

**CIDER 2006 Summer Program****Mineral Physics Component**

- Min Phys 1 Thermodynamics (Lars)
- Min Phys 2 Mantle Mineralogy (Lars)
- Tutorial 1 Constructing Earth Models (Lars)
- Tutorial 2 Melts (Marc)
- Min Phys 3 Equation of state and Lattice Dynamics (Tom)
- Min Phys 4 Phase Equilibria (Marc)
- Min Phys 5 Elasticity (Tom)
- Tutorial 3 Equation of state data analysis (Tom)
- Min Phys 6 Fluids and Melts (Marc)

**Questions:**

-- What bulk compositions are compatible with seismic velocity and density data for the transition zone and upper mantle?

*How do these compare to inferences from peridotites, meteorites?*

*How much heterogeneity is allowed?*

-- What is the origin of seismic discontinuities?

*Can there be chemical changes in addition to or instead of phase changes?*

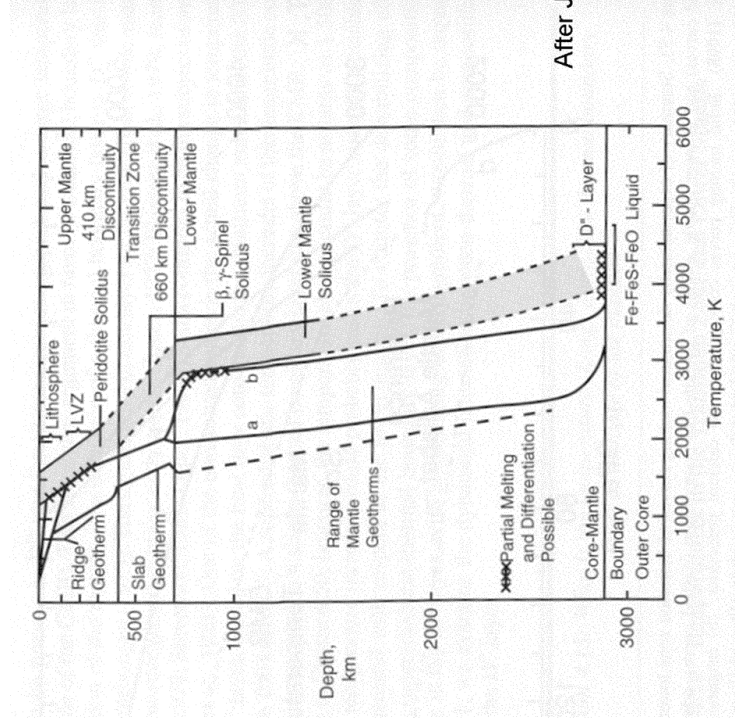
-- How do slabs interact with the transition zone?

*What is the density contrast between the slab and surrounding mantle?*

-- How can we interpret tomographic images?

*What is the sensitivity of density, velocity to lateral temperature, phase and chemical changes?*

What is the thermal structure of the transition zone?



**Overview: Fundamental Thermodynamic Relation**

Energy functions: E H F G

Independent Variables: P, V, T, S + .....

Maxwell's relations:  $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Higher order derivatives – the quantities we would really like to know:

Bulk modulus:  $K_T = -V \left(\frac{\partial P}{\partial V}\right)_T$  Specific Heat:  $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$   
 (adiabatic or isentropic) (isochoric or isobaric)

Thermal expansivity:  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$  Gruneisen parameter:  $\gamma = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S$

These quantities are not independent:  $\gamma = V \left(\frac{\partial P}{\partial E}\right)_V = \frac{\alpha K_T V}{C_V}$

Thermodynamic path is important:  $\frac{K_S}{K_T} = 1 + \alpha \gamma T$

### Equation of state

-- Relationship between **pressure**, **volume**, and **energy** (or **temperature**)

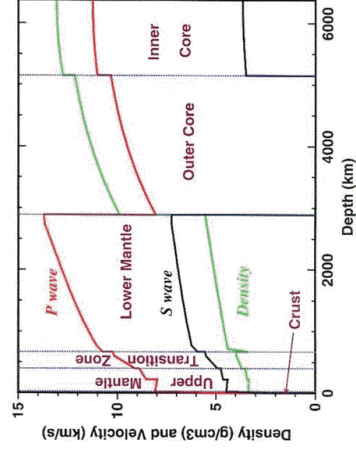
Volume:  $V$

$$\text{Seismic Parameter: } \Phi = K_s / \rho = \left( \frac{\partial P}{\partial \rho} \right)_s = V^2 - 4/3 V^2_s$$

$$\text{Bulk Modulus: } K_T = -V \left( \frac{\partial P}{\partial V} \right)_T$$

Bullen parameter

$$\eta = \frac{(d\rho/dz)_{\text{Earth}}}{(d\rho/dz)_{\text{adiabat}}}$$



One approach to developing an equation of state involves a series expansion of the Helmholtz free energy,  $F$ , as a function of strain:

$$F = a_0 + a_1 f + a_2 f^2 + a_3 f^3 + a_4 f^4 + \dots$$

Two main considerations:

- Truncation of the series
- Appropriate measure of finite strain

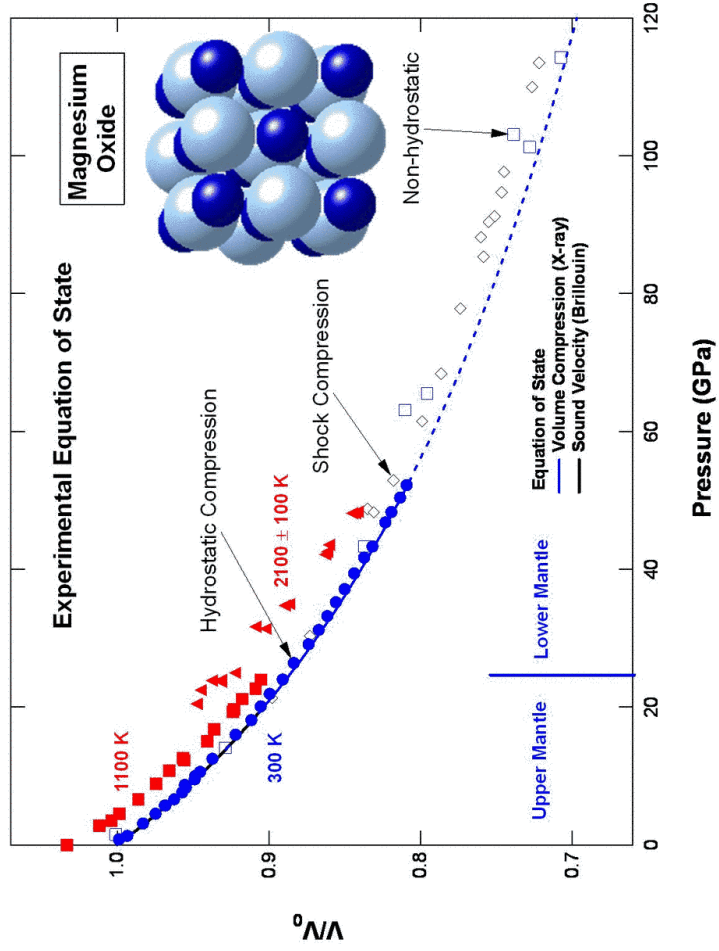
Empirically, the Eulerian finite strain has been shown to be superior:

$$\frac{\rho}{\rho_0} = \frac{V_0}{V} = (1 + 2f)^{3/2}$$

Keeping terms to third order in strain, taking appropriate derivatives, and evaluating the constants yields the Birch-Murnaghan Equation:

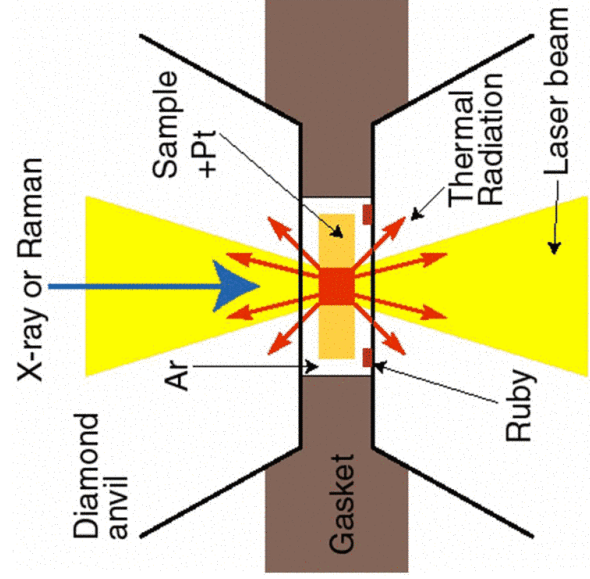
$$P = \frac{3K_{T0}}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4} (4 - K_{T0}') \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

$$K_T' = \left( \frac{\partial K_T}{\partial P} \right)_T$$



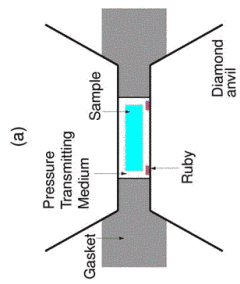
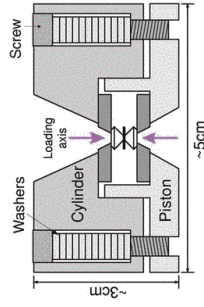
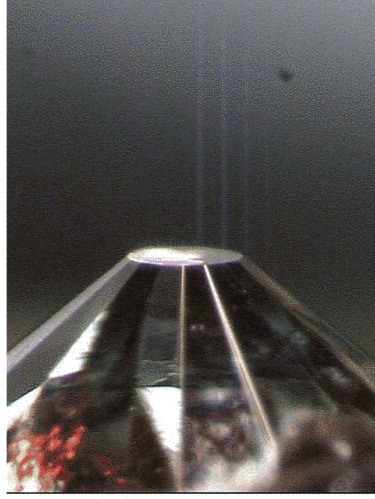
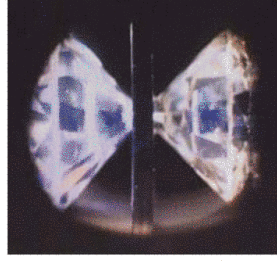
$$V_0 = 74.71 \text{ \AA}^3, K_{0T} = 160.3 \text{ GPa}, K_{0T}' = 3.9$$

### Diamond Anvil Cell

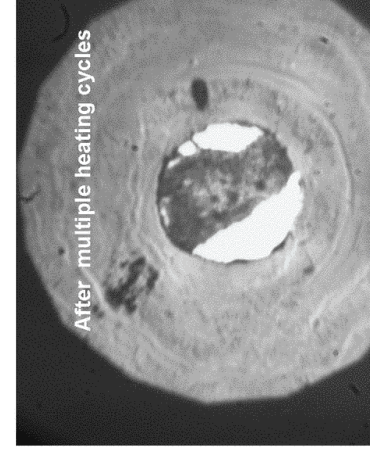
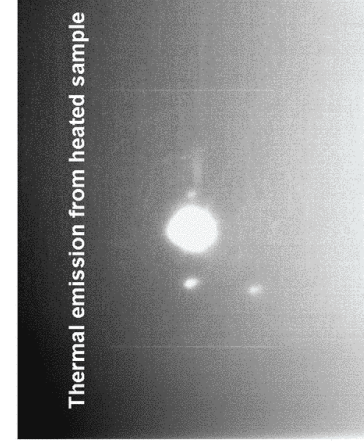
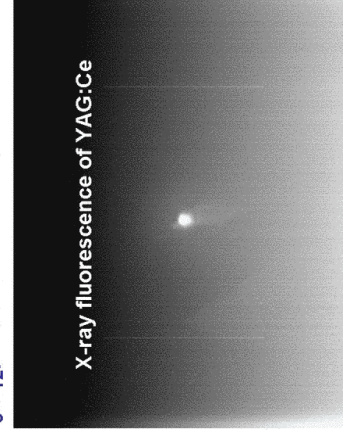
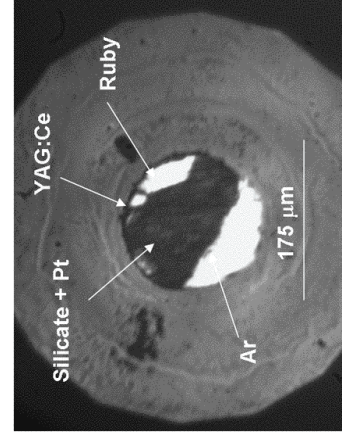




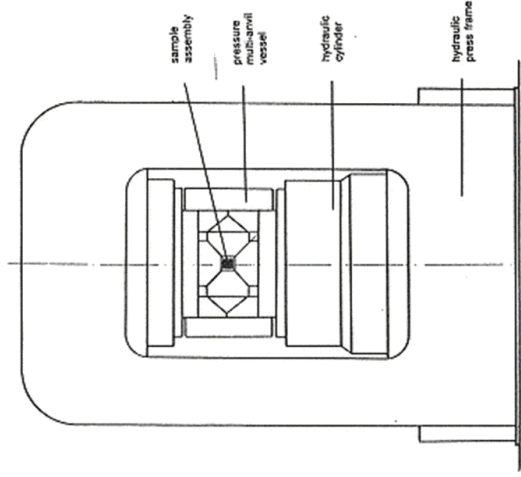
**Diamond Anvil Cell and Sample Configuration**



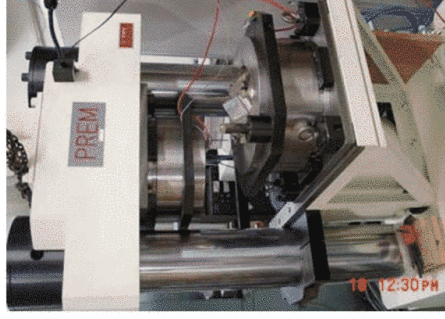
**Laser heating of Pyrope ( $Mg_3Al_2Si_3O_{12}$ ) Garnet at ~30 GPa**



Multi-Anvil Apparatus  
(Large-Volume Press)



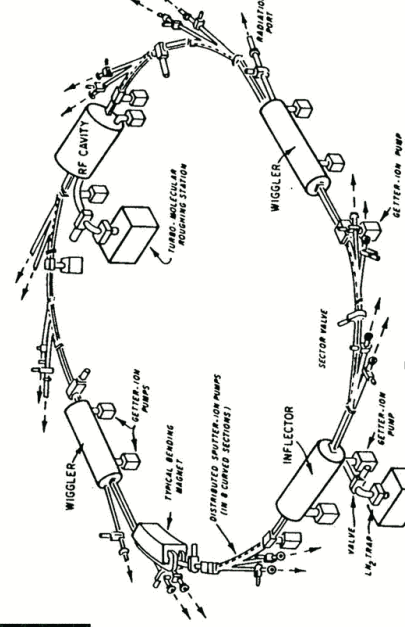
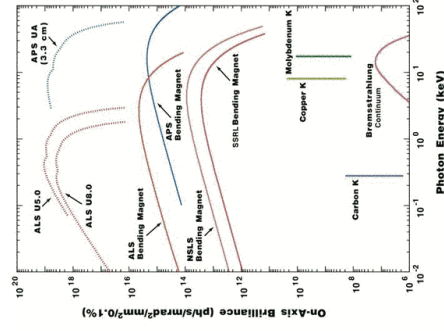
The Multi-Anvil High Pressure System



Synchrotron X-ray source



Advanced Photon Source,  
Argonne National Lab.



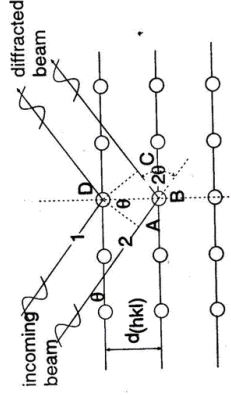


Figure 8 Bragg's law, assuming the planes of atoms behave as reflecting planes.

$$n\lambda = 2d\sin\theta$$

$\lambda$  = x-ray wavelenth (~1 Ang.)

$2\theta$  = diffraction angle

$d$  = interplanar spacing

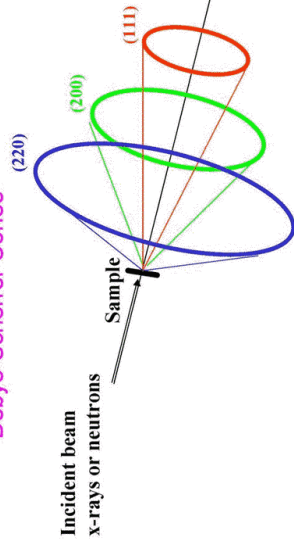
Miller indices: (100) (220) (311)

**X-Ray Diffraction:**

Powder—most widely used

Single crystal --best results but generally restricted to very low pressures

**Powder Diffraction gives Scattering on Debye-Scherrer Cones**



Powder diffraction

**From peak positions:**

- Crystal system
- Unit cell dimensions (volume)
- Phase identification

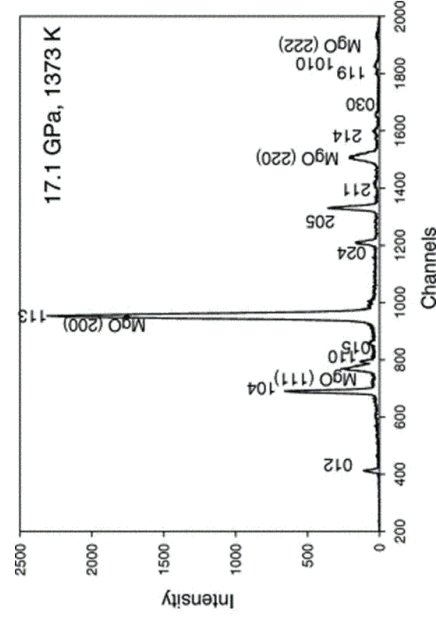
**From peak intensities**

Atomic positions (Rietveld method)

**From peak widths**

- Crystal size
- Differential stress

**Akimotoite – MgSiO<sub>3</sub>**  
(ilmenite structure)



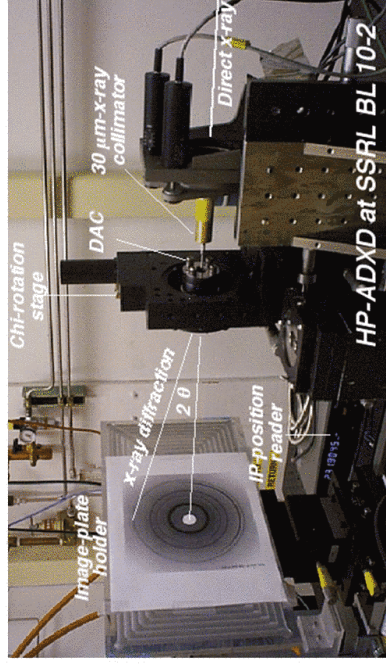


### Simplified experimental setup for angle-dispersive x-ray diffraction

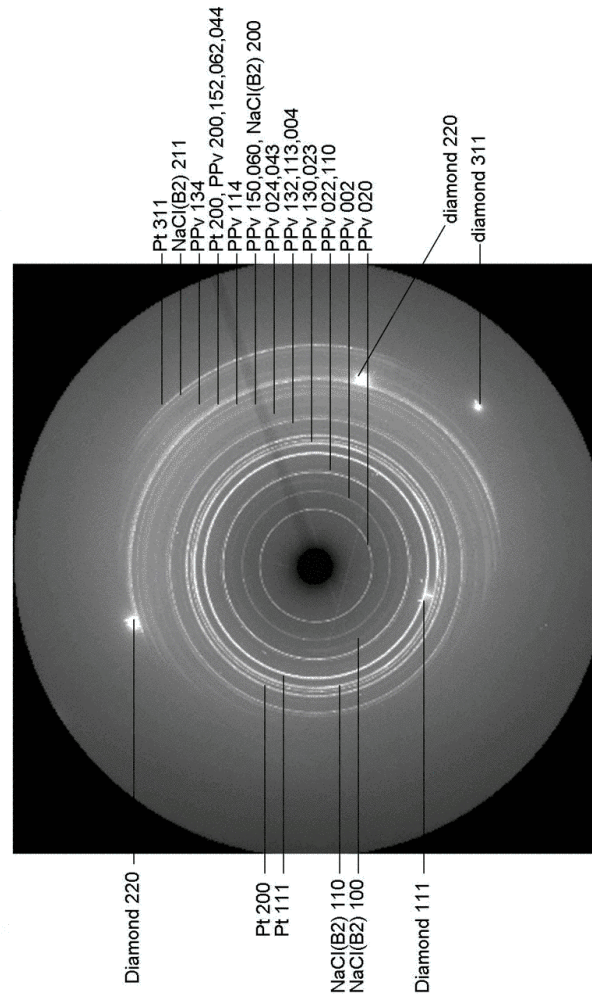
**Monochromator** is used to select a single wavelength for incoming x-rays ( $\Delta\lambda/\lambda \sim 10^{-4}$ )

**Collimator, slits, focusing mirror** is used to shape beamsize appropriately

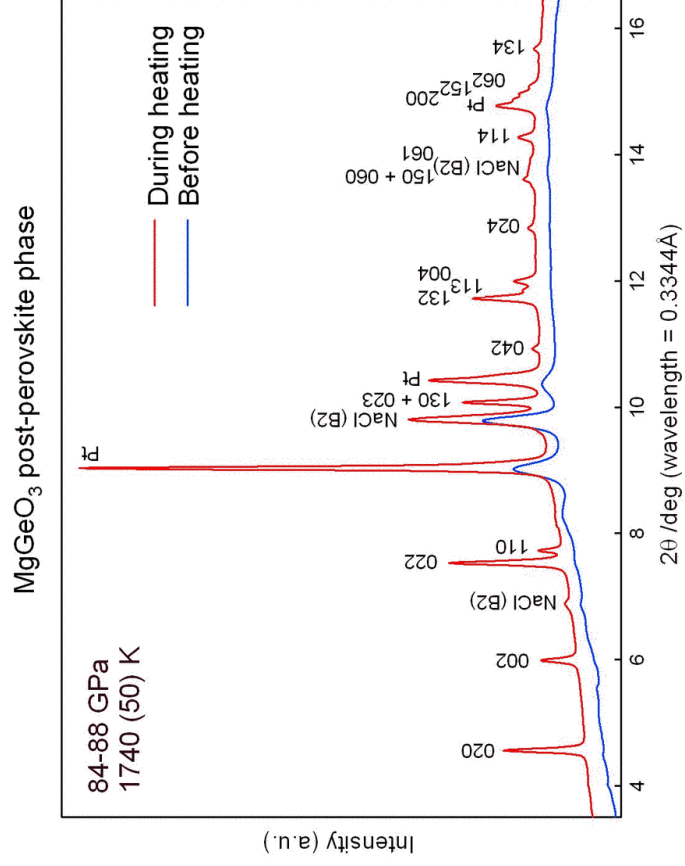
**Two-dimensional detector** (e. g. Image Plate) located a few hundred mm behind the sample records diffracted x-ray intensity.



### Example: $\text{MgGeO}_3$ in the post-perovskite phase (CaIrO<sub>3</sub>-type)







d-spacing obtained from Bragg's Law:  $\lambda = 2d\sin\theta$

Interplanar (d) spacings for a given (hkl) reflection depend on the unit cell dimensions

cubic (lattice parameter: a)

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

Orthorhombic system (a,b,c):

$$1/d^2 = (h^2/a^2 + k^2/b^2 + l^2/c^2)$$

Hexagonal system (a,c):

$$1/d^2 = 4/3(h^2 + hk + k^2) + l^2/c^2$$

Unit cell volume:

Cubic:  $V = a^3$

Orthorhombic:  $V = abc$

Hexagonal:  $V = (3)^{1/2}a^2c/2$

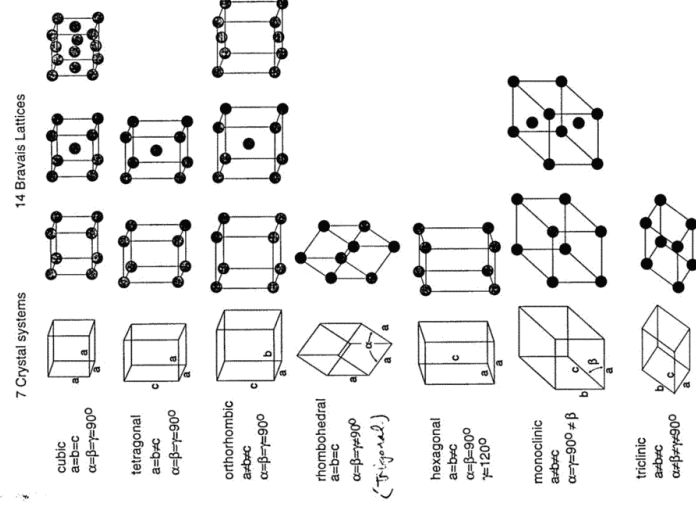
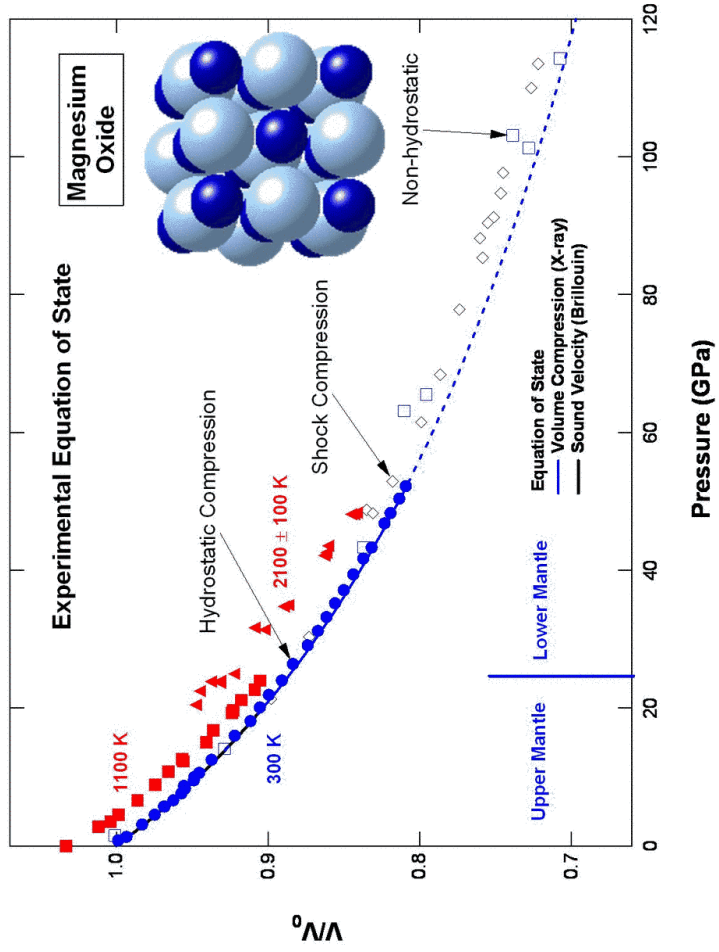
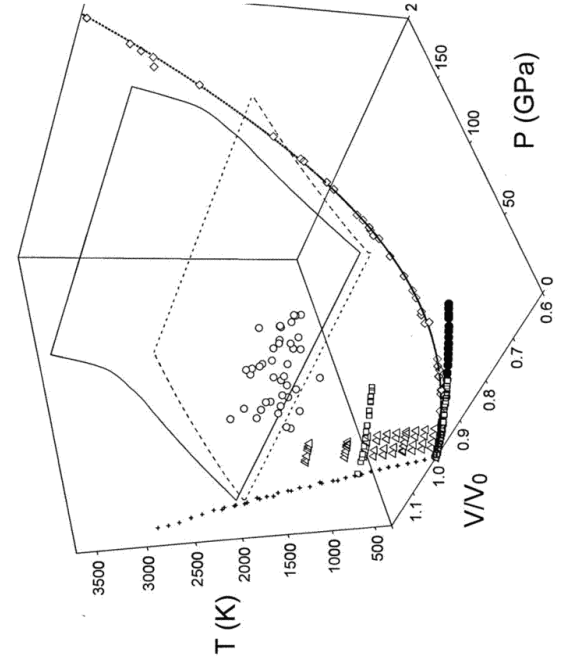
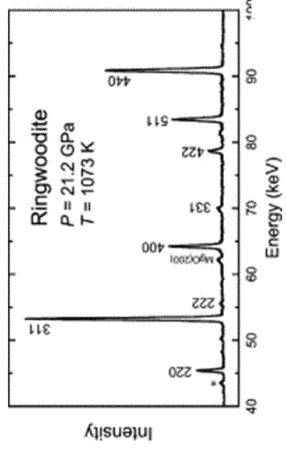


Figure 4. The 7 crystal systems and the 14 Bravais lattices

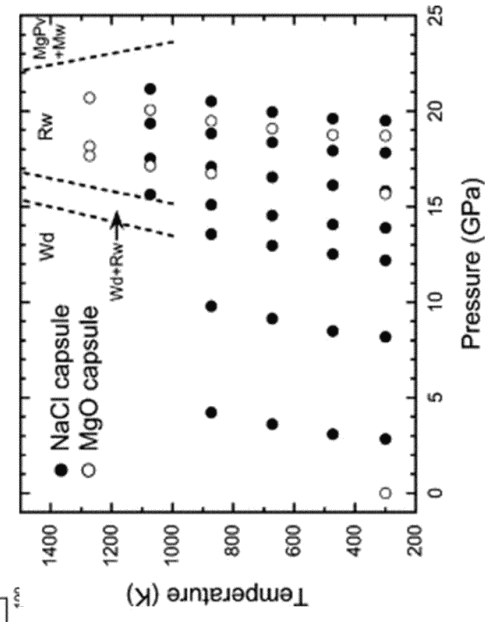


Magnesium Oxide – P-V-T Equation of state





Thermal equation of state of Ringwoodite

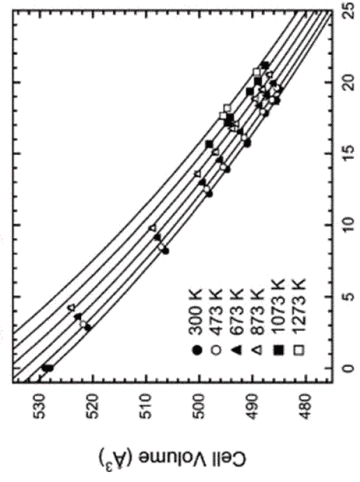


Nishihara et al., 2004

- Caveats:
- Non-hydrostatic stress
- Metastability
- Pressure scale

Thermal equation of state:

1. High Temperature Birch-Murnaghan Equation



Parameter	[187]
$K_{T0}$ (GPa)	4.4(1)
$K'_T$	-0.028(5)
$(\partial K_T / \partial T)_P$ (GPa K <sup>-1</sup> )	1.9(2)
$\alpha = a + bT$	1.2(4)
$a$ (10 <sup>-5</sup> K <sup>-1</sup> )	Au-A
$b$ (10 <sup>-8</sup> K <sup>-2</sup> )	
P-Marker <sup>b</sup>	

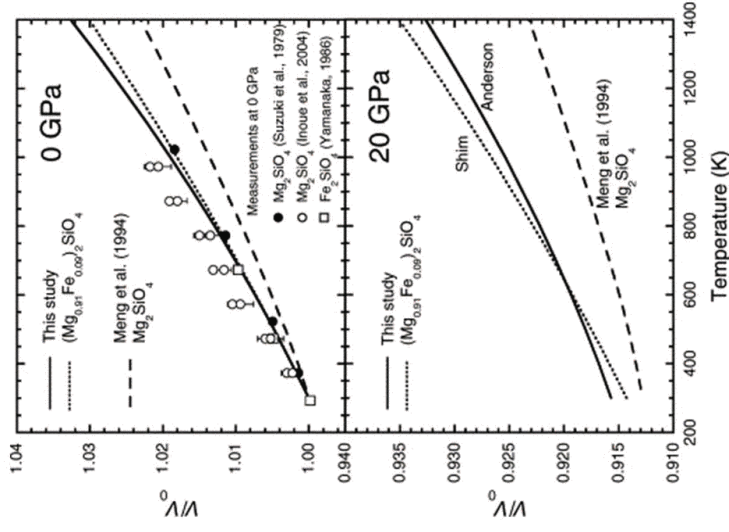
$$P = \frac{3K_{T0}}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4} (4 - K_{T0}') \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

$$K_{T0}(T) = K_{T0}(T_0) + \left( \frac{\partial K_T}{\partial T} \right)_P (T - T_0)$$

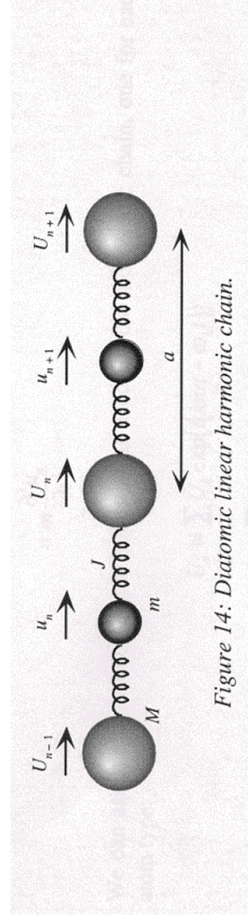
$$V_0(T) = V_0(T_0) \exp \int_{T_0}^T \alpha(T) dT \quad \alpha(T) = a + bT - \frac{c}{T^2}$$

**High-Temperature Birch Murnaghan Equation**

- Simple and effective for fitting
- Not thermodynamically self-consistent



**Lattice dynamics:** Contribution to the internal energy that arises from the vibrations of atoms about their equilibrium positions.



Consider a 1-dimensional (diatomic) chain of atoms

- Lattice spacing:  $a$
- Each atom experiences a *harmonic* force (i.e. restoring force proportional to displacement) due to nearest neighbors only.
- Longitudinal motions only
- Solve equations of motion.....



$$\omega^2 = J \frac{M+m}{Mm} \pm \frac{J}{Mm} \sqrt{(M+m)^2 - 4Mm \sin^2(ka/2)}$$

Dispersion curves:  $\omega = f(k)$

Solution is periodic reflecting that of the lattice

Two types of modes:

Acoustic modes

Optic modes

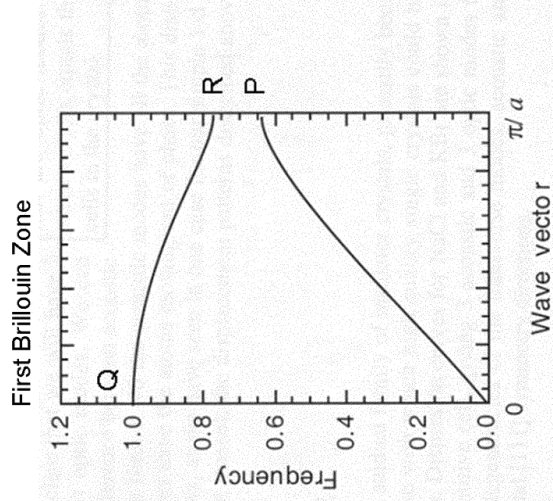


Figure 16: Dispersion curves for the one-dimensional diatomic chain

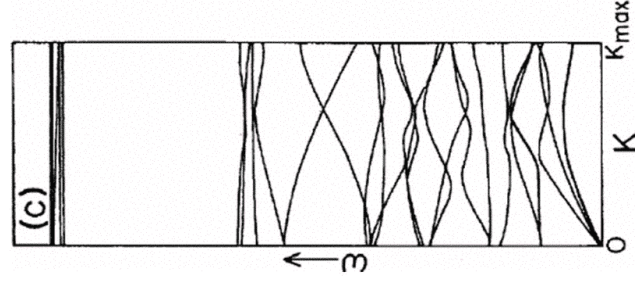
**Generalization for real crystals:**

-- 3Z branches where Z is the number of atoms in the unit cell

- 3 acoustic branches
- 3Z-3 optic branches

--Experimental Probes

- Optic zone center
- Raman
- Infrared
- Acoustic near zone center
- Brillouin
- Full phonon spectrum
- Inelastic neutron scattering



Quartz - 27 branches

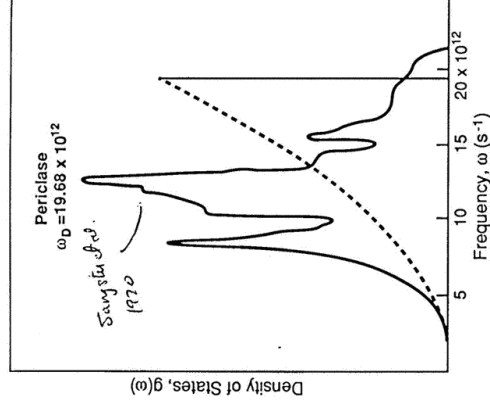
Thermodynamic functions are obtained by summing over all vibrational modes

-- Lattice vibrations are quantized:  $E = \left(n + \frac{1}{2}\right) \hbar \omega$

where n is the number of phonons with frequency  $\omega$  at temperature T.

-- Periodic lattice structure

We can describe the vibrational spectrum by a density of states,  $g(\omega)$ , which specifies the number of oscillation modes in some frequency range,  $d\omega$ .



$$E_{th} = \int_0^{\infty} \frac{g(\omega) \hbar \omega d\omega}{\exp(\hbar \omega / kT) - 1}$$

Specific heat obtained by taking derivative w.r.t. T

$$E(V,T) = E_c(V) + E_{th}(V,T) + E_{el}(V,T)$$

Debye model –

Approximate the density of states as:

$$g(\omega) = A\omega^2$$

with a maximum value,  $\omega_D$ , called the Debye frequency

This maximum frequency is derived by approximating all vibrational modes as acoustic modes with the same velocity

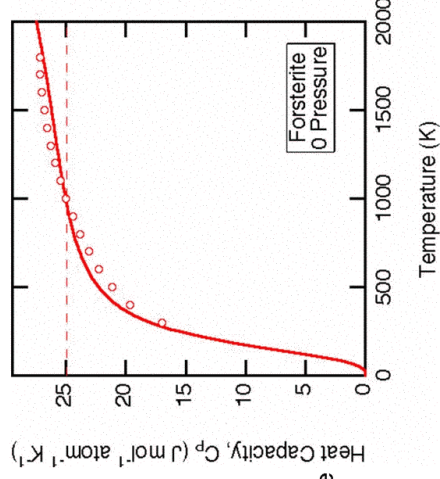
$$\omega_D^3 = \frac{6\pi N}{V} V_M^3$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = 3NkD\left(\frac{\theta_D}{T}\right)$$

$$D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x) dx}{(\exp(x) - 1)^2}$$

At high T,  $C_v \rightarrow 3R$   
At low T,  $C_v \rightarrow T^3$

$$\text{Debye Temperature } \theta_D = \frac{\hbar}{k} \omega_D$$



**Thermal Equation of state: Mie-Gruneisen-Debye model**

Fitting parameters:

$V_0, K_0, K_0'$  (reference equation of state)

$\theta$  – Debye temperature

$\gamma$  -- Gruneisen parameter

$q$  -- volume dependence of  $g$

$$P(V, T) - P_r(V, T_r) = \frac{\gamma}{V} [E(V, T) - E_r(V, T_r)]$$

$$\frac{d \log \Theta}{d \log V} = -\gamma \quad \text{Quasi-harmonic Approx.}$$

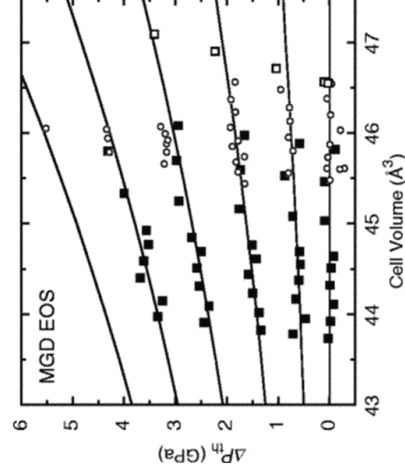
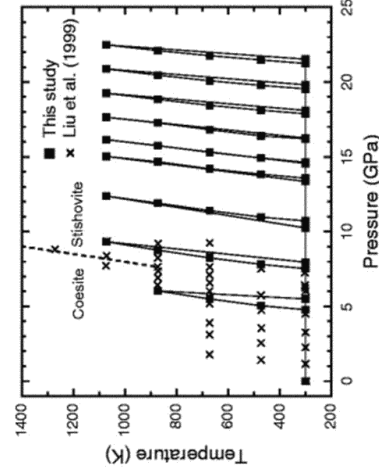
$$E_{th} = E_0 + 3NkTF \left( \frac{\theta_D}{T} \right)$$

$$\gamma = \gamma_0 \left( \frac{V}{V_0} \right)^q$$

Advantages: thermodynamically self-consistent. Can readily derive all higher order quantities, useful for extrapolation not just fitting

Disadvantages: Ability to recover  $q$  limited for "realistic" data sets; validity of model open to questioned (too simple?)

**Stishovite – SiO2 (Nishihara et al. 2005)**



- $V_0 = 46.55(1) \text{ \AA}^3$
- $K_0 = 299(4) \text{ GPa}$
- $K_0' = 4.0(4)$
- $\gamma = 1.33(6)$
- $q = 6.1(8)$
- $\theta = 1160 (120)$

For each vibrational mode, a mode Grüneisen parameter can be defined:

$$\gamma_i = - \frac{\partial \ln \omega_i}{\partial \ln V} = - \frac{V}{\omega_i} \frac{\partial \omega_i}{\partial V}$$

$$\omega_i = \frac{V_i}{\lambda_i} = \frac{\text{sound velocity}}{\text{lattice spacing}}$$

$$\gamma_i = - \frac{\partial \ln \omega_i}{\partial \ln V} = \frac{K'_s}{2} - \frac{1}{6}$$

Slater formula

Seismic data + Debye model yield a complete thermodynamic model for the Earth

$$\gamma = \frac{\alpha K'_s}{\rho C_p}$$

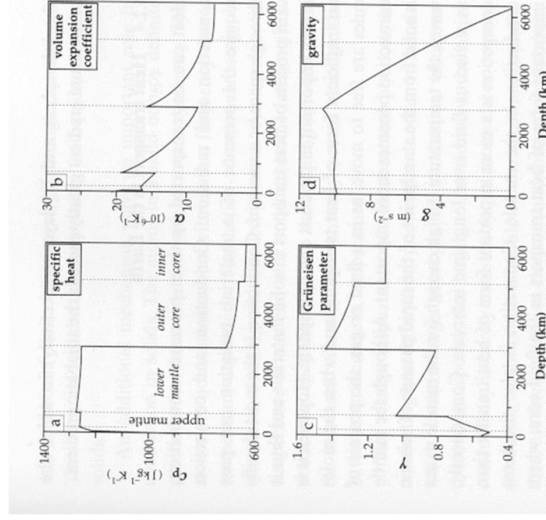


Fig. 4.13 Variations with depth in the Earth of (a) specific heat at constant pressure, (b) volume coefficient of thermal expansion, (c) Grüneisen parameter, and (d) gravity (based upon data from Stacey, 1992).

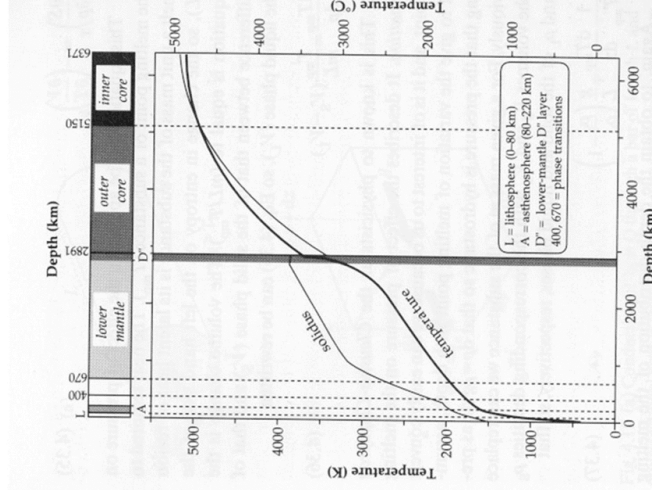


Fig. 4.14 Variations of estimated temperature and melting point with depth in the Earth (based upon data from Stacey, 1992).



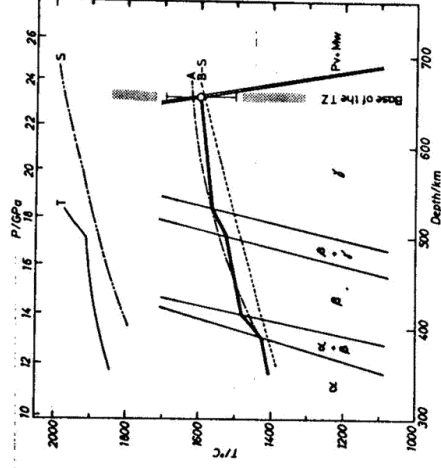


Fig. 2. Pressure-temperature stability diagram for  $(\text{Mg}_{0.89}\text{Fe}_{0.11})_2\text{SiO}_4$  bulk composition. The heavy solid curve represents the temperature profile for the peridotitic mantle model (see text). The curves denoted by B-S, A, and S are temperature profiles by Brown and Shankland [1981], Anderson [1981], and Stacey [1977], respectively. T is the solidus curve for dry peridotite determined by Takahashi [1986]. The shaded area denotes the reference depth with uncertainty  $(655 \pm 5 \text{ km})$ . The open circle shows the fixed temperature  $(1600 \pm 100 \text{ }^\circ\text{C})$  at the reference depth.

$$\left(\frac{\partial T}{\partial V}\right)_z = -\frac{\gamma T}{V}$$

$$\left(\frac{\partial T}{\partial V}\right)_z = \left(\frac{\partial T}{\partial P}\right)_z \left(\frac{\partial P}{\partial V}\right)_z = \left(\frac{\partial T}{\partial P}\right)_z \left(-\frac{K_z}{V}\right) = -\frac{\gamma T}{V}$$

$$\left(\frac{\partial T}{\partial P}\right)_z = \left(\frac{\partial T}{\partial z}\right) \left(\frac{\partial z}{\partial P}\right) = \left(\frac{\partial T}{\partial z}\right) \frac{1}{\rho g} = \frac{\gamma T}{K_z}$$

$$\left(\frac{\partial T}{\partial z}\right) = \frac{\gamma T \rho g}{K_z} = \frac{\gamma T g}{\phi}$$

Using  $\gamma = 1$ ,  $K_z = 500 \text{ GPa}$ ,  $T = 2500 \text{ K}$ :

$$\left(\frac{\partial T}{\partial P}\right)_z = \gamma \frac{T}{K_z} \approx 5 \text{ K/GPa}$$

or using  $g = 0.01 \text{ km/s}^2$  and  $\phi = 100 \text{ km}^2/\text{s}^2$ :

$$\left(\frac{\partial T}{\partial z}\right) = 0.25 \text{ K/km}$$

Or a modest 250 K rise over 1000 km depth.

In contrast, the average (conductive) thermal gradient near the Earth's surface is 2 orders of magnitude larger: 30 K/km.