$***

➌ **Compression at high temperature: *$V(T,P)$***

$$P(V,T) = P(V,T_0) + \Delta P_{th}(V,T) = \sum b_i X_i\left(V/V_0, T\right)$$

$$X_i\left(V/V_0, T\right) = 2 f_E^i (1 + 2 f_E)^{5/2} \quad \text{with} \quad b_1 = 3K_{T_0}/2 \quad \text{and} \quad b_2 = 9K_{T_0}\left(K'_{T_0} - 4\right)/8$$

III order Birch-Murnaghan EoS for reference isotherm

$$X_3 = T - T_0 \qquad X_4 = (T - T_0)\ln(V/V_0) \qquad X_5 = (T - T_0)^2 \qquad X_6 = (T - T_0)^3$$

Mie-Grüneisen EoS

Lattice dynamics approach: the thermal pressure is related to the vibrational density of state

$$\Delta P_{th} = \frac{\gamma(V)}{V}\left[E_{th}(V,T) - E_{th}(V,T_0)\right]$$

Grüneisen parameter: $$\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^q \qquad q = \frac{d\ln\gamma}{d\ln V} = const.$$

Thermal free energy: $$E_{th} = \frac{9nRT}{(\theta/T)^3}\int_0^{\theta/T}\frac{\xi^3}{e^{\xi}-1}d\xi$$

$$\theta(V) = \theta_0 \exp\{[\gamma_0 - \gamma(V)]/q\}$$

γ and θ independent of temperature, functions of volume only

Experimental details

Pressure medium

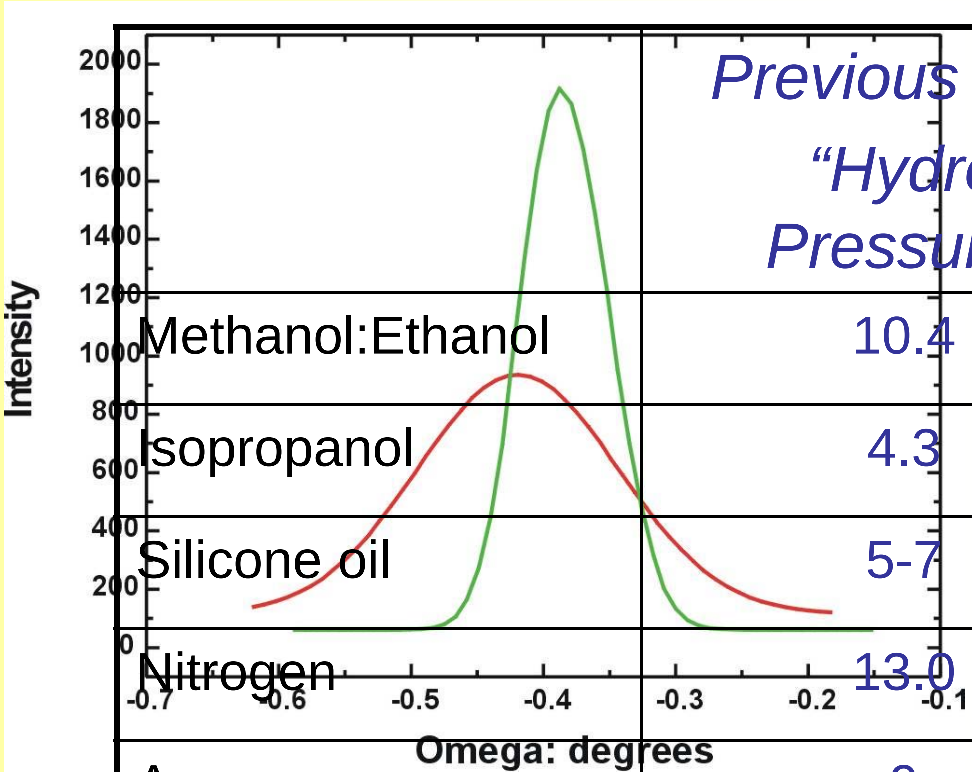
❶ Requirements

- Hydrostatic
- Does not dissolve sample
- Does not penetrate sample

❷ Non-hydrostatic stresses

- Cannot be measured accurately
- Reduce the data quality
- Result in different EoS
- affect structural phase transitions

Broadening of diffraction peaks



	Previous max "Hydro Pressure"	*Diffraction broadening (GPa)*
Methanol:Ethanol	10.4	10.1
Isopropanol	4.3	3.9
Silicone oil	5-7	< 2.0
Nitrogen	13.0	3
Argon	9	2
Fluorinert	5-10	1

Non-hydrostatic stresses give rise to broadening of the diffraction profiles

Angel et al. 2007 J Appl Cryst 40:26

Gas loading

He and Neon

No broadening observed so far up to 22 GPa with a point detector.

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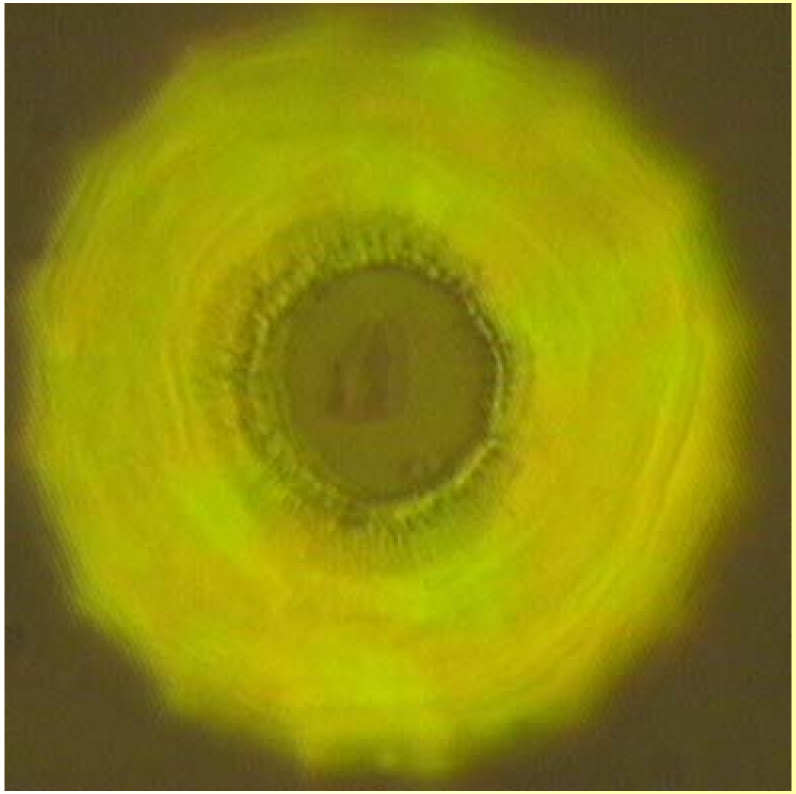


75 GPa (ESRF)

Pressure scales

❶ **Single-crystal room *T* up to 10 GPa:**
quartz crystal (Angel et al. 1997)

❷ **Single-crystal and powder room *T* any pressure:**
ruby fluorescence

❸ **Powder H*T* and H*P*:**
EoS of metals like Au, Pt, Cu, Ag ...
EoS of non metal like MgO, NaCl ...
(Fei et al. 2004)

❹ **Single-crystal H*T* and H*P*:**
? ... EoS of Neon and He

Ruby scales

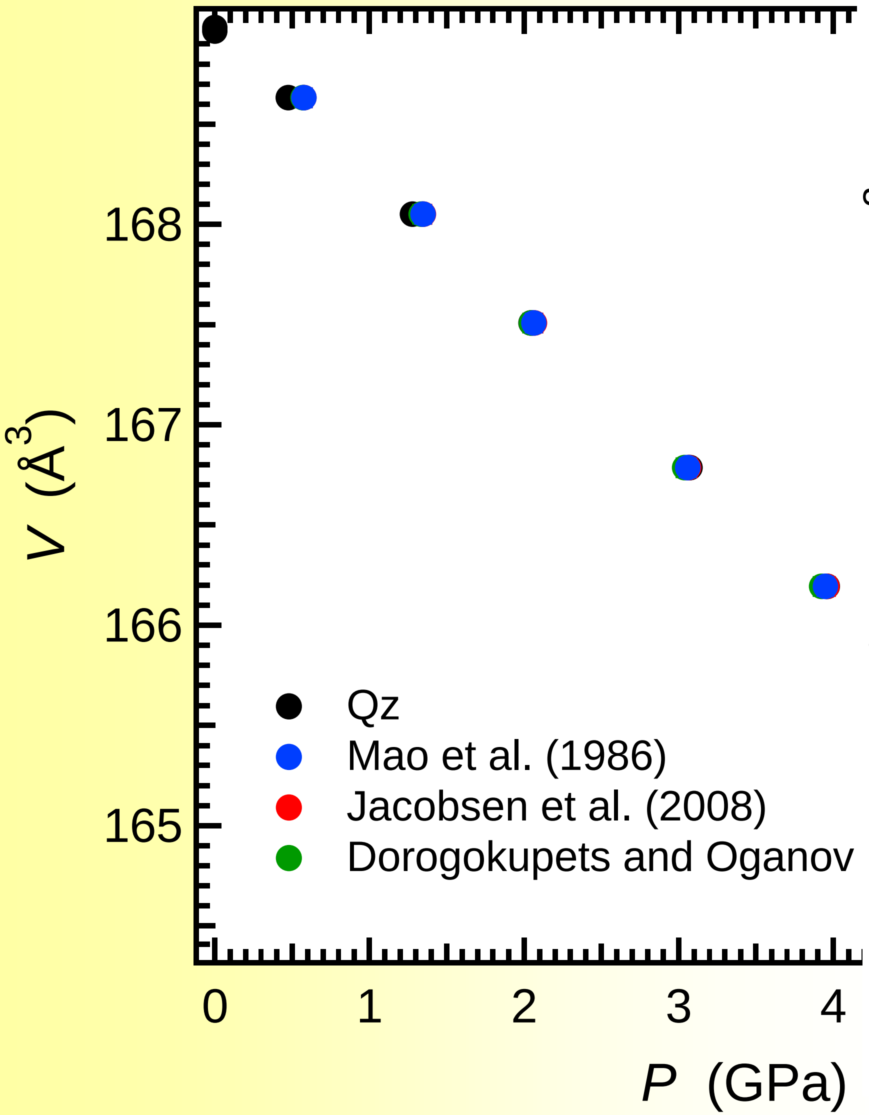
The ruby scales are based on the calibration of the shift of the ruby R_1 luminescent line and the specific volume of some standard material with increasing pressure

➊ **Mao et al. (1996): ruby vs Cu in Ar pressure medium**

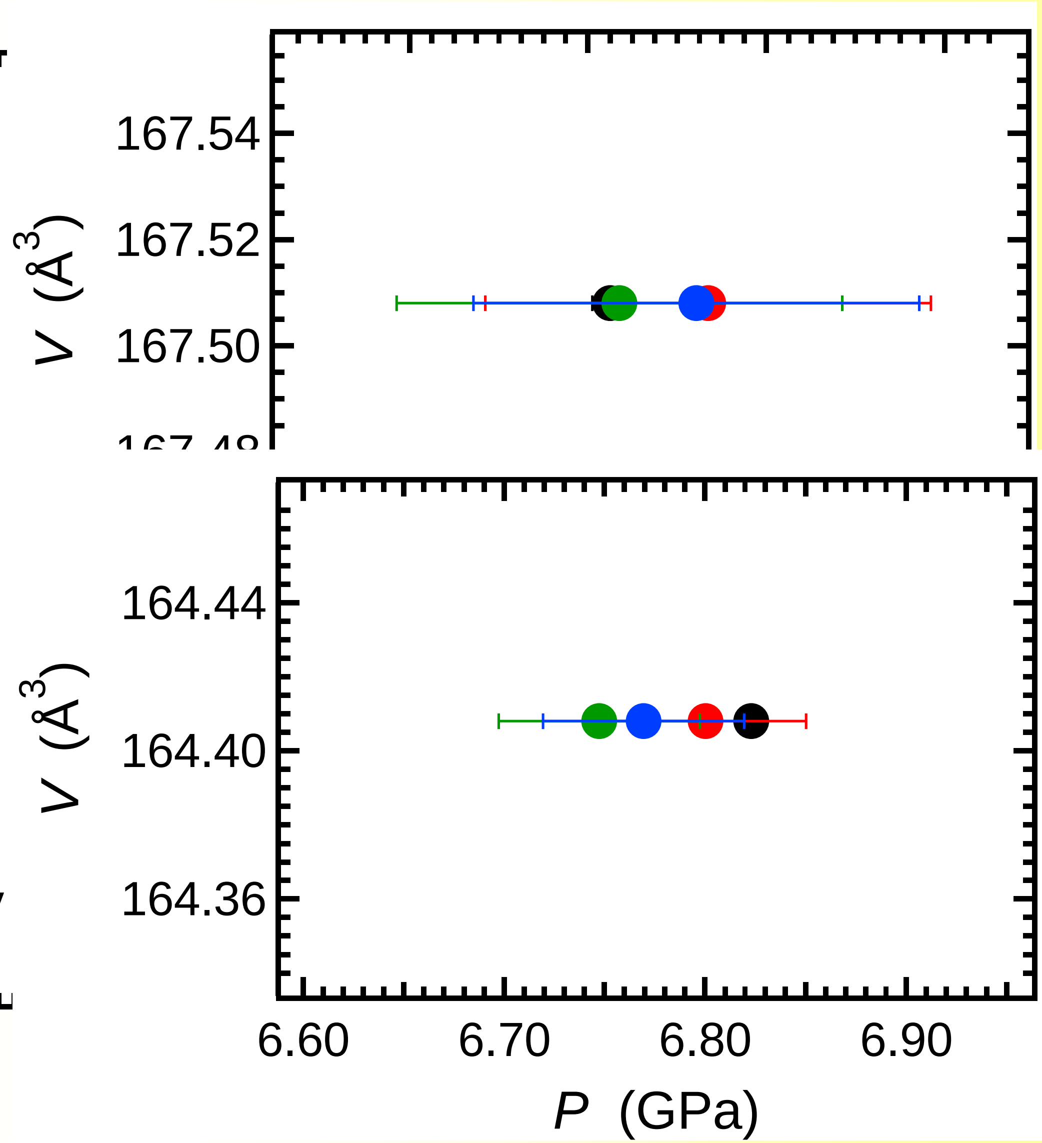
➋ **Dorogokupets and Oganov (2007): ruby vs semiempirical EoS of standard metals**

➌ **Jacobsen et al. 2008: ruby vs MgO in He pressure medium**

Ruby scales



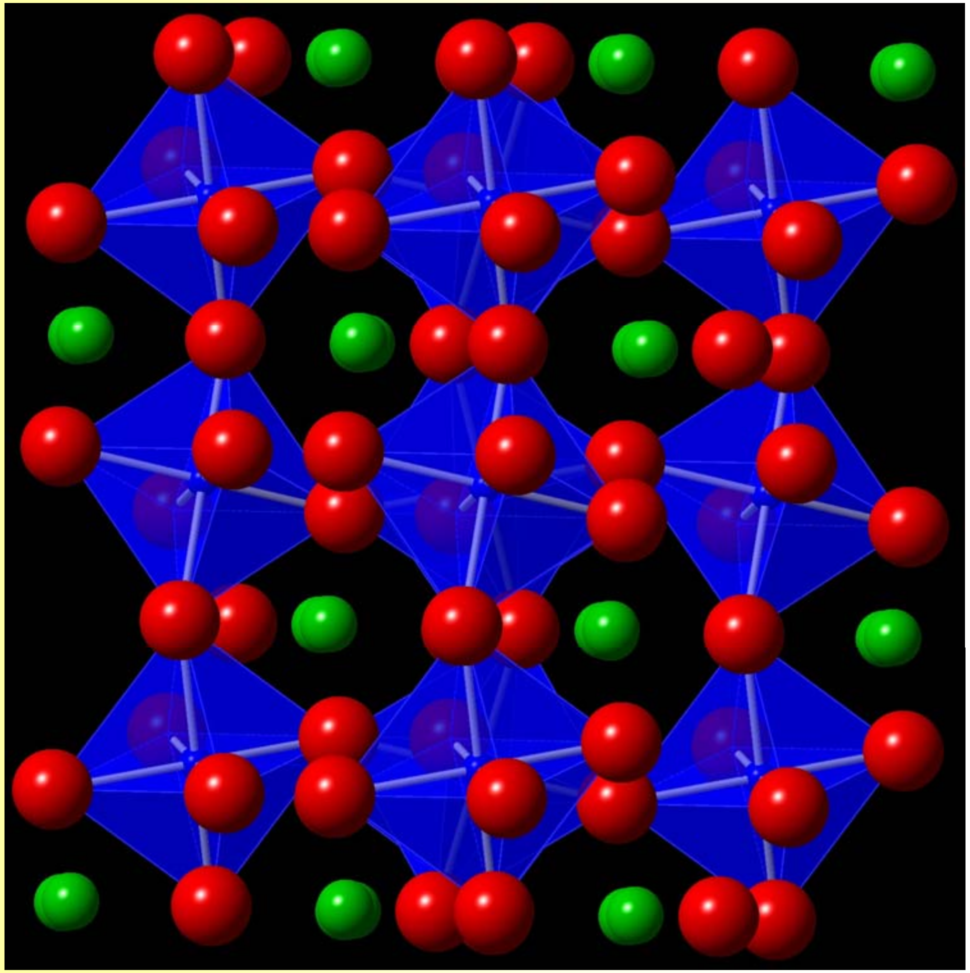
V (Å³)
P (GPa)
0
1
2
3
4
165
166
167
168
Qz
Mao et al. (1986)
Jacobsen et al. (2008)
Dorogokupets and Oganov



V (Å³)
167.54
167.52
167.50
V (Å³)
164.44
164.40
164.36
6.60
6.70
6.80
6.90
P (GPa)

In practice

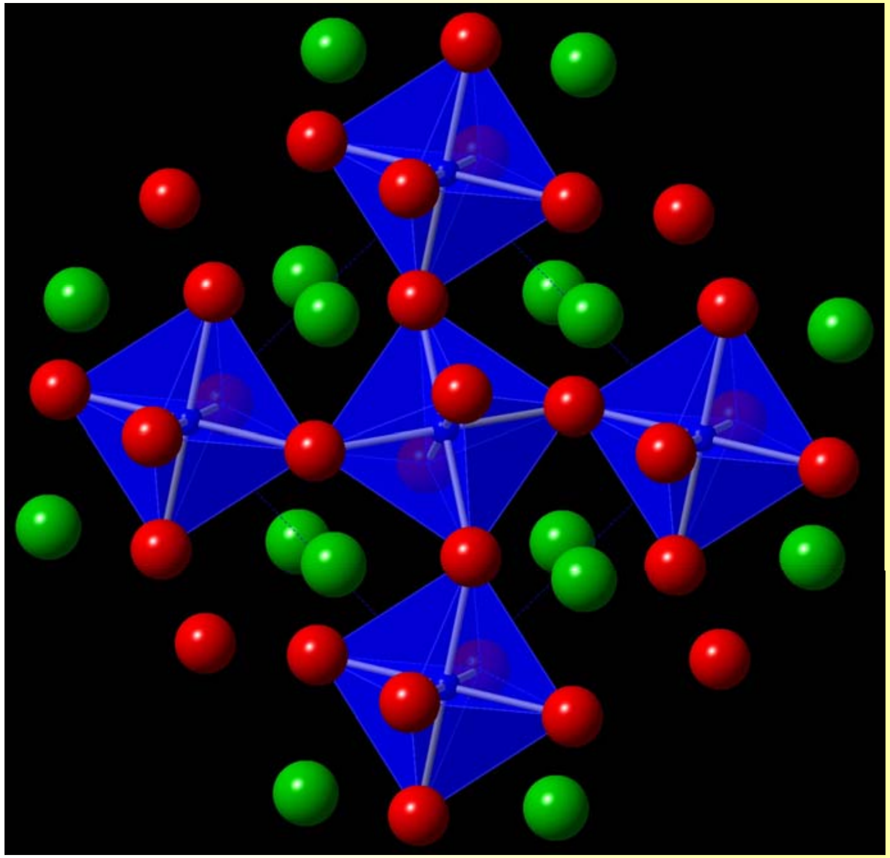
Orthorhombic $MgSiO_3$ perovskite



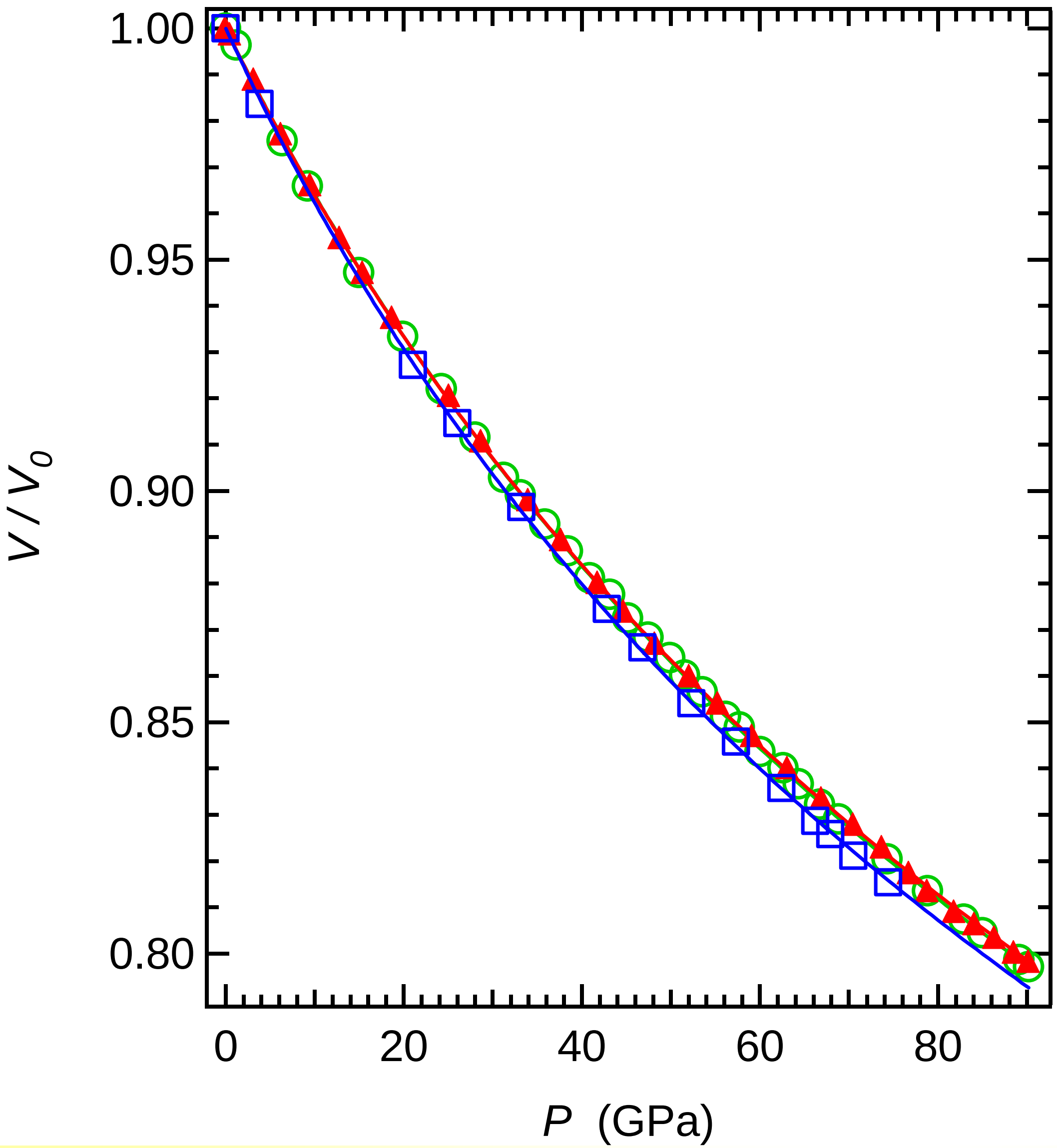
out-of-phase tilting along [110]

Pbnm $a^- a^- c^+$

in-phase tilting around [001]



Volume compressibility



V_0 = 162.36 (4) Å

K_0 = 251 (2) GPa

K' = 4.11 (7)

V_0 = 163.09 (6) Å

K_0 = 253 (2) GPa

K' = 3.99 (7)

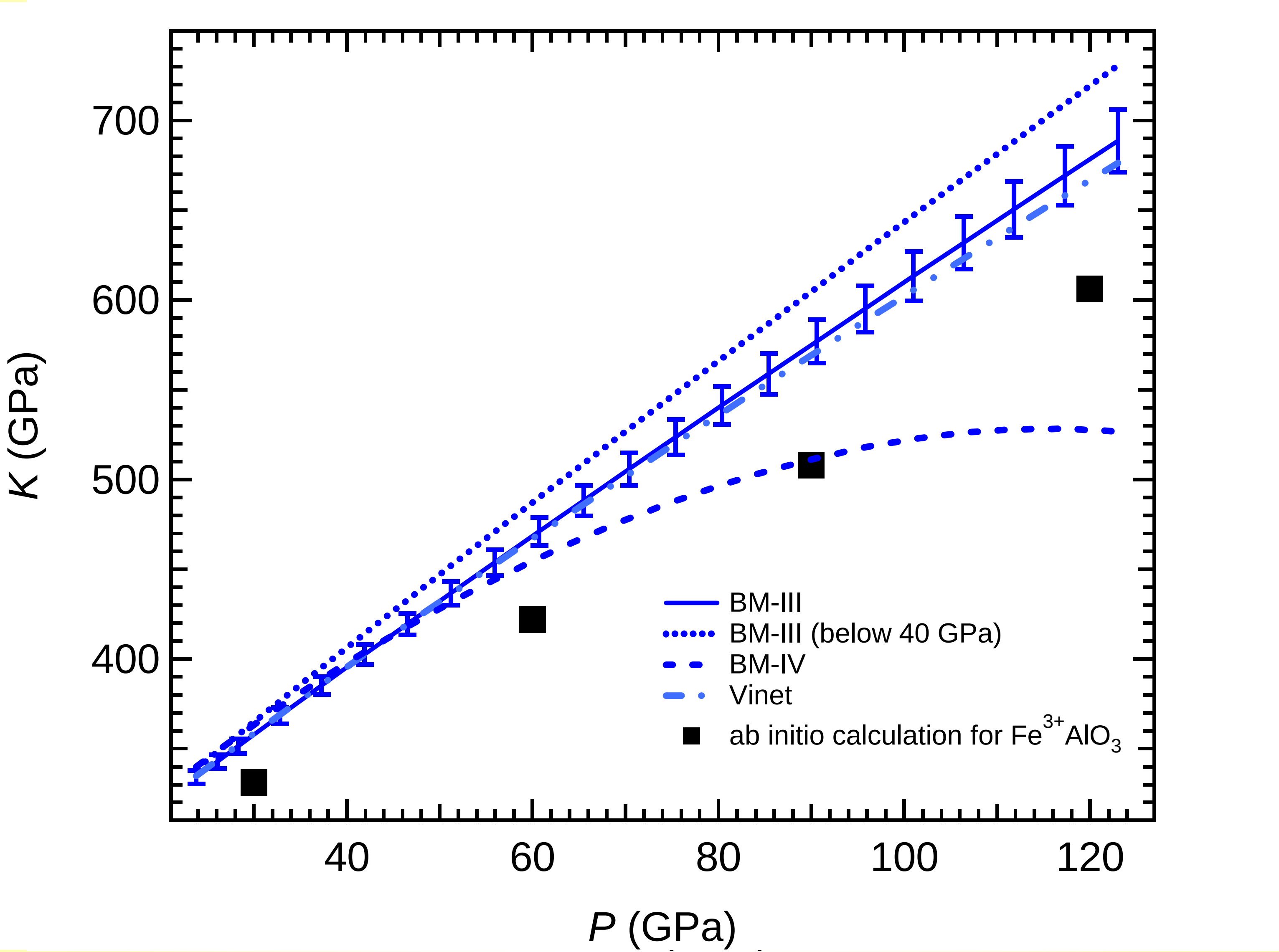
V_0 = 168.93 (5) Å

K_0 = 240 (2) GPa

K' = 4.12 (8)

Boffa Ballaran et al. 2012

Bulk moduli



700
600
500
400
K (GPa)
40
60
80
100
120
P (GPa)
BM-III
BM-III (below 40 GPa)
BM-IV
Vinet
ab initio calculation for $Fe^{3+}AlO_3$

F-f plot

Angel 2000

Normalised stress vs finite strain

➊ Visual diagnostic tool to determine which higher order term is significant in an EoS

➋ Can be applied to any isothermal EoS based upon finite strain

Birch-Murnaghan EoS

$$f = -\varepsilon = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]$$

IV order Birch-Murnaghan EoS

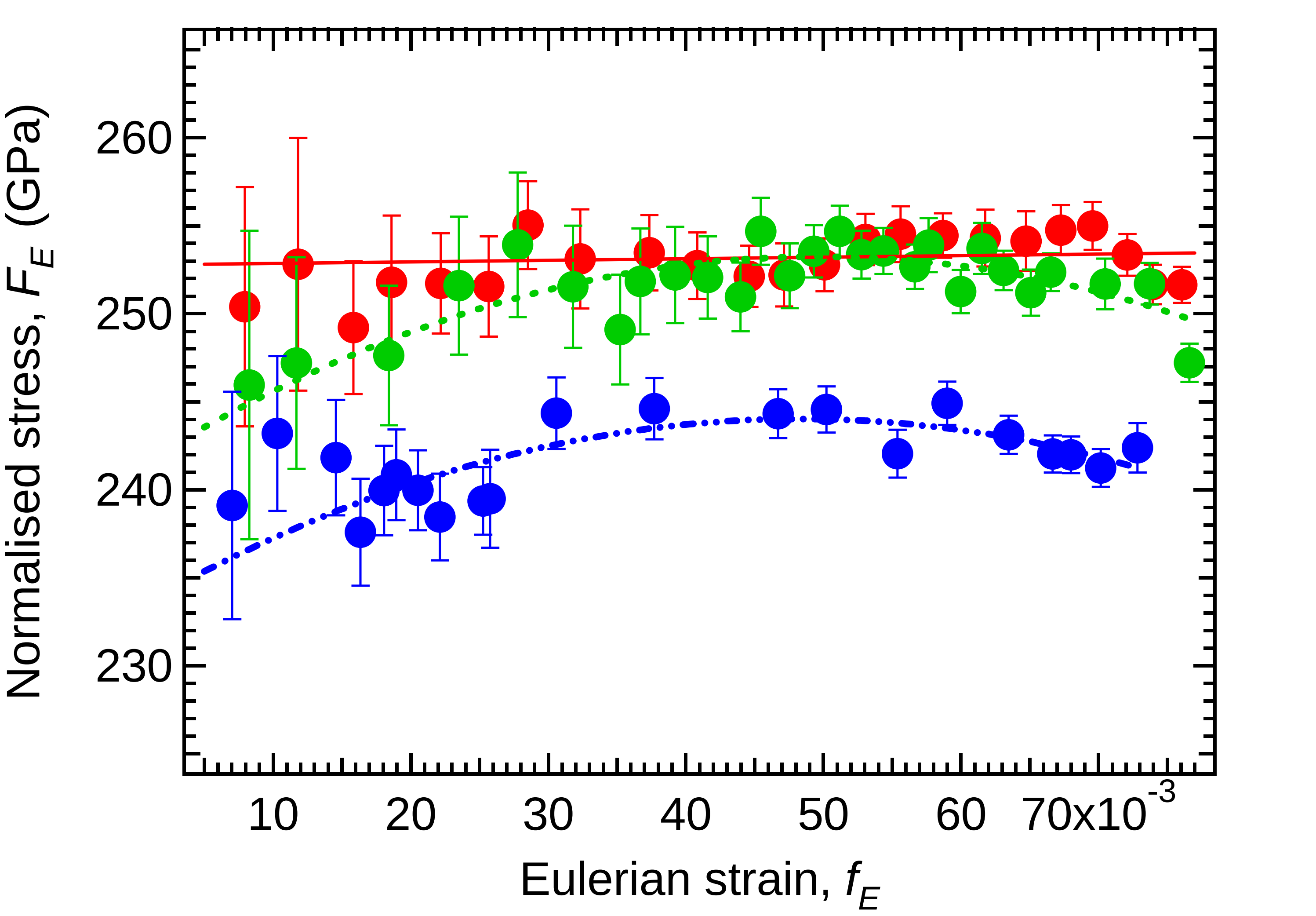
$$P = -\frac{dA}{df}\frac{df}{dV} = 3K_0 f\left(1+2f\right)^{5/2}\left(1+\frac{3}{2}\left(K_0'-4\right)f + \frac{3}{2}\left(K_0K_0''+\left(K_0'-4\right)\left(K_0'-3\right)+\frac{35}{9}\right)f^2\right)$$

Normalised stress

$$F = \frac{P}{3f\left(1+2f\right)^{5/2}}$$

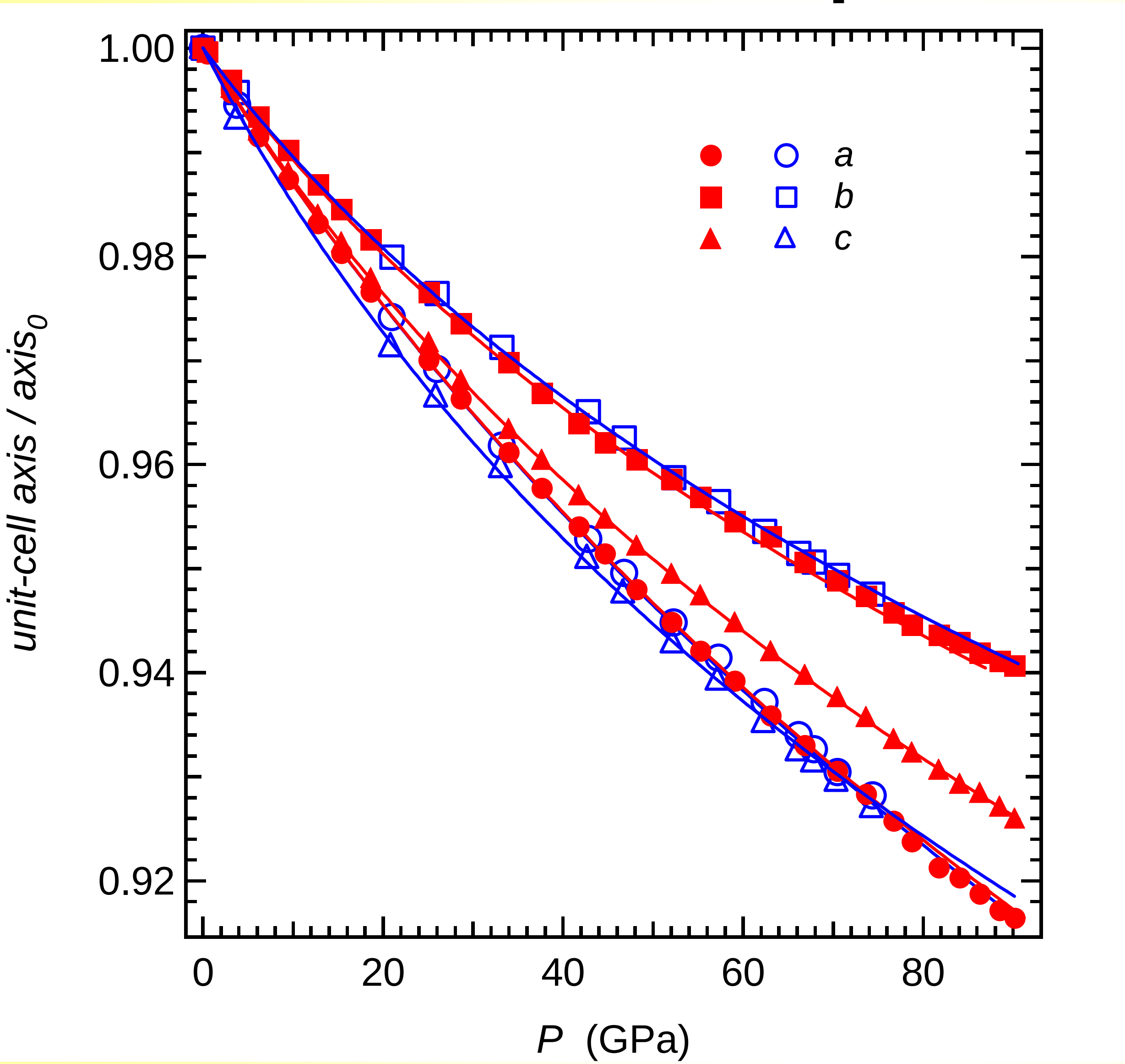
$$F = K_0 + \frac{3}{2}K_0\left(K_0'-4\right)f + \frac{3}{2}K_0\left[\left(K_0K_0''\right)+\left(K_0'-4\right)\left(K_0'-3\right)+\frac{35}{9}\right]f^2$$

F-f plot



Normalised stress, F_E (GPa)
260
250
240
230
10
20
30
40
50
60
70x10^{-3}
Eulerian strain, f_E

Axial compressibility

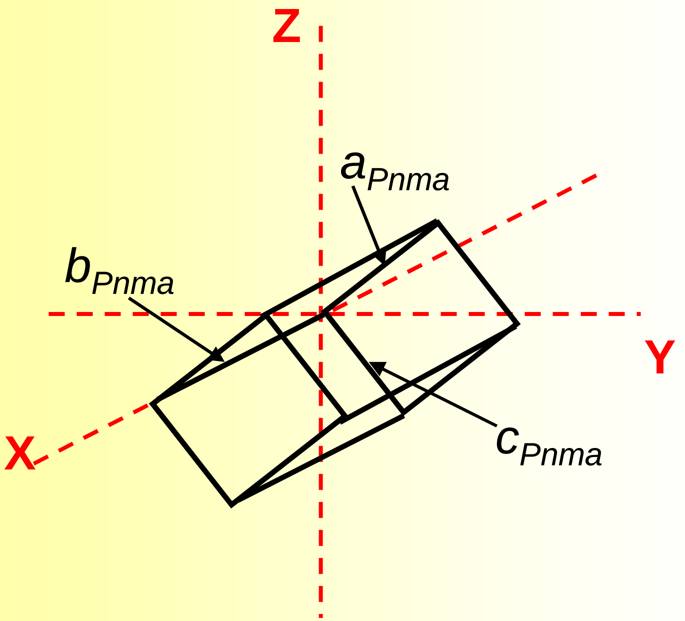


K_0 (*a*) : K_0 (*b*) : K_0 (*c*)

0.81	:	1	:	0.82
0.83	:	1	:	0.69
0.84	:	1	:	0.85

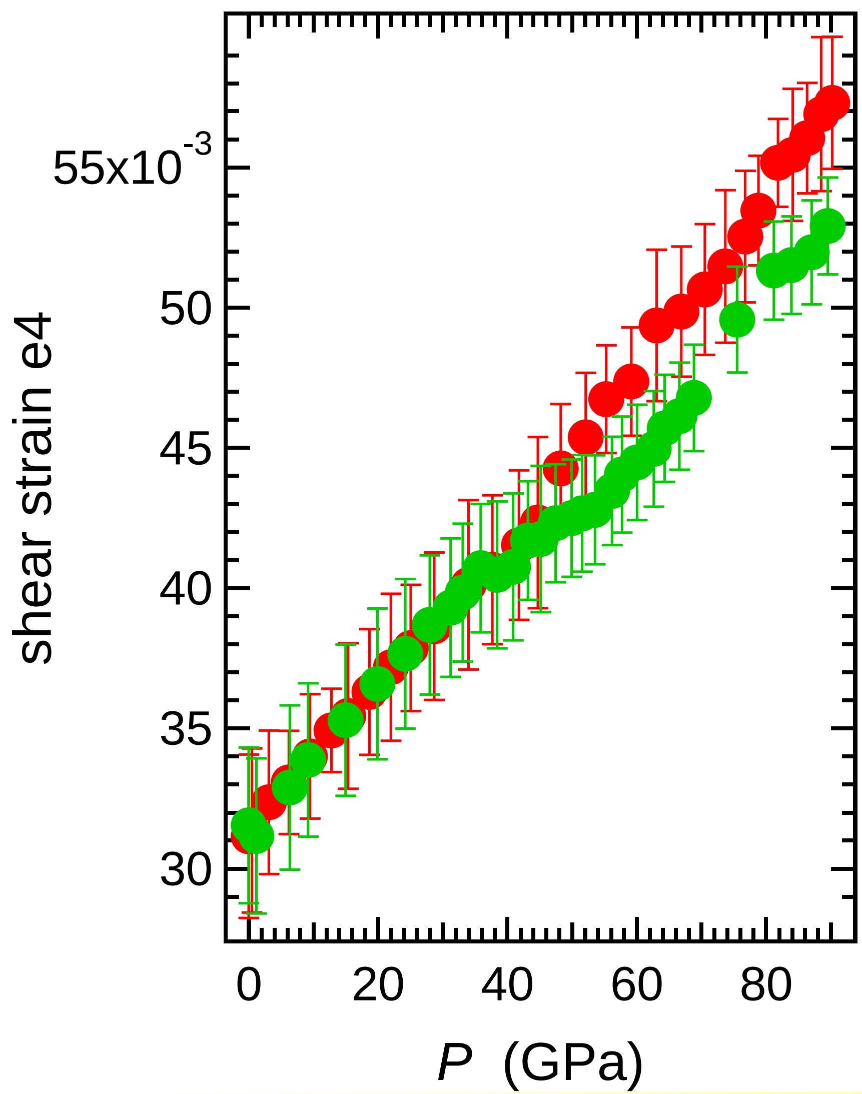
Lattice strain

Pnma



$$e_4 = \frac{c/\sqrt{2} - a_0}{a_0} - \frac{a/\sqrt{2} - a_0}{a_0}$$

Carpenter et al. 2006



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