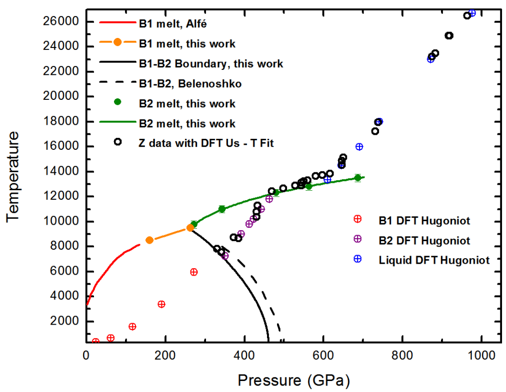
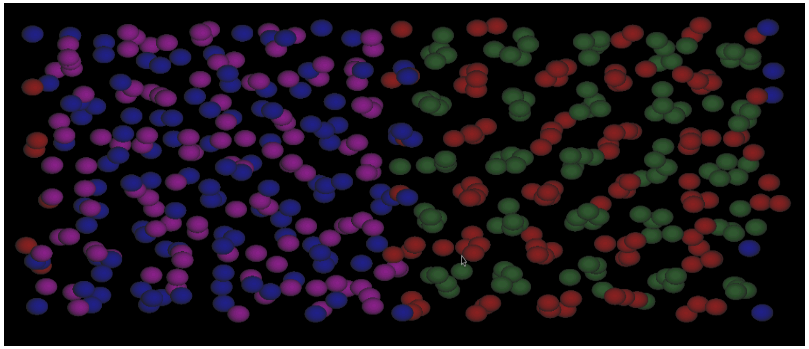
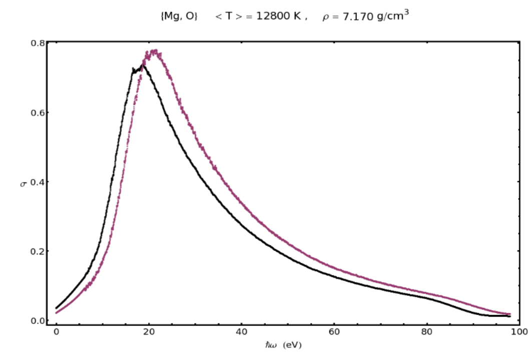
SAND2013-5427C

Exceptional service in the national interest

Sandia National Laboratories







The phase diagram and transport properties of MgO from theory and experiment

Luke Shulenburger

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

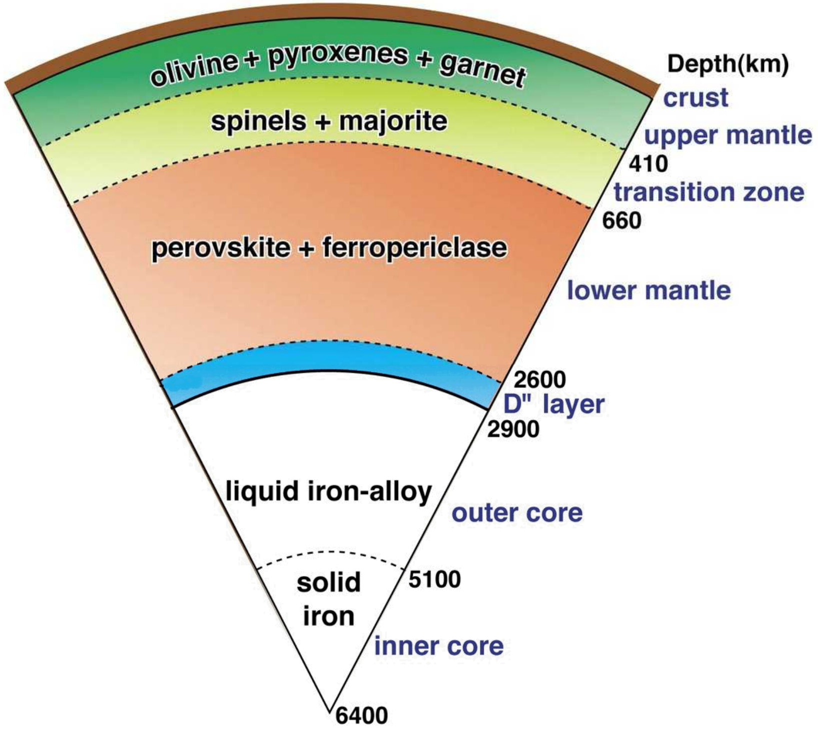
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

Acknowledgements

- Seth Root
- Kyle Cochrane
- Mike Desjarlais
- Dan Dolan
- Marcus Knudson
- Thomas Mattsson
- Z operations and target fabrication teams

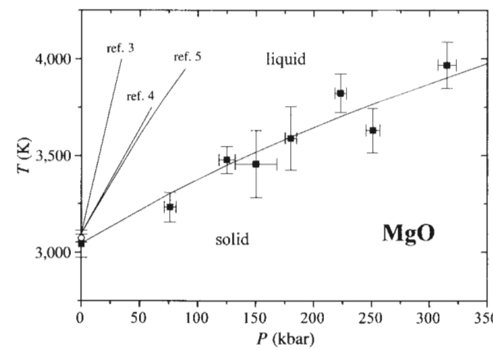
An understanding of MgO is important to planetary modeling

- MgO is an end member of the (Mg,Fe)O mineral that comprises a large fraction of the earth's mantle
- The shock behavior and transport properties are important to the study of giant impacts (A1.01)
- Useful check of experimental methodology: simple structure and transport properties

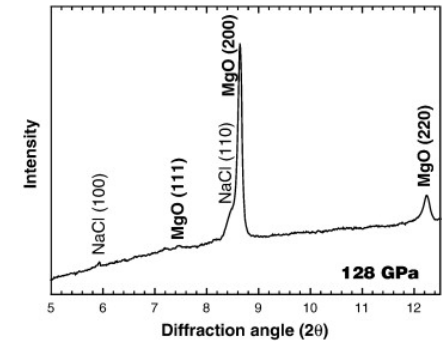


State of experiments prior to 2012

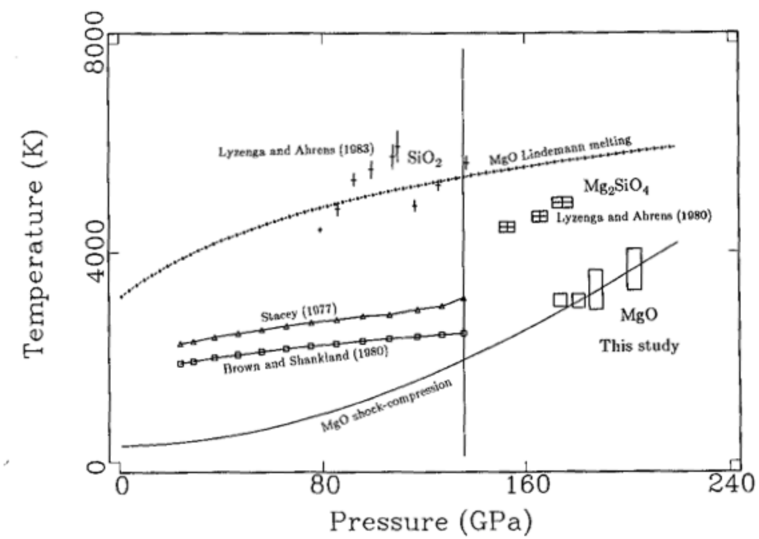
- Diamond anvil cell measurements of melt
- Diamond anvil cell XRD, Brillouin spectroscopy etc.
- Gas gun driven Hugoniot measurements of us-up and temperature
- Possibility of shock melting was unclear



Zerr and Boehler, Nature **371**, 506 (1994)



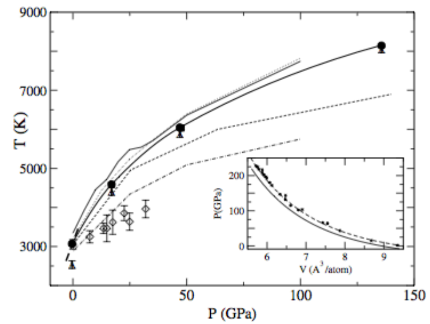
Murakami et al., EPL **277**, 123 (2009)



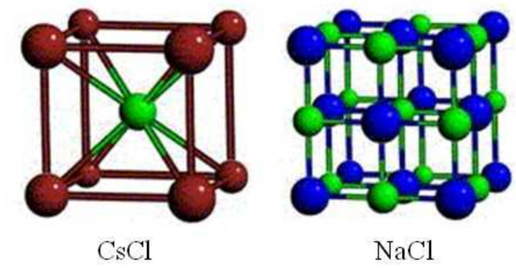
Svendsen and Ahrens, Geophys. J. R. astr. Soc. **91**, 667 (1987)

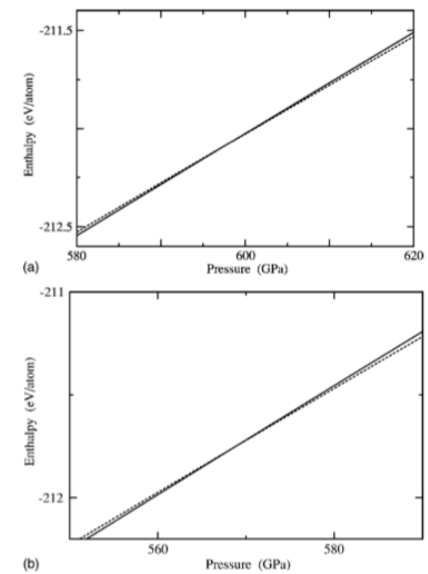
State of theory prior to 2012

- DFT and QMC predicted solid-solid phase transition at ~ 570-600 GPa
- Melt curve as a function of pressure from DFT-MD
- Wide range phase diagram utilizing ab initio calculations

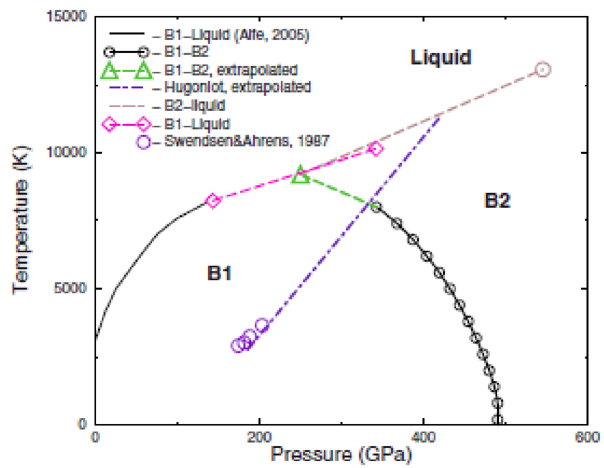


Alfe, PRL **94**, 235701 (2005)



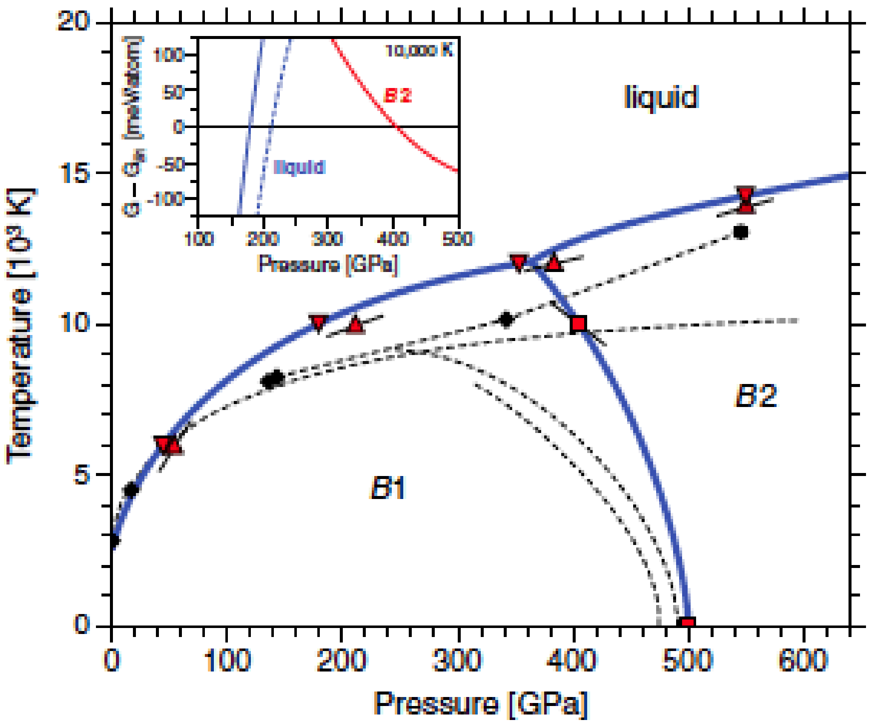


Alfe et al., PRB **72**, 014114 (2005)

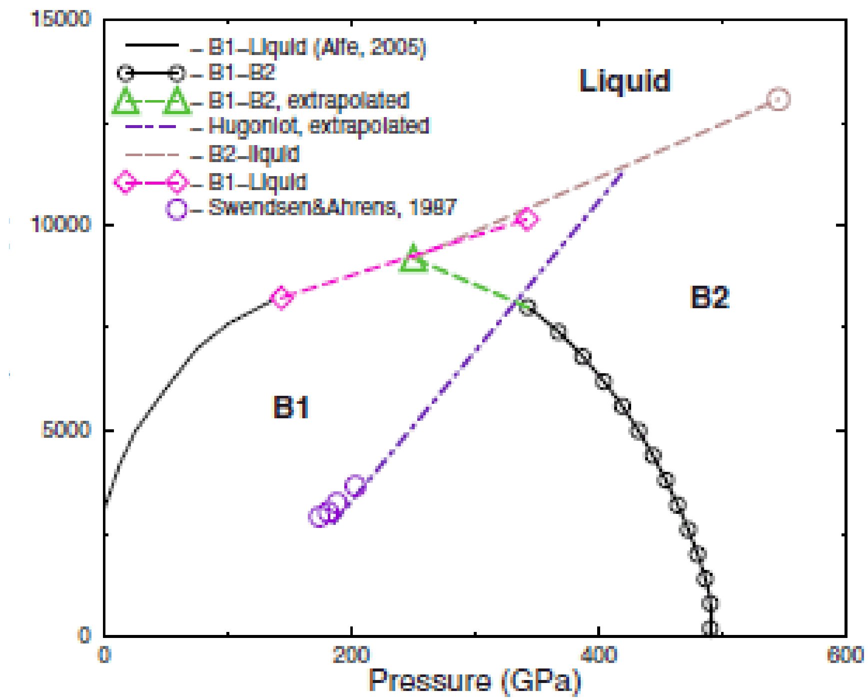


Belonoshko *et al.*, PRB **81**, 054110 (2010)

New theory paper refines phase boundaries



B. Boates and S. Bonev, PRL **110**, 135504 (2013).



Belonoshko *et al.*, PRB **81**, 054110 (2010)

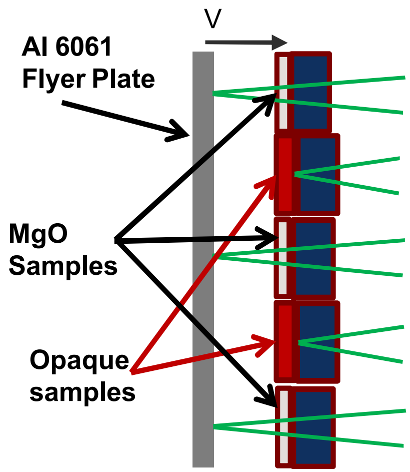
Opportunity exists for theory and experiment to complement each other

- DAC experiments in 3+ Mbar and 5,000K + regime are technologically difficult (currently impossible?)
- Dynamic experiments are typically limited by the ability to diagnose the product states
- Ab inito methods have potential theoretical limitations for studying the EOS of MgO
  - Free energy is difficult to compute and subject to uncertainties (H4.02)
  - "Band gap problem" in DFT will lead to premature metallization
  - Modest system sizes leave molecular dynamics calculations subject to difficult to converge errors

Two recent dynamic experiments offer new data

Steady shock from flyer plates

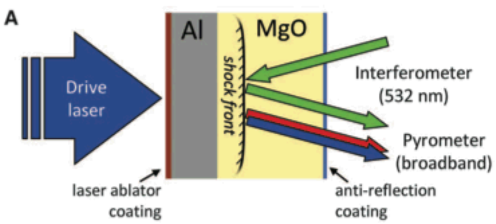
- Root et al.



- Measure u_s, reflectivity and u_p via impedance matching
- Longer transit times (~25 ns)
- Large number of shots to different final pressures (>30)

Laser driven decaying shock

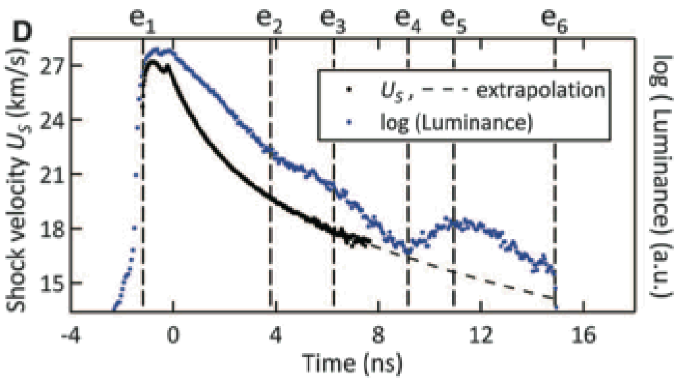
- McWilliams et al. Science **338**, 1330 (2012)

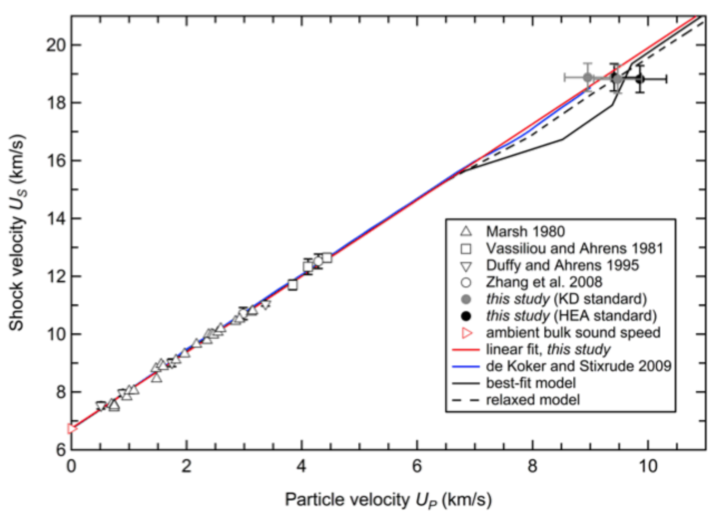


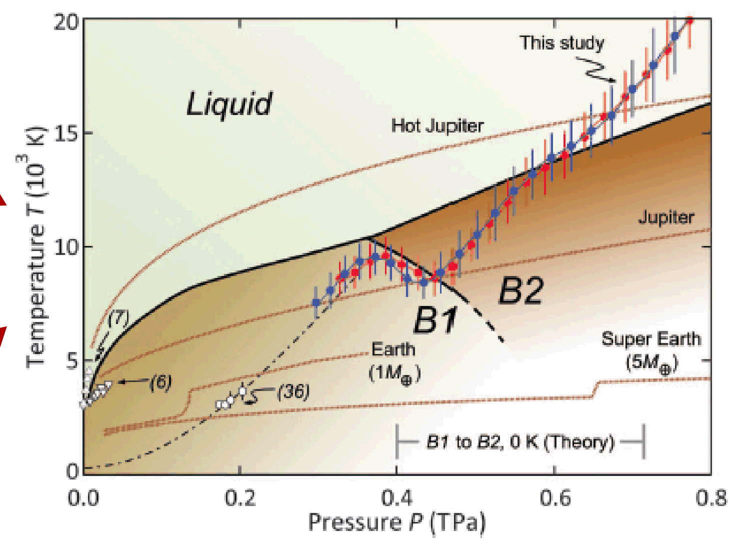
- Measure u_s, reflectivity and T as a function of time
- Potentially map entire Hugoniot in a single shot
- Must infer u_p from knowledge of Hugoniot
- Short time scales (transit through MgO lasts ~10 ns)

Experiments do not perfectly agree, leading to difference in interpretation

- McWilliams et al. measures u_s and T, using preexisting knowledge of Hugoniot to infer pressure



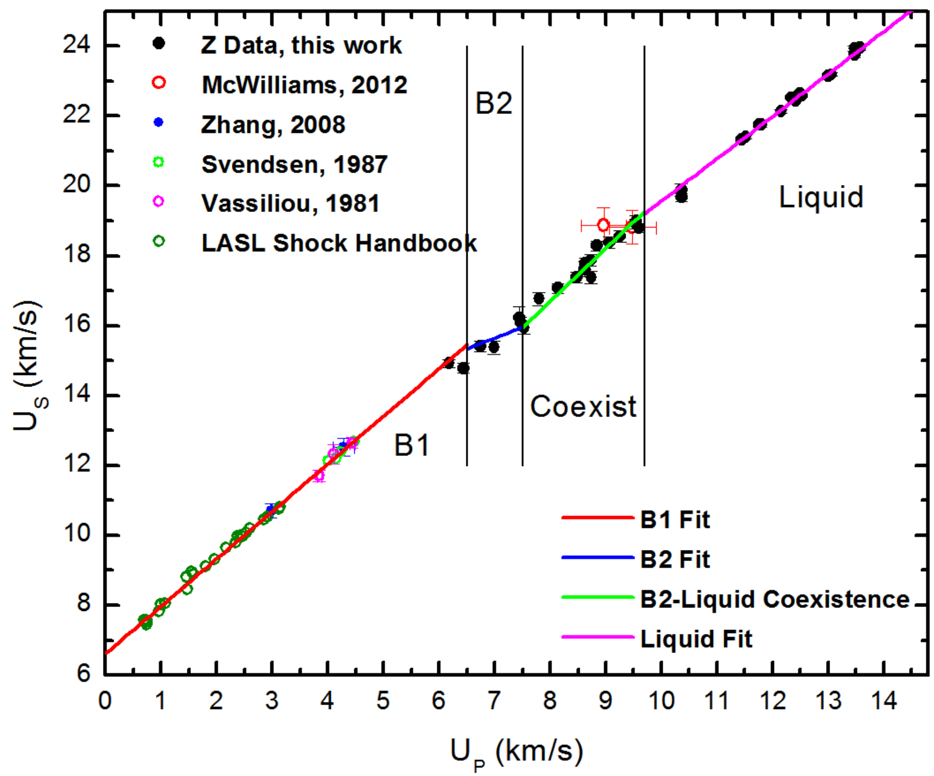




- Suggests large latent heat from B1-B2 solid, combined with small change at melt boundary

Experiments do not perfectly agree, leading to difference in interpretation

- Root et al. use many shots to map u_s vs u_p along the Hugoniot
- Phase changes are inferred by assuming u_s vs u_p is linear in any given phase
- Similar method applied to diamond (Knudson et al, Science **322**, 1822 (2008).
- Coincident with last break, shock becomes reflective
- Implies large coexistence between B2 and liquid

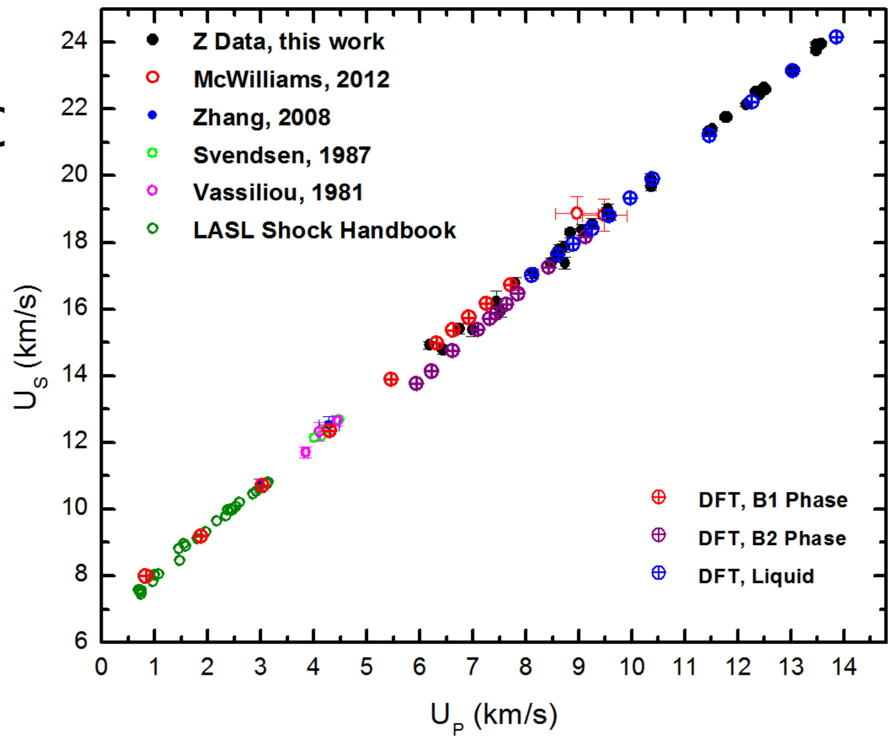


Gain insight by comparing experiments to ab inito calculations

- Calculate Hugoniot using DFT-MD as implemented in VASP*
- Electronic states occupied according to Mermin's finite-temperature formulation with AM05 functional
- Satisfy the Hugoniot Condition:

$$2\left(E - E_{ref}\right) - \left(P + P_{ref}\right)\left(v_{ref} - v\right) = 0$$

- Finite size (~250 atoms) and duration (~3 ps) of simulations require symmetry to be imposed in the solid phase



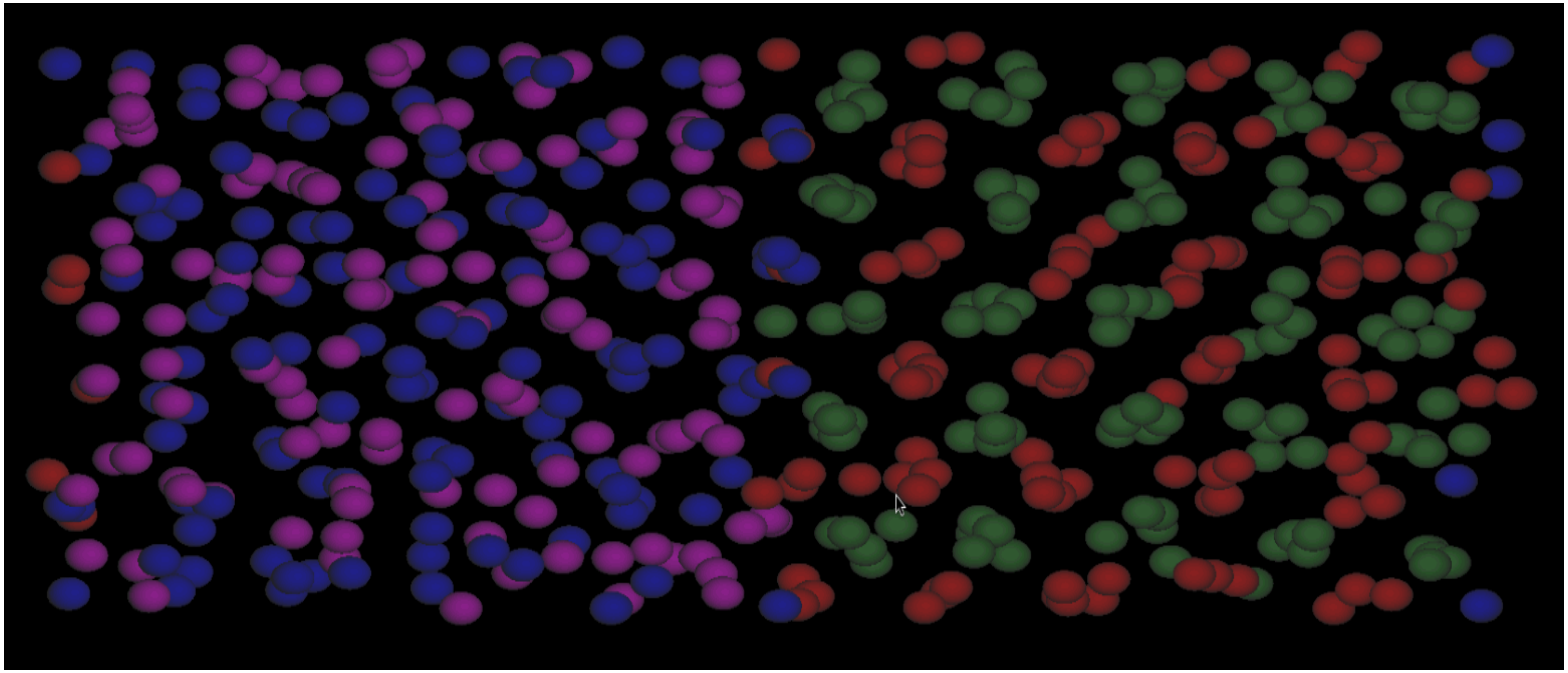
$$u_p = \sqrt{P\left(\frac{1}{\rho_0} - \frac{1}{\rho}\right)}$$

$$u_s = \sqrt{\frac{P/\rho_0}{(1-\rho_0/\rho)}}$$

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

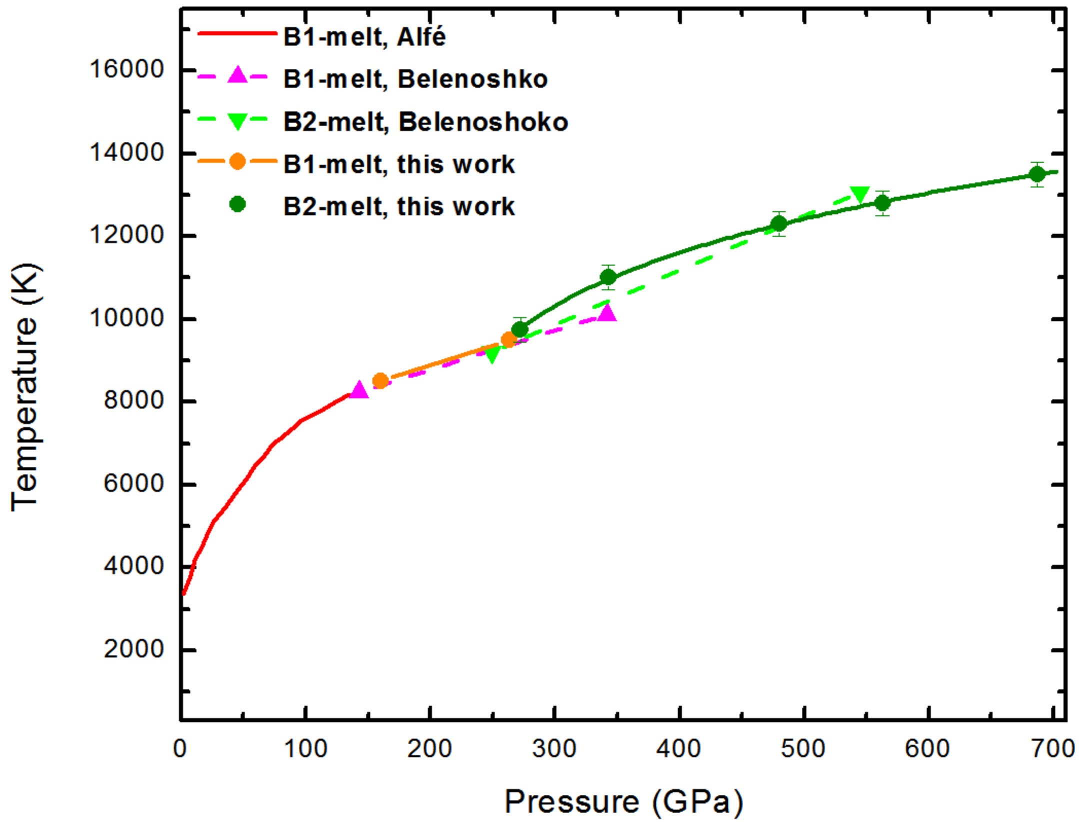
Directly calculate Solid-Melt Boundaries

- For melting boundary use two phase coexistence simulations
- Place solid and liquid in contact with each other
- Run at different temperatures and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of coexistence



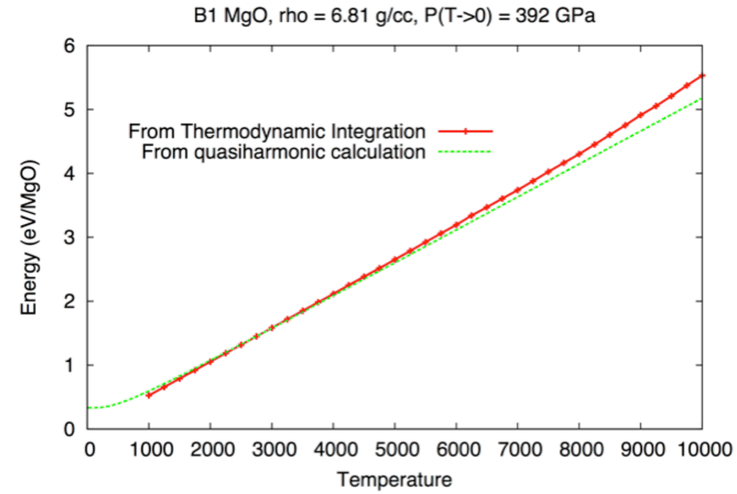
Directly calculate Solid-Melt Boundaries

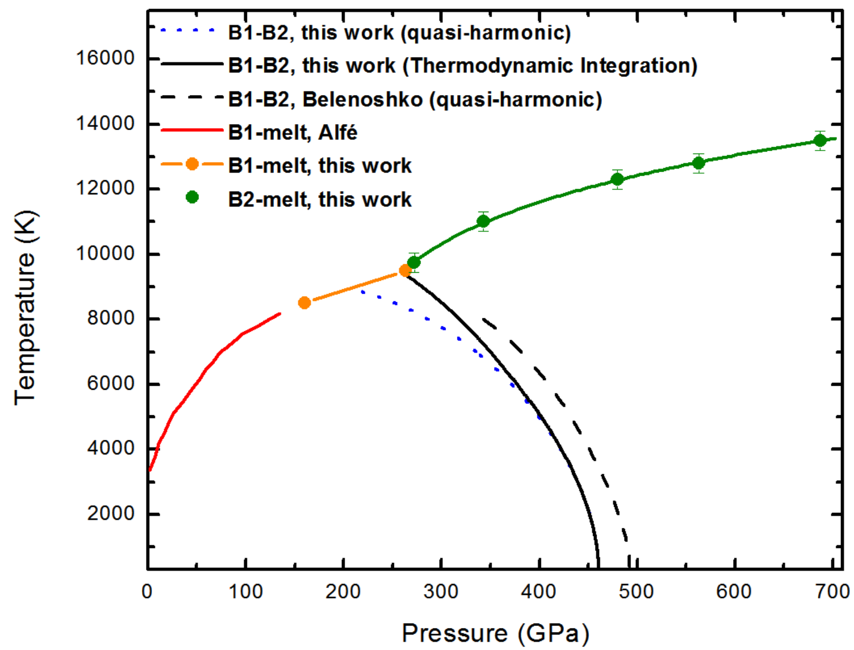
- For melting boundary use two phase coexistence simulations
- Place solid and liquid in contact with each other
- Run at different temperatures and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of phase coexistence
- Follow work of Belonoshko, but include quantum calculations of B2 phase melting



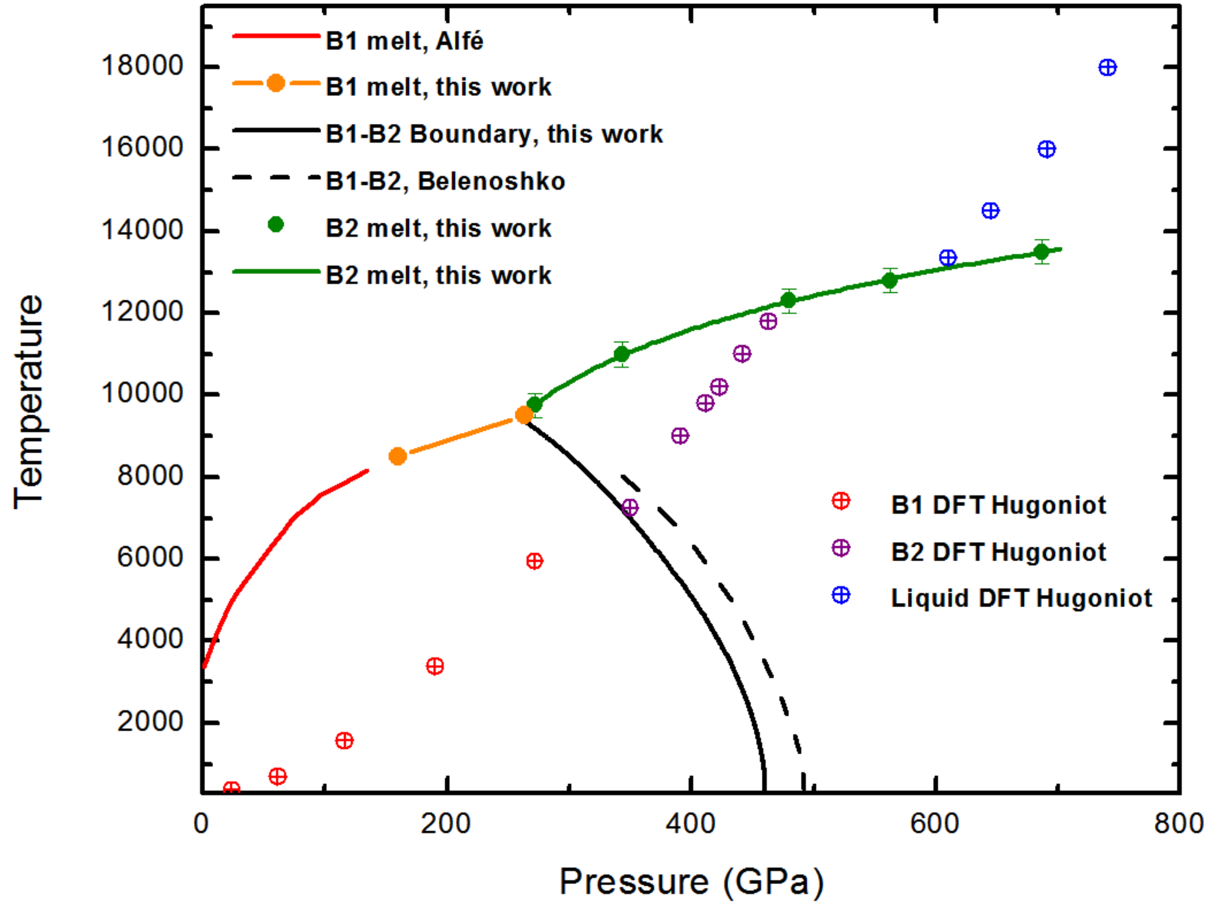
Calculation of solid-solid phase boundary

- At low temperatures, harmonic phonon approximation provides free energies
- Entropy can be calculated directly using analogy to finite temperature quantum harmonic oscillator
- Approximation breaks down for moderate temperatures
  - Effect is strongest in B1 phase
- Switch to thermodynamic integration using multiple DFT-MD calculations along each isochore
- Resulting phase boundary finds triple point between B1, B2 and liquid





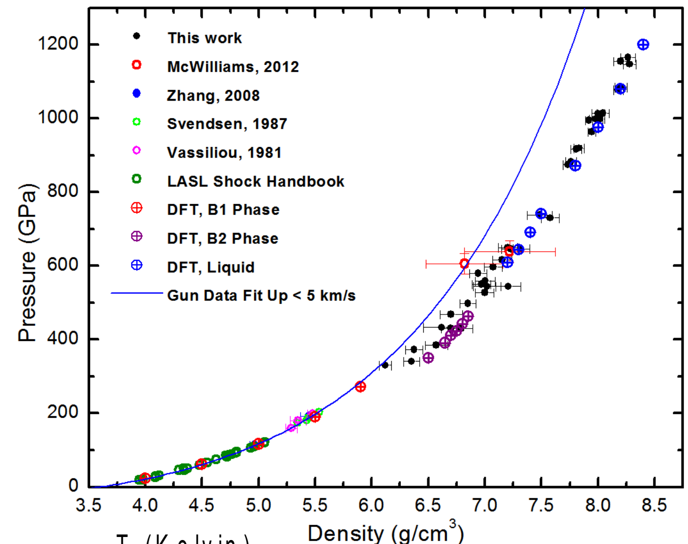
New phase diagram with Hugoniot

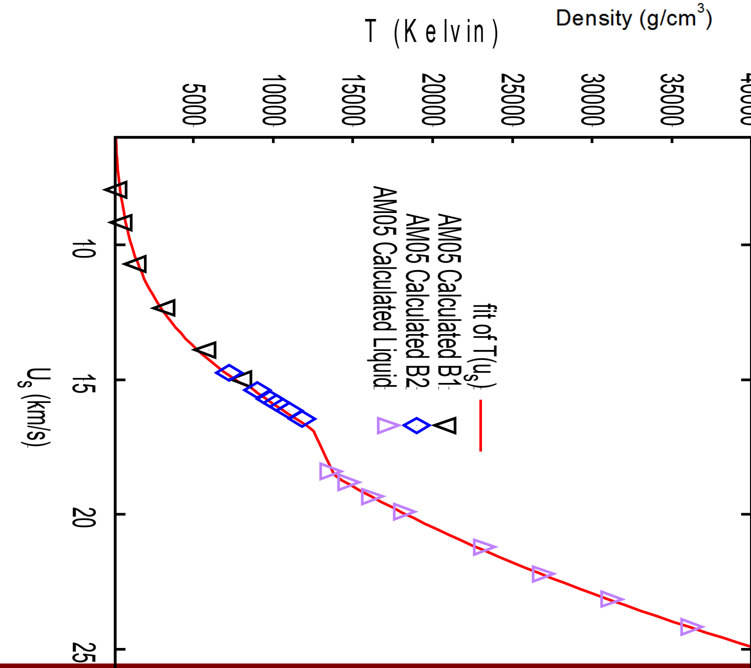


- Knowledge of phase boundaries allows for the metastable simulations to be eliminated
- How does this compare to experiments

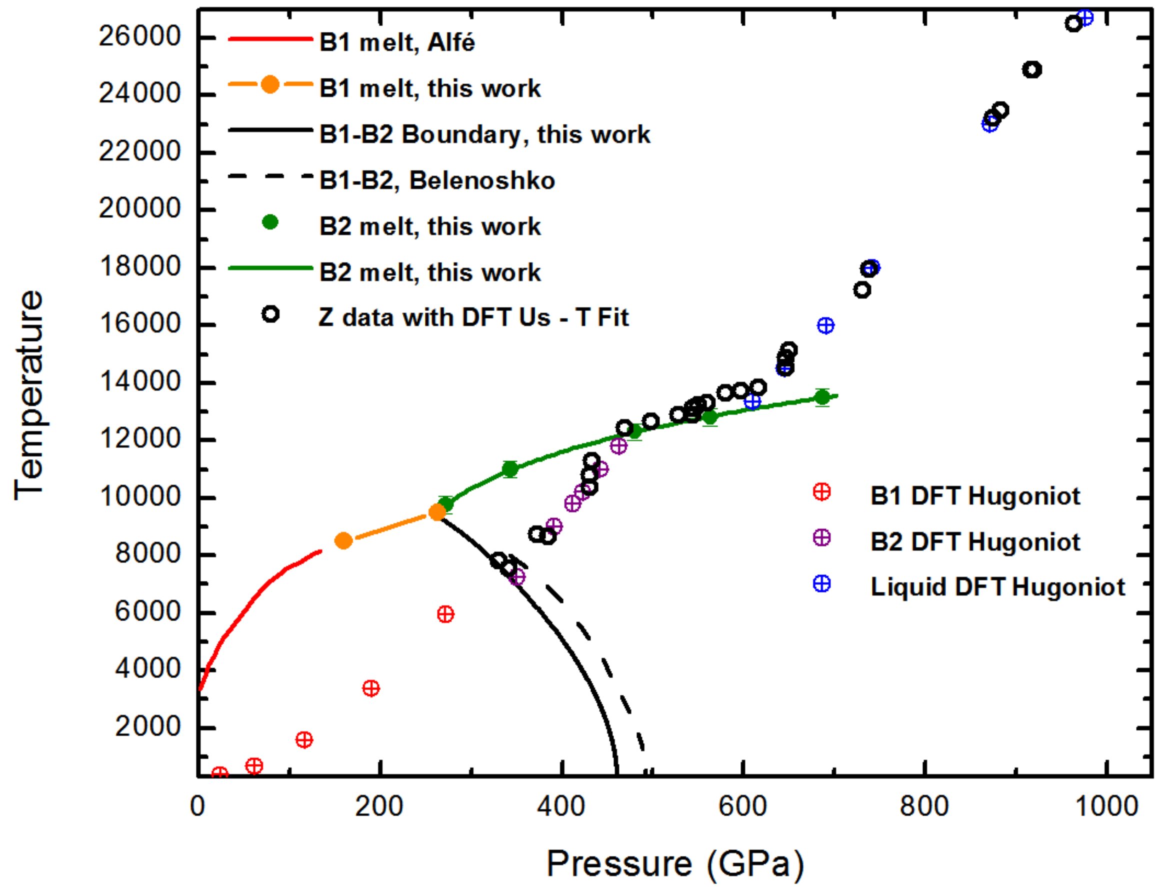
Use QMD to assign temperatures to the Sandia experiment

- No pyrometry is available for the Root et al data set
- Close agreement with QMD allows for possibility of using theoretical temperatures
- Construct $T(u_s)$ along the Hugoniot from QMD



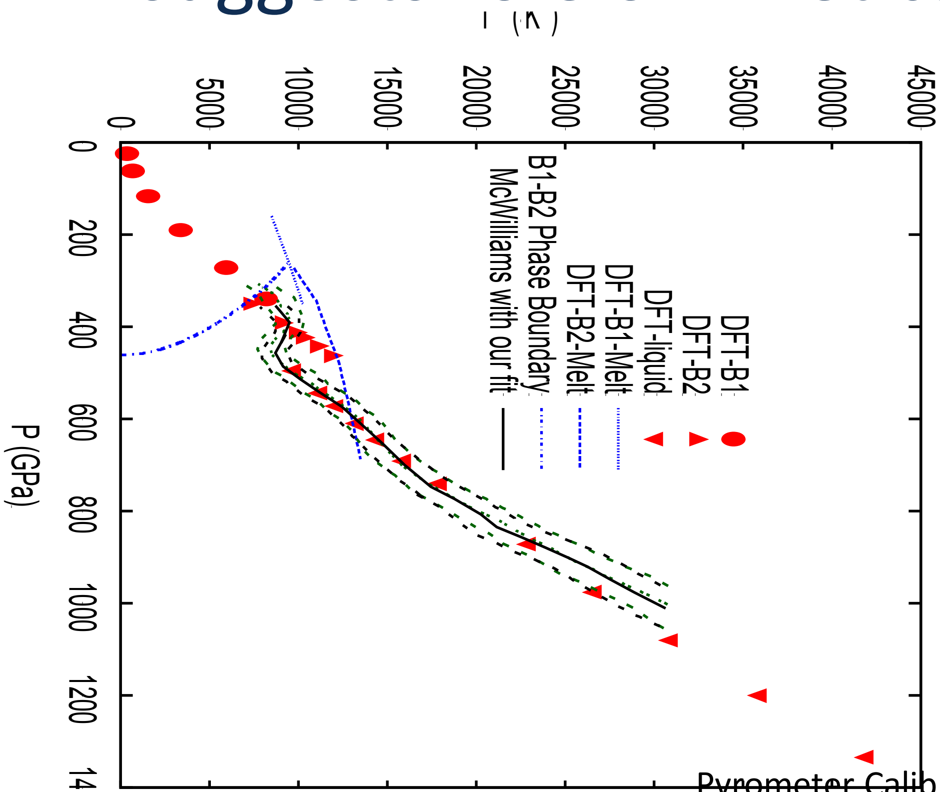


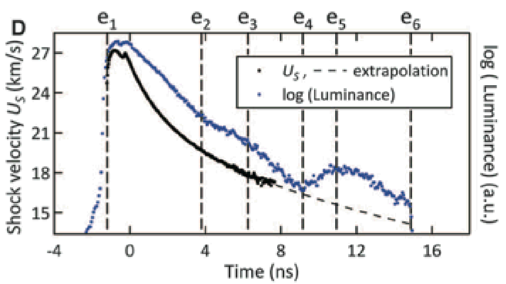
Theory and experiment agree on Hugoniot



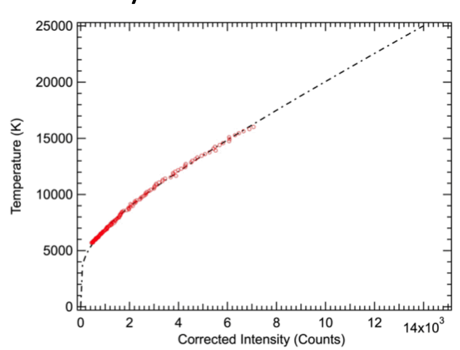
- Use U_s vs T fit from DFT calculations and apply to Root data
- DFT confirms a large coexistence region between B2 and liquid on the Hugoniot

Comparison to McWilliams results suggests role of kinetics





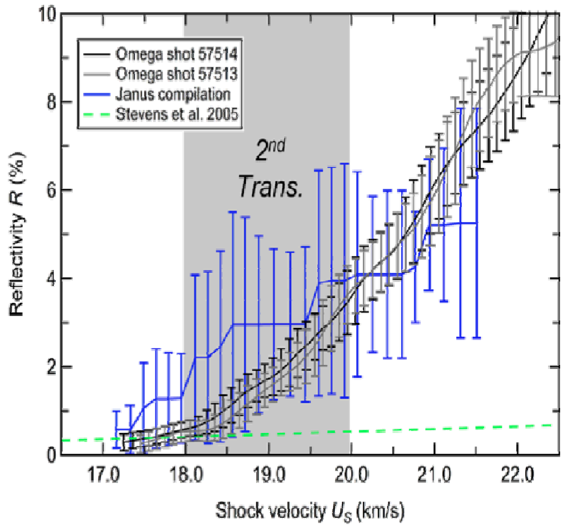
Pyrometer Calibration



- Excellent agreement at higher pressures in liquid phase
- Slight discrepancy with temperature at high pressure explained by calibration
- Disagreement occurring at B2 – Melt boundary
  - Decreased luminance due to scattering in two phase region?
  - Extrapolation of $u_s(t)$ for nonreflective shocks?
  - Metastable liquid observed in decaying shock front?

Reflectivity change provides additional evidence of melt boundary

- McWilliams and Root both measure reflectivity at 532nm as a consequence of their use of VISAR interferometry
- In each case, the reflectivity disappears for shock speeds less than ~18 km/s
- Explanation due to metal to insulator transition going from liquid to B2 phase



McWilliams et al. Science. **338**, 1330 (2012)

Confirm melting hypothesis by calculating reflectivity using QMD

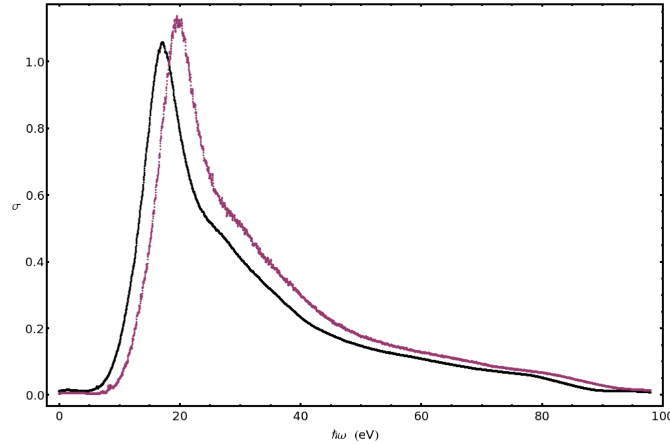
- Use Kubo-Greenwood formulation on snapshots from the B2 solid and liquid near the melt boundary

- Kramers-Kronig relation allows calculation of complex dielectric function

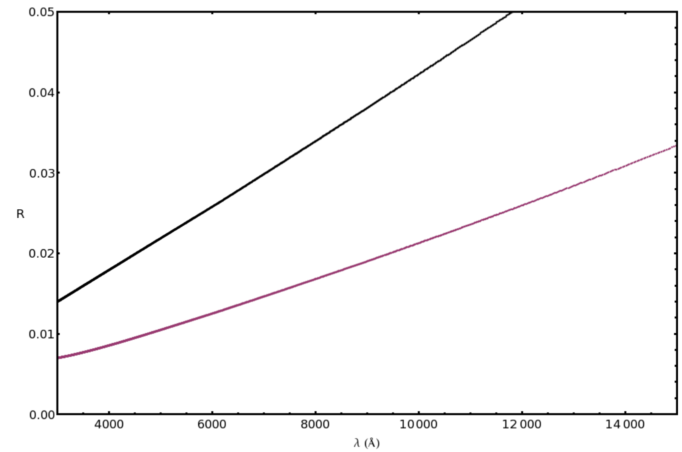
$$\sigma_2(\omega) = -\frac{2}{\pi} P \int \frac{\sigma_1(\nu)\omega}{(\nu^2 - \omega^2)} d\nu$$

- Use of HSE functional provides a better description of the gap and the reflectivities agree with experiment

Optical conductivity of solid



Reflectivity of liquid



Solid reflectivity at 532 nm: 0.02%
Liquid reflectivity at 532 nm: 1.1%

New experimental techniques combined with theoretical tools allow quantitative exploration of an unprecedented region of phase space for geomaterials

- Accurately measured the MgO Hugoniot from 330 GPa to 1160 GPa
  - Data starts at pressures and temperatures that had never been probed prior to 2012
- MgO has a large coexistence region along the Hugoniot between B2 and liquid
  - Significant to planetary and moon formation
  - Shock pressures of ~7 Mbar or greater needed to completely melt cold MgO
- Vastly expanding the domain of quantitative understanding for geomaterials