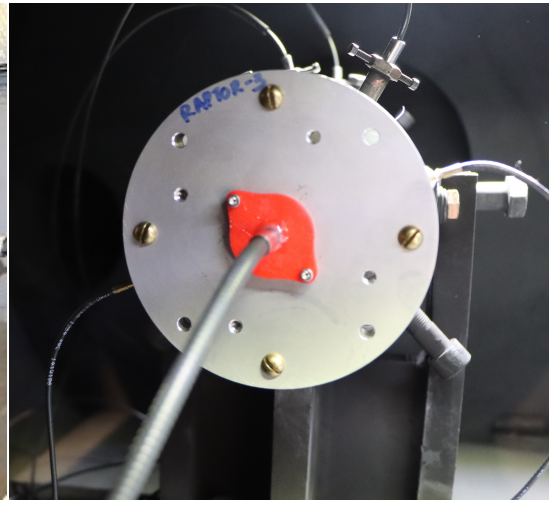
SAND2022-3062C



Structural evolution of f-electron system under dynamic compression

Presented by: Sakun Duwal

Team members: Chad McCoy, Dan Dolan, Cody Melton, Marcus Knudson, Chris Seagle, Seth Root, Richard Hacking, Bernardo Farfan, Chris Johnson, C. S. Alexander

APS March meeting
March 16th, 20220
Chicago, IL

Sandia National Laboratories

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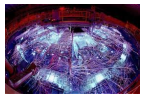
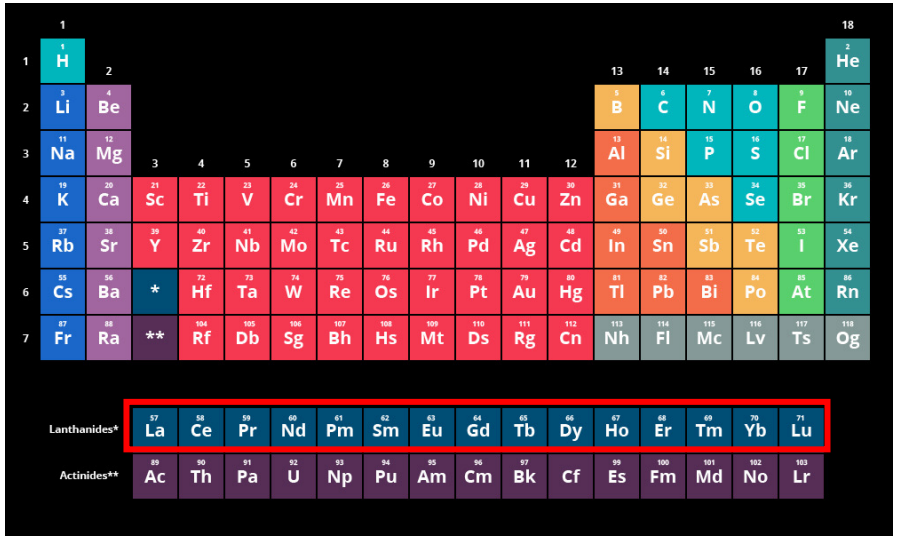
Outline



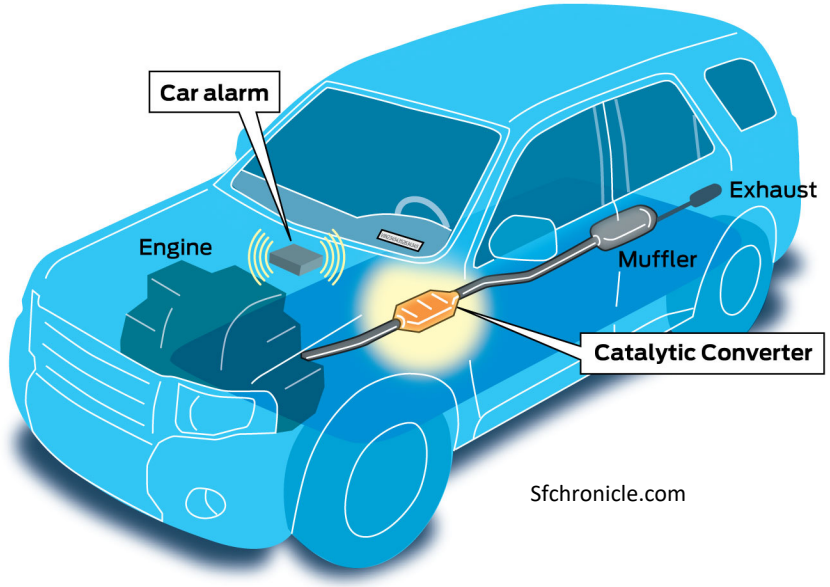
- Lanthanide -motivation
- Experimental methods
  - Laser shock, x-ray diffraction, Pyrometry (gas-gun)
- Results –XRD, Temperature measurements, Hugoniot data, DFT
- Summary

S. Duwal, C. McCoy, C. Melton, M. Knudson, S. Root, C. Seagle, D. Dolan.R. Hacking. In Preparation.

Properties of Lanthanides matter to many applications

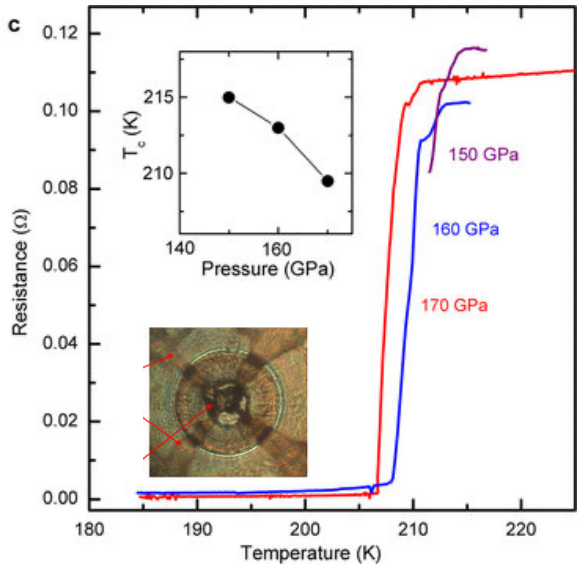


- Rare earth metals; technology metals
- Cell phones, color TVs
- A single iPhone contains eight different rare-earth metals; Vibration: Nd, Dy
- Batteries, lasers



Sfchronicle.com

- Catalytic convertors: Sm, Eu, Gd, Tb

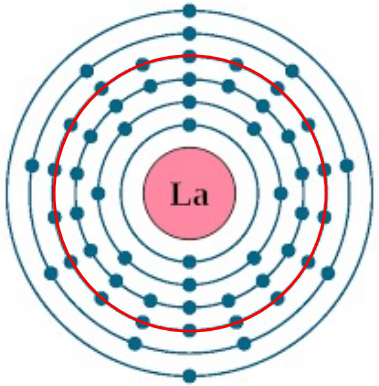


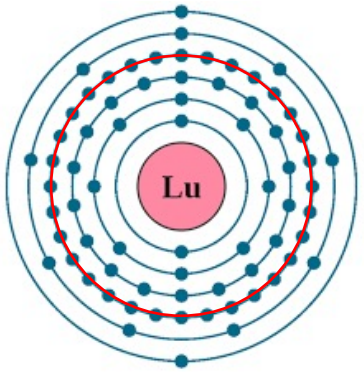
Drozdov. Nature. 2019

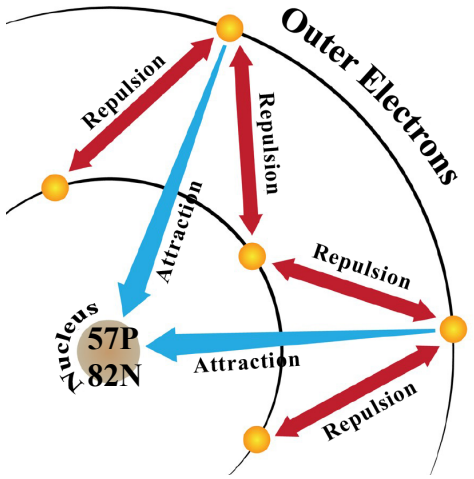
- Superconductors
  - La, Ce, Eu, Lu
- High-T_c superconductors, LaH_{10}, CeH_9

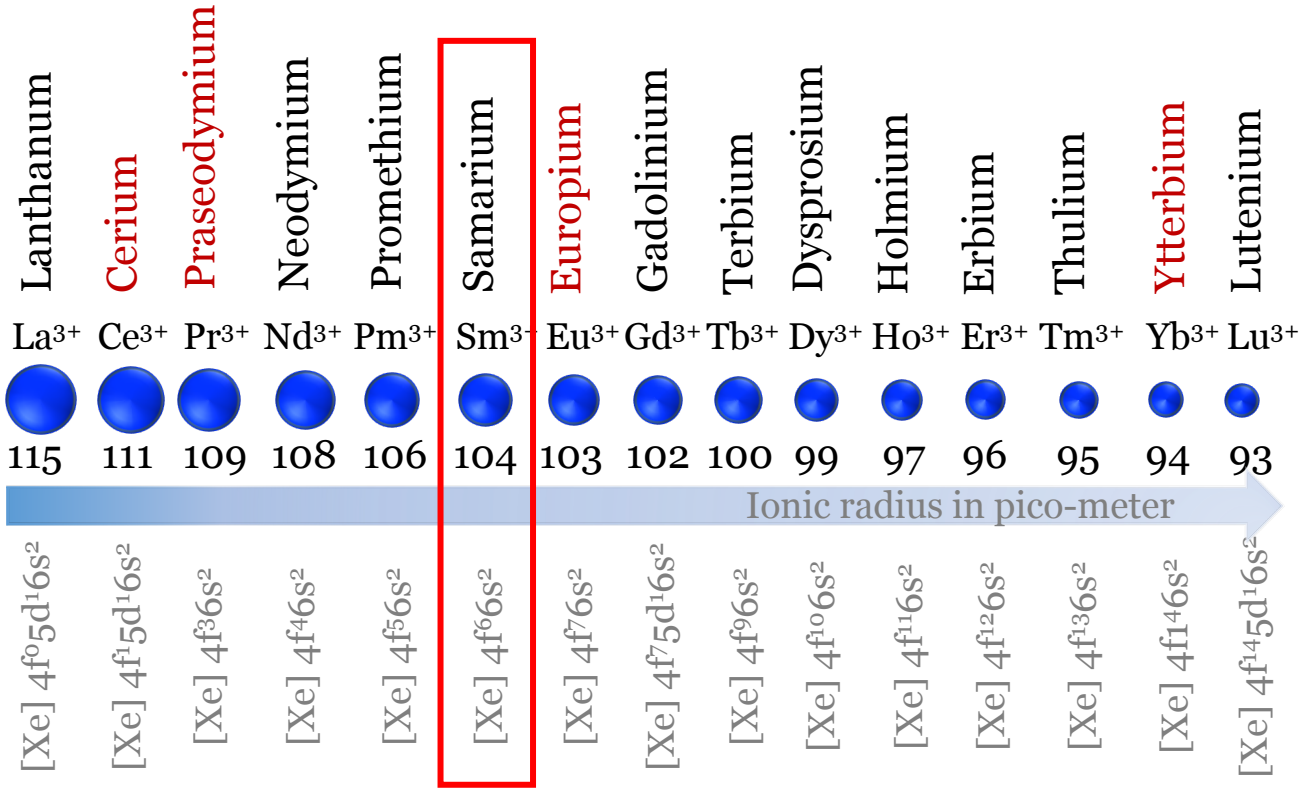
Properties of lanthanides has brought attention to the physics of f-electron metals

Lanthanides at high pressure: ideal for studying f-electron physics



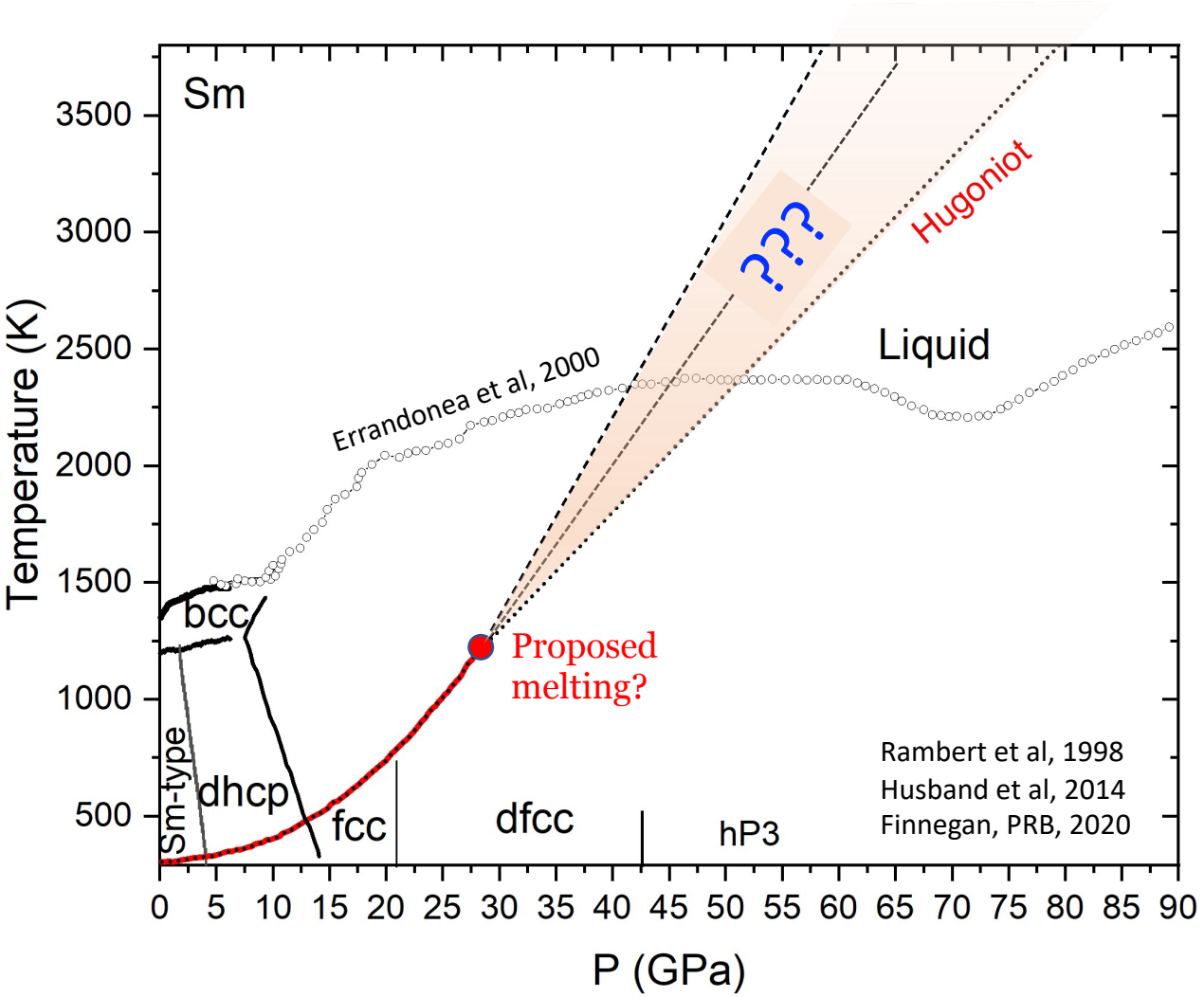






- 4f shielding in lanthanides → decrease in radius →inertness from 4f characters
- **Shielding or screening effect** of **f-orbital <s , p, d-orbital** → lanthanide contraction
- High P phase transition sequence: hcp → Sm-Type → dhcp → fcc → dfcc. However, in Ce from fcc → fcc' →bcm → bct (4f electron hybridization)
- Systematic study of lanthanides to understand the effects of f-electrons
- Samarium –phase transitions at high pressure

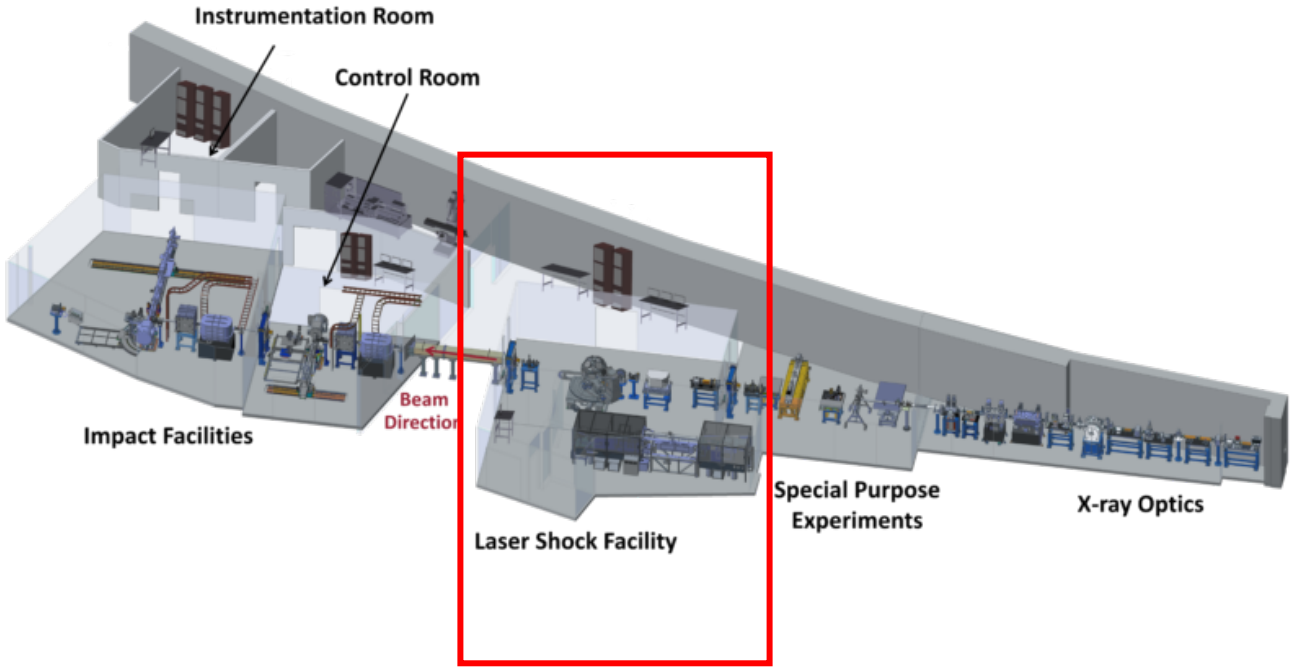
Sm at high pressure: many phases and large uncertainties



- DAC studies: Sm-type →dhcp → fcc → dfcc →hP3
- Gas-gun studies below 100 GPa (1975)
- Very few DFT studies
- Huge uncertainty in P-T Hugoniot space

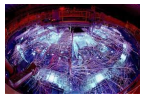
Unique measurements at DCS @ APS to reveal complex behavior of Sm

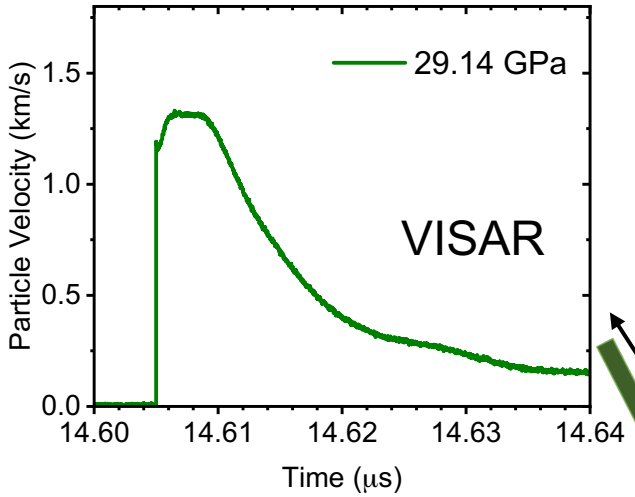
www.dcs-aps.wsu.edu



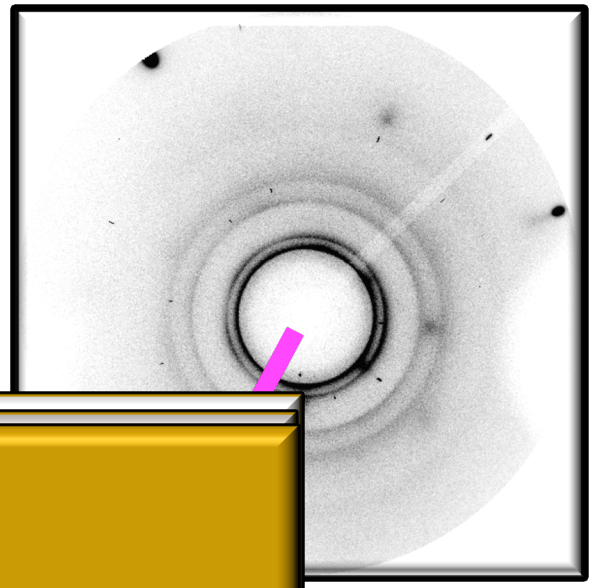
- Single- and two-stage gas guns, laser shock capability, multi-event hutch
- Time-resolved, in-situ measurements utilizing the tunable, high energy X-ray capabilities at the Advanced Photon Source (APS)
- Focus on diffraction, imaging, and scattering measurements; simultaneous continuum measurements

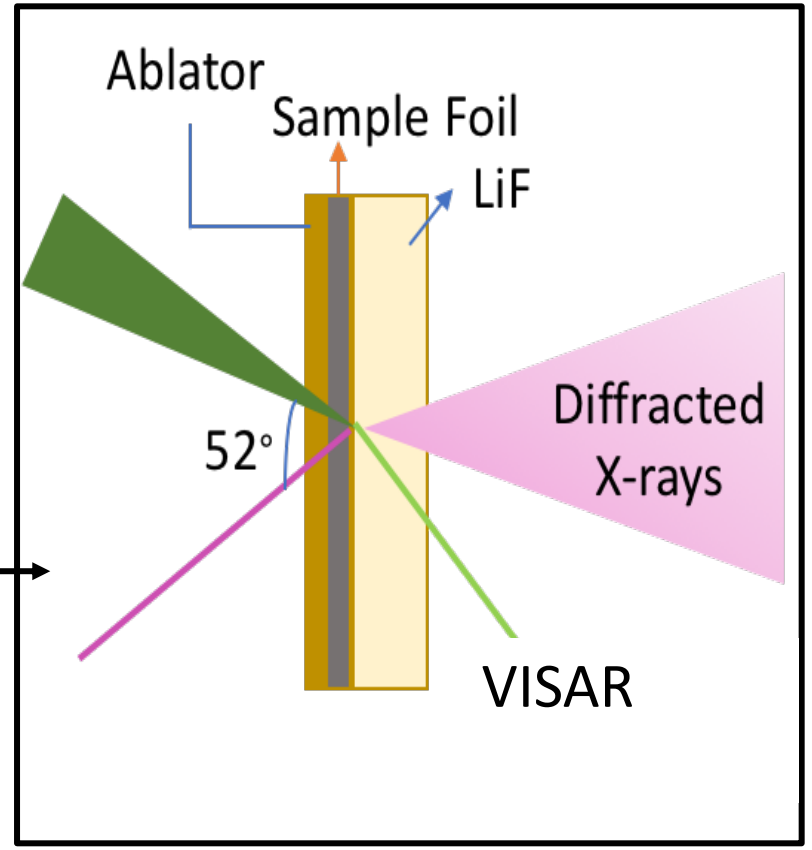
Multi-probe experiments yield simultaneous phase, P, density state

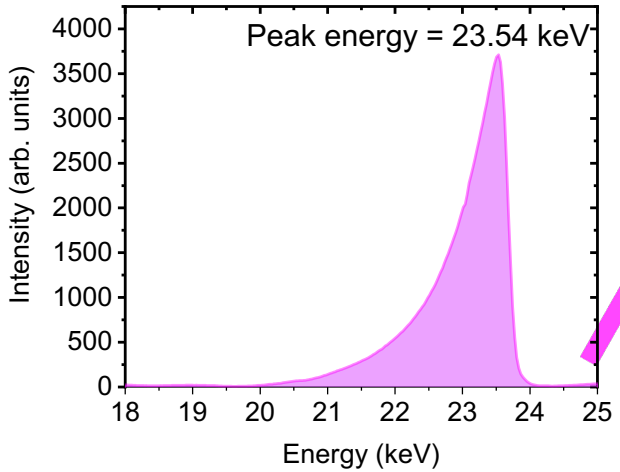




Laser interferometry to measure the surface velocity of solids moving at high speeds.



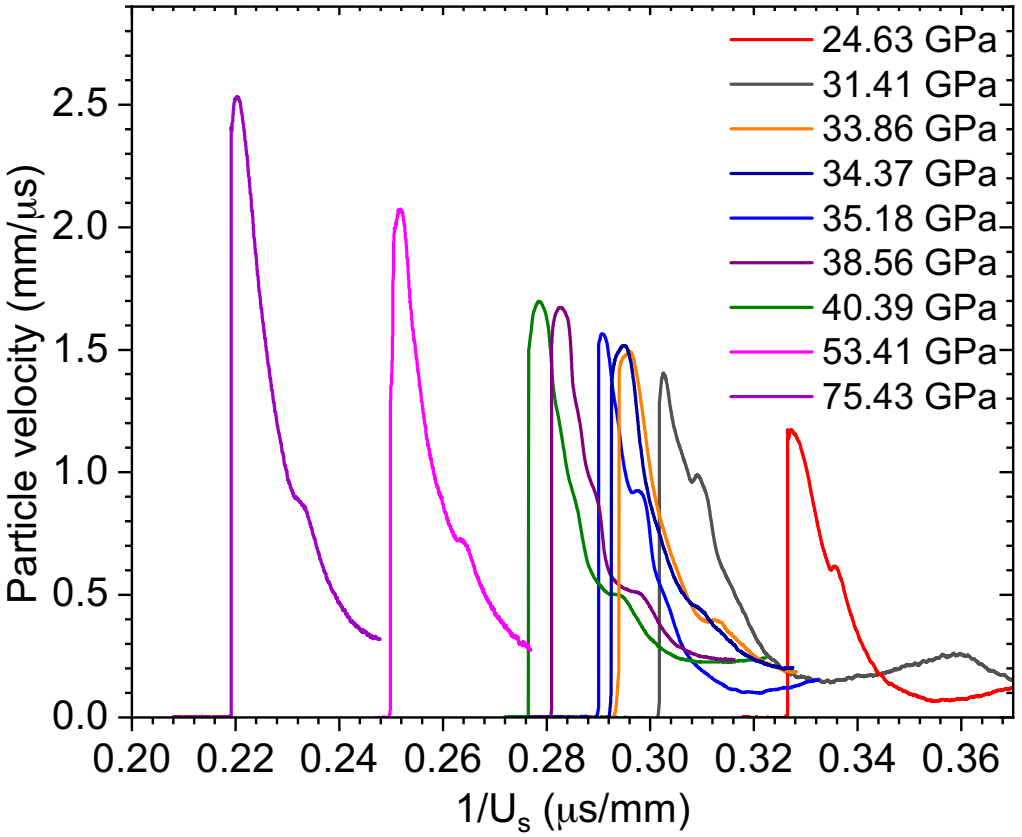


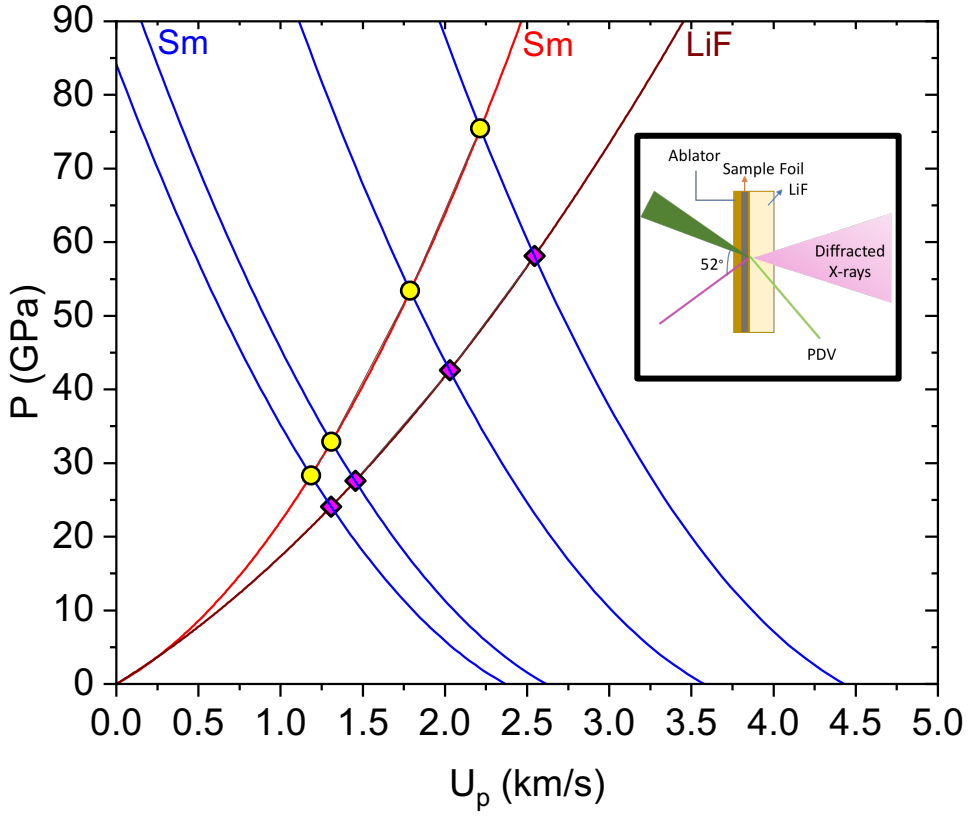


X-ray
23 keV

Laser, 351 nm
5 or 10 ns pulse
~100J
500 um spot size

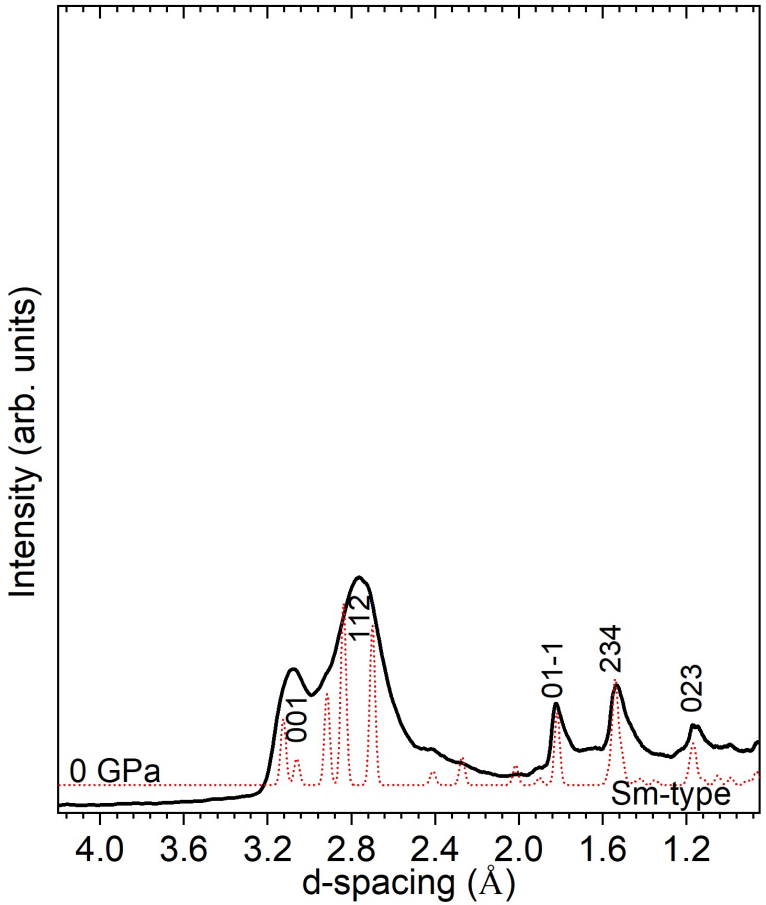
Velocimetry to determine pressure

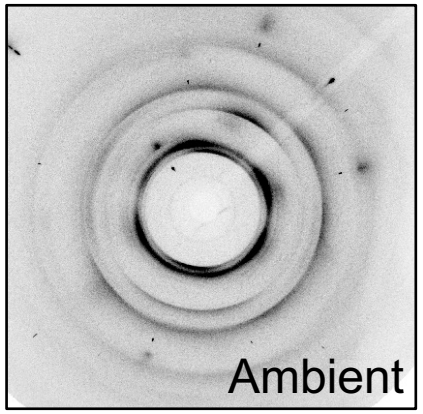




- Velocimetry measurements at Sm/LiF interface
- Impedance matching method to determine the in-material states

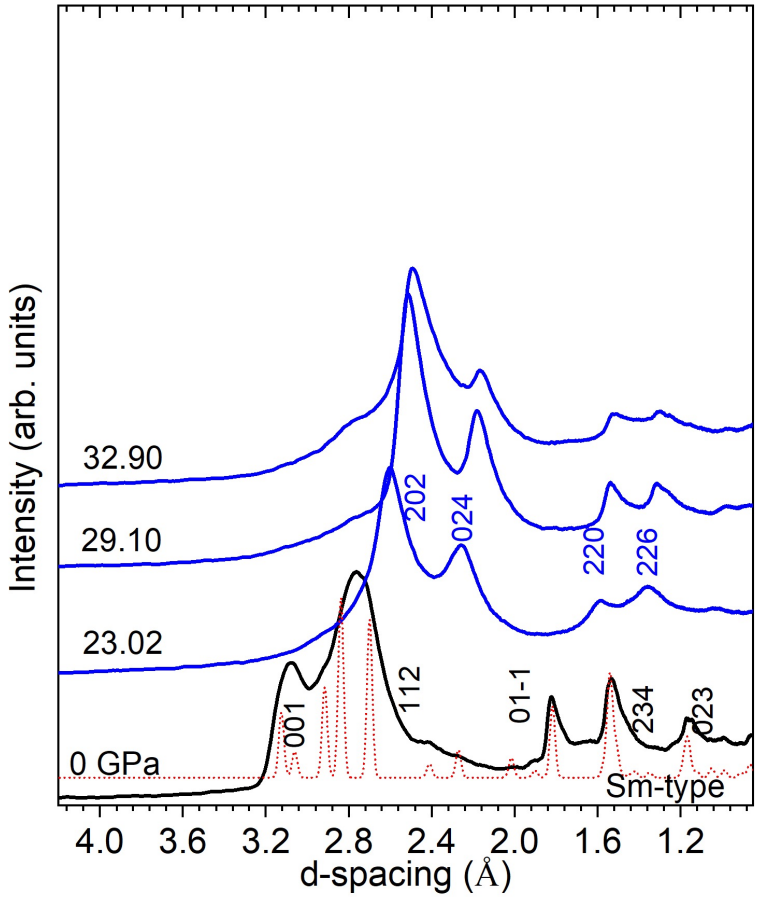
Structural evolution at high pressure

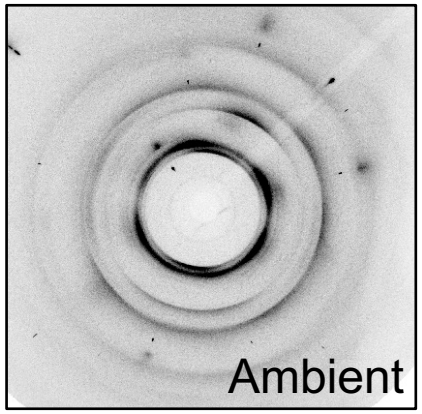


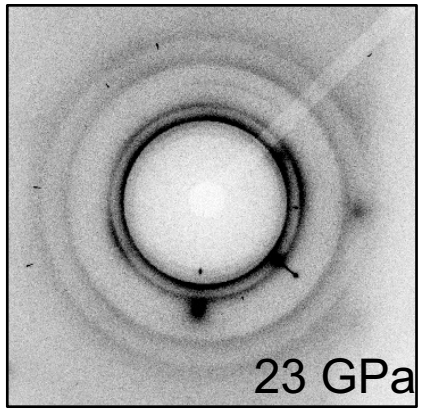


- Sm-type phase stable at ambient conditions

Structural evolution at high pressure

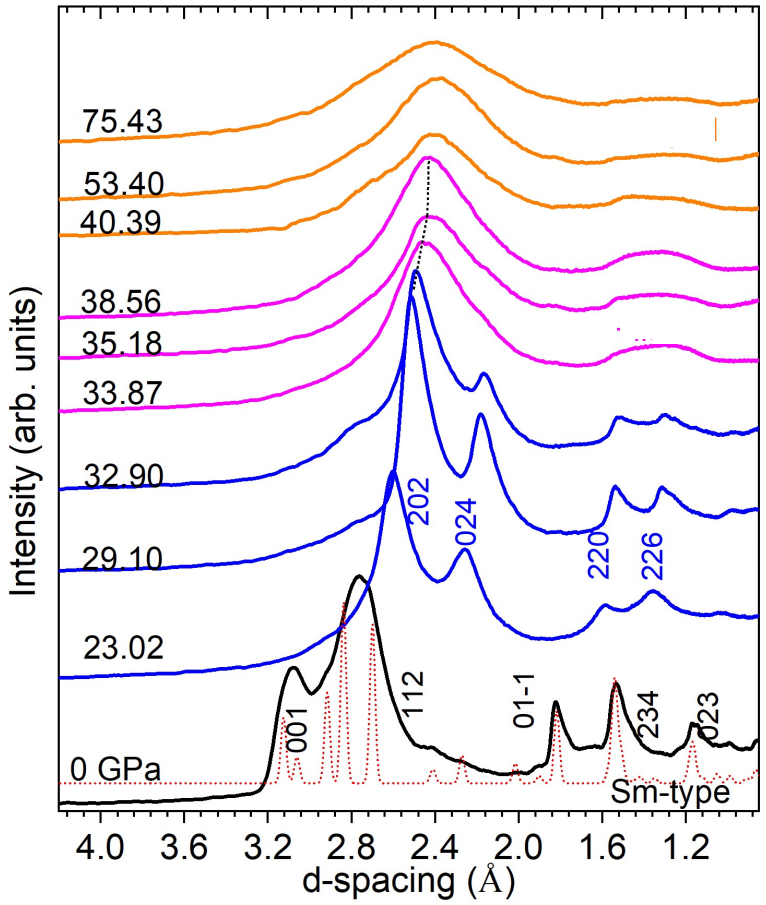


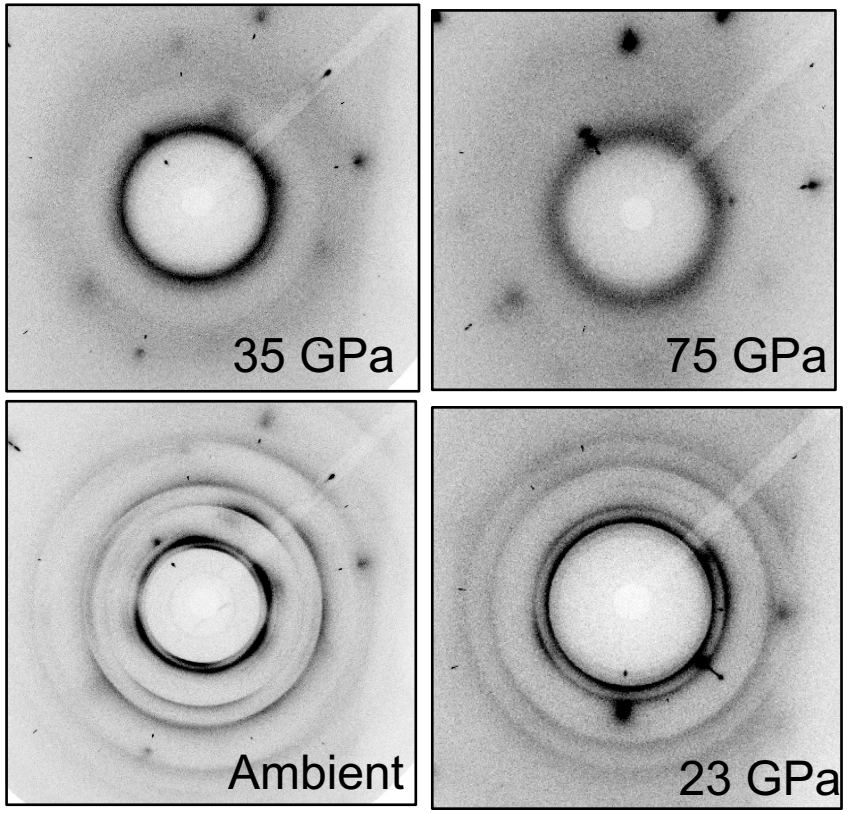




- Sm-type phase stable at ambient conditions
- A new solid-solid phase observed at 23 GPa

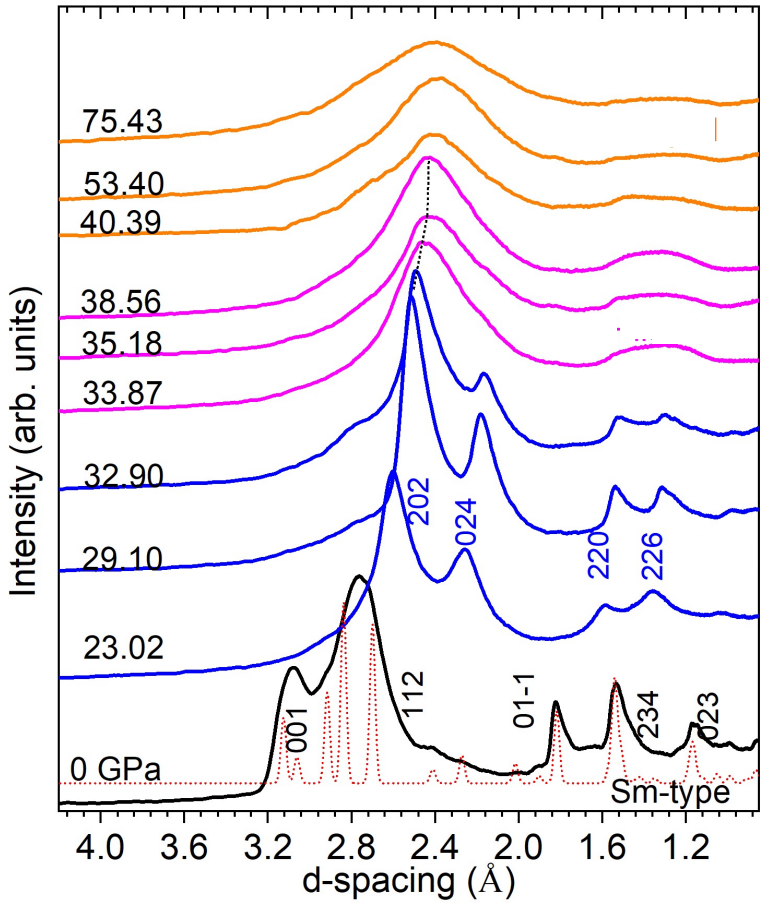
Structural evolution at high pressure

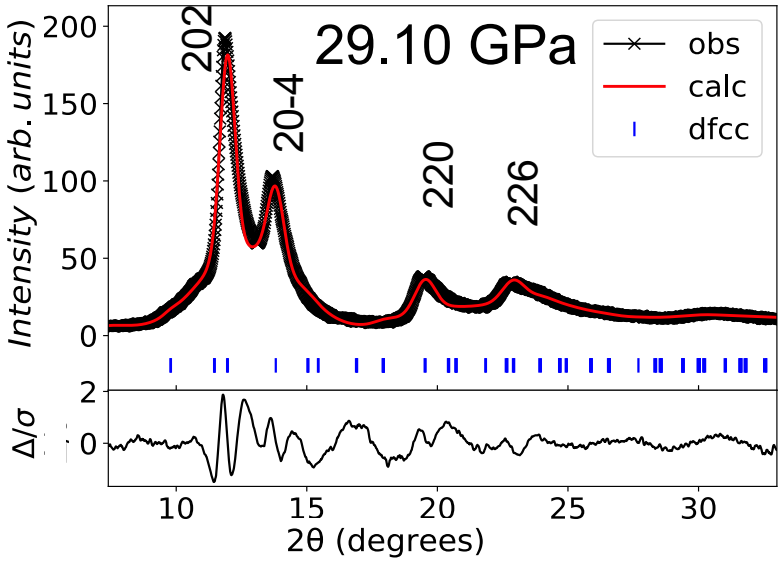


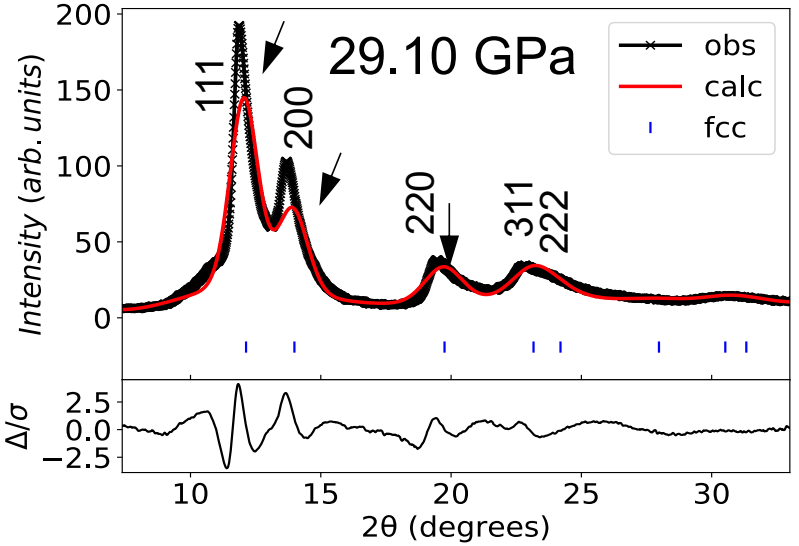


- Sm-type phase stable at ambient conditions
- A new solid-solid phase observed at 23 GPa
- Onset of melting at 33 GPa

Structural evolution at high pressure

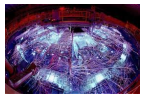


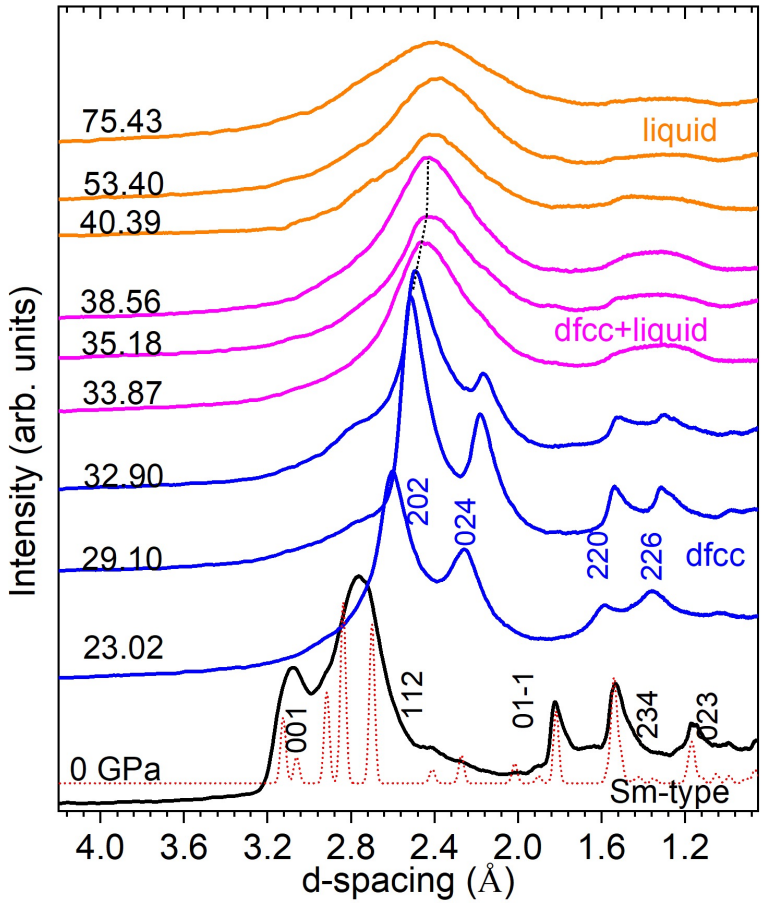


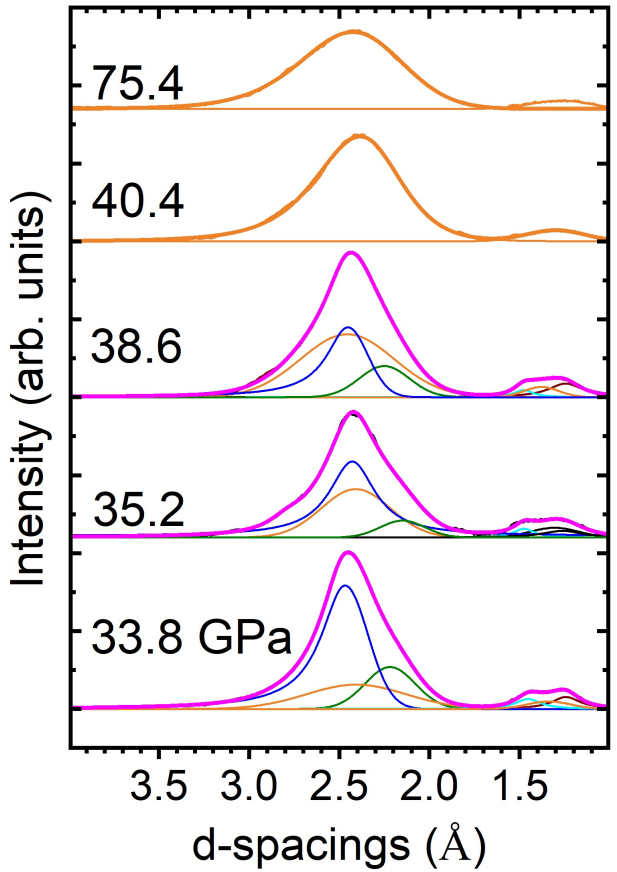


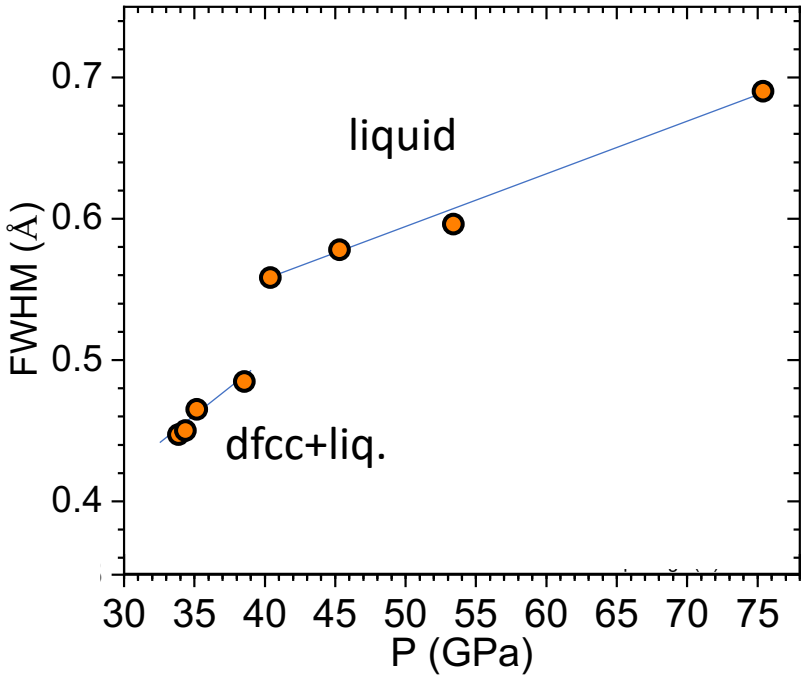
- Rietveld refinement suggest dfcc phase

Structural evolution at high pressure



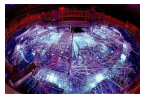


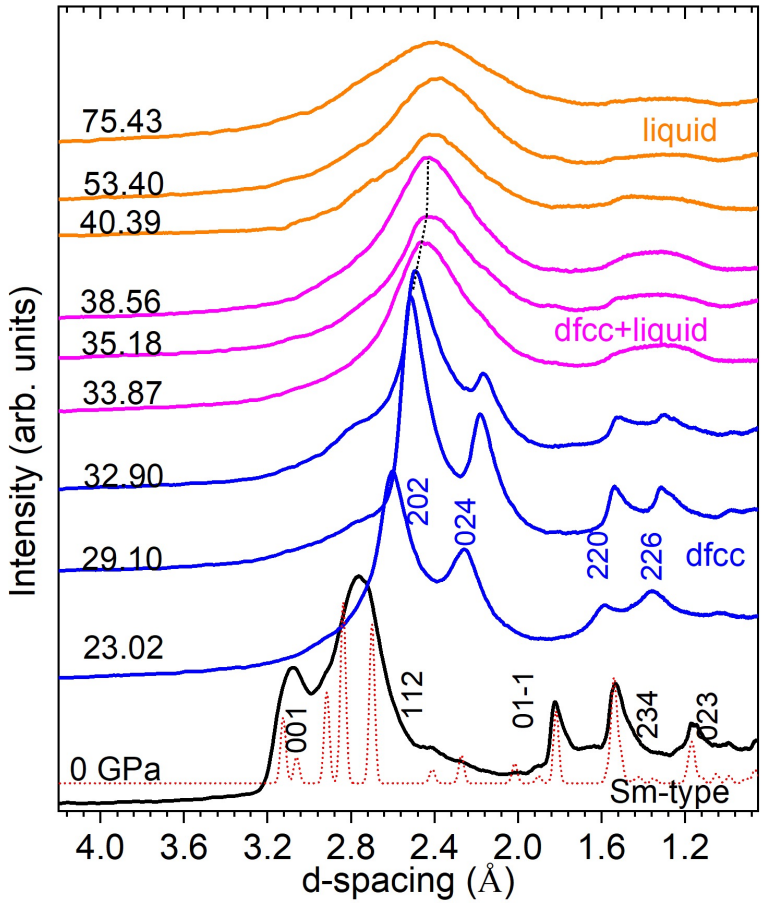


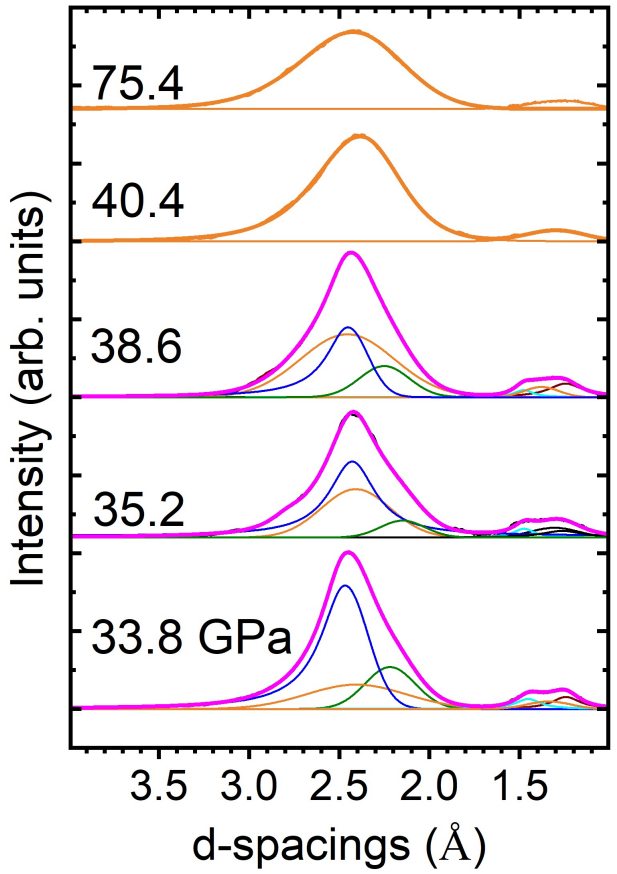


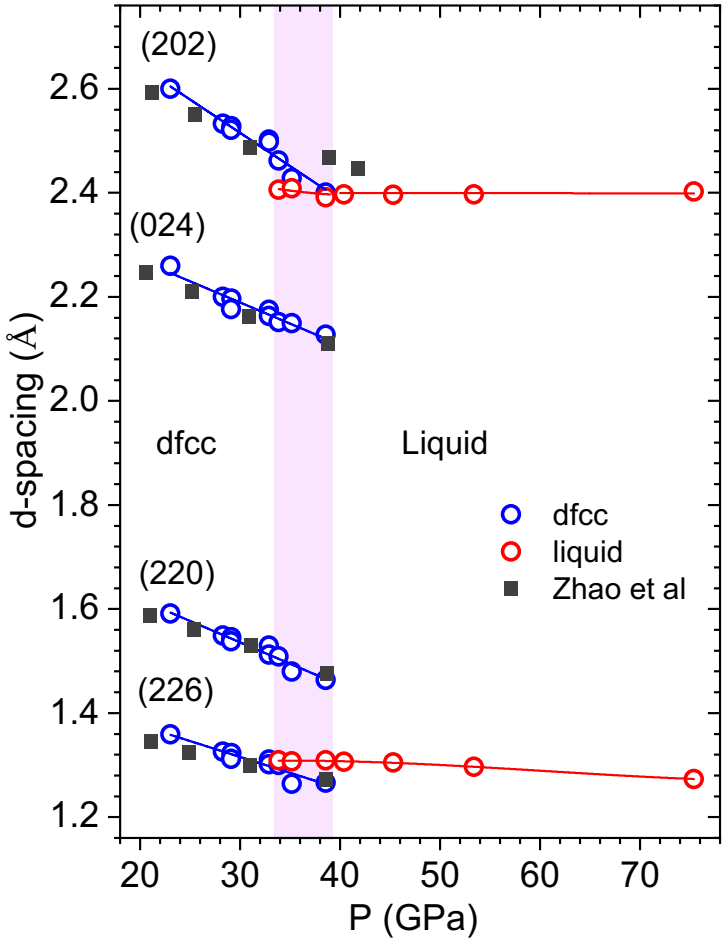
- Sm-type phase stable at ambient conditions
- A new solid-solid phase observed at 23 GPa
- Onset of melting at 33 GPa

Structural evolution at high pressure









- Sm-type phase stable at ambient conditions
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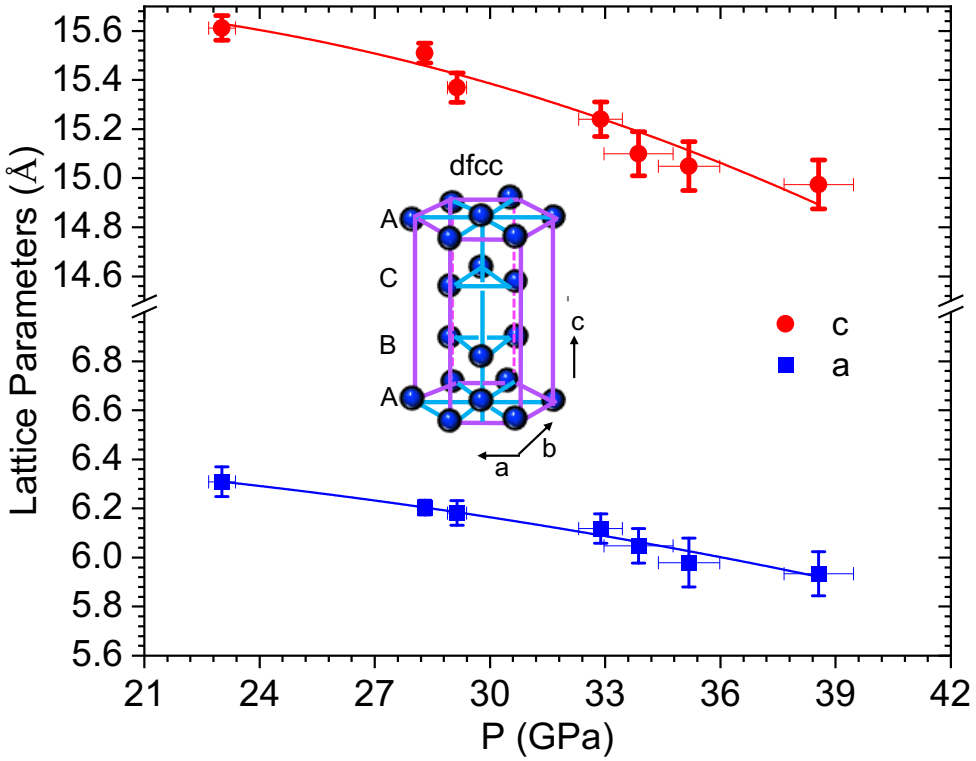
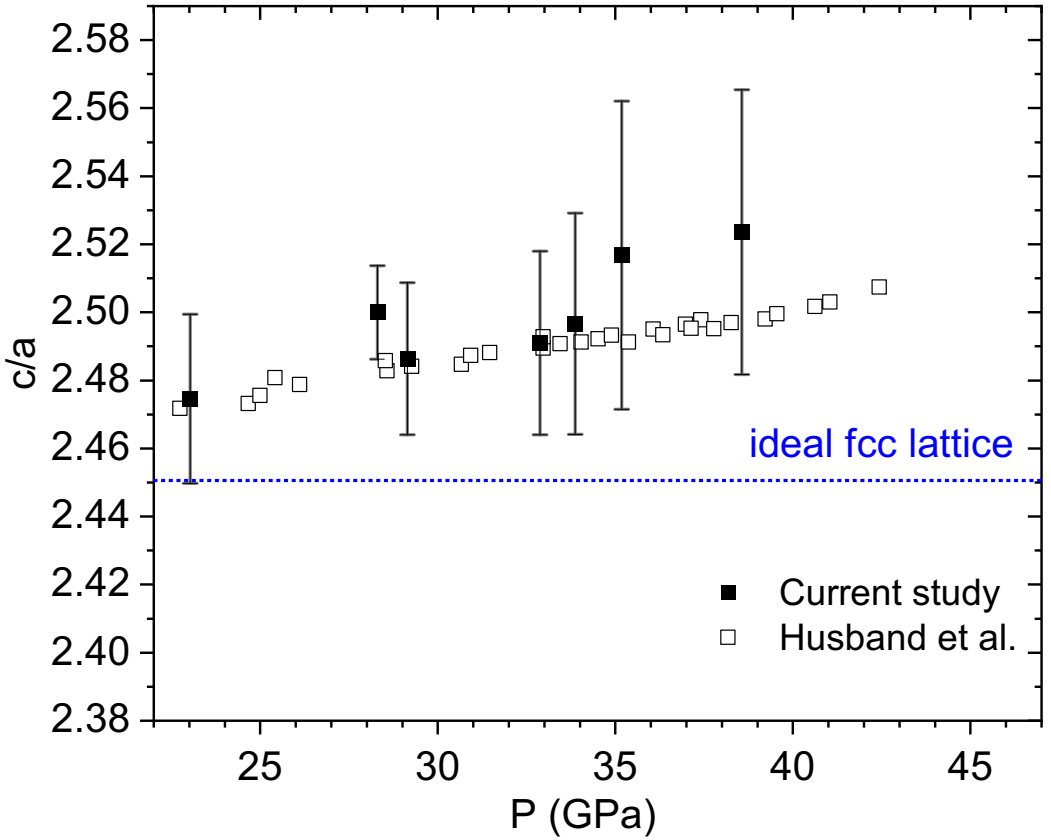
c/a ratio deviates from ideal fcc lattice

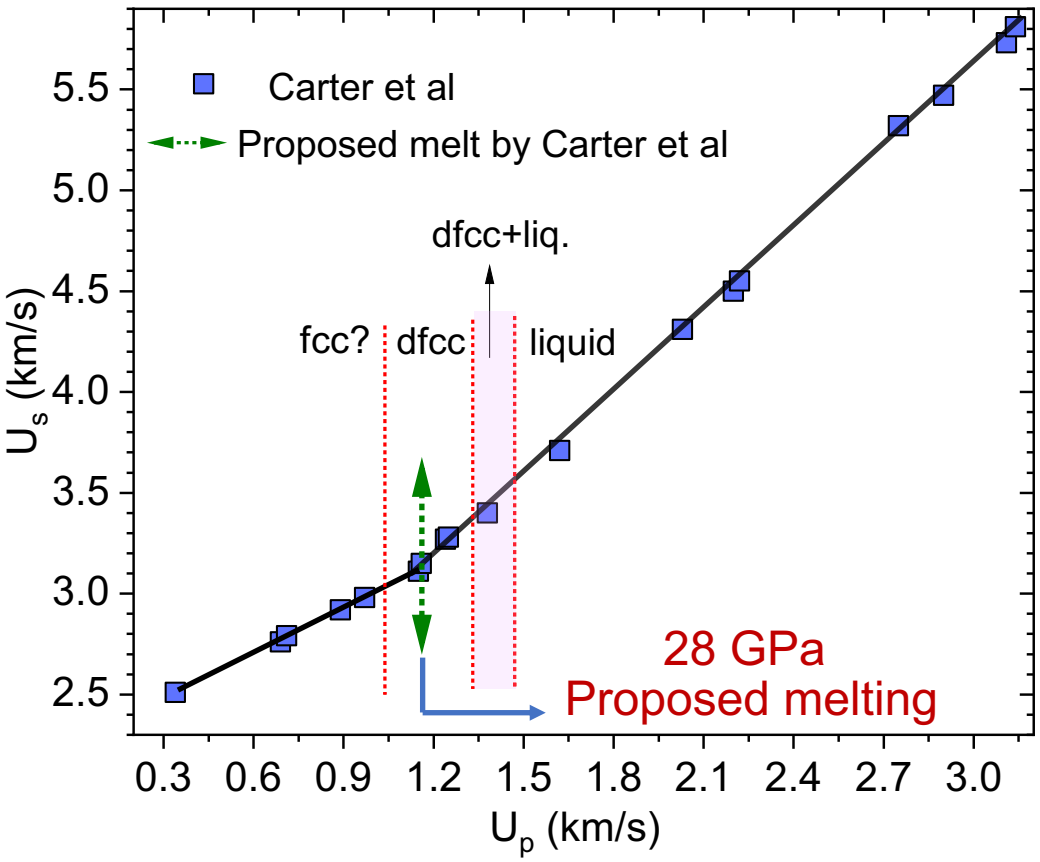


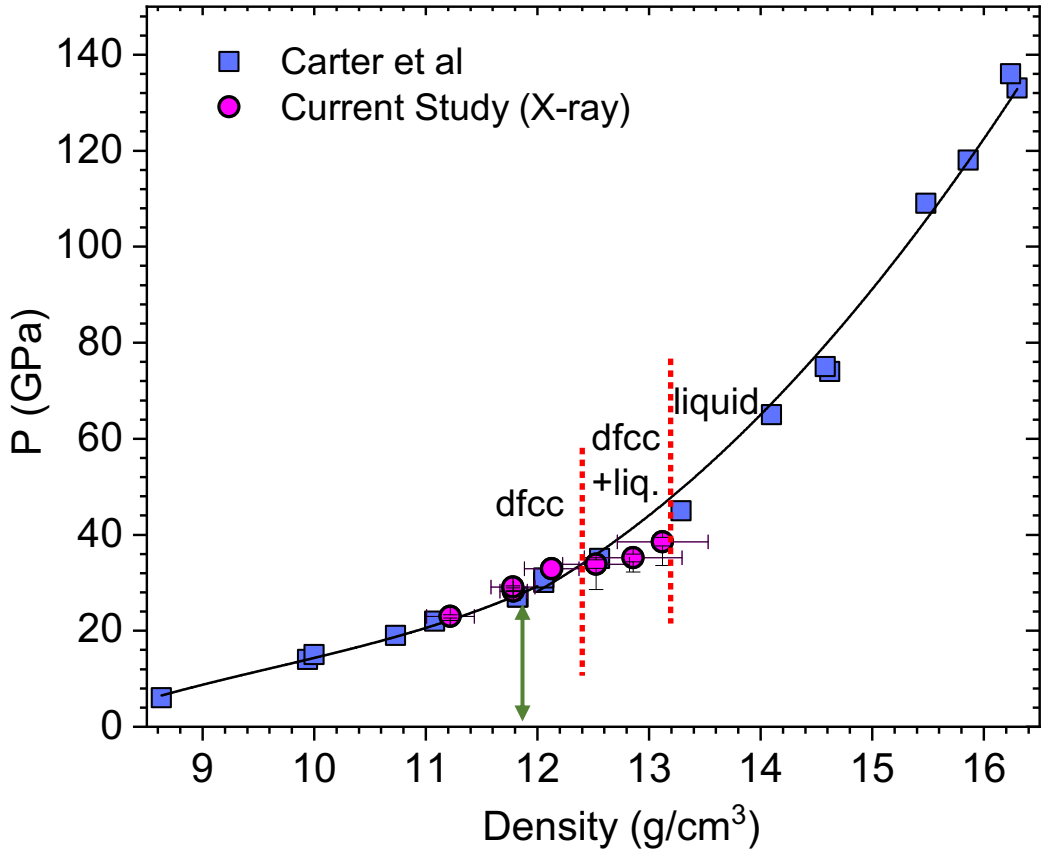
- Decreasing lattice parameters with increase in pressure
- c-axis is more compressible than a-axis



- c/a ratio deviates from ideal fcc value, 2.45

Current work disagrees with the previously proposed melting

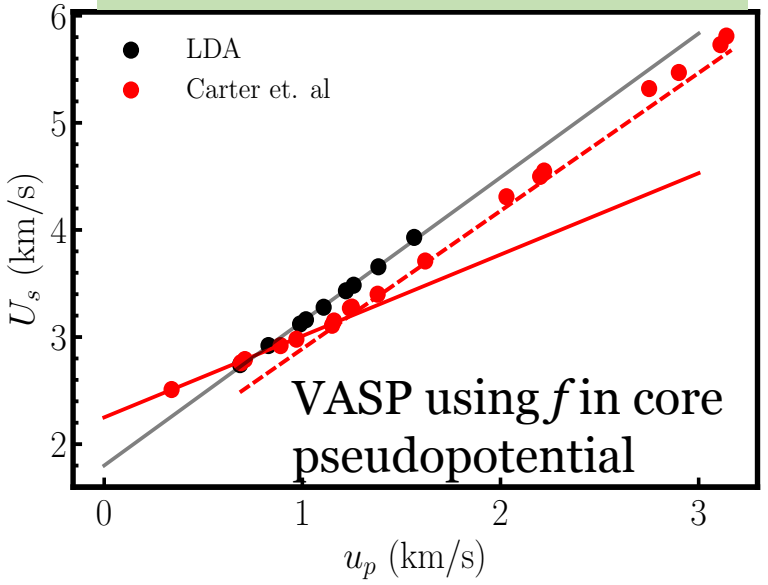




- Early shock work indicated melting based on U_s-U_p discontinuity
- XRD results suggests melting occurs at a higher pressure along the Hugoniot

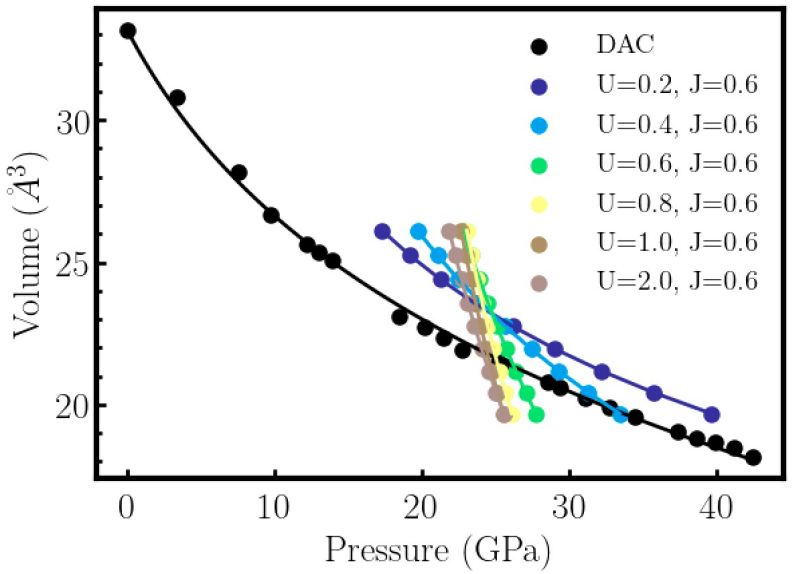
DFT sparks insights into f-electron physics at play

DFT-MD, localized f-electrons



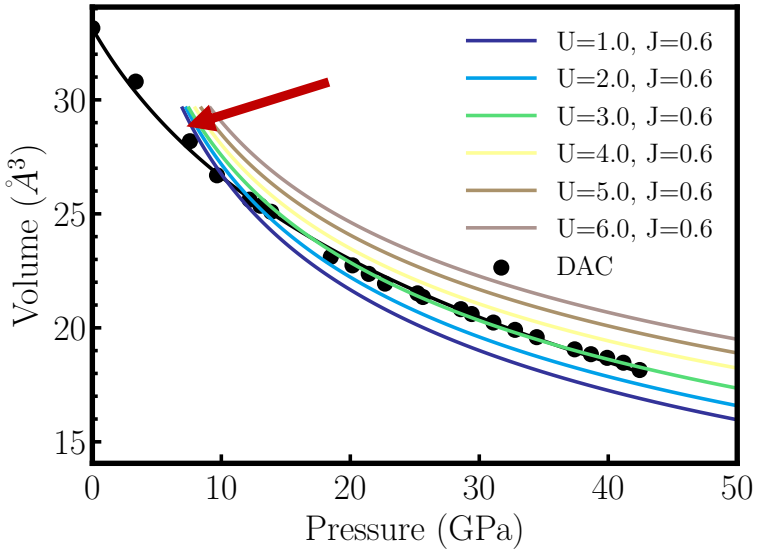
- Clear discrepancy in U_S-u_p

DFT+U, localized f-electrons



- DFT+U using ELK; f-electrons are localized, but no SOC

DFT+U+SOC, "valence" f-electrons

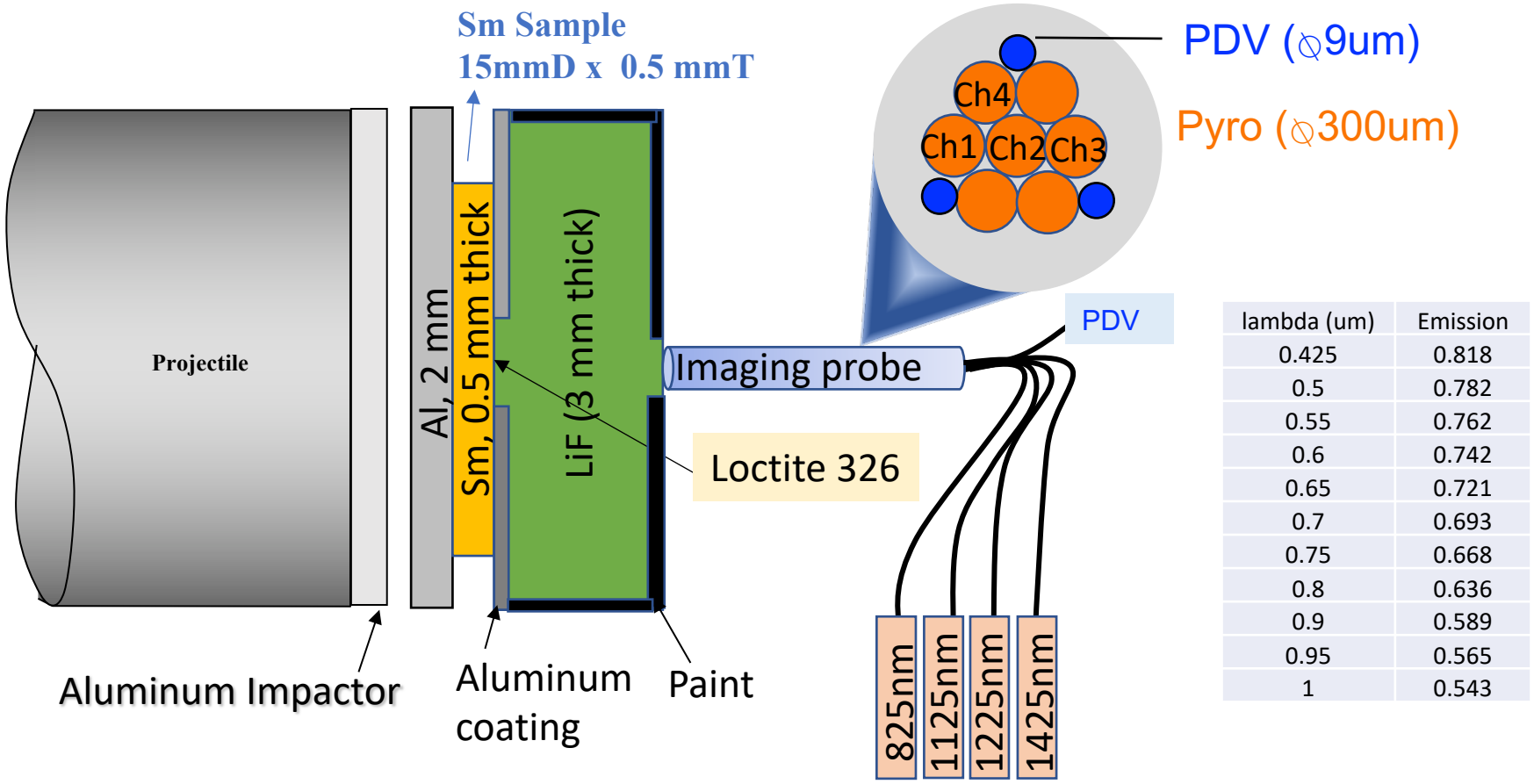


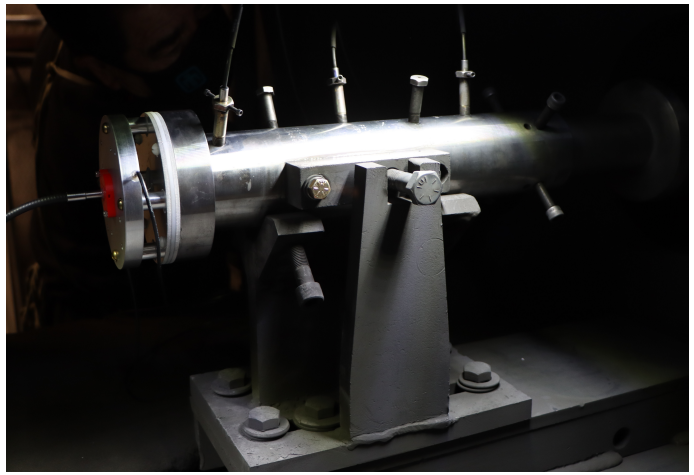
- DFT+U+SOC using ELK; valence f-electrons
- Low pressure agreement still poor
- **Cold curve needs to be reproduced well before moving to Hugoniot**
- f-electrons participate in bonding at high pressure, but not at low pressure

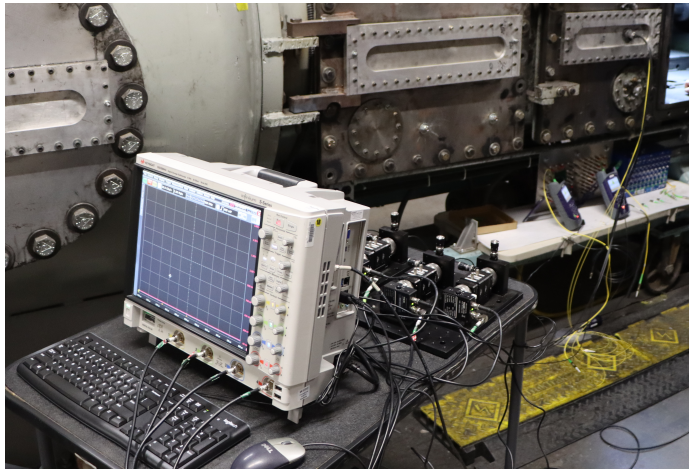
- Quality of results are highly sensitive to U/J/SOC treatment.
- Current DFT efforts struggle to reproduce cold curves near ambient when *f*-electrons are treated as valence , which will bias Hugoniot pressures and temperatures. **More investigation is needed for ab-initio Hugoniot for lanthanides**

Cody Melton

Temperature measurements using pyrometry to constrain the Hugoniot





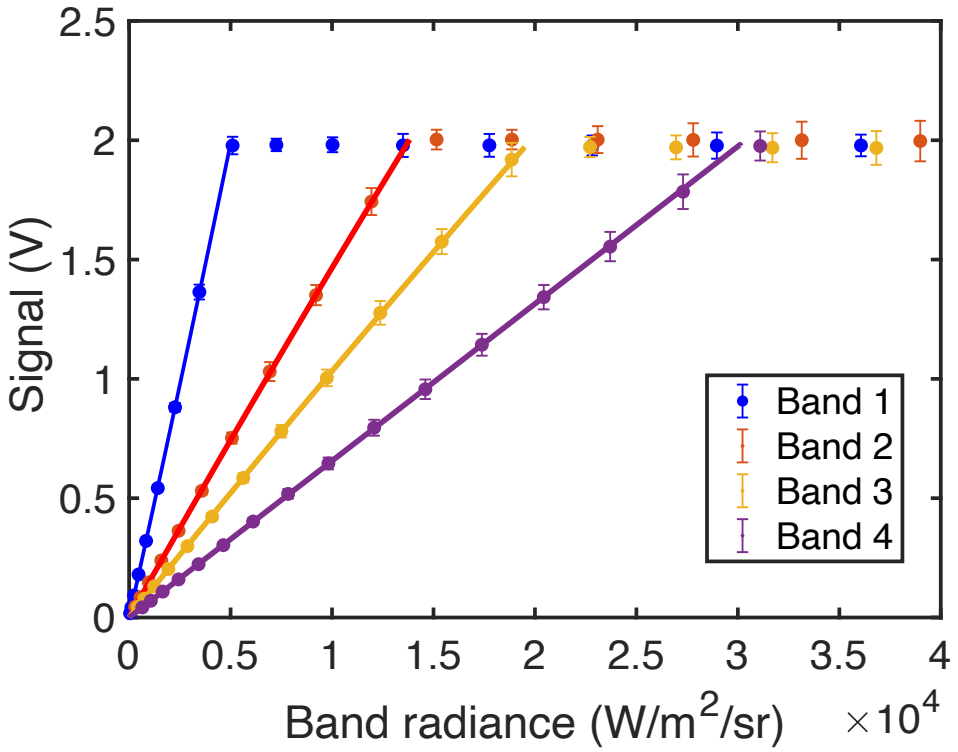


lambda (um)	Emission
0.425	0.818
0.5	0.782
0.55	0.762
0.6	0.742
0.65	0.721
0.7	0.693
0.75	0.668
0.8	0.636
0.9	0.589
0.95	0.565
1	0.543

- Temperature measurements made using multi-channel optical pyrometers (Avalanche photo diodes, APDs) using 4 channel system
- Sample needs to be a great emitter
- Well impedance matched with LiF (Z_{LiF}: 17.42; Z_{Sm}:15.75)

Temperature calibration for high quality data

Blackbody Source

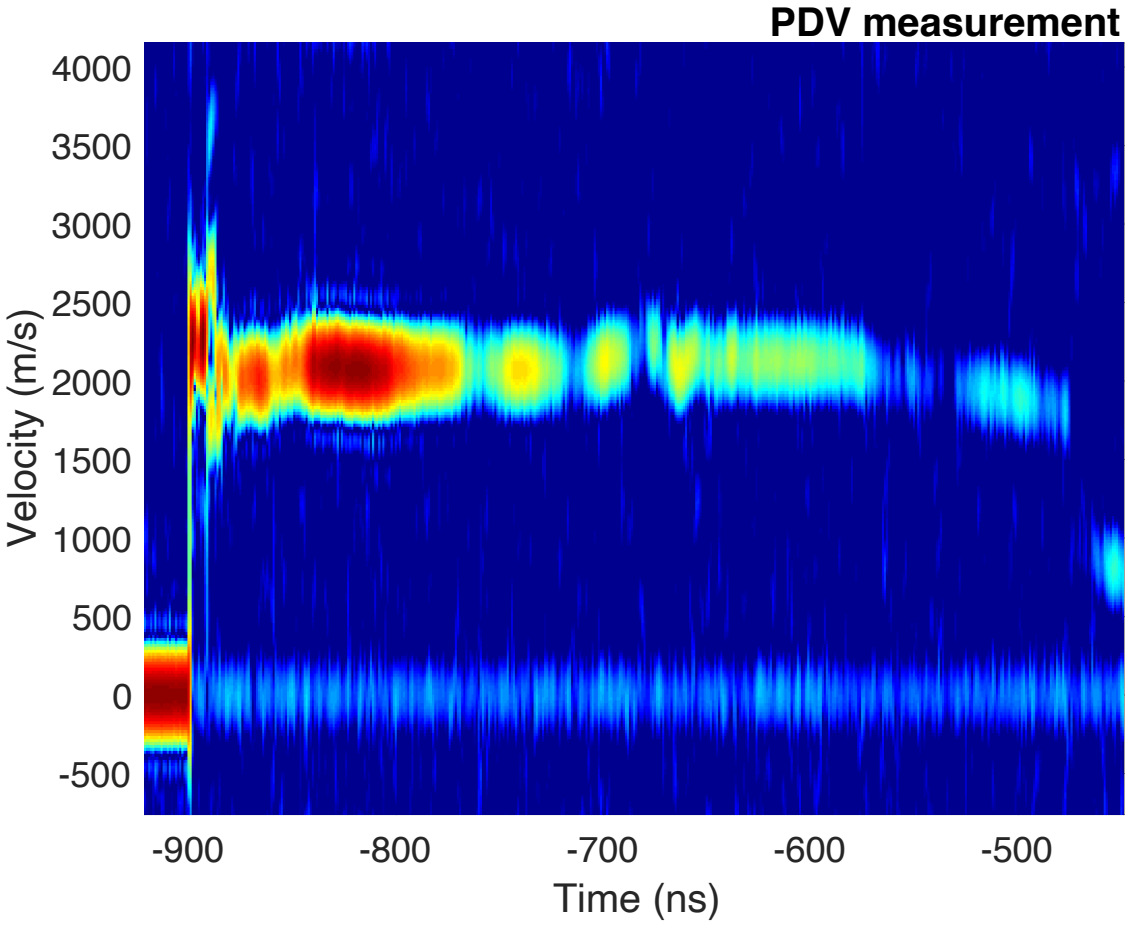


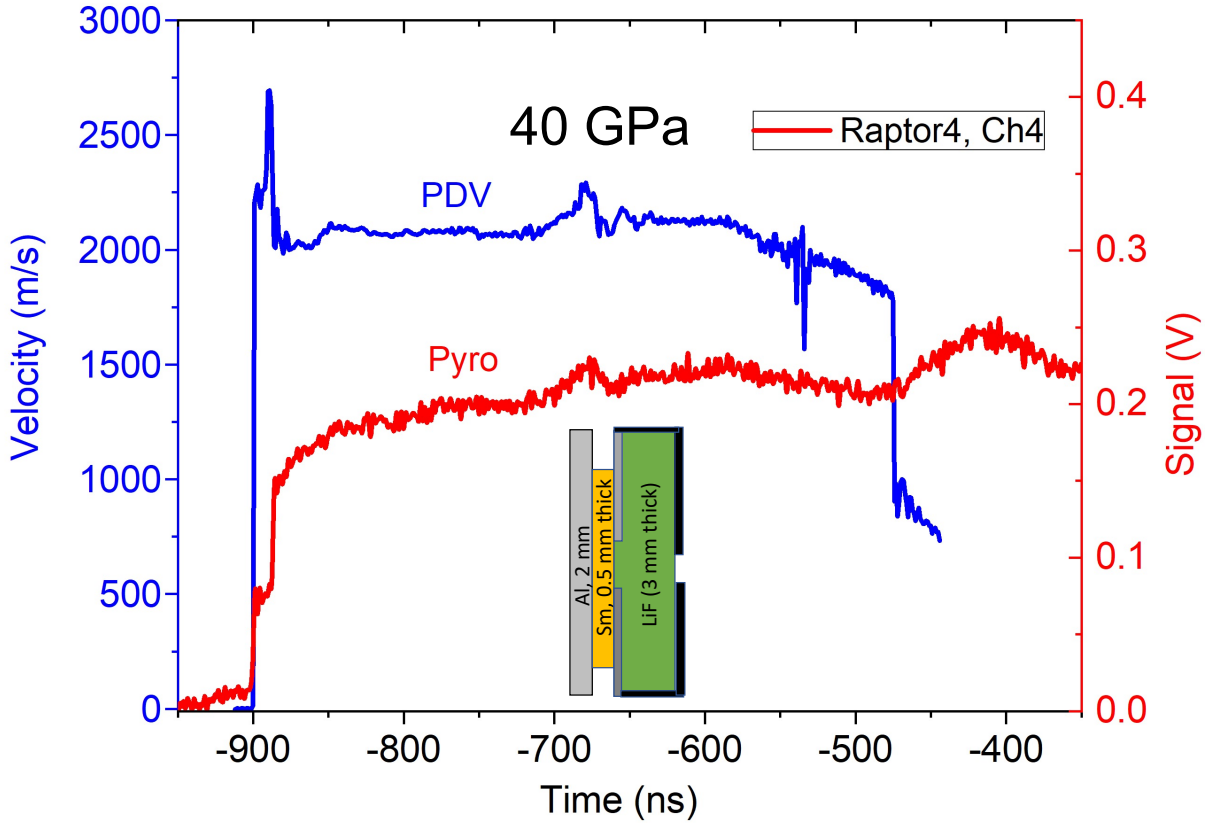
$$T = \frac{c_2}{\lambda_m} \frac{1}{\ln(\frac{\epsilon_m c_1}{L_m \lambda_m^5} - 1)}$$

- Radiance detectors are calibrated by placing the radiance optical fiber into a blackbody source, varying the blackbody temperature over the expected range of experiment temperatures, and recording the signals, V_{Cal} (T), at each temperature.

- For each detector, these calibration temperatures and signal voltages were fit to a numerical equation, to obtain smooth calibration interpolations at all relevant temperatures.

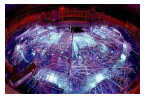
Velocimetry and emission measurements follows the same trend

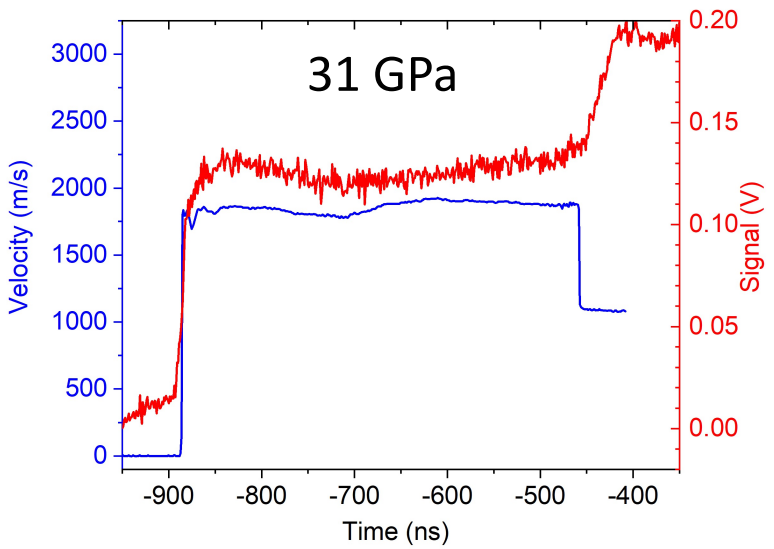


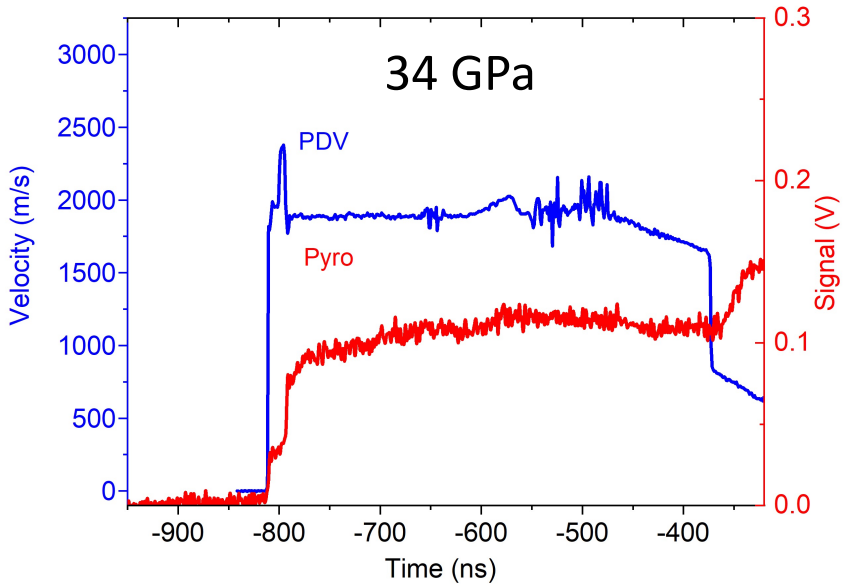


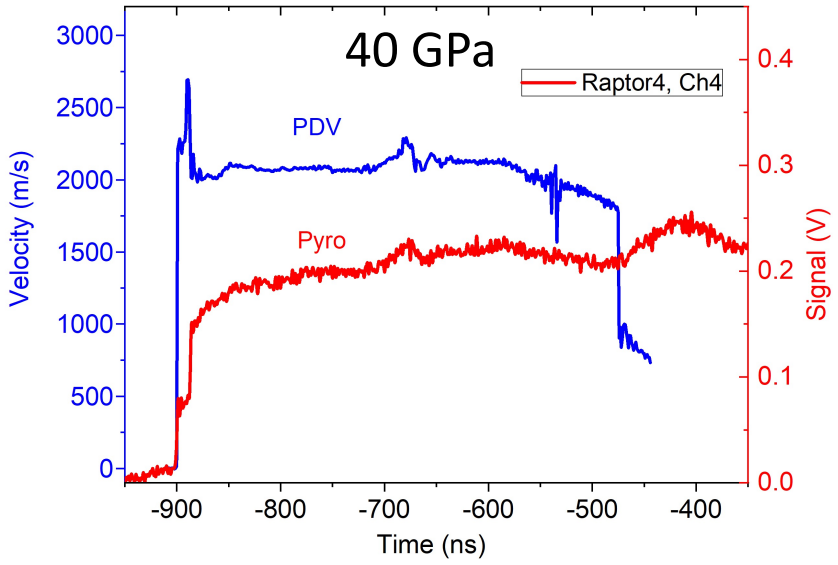
Detector signals vs time, V(t), are recorded on high-speed digital oscilloscopes.

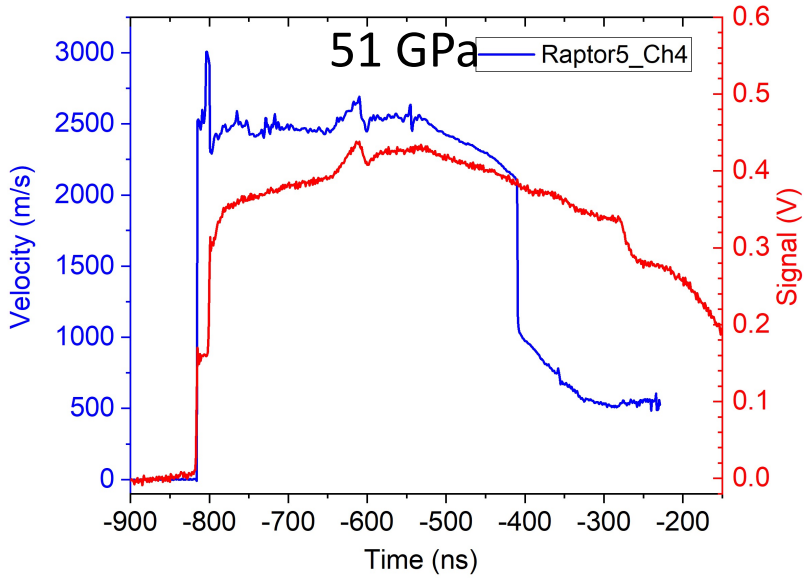
Four simultaneous velocimetry and temperature measurements



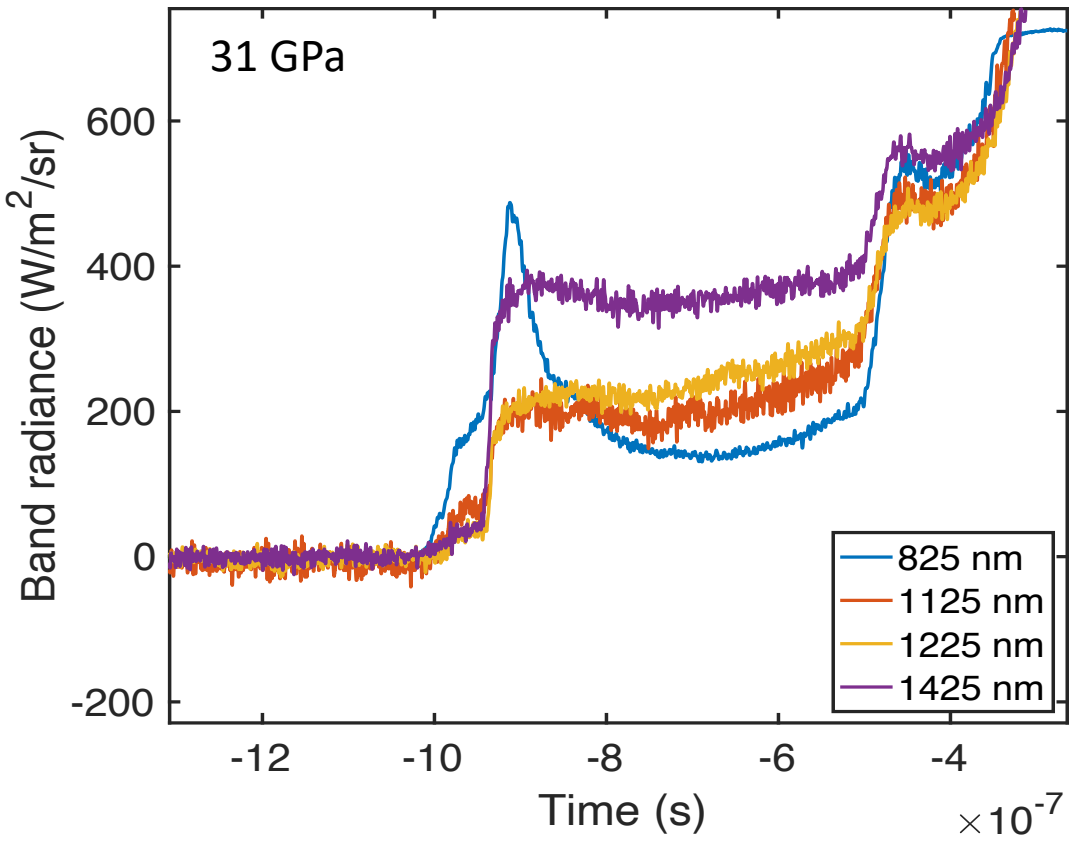


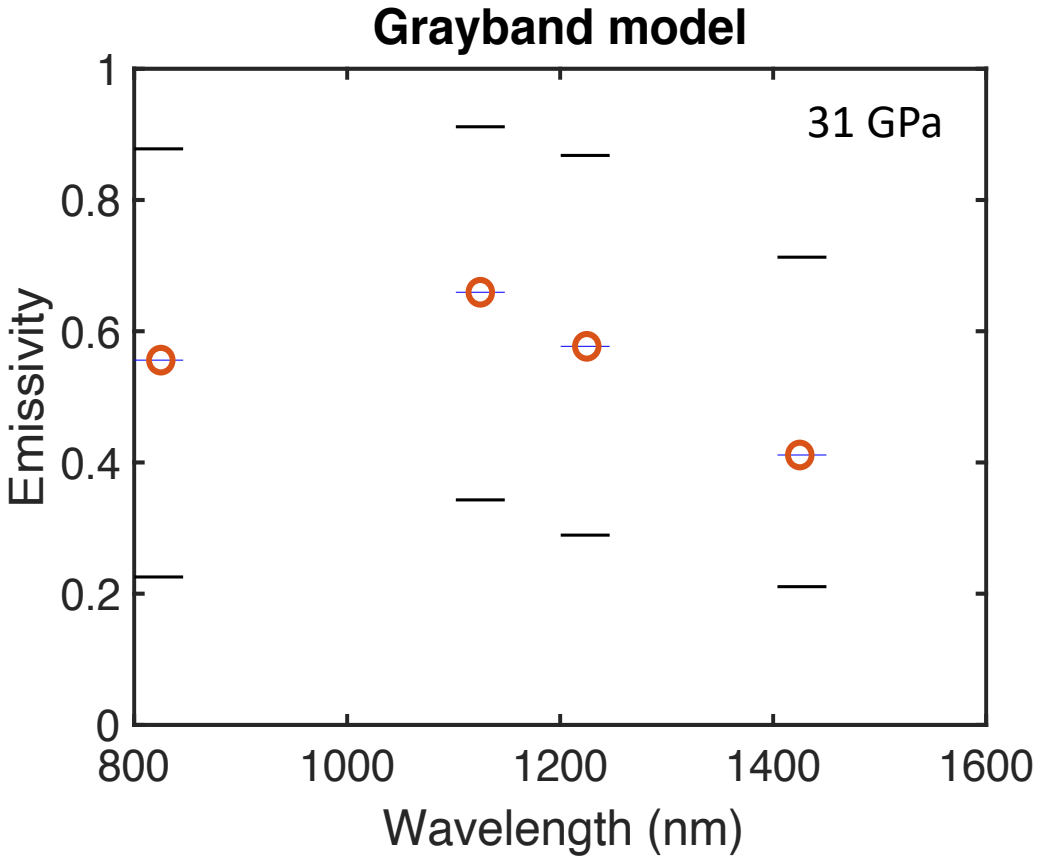






Sm-Temperature calculations





$$T = \frac{c_2}{\lambda_m} \frac{1}{\ln\left(\frac{\epsilon_m c_1}{L_m \lambda_m^5} - 1\right)}$$

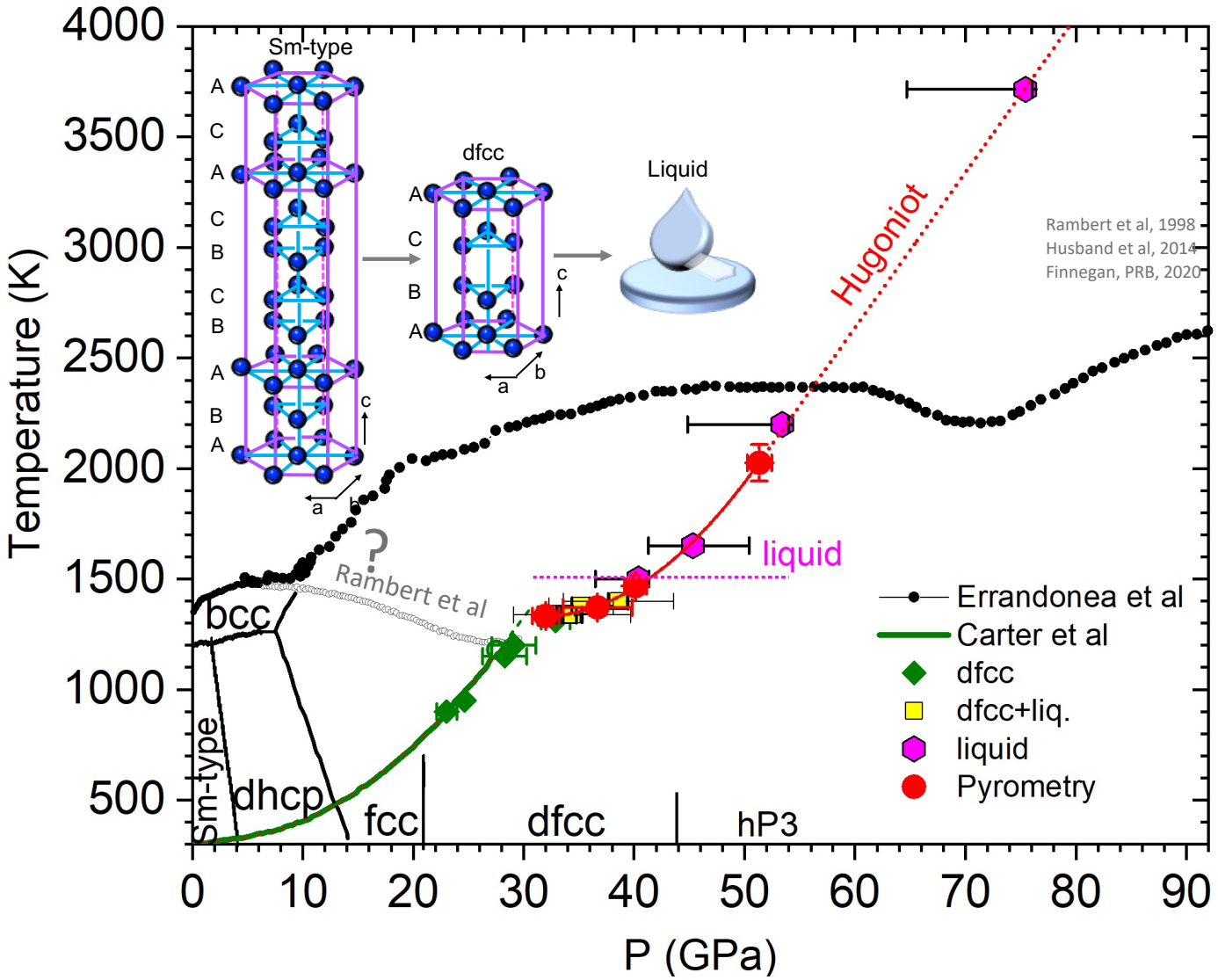
ε: emissivity **(0< ε<1);** L_m: measured band radiance
c_1, c_2: radiation constants
λ: wavelength

Gray band model

- 5 adjustable parameters to describe emissivity within each spectral band
- One emissivity changed per iteration, randomly alternating between spectral bands

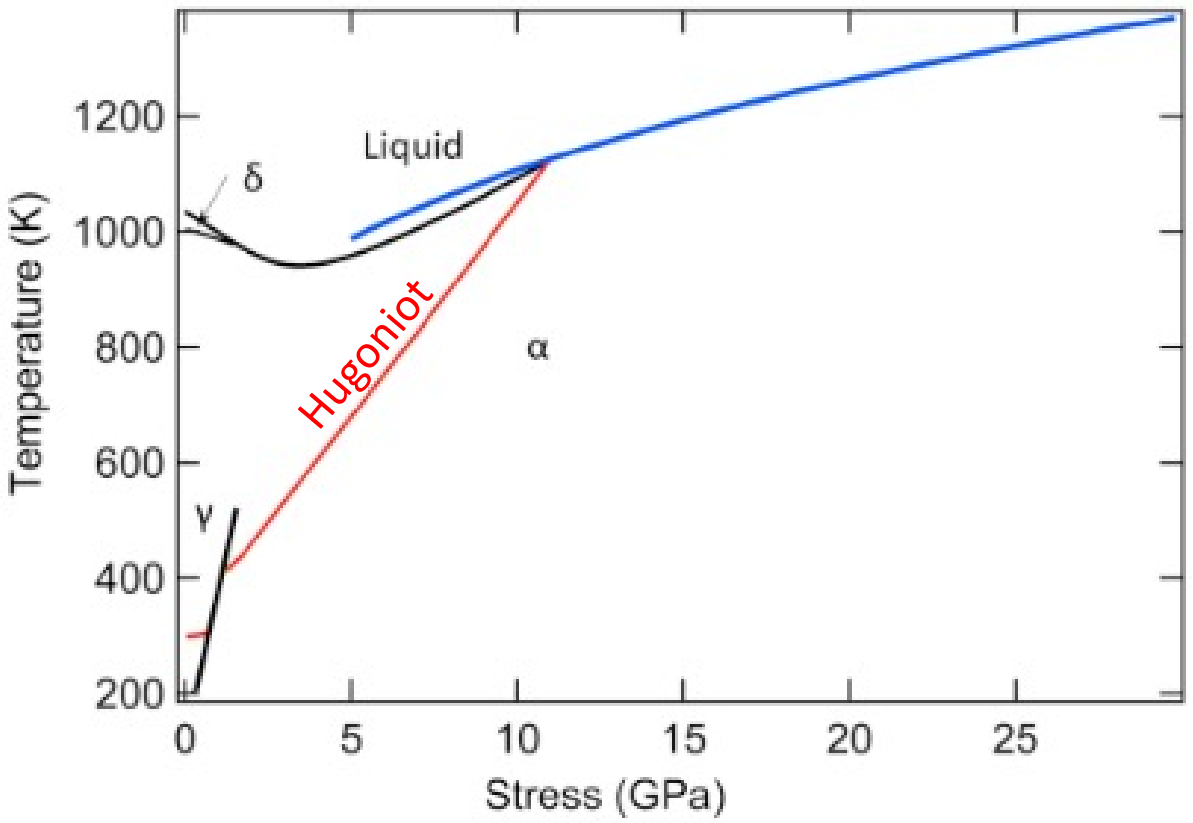
D. H. Dolan

Proposed phase diagram suggests melt occurs at much lower T



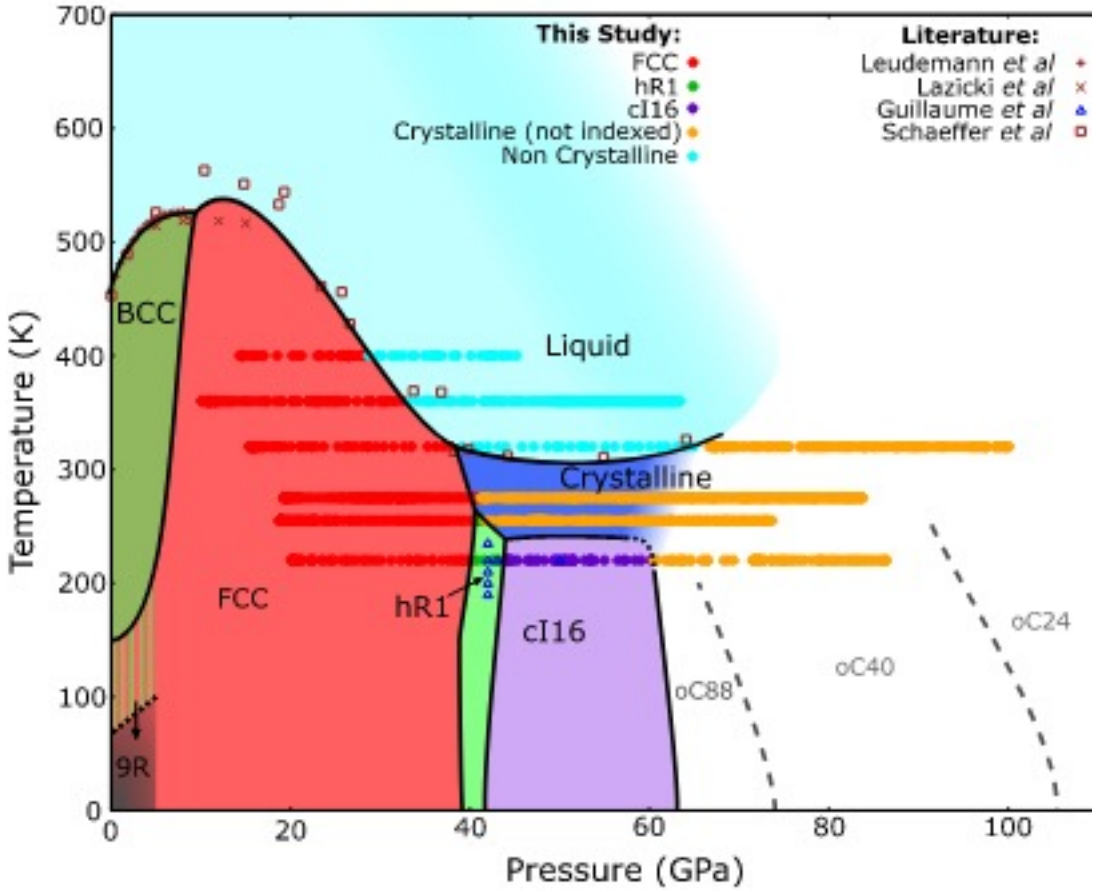
Melting curves of some other metals

Cerium



Jensen, JAP, 2021

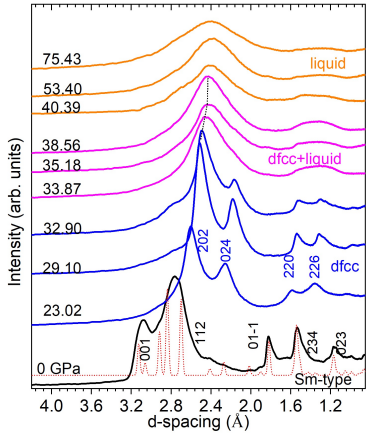
Lithium

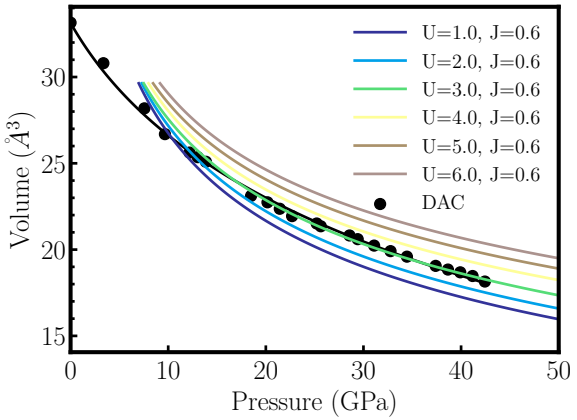


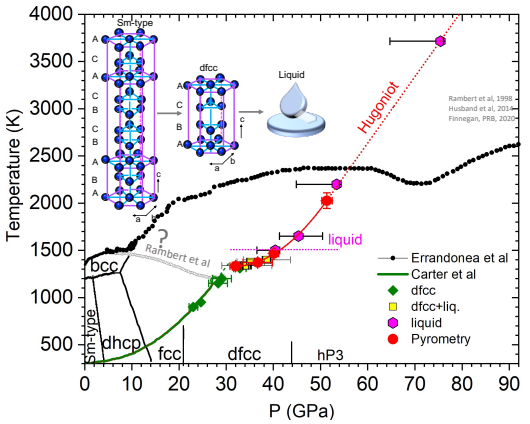
Guillaume et al, Nature Physics, 2011

Summary

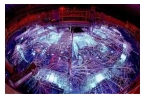
- Structural study of Sm–type to dfcc to liquid
- DFT suggests f-electrons participate in bonding at higher pressure
- Temperature measurements constraining Hugoniot in P-T-Rho space
- Melting reported at lower temperature than DAC experiments







Acknowledgements



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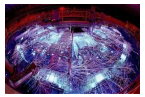

Thank you!