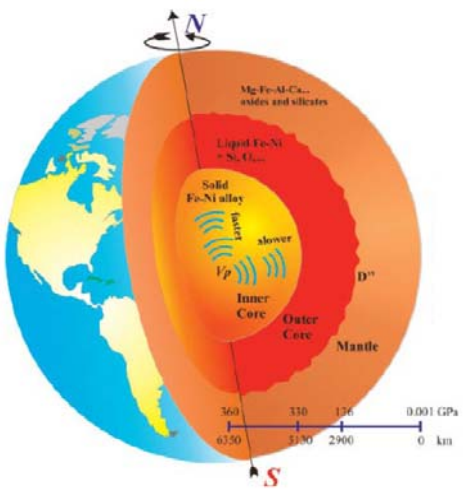
Studying elasticity of materials in extreme environments using high-energy resolution IXS (HERIX)

Jung-Fu “Afu” Lin

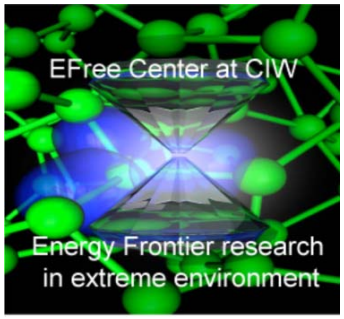
Department of Geological Sciences, Jackson School of Geosciences

The University of Texas at Austin

1. Introduction and Motivation
2. Velocity-Density Relation of Fe Alloys in Earth’s Core
3. Elasticity across Electronic Transitions in the Mantle
4. Conclusions and Outlook

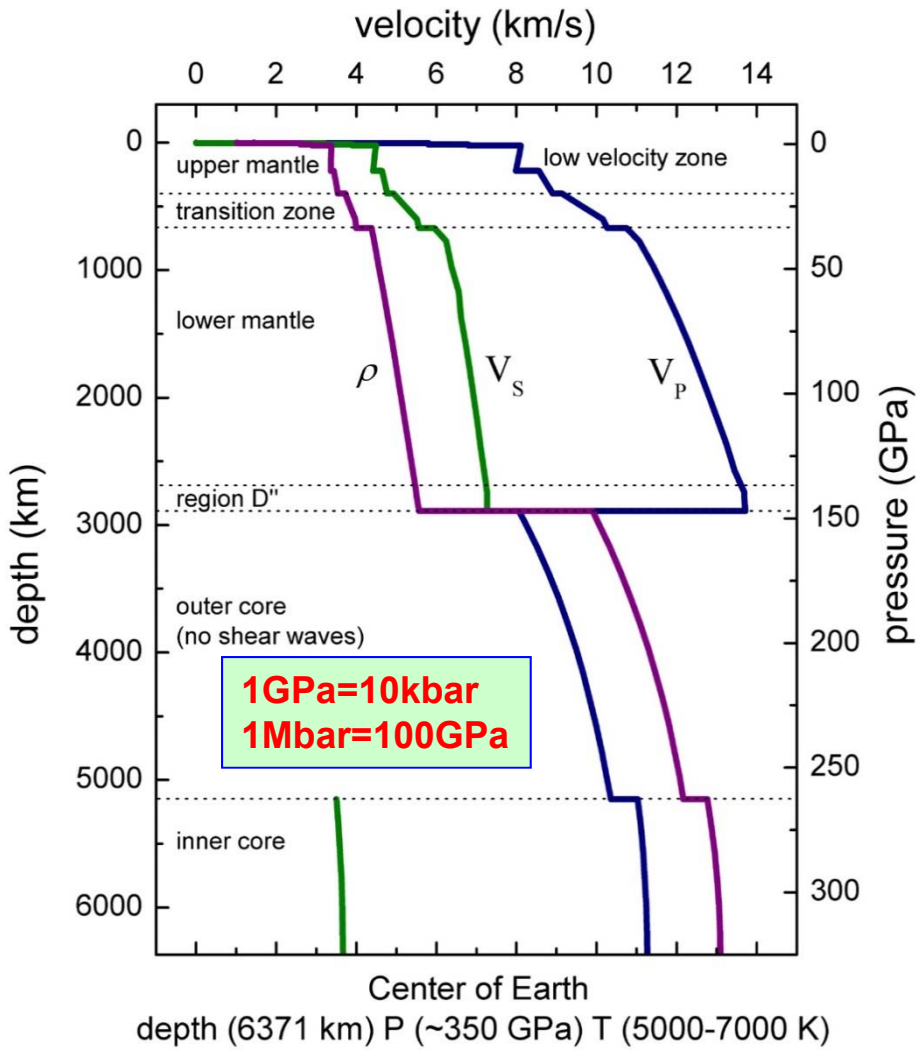


NSF Geophysics
Early Career Award
Instrumentation & Facility



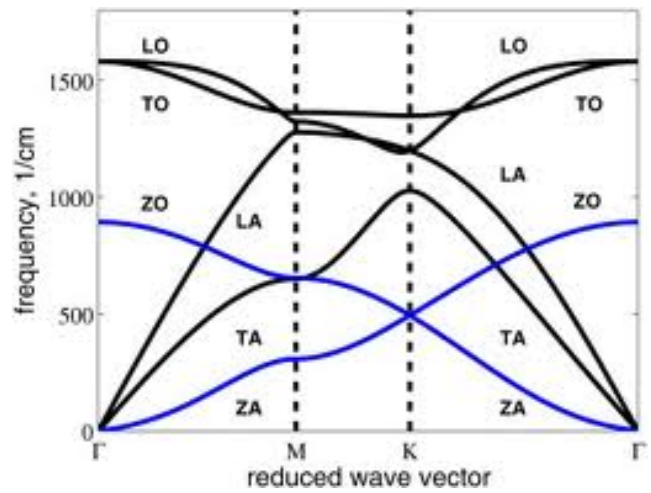
Energy Frontier Research Centers

1. Understanding Elasticity & Acoustic Phonons

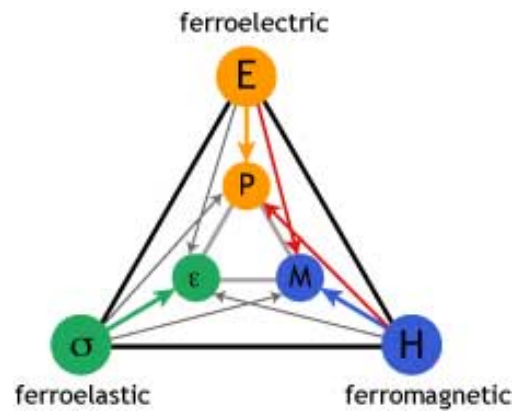


PREM (Dziewonski & Anderson , 1981)

Acoustic Phonons



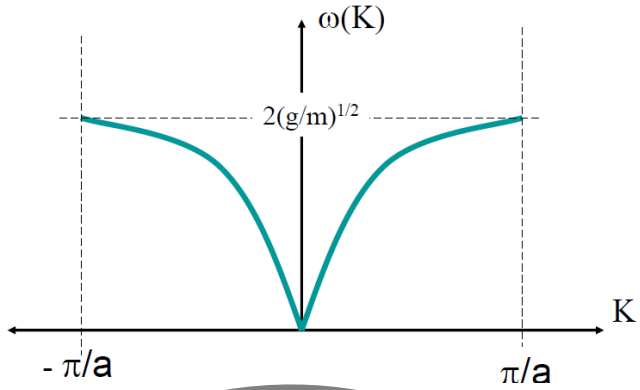
Elasticity vs. Electric/Magnetism

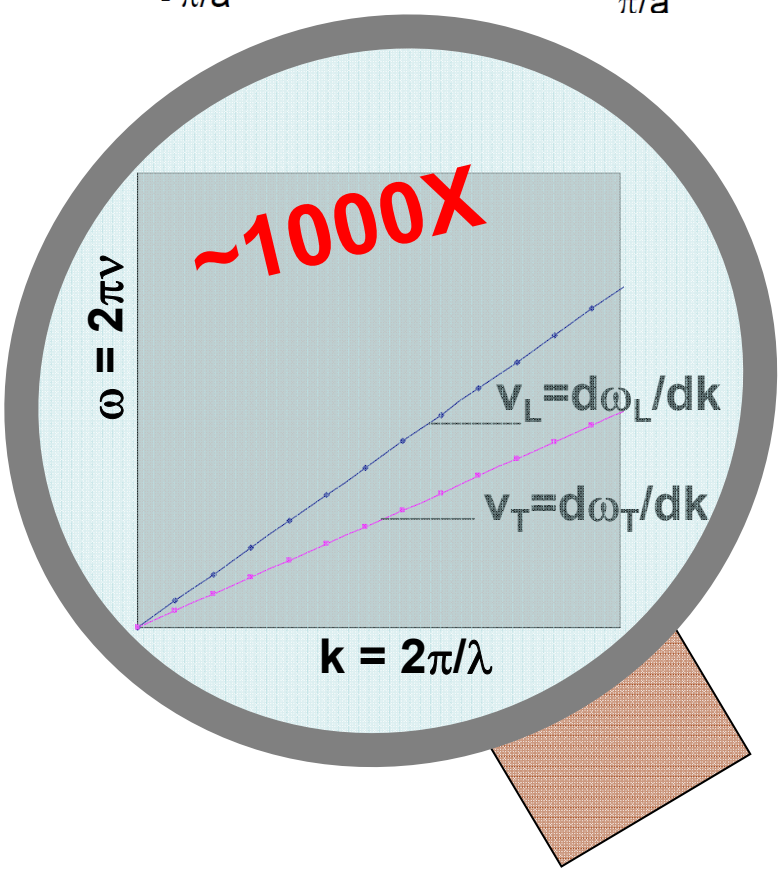


The speed of seismic waves in the Earth's interior is governed by the elastic properties of constitute materials. Knowledge of the elasticity at high pressures and temperatures is thus essential to our understanding of materials properties.

Longitudinal and Transverse Acoustic Wave

Phonon Dispersion Curve





$$V_P = \sqrt{\frac{K + 4/3G}{\rho}} \qquad V_S = \sqrt{\frac{G}{\rho}}$$

$$\rho V^2 \longrightarrow c_{ij}$$

K bulk modulus
G shear modulus
ρ density

$$\sigma_{ij} = \sum c_{ijkl}\varepsilon_{kl} \quad \text{(Hooke's law)}$$

σ_{ij}: stress tensor
ε_{kl}: strain tensor
c_{ijkl}: elastic constant

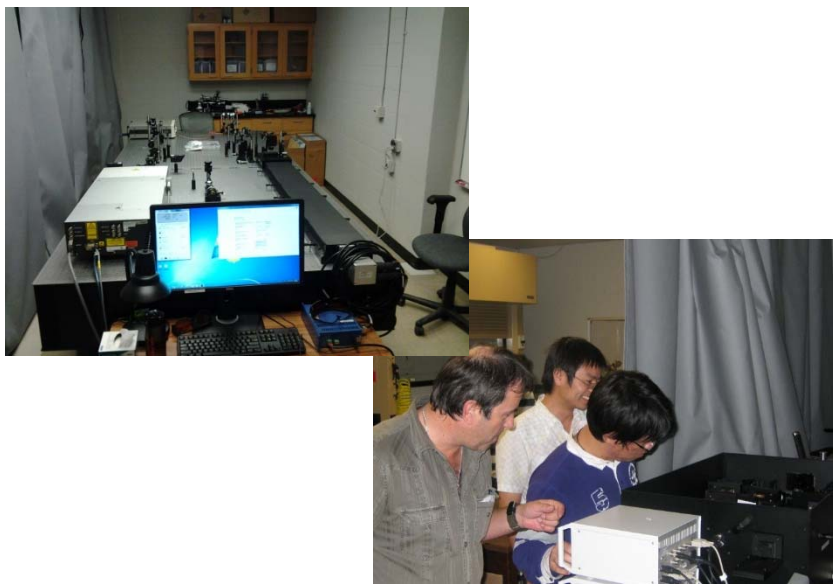
- From acoustic velocities as a function of crystal direction one can calculate single-crystal elastic moduli (C_{ij}), which completely characterize the elasticity of the crystal:

e.g. $C_{11} = \rho V^2_{P(100)}$

$$\left| C_{ijkl} a_j a_l - \rho V^2 \delta_{ik} \right| = 0$$

Methods to Determine Sound Velocities at HP

- Brillouin Light Scattering Spectroscopy (BLS)
- Impulsive Stimulated Light Scattering (ISS)
- Ultrasonic Interferometry
- Nuclear Resonant Inelastic X-ray Scattering
- High-Resolution Inelastic X-ray Scattering



ISS and Brillouin Systems at UT Austin

$$V_P = V_P(P, T, X)$$

$$dVp = \frac{\partial V_P}{\partial P} dP + \frac{\partial V_P}{\partial T} dT + \frac{\partial V_P}{\partial X} dX$$

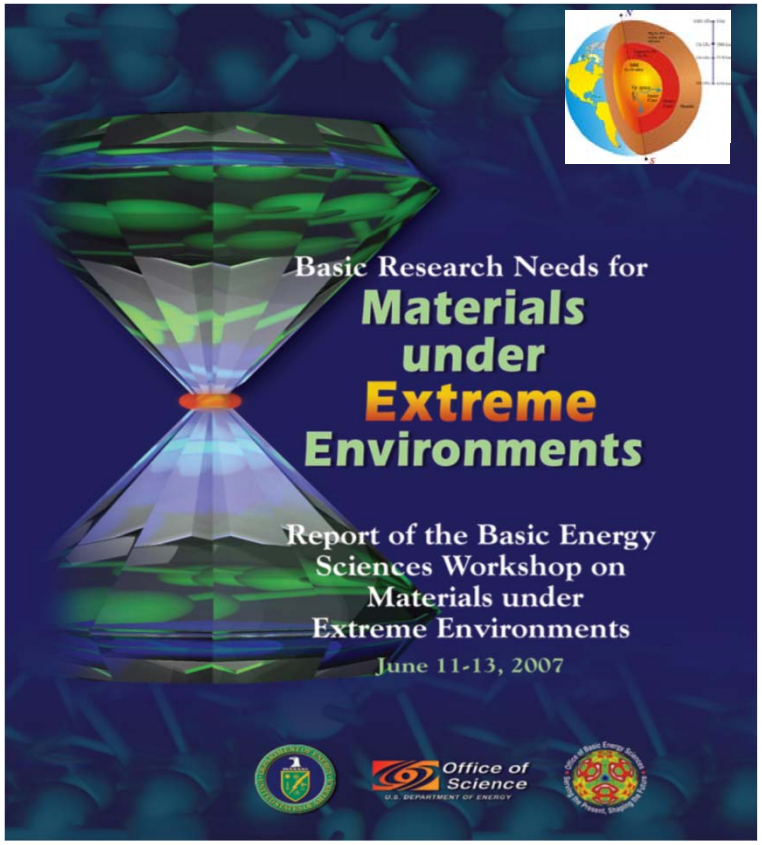
Since we know P well, we can write:

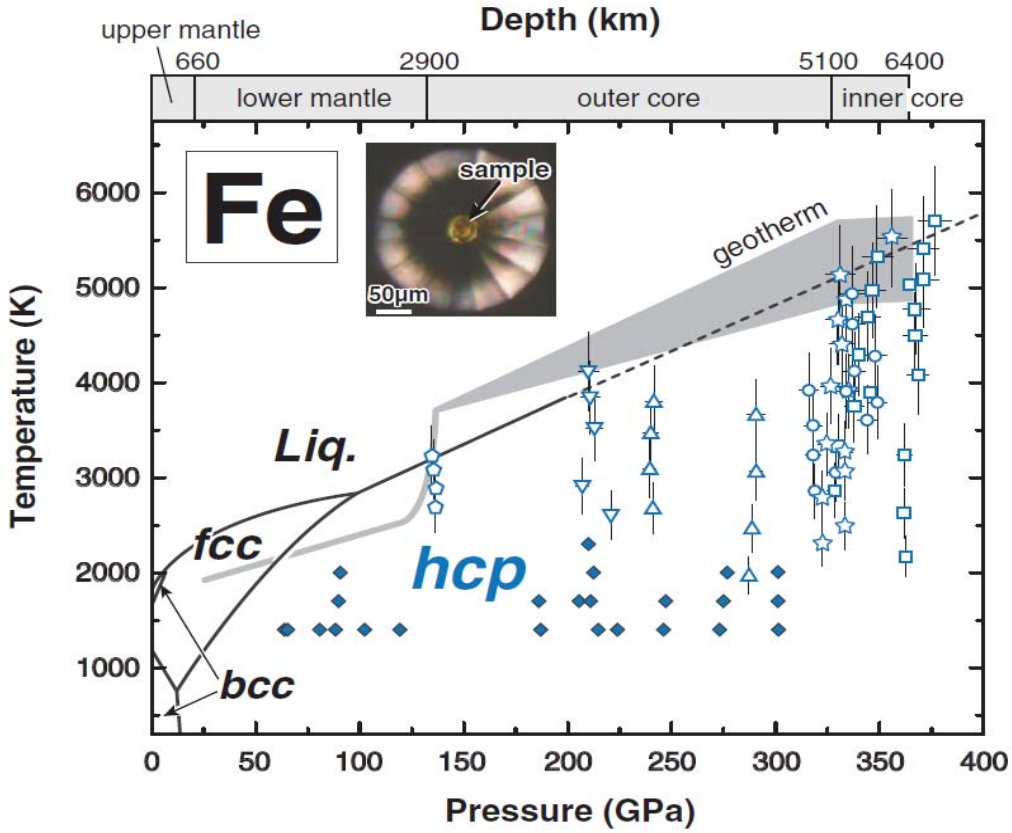
$$dVp = \frac{\partial V_P}{\partial T} dT + \frac{\partial V_P}{\partial X} dX$$

X can be composition or mineral content.

Science Case for HERIX:

Planetary Materials under Extreme Pressures and Temperatures





Tateno et al., Science, 2010

Why HERIX is needed?

- **Study micro, opaque samples at P-T reaching the center of the Earth's core**
- **Measure wave velocities, elastic anisotropy, lattice dynamics under *real* P-T.**
- **Other techniques have limitations (e.g., Brillouin light scattering, neutron)**

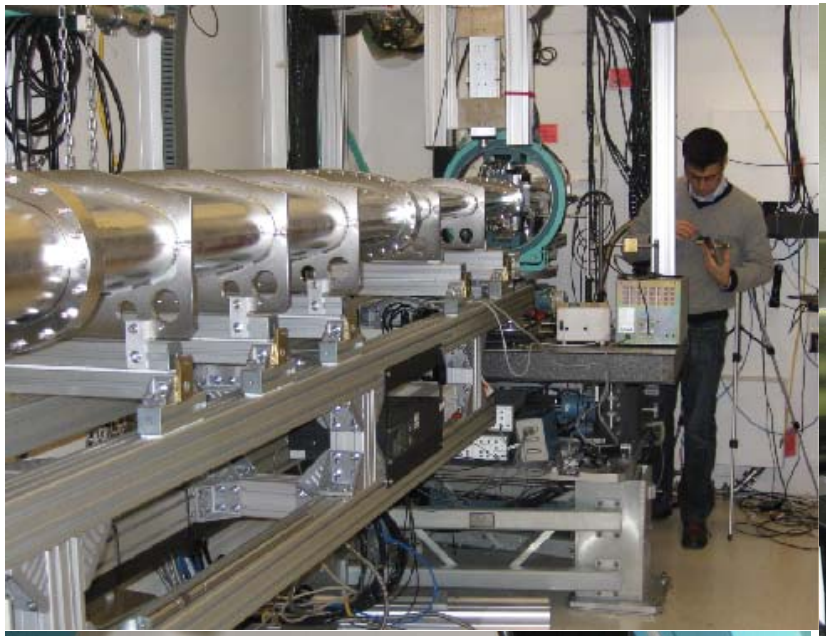
Current Status of the HERIX Programs at APS

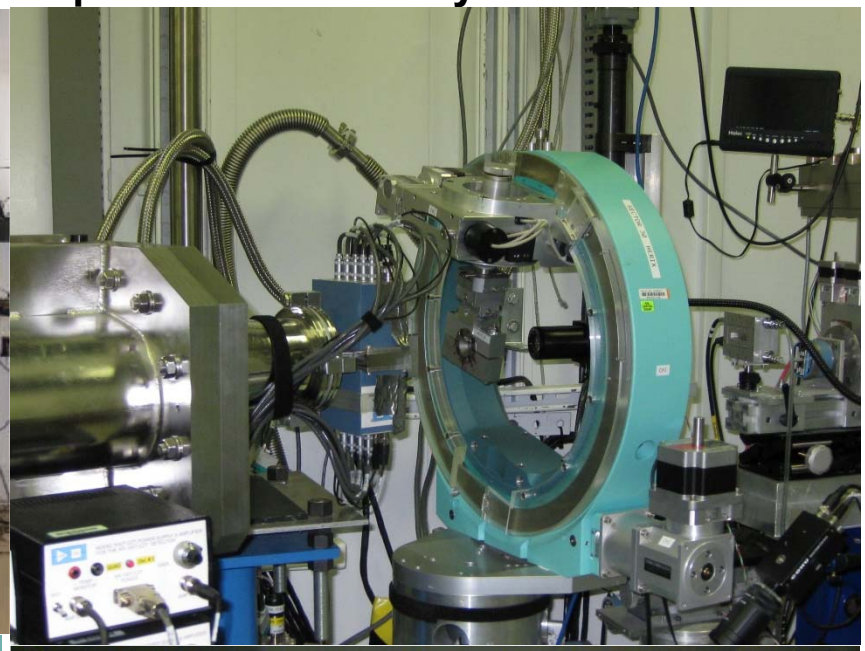
	HERIX-3 Started in 1999	HERIX-30 Started in 2007
Sector	3	30
Available beamtime	40% (60% NRS)	50% (50% MERIX)
Working energy (keV)	21.6	23.7
Energy resolution (meV)	2-2.4	1.5-1.7
Number of analyzers	4	9
Maximum momentum transfer (nm^{-1})	**35**	**72**
Beam size at sample (VxH) (μm^2)	**17x17**	**20x35**
Flux at sample (GHz)	**3.5-4.5**	**1.8**

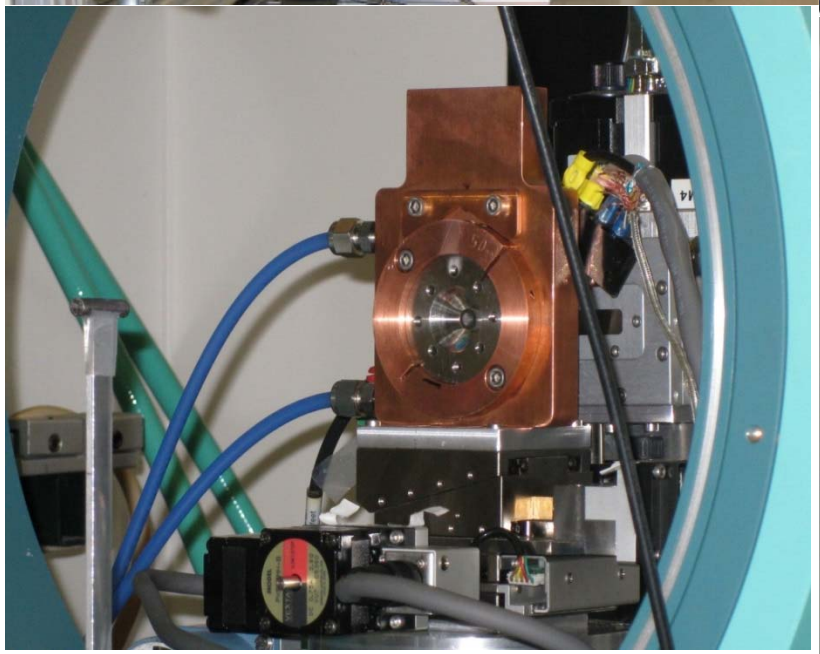
HERIX with the meV energy resolution and small beamsize at extreme environments is regarded as "photon hungry" technique.
APS-U: a factor of 10-15 gain in signal throughput:
More flux, more beamtime, more results, more publications, more opportunities

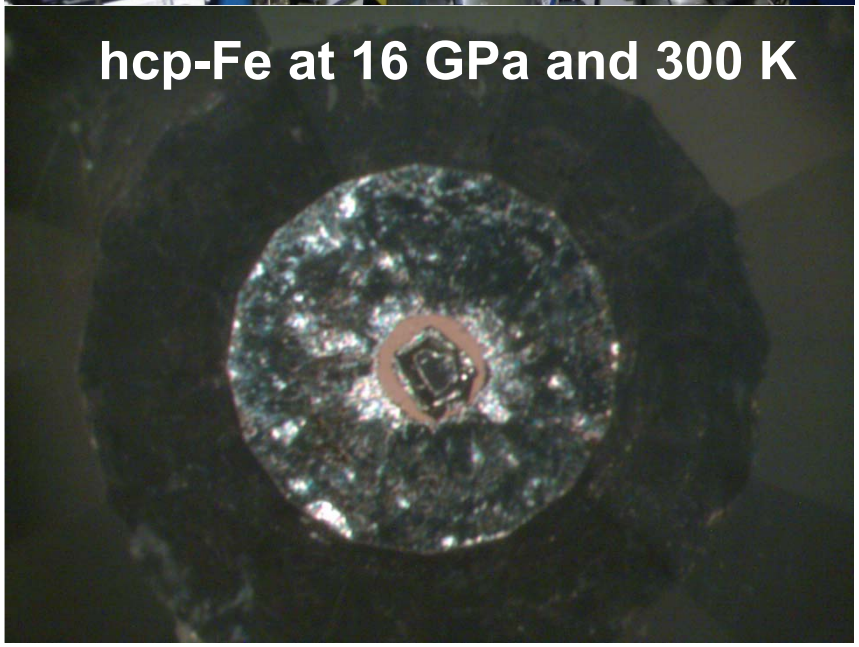
High P-T HERIX Experiments at XOR3 of the APS

- 21.657 keV ~2.3 meV resolution ~20 μm beam 4 analyzers 3 GHz flux

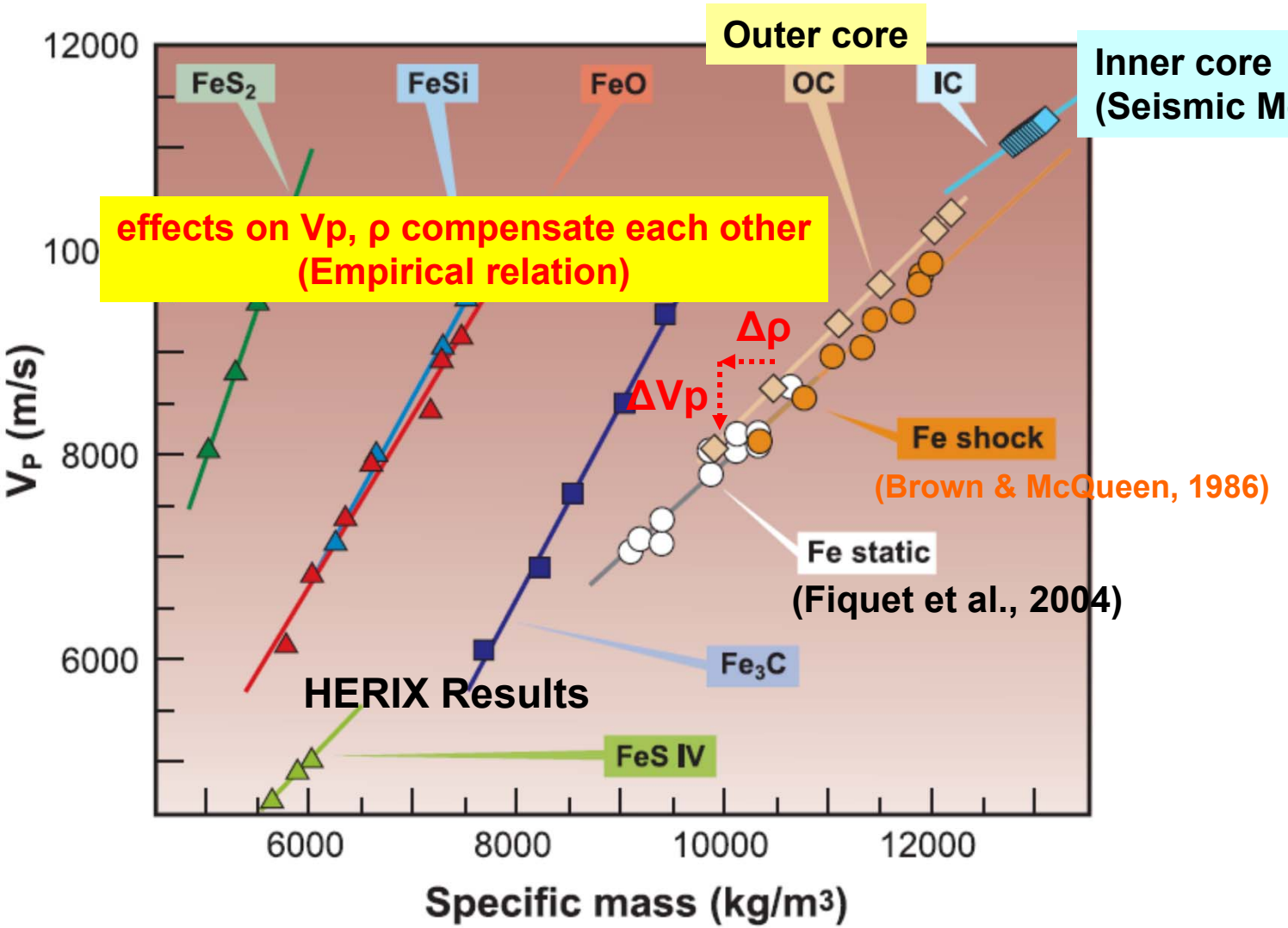








2. Sound Velocities of Iron and Birch's Law



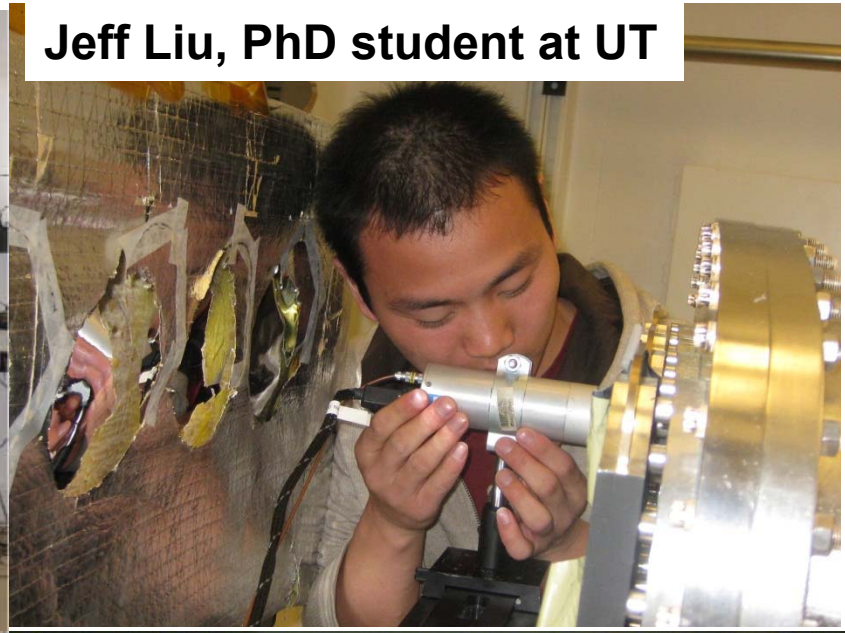
Birch, 1952, 1961; Badro et al., 2007

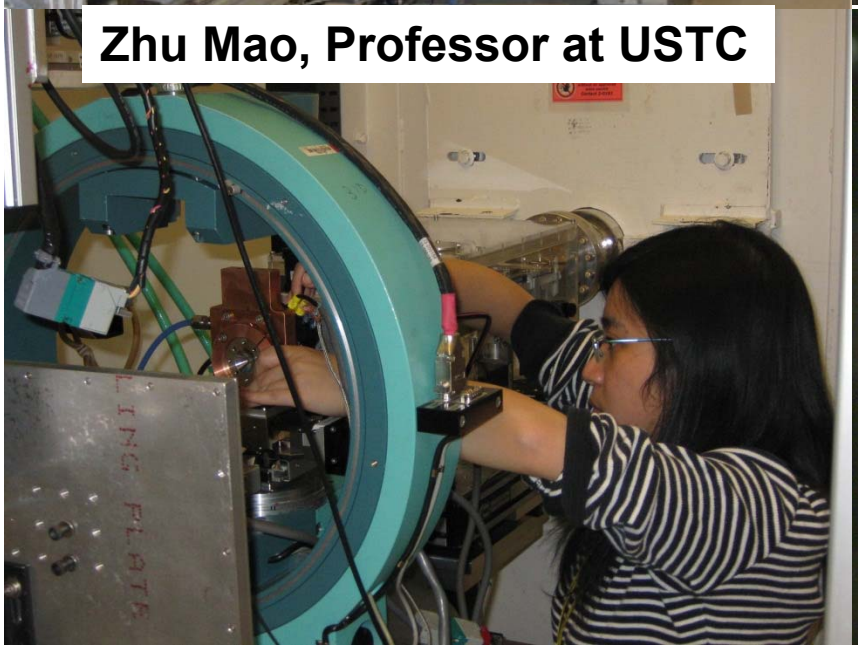
Birch's law, a linear sound velocity–density relation, has been used to extrapolate Vp of iron compounds at high pressures and room temperature to inner core conditions.

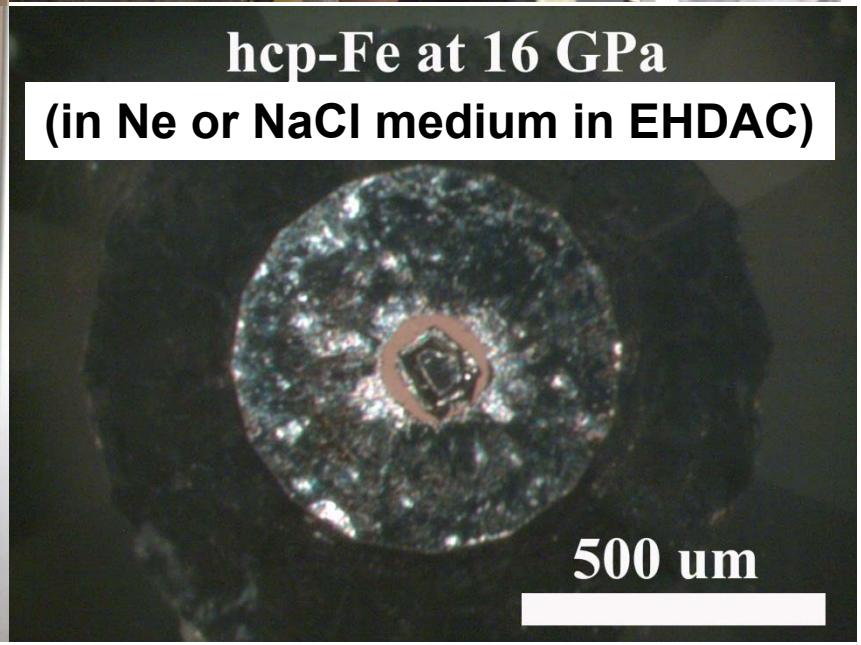
P-T effects on sound velocities of Fe remains largely unknown!

In Situ High P-T Experiments in an Externally-Heated DAC

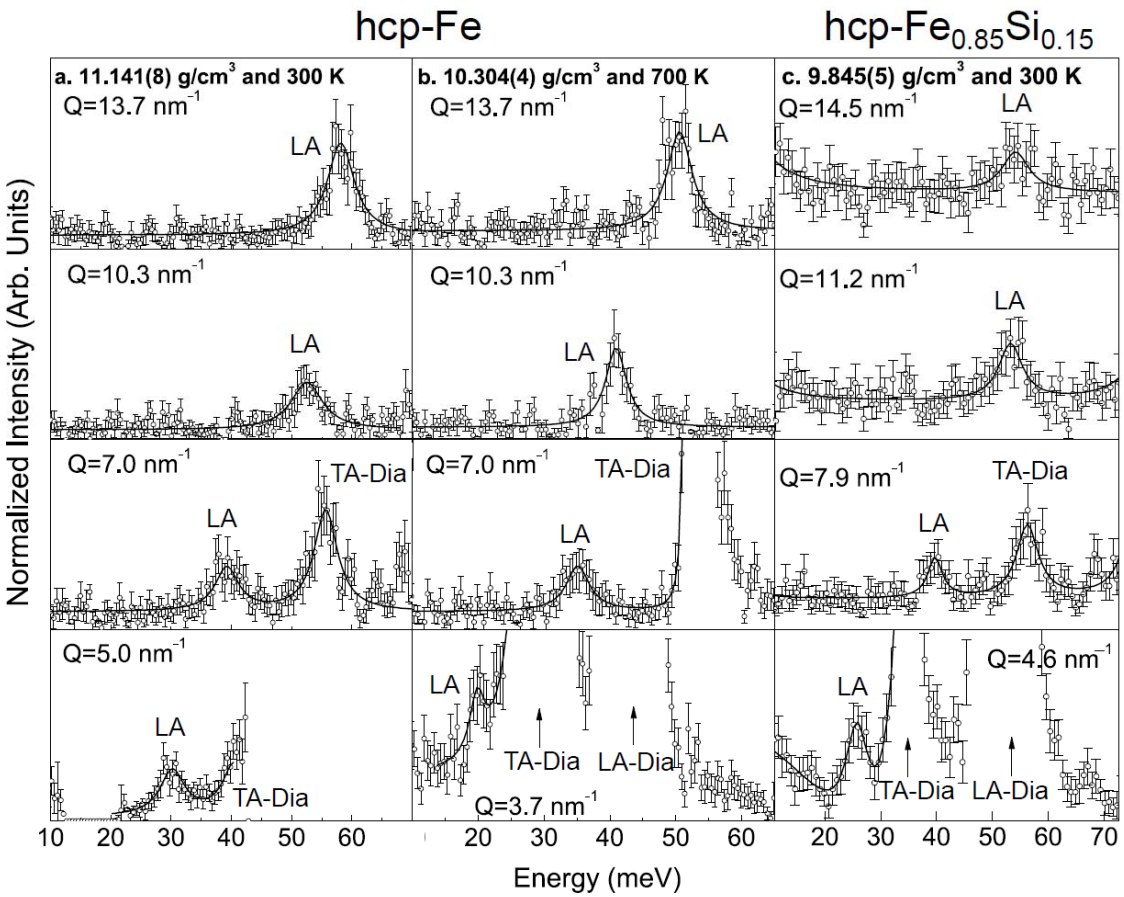
21.657keV; ~2.2meV resolution; ~20μm beam; 4 analyzers; 3GHz flux





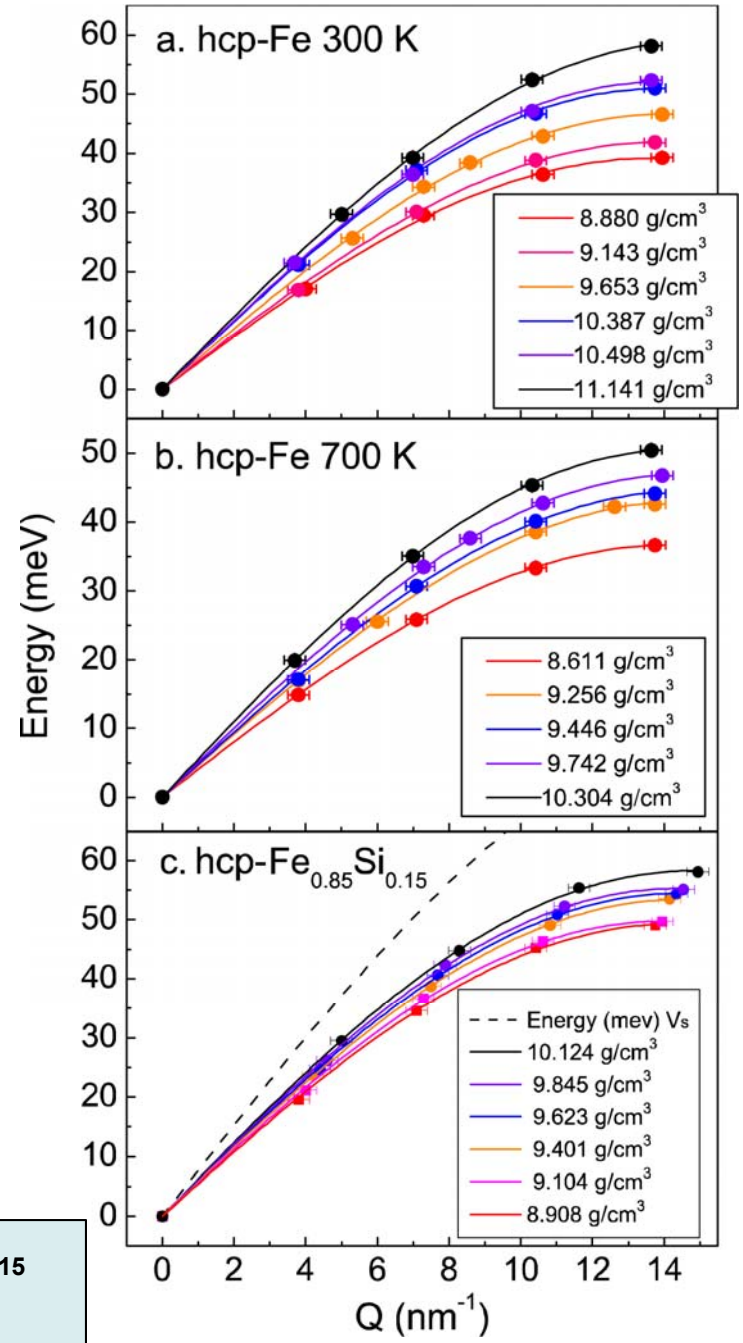


Phonon Dispersion Curves by HERIX



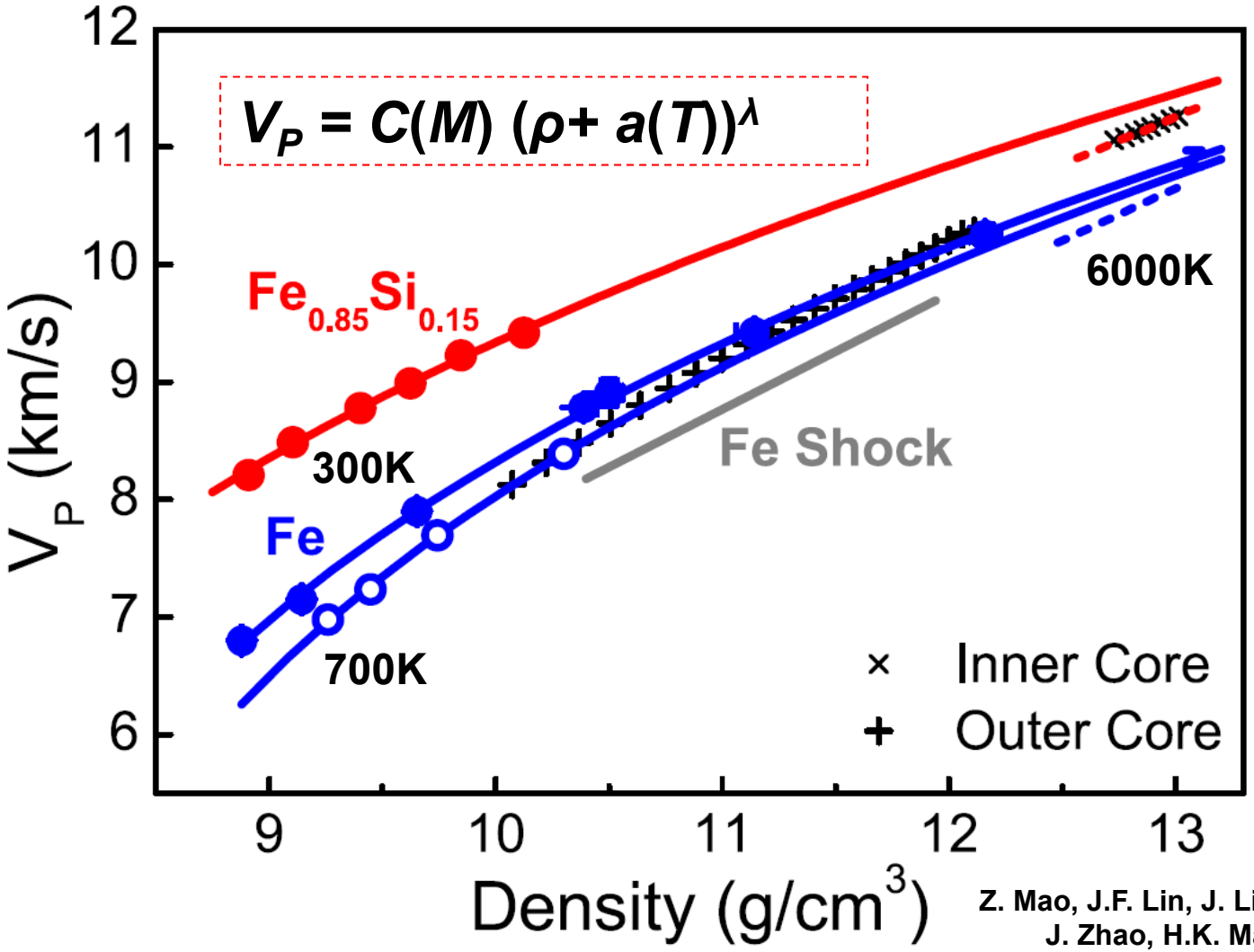
Z. Mao, J.F. Lin, J. Liu, A. Alatas, L. Gao, J. Zhao, H.K. Mao, PNAS, 2012

$$Q = 2k_1 \sin\left(\frac{\theta}{2}\right)$$



Longitudinal acoustic dispersion curves of hcp-Fe and $Fe_{0.85}Si_{0.15}$ alloy are fitted to a sine function to derive the Vp (within the framework of the Born–von Karman lattice-dynamics theory).

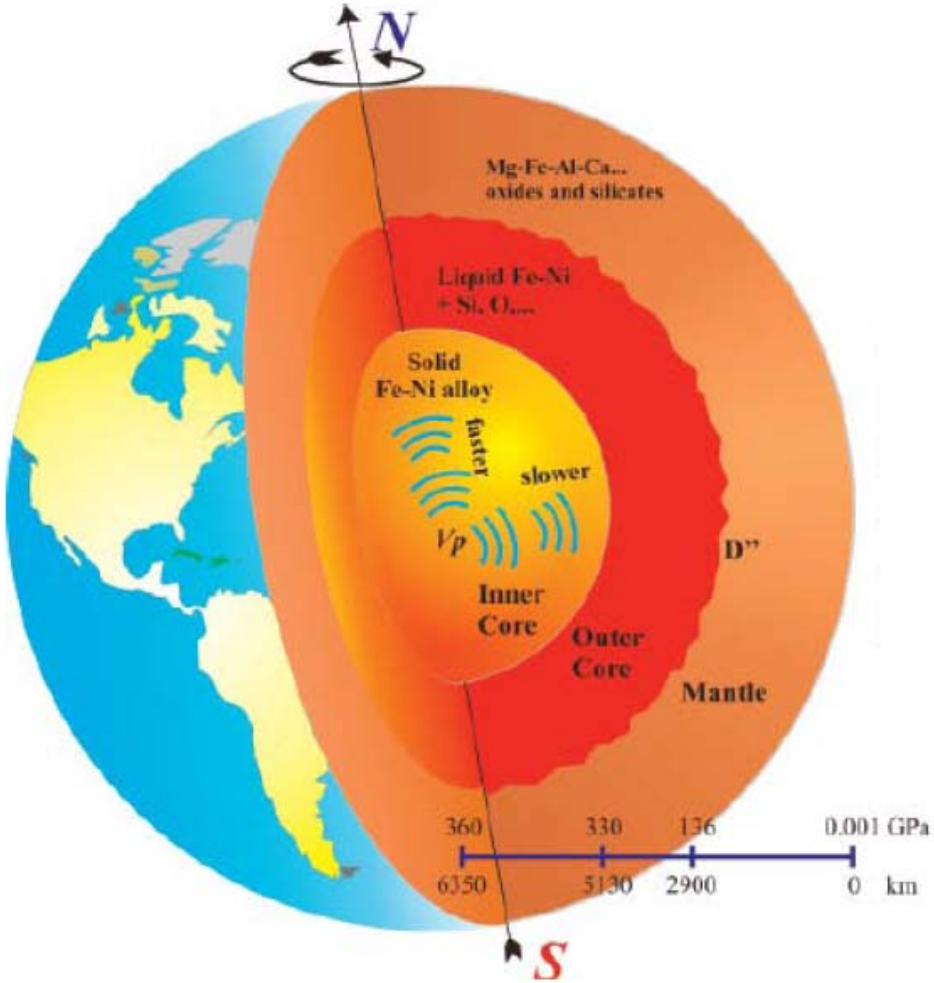
Velocity-Density Relation of Iron in Earth's Core



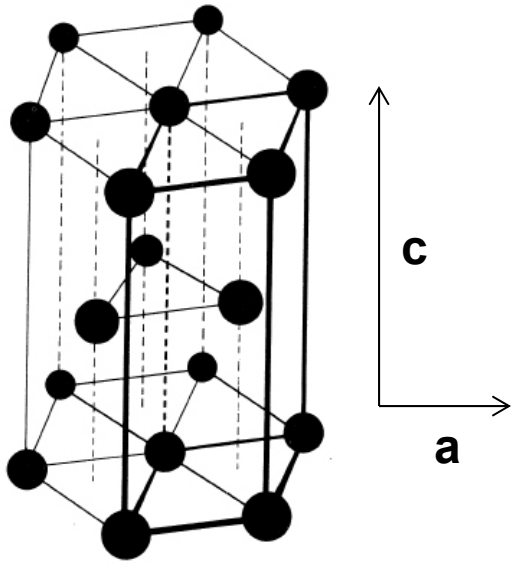
Z. Mao, J.F. Lin, J. Liu, A. Alatas, L. Gao, J. Zhao, H.K. Mao, PNAS, 2012

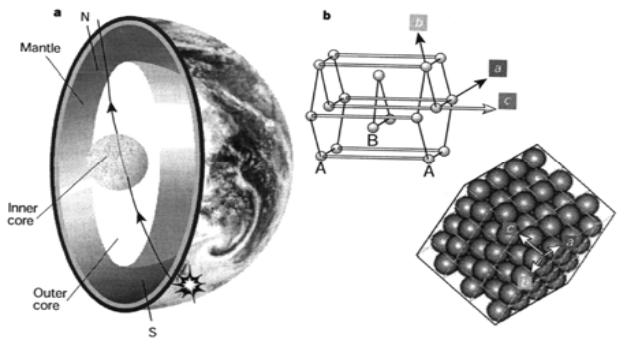
Extending our results to relevant inner core conditions using the power-law function and previous shock wave results, V_P of hcp-Fe at 300 K is 5-6% and 3.5% lower than that of the linear extrapolation and seismic references, respectively.

Sound Velocity of Fe in Earth's Inner Core



Lin et al., EoS, 2008; Tateno et al., Science, 2010

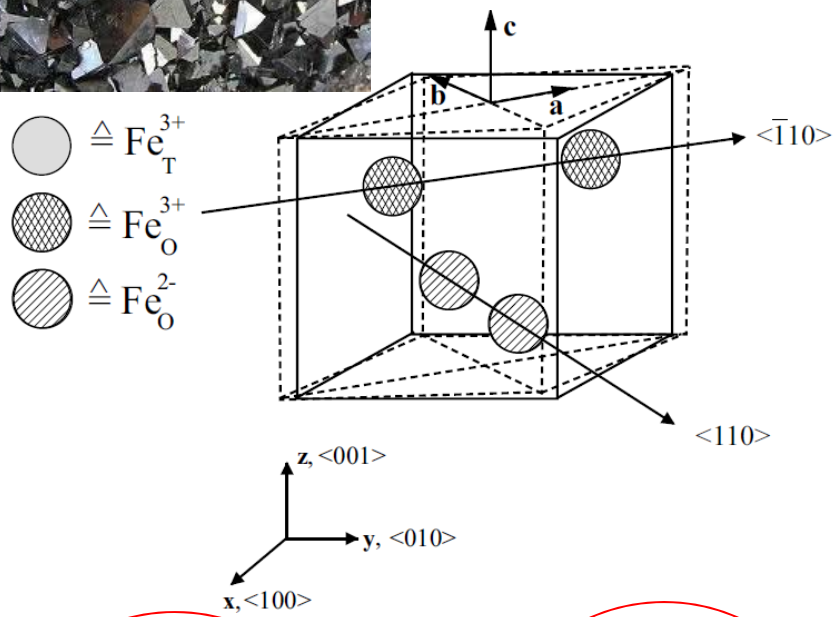


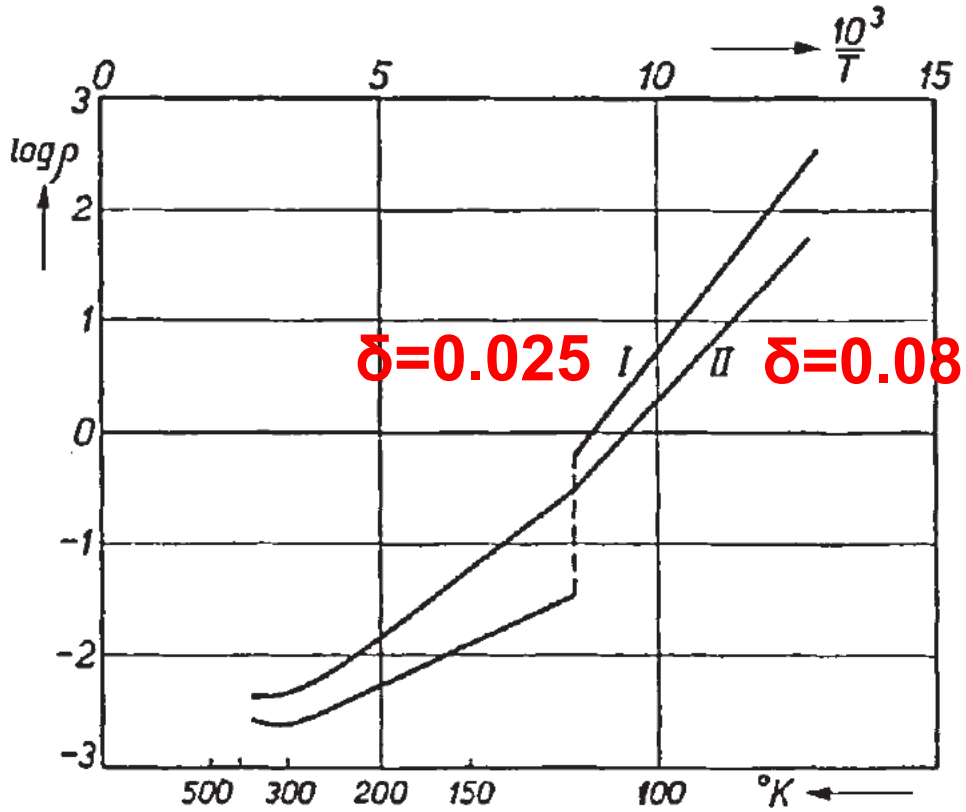


Steinle-Neumann et al., Nature, 2001

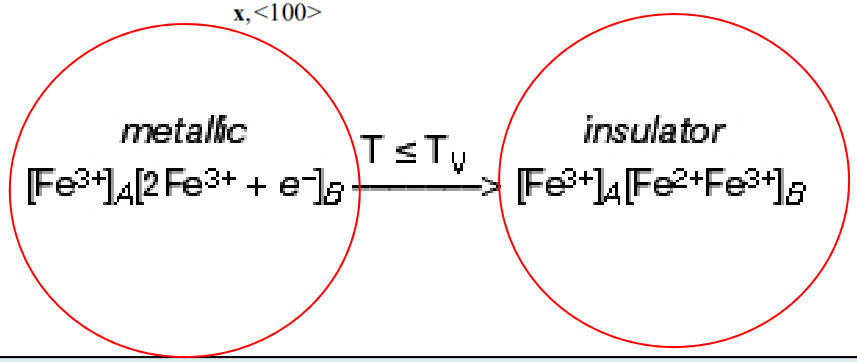
hcp-Fe is likely stable under the P-T conditions of the inner core, although bcc-Fe has also been proposed theoretically. Preferred orientation of Fe crystals may help explain the seismic wave anisotropy in the inner core.

3.1. Magnetite (Fe_3O_4) in Extreme Environments





The accompanying graph shows log ρ against $1/T$ for two bars: I with $FeO : Fe_2O_3 = 1 : 1{\cdot}025$, and II with $FeO : Fe_2O_3 = 1 : 1{\cdot}08$.



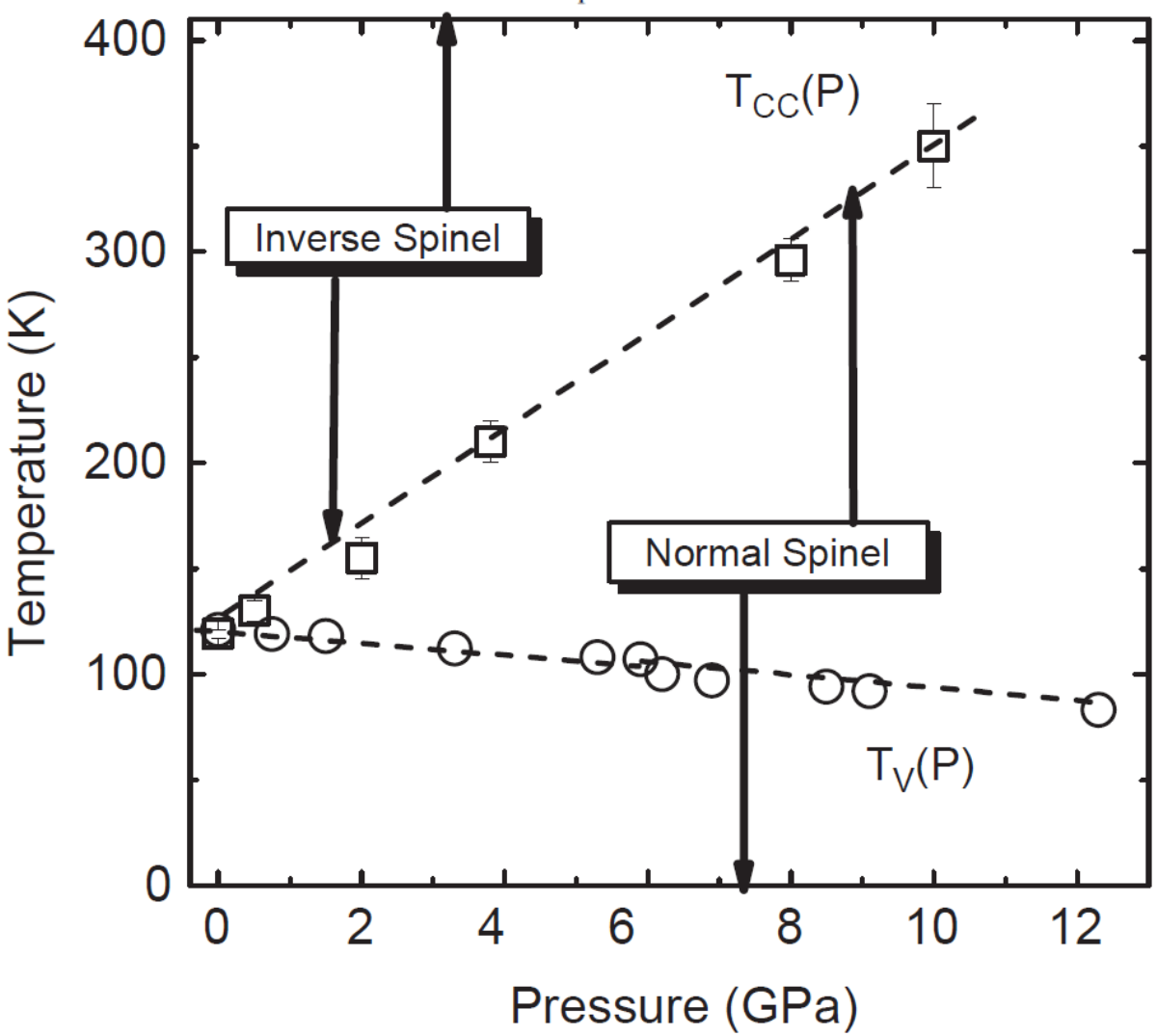
Verwey, Nature, 1939

Magnetite (Fe3O4) is a metallic ferrimagnet at ambient conditions. It is the only mixed-valence iron oxide with an inverse spinel structure at ambient conditions. The Verwey transition was first discovered in 1939.

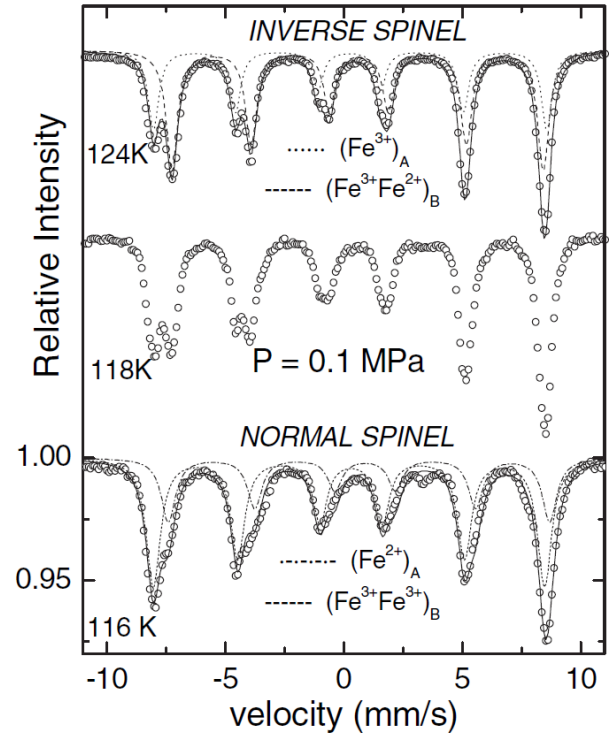
Electronic Transition in Magnetite

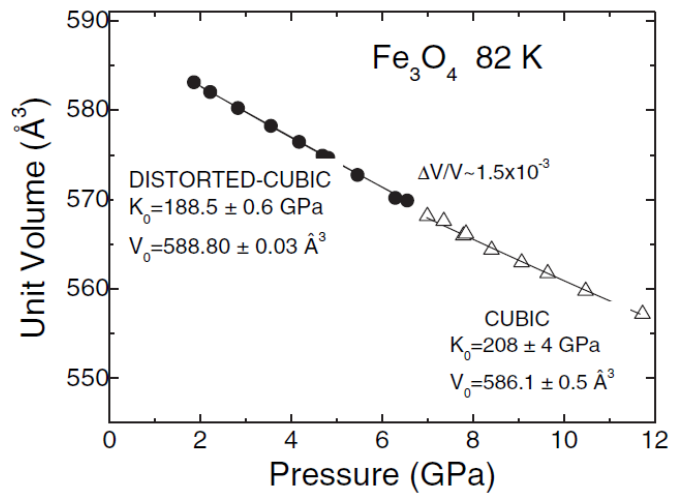
$$\underset{\text{inverse spinel}}{[Fe^{2.5+}Fe^{2.5+}][Fe^{3+}]} \underset{T}{\overset{P}{\rightleftarrows}} \underset{\text{inverse spinel}}{[Fe^{2+}Fe^{3+}][Fe^{3+}]}$$

$$\underset{T}{\overset{P}{\rightleftarrows}} \underset{\text{normal spinel}}{[Fe^{3+}Fe^{3+}][Fe^{2+}]}.$$



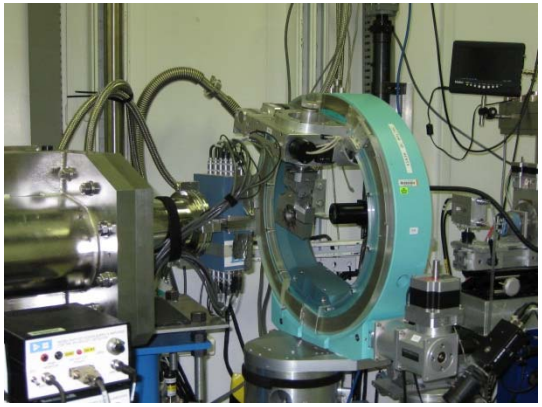
Pasternak et al., JMMM, 2003

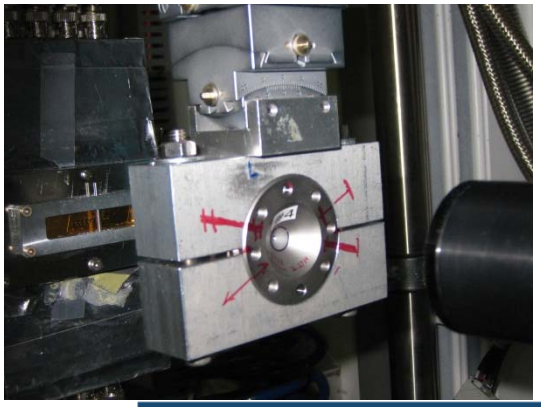




Rozenberg et al., PRL, 2006

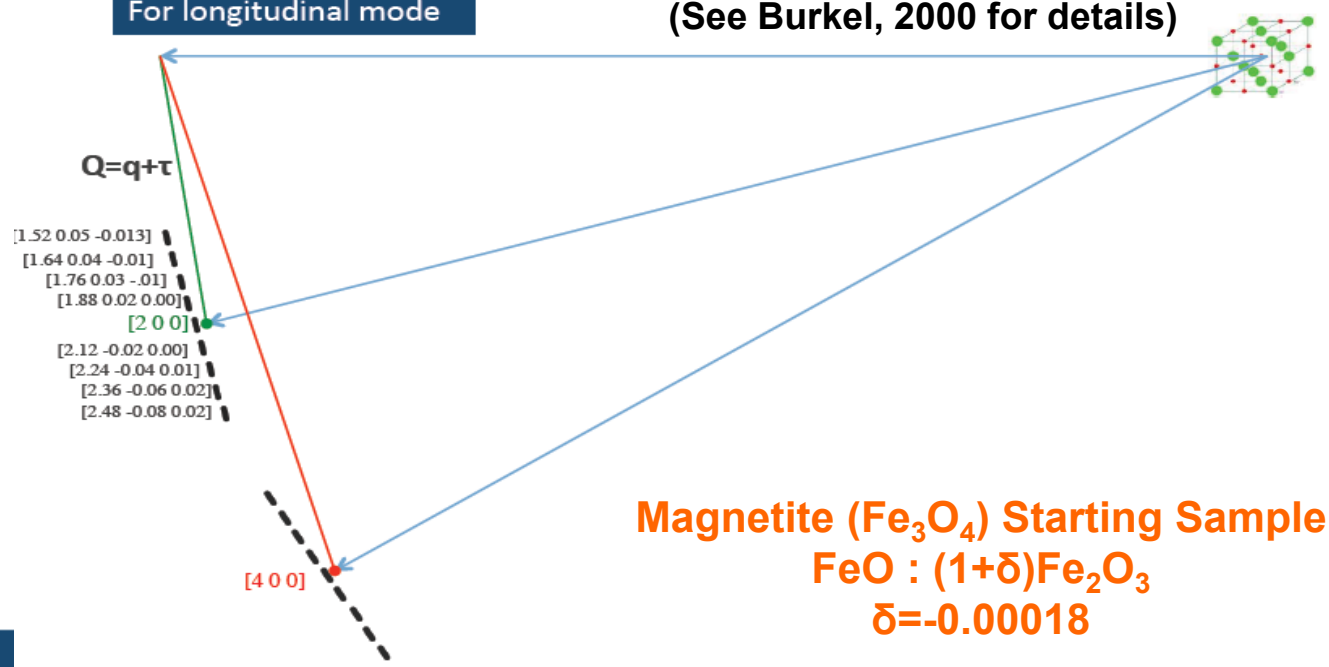
Cij by Acoustic Phonons in HERIX





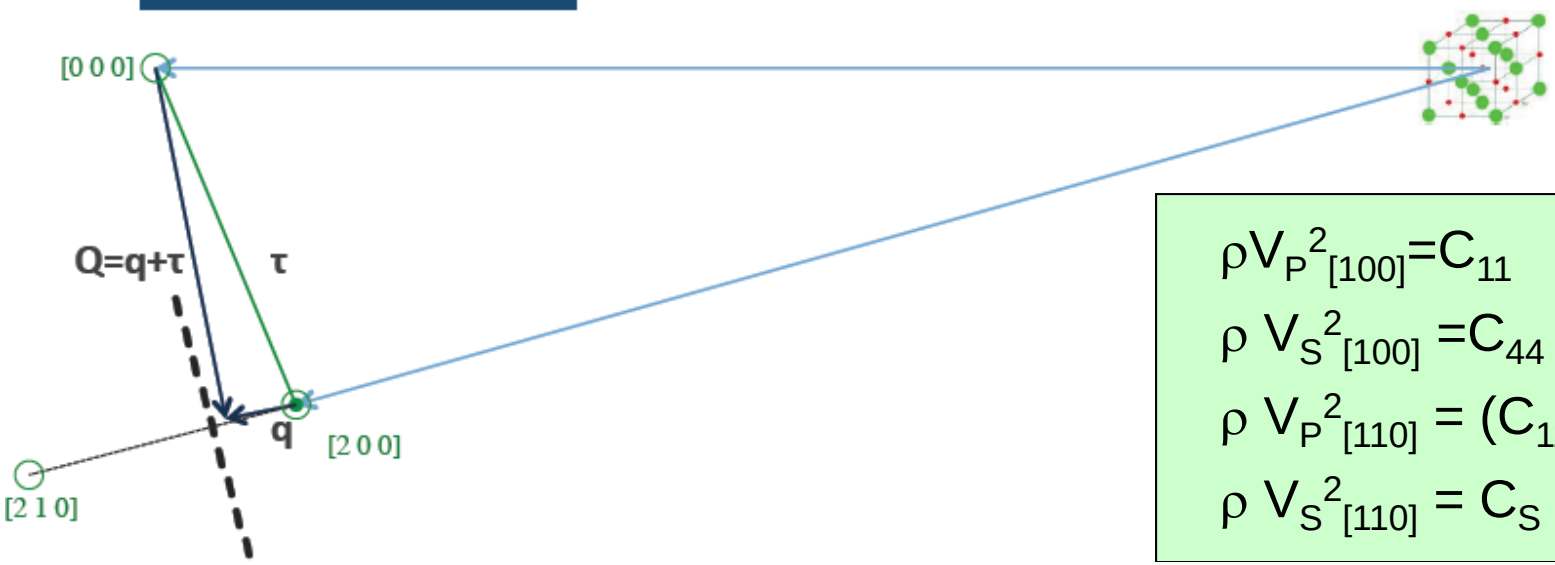
Pictures Courtesy: Dr. Ayman Said of XOR30
(See Burkel, 2000 for details)

For longitudinal mode



Magnetite (Fe_3O_4) Starting Sample
FeO : $(1+\delta)Fe_2O_3$
δ=-0.00018

For transverse mode



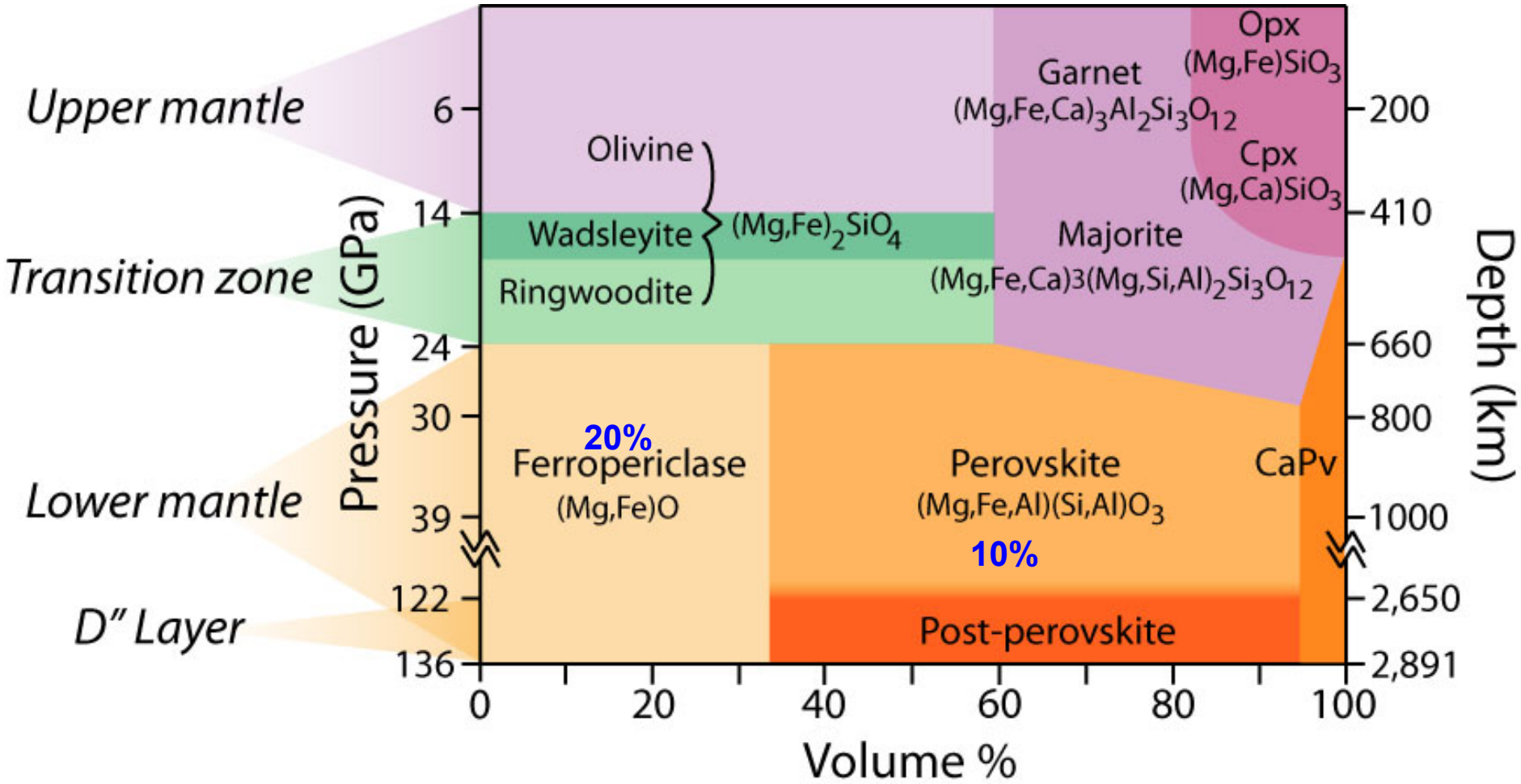
$$\rho V_P^2{}_{[100]} = C_{11}$$

$$\rho V_S^2{}_{[100]} = C_{44}$$

$$\rho V_P^2{}_{[110]} = (C_{11}+C_{12}+2C_{44})/2$$

$$\rho V_S^2{}_{[110]} = C_S = (C_{11}-C_{12})/2$$

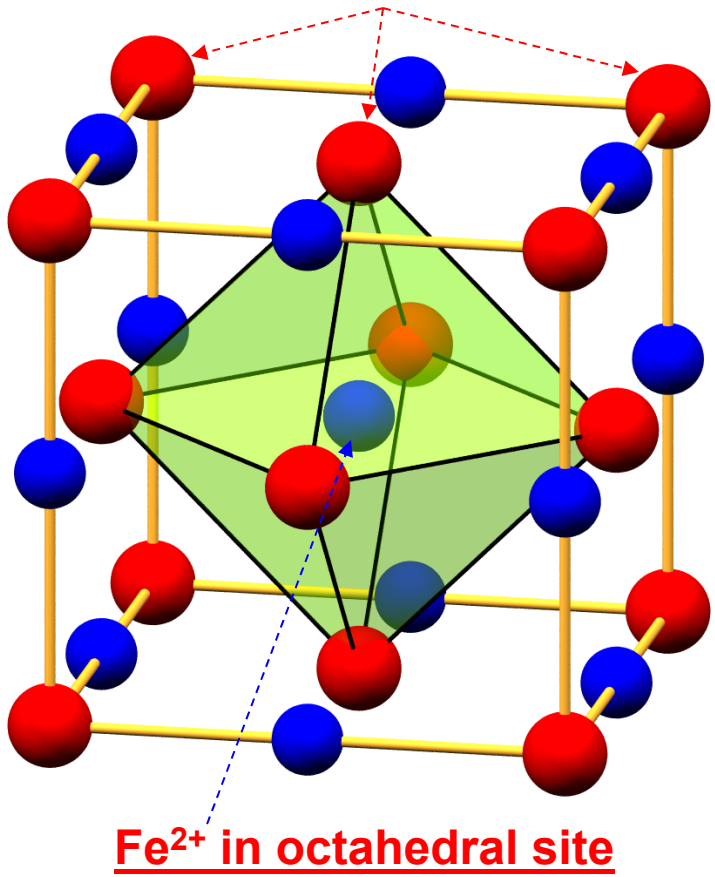
3.2 Mineralogy of the Earth's Mantle

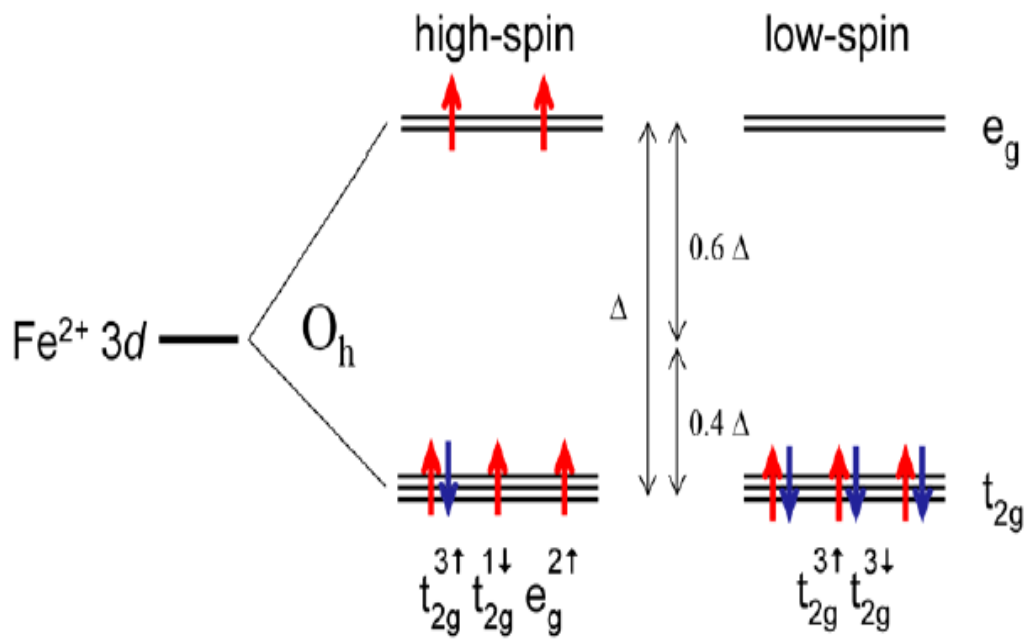


Lin, Speziale, Mao, Marquardt, Review of Geophysics, 2013

Spin States of Fe^{2+} in Ferropericlase

$(Mg_{0.8}Fe_{0.2})O$





Pauli's Exclusion Principle: prevents two electrons of the same spin from being at the same place at the same time.

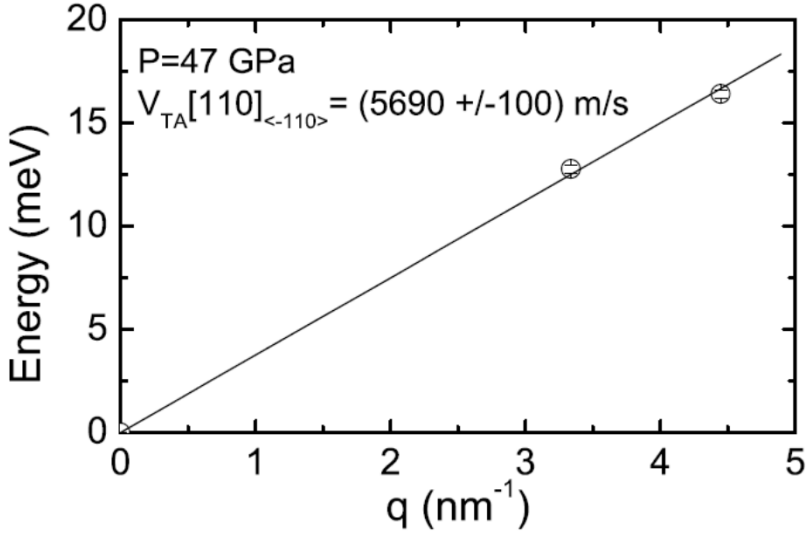
Δ: crystal splitting energy

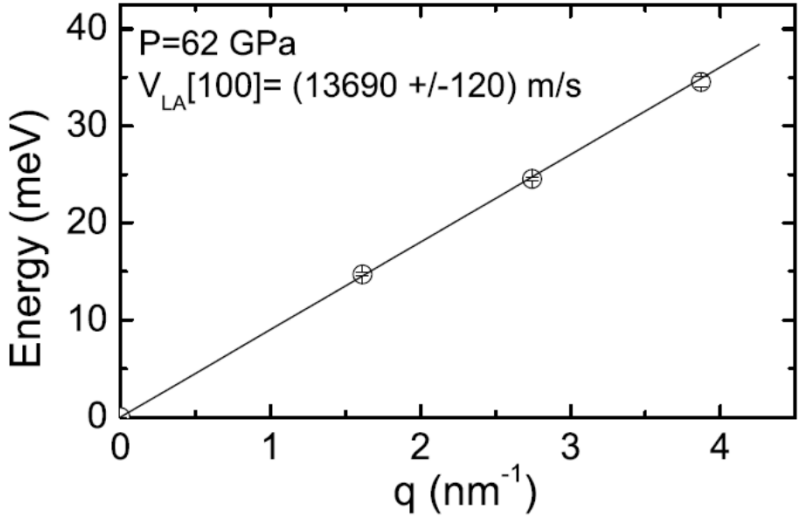
Π: spin-pairing energy

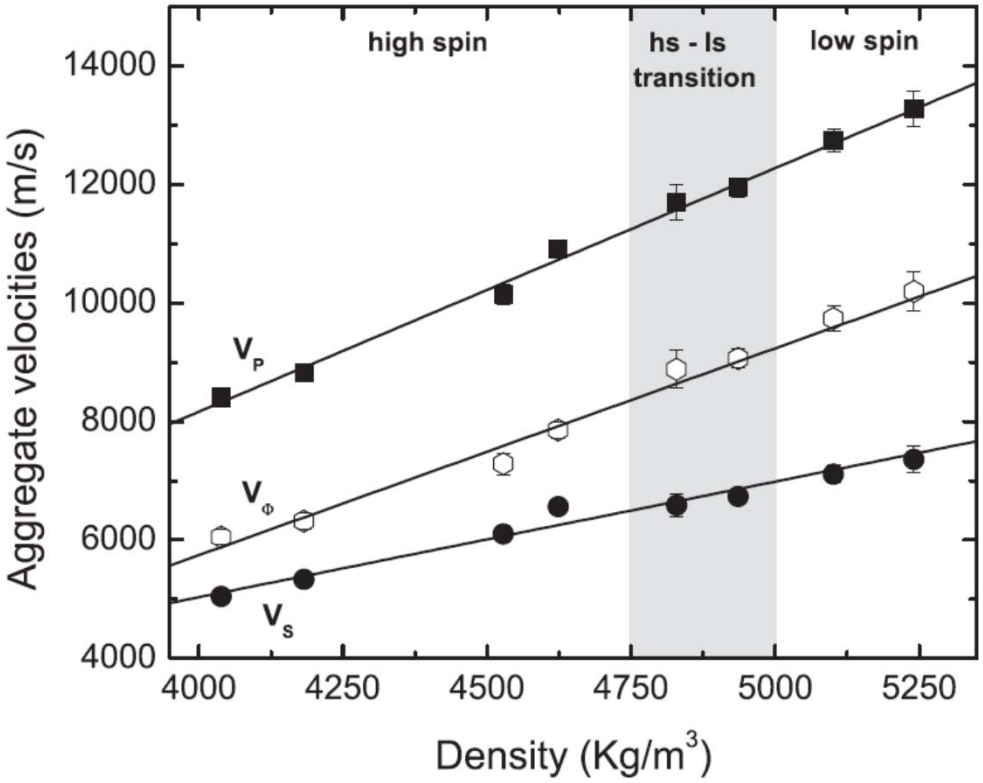
At high pressures, Δ overcomes Π, resulting in the occurrence of the low-spin state

Fe^{2+} in ferropericlase is in the high-spin state under ambient conditions. Applied pressure forces 3*d* electrons to pair up in the low-spin sate—the electronic spin transition.

Elasticity in Ferropericlase across the Spin Transition

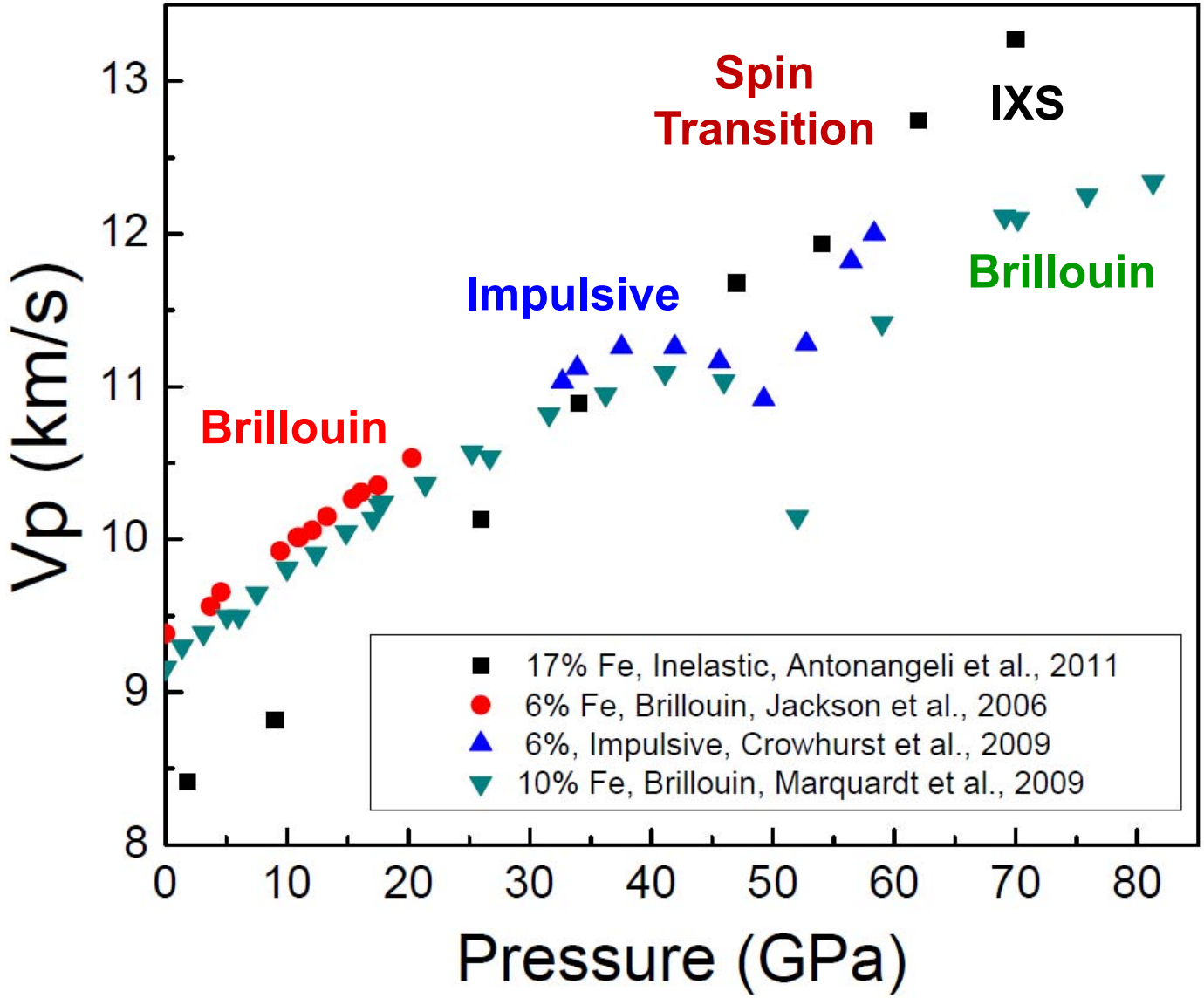






Antonangeli et al.,Science,2011

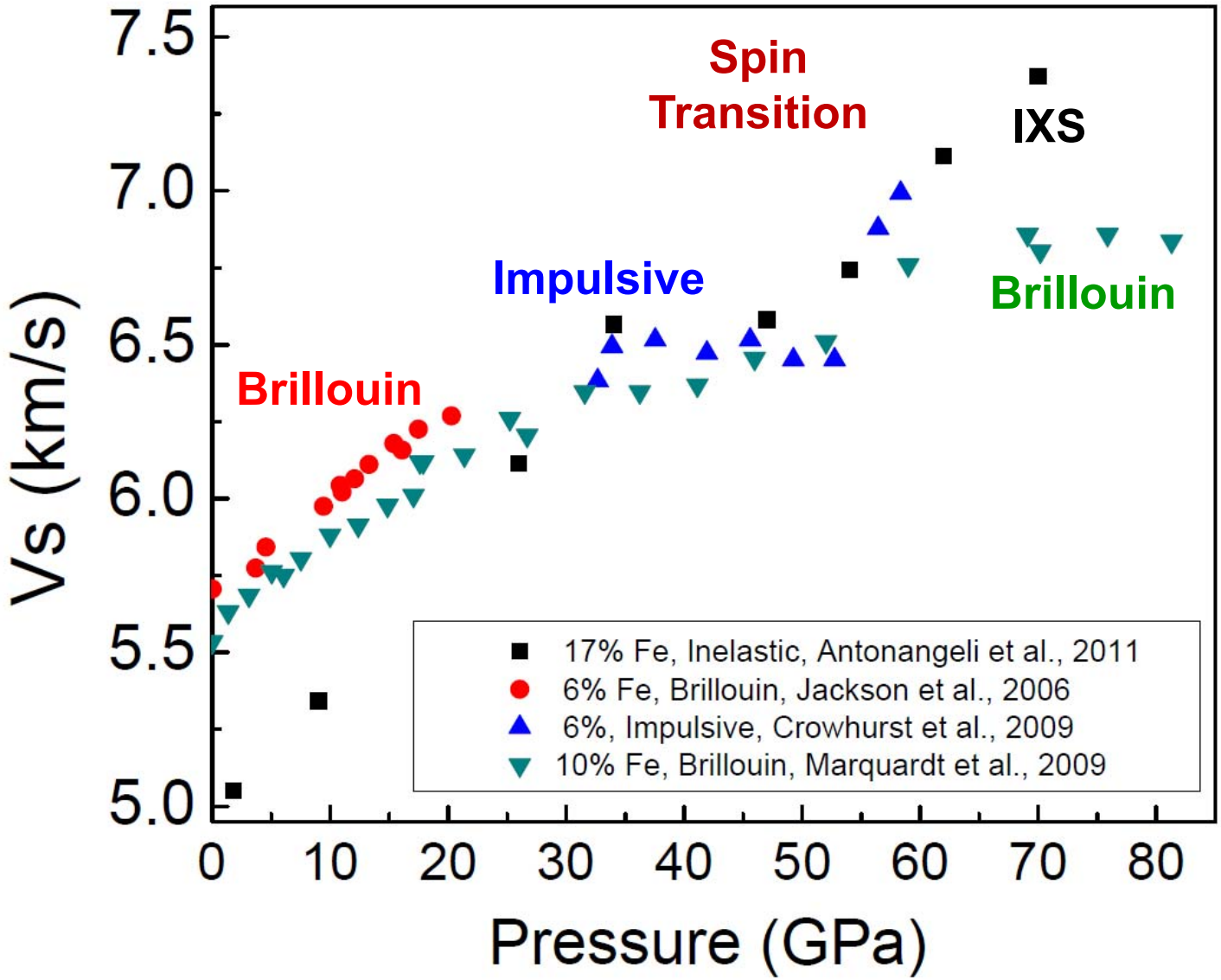
Compressional Wave Velocity (Vp) of Ferropericlase



Lin, Mao, Sergio, Marquart, Rev. Geophys., 2013

Compressional wave velocity of ferropericlase is significantly reduced within the transition.

Shear Wave Velocity (Vs) of Ferropericlase



Lin, Mao, Sergio, Marquart, Rev. Geophys., 2013

Shear wave velocity of ferropericlase may be reduced within the transition.
Elastic anisotropy is significantly enhanced across the transition

New Research Capabilities & Opportunities with the HERIX Facilities

"The Right Source for the Right Experiment":

Micro-sized sample environments: µm-sized beam, flux, wide Q range, multi-detectors.

Material science at high pressure/low temperature

Quantum phase transitions in complex and correlated systems

Superconducting transitions, lattice dynamics in real time…

Planetary sciences under real high P-T conditions

Seismic wave velocities, geodynamics, geochemistry (up to a few Mbars and thousands kelvins)

***In-situ* X-ray diffraction (all user groups):**

Structural identification and sample alignment

Density measurements during the experiment