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Dynamic Loading Response of CaF_2 under Shock and Shockless Compression

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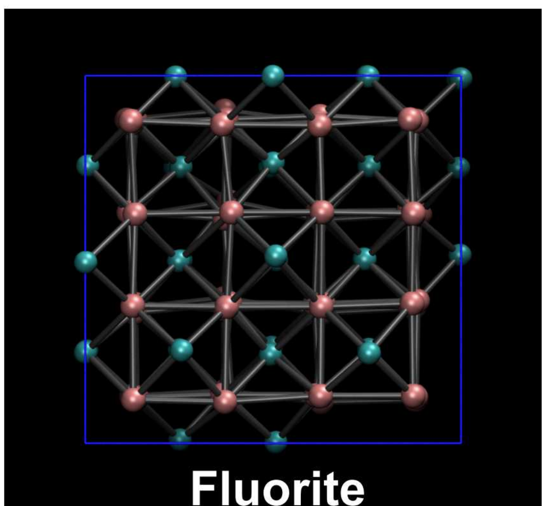
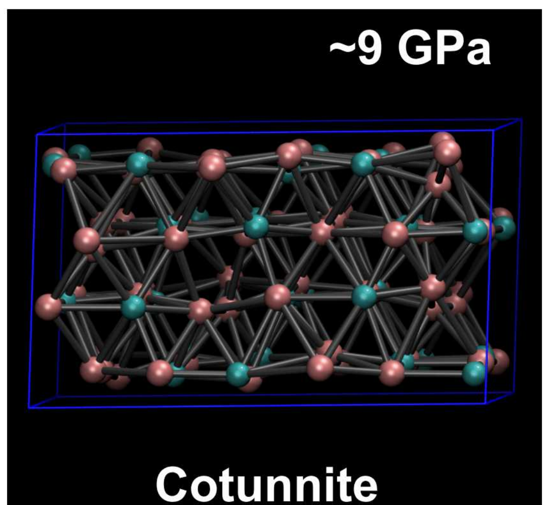
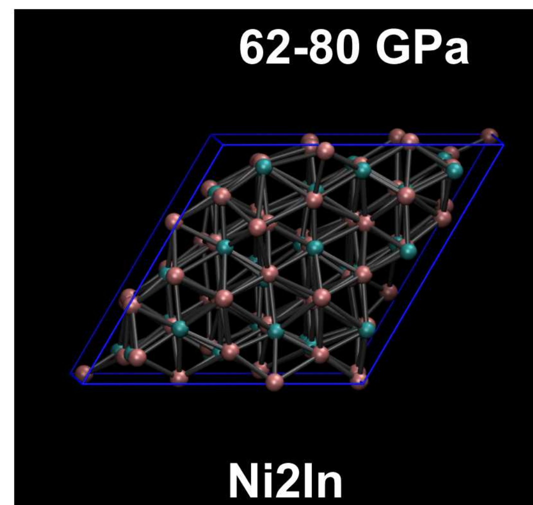
Calcium Fluoride

- The fluorite structure and associated pressure-induced transitions are common to many compounds
- At ambient conditions, Calcium Fluoride (CaF_2) crystallizes into the fluorite structure
- Static compression at ambient temperatures shows two solid-solid phase transitions: fluorite → cotunnite → Ni_2In
- CaF_2 has an orientation dependent elastic behavior
- CaF_2 samples are cheap, well-characterized, and easy to acquire in multiple orientations

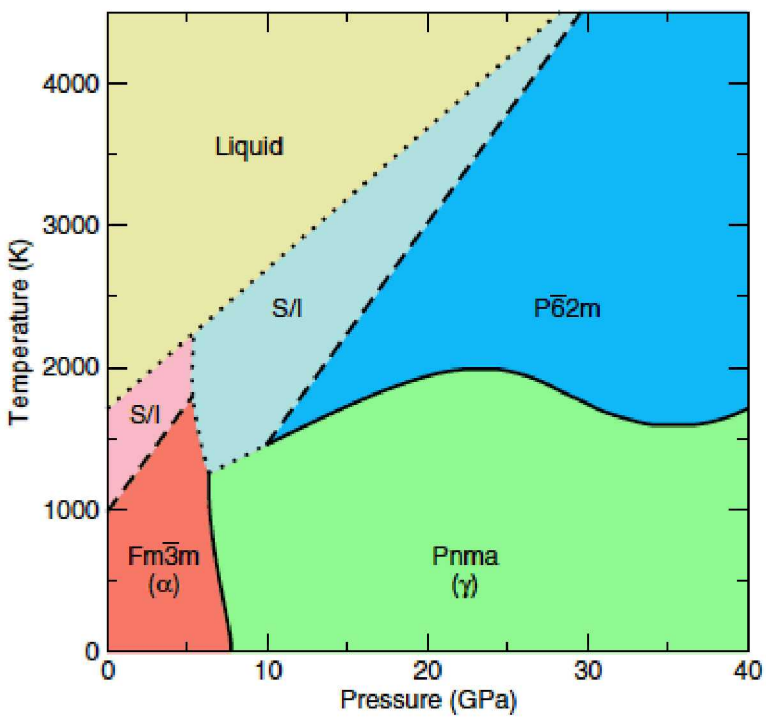




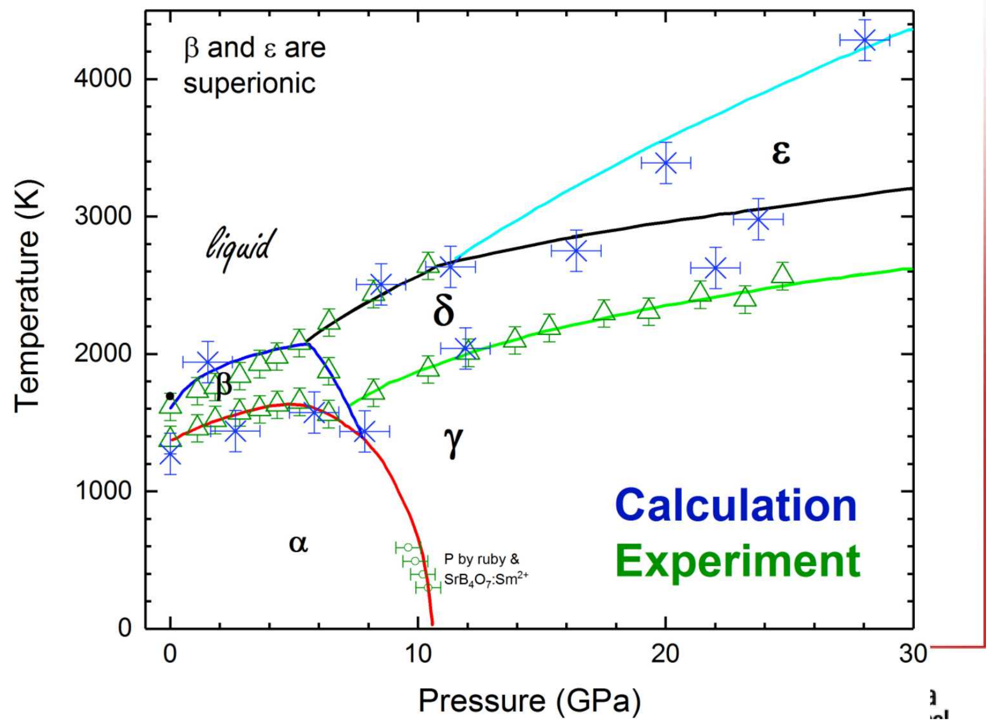


CaF_2 Phase Diagram

- **Extended phase diagram is undetermined determined**
- **Phase diagrams determined using QMD combined with limited static compression work below 30 GPa and elevated temperatures**
- **Both suggest two super ionic phases and a high P-T phase**
- **The high P-T phase does not correspond to the Ni_2In phase**
- **Location and range of the Ni_2In phase is unknown**



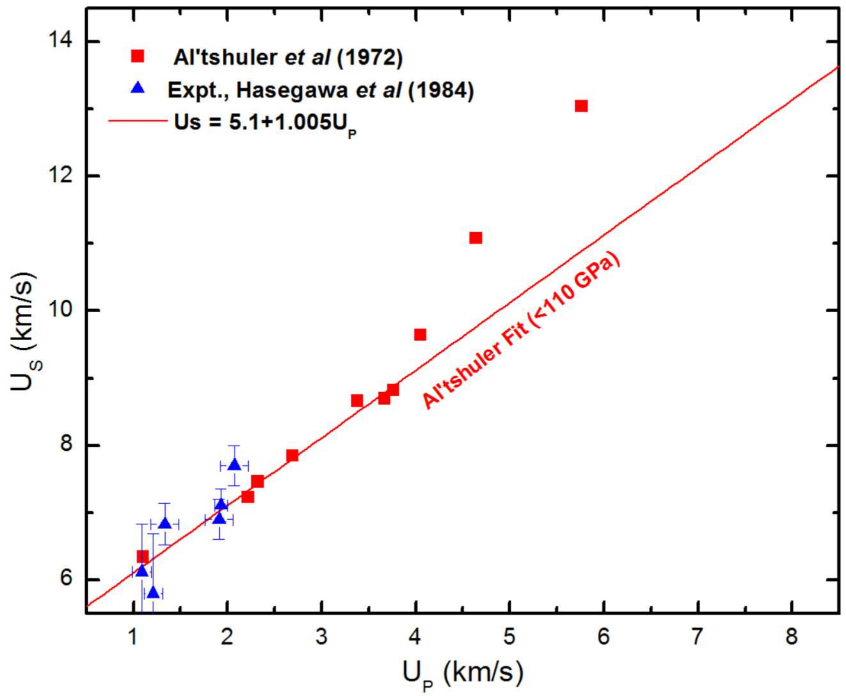
J. R. Nelson *et al*, PRB **95**, 054118 (2017)

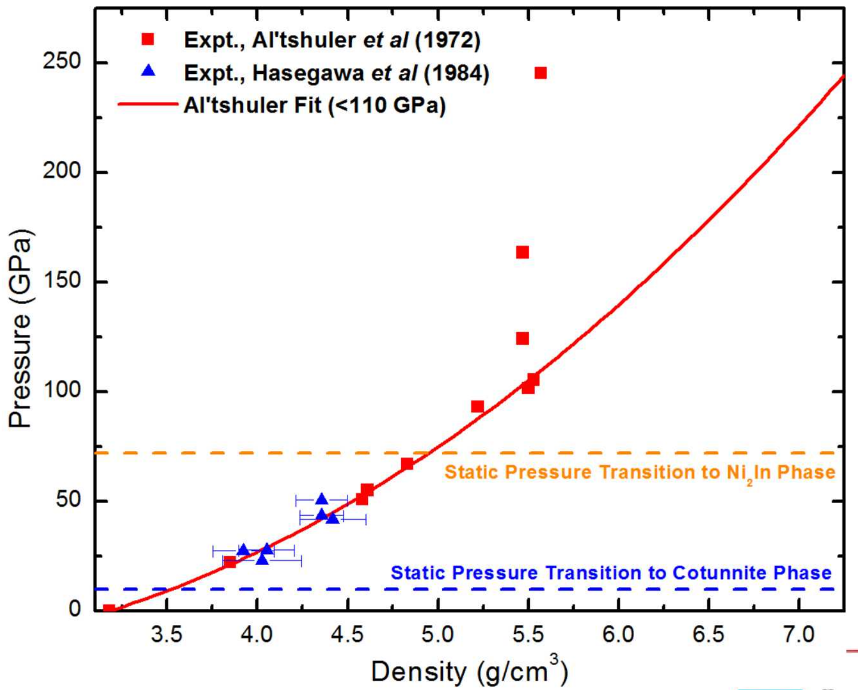


C. Cazorla and D Errandonea, PRL **113**, 235902, (2014)

Prior Shock Compression Work

- **Observation of fluorite → cotunnite phase along Hugoniot in wave profile[1] and x-ray diffraction[2] experiments (~12 GPa)**
- **Al'tshuler *et al* measured the Hugoniot to 250 GPa (no uncertainties listed)**
- **Monotonic increase to 100 Gpa, but becomes highly incompressible above 100 GPa**
- **They attributed the incompressibility to F-F repulsion**





1. T. Sekine and T. Kobayashi, **Phys. Chem. Minerals 38**, 305 (2011)
2. P. Kalita *et al*, **Phys. Rev. Lett. 119**, 255701 (2017)

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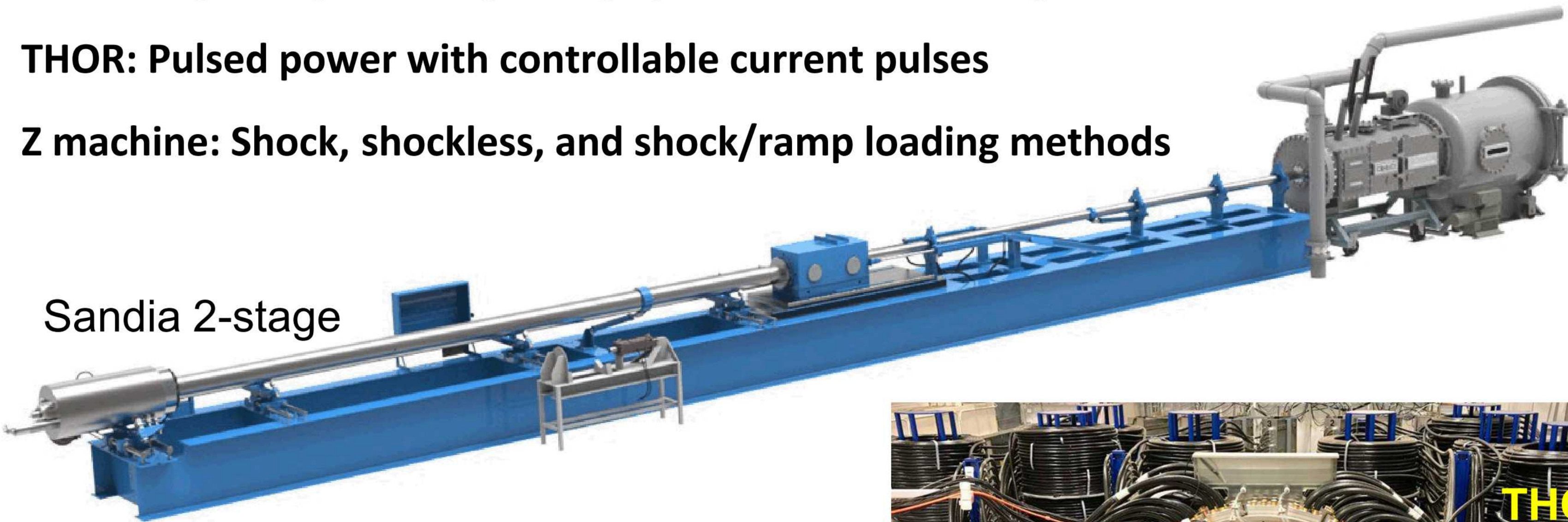
Collaboration Objectives

- **Develop a data-driven, multiphase equation of state**
  - Understand phase diagram over a broad range of pressure and temperature
  - Understand the kinetics of the phase transitions
  - Using shock, shock-ramp, shockless, static compression methods
  - Using density functional theory methods

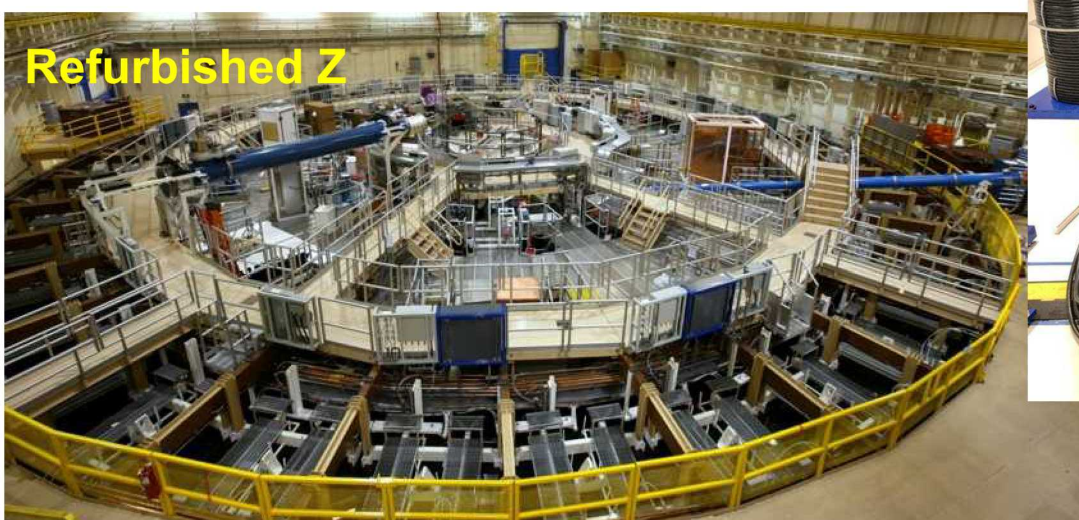
- **Develop or validate a constitutive model**
  - Examine the dynamics of the constitutive response
  - Orientation, temperature, loading rate dependencies
  - Using shock and shockless compression methods

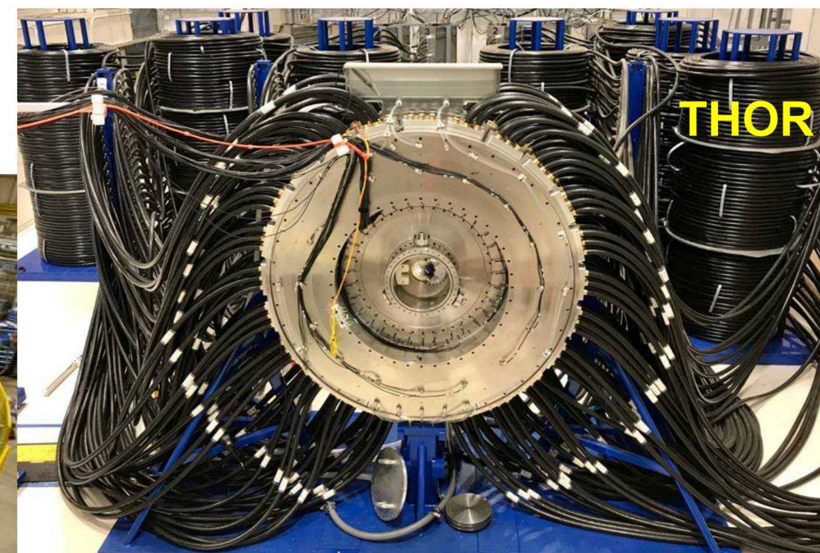
Sandia's Experimental Platforms

- **Guns: Single stage air, single stage powder, and two-stage launchers**
- **THOR: Pulsed power with controllable current pulses**
- **Z machine: Shock, shockless, and shock/ramp loading methods**



Sandia 2-stage





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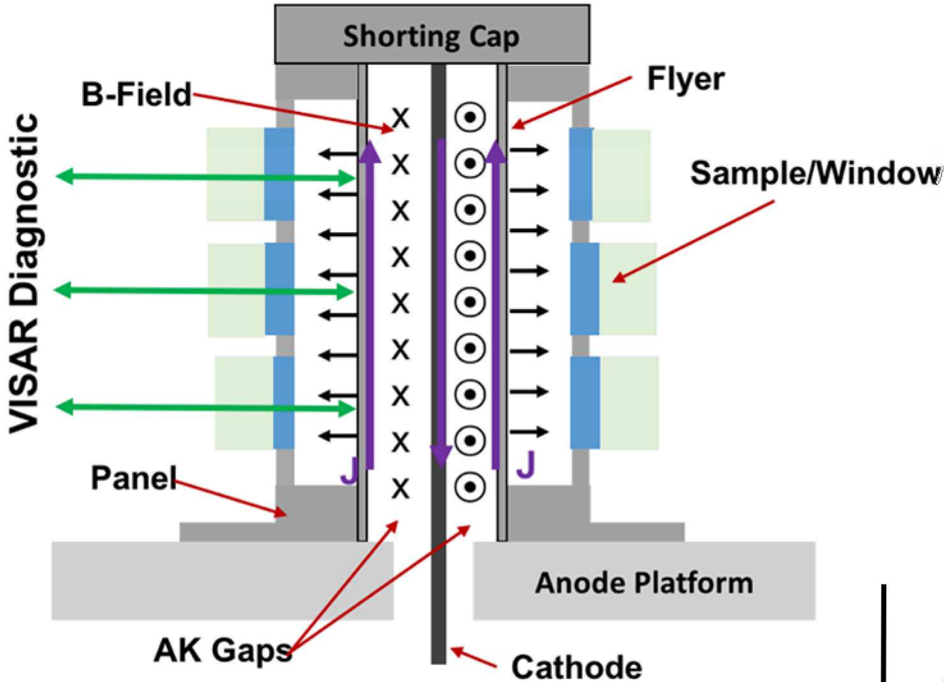
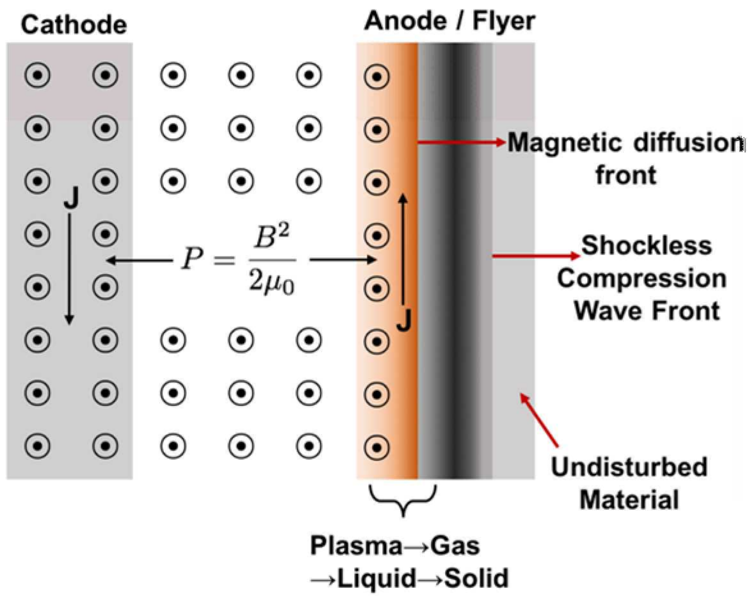
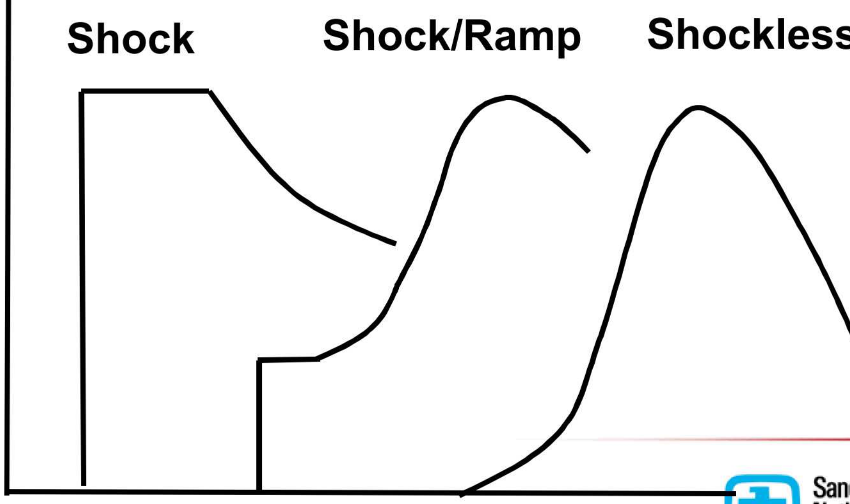
Z Machine





- Shock compression with flyers
  - Up to 45 km/s
- Shockless Compression
  - Quasi-isentropic loading
- Samples are 100s of μm to a few mm



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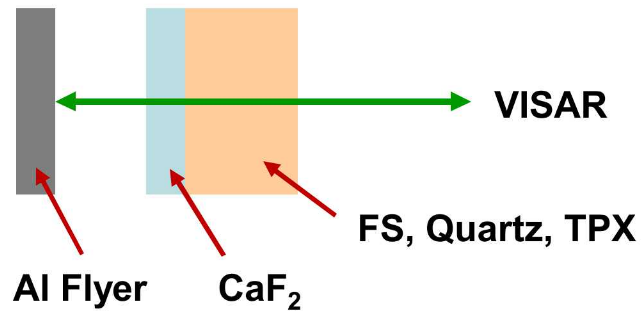
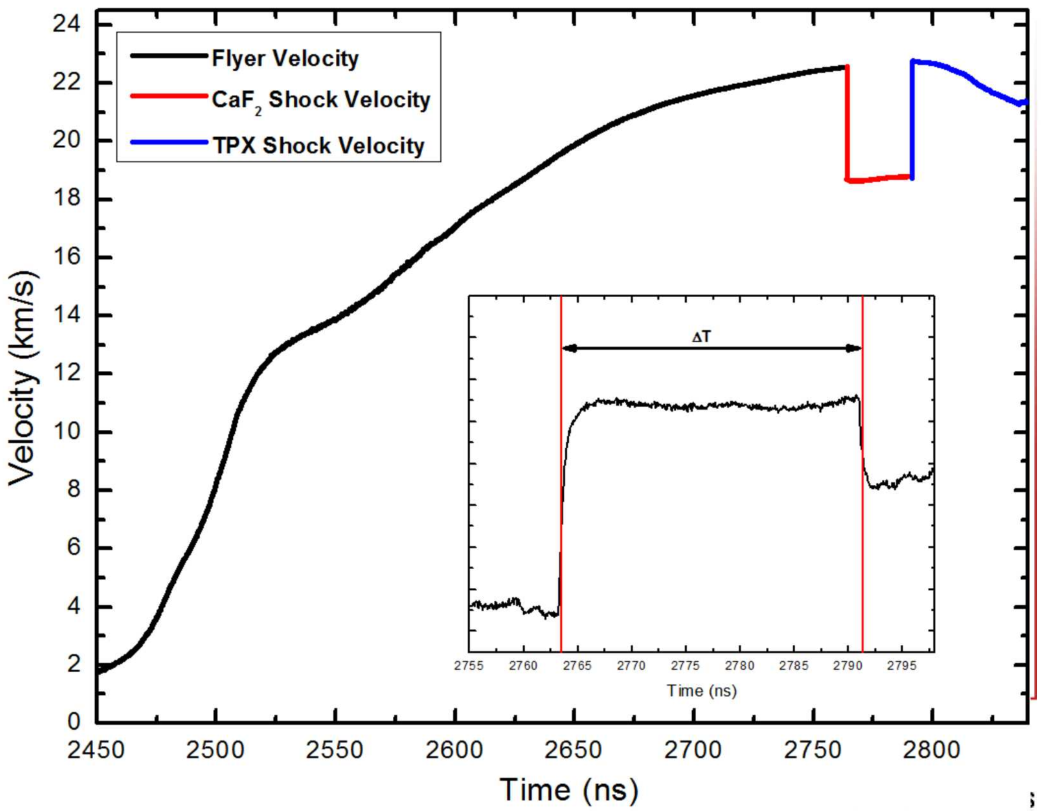
Z Experiments Along the Hugoniot

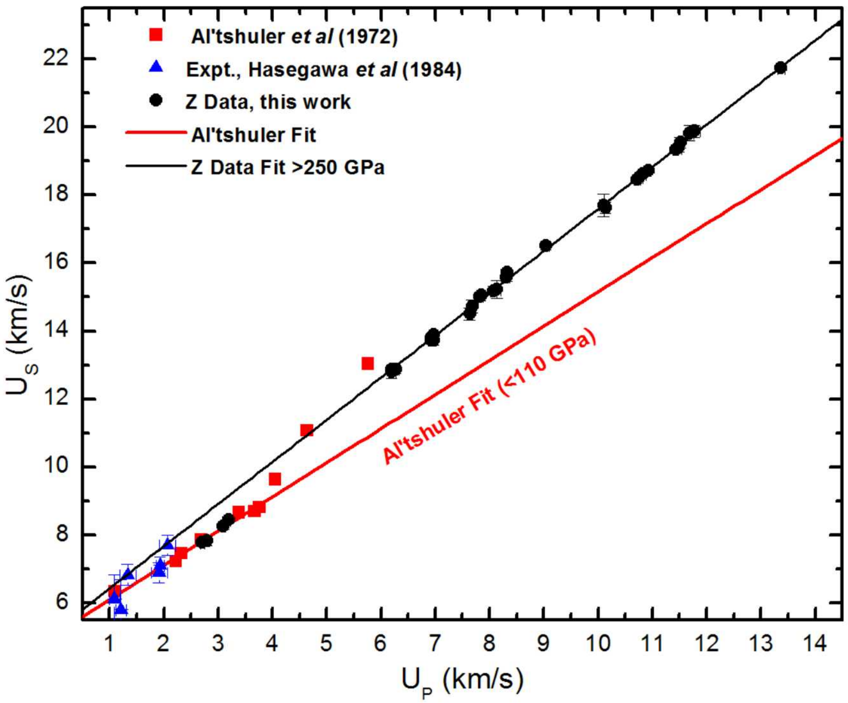
- Single crystal CaF_2 [111]
- Initial density = 3.18 g/cm^3
- CaF_2 backed by various windows for release measurements
- Z machine shocklessly accelerate Aluminum flyers
- Flyer Velocities: 12 to 28 km/s
- Generating steady shocks in CaF_2
- At impact velocities < 18 km/s the shock front is not reflective
- VISAR measures impact velocity, shock velocities and transit times

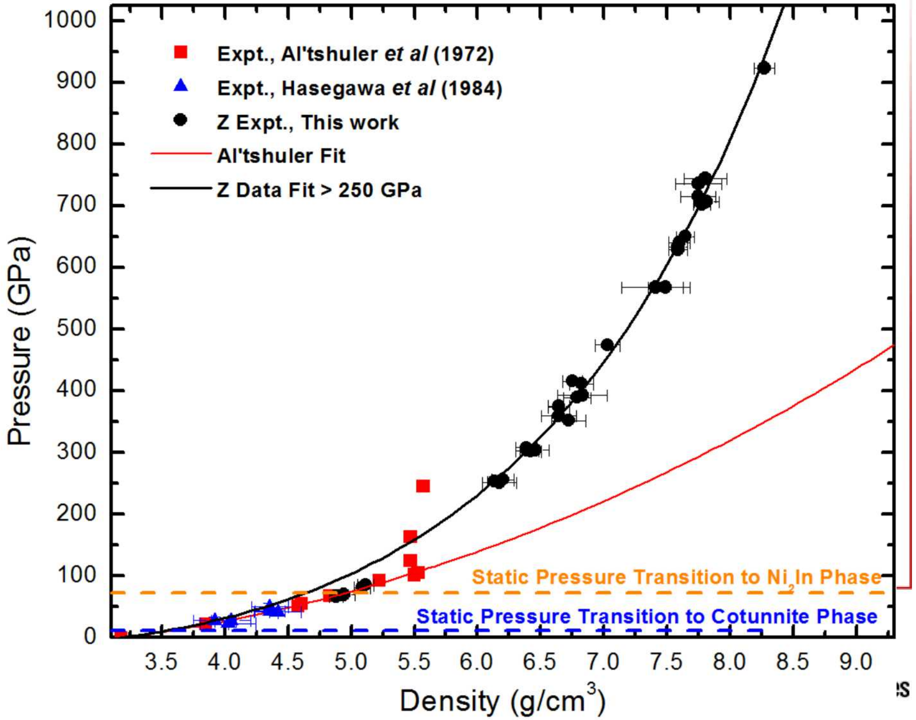




Z Experimental Results

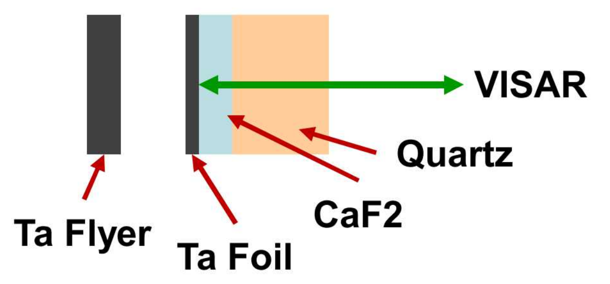
- **Measured the Hugoniot from 250 GPa to 950 GPa**
- **One shot at 65 – 85 GPa – consistent with Al'tshuler data below 100 GPa**
- **Hugoniot determined using *Monte Carlo* impedance matching**
- **Data show a monotonically increasing trend above 250 GPa**
- **Data deviate from the <110 GPa Al'tshuler fit**
- **Data are not consistent with the observed incompressible behavior**

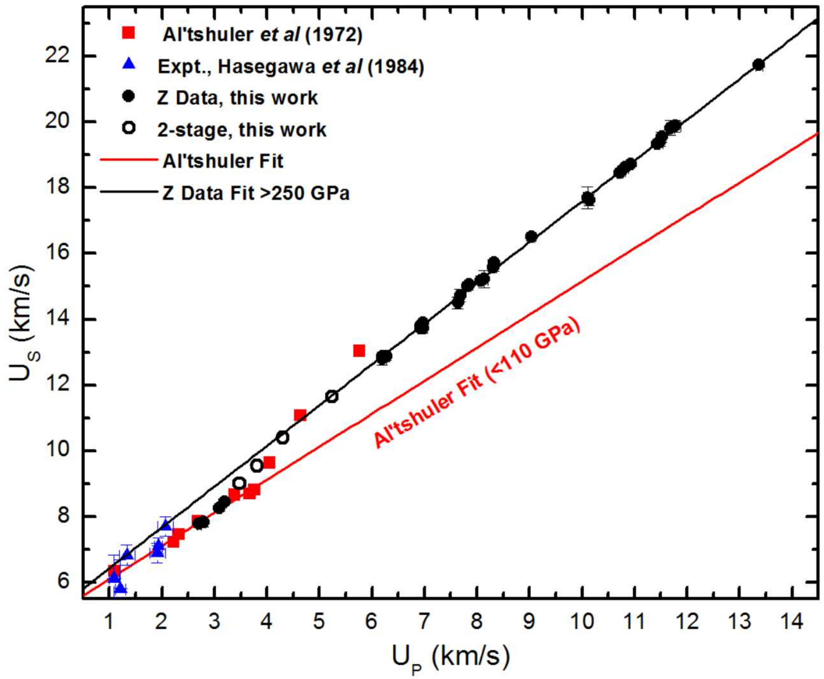


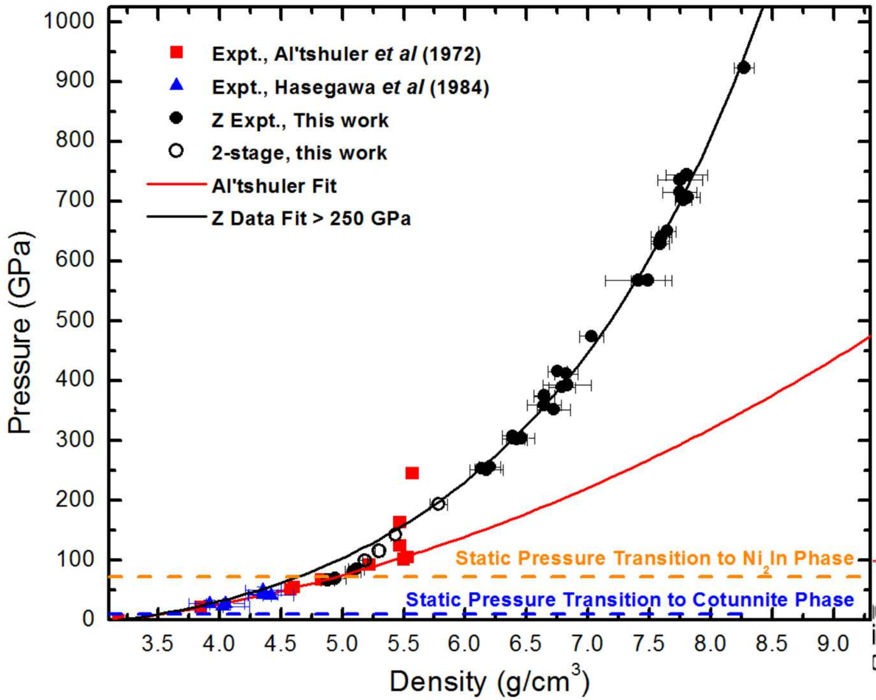


Two-Stage Experimental Results

- **Two-stage experiments using Ta impactors and [111] CaF2**
- **Impact velocities from 4.7 km/s to 7 km/s**
- **Transit time measurement with *Monte Carlo* impedance matching to Ta**
- **Higher pressure data (~200 GPa) consistent with the Z data**
- **Data between 100 GPa and 150 GPa show a slope change suggesting a phase transition**







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Density Functional Theory Simulations

- Use DFT-MD to assess the CaF_2 Hugoniot at high pressures and temperatures

- DFT-MD simulations performed using VASP 5.4.1*
- Electronic states occupied according to Mermin's finite-temperature formulation
- Calculate energy and pressure for a given density and finite temperature
- Satisfy the Hugoniot Condition: $2\left(E - E_{ref}\right) - \left(P + P_{ref}\right)\left(v_{ref} - v\right) = 0$

- Atoms/Simulation: Fluorite, Cotunnite, and Liquid = 96; Ni2In = 108
- PBEsol exchange correlation functional
- Energy cutoff is 900eV
- Checked for convergence: number of atoms, energy cutoff, etc
- VASP PAW potentials: Ca_sv_GW_31Mar2010 (10e-), F_GW_19Mar2012 (7e-)

* G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993) and Phys. Rev. B **49**, 14251 (1994).

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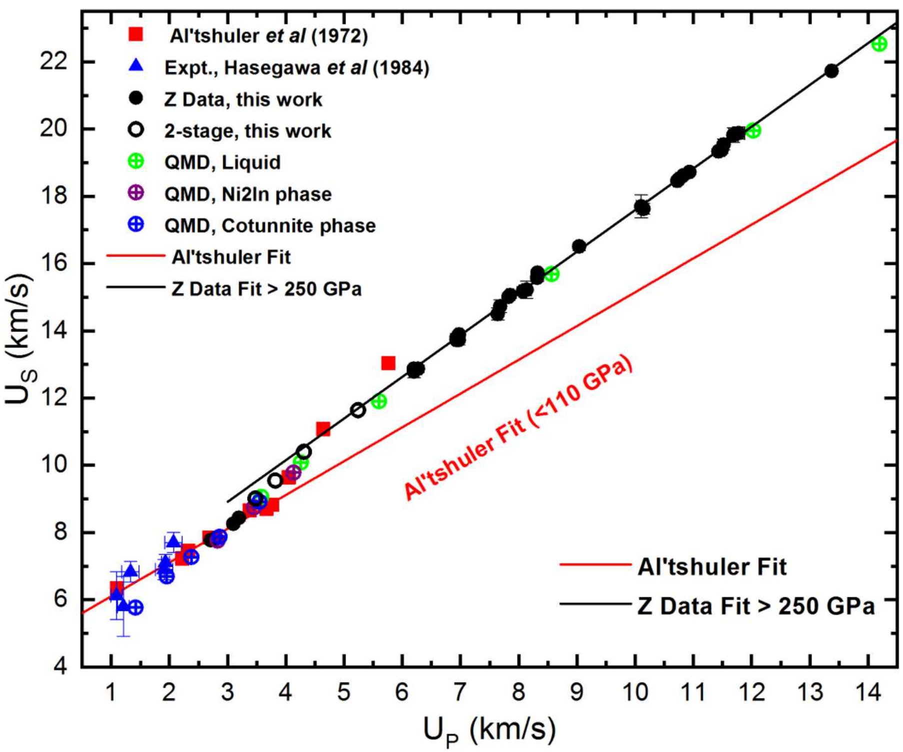
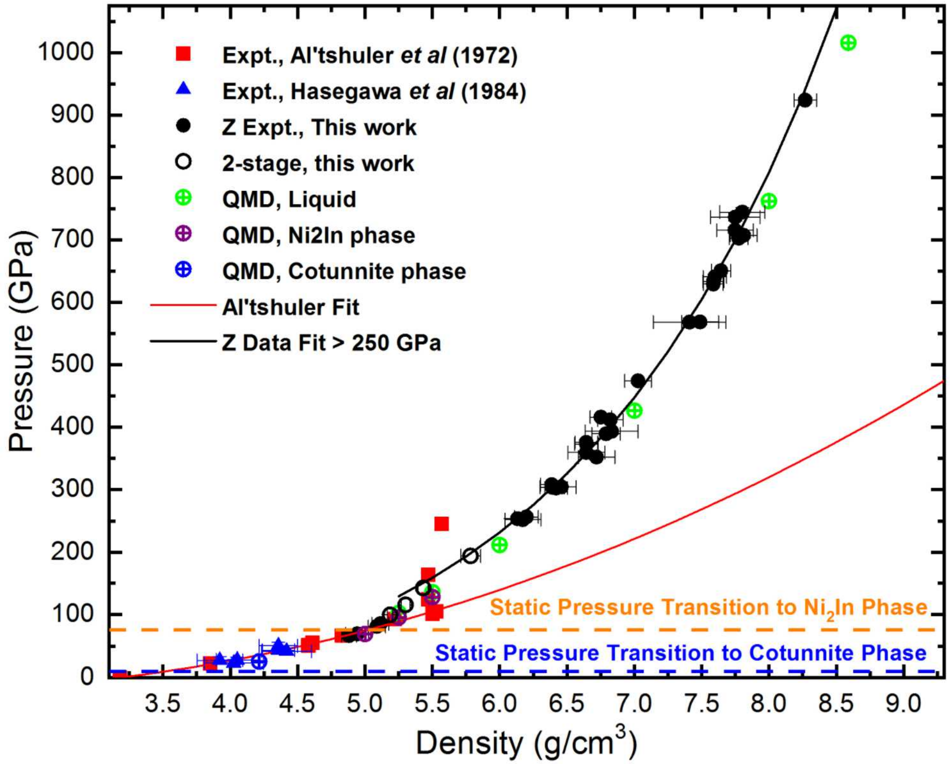
DFT Results and Comparison

- **DFT Liquid Hugoniot is consistent with the Z data above 200 GPa**
- **DFT simulations do not show Al'tshuler incompressibility**
- **Simulations on the liquid are consistent with the slope change between 100 GPa and 150 GPa**
- **Simulations on Ni_2In phase are also consistent**
- **Cotunnite simulations melt at a density of 5.5 g/cm^3**





DFT Results and Comparison

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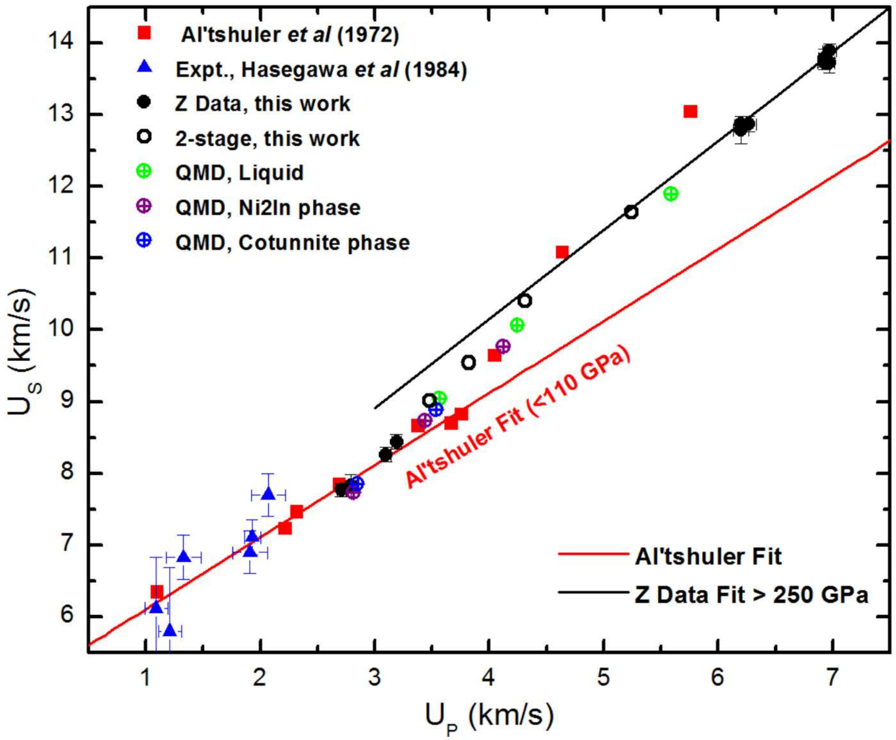
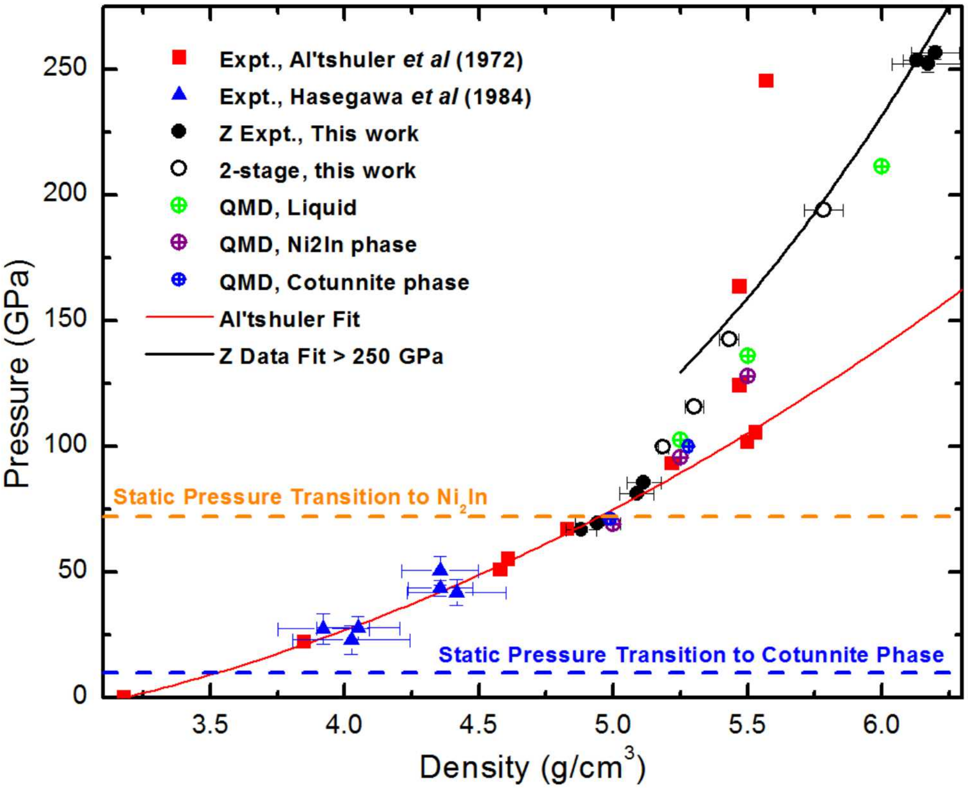
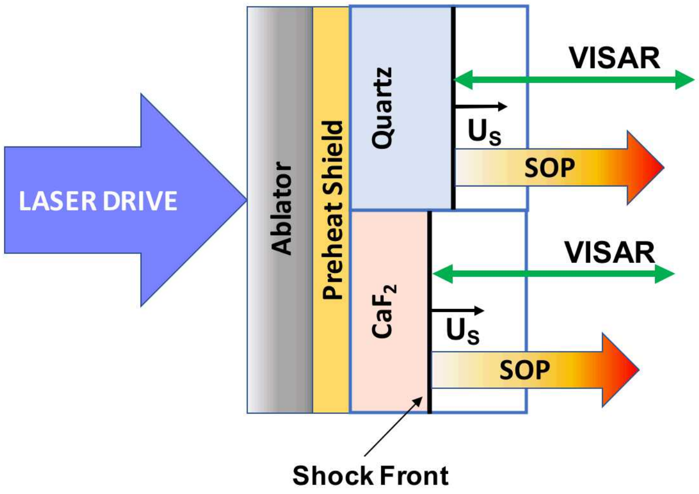
- Simulations on the liquid are consistent with the slope change between 100 GPa and 150 GPa
- Simulations on Ni_2In phase are also consistent
- Cotunnite simulations melt at a density of 5.5 g/cm^3
- CaF_2 is likely melting, but further work is needed

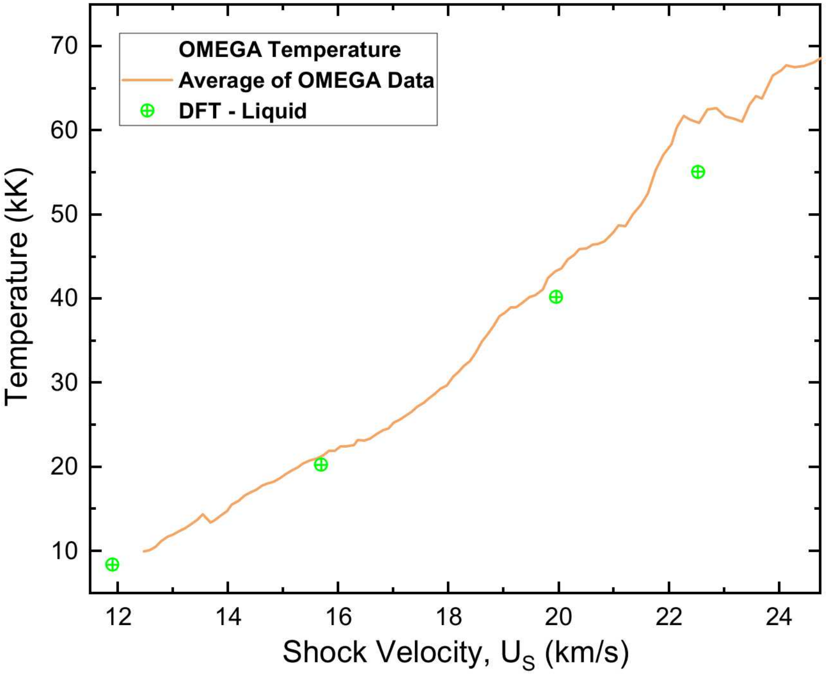


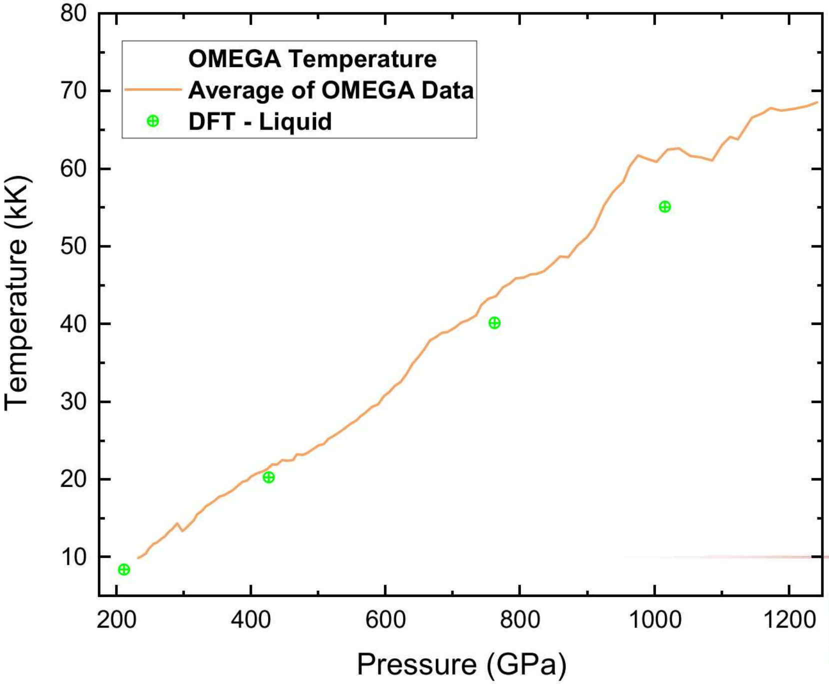


Hugoniot Temperatures

- Z has temperature measurement capability
- Hugoniot temperature easily measured using decaying shocks at OMEGA facility
- The QMD provides temperature automatically
- QMD and OMEGA temperatures are in good agreement







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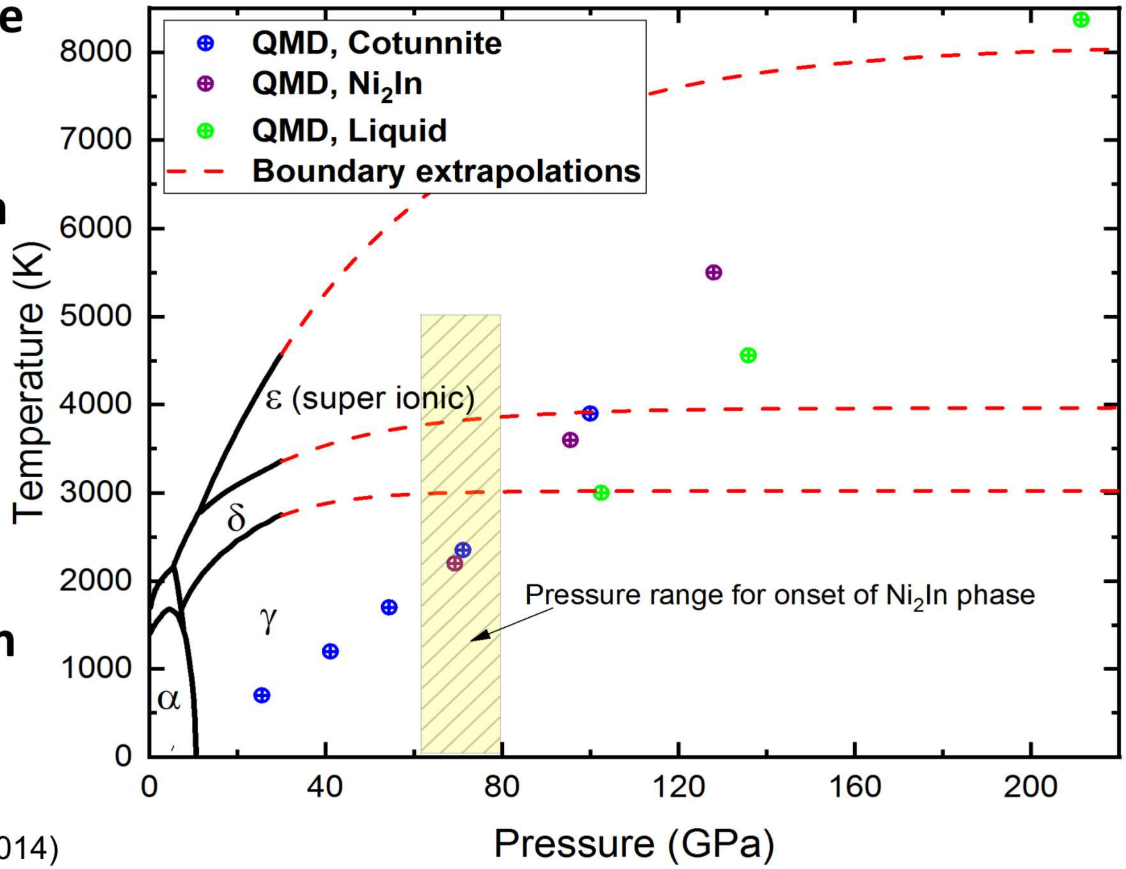
Calcium Fluoride Phase Diagram

- The extended phase diagram is unknown
- Both Carzola and Nelson predict a high pressure, high temperature phase δ
- Both Carzola and Nelson predict a super-ionic phase
- Dorfman's results show a high pressure phase starting around 62 GPa

- Comparison of QMD and phase boundary extrapolations suggest the melt boundary is lower than Carzola and Nelson predict
  - Extrapolations are not unique
- Range of the δ phase is undetermined
- Location and range of the Ni_2In phase are undetermined

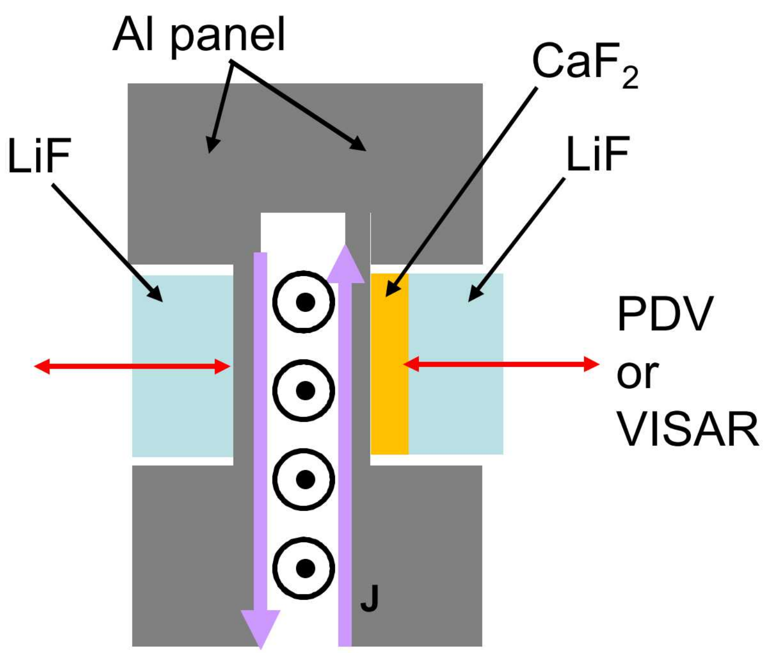


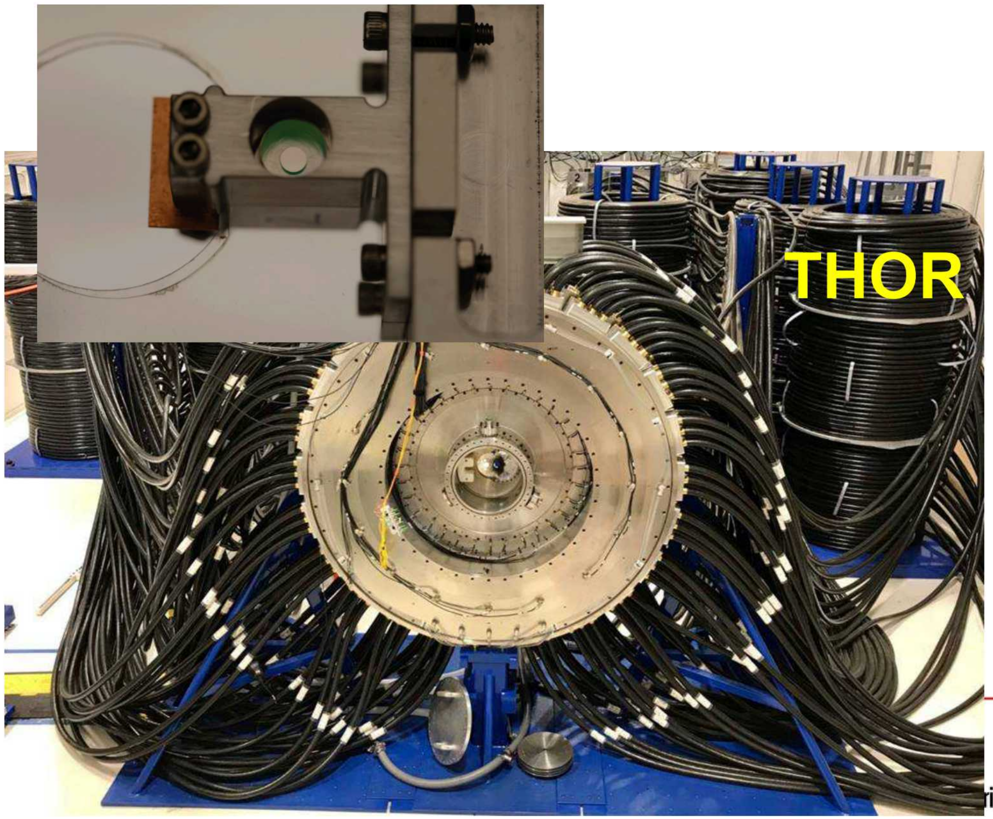
J. R. Nelson *et al*, PRB **95**, 054118 (2017)

C. Cazorla and D Errandonea, PRL **113**, 235902, (2014)

Shockless Compression Experiments

- **Preliminary experiments and analysis**
- **Used THOR to drive increasing loading rates into CaF2 [111] to examine elastic precursor behavior**
- **Comparison of [100] and [111] compressed above fluorite – cotunnite phase transition**





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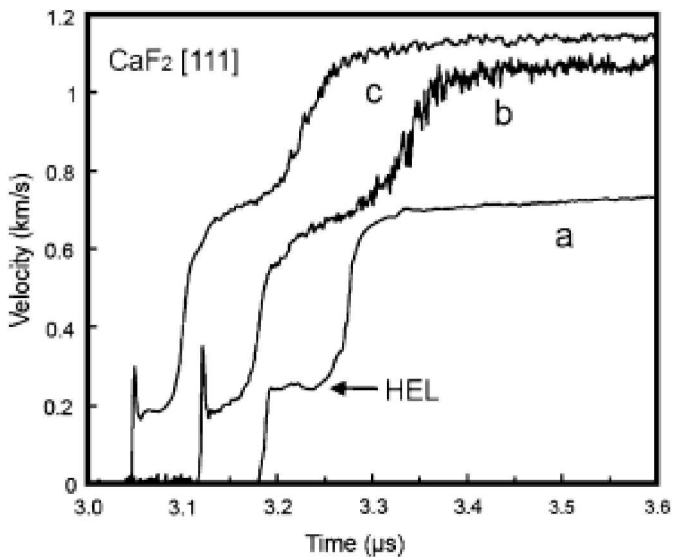
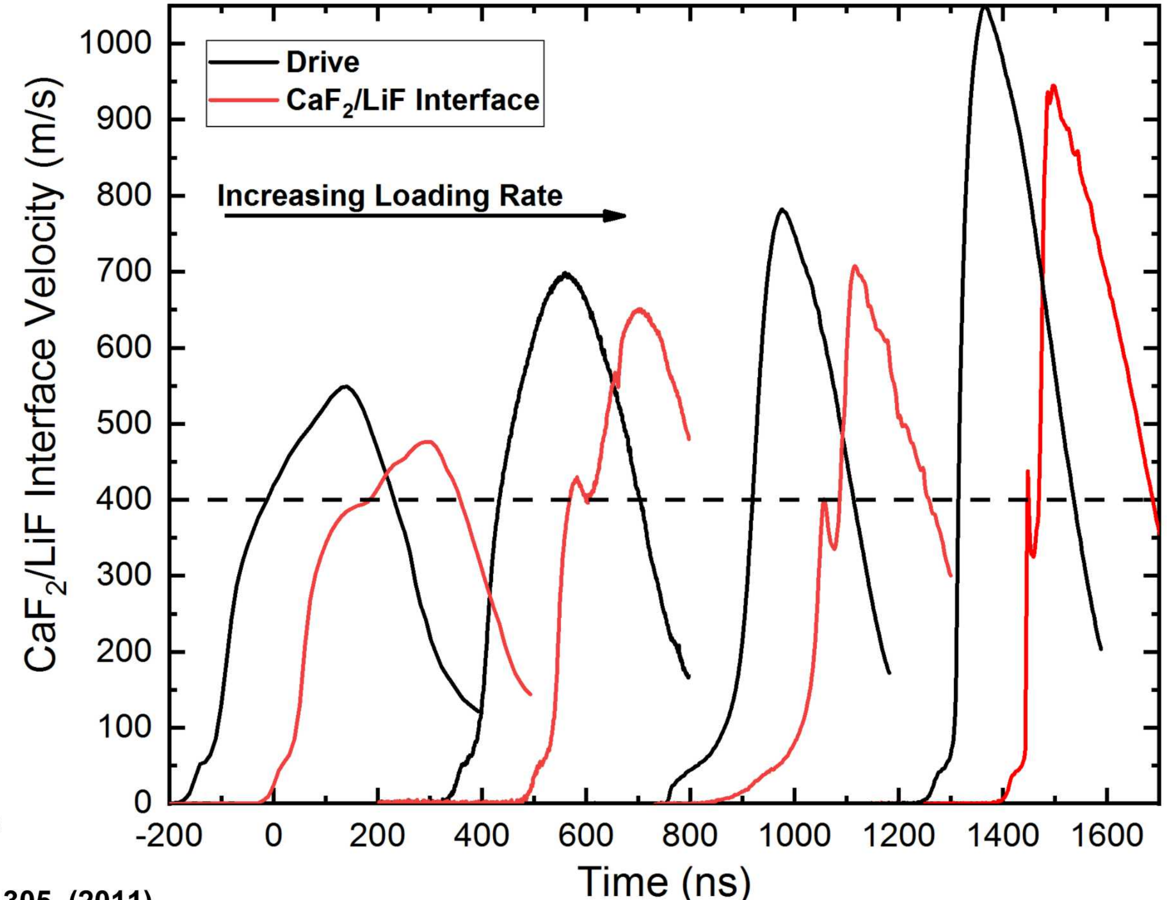
Shockless Compression Experiments

- **Preliminary experiments and analysis**
- **Used THOR to drive increasing loading rates into CaF_2 [111]**
- **As loading rate increases, elastic precursor qualitatively looks like earlier shock work**
- **Lowering the loading rate changes the elastic peak**
- **Lowering rate also lowers the peak stress state**

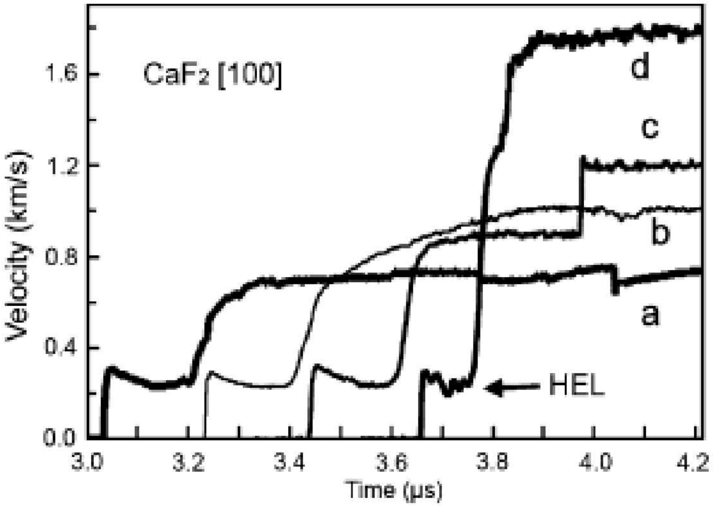


Sekine and Kobayashi, Phys. Chem. Minerals 38, 305, (2011)



Shockless Compression Experiments

- Preliminary experiments and analysis
- Used THOR to drive CaF2 above the fluorite-cotunnite transition
- High loading rate: both [111] and[100] show a sharp elastic precursor
  - Contrasts with Sekine's results on [100]
- Phase transition shows at velocities near 1000 m/s
- Under static compression the transition reduces volume by ~6%



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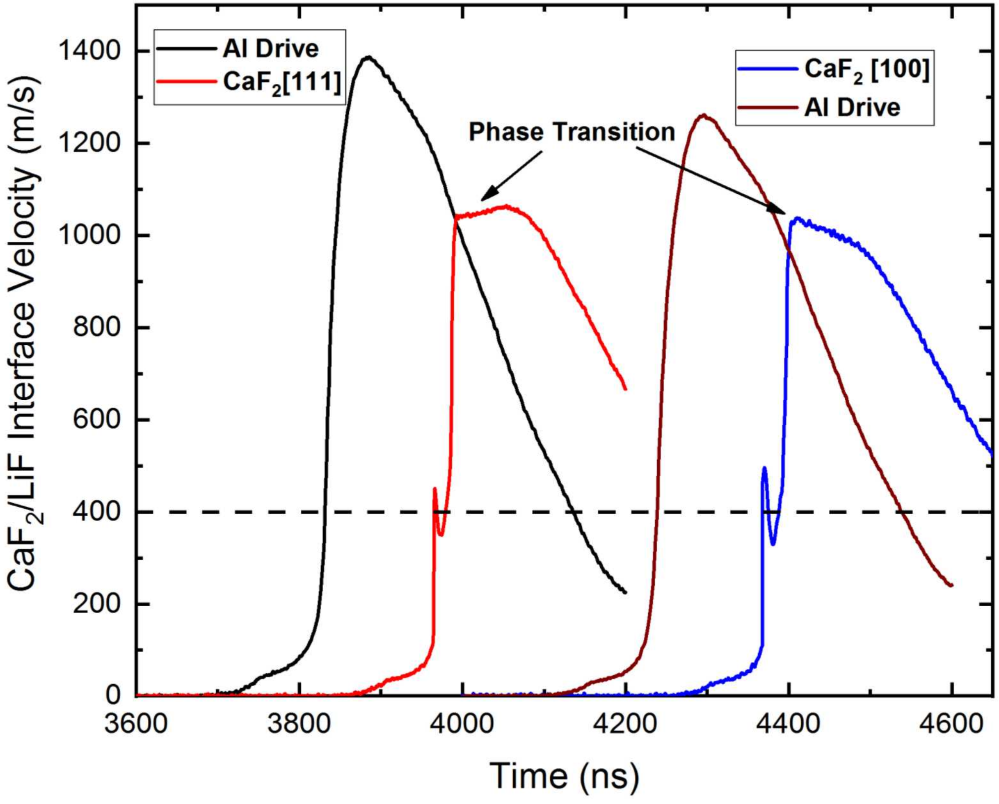
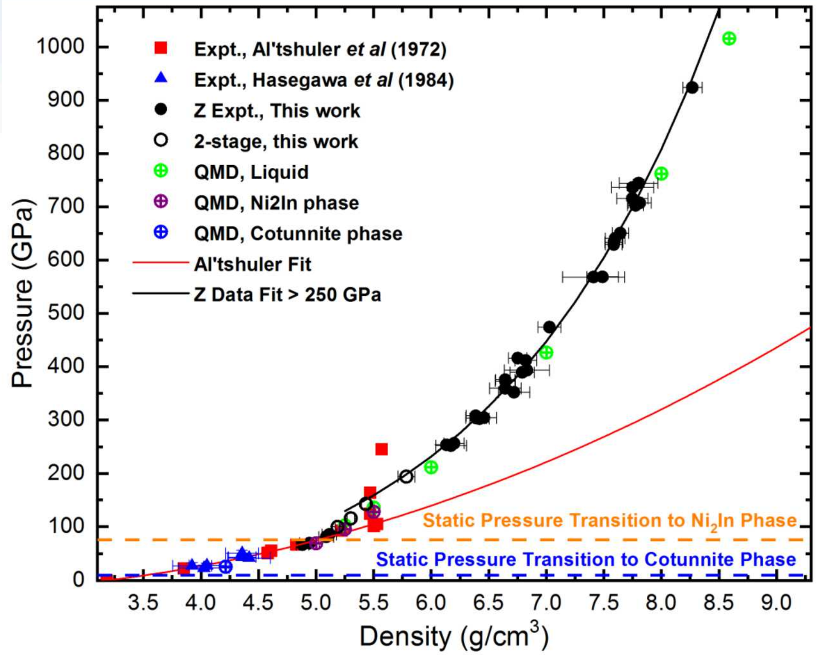
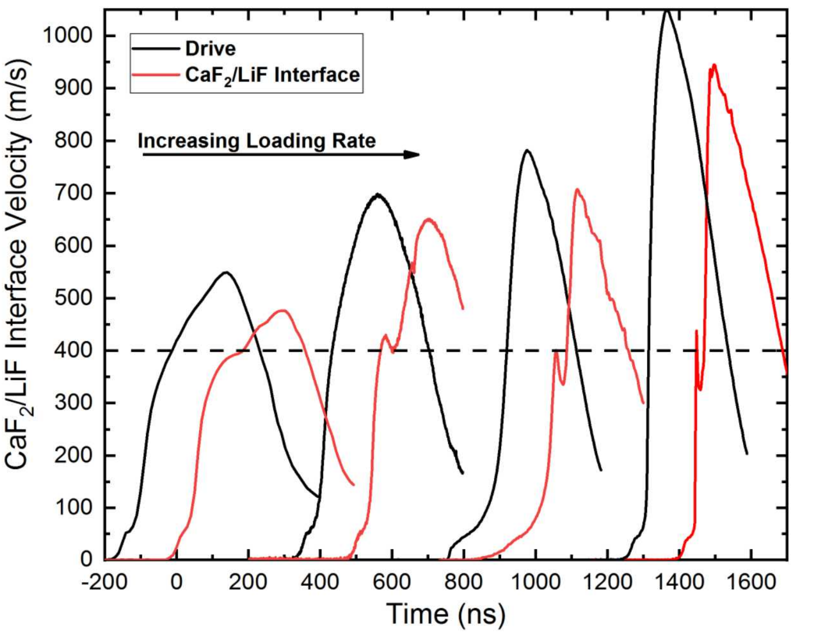


Summary

- Shock compressed CaF_2 from 65 GPa to 950 GPa
- Above 200 GPa, CaF_2 is likely melted
- DFT simulations in liquid state are consistent with the Z data > 200 GPa
- Between 100 and 150 GPa, the QMD results using solid CaF_2 and liquid are consistent with the data
- Further DFT work is needed – comparison of Gibbs energies
- Phase boundaries are undetermined
- Loading rate affects the behavior of the elastic precursor





Collaboration Objectives and Questions

Phase Transitions and Phase Diagram

- **Develop a data-driven, multiphase equation of state for CaF_2**
- **Understand phase diagram over a broad range of pressure and temperature**
- **Understand the kinetics of the phase transitions**
    - The Hugoniot below 100 GPa is complicated by multiple wave structures – can we understand these?
    - Along the Hugoniot, does melt start from the cotunnite phase or do other solid phases exist?
    - What does the extended phase diagram look like?
    - Shock, Shock-Ramp, and DAC experiments and DFT-QMD calculations

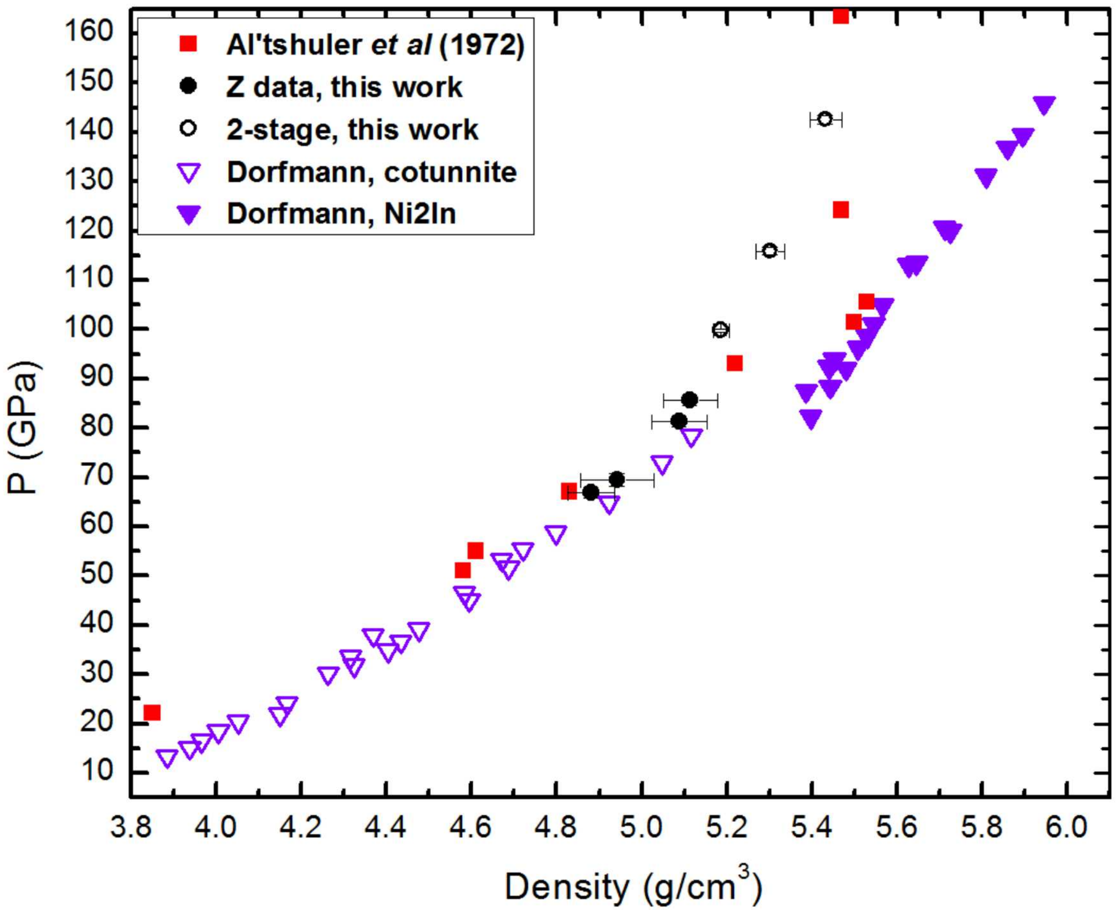
Elastic – Plastic Behavior

- **Examine the dynamics of the constitutive response and develop or validate a constitutive model**
    - How does loading rate and peak stress affect elastic precursor behavior?
    - Temperature and orientation effects on the elastic precursor?
    - Shock and shockless compression experiments

Extra Slides

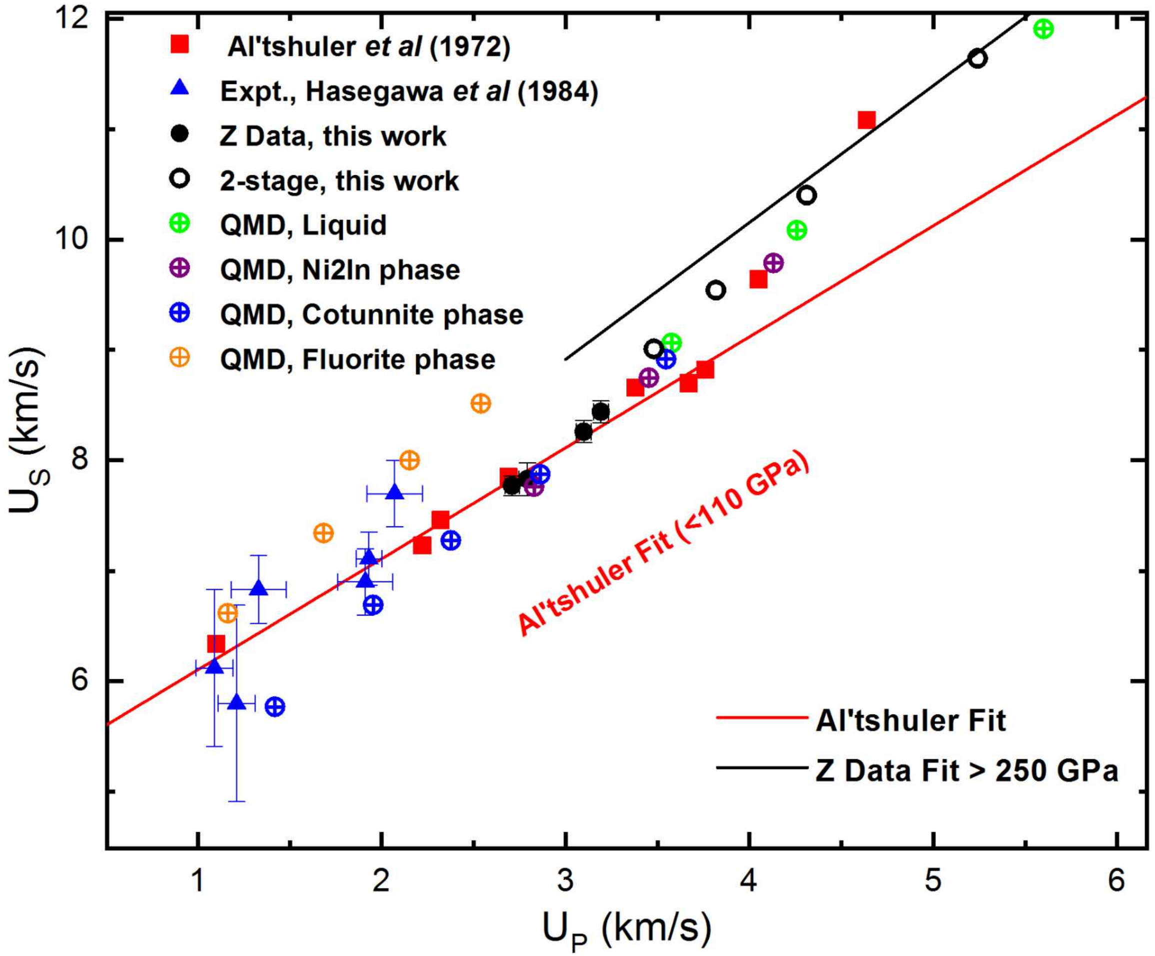
Melting Transition

- CaF_2 is likely melting
- CaF_2 becomes less compressible between 100 – 150 GPa range
- Dorfman's data show the Ni_2In transition has a volume reduction



* S. Dorfman *et al*, Phys. Rev. B **81**, 174121 (2010)
Dorfmann, private communication

Fluorite phase Hugoniot calculations



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