

X-ray Powder Diffraction, Part 1: Principles & Theory

February 1, 2010

Jennifer Jackson

(Lecture was given on the white board)

Outline from white board notes

- Discovery of x-rays
 - Electromagnetic spectrum
 - Hard vs. soft x-rays
 - Radiation training (1st week of lab)
- Principles
 - atoms act as source reflectors
 - The electron cloud around each atom interacts with the x-rays and elastically scatters the x-rays coherently
- Bragg's law: $n\lambda = 2d\sin\theta$
- Generating x-rays

Outline from white board notes, cont.

- **Methods & Geometry**
 - In-house
 - Requires milligrams of sample
 - Decent flux at low energies
 - Unfocused radiation, but can be collimated
 - Synchrotron
 - Requires less than a microgram
 - High-flux at high-energies
 - Can be focused (no need for a collimator)
- **Brief overview of applications**
- **Sample preparation**
 - Grind under alcohol using agate mortar & pestle
 - Grain size should be $\sim 100 \mu\text{m}$
 - Spread on glass disc or zero-background Si wafer

X-ray Powder Diffraction, Part 2: Practical Applications

February 8, 2010

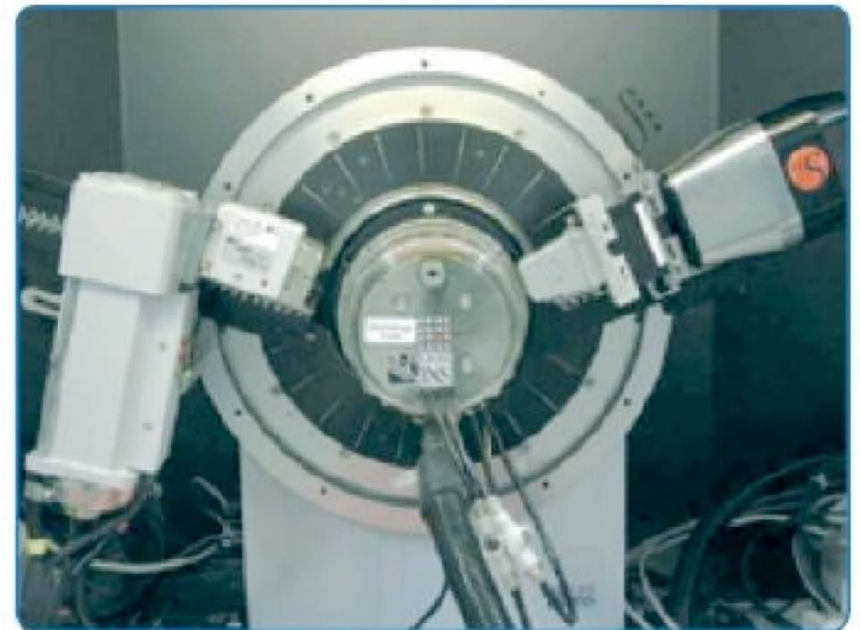
Jennifer Jackson

Outline

- Target material
 - Cu, Mo Ag (increase in incident energy from Cu to Ag)
- Determining the unit cell volume
 - Diffraction determines atomic spacing for a regularly spaced lattice
 - Structural information: clear mineral ID
 - Lattice parameters
 - Volume
 - Density (if chemistry is known)
- Phase proportions
 - Using relative intensities
- Peak Widths
 - Adsorbed materials
 - disorder
 - Strain analysis
- Structural Phase transitions
 - Identify polymorphs with certainty
 - In-situ monitoring of phase transitions
 - Kinetics of reactions & phase transitions
- Synchrotron x-ray diffraction
 - Very small samples (micro- to nano-grams of sample); in-house XRPD instruments require mgrams
 - Excellent tool for high-pressure studies and structures fo nano-phases
- Other x-ray diffraction methods
 - Small angle x-ray scattering
 - Single-crystal x-ray diffraction

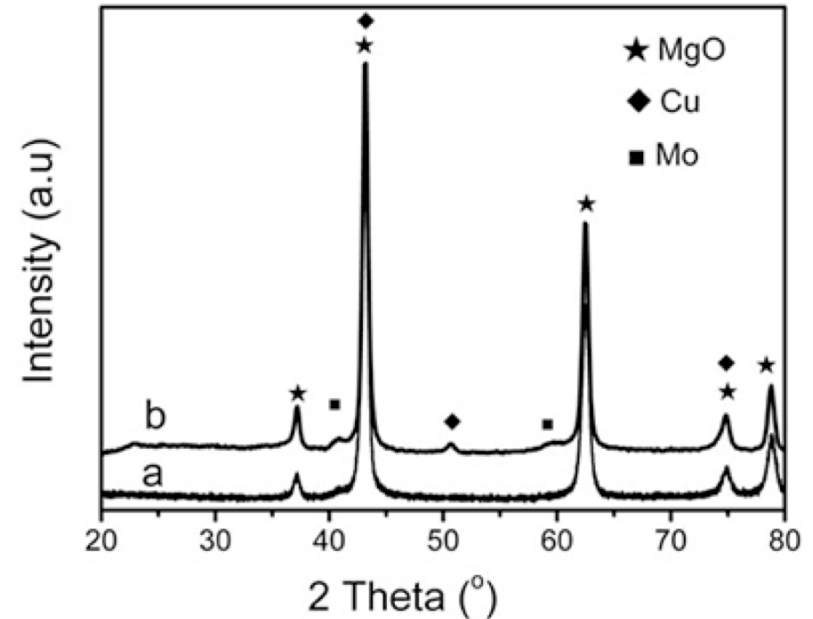
Target material

- Copper target
- Ni filter
- Cu $K\alpha_1$, $\lambda = 1.54056 \text{ \AA}$
- Cu $K\alpha_2$, $\lambda = 1.54439 \text{ \AA}$
- Bragg's law:
$$n\lambda = 2d\sin\theta$$



Determining volume

- cubic:
 $d^2 = a^2(h^2+k^2+l^2)$
- Important to fit all the peaks using weighted fits
 - Increased resolution at higher angles
- e.g., Celref: Fits peak positions, assuming space group & atomic positions
- If chemistry is known, one can accurately determine the density

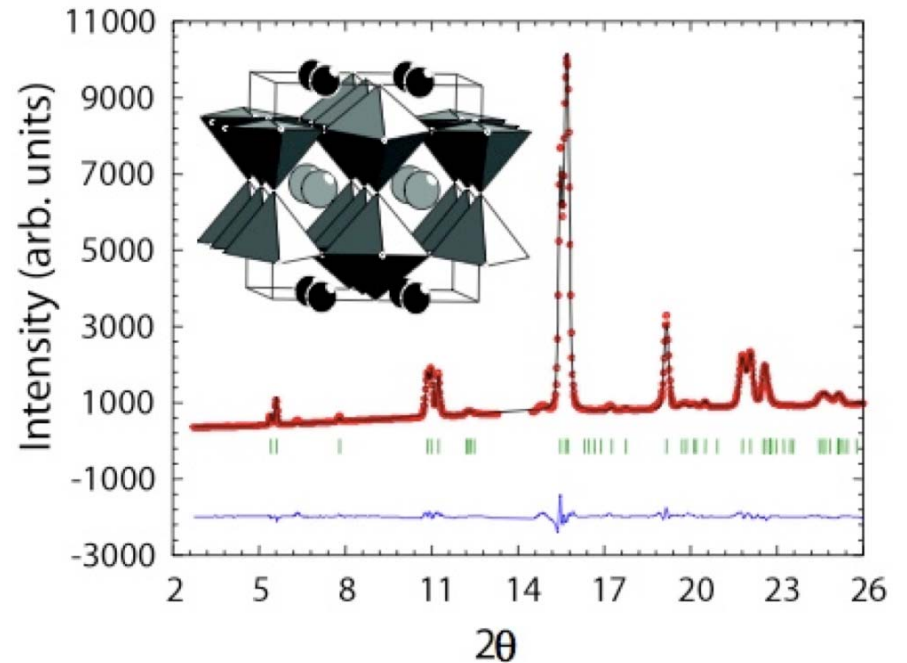


Determining structure & volume

- Rietveld approach to powder XRD
 - Refines *atomic positions*
 - It can *solve* the structure if quality of powder pattern is high

- e.g., GSAS

General Structure Analysis System



TbBaCo₂O_{5.48}

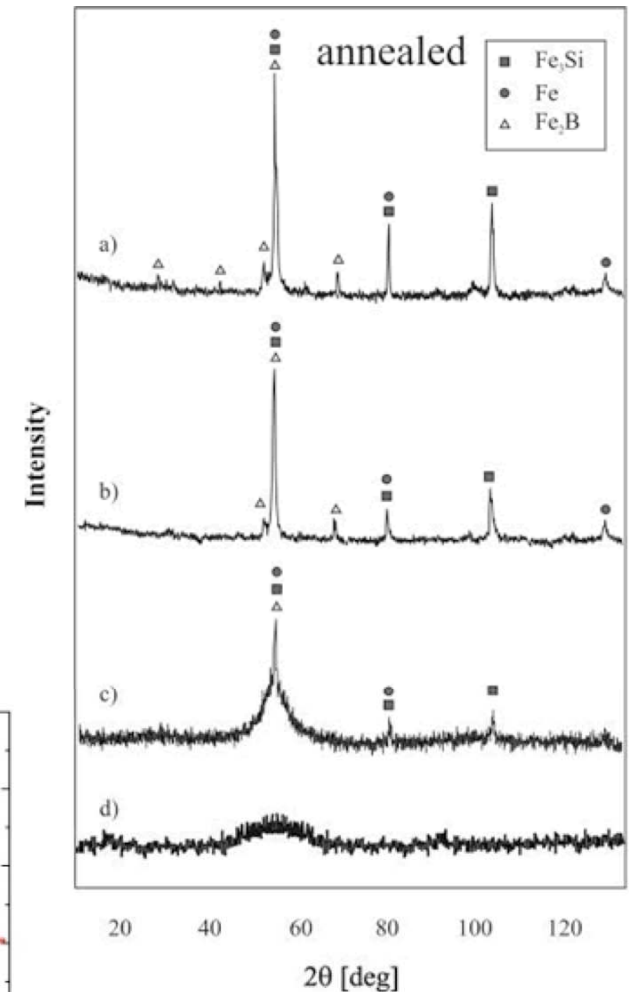
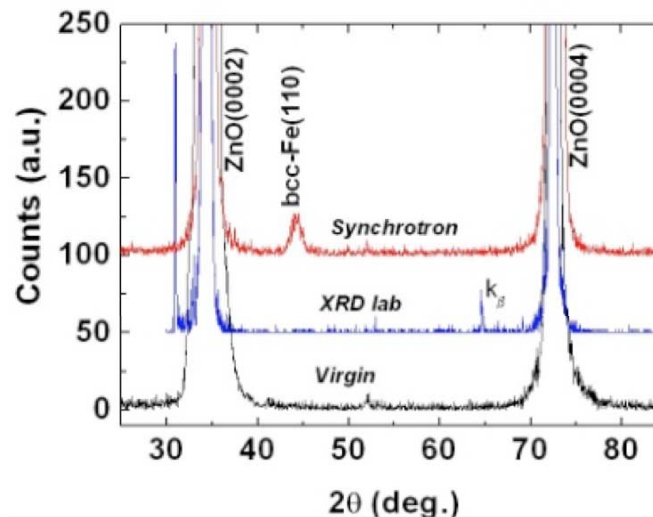
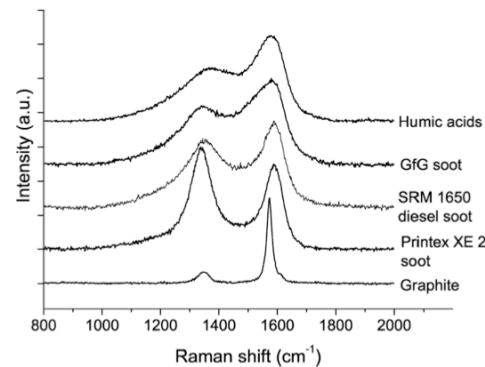
Origin of peak widths

Instrument

- Source wavelength
- Detector resolution

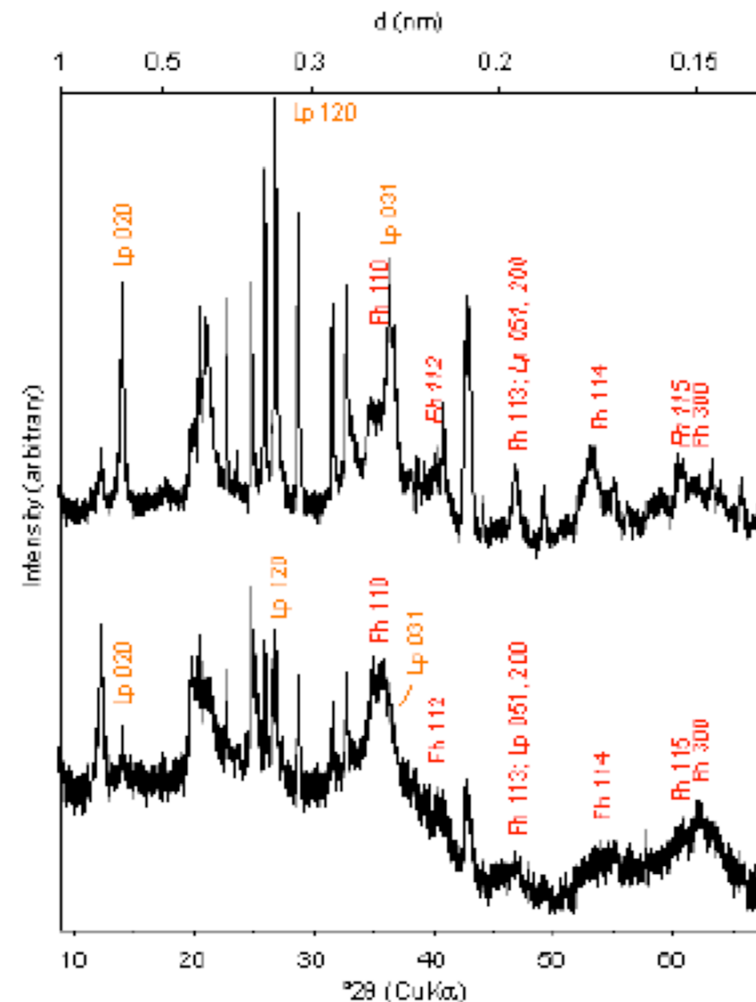
Sample

- Adsorption:
 - OH, organics
- Disorder
 - Mg-Fe, Ca-Na
- Strain
 - Tempered steel
- Grain size
 - If grain size is $\sim\lambda$, get broadening
- Temperature
 - Debye-waller factor
 - Thermal ellipsoids
 - Exists at 300 K



Mixed phases: determining proportion

- Environmental sciences
- Quantity and type of clay is important
- Acid mine drainage areas
- Requires an analysis of relative intensities
 - Watch out for preferred orientation



Two iron oxide coatings on lignite from Sokolov showing different relative proportions of kaolinite (not marked), ferrihydrite and lepidocrocite.

Synthesizing mineral-analogues

- Gas-mixing furnace
- Piston-cylinder
- Multi-anvil
- MgSiO_3 polymorphs
 - Enstatite, Ilmenite, majorite?
- Mg_2SiO_4 polymorphs
 - Olivine, wadsleyite, ringwoodite?



Gas-mixing furnaces



Piston cylinder

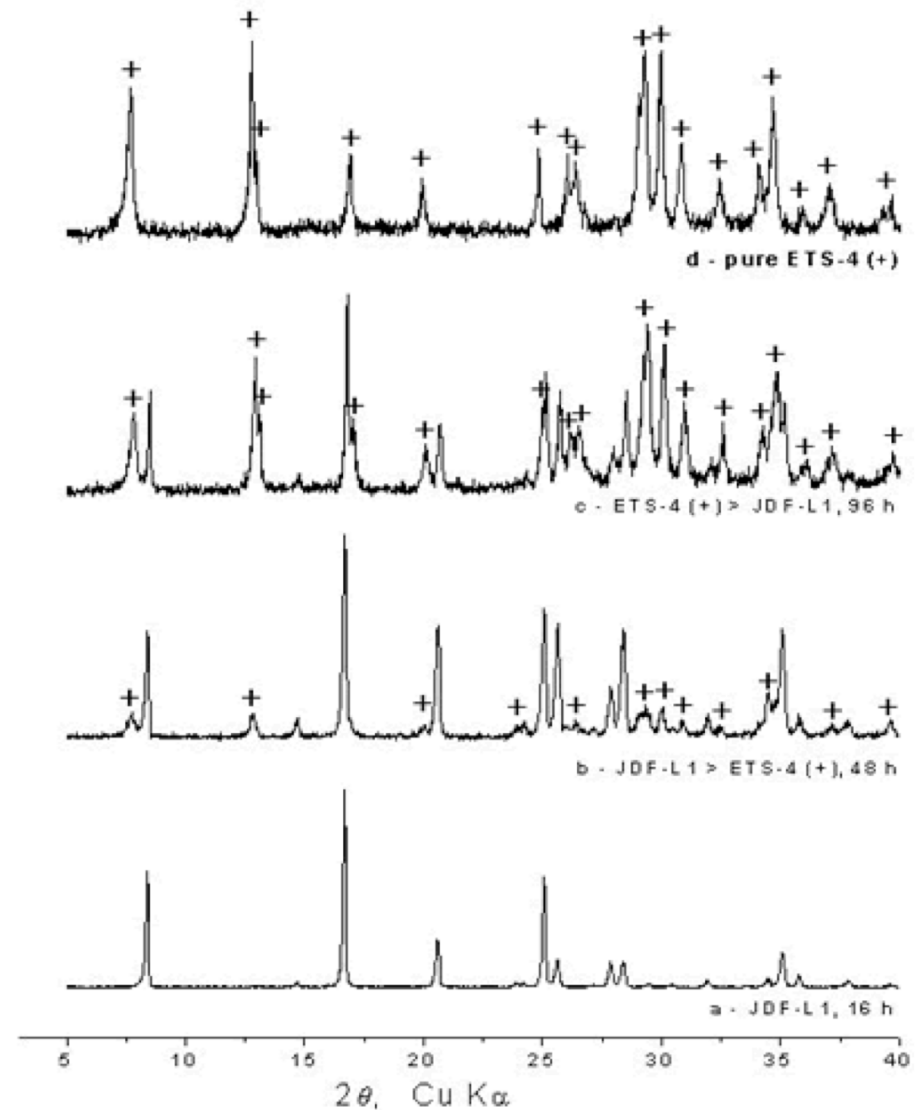


Multi-anvil



Determining phase transitions

- See evolution of diffraction peaks as a function of temperature, time, pressure, hydration, etc.
- Example: hydrothermal studies on titanosilicates:
 $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22} \cdot 4\text{H}_2\text{O}$ to
 $\text{Na}_9\text{Si}_{12}\text{Ti}_5\text{O}_{38}(\text{OH}) \cdot 12\text{H}_2\text{O}$

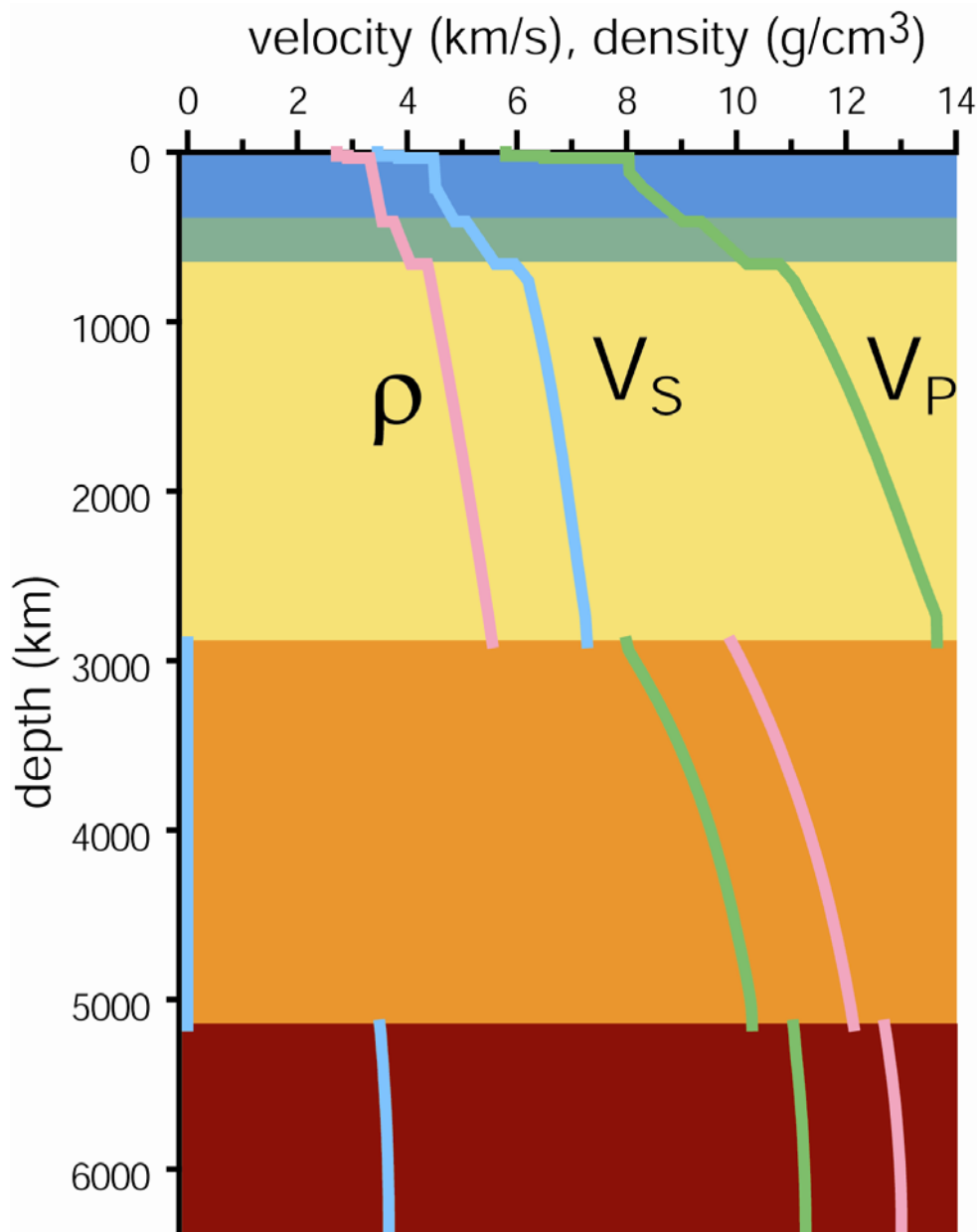


Synchrotron x-radiation



**Advanced Photon Source (APS)
Argonne National Laboratory, Chicago, IL**

Determining the density of minerals in the interior of Earth



*Preliminary Reference
Earth Model (PREM)*

*Measure candidate minerals
At high-PT conditions:*

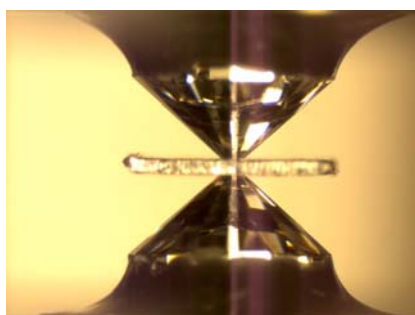
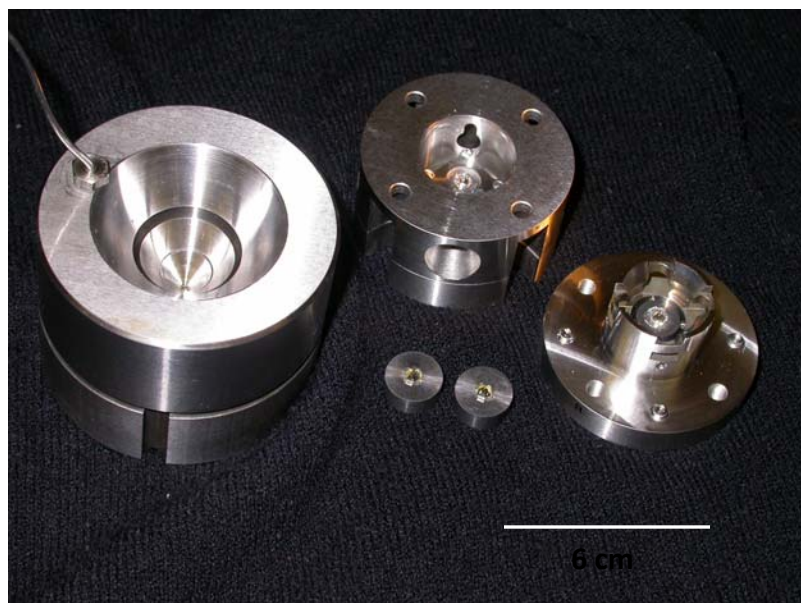
V_p

V_s

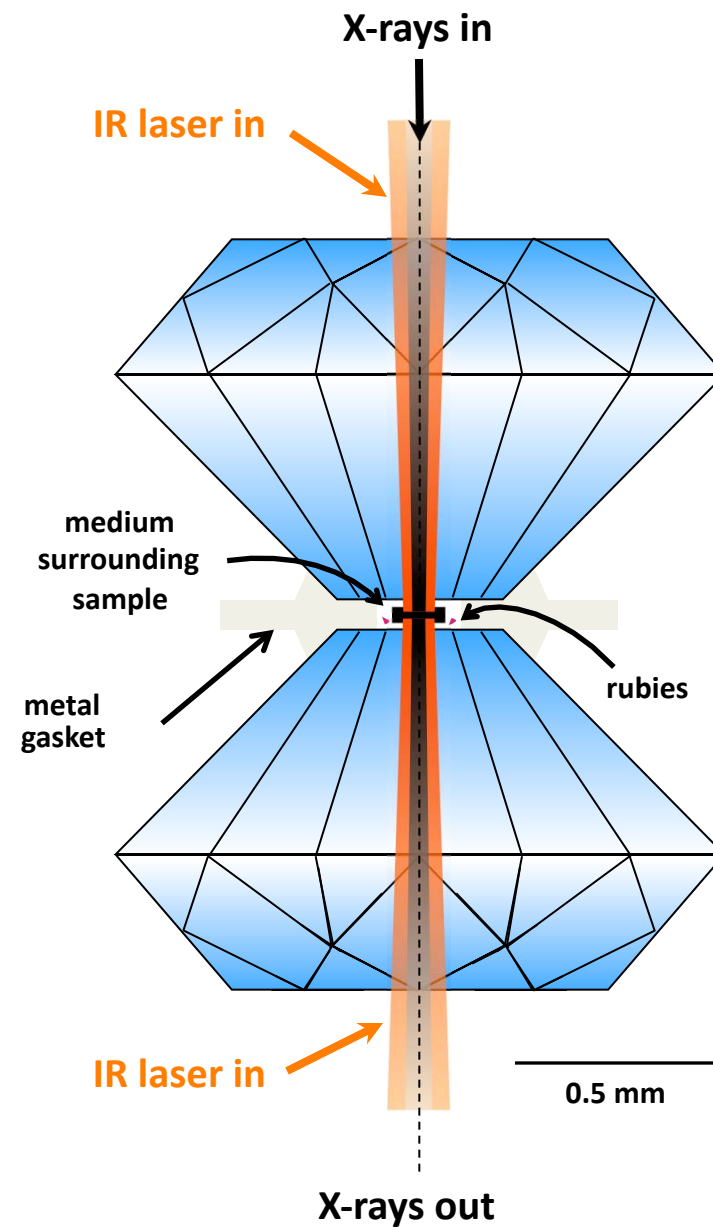
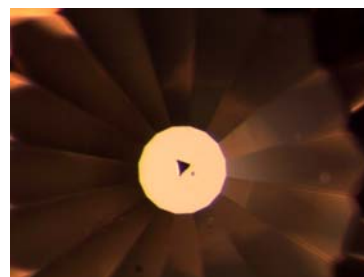
Density (XRD + chemical info)

(Dziewonski & Anderson 1981)

The diamond anvil cell

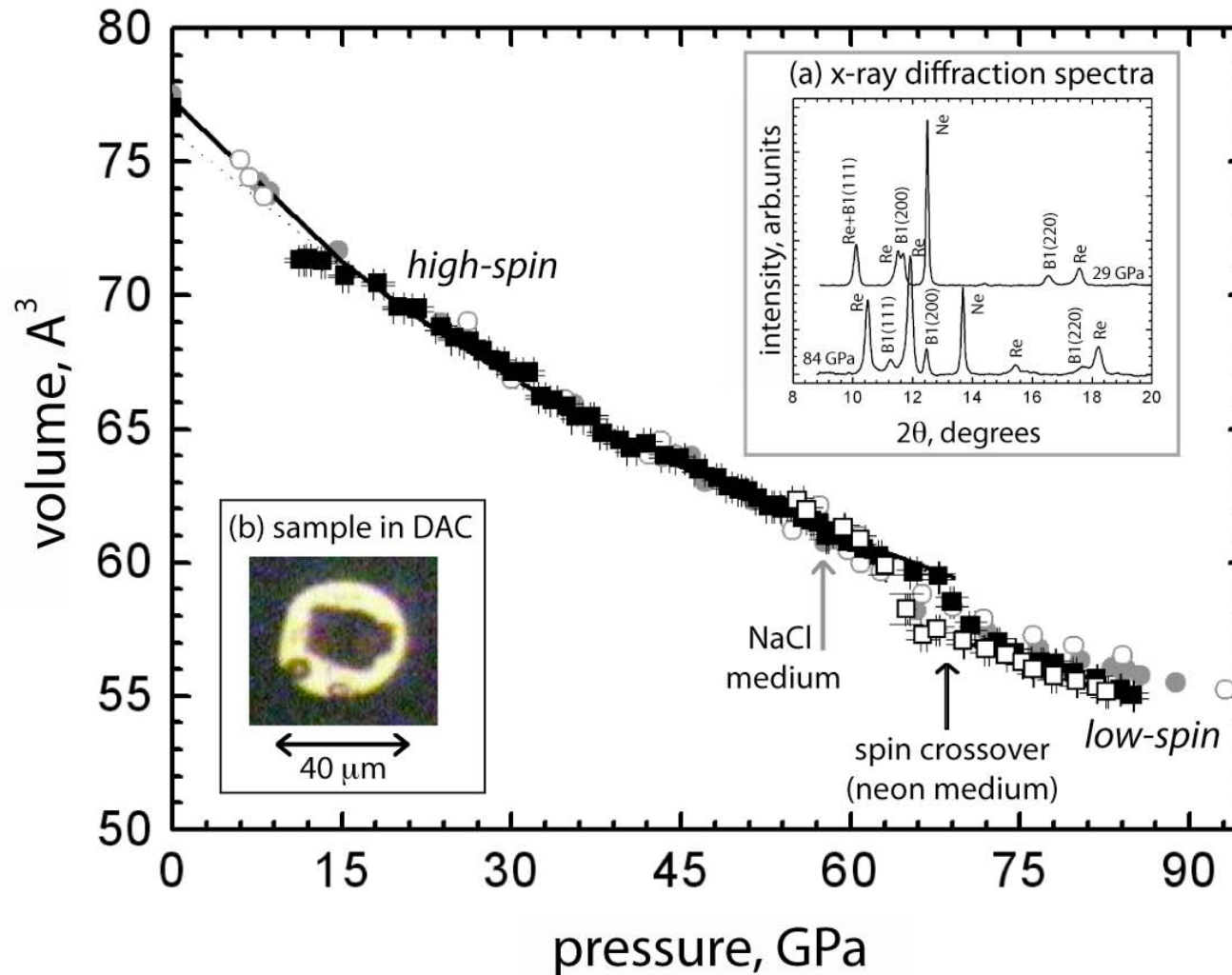


Diamond-anvil-cell laboratory,
Caltech



Volume (density) change of $(\text{Mg}_{0.61}\text{Fe}_{0.39})\text{O}$ through the spin crossover

Experiments conducted at The Advanced Light Source, Berkeley, CA



Zhuravlev, Jackson, Wolf, Wicks, Yan, Clark (2009)
Phys. Chem. Min.

Other X-ray Diffraction Methods

- Small angle x-ray scattering
 - Structural deviations
 - Local scale
- Single-crystal x-ray diffraction
 - Can be done in-house or at the synchrotron
 - Solves for atomic positions
 - Solves structure
 - Structures of minerals
 - Protein crystallography

Specific information from x-ray diffraction

- Atomic spacing
 - Structural information: clear mineral ID
 - Lattice parameters
 - Volume
 - Density (if chemistry is known)
- Phase proportions
 - Using relative intensities
- Strain analysis
 - Using the peak widths
- Structural Phase transitions
 - Identify polymorphs with certainty
 - In-situ monitoring of phase transitions
 - kinetics