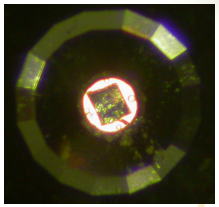
Sample synthesis, preparations, and analysis

Ambient pressure synthesis:
Gas mixing furnace
Arc melting

For nuclear resonant measurements:
$^{57}Fe_2O_3$ and ^{57}Fe synthetic starting material (~95% enriched)

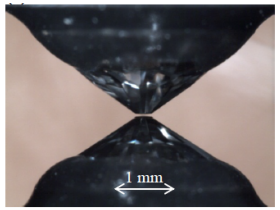
Chemical analysis:
EMPA, SEM, nanoSIMS, EBSD, XRD

Hyperfine fields (e.g., $Fe^{3+}/\Sigma Fe$):
Mössbauer spectroscopy

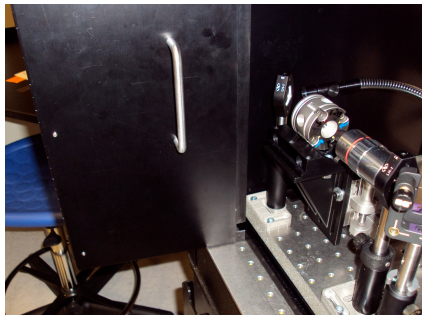


The Zephyr (new!):
Pressurized gas-loading of noble and reactive gases

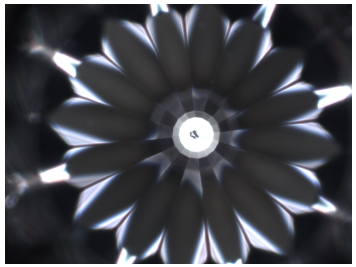
Diamond-anvil cell laboratory:



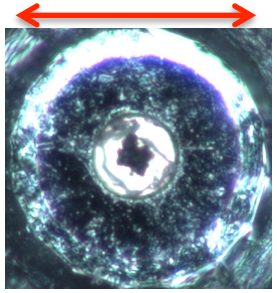
Fluorescence/Raman measurements

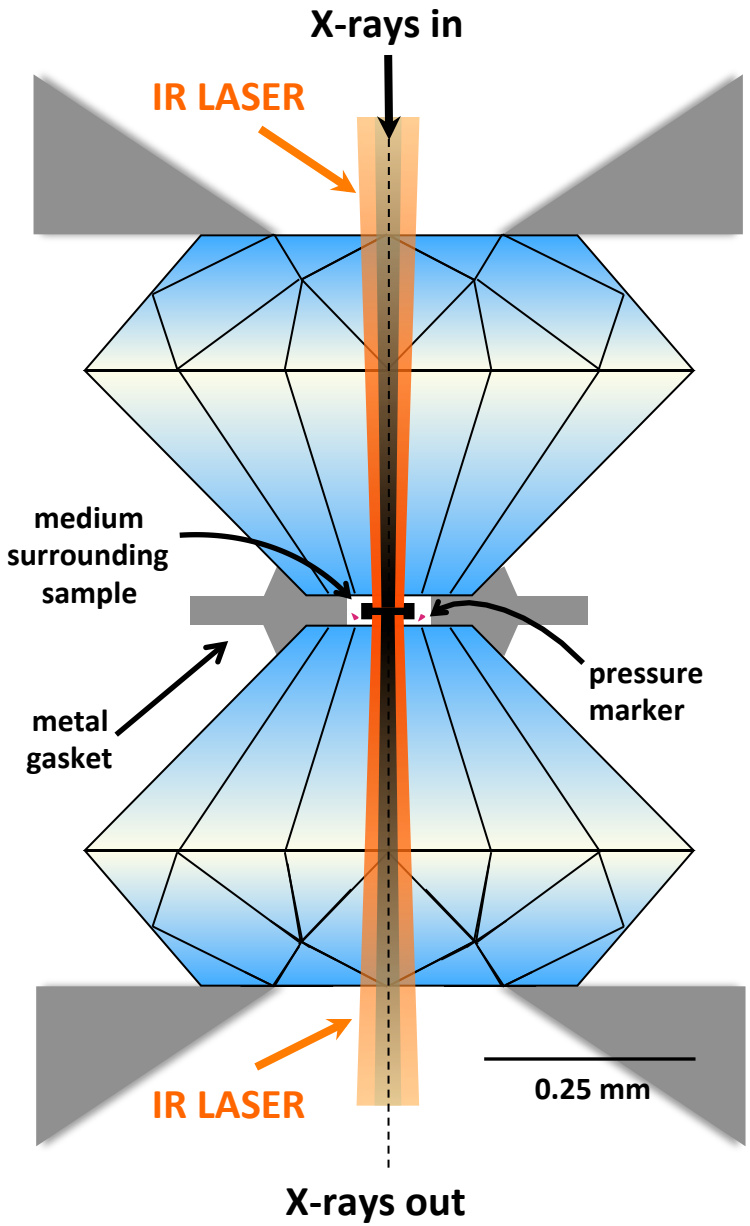


The diamond-anvil cell



250 um

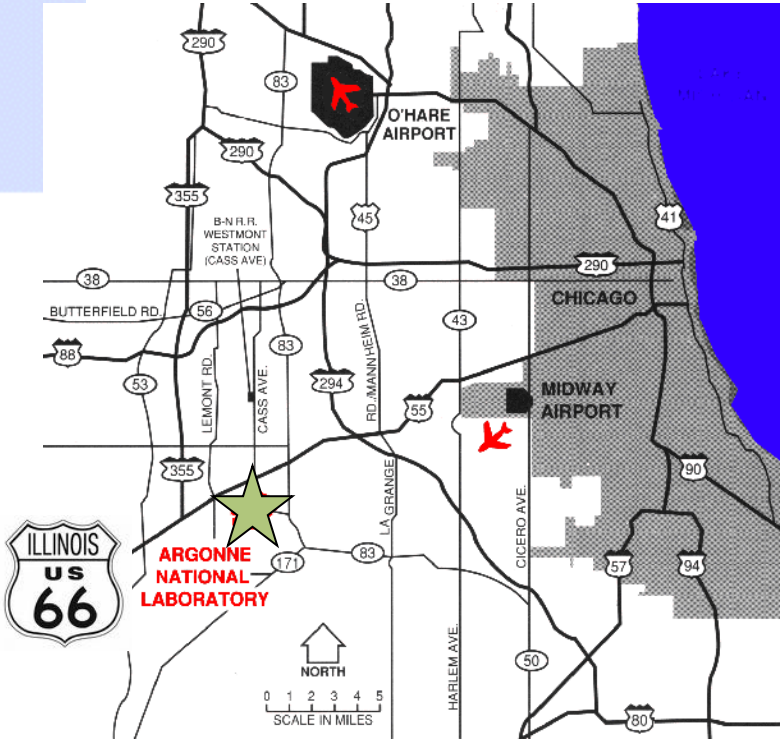




1 bar

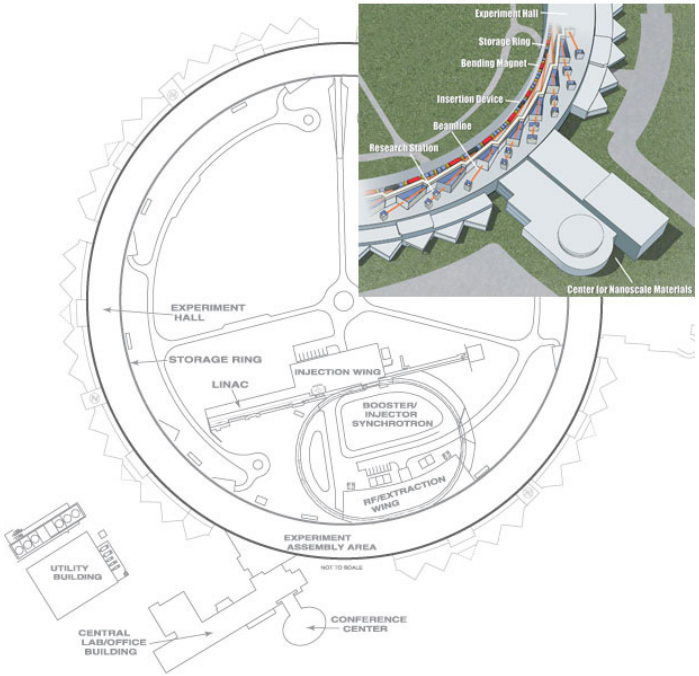
1 megabar (100 GPa)

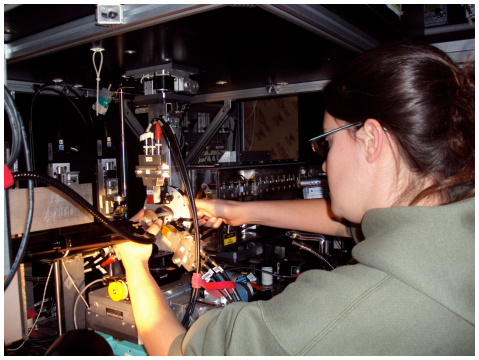
Journeying across the country for brilliant x-rays….

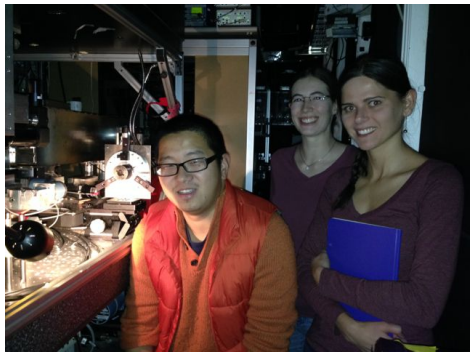


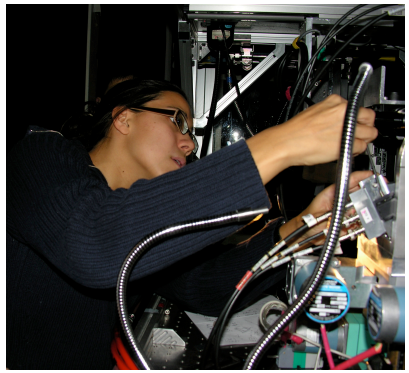
The Advanced Photon Source

Nuclear resonant scattering experiments

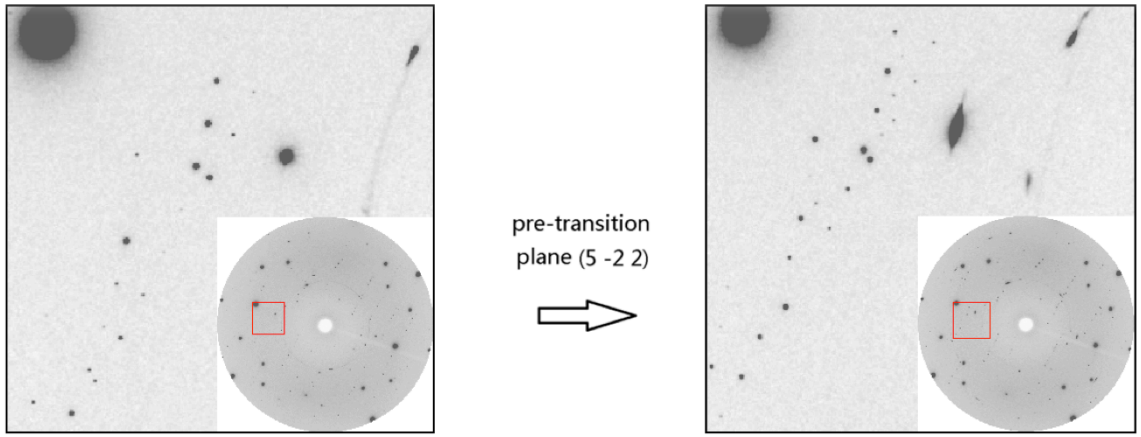






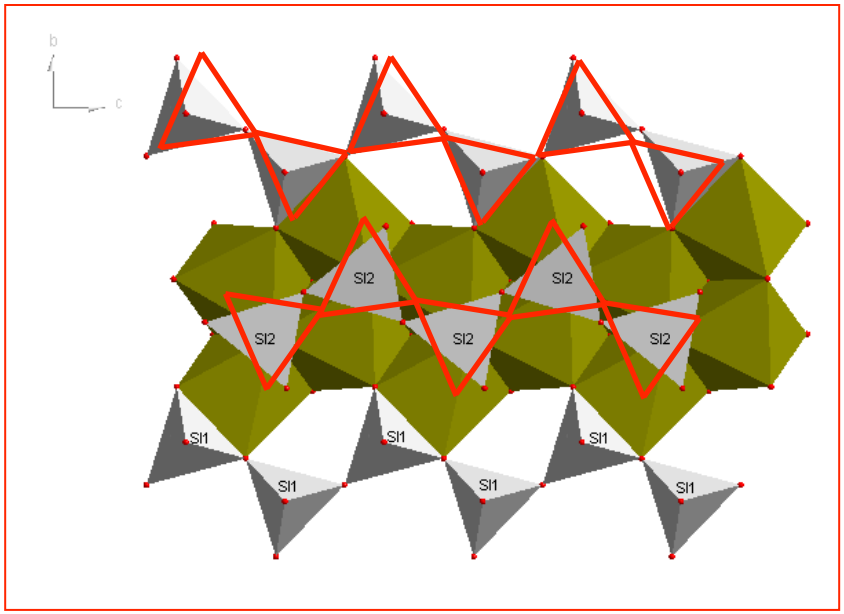


A starting point: the Static arrangement of the atoms
PX^2, eXtreme Xtallography (APS 13-ID-D)



OEN (Pbca) 11.54 GPa

HPCEN2 ($P2_1/c$) 14.53 GPa



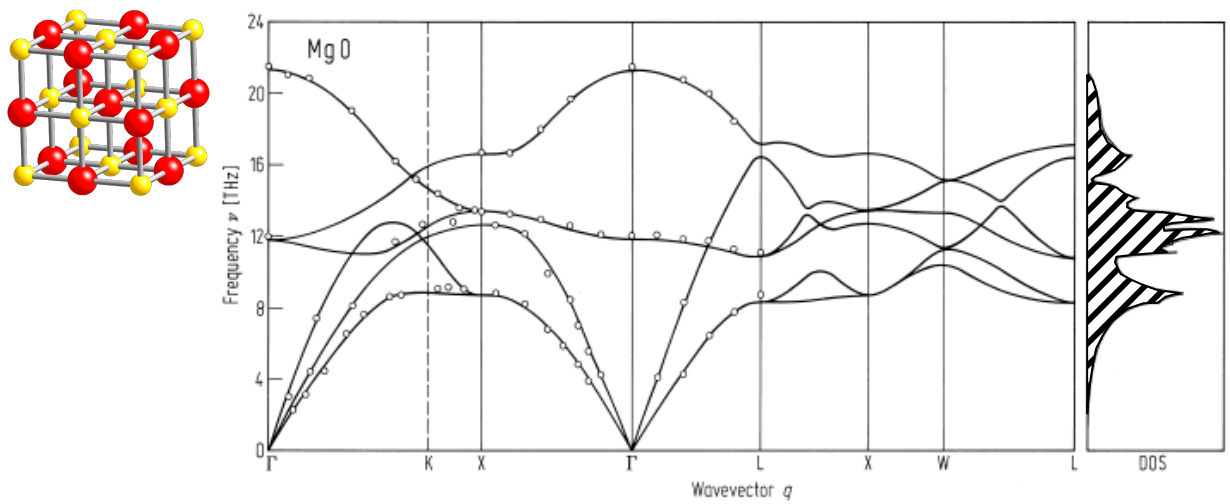
Orthoenstatite
$MgMg(SiO_3)_2$

Zhang, Dera and Bass,
Amer. Mineral. 2012

Determining vibrational pressure (energy) (P_{vib})

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F_{elastic}}{\partial V}\right)_T - \boxed{\left(\frac{\partial F_{phonon=vib}}{\partial V}\right)_T} - \left(\frac{\partial F_{electronic}}{\partial V}\right)_T$$

Measure all the phonon (vibrational) states



Phonon density of states (DOS)

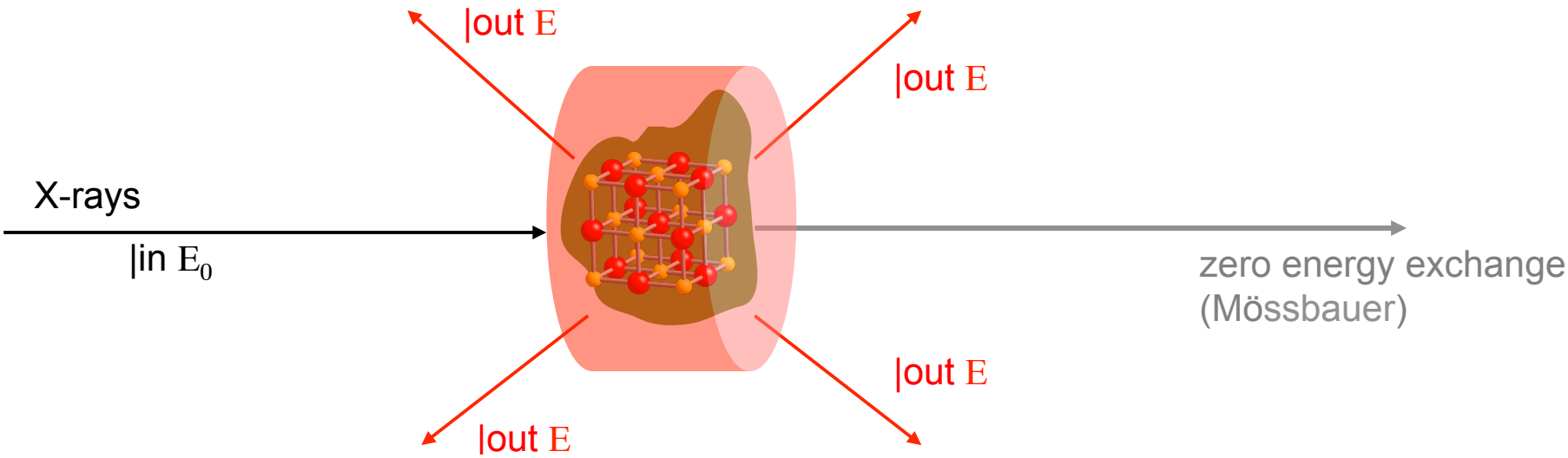
$$g(\omega)d\omega$$

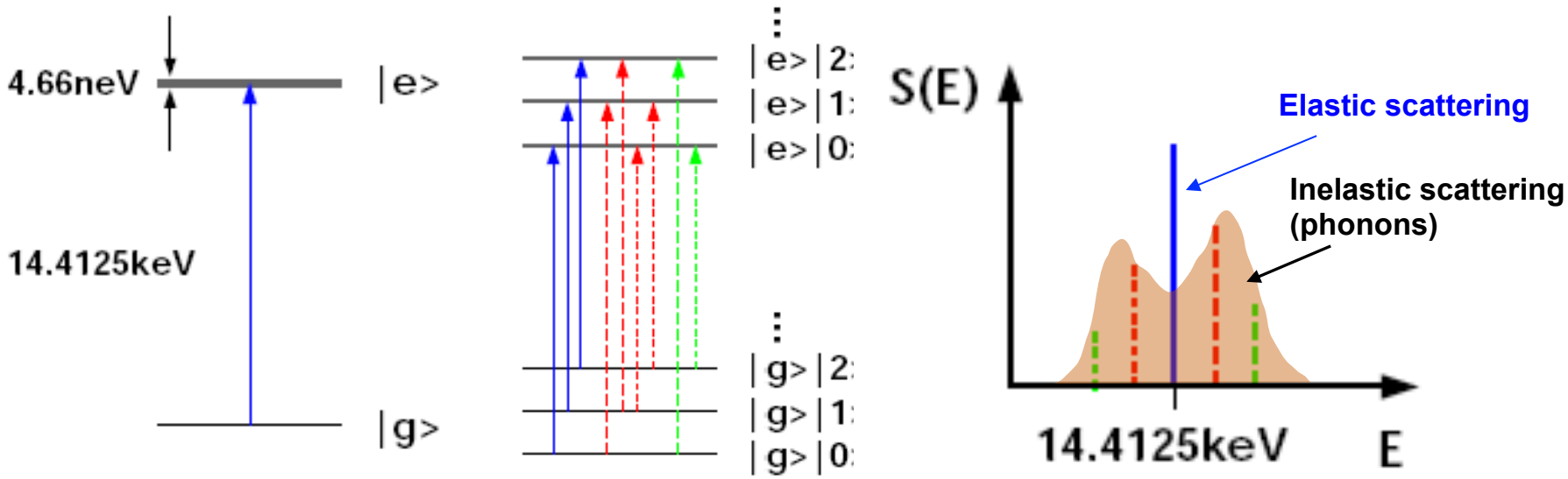
$$P_{phonon=vibrational} = F_{vib} = E_{vib} = \int_0^{\omega} \langle n \rangle \hbar\omega g(\omega) d\omega,$$

Where we have the phonon occupation in thermal equilibrium, given by the Bose-Einstein distribution:

$$\langle n \rangle = [e^{\frac{\hbar\omega}{k_B T}} - 1]^{-1}$$

Measuring vibrational properties with nuclear resonant inelastic x-ray scattering (APS 3-ID-B)





e.g., Sturhahn *JCMP* (2004)

Information from nuclear resonant inelastic x-ray scattering spectra

Directly from the data, *S(E)*

Temperature (M_1)

$$T = -\frac{E}{k_B}\ln\left[\frac{S(-E)}{S(E)}\right]$$

Mean square displacement (M_1)

$$\langle u^2 \rangle = \frac{1}{k^2}\ln\left[1 - \int \{S(E) - S(0)\} dE\right]$$

Kinetic energy (M_2)

$$E_k = \frac{1}{4E_R}\int (E - E_R)^2 S(E) dE$$

Average force constant (M_3),
Mass-dependent isotopic fractionation

$$\Phi = \frac{k^2}{2E_R^2}\int (E - E_R)^3 S(E) dE$$

$$\ln \beta(V,T) = -\frac{\Delta m \hbar^2 \Phi(V,T)}{m m^* 8 (k_B T)^2}$$

k : wave number of nuclear transition
E_R : recoil energy

Quasi-harmonic lattice model

(Partial) Projected phonon density of states

$$D(E,V)$$

Debye sound velocity

$$D(E \to 0) = \frac{M}{2\rho\pi^2\hbar^3}\frac{1}{v_D^3}E^2$$

Grüneisen parameter

$$\gamma_{vib} = \frac{\partial \ln \xi(V/V_i)}{\partial \ln V_i}$$

Thermal expansion

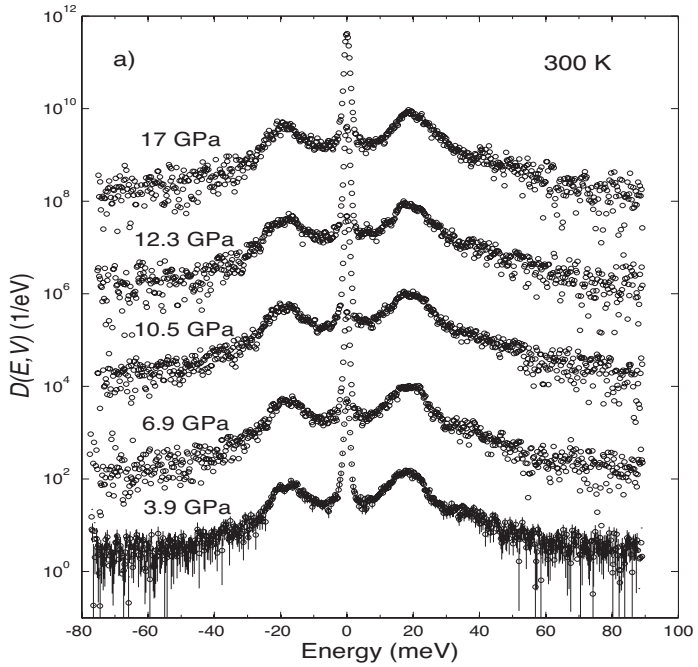
$$(\partial S_{vib}/\partial V)_T = \alpha_{vib} K_T$$

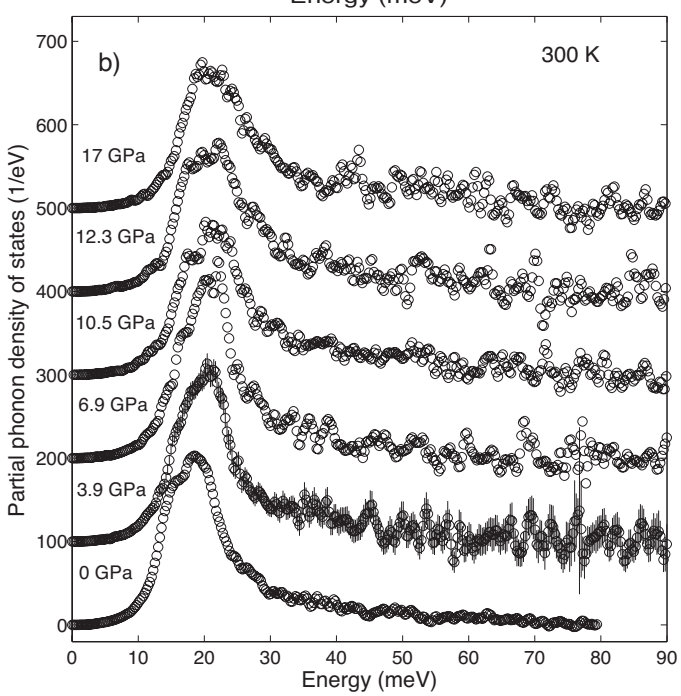
Complete phonon density of states (per atom):
Entropy (S_{vib}), Specific Heat (C_V), and
free energy, e.g.,

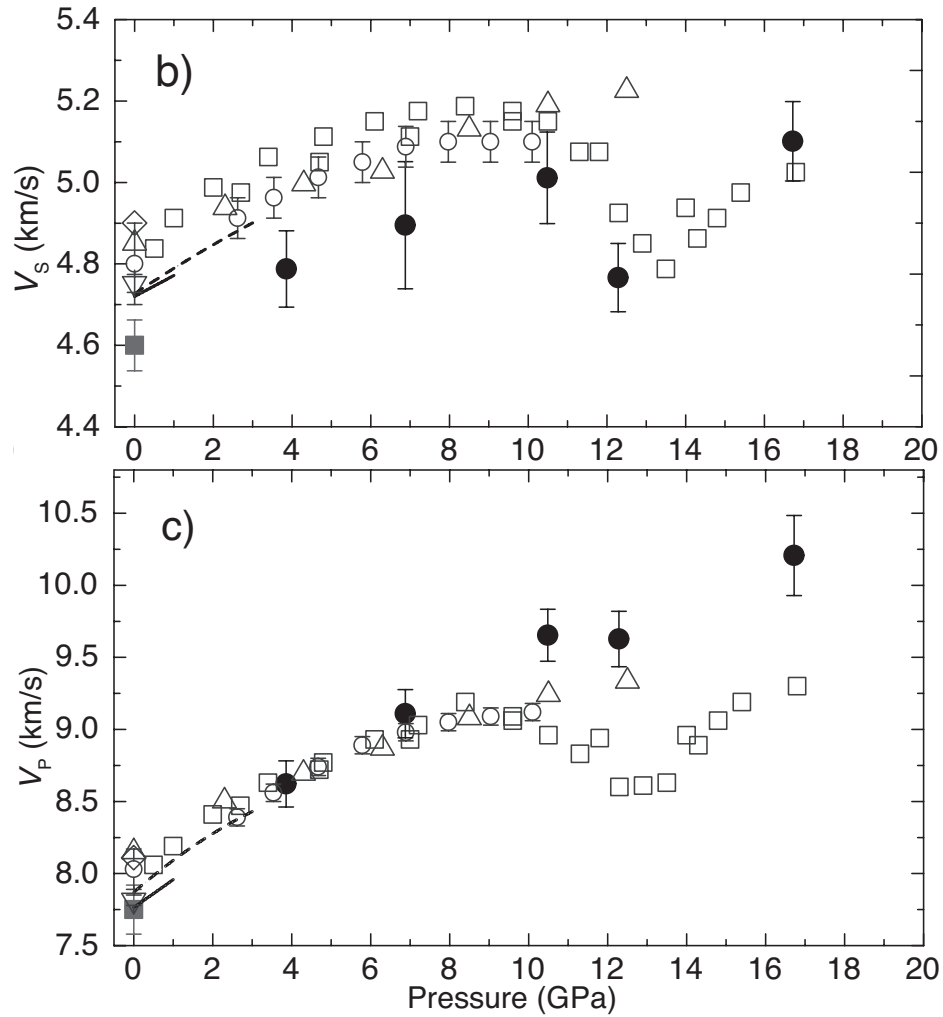
$$F_{vib}(V,T) = \frac{1}{\beta}\int \ln\left(2\sinh\frac{\beta E}{2}\right) D(E,V) dE$$

e.g., Sturhahn *HI* (2000, www.nrixs.com); Sturhahn *JCMP* (2004); Sturhahn & Jackson *GSA Mono.* (2007)

Phase transitions in upper mantle minerals: Enstatite







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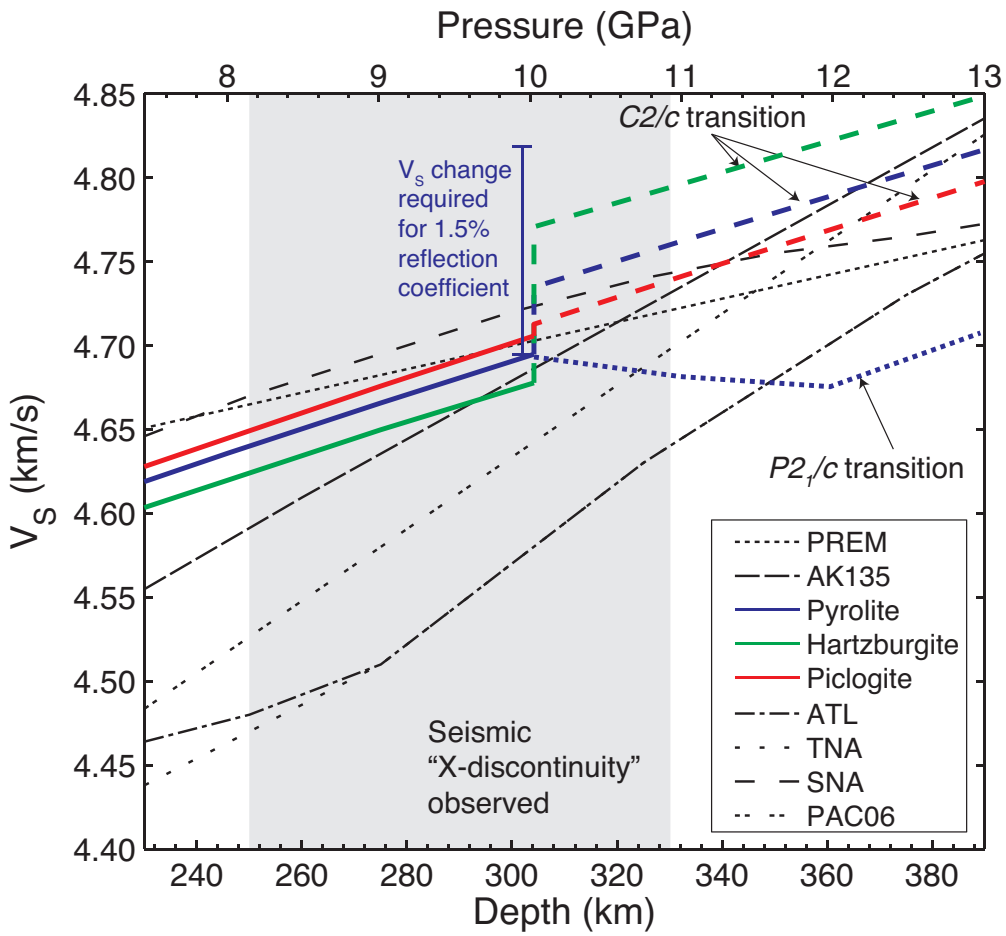
Phase transitions in upper mantle minerals: Enstatite

Comparison with seismic observations



- Experiments done at high-pressures to determine V_P, V_S, and density of iron-bearing enstatite (pyroxene)
- Phase transition occurs around 12 GPa (360 km depth), characterized by low velocities
- Note global models do not agree – regional studies are crucial to understand chemistry
- Enstatite-rich rocks not as low as active tectonic regions, but lower than stable regions

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