Oak Ridge National Laboratory

Extreme Environments in Neutron Scattering

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About me…

SNAP Beamline

NOVA
FACULDADE DE
CIÊNCIAS E TECNOLOGIA

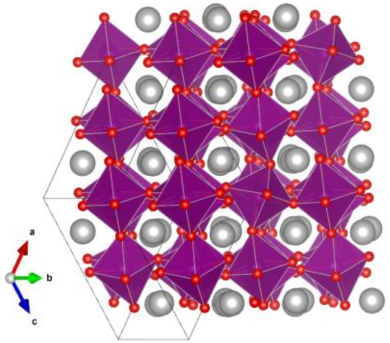
PHYSICS OF MATTER UNDER EXTREMES

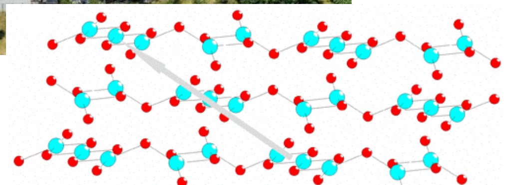
For the study of materials in extreme stimuli to develop new materials and elicit optimized properties, and to characterize these far from equilibrium states with fine spatial resolution and short times.

ARCS, BASIS, BIO-SANS, CNCS, CORELLI, CTAX, DEMAND, GP-SANS, HYSPEC, IMAGINE-X, MARS, POWDER, POWGEN, PTAX, SEQUOIA, SNAP, TAX, USANS, VERITAS, VISION, WAND²

universidade
de aveiro

Multiferroic $BiMnO_3$





Ferrimagnet $Na_2Cu_5Si_4O_{14}$

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Extreme Environments in Materials Science

Temperature

Pressure/Strain

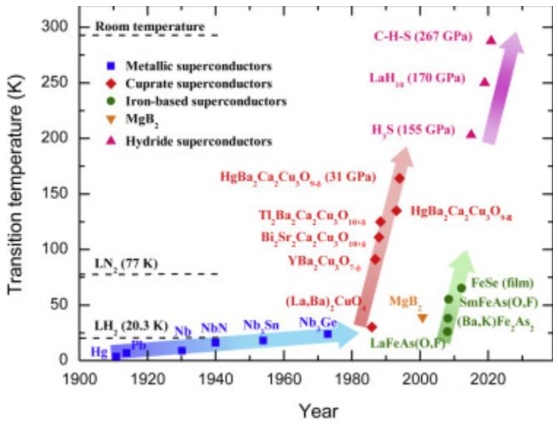
Magnetic Field

Corrosion

Radiation

Fundamental Research

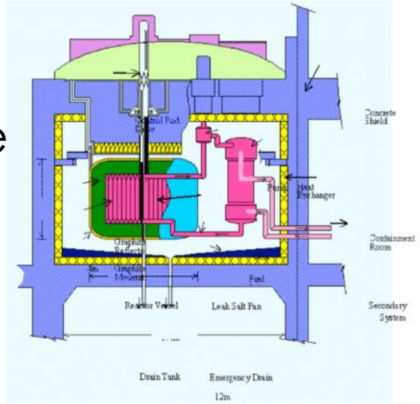
Superconductivity



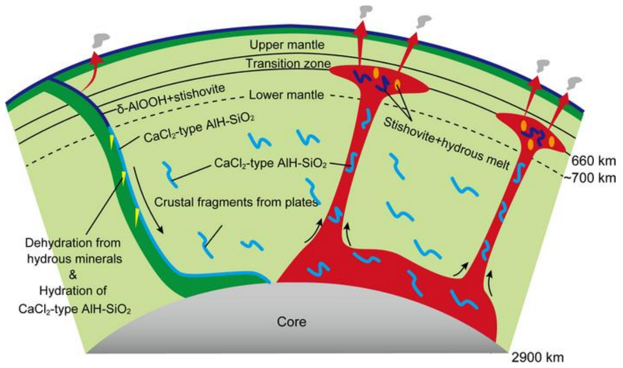
Structural Materials

High-Temperature Metals/Ceramics

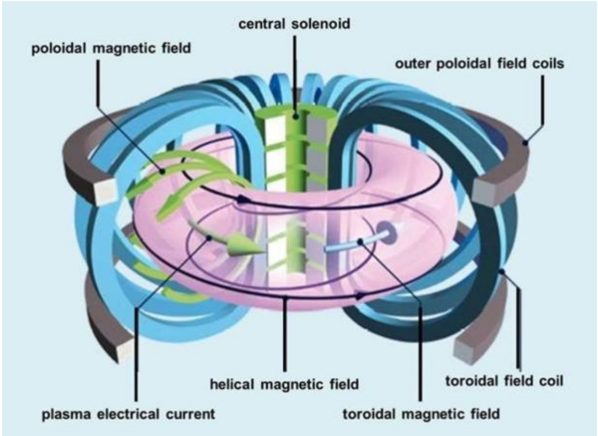
Corrosion Resistance



Planetary interiors



Materials for Fusion



Superhard Materials

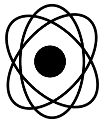
Real world applications

Outline

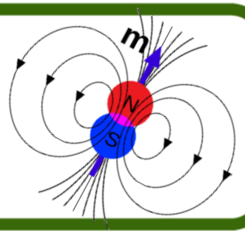
- Neutron Scattering Role in Extreme Environments
  - Pressure
  - Magnetic Field / Pulsed Magnets
  - High Temperature / Levitators
- Opportunities and Conclusions

Neutron Scattering under Extreme Environments

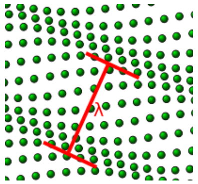
Crystal / Nuc. Structure



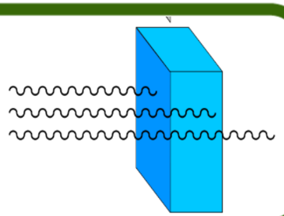
Magnetic Structure



Inelastic Neutron Scattering



Penetrating Access to mK Complex env.

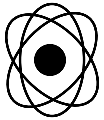


- Tracking phase evolution and transitions even low Z species
- Detailed information on magnetic and crystal structure.
- Sensitive to lattice dynamics and accurate thermal parameters
- Instruments compatible with high magnetic field

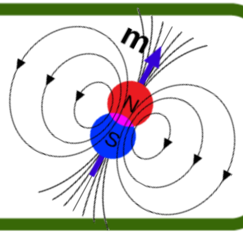
- Bulk sample characterization
- Complex sample environments
- Time of Flight (Pulsed sources)
  - Access to extended q – highest momentum transfer/real space resolution
  - Energy resolved - ideal for spatially constricted samples

Neutron Scattering for Extremes

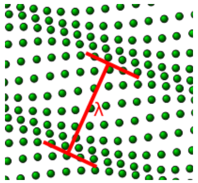
Crystal / Nuc. Structure



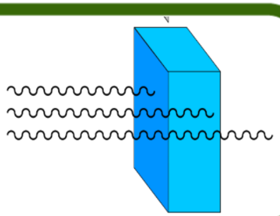
Magnetic Structure



Inelastic Neutron Scattering



Penetrating Access to mK Complex env..



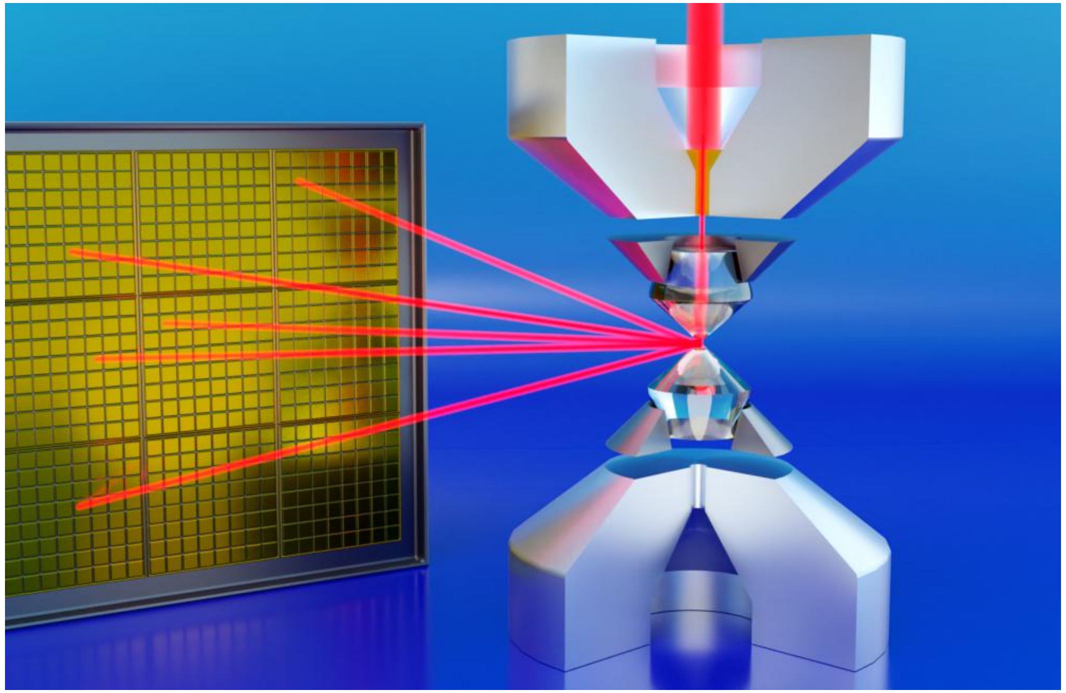
<u>Neutron Experiments</u>

- Low Flux
- Weak scattering cross section
- Slow measurements
- Medium instrument resolution
- “Large” samples

<u>Under extreme environments</u>

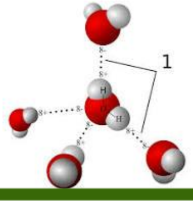
- Smaller samples - long collection times
- Mixed phases
- Fine spatial and temporal resolution
- (Very) complex and often hazardous sample environment
- Development of new data acquisition reduction and analysis tools

High-Pressure



High-Pressure Neutron Diffraction

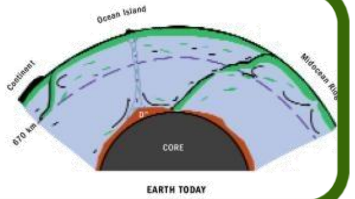
Hydrogen-Bonded systems



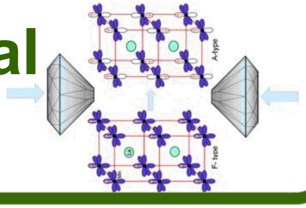
Melts and glasses at high pressure

In-Situ synthesis

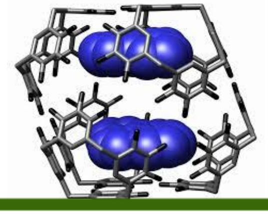
Light elements in Mantle Minerals



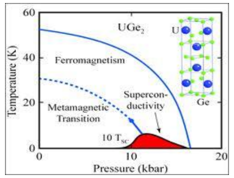
Magneto-Structural Coupling



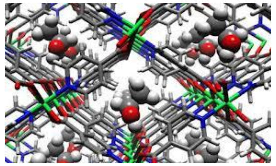
Guest-Host systems



Quantum phenomena

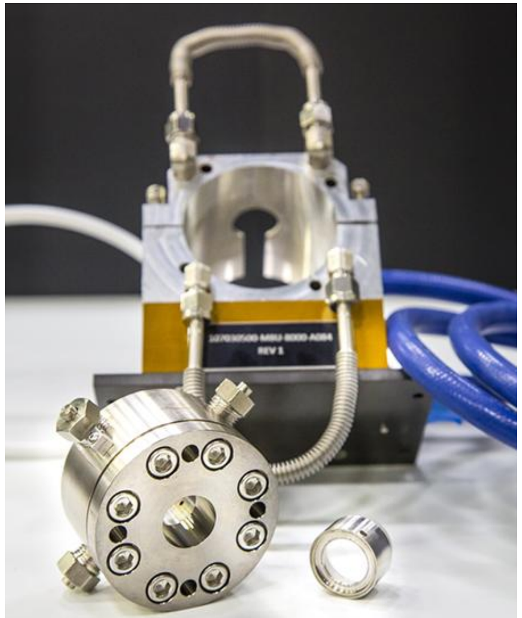


Gas Storage



High-Pressure Devices – an Overview:

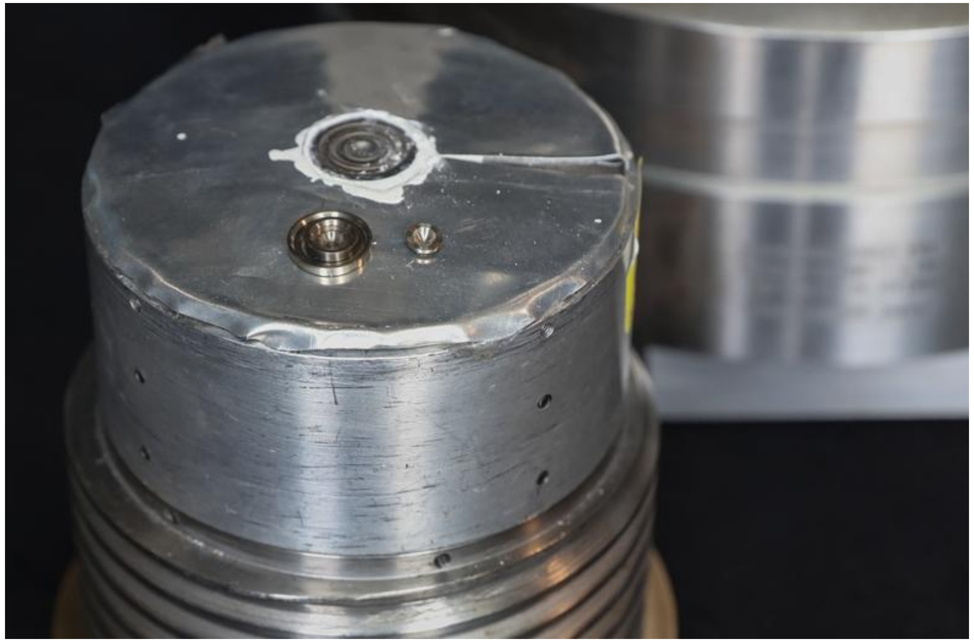
Science	Cell Type	Max. Pressure (GPa)	Temperature range (K)	Sample size (mm³)
Gas Storage, Biology Organic Chemistry	Gas	0.5 (1)	10-350	<700
Quantum Phenomena Magnetism	Clamp	2	mK-350	<150



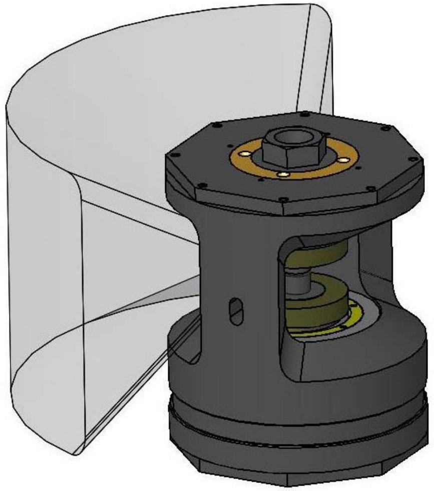
Chemistry / Materials – The Workhorse:

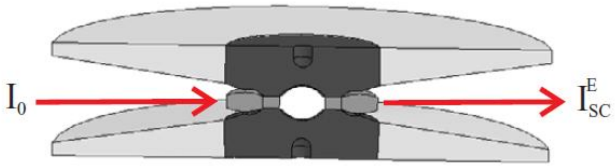
PE – Paris-Edinburgh press

Science	Cell Type	Max. Pressure (GPa)	Temperature range (K)	Sample size (mm^3)
Chemical Synthesis Mineral Physics	PE- heater	6	300-2000	<68
Phase transitions Crystallography	PE	10-20	(1.8) 80-350	<87

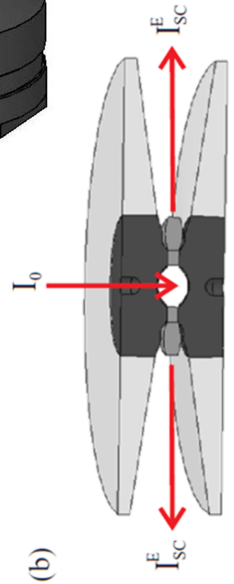


Paris-Edinburgh Press



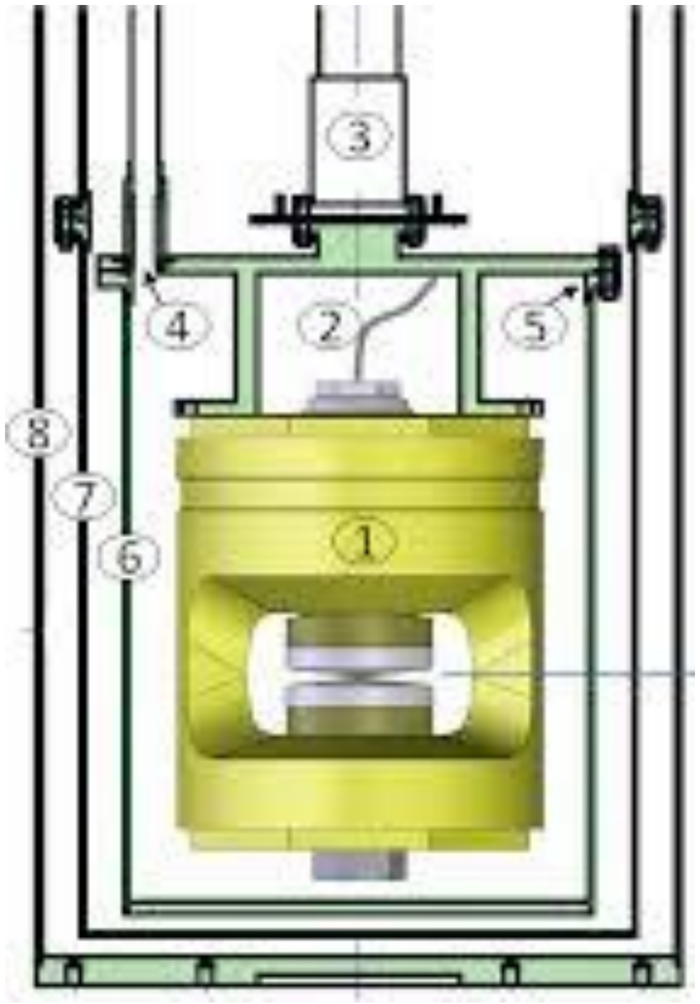


- Wide angle: large q
- Cubic BN anvils
- Self collimating
- Max. pressure : up to 10 GPa



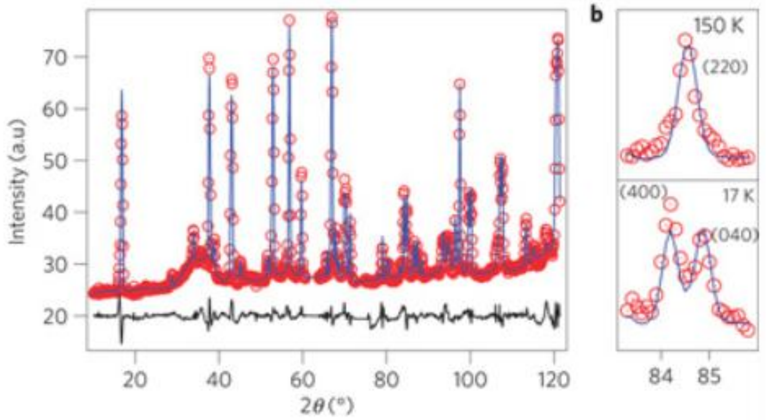
(b)

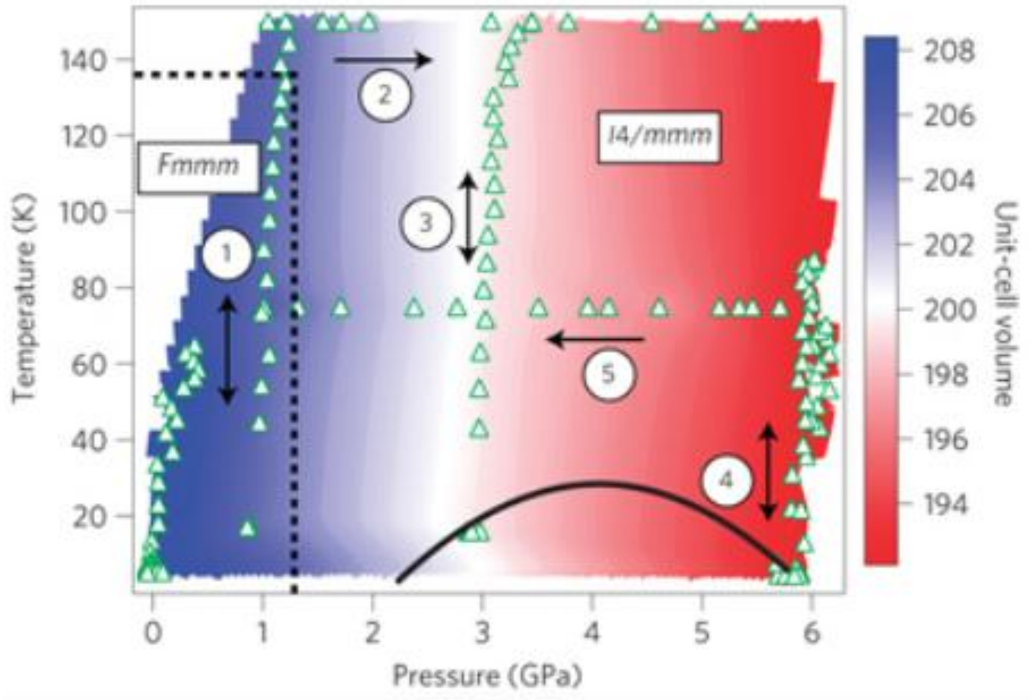
- Narrow angle: limited q
- PCD / WC / ZTA anvils
- Transparent anvils
- Max. pressure : up to 20 GPa

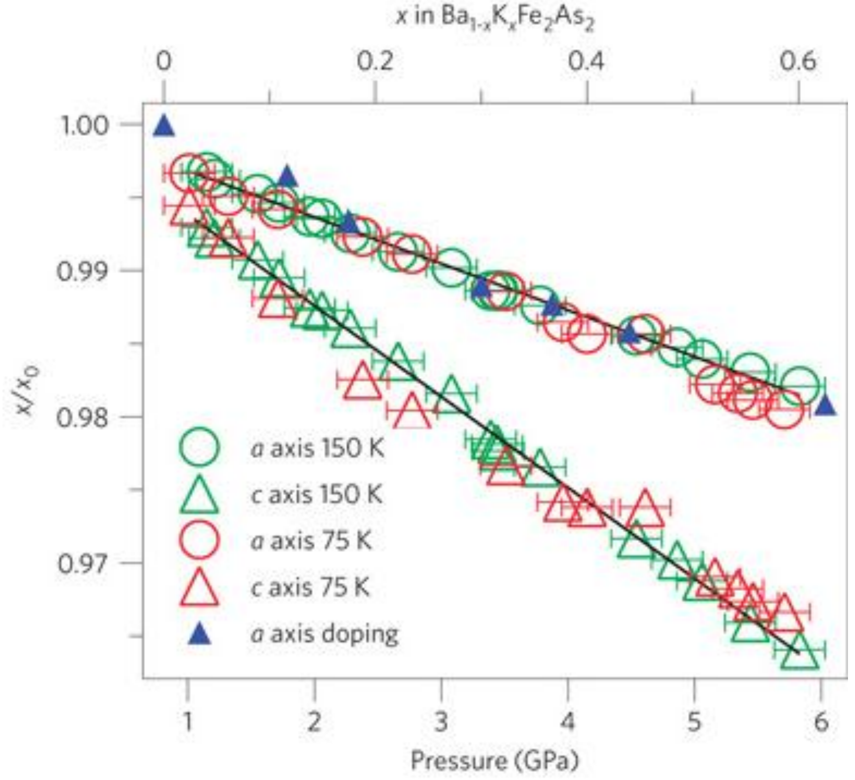


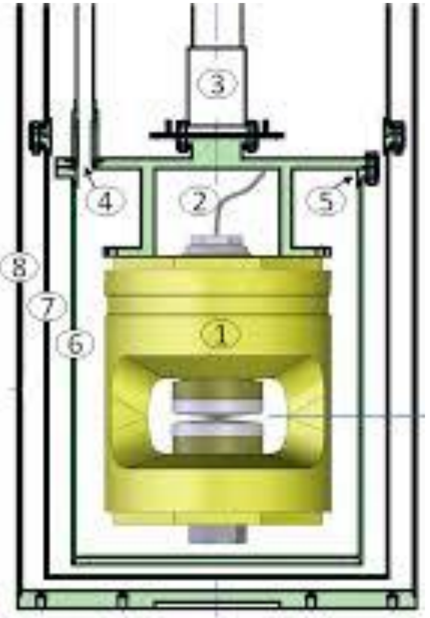
High pressure neutron ~~diffraction~~ scattering to 20 GPa and below 1.8 K

Pressure vs chemical doping in $BaFe_2As_2$



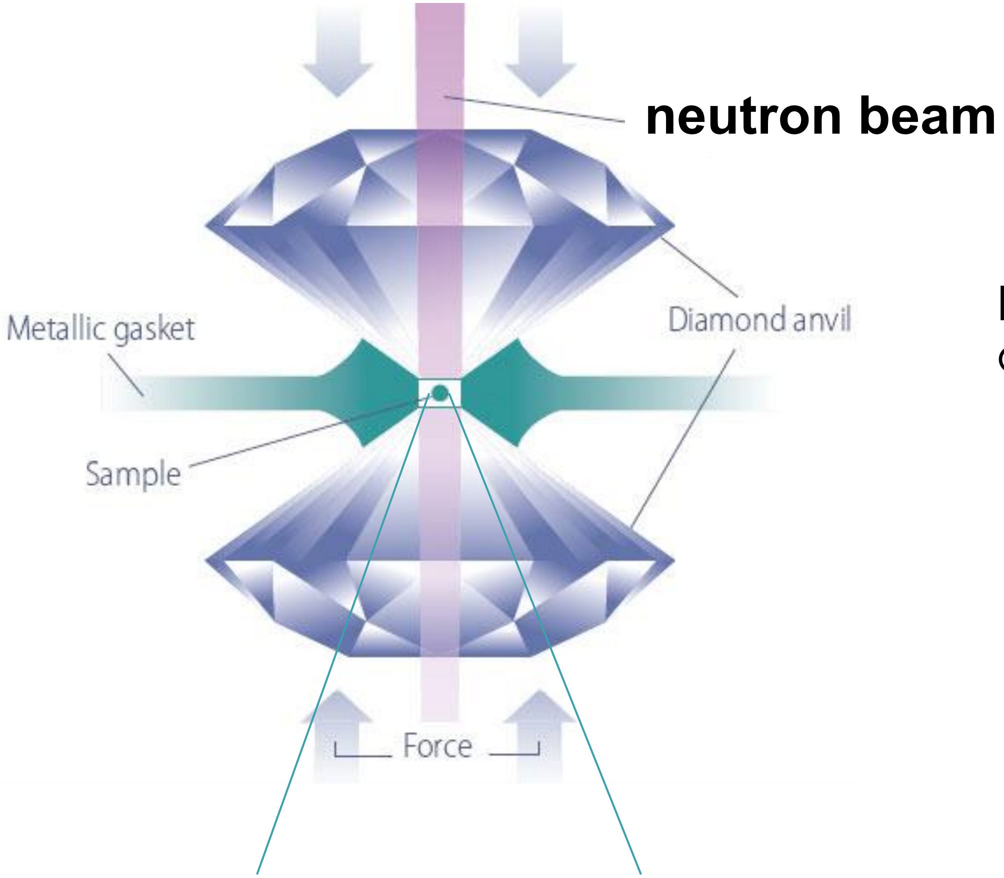






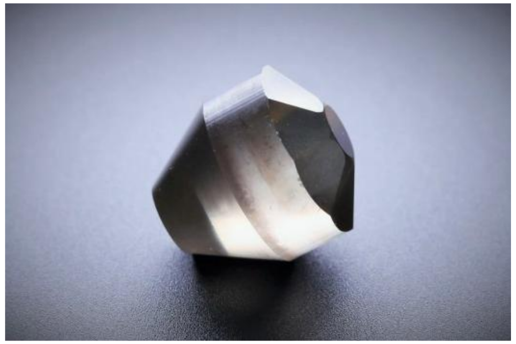
S. Kimber, A. Kreyssig, et al. Nature Materials 8, 471 - 475 (2009)

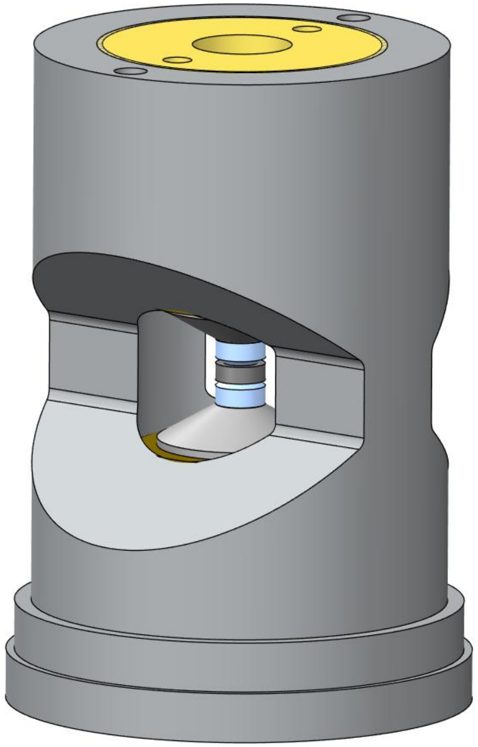
Neutron Diamond Anvil Cells



500 µm x 100 µm sample

Enabled by the availability of CVD-grown diamonds

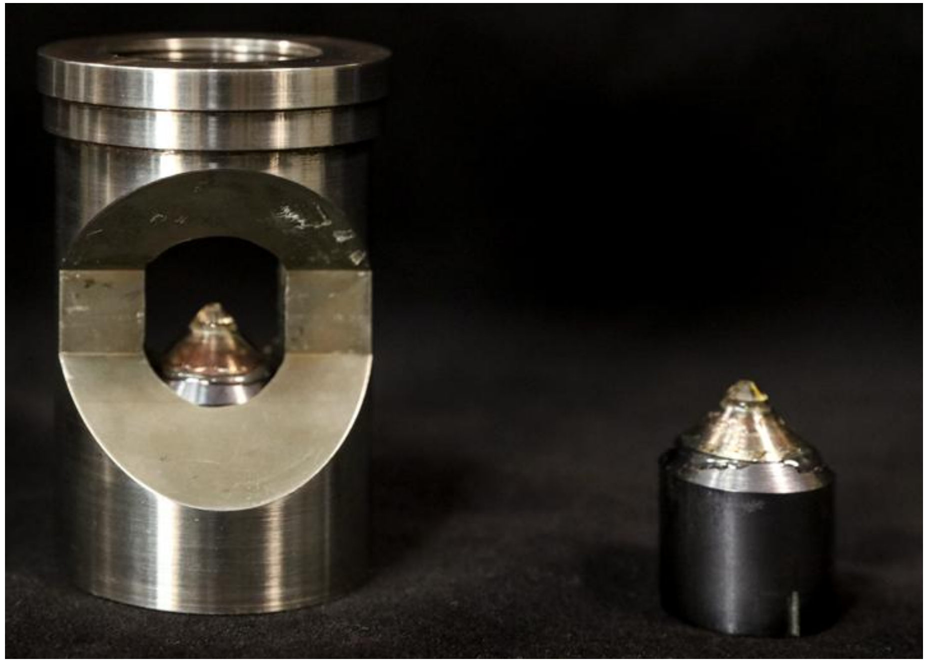




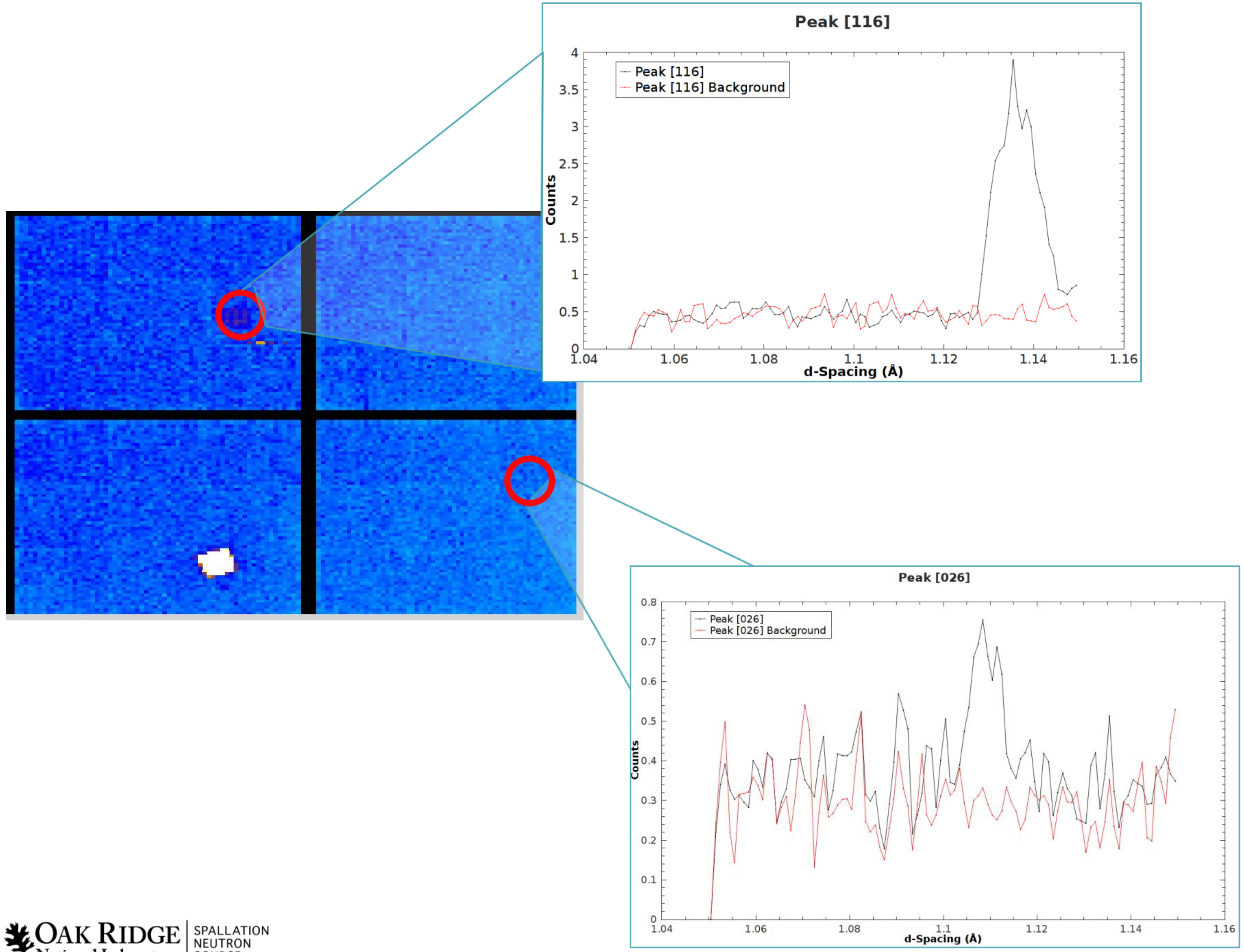
Extreme Pressure

Science	Cell Type	Max. Pressure (GPa)	Temperature range (K)	Sample size (mm^3)
Extreme Chemistry	DAC	40 (95 max)	6-700	<0.15

Gas Loading compressor

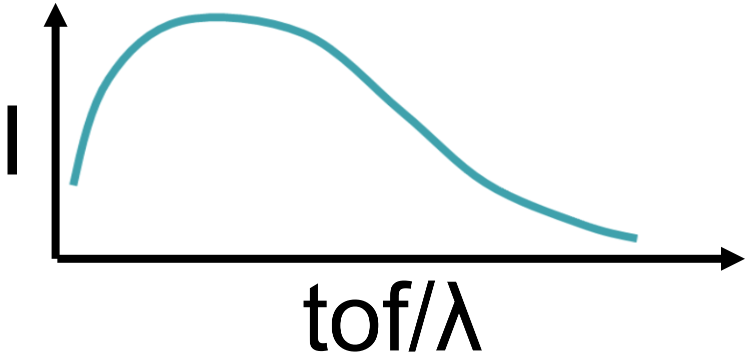


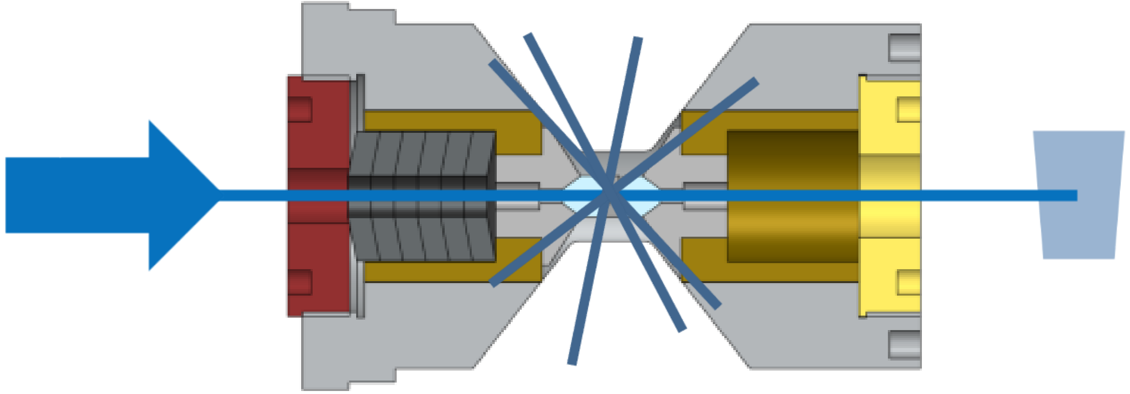
Benefits of area detectors

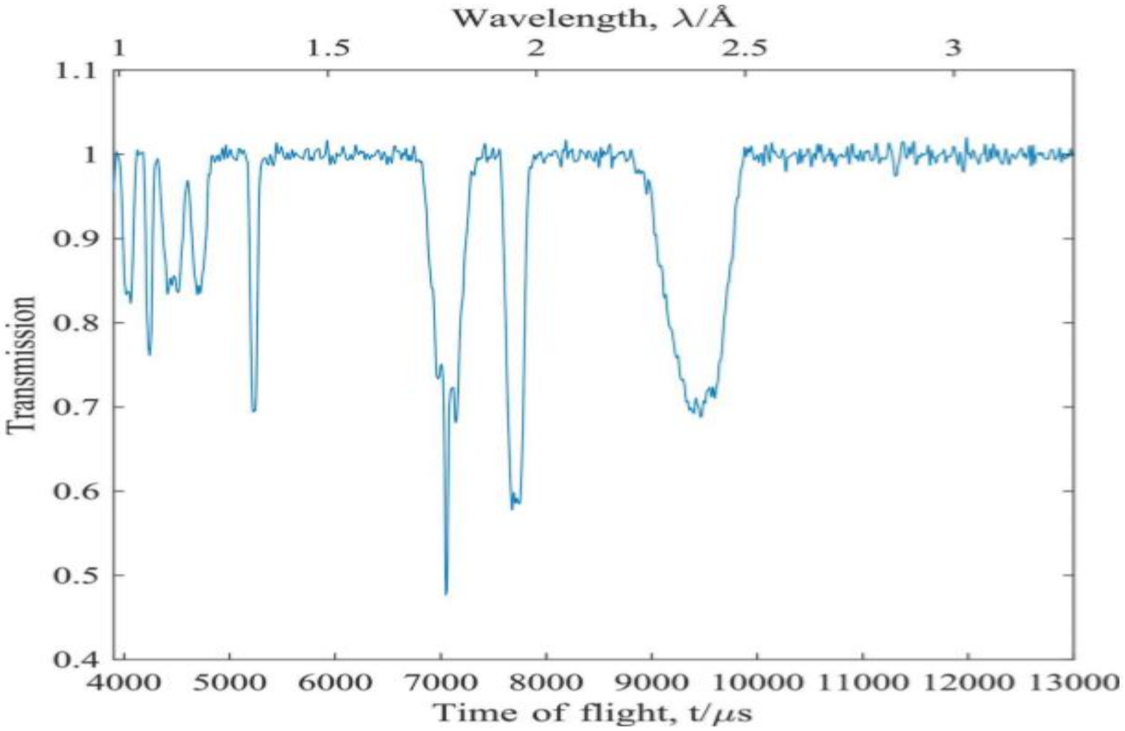


- Single crystal capability
- Enhanced sensitivity
- Masking spurious signal
- Sensitive to non ideal samples
- Large datasets
- Complex data reduction

New data reduction challenges

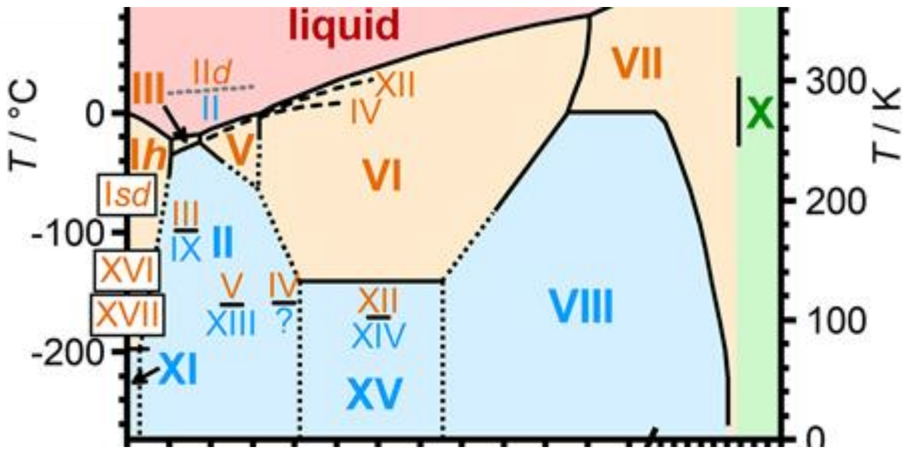


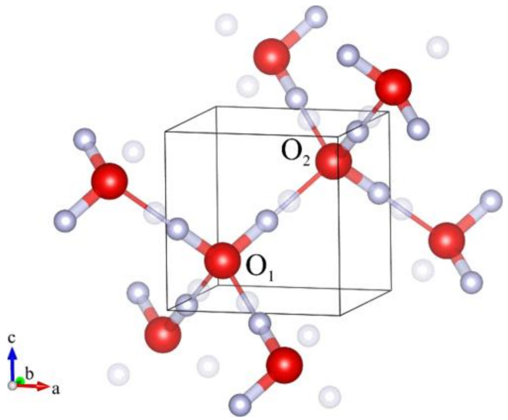


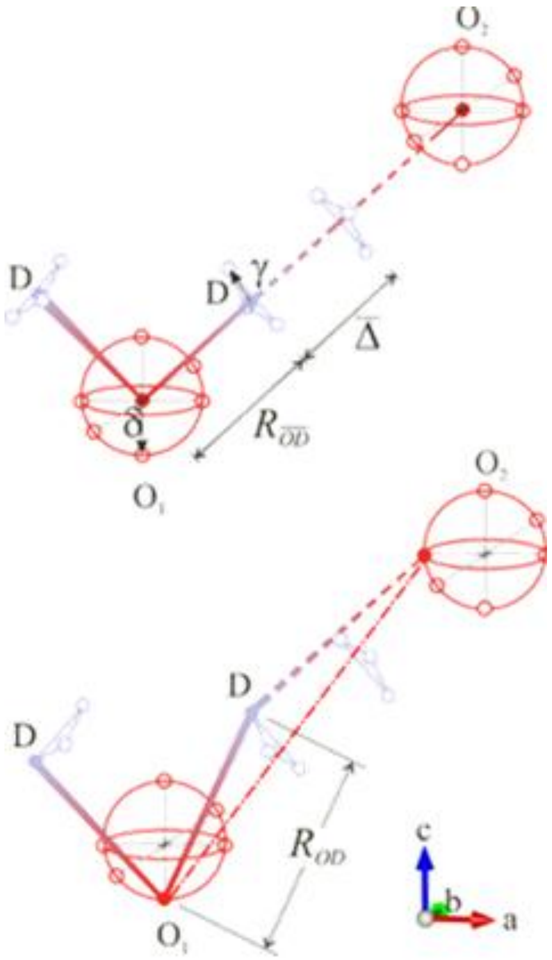


Guthrie, M.; Pruteanu, C. G.; et al. J. App. Cryst. 50 76-86

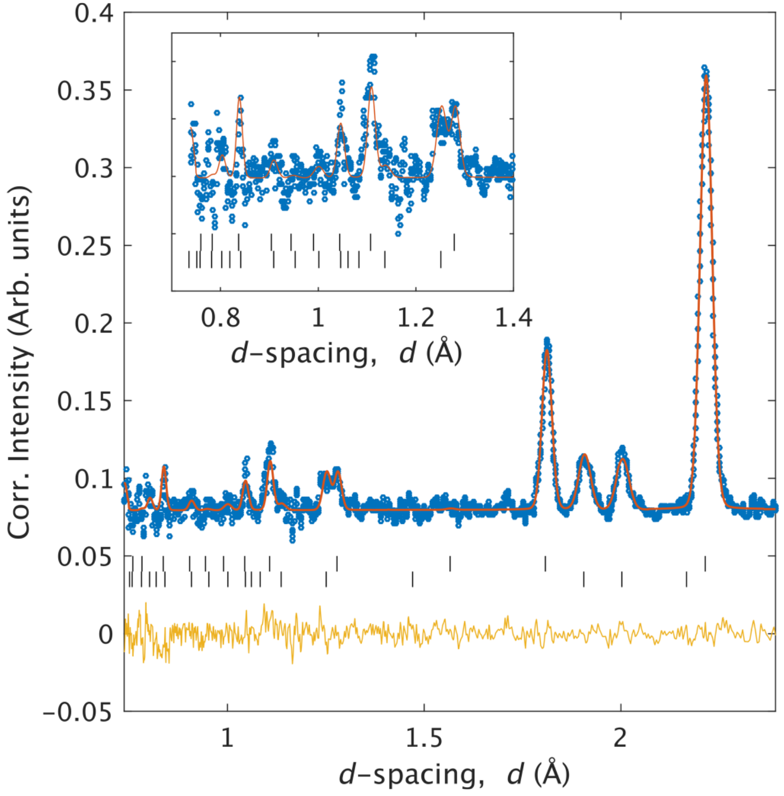
Quantitative Rietveld Refinment @ Pressure





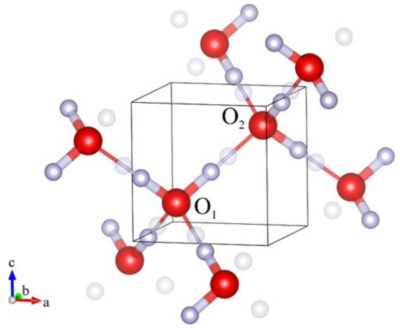


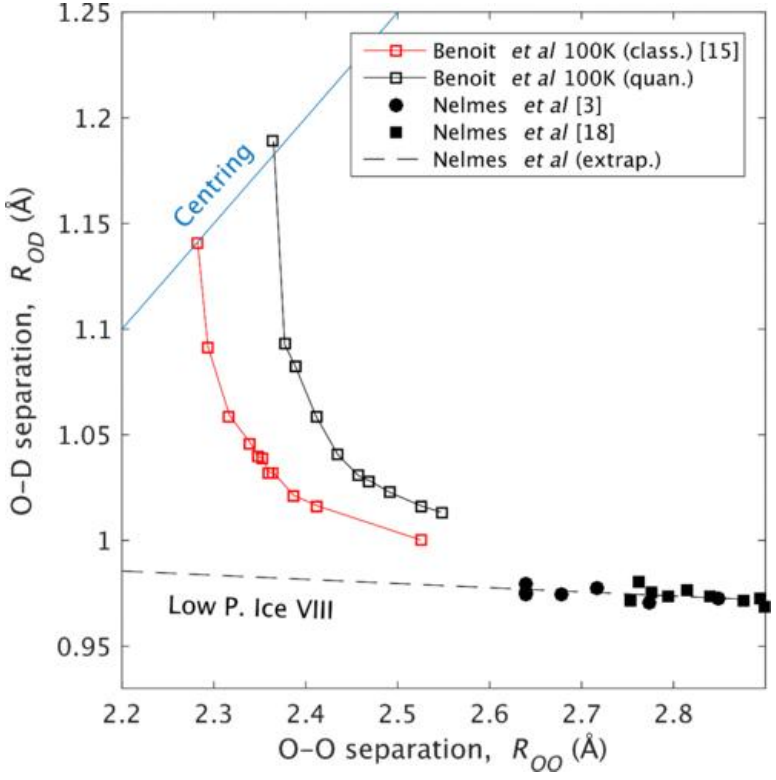
Structural refinement
Ice VII at 12.5 GPa

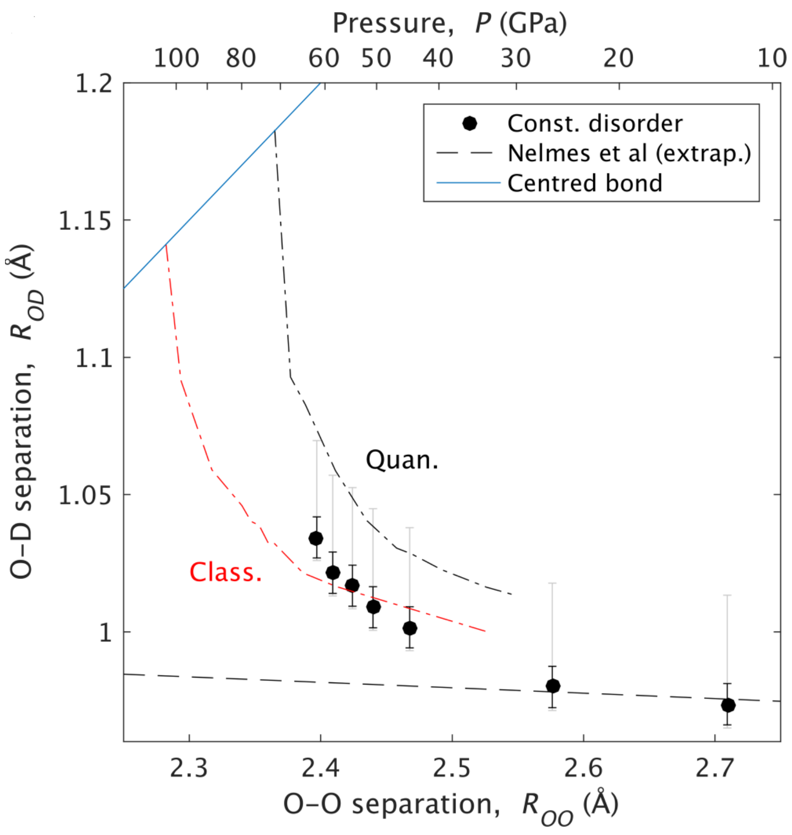


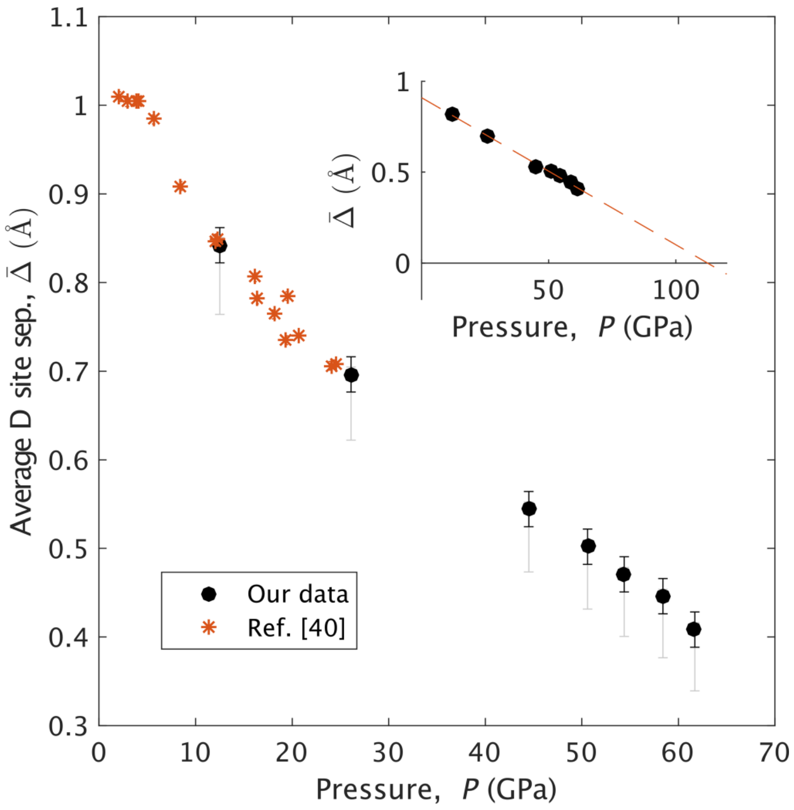
M. Guthrie, et. al; Phys. Rev. B 99, 184112

Ice VII on the approach to H-bond symmetrization









M. Guthrie, et. al; Phys. Rev. B 99, 184112

Ongoing Developments

In-situ ~~clamp~~ cell

Clamp Cell

Advantages

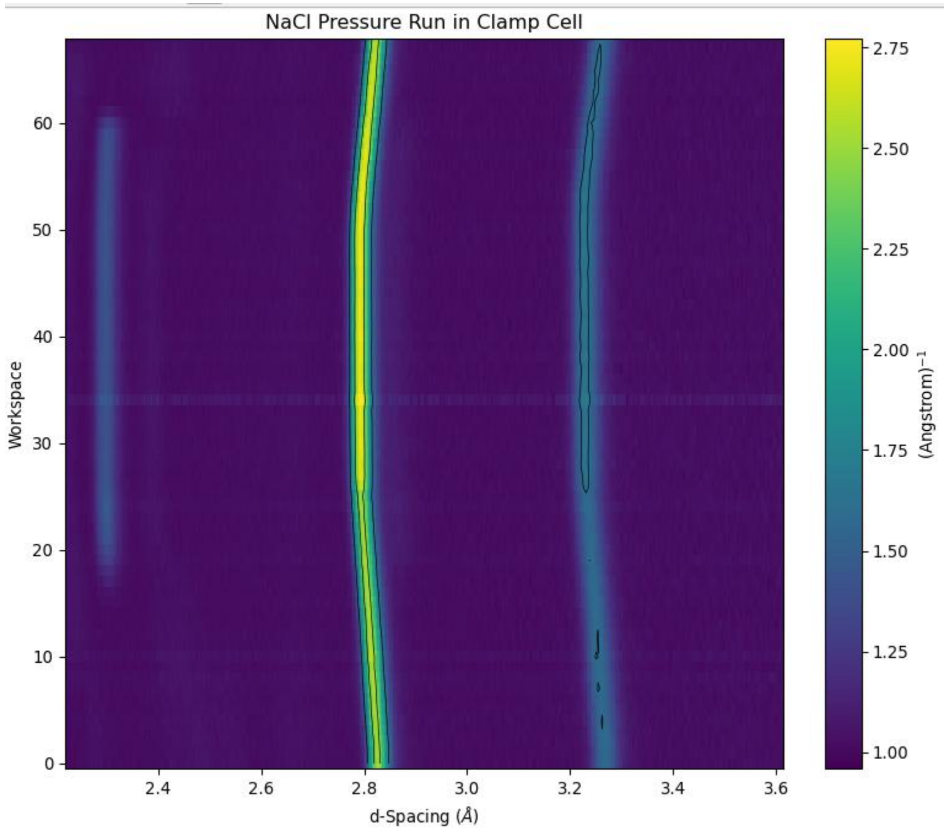
- Large sample size
- Easily customizable
- Full detector coverage
- Compatible with single crystals
- Amenable to fast cooling

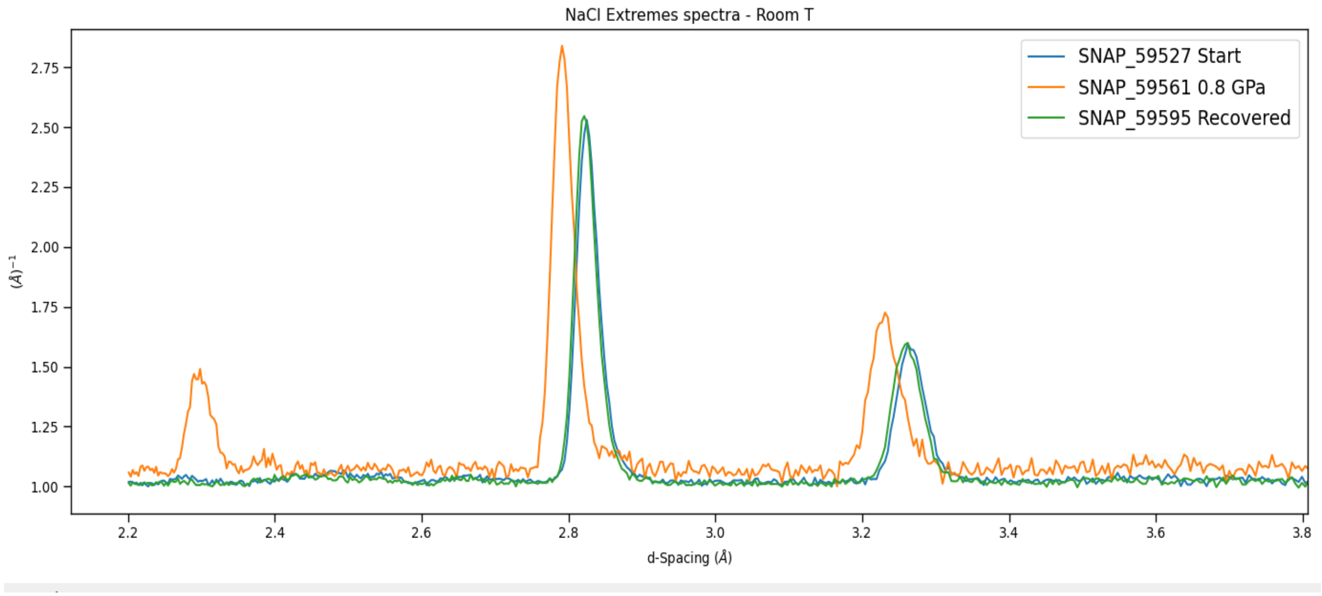
Drawbacks

- Low/Medium pressure (2-3 GPa)
- No continuous pressure control/monitoring
- Laborious pressure changes

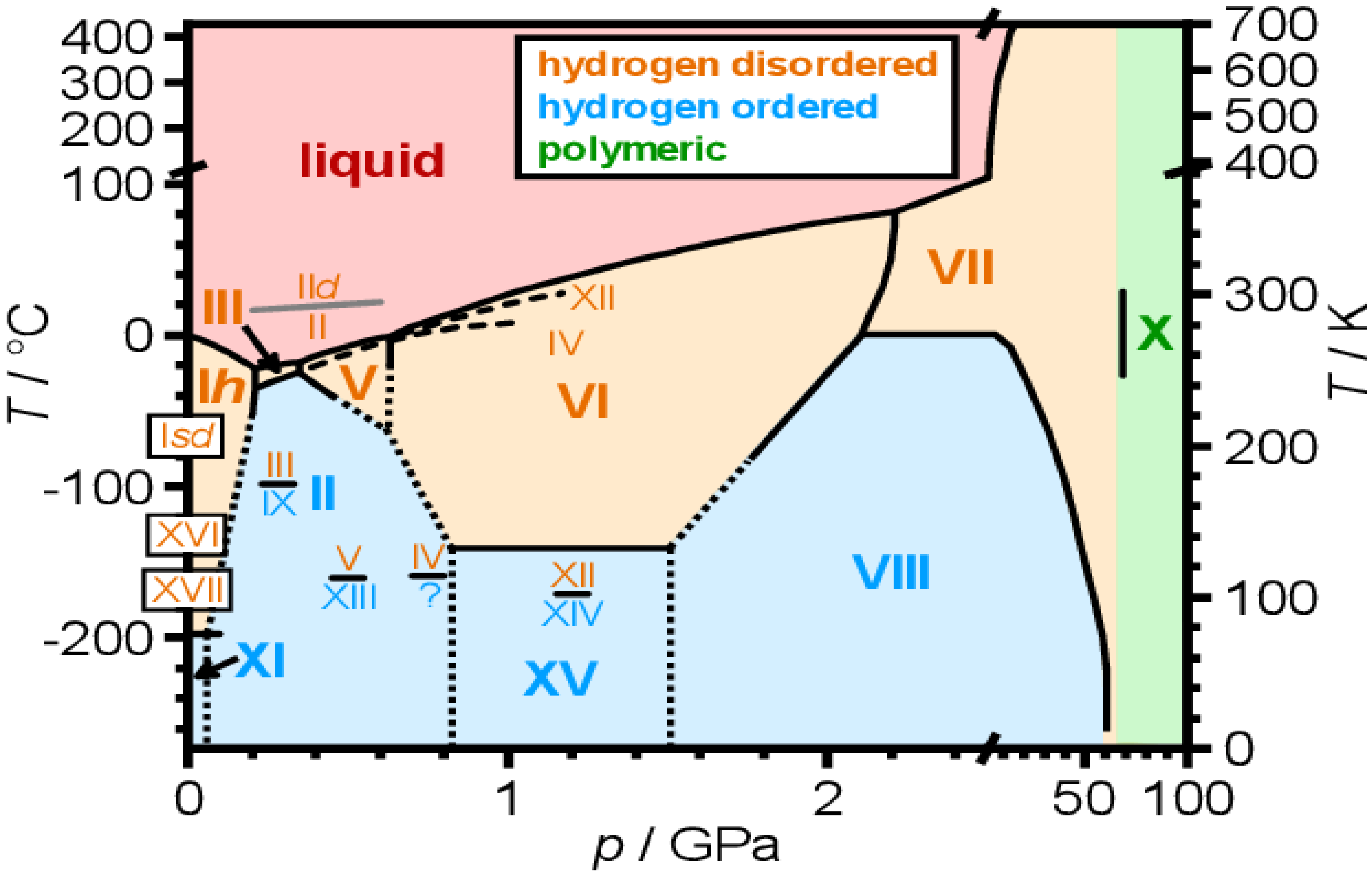
Collaboration with DAC-Tools and Jamie Molaison

NaCl Test Pressure Run





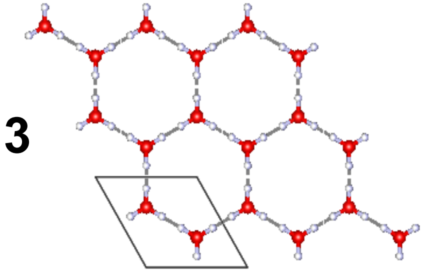
The “impossible” clamped experiment



C.G. Salzman, J.Chem. Phys. 150(6) 2019

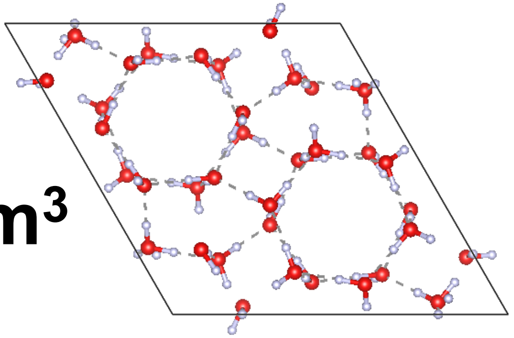
Ice Ih

0.91 g/cm^3



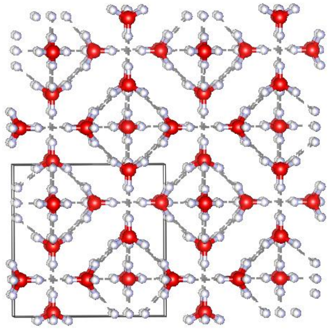
Ice II

1.16 g/cm^3

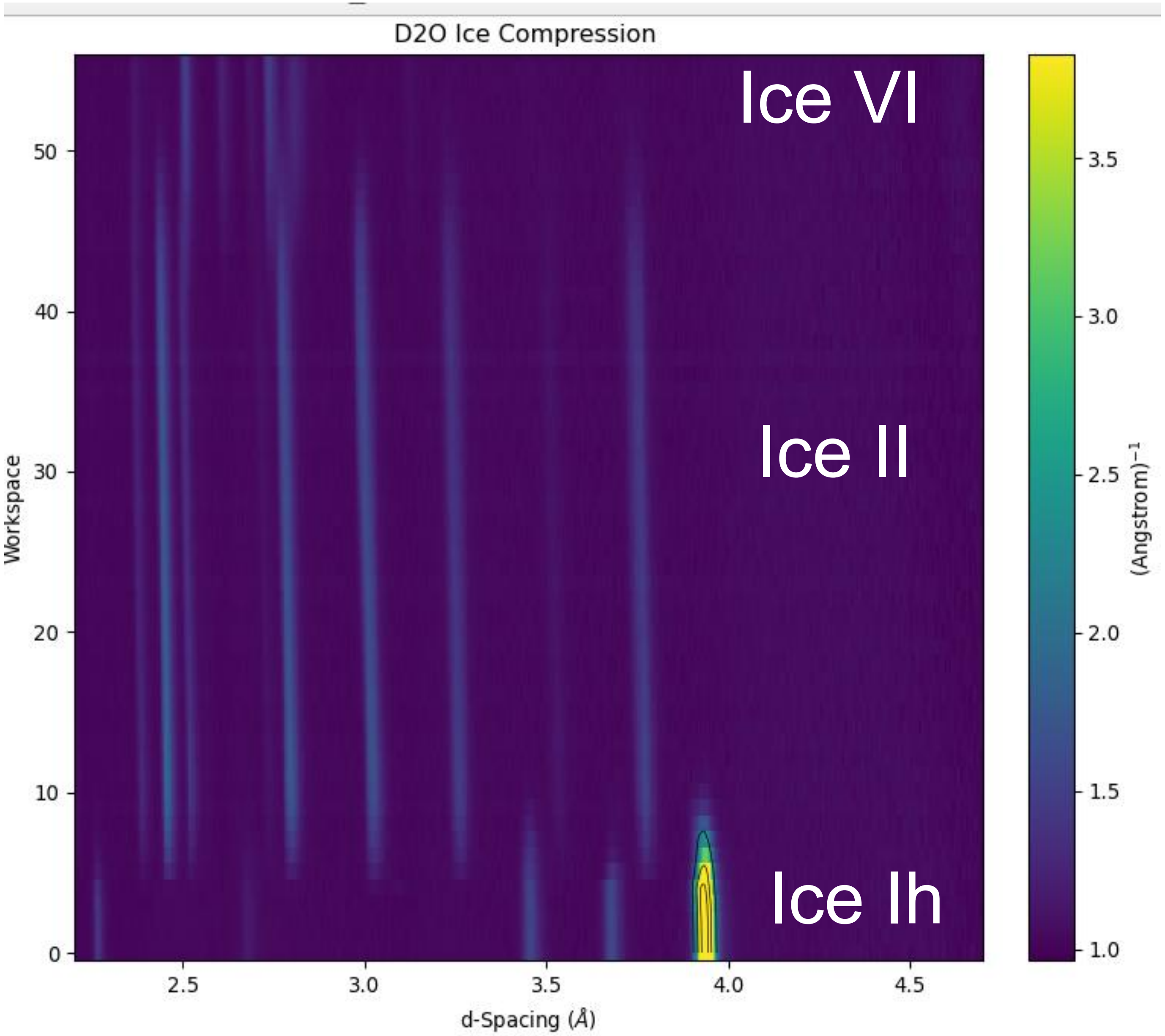


Ice VI

1.272 g/cm^3



D_2O Ice Compression



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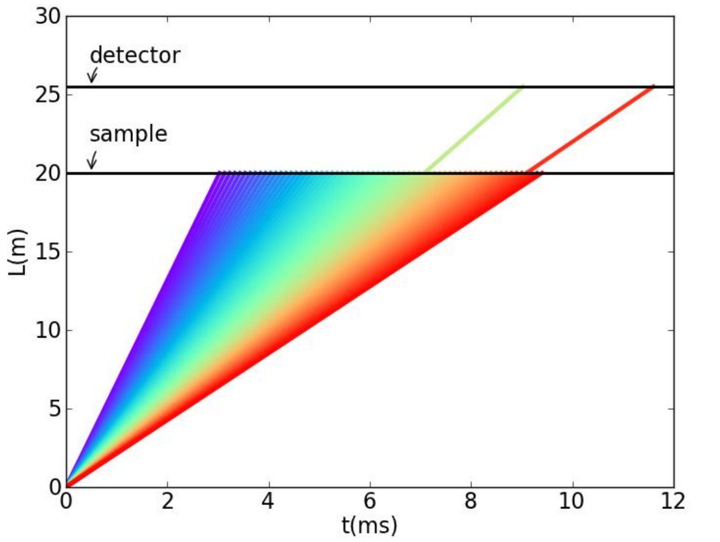
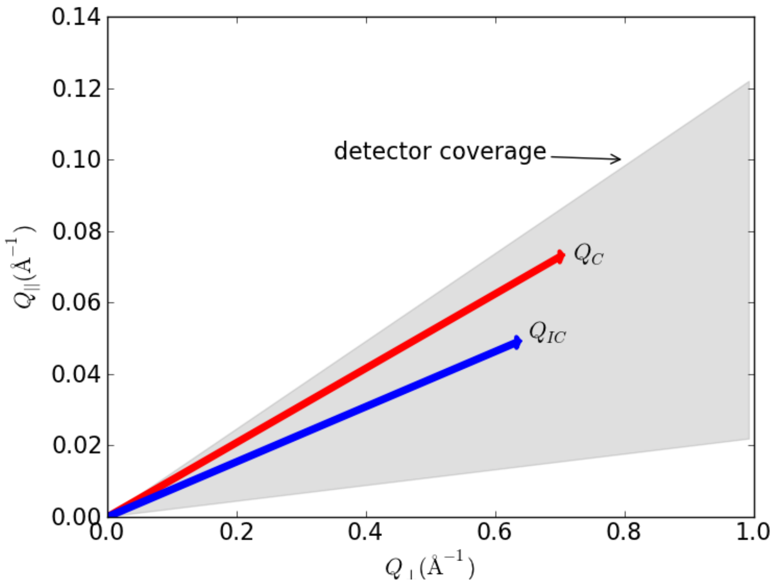
Pulsed Magnetic Field

Slides Contributed by Garrett Granroth

TOF Neutron Diffraction

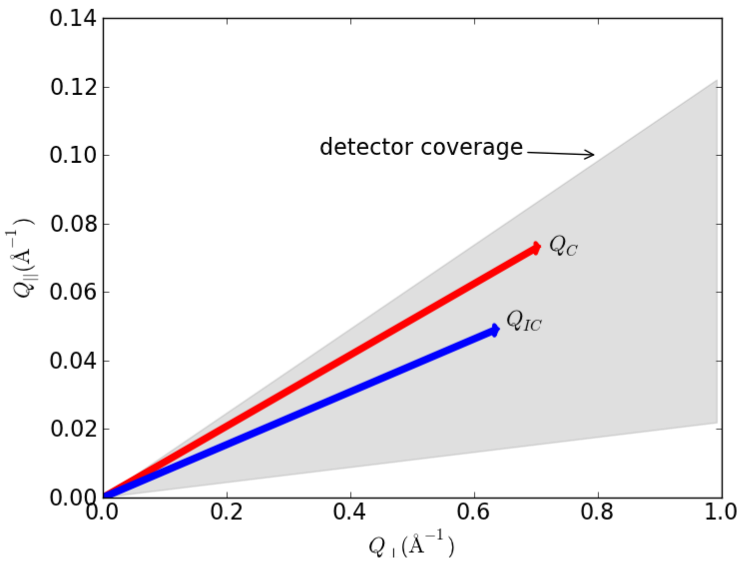
- Wavelength is encoded in TOF
- Fixed detector array
- Laue pattern; but TOF allows identification of individual peaks
- Means multiple Bragg reflections for a single orientation

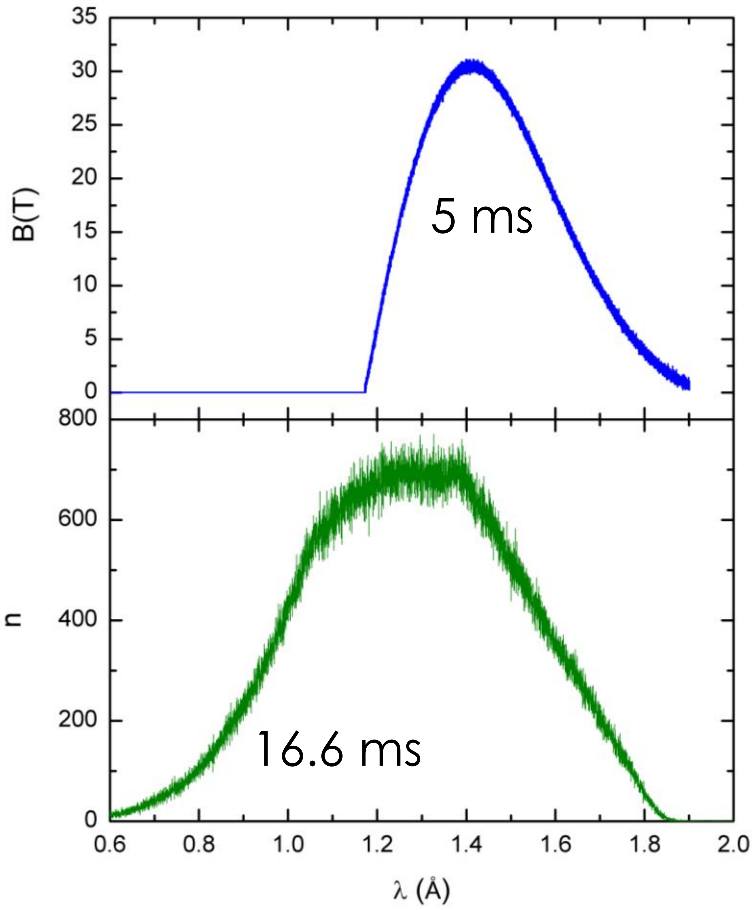


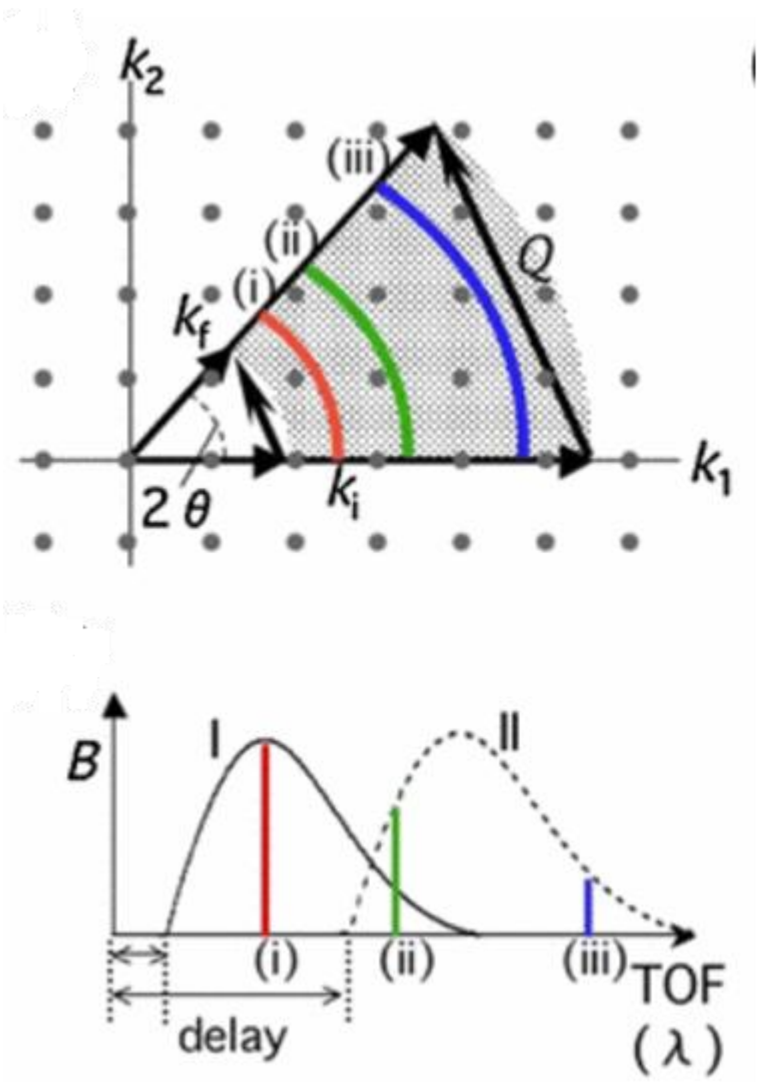


TOF neutrons + pulsed magnet

- Independently vary field and wavelength band as a function of time







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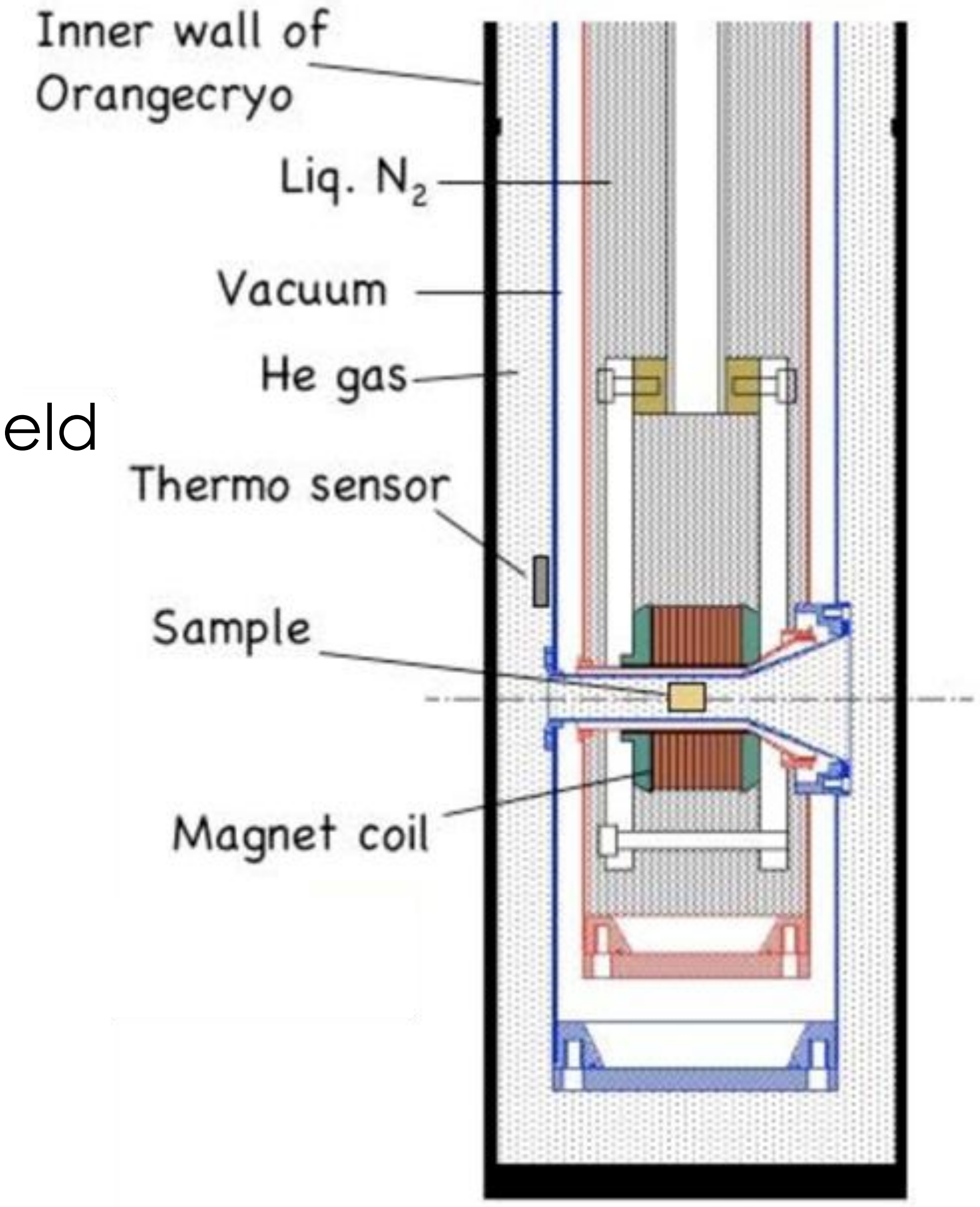
The Magnet

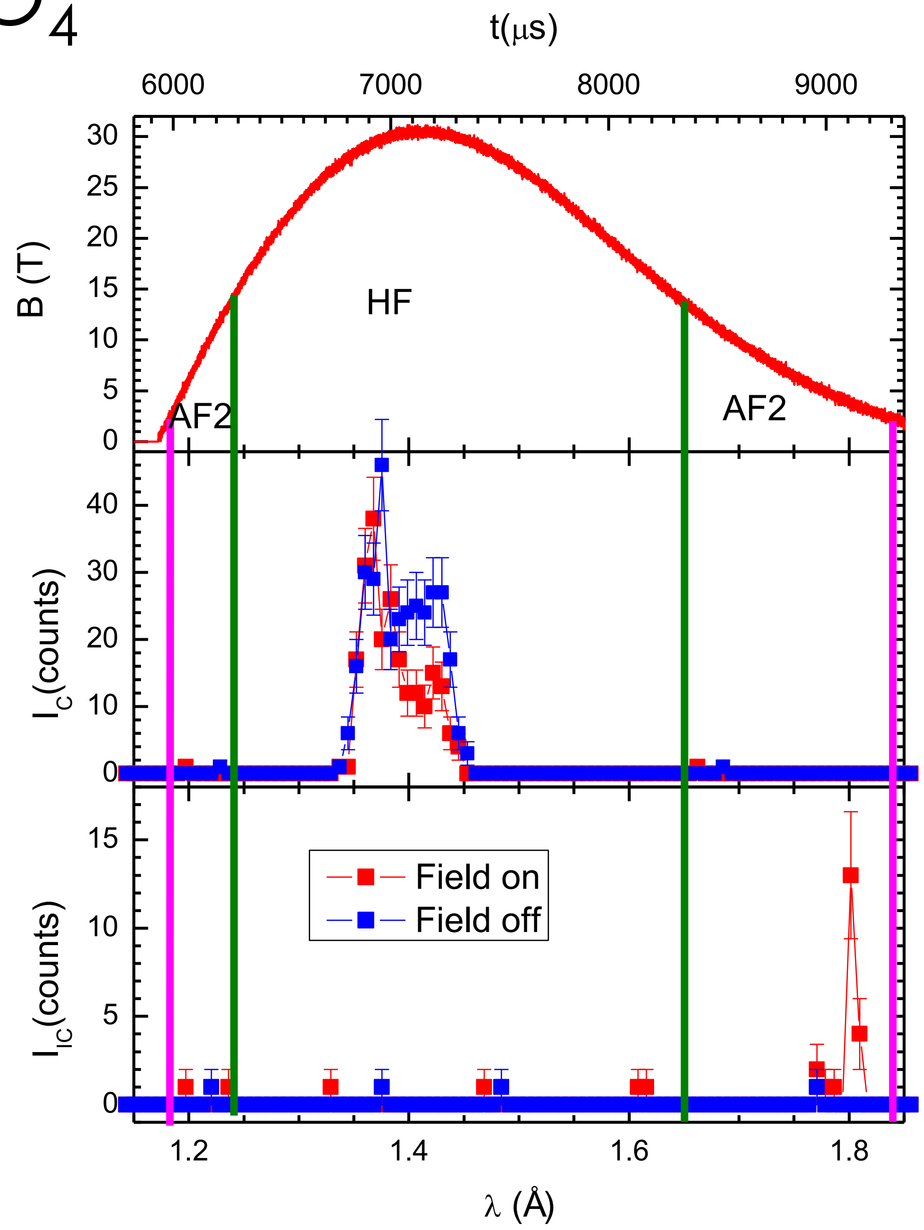
- Insert for an orange cryostat
- Can apply up to 30 T on a sample
- Time synced to facility timing signal
- 1 pulse every 2-5 min depending on peak field
- 14 degrees of forward scattering angle

Design of Prof. H. Nojiri



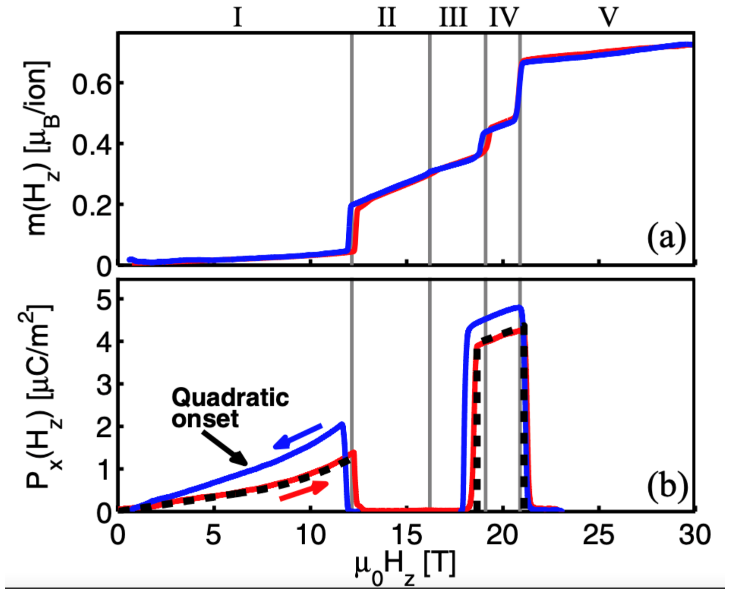
First High field measurement $MnWO_4$

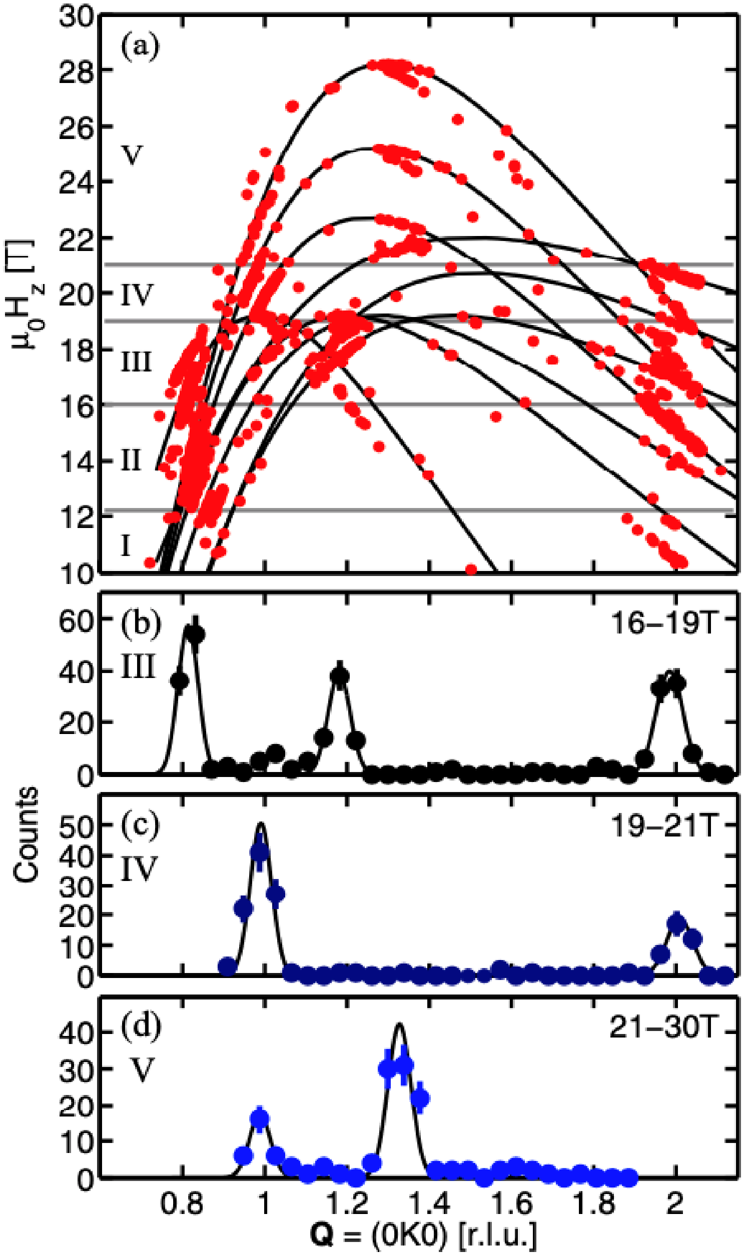
- SEQUOIA in white beam mode
  - No Fermi Chopper; T0 @ 30 Hz ~ 0.5 Å bandwidth
  - Phase magnet pulse for commensurate peak at 30 T
  - Peak is for 30 pulses; 5 minutes between pulses
  - Sum over two tubes and pixels 50-70
  - T = 2 K
- Peak shape change in HF phase
- Two reflections observed in single angle setting!
- Details in H. Nojiri *et al.* PRL **106**, 237202 (2011)

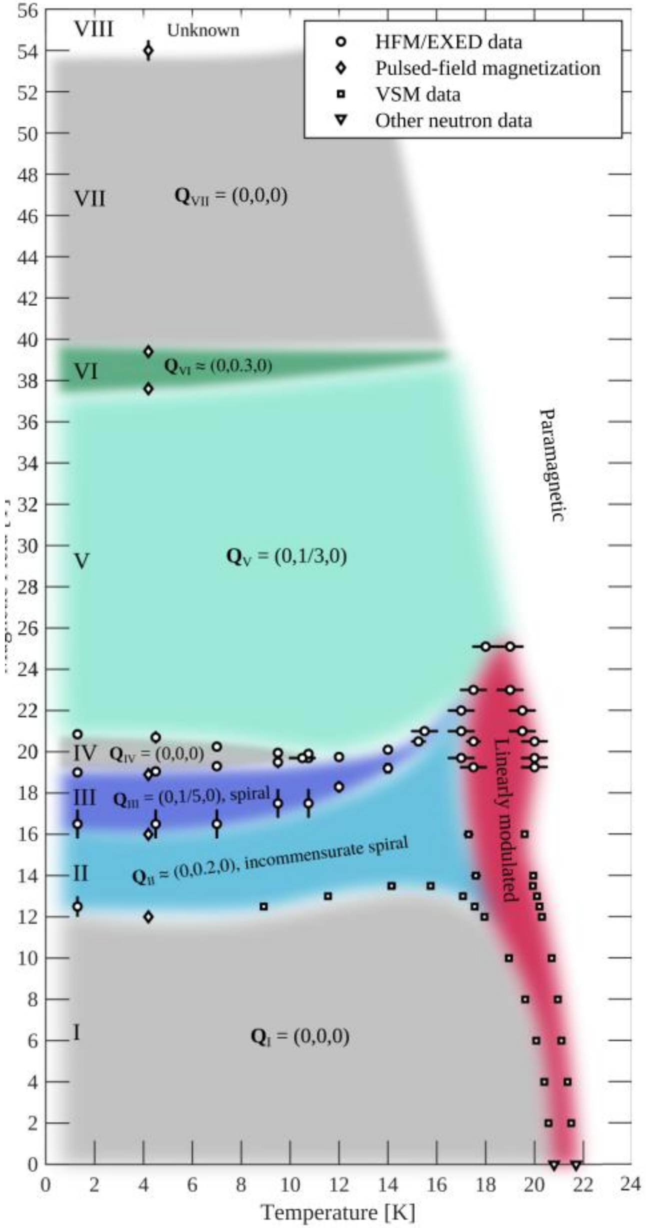


MultiFerroics – $LiNiPO_4$

- Correlation between charge Polarization and magnetism is useful.
- Lots of structural data from neutron Laue with pulsed magnets







R. Toft-Petersen *et al.* Phys. Rev. B **95**, 064421 (2017).

E. Fogh *et al.* Phys. Rev. B **101**, 024403 (2020).

Extreme High Temperature Levitators

Slides Contributed by Dante Quirinale

Containment is **not** simple at high temperatures

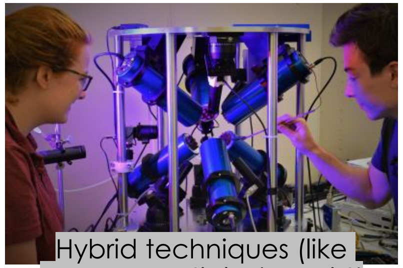
- For neutrons, we generally need large samples and long measurement times
  - Samples usually *stay* hot for hours
- There aren't *that* many materials that are low background – Al, V, Nb….
- Loss of containment can be *very* bad if the sample is activated
- We support lots of different samples per year. Sometimes, things don't go great – **hopefully** things break on a pre-beamtime test!

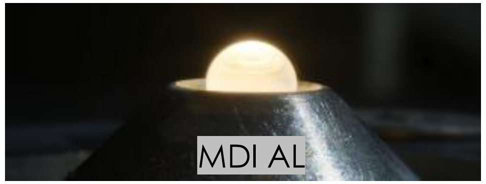
FIG. 3. Niobium embrittled by water at elevated temperature.

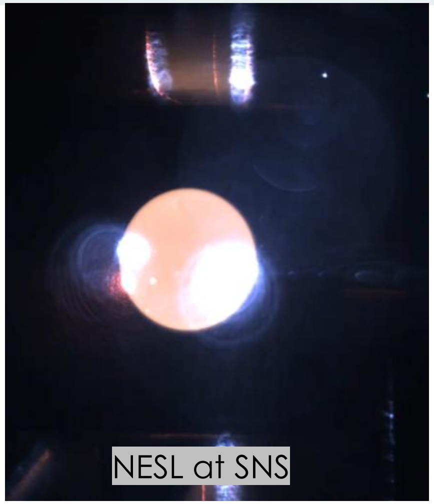
"At sufficiently high temperatures, **everything** reacts with **everything**."

Pushing materials to extremes temperatures

	Aerodynamic* (AL)	**Electrostatic* (ESL)**	**Electromagnetic (EML)**	**Acoustic (ACL or USL)**
Optimal Use	Ceramics	Metals, Semiconductors	Metals	Solutions, low density solids
Material Limitation	Density, Viscosity, Atmosphere	Conductivity, Vapor Pressure	Conductivity, Vapor Pressure	Density, surface tension
Max Temperature	~3000 °C	~3000 °C?	~4000 °C?	~1000 °C (under MG)
Complexity	Low-Medium	Very High	Low	Low-Medium
Thermophysical property meas.	With Difficulty	Fully Capable	Limited (on earth)	Limited
Atmosphere capability	Atm-pressure	UHV – pressure	UHV – pressure	Atm-pressure


Hybrid techniques (like Aero-Acoustic) also exist!


MDI AL

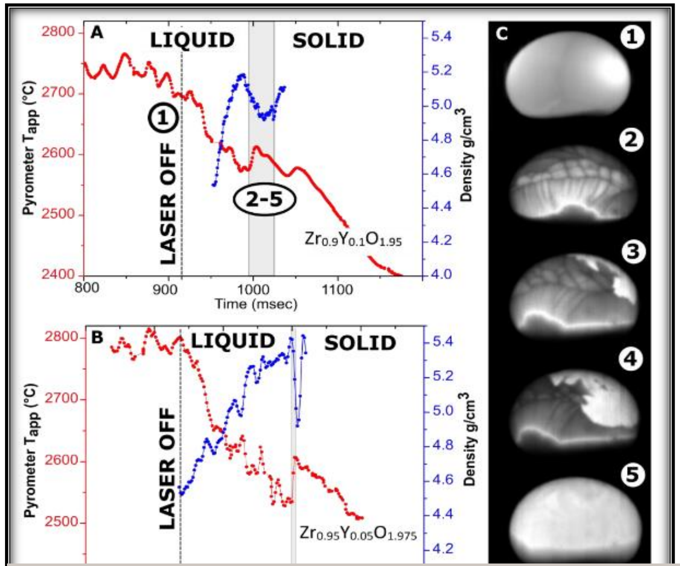

NESL at SNS


EML at SNS

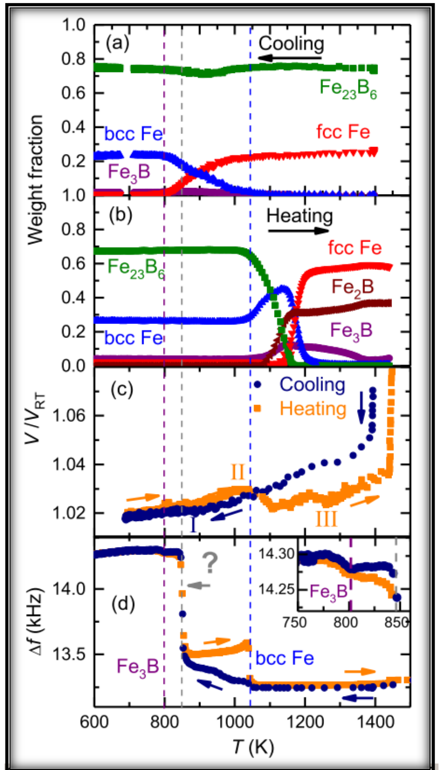

ORNL BigLev

Thermophysical Properties

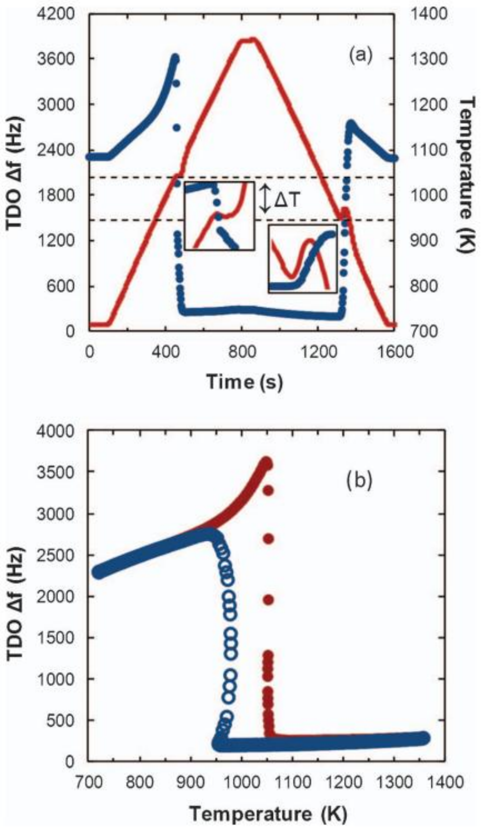
- Density, viscosity, surface tension, some calorimetry, even possible to map magnetic transitions
- Errors often much smaller than conventional experiments ….tradeoff is that these experiments are often much more challenging!



Ushakov, Sergey V., Jonas Niessen, Dante G. Quirinale, Robert Prieler, Alexandra Navrotsky, and Rainer Telle. "Measurements of Density of Liquid Oxides with an Aero-Acoustic Levitator." *Materials* 14, no. 4 (2021): 822.

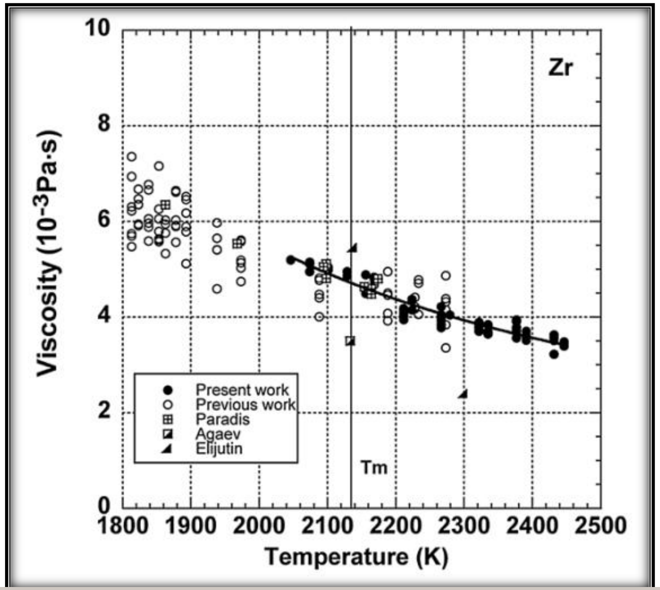


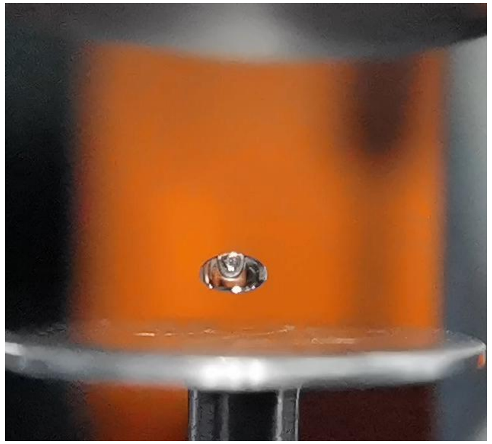
Quirinale, D. G., et al. "In situ Investigation of Magnetism in Metastable Phases of Levitated Fe 83 B 17 During Solidification." *Physical Review Applied* 8, no. 5 (2017): 054046.



Curie Temperature observed in steel

Rustan, G. E., N. S. Spyrison, A. Kreyssig, R. Prozorov, and A. I. Goldman. "Noncontact technique for measuring the electrical resistivity and magnetic susceptibility of electrostatically levitated materials." *Review of Scientific Instruments* 83, no. 10 (2012): 103907.



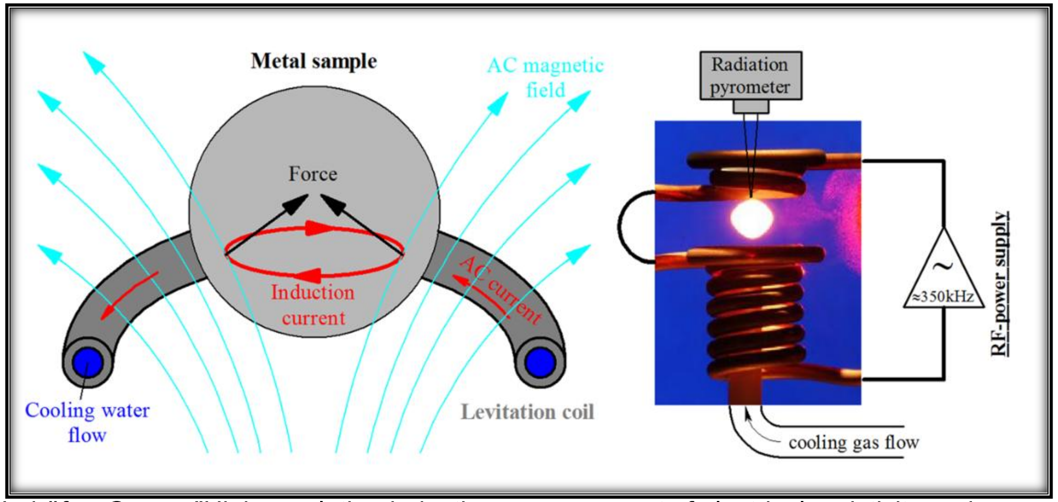


Ishikawa, Takehiko, Paul-François Paradis, Junpei T. Okada, and Yuki Watanabe. "Viscosity measurements of molten refractory metals using an electrostatic levitator." *Measurement Science and Technology* 23, no. 2 (2012): 025305.

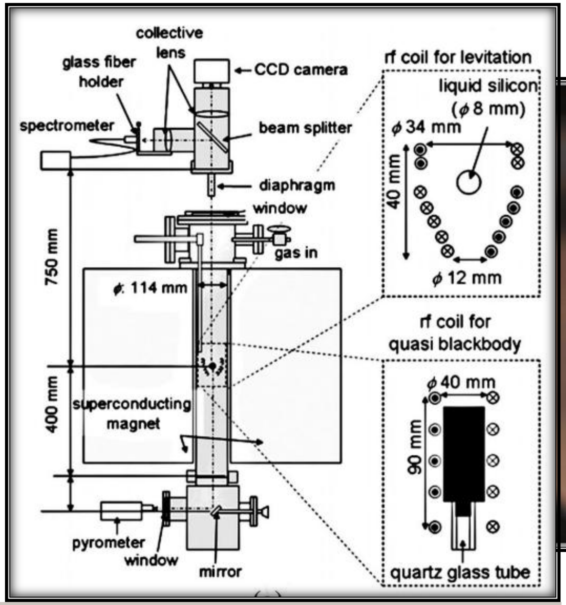
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

Modern EML

- Requires material to conduct (or be heated to conductive state)
- Heating intrinsically linked to levitation
- Operates in vacuum or under atmosphere
- Expect deformation of sample terrestrially, not in microgravity…
- Methods exist for measurement of temperature, and thermophysical properties…..
- Natural stirring mechanism; low thermal gradients



Lohöfer, Georg. "High-resolution inductive measurement of electrical resistivity and density of electromagnetically levitated liquid metal droplets." *Review of Scientific Instruments* 89, no. 12 (2018): 124709.

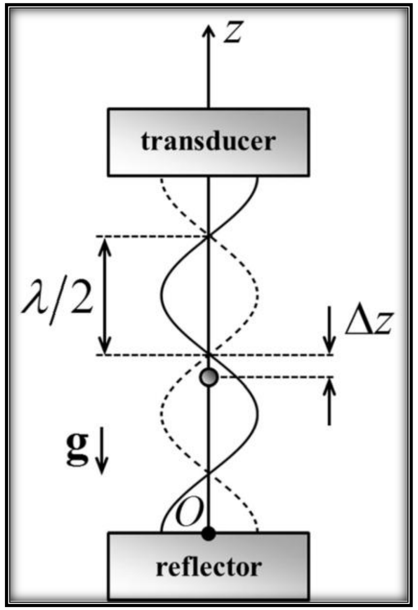


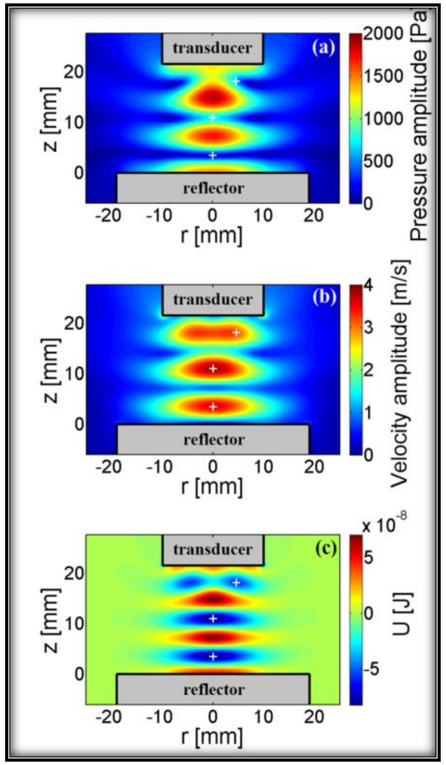
Fun times at the National High Magnetic Field Lab

Gao, L., Shi, Z., Li, D. *et al.* Applications of Electromagnetic Levitation and Development of Mathematical Models: A Review of the Last 15 Years (2000 to 2015). *Metall Mater Trans B* **47,** 537–547 (2016). https://doi.org/10.1007/s11663-015-0522-8

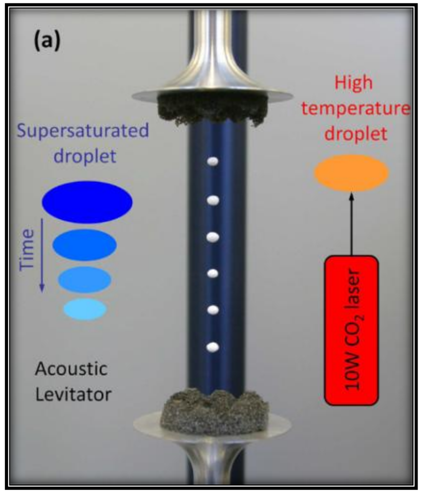
Acoustic Levitation

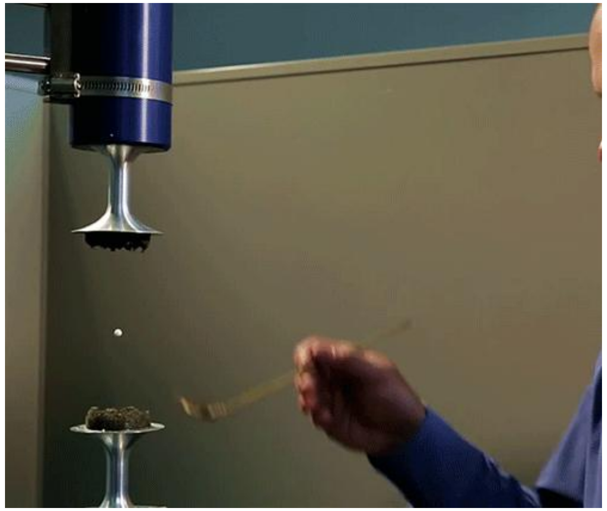
- Samples rest in pressure nodes created by standing waves
- Levitation limited by density, but possible with correct optimization to float refractory metals
- Temperature generally limited to less than 1200 C
- Originally, just a transducer/reflector pair was most common configuration
- Investigated by NASA in the 1980s as microgravity technique; managed to get up to 1000 °C…





Andrade, Marco AB, Nicolás Pérez, and Julio C. Adamowski. "Review of progress in acoustic levitation." *Brazilian Journal of Physics* 48, no. 2 (2018): 190-213.

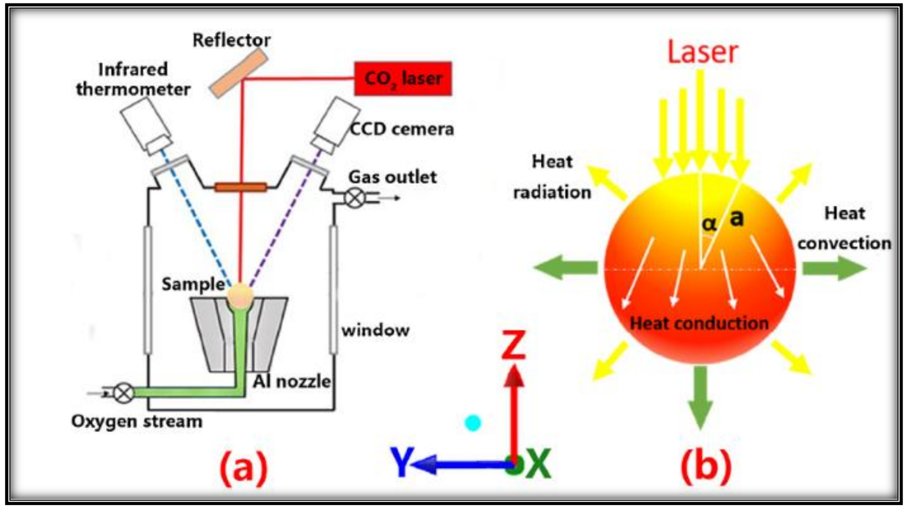




Benmore, C. J., and J. K. R. Weber. "Amorphization of molecular liquids of pharmaceutical drugs by acoustic levitation." *Physical Review X* 1, no. 1 (2011): 011004.

Aerodynamic Levitation

- Float on a gas stream in a special nozzle
- Heat from above (and sometimes below) with a CO_2 laser, or use induction coils
- Pronounced thermal gradients can exist across the sample….
- Allows rapid, easy heating of many different materials, quick sample changes

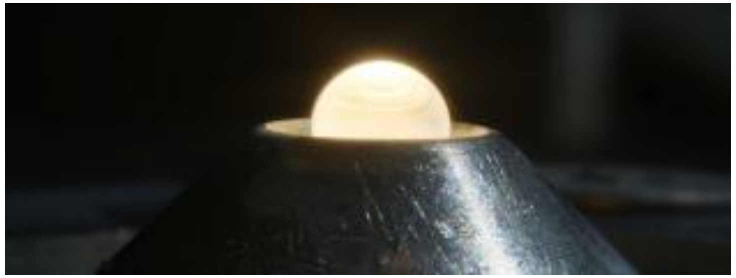


Ge, Xuan, Xiaowei Xu, Qiaodan Hu, Wenquan Lu, Liang Yang, Sheng Cao, Mingxu Xia, and Jianguo Li. "Ambiguous temperature difference in aerodynamic levitation process: Modelling, solving and application." *Journal of Materials Science & Technology* 35, no. 8 (2019): 1636-1643.

TABLE II. Summary of the temperature gradients (°C) found in liquid and solid samples.

Top $T_A - T_B$	1000–1500 °C	1500–2500 °C	2500–3000 °C
Single crystal ruby[a]	0	0	…
Spherical ZrO_2 (Ball mill)	0	0–30	…
Liquid (ZrO_2, Y_2O_3, Al_2O_3, $CaO.Al_2O_3$)[b]	…	10–20	10–30
ZrO_2 solid (Molten hearth)	20–60	60–180	250–320
ZrO_2 solid (Vibrating table)	80–120	120–180	180–310
Entire $T_A - T_D$	1000–1500 °C	1500–2500 °C	2500–3000 °C
Single crystal ruby[a]	0	0–10	…
ZrO_2 Rotating (Ball mill)	0	0–30	…
Liquid (ZrO_2, Y_2O_3, Al_2O_3, $CaO.Al_2O_3$)[b]	…	30–60	100–200
ZrO_2 solid (Molten hearth)	110–260	260–590	590–900
ZrO_2 solid (Vibrating table)	~650[c]	650–970	970–1120

[a]Single crystal ruby melts at ~2050 °C.
[b]Different samples were used to achieve a larger liquid range, i.e., $CaO.Al_2O_3$ T_m = ~1371,[32] Al_2O_3 T_m = ~2050 °C,[32] Y_2O_3 T_m = 2425 °C,[31] and ZrO_2 T_m = 2715 °C.[31]
[c]Below T_A = 1450 °C, position T_D (towards the bottom of the spheroid) had temperatures below what the filament disappearing pyrometer could detect (<700 °C).



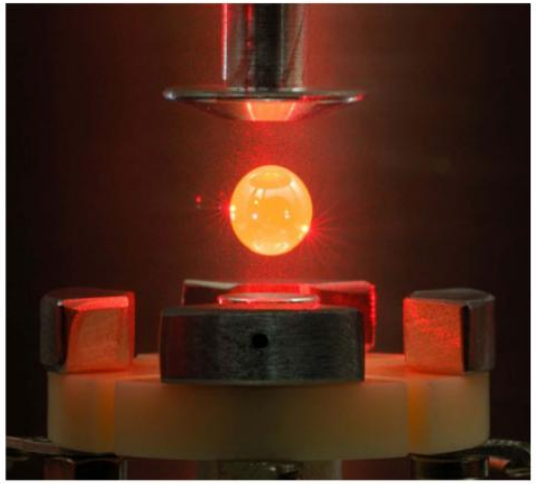
MDI, www.matsdev.com

McCormack, Scott J., Anthony Tamalonis, Richard JK Weber, and Waltraud M. Kriven. "Temperature gradients for thermophysical and thermochemical property measurements to 3000 C for an aerodynamically levitated spheroid." *Review of Scientific Instruments* 90, no. 1 (2019): 015109.

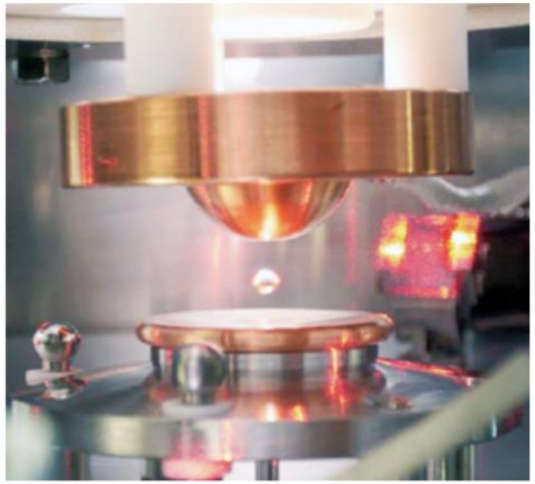
Electrostatic Levitation

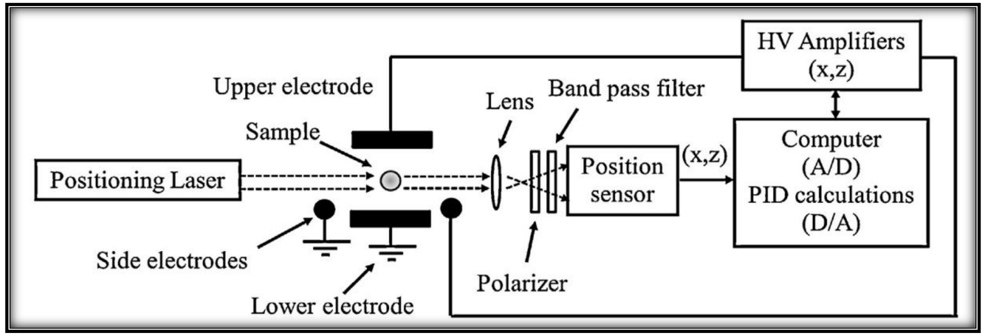
- The most challenging technique, but the most stable and precise
- Requires conductive material
- Sample recharged by high energy UV lamp
- Heating is decoupled from levitation

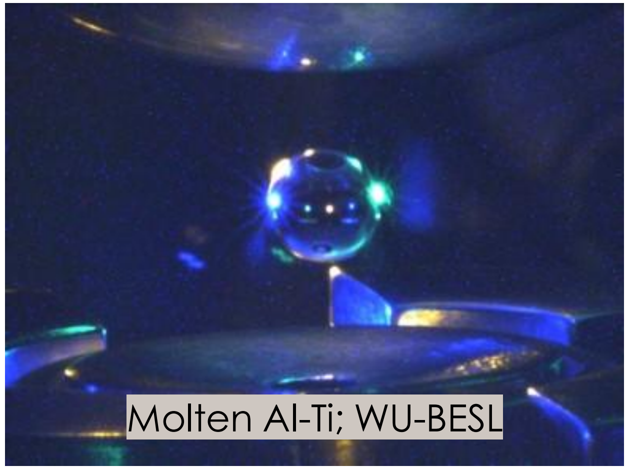
DLR



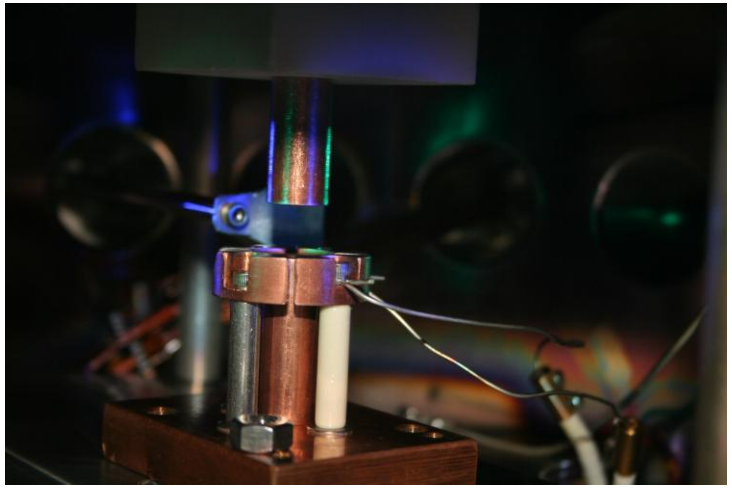
JAXA







Molten Al-Ti; WU-BESL

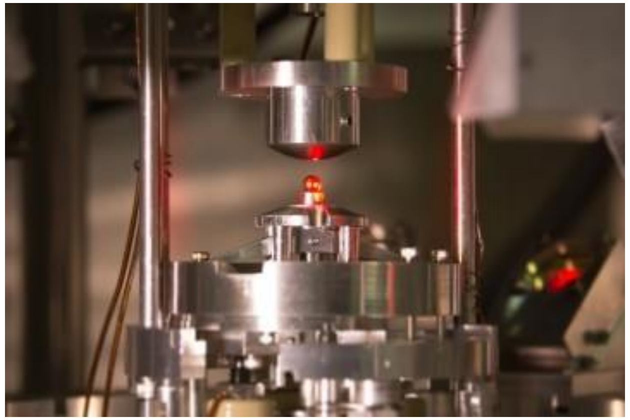


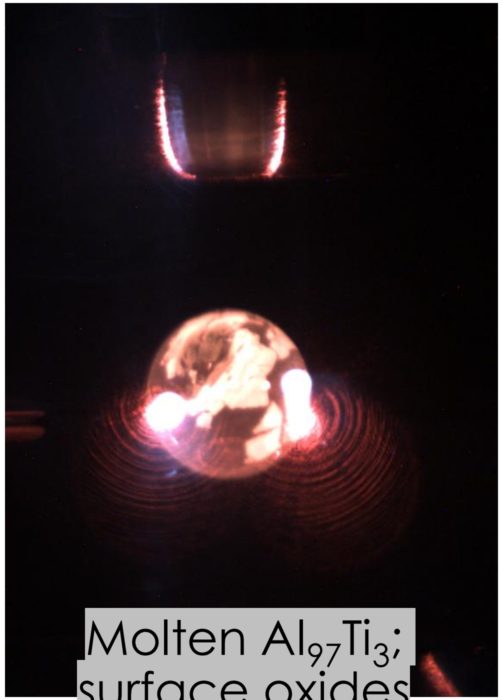
Iowa State University

Paradis, Paul-François, Takehiko Ishikawa, Geun-Woo Lee, Dirk Holland-Moritz, Jürgen Brillo, Won-Kyu Rhim, and Junpei T. Okada. "Materials properties measurements and particle beam interactions studies using electrostatic levitation." *Materials Science and Engineering: R: Reports* 76 (2014): 1-53.

Neutron ElectroStatic Levitator (NESL)

- **Samples must be able to charge (metals, semiconductors)**
- Operated at high vacuum (~10^{-7} torr)
- Unobstructed view of sample
- Internal sample changer with 30 slots
- Runs at **NOMAD** (pair distribution function), **ARCS** (inelastic scattering), **CNCS** (quasi-elastic scattering)



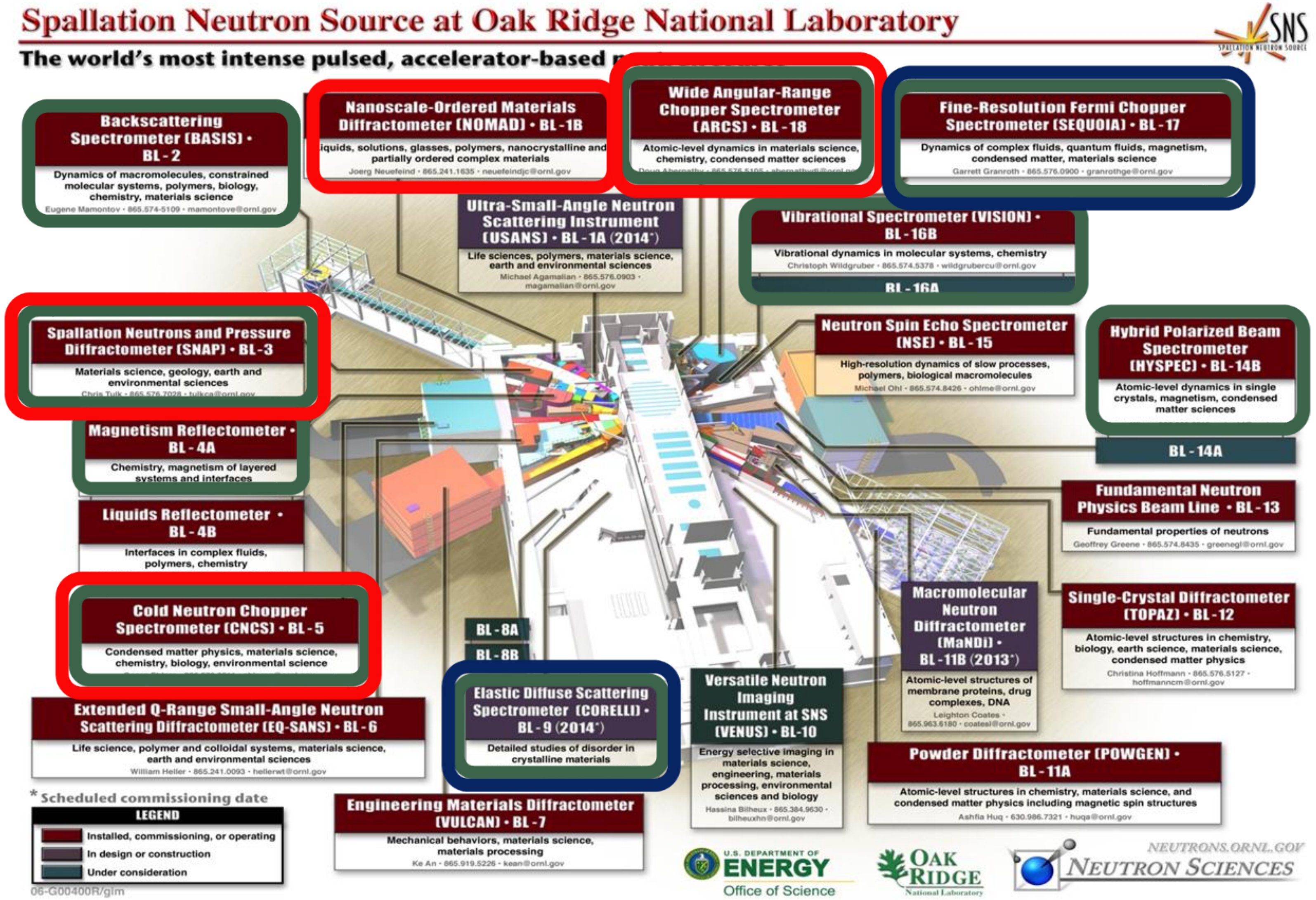


Extreme conditions at the SNS

Pressure

Levitators

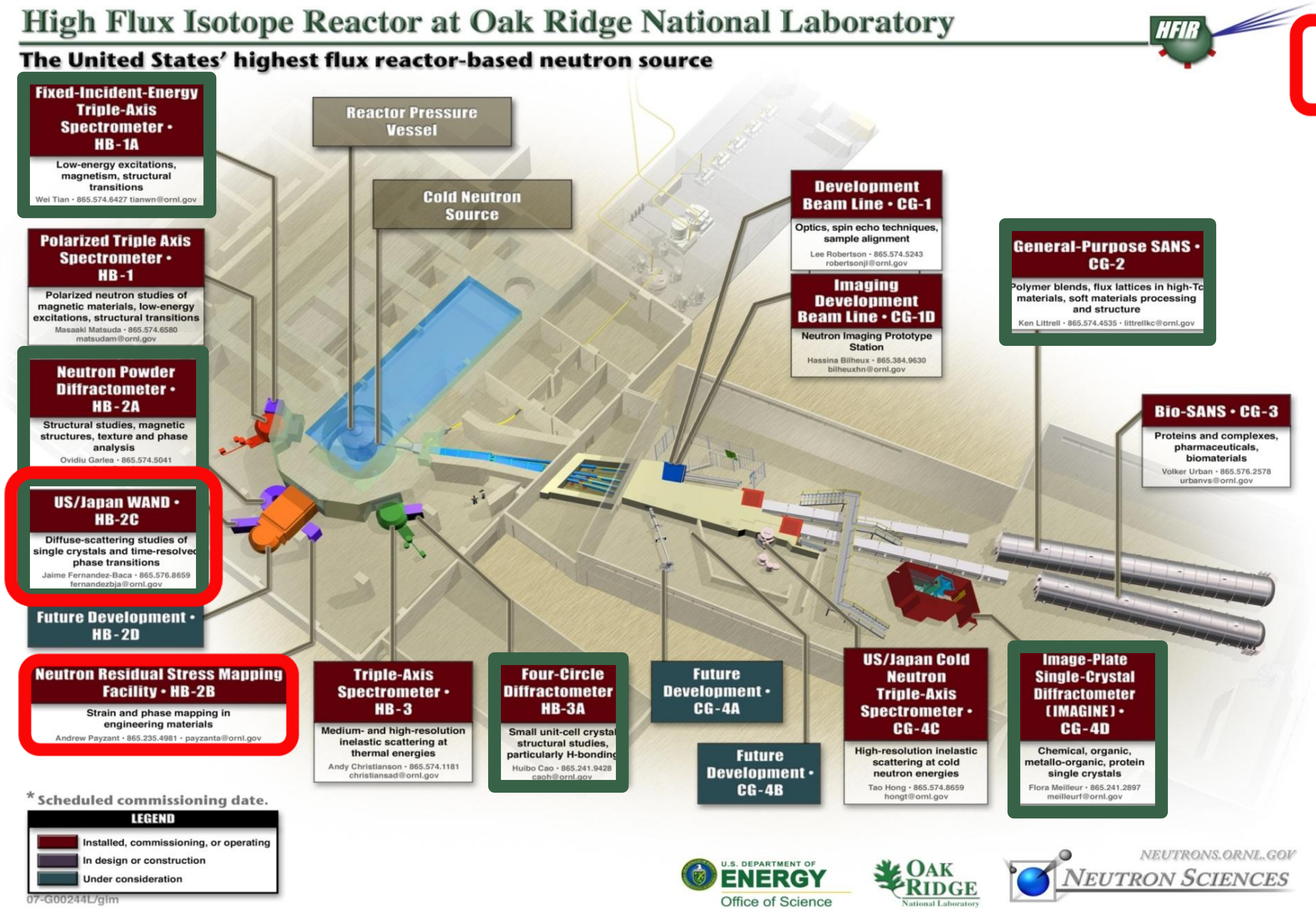
Pulsed Magnets



Extreme conditions at the HFIR

Pressure

Levitators



Neutron study of material under extreme conditions:

Poses new challenges.

Allows unique understanding of materials' behavior both at the fundamental level and their operating Limits.

Neutron scattering techniques can provide unique insights in this space:

- Track phase transitions,
- Assess the coupling between lattice spin and charge DoF.
- Determine magnetic structures.
- Evaluate the relative strength of competing interactions.

Beyond its own merits, the challenges addressed when performing these experiments can be translated into better experiments across the board:

- Smaller samples
- Improved experimental control
- Sophisticated data collection, reduction and analysis

Suggested Reading:

Pressure (Antonio dos Santos):

- Techniques in High Pressure Neutron Scattering" by Stefan Klotz, CRC Press (2016).
- "High-Pressure Physics, J. Loveday", CRC Press (2012)

Pulsed Magnets (Garrett Granroth):

- *"Pulsed High Magnetic Fields for Neutron and X-ray Scattering Experiments"* by Nojiri, H. Journal of Neutron Research 12(4):279-281 December 2004
- *"Automated Pulsed Magnet System for Neutron Diffraction Experiments at the MLF in J-PARC"* by Watanabe, M.; Kihara, T.; Nojiri, H. Quantum Beam Sci. 2023, 7, 1.

Levitators (Dante Quirinale):

- *"Electrostatic levitation facility optimized for neutron diffraction studies of high temperature liquids at a spallation neutron source."* by Mauro, Nicholas et al, Review of Scientific Instruments. 87. 013904. (2016)
- "Review of Progress in Acoustic Levitation." By Andrade, Marco Aurelio, et al. Brazilian Journal of Physics. 48. (2017)