

High pressure crystallography for the future

Dr. Przemyslaw Dera
*Hawaii Institute of Geophysics and
Planetology*

ChemMatCARS Workshop,
December 14, 2019, Argonne, IL

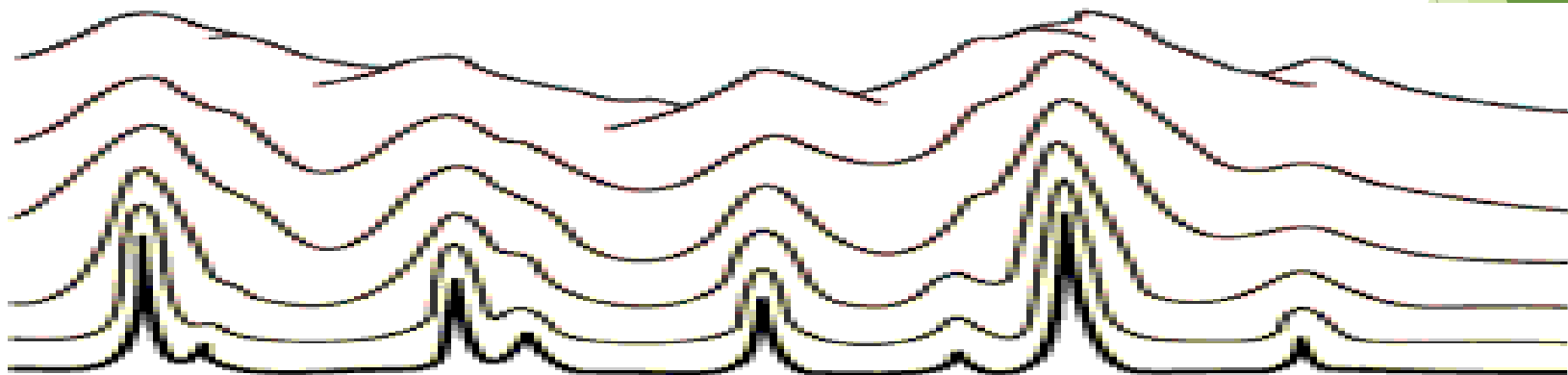


Physical and Chemical phenomena

- Elastic deformation
- Plastic deformation
 - Structural phase transitions
 - Reconstructive
 - Displacive
 - Order-disorder
- Electronic transitions
 - Metal-insulator
 - High-spin low-spin
- Magnetic transitions
- Melting
- Amorphisation
- Chemical transformations
- Continuous changes in the physical properties at high pT

Geological processes

- Earthquakes
- Plate tectonics and subduction
- Geodynamo and core convection
- Planet formation and accretion
- Impact metamorphism
- Volcanism



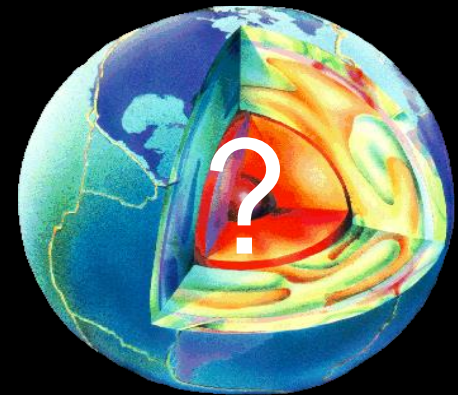
Knowledge of the crystal structure and physical properties of Earth forming minerals at varying pT conditions is essential for reliable and realistic modeling of geophysical phenomena and environments

Earth is a complex and dynamic system.

Major geologic events have significant effect on the human civilization.

Human activity can significantly affect the stability of the Earth system in the long run.

Understanding of the structure, composition and properties of the Earth interior offers us a better chance to live in harmony with our planet (e.g. geo-hazards, mineral resources, etc.).



99% of the Earth interior is inaccessible for direct observations

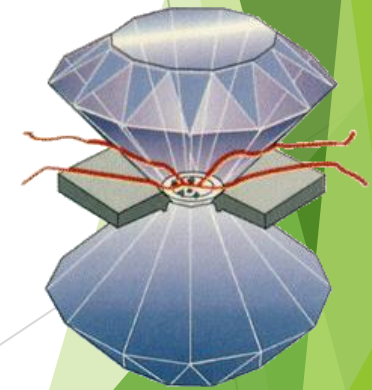
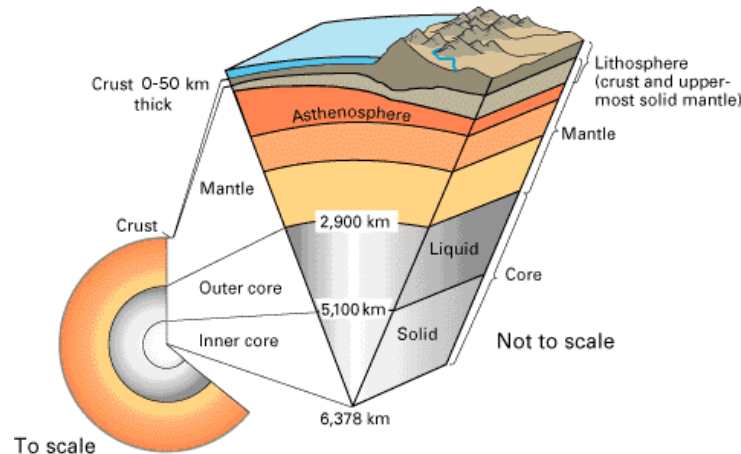


In 1960s at the north Kola peninsula Russian geologists drilled for more than 15 years to reach a crust depth of 11 km, a record that has not yet been broken.



Virgil drilling vehicle capable of reaching depth of Earth's core from science fiction movie "The core"

Integrated Ocean Drilling Program: A new \$1 billion mission to drill 6 km (3.7 miles) beneath the Pacific seafloor to reach the Earth's mantle – a 3000 km-thick layer of slowly deforming rock between the crust and the core which makes up the majority of our planet - and bring back the first ever fresh samples.

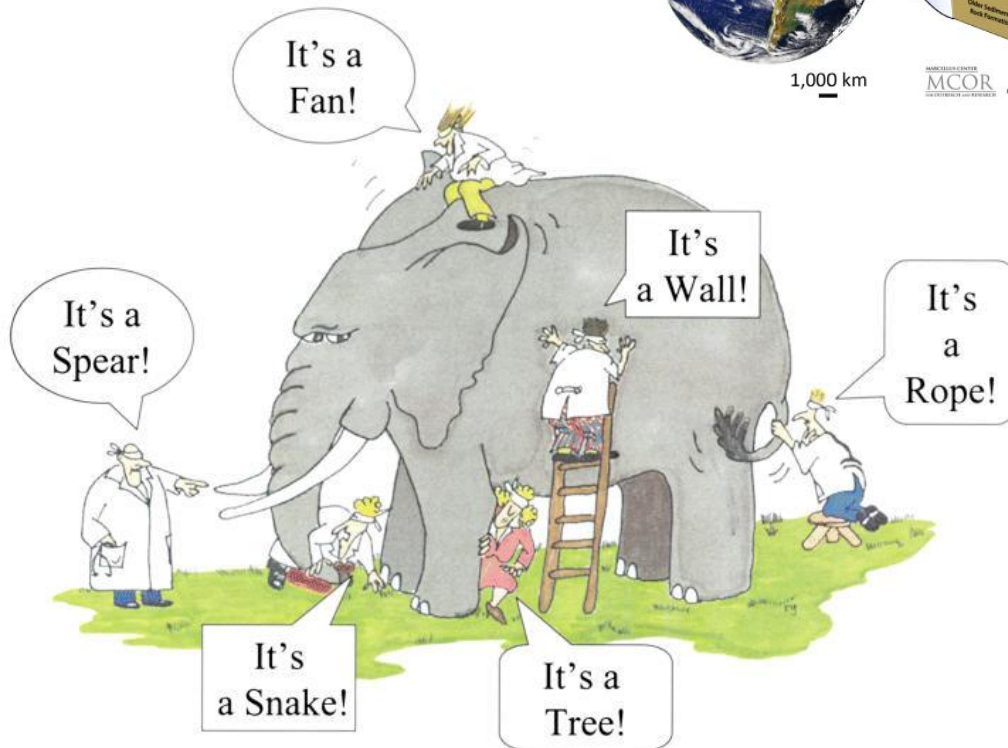
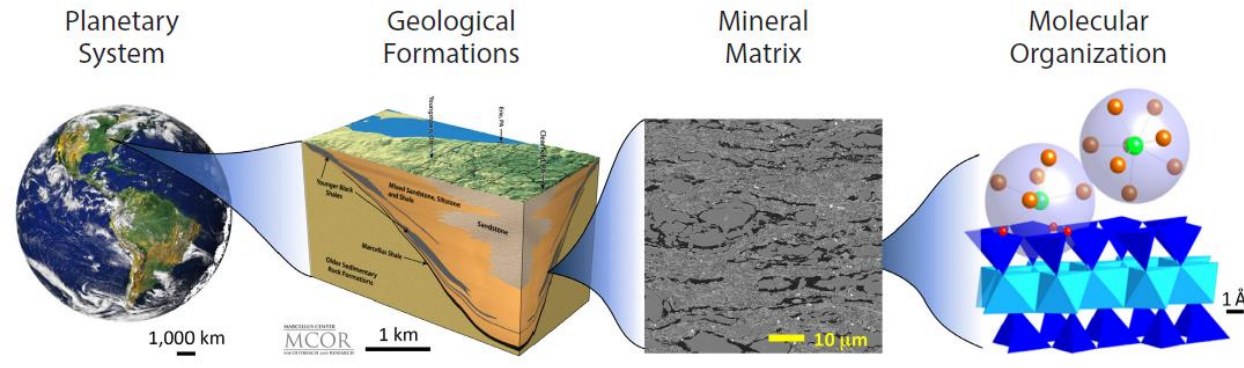


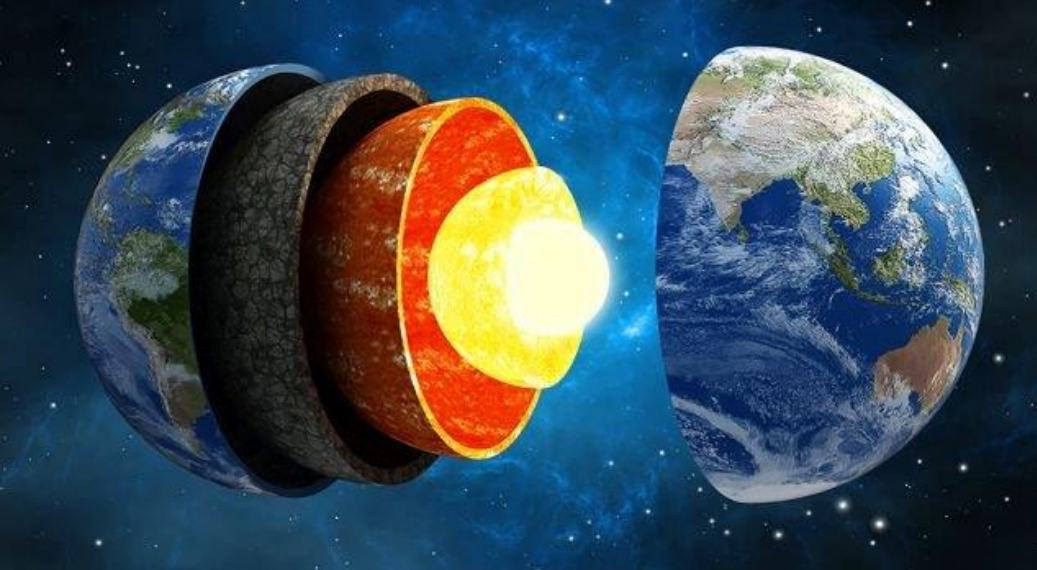
Diamond anvil cell, a miniature device developed in 1960s allows to simulate in a laboratory conditions present in the Earth lower mantle and core.

Earth interior

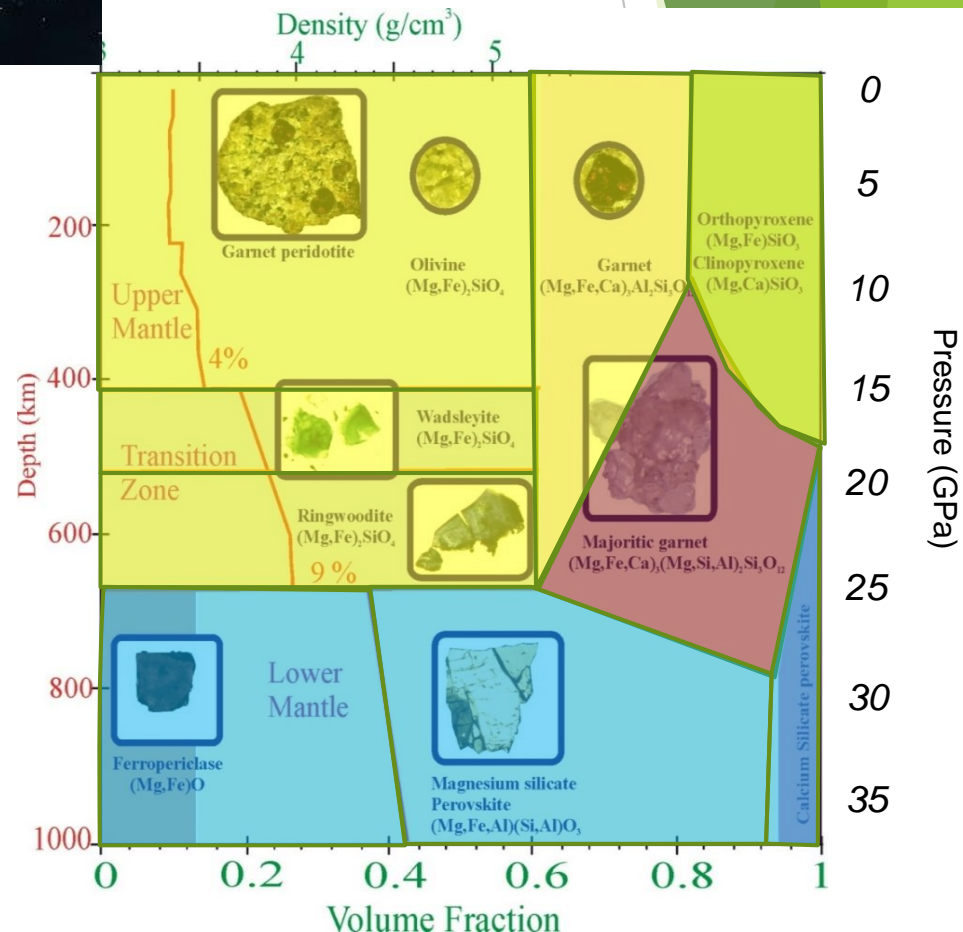
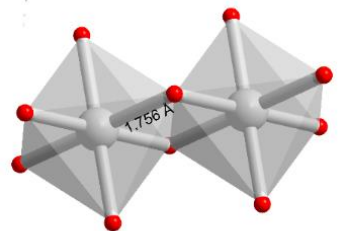
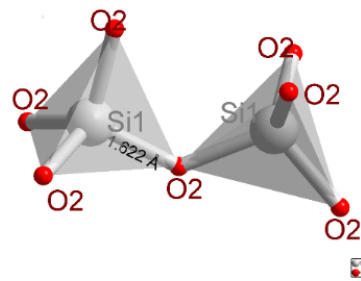
Main information about conditions and properties of constituent materials of the Earth interior is indirect, derived from:

- ▶ analysis of material accessible on the surface, including excavated mantle rocks (xenoliths, ophiolites)
- ▶ seismic observations
- ▶ study of meteorites
- ▶ Mineral physics research





Crystal chemistry of Si in the mantle



Penta-Si in chemistry

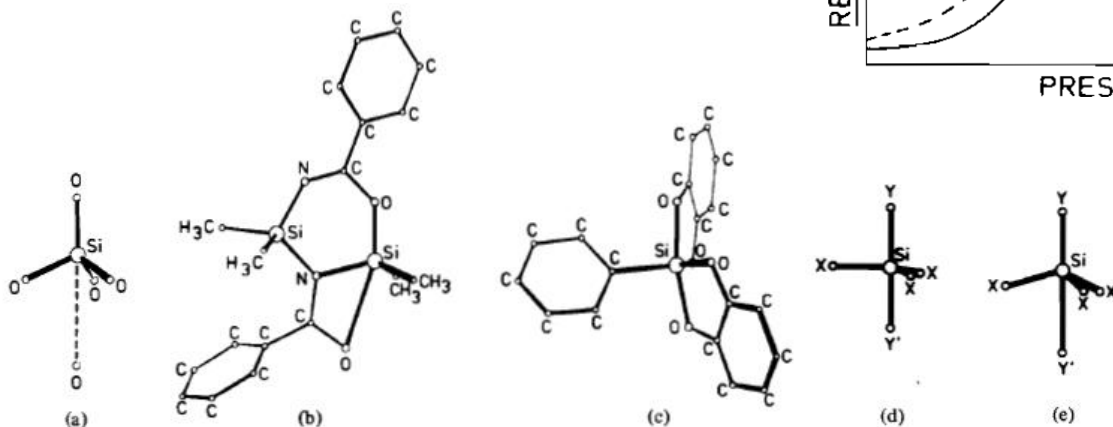
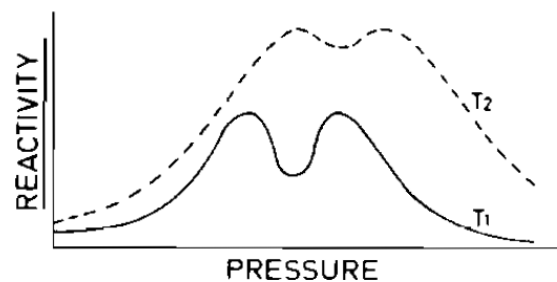
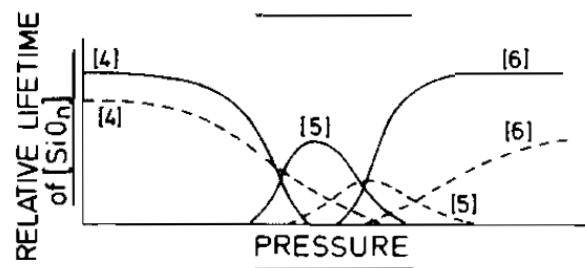
Inorganica Chimica Acta, 89 (1984) 1-7

Pentacoordinate Silicon Intermediate States During Silicate Condensation and Decondensation. Crystallographic Support

F. LIEBAU

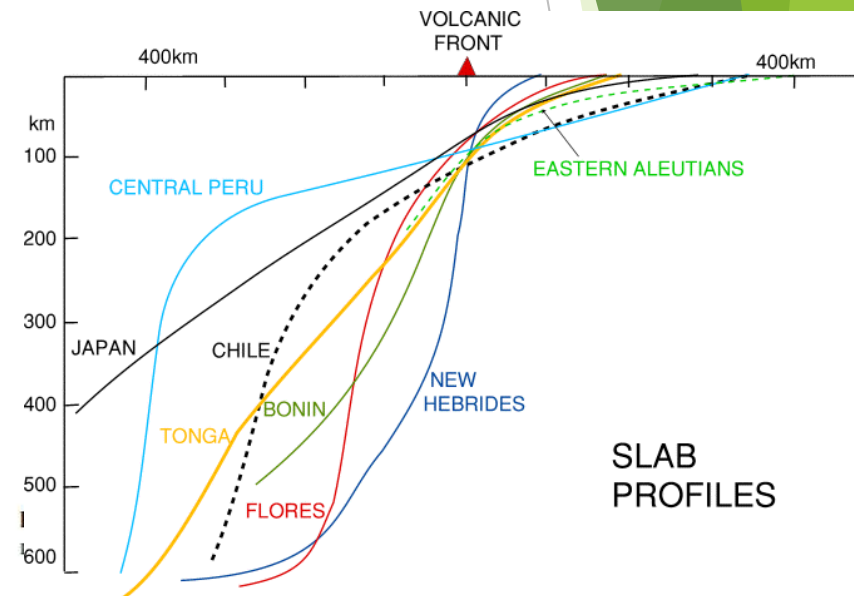
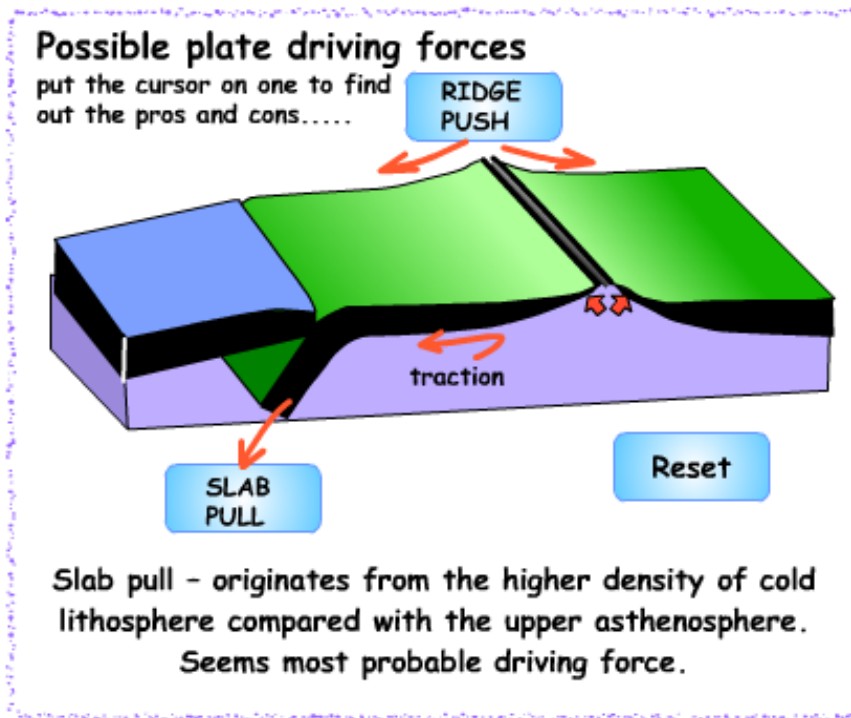
Mineralogisches Institut der Universität, 2300 Kiel, FRG

Received December 20, 1983



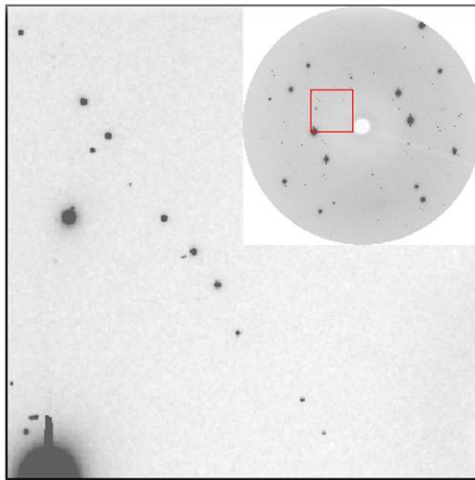
Penta-Si needs cold(er) conditions

- Subduction zones are regions where cool oceanic plates sink back into the mantle beneath warmer, continental plates.
- The "slab-pull" force which derives from the negative buoyancy of the heavy, cold slab in the surrounding warm and less dense mantle, is thought to play important role in controlling plate tectonics.
- Depending on the age of the oceanic plate, the geometry (e.g. dip angle), subduction rate, as well as thermal structure of the subduction zones vary significantly.
- Some subducted slabs are believed to penetrate to the lower mantle, whereas others stagnate around transition zone.



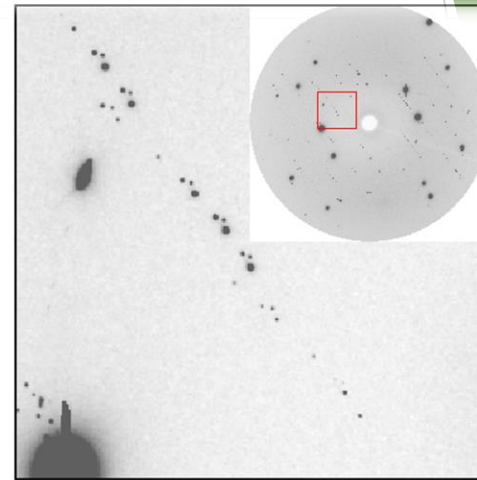
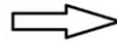
<http://www.le.ac.uk/gl/art/gl209/lecture5/lecture5.html>

SXD experiment

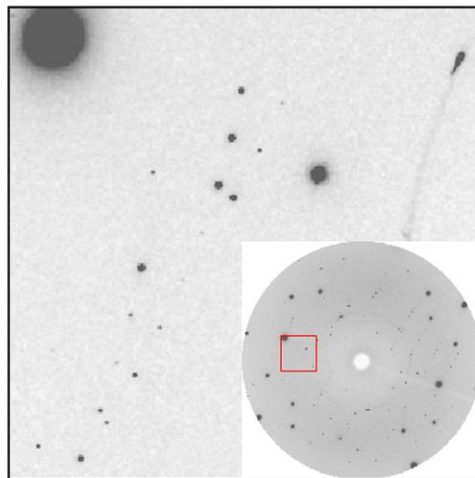


OEN (Pbca) 12.66 GPa

pre-transition
plane (0 1 -1)

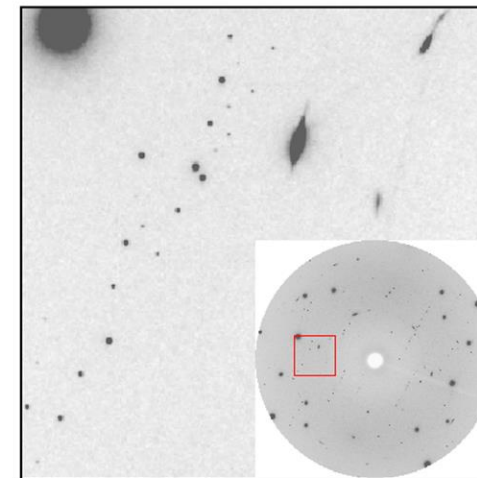
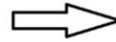


HPCEN2 (P2₁/c) 14.26 GPa



OEN (Pbca) 11.54 GPa

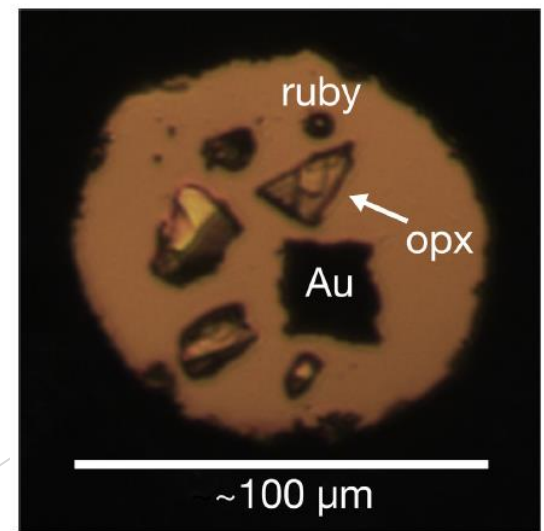
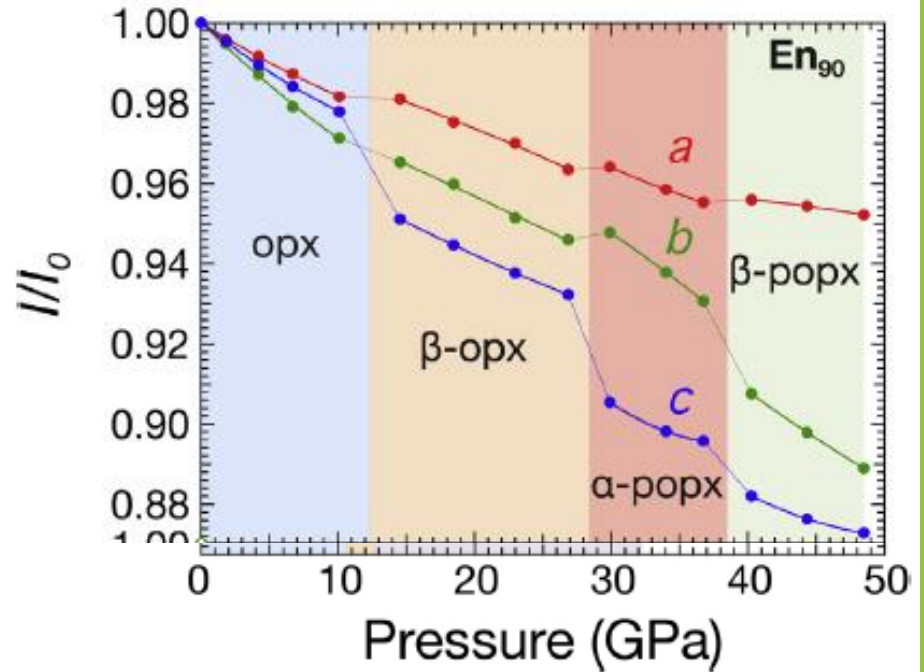
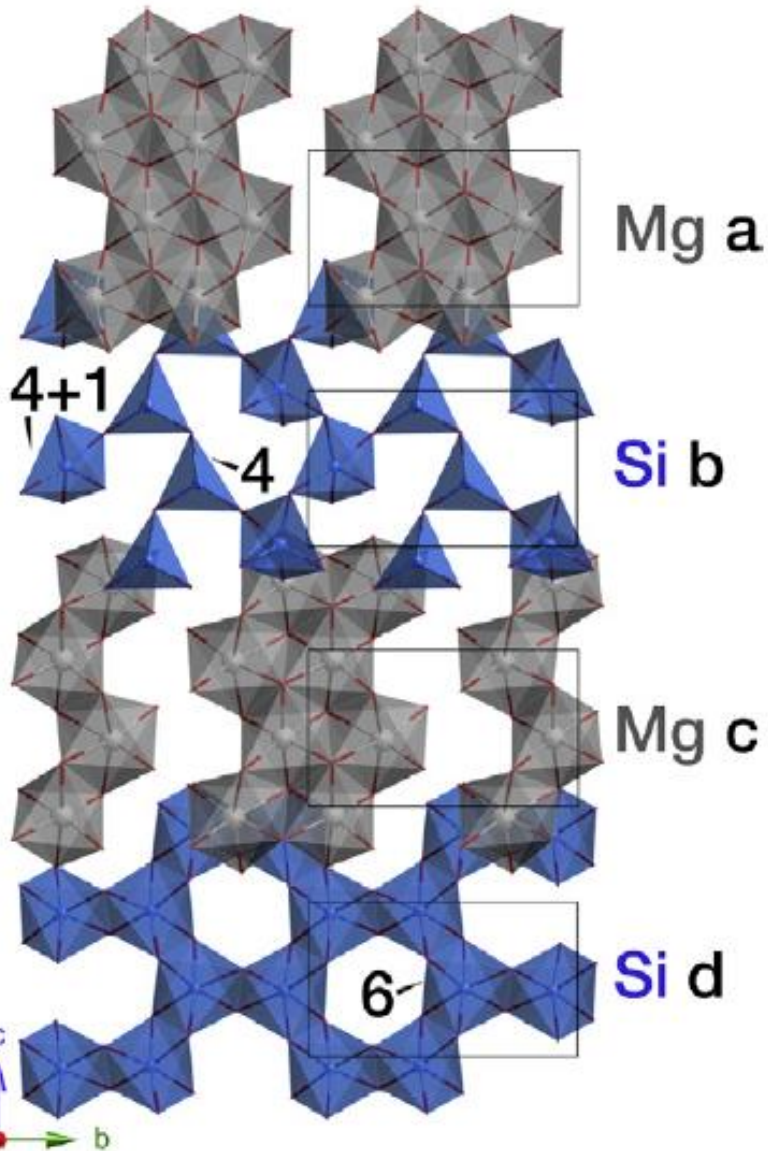
pre-transition
plane (5 -2 2)



HPCEN2 (P2₁/c) 14.53 GPa

More displacive transitions

Finkelstein, Dera et al. 2015



Materials chemistry at high pressure and temperature

Discovery of the recoverable high-pressure iron oxide Fe_4O_5

Barbara Lavina^{a,b,1}, Przemyslaw Dera^c, Eunja Kim^b, Yue Meng^d, Robert T. Downs^e, Philippe F. Weck^f, Stephen R. Sutton^c, and Yusheng Zhao^{a,b}

Known iron oxides:

FeO - wustite

Fe_2O_3 - hematite

Fe_3O_4 – magnetite

Fe_2O_3 - maghemite

- Heating of Fe-O mixture from Fe_2O_3 to Fe_4O_5 composition at pressures between 8 and 20 GPa to temperatures above 2000 K induces formation of iron oxide with new stoichiometry – Fe_4O_5
- Fe_4O_5 also forms by thermal decomposition of Fe-carbonate at similar conditions
- The structure of the new oxide is a derivative of post-spinel structure (CaFe_2O_4)
- The new phase is quenchable and has unique magnetic properties.

Lavina, Dera et al. PNAS 2011

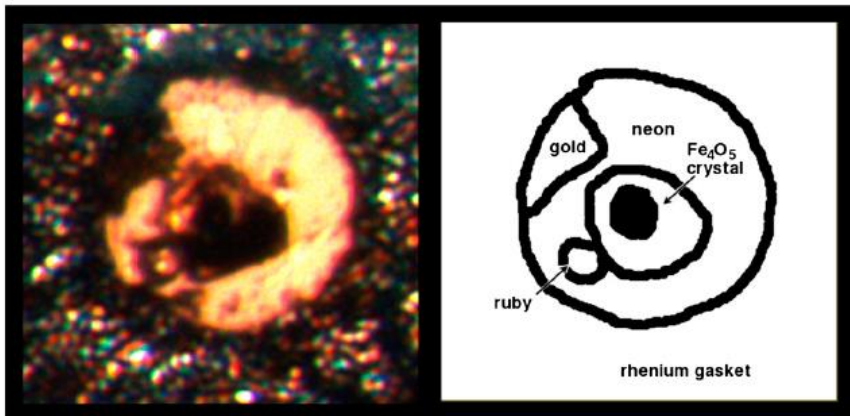


Fig. 1. The single crystal of Fe_4O_5 synthesized in the diamond anvil cell at high pressure after laser heating. The sample chamber, about 60 μm in diameter, viewed through a diamond anvil at 10 GPa and its sketch show the rounded opaque crystal of Fe_4O_5 grown in the heated area. The sample is well separated from the gasket, ruby, and the anvils by the inert neon medium.

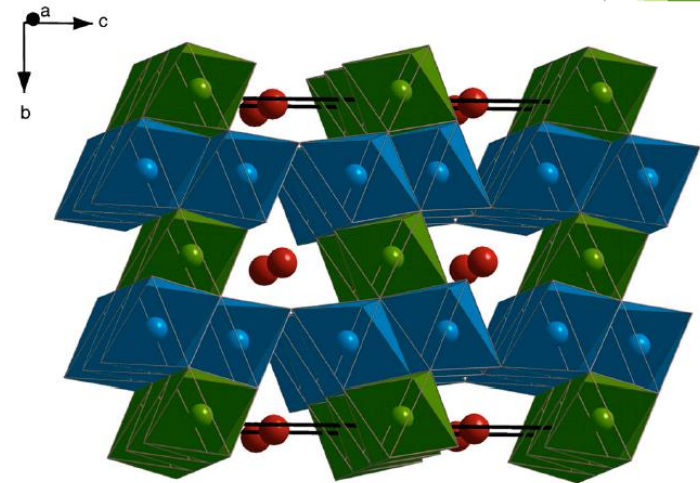


Fig. 2. Structure of Fe_4O_5 . Green and blue octahedra (sites Fe1 and Fe2, respectively) illustrate nonequivalent edge-sharing FeO_6 groups forming layers perpendicular to the c axis. Layers are alternated by channels where iron, represented as red spheres (Site Fe3), is arranged in larger triangular prisms sharing faces along the direction of the a axis.

FACEBOOK DIGG STUMBLEUPON REDDIT PRINT

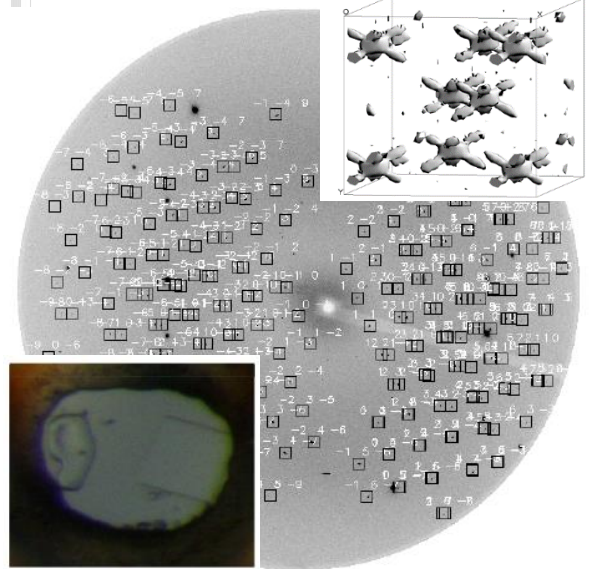
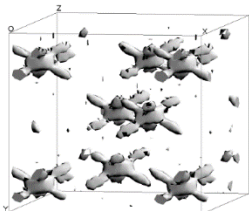
High-Pressure Diamond Anvil Creates a New Solid from Xenon and Hydrogen

The useful noble gas may provide a breakthrough way to store hydrogen for fuel
 By Jeremy Hsu Posted 11.23.2009 at 6:14 pm 13 Comments



Hydrogen Storage: Store me some hydrogen Nature Chemistry/H-Racer

Science under pressure can produce marvelous results, such as an entirely new way to store hydrogen fuel. Researchers combined the noble gas xenon with molecular hydrogen (H₂) to make a never-before-seen solid that opens the doors to an entire new family of materials for hydrogen storage.



• Unlike each of the components (which form simple close packed solids), mixture of H₂ and Xe pressurized above 4.8 GPa was found to form a complex Van der Waals solid with Xe(H₂)₇ featuring weak Xe..Xe bonding interactions.



• Xe acts as “molecular glue” and provides remarkable stability to the new solid (stable to at least 250 GPa)

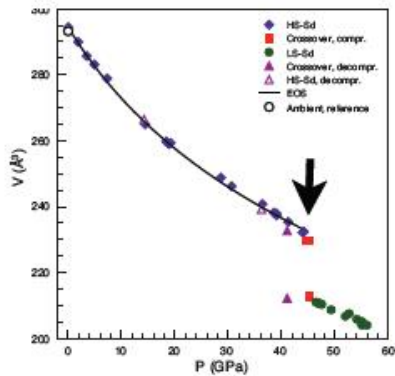
• The Xe(H₂) solid is pressure quenchable at LN₂ temperatures

Somayazulu, Dera et al. Nature Chemistry 2009

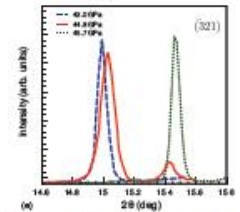
Spin crossover

Lavina, Dera et al. Phys. Rev. B (2010)

10% shrinkage at 44 GPa

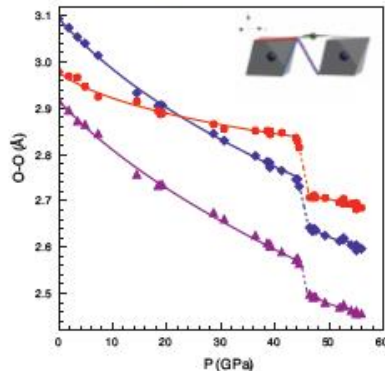


raise of absorption bands in the visible range



splitting of diffraction peaks: formation of high and low spins domains

anisotropic octahedral compression



We have provided the first evidence of the lack of an intermediate spin state or a random spin distribution in a pressure-induced spin transition.

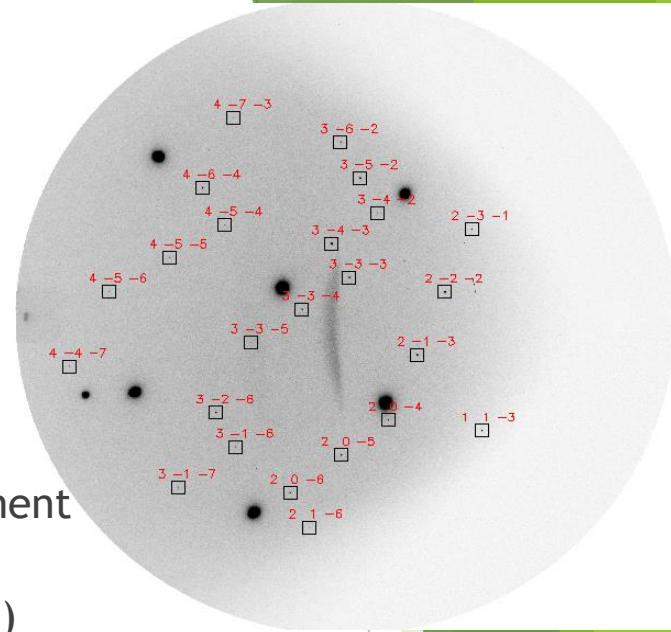
Iron rich minerals with regular octahedral Fe²⁺ coordinations are likely to show sharp transitions in the Earth's mantle.

Graphics modified from refs. 5, 6

High-pressure crystallography: experimental challenges

Experimental challenges:

- ▶ Very small sample (<0.050mm)
- ▶ Angular access restricted (low completeness)
- ▶ Absorption limits the incident energy to >15 keV
- ▶ Absorption and extinction affect intensity measurement
- ▶ High background (scattering)
- ▶ Poor sample quality (strain, multi-grain assemblages)



High-pressure “mind-set” on crystallography 5 years ago:

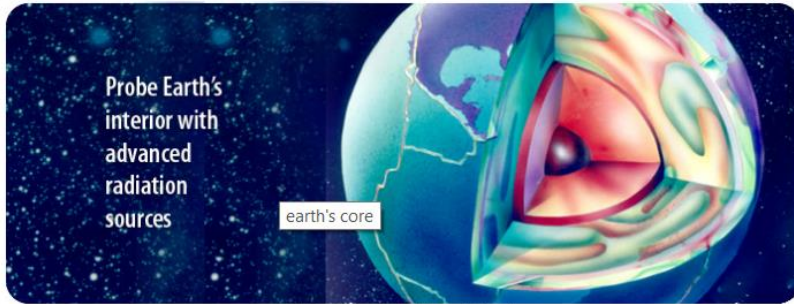
- ▶ 99% of experiments above 10 GPa are performed at synchrotrons
- ▶ Dominating tool (90% studies) is powder diffraction. It is sufficient for simple solids, but usually fails for more complex/interesting cases.

High-pressure “mind-set” on crystallography today:

- ▶ 90% of experiments above 10 GPa are performed at synchrotrons
- ▶ >20 single crystal HP XRD papers from PX² per year

High-pressure “mind-set” on crystallography tomorrow:

- ▶ Electron density modeling
- ▶ Defect modeling
- ▶ Time-resolved phenomena
- ▶ Multigrain experiment



Original Drawing Created by Keelin Murphy

2015 ANNUAL MEETING

2015 ANNUAL MEETING
July 6-9, 2015
[Cheyenne Mountain Resort](#)
Colorado Springs, CO

Registration Info Soon!

PRESIDENT SEARCH

COMPRES SEEKS PRESIDENT

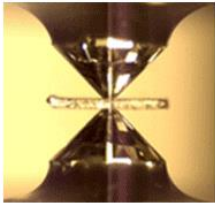
The President works with the elected committees, the community, and administrative support to advance the goals of COMPRES.

[Official Search Announcement](#)

LECTURE SERIES

COMPRES DISTINGUISHED

COMPRES Facilities



[Nslf Synchrotron Light Source \(NSLS\) - Diamond Anvil Cell \(X-ray\)](#)

[NSLS - Multi-anvil \(X-ray\)](#)

[NSLS - Diamond Anvil Cell \(Infrared\)](#)

[Advanced Light Source \(ALS\) - Diamond Anvil Cell \(X-ray\)](#)

Home

Welcome

COMPRES, the Consortium for Materials Properties Research in Earth Sciences is a community-based consortium whose goal is to enable Earth Science researchers to conduct the next generation of high-pressure science on world-class equipment and facilities. It facilitates the operation of beam lines, the development of new technologies for high pressure research, and advocates for science and educational programs to the various funding agencies.



High Pressure Science at NSLS-II

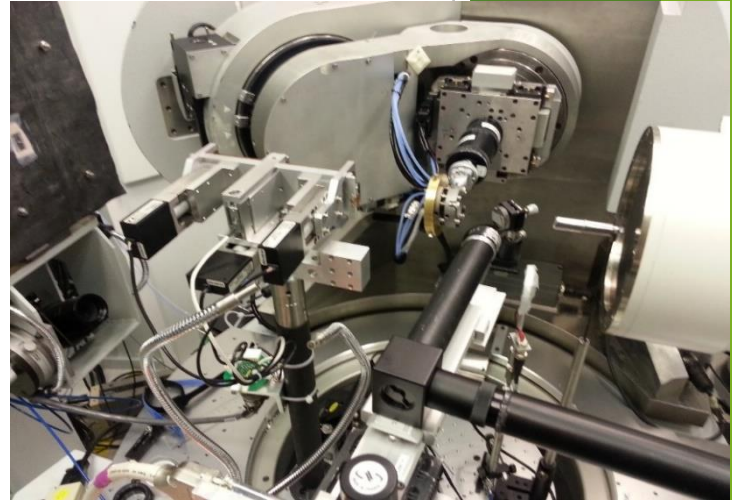
NSLS-II ANNOUNCES SUCCESSFUL BEAMLINE DEVELOPMENT PROPOSALS

3 COMPRES - Affiliated Proposals Awarded Type I Status for Beamline Development

What is COMPRES?

- NSF-funded consortium since 2001
- Institutional membership (>60 member institution in USA). Requires a faculty representative/elector.
- Annual meetings every year (in 2020 Palisades Resort, NJ, July 7-10). Rich student-focused program, including job-search workshops, breakout sessions, etc. Student travel grants are available.
- Operates several national facilities (synchrotron beamlines) for mineral physics research.
- Outreach program includes on line course Mineral Physics 101 and Distinguished Lecture Series.

PX² - Partnership for eXtreme Xtallography (APS 13BM-C)

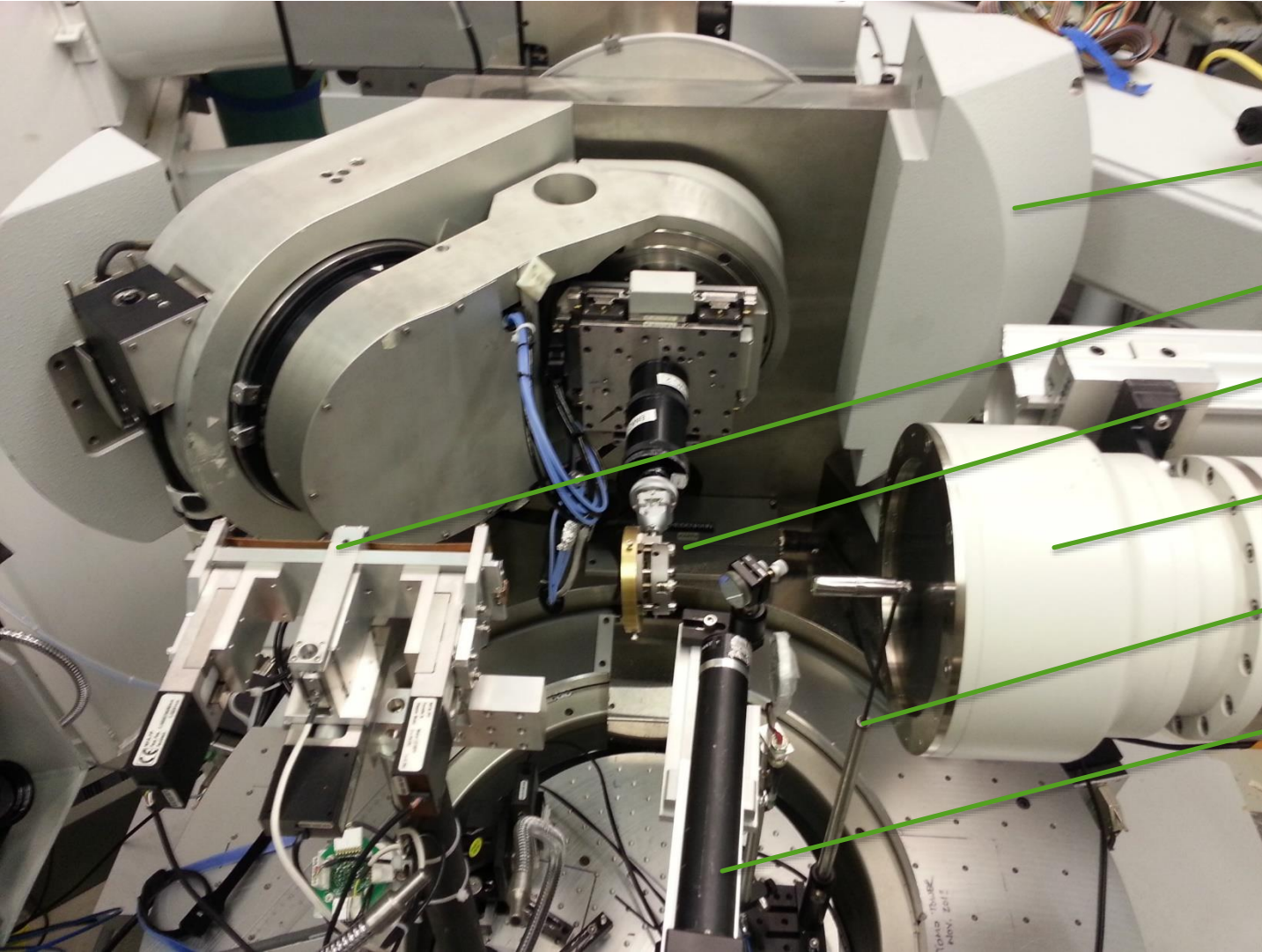


Key characteristics:

- X-ray beam: Bending magnet source, 30 keV fixed energy, 15x15 micrometers focal spot size
- Goniometer: Unique six-circle diffractometer
- high rotation speed (up to 15deg/sec),
 - high precision of rotation
 - less than 10 micrometers sphere of confusion)
 - high load capacity (up to 25 lb)
- Detector: Mar165 CCD
Pilatus 100K
Pilatus 1M (1mm Si)
- Laser optics: Online Raman spectroscopy
Unique laser heating system for SXD (200W NIR fiber laser)

Project milestones

- ▶ COMPRES funding starts Jun 2014
- ▶ Si-311 monochromator crystal: Sep 2014
- ▶ Small K-B mirror, manual camera stage: Jan 2015
- ▶ First GUP user: Feb 2015
- ▶ Motorized zoom stage: Jun 2015
- ▶ Big K-B mirror with enclosure: Sep 2015
- ▶ Resistive heating, membrane pressure control: Oct 2015
- ▶ 532 nm laser, spectrometer, ruby fluorescence: Jan 2016
- ▶ First user paper: Jun 2016
- ▶ Remote experiments: Oct 2016
- ▶ Laser interlock approved: Jan 2017
- ▶ 200 W IR laser, LH diffraction at ambient pressure: Jun 2017
- ▶ Permanent laser interlock approved: Feb 2018
- ▶ New Pilatus 1M detector: Sep 2018
- ▶ Second Beamline Scientist: March 2019



Goniometer

Focusing mirror

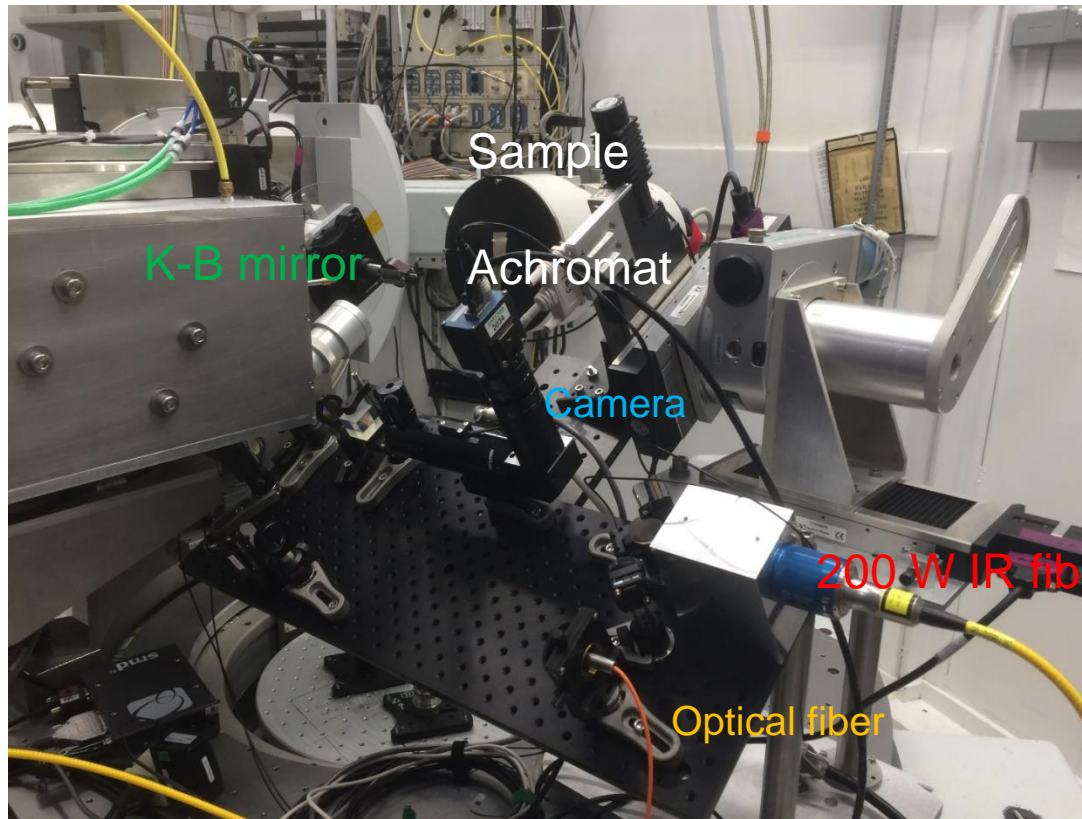
DAC

CCD

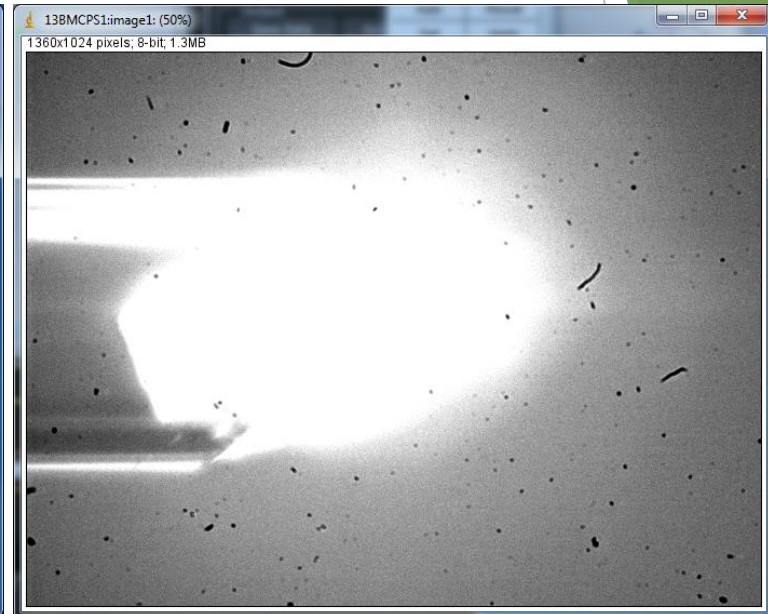
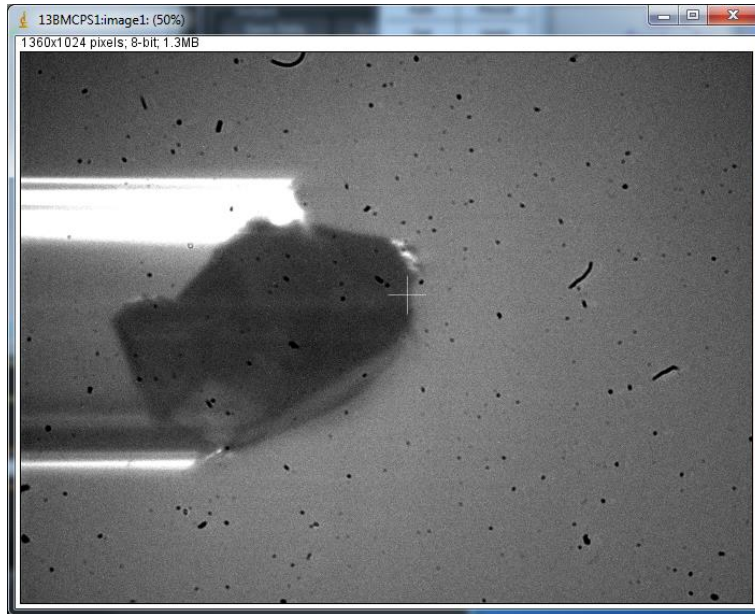
Beam stop

HR microscope

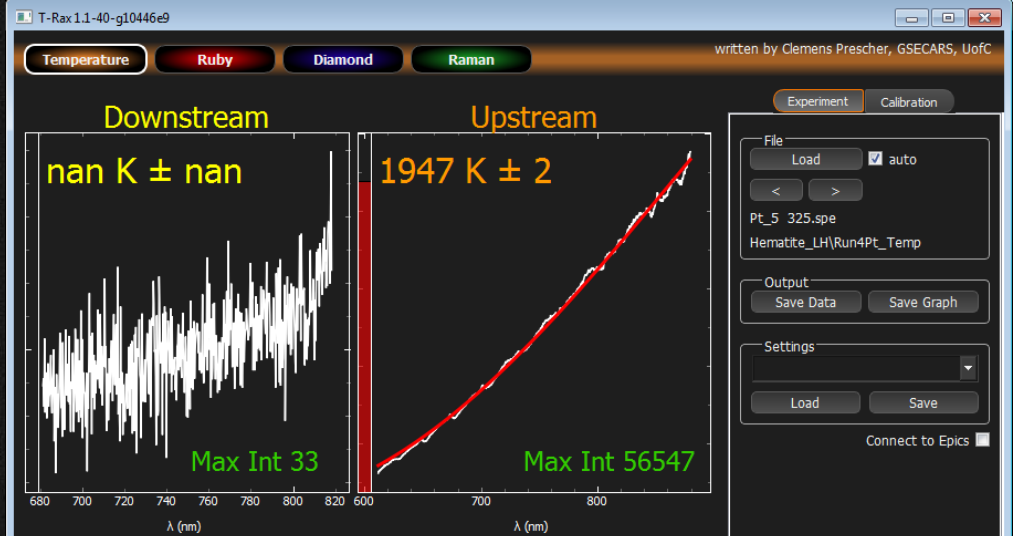
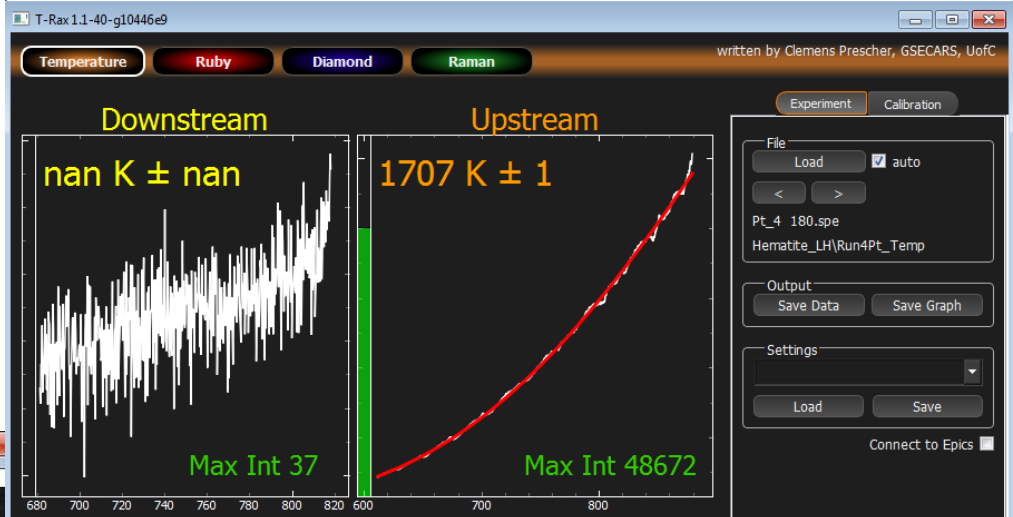
Beamline developments: laser heating



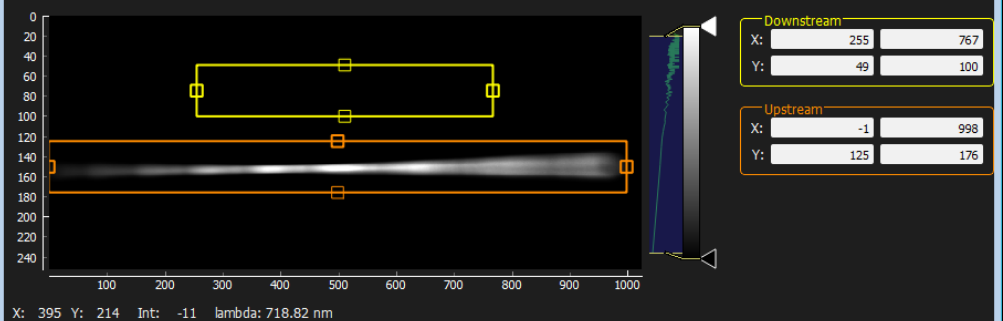
Heating Fe_2O_3 single crystal in air: Optical images of hematite sample before and during heating



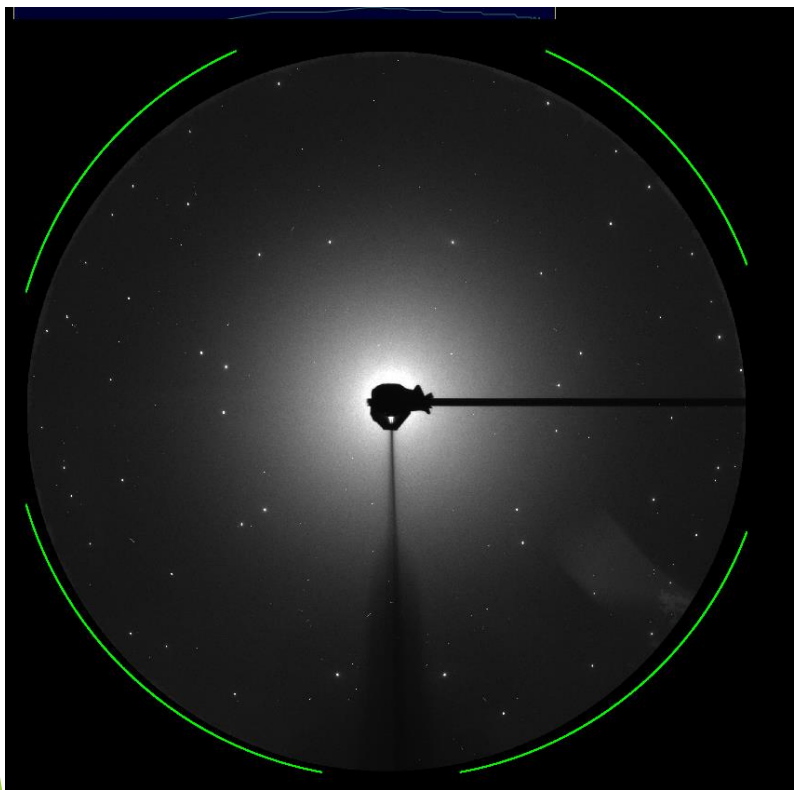
Pt single crystal diffraction at high temperatures



X: 665.29 Y: 1395.92 Exp. Time: 0.049999999999999996 | Grating: 750nm 300 | Detector: PIXIS: 256BR



Diffraction of Pt at 1950 K



RSV for SXD ver 2.5.4, November 02, 2011

Total: 46
Selected: 0

File View Filter Index Refine

triclinic
 monoclinic a-unique
 monoclinic b-unique
 monoclinic c-unique
 orthorhombic
 tetragonal
 hexagonal
 cubic

Refine w/ xyz Refine w/ d-spc Refine omega

0	0	-2	2	2	1.13169	74.0810
0	1	-1	1	1	2.26079	81.5209
0	2	-1	3	1	1.18194	80.7615
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0	7	-1	3	-1	1.18360	56.5212
0	8	0	-2	2	1.38543	66.4640
0	9	2	-2	0	1.38713	68.8334
0	10	3	-1	-1	1.18397	63.6153
0	11	-3	1	1	1.18125	32.5978
0	12	-2	0	2	1.38437	35.4989
0	13	-1	-1	3	1.18124	46.6428
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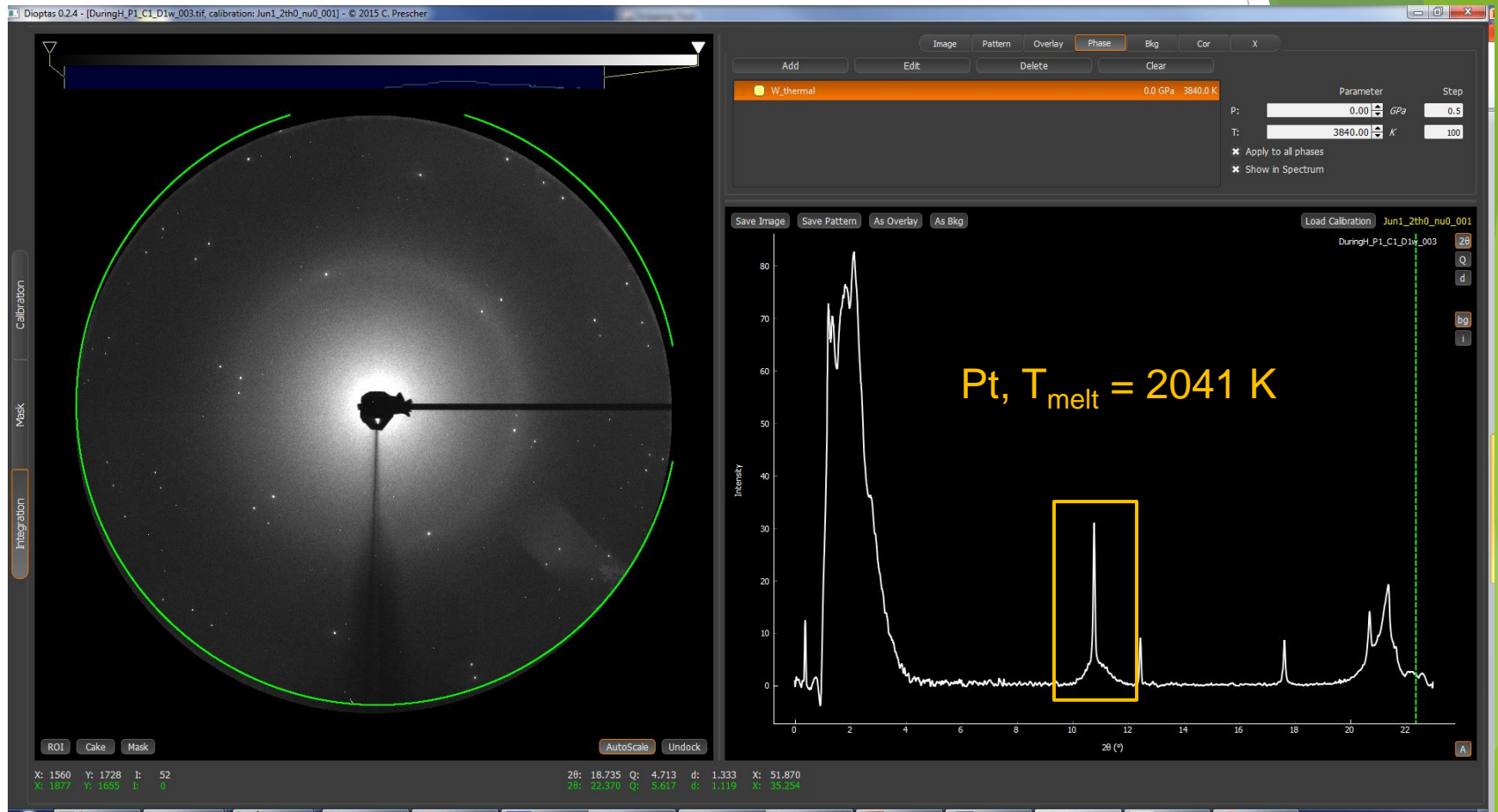
UB matrix:
0.0498815 -0.247606 -0.0346943
-0.190368 -0.0146772 -0.168953
0.162087 0.0589614 -0.187755

Unit cell parameters:
3.92231 3.92231 3.92231
90.0000 90.0000 90.0000

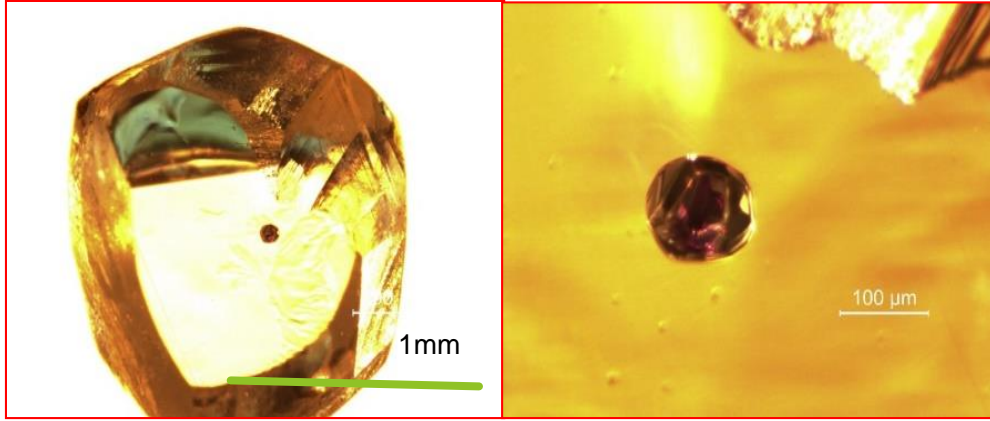
Estimated standard deviations:
0.000911278 0.000911278 0.000911278
0.000000 0.000000 0.000000

Chi²= 0.00878974

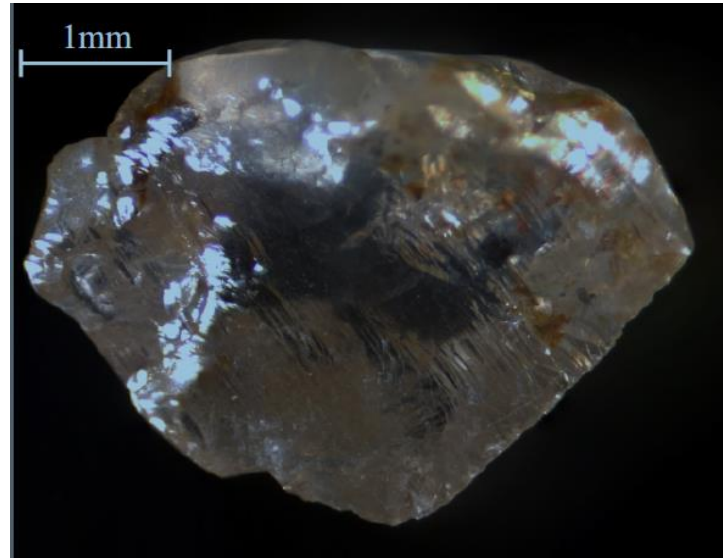
Diffraction of melt: diffuse scattering rings



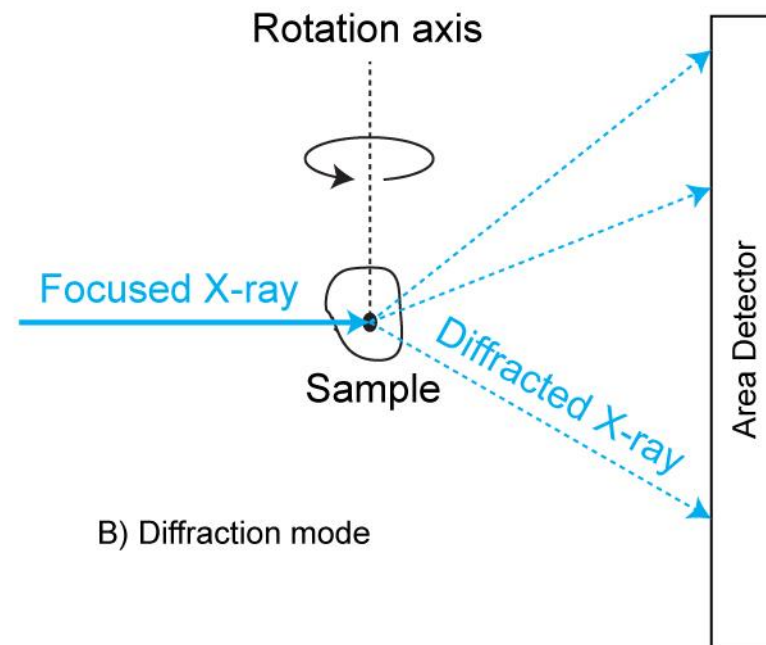
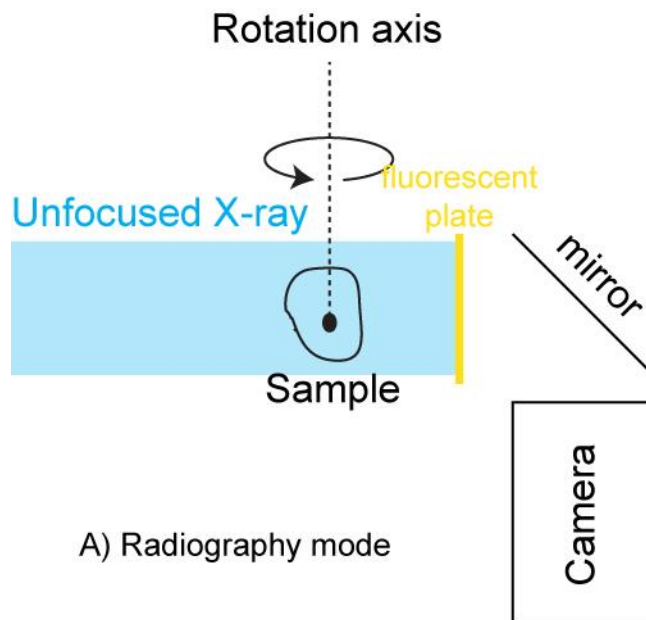
Solid inclusions in diamonds: diffraction and radiography



Collaboration with Northwestern Univ. Steve Jacobsen's group



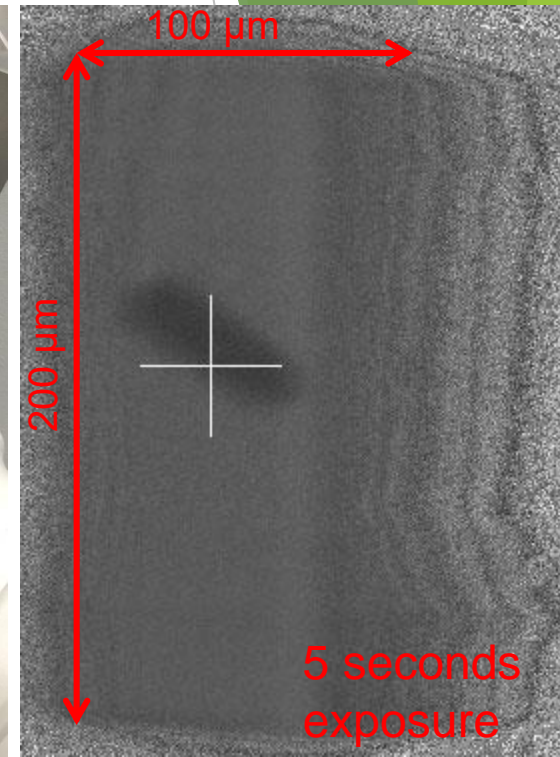
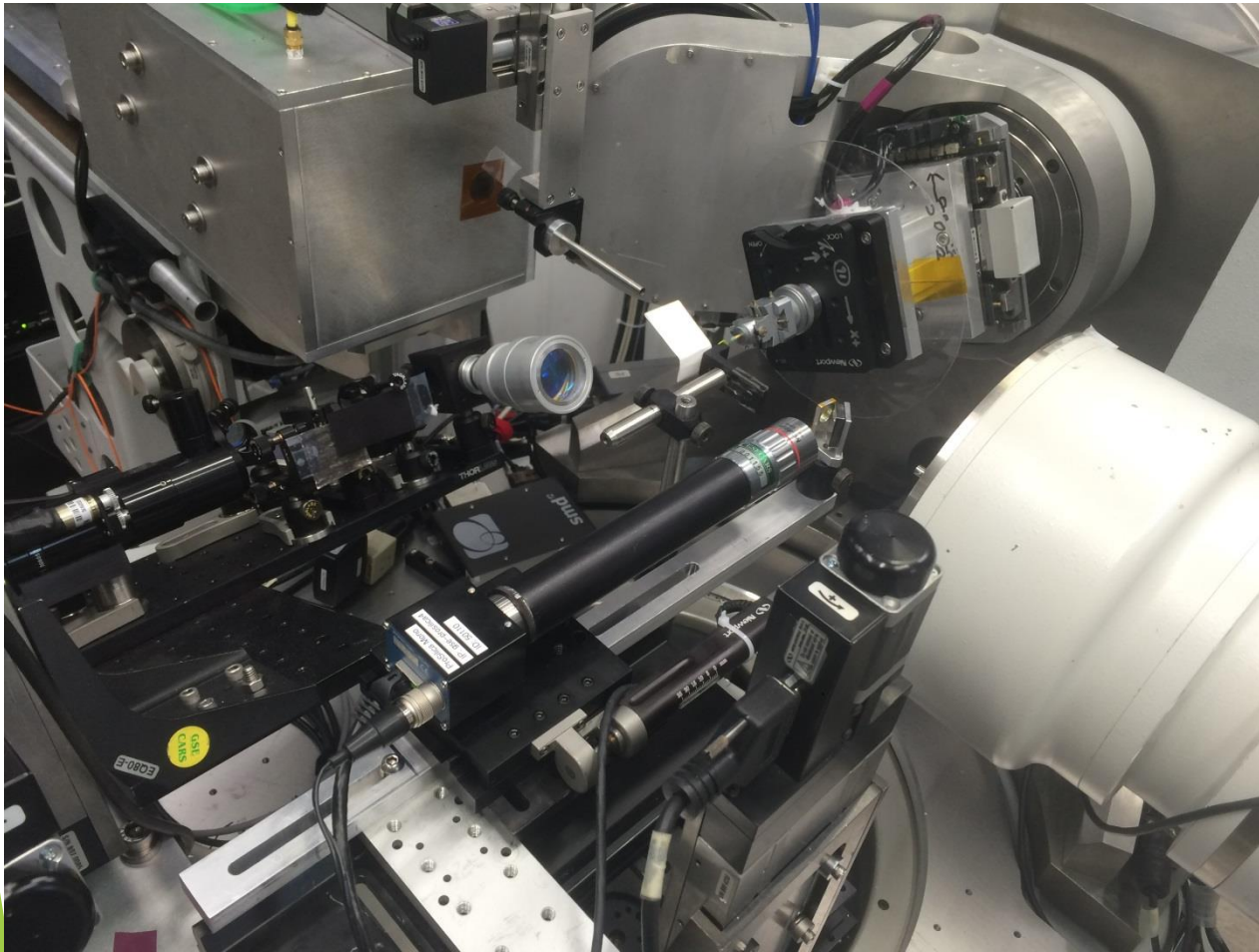
Beamline developments: radiography setup for inclusion-host diffraction



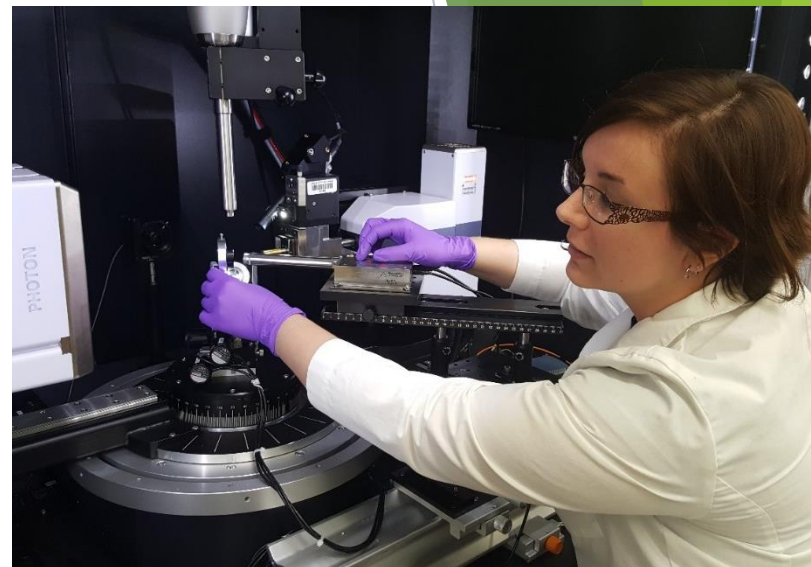
Defocused X-ray field of view: $\sim 200 \times 100 \mu\text{m}^2$
Focused beam size: $\sim 18 \times 12 \mu\text{m}^2$

Collaboration with M.
Wenz and S.
Jacobsen
(Northwestern U)

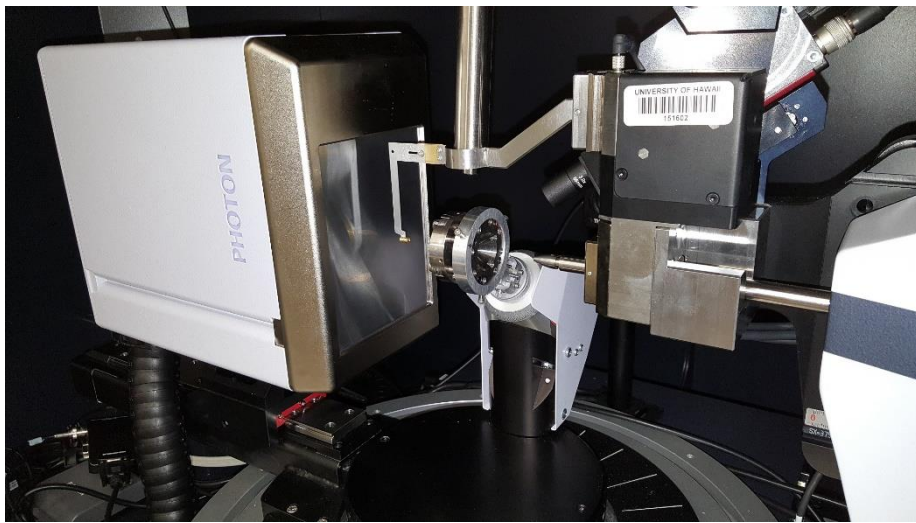
Beamline developments: radiography setup for inclusion-host diffraction



Collaboration with M. Wenz and S. Jacobsen (Northwestern U)



- X-ray Atlas is an NSF-funded instrument development project aimed at creating “your little synchrotron at home” solution for single crystal diamond anvil cell experiments.
- Within this project, we are customizing a commercial instrument, Bruker D8 VENTURE single-crystal diffractometer with a fixed-chi 3-circle goniometer, innovative PHOTON II CPAD detector, and $1\mu\text{S}$ 3.0 AgK α Incoatec microfocus source with Helios focusing optics to enhance and improve performance for diamond anvil cell experiments beyond 20 GPa.
- The customizations include most of the synchrotron-specific solutions, including motorized sample translation, automated radiographic scanning, and online laser spectroscopy.

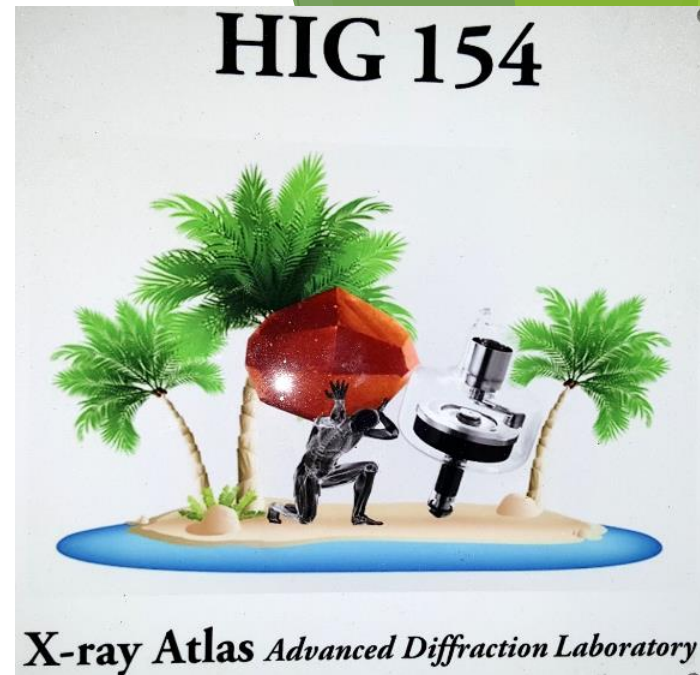


X-ray Atals: Our “little synchrotron” at home

Bruker D8 Venture
 Fixed-chi goniometer
 AgK α Incoatec ImS 3.0 with Helios optics
 22 keV
 100 microns focal spot at sample
 Long sample-to-focusing optics distance
 Photon-II CPAD detector
 APEX 3 software

XXI Atlas HP System

1. Heavy duty omega-platform sample stage with motorized translations and optional chi
2. Online ruby system with high-magnification optics
3. Photodiode-based beam intensity monitoring and scanning
4. Micro-XRF capability
5. EPICS control



X-ray mass attenuation coefficients μ/ρ
for carbon [cm²/g]

5.0 keV	1.912E+01
10 keV	2.373E+00
15 keV	8.071E-01
20 keV	4.420E-01
30 keV	2.562E-01
40 keV	2.076E-01
50 keV	1.871E-01

CuK α

MoK α

AgK α

APS PX²

APS 13IDD

Heavy-duty motorized sample stage

- Standard lab diffractometer are designed to only hold a small sample crystals. There is typically no space on the goniometer to accommodate heavy-duty motorized stages. Sample position is controlled manually with screws (goniometer head).
- Motorized goniometer heads are available, but are bulky and have very low load capacities.
- The heart of X-ray Atlas is a motorized heavy-duty (10lb) XYZ sample stage. The stage is small enough to fit underneath the detector, on top of the omega-platform.
- The motorized stage features long, 10mm translation range in each direction, can accommodate cooling sample holder for resistive heating experiments, as well as motorized open cradle chi-stage.
- Motorized sample translation allows automated data collection from multiple sample crystals at ambient pressure, e.g. for crystal screening.
- The XYZ stage is controlled via EPICS protocol, widely used at synchrotron facilities, with built-in capabilities to seamlessly combine control for multiple devices, providing scanning capabilities, etc.



The image displays several software windows for instrument control:

- USB-1608G Dera:1608G:** Controls for analog input (8 channels) and waveform digitizer (current point, # points, time/point, total time, etc.).
- scan_more.adl:** Controls for positioners (Dera:m1.RBV, Dera:m1.VAL) and detectors (Dera:1608G:A11). Includes a 'SCAN' button and 'GO/PAUSE/ABORT' controls.
- DeraLab.adl:** A central control panel for 'Dera DAC Lab' with checkboxes for various hardware components.
- SR570.adl:** Controls for the SR570 current preamplifier, including filter settings (lowpass/highpass 3dB freq) and gain mode.
- 3motors.adl:** A 'Sample_Stage' control panel with a table for motor limits and move controls.

Motor	Description	Limits	Readback	Move Absolute	Tweak Jog	Mode	More Controls
X		3.3500	3.3500	< 0.5000 >	JogR JogF	Use Set	Stop Move Pause Go
Y		2.8292	2.8292	< 0.1000 >	JogR JogF	Use Set	Stop Move Pause Go
Z		2.0900	2.0900	< 0.0100 >	JogR JogF	Use Set	Stop Move Pause Go

EPICS is a proven industry standard for synchrotron instrument control. Compatibility of this Bruker lab diffractometer interface with synchrotron beamlines allows students to learn fast and perfect their skills in the home lab setting, without the stress and restrictions of beam time.

Conclusions

- ▶ High pressure crystallography can offer significant breakthroughs to advance mineral physics and extreme materials science.
- ▶ High pressure crystallography desperately needs more advanced synchrotron crystallography facilities like ChemMatCARS, with sufficient specialized equipment (motorized sample translation, ruby fluorescence, etc.).
- ▶ Collaboration with PX² and UH X-ray Atlas lab may offer opportunities for technology transfer for development of new HP crystallography capabilities at ChemMatCARS.
- ▶ Co-funding opportunities with NSF-EAR, COMPRES, etc. might be worth exploring.

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