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Phase Transitions of MgO Along the Hugoniot

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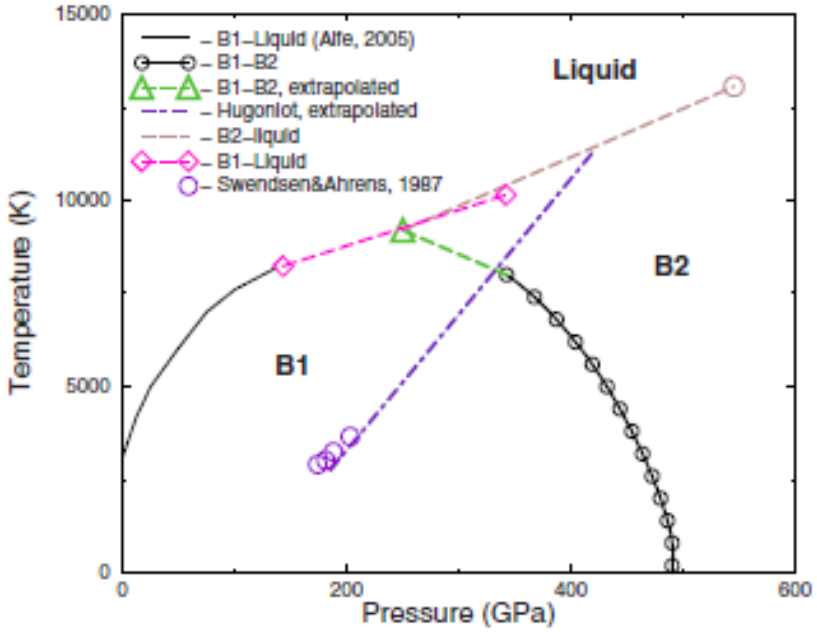
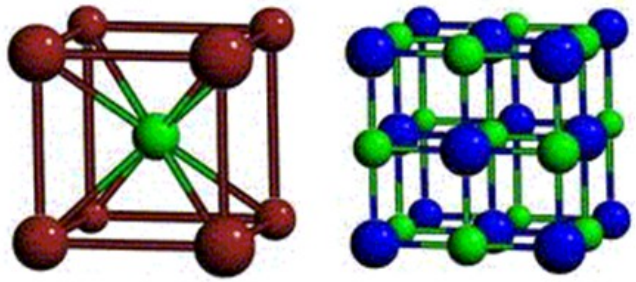
MgO Background

- MgO is abundantly found the Earth's mantle and likely other terrestrial exo-planets
- Understanding the high P-T behavior of MgO is important for modeling Earth's interior and planetary formation
- Static pressure data show no phase transition up to 227 Gpa at ambient temperature
- Hugoniot data (starting at ambient temperature) to ~ 200 GPa – no phase transition
- Belonoshko et al predict a B1-B2 phase transition near 350 GPa and melt near 5 Mbar and 12000 K.
- McWilliams *et al* predict B1-B2 transition at 440 GPa and melt at 650 GPa



Belonoshko *et al.*, Phys. Rev. B **81**, 054110 (2010)



CsCl NaCl

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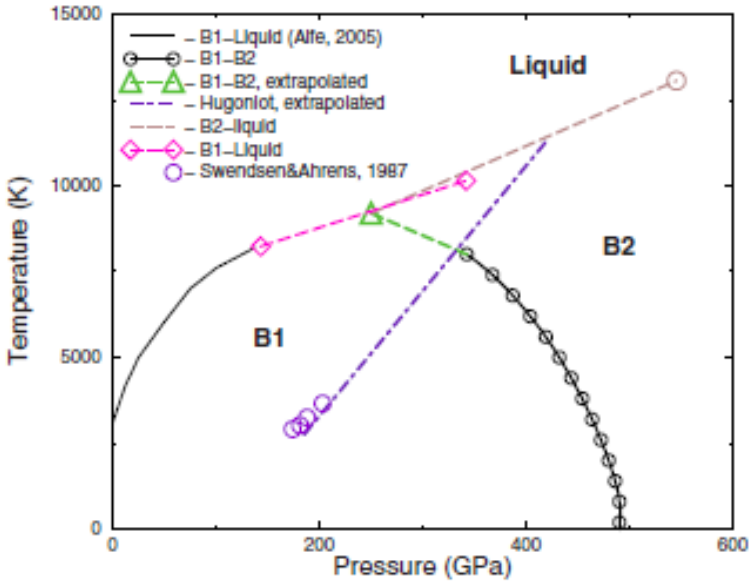
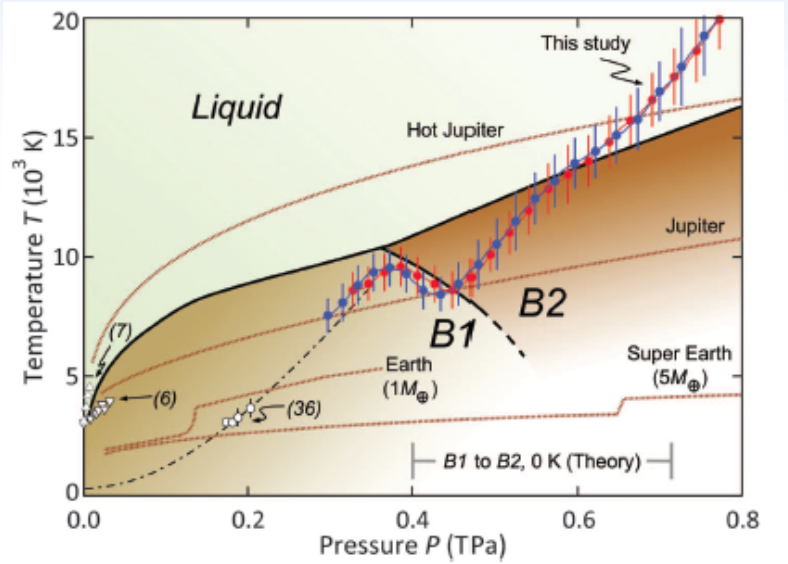
MgO Phase Diagrams

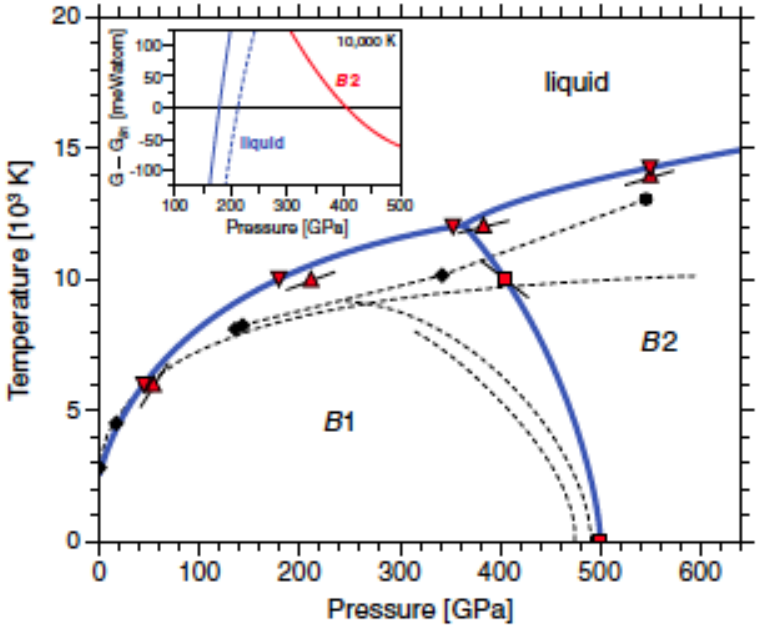


Belonoshko *et al.*, PRB **81**, 054110 (2010)



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

- **Multiple phase diagrams published**
- **B1-B2 phase boundary in disagreement in all phase diagrams**
- **Melt boundary in disagreement**
- **No consensus on phase boundaries**



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

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Objectives

- Measure the MgO Hugoniot to 12 Mbar using the Sandia Z - Machine

- Experimental determine the proposed solid-solid phase transition

- Determine melt on the Hugoniot

- Apply Density Functional Theory methods to corroborate experimental findings

- Update the MgO phase diagram

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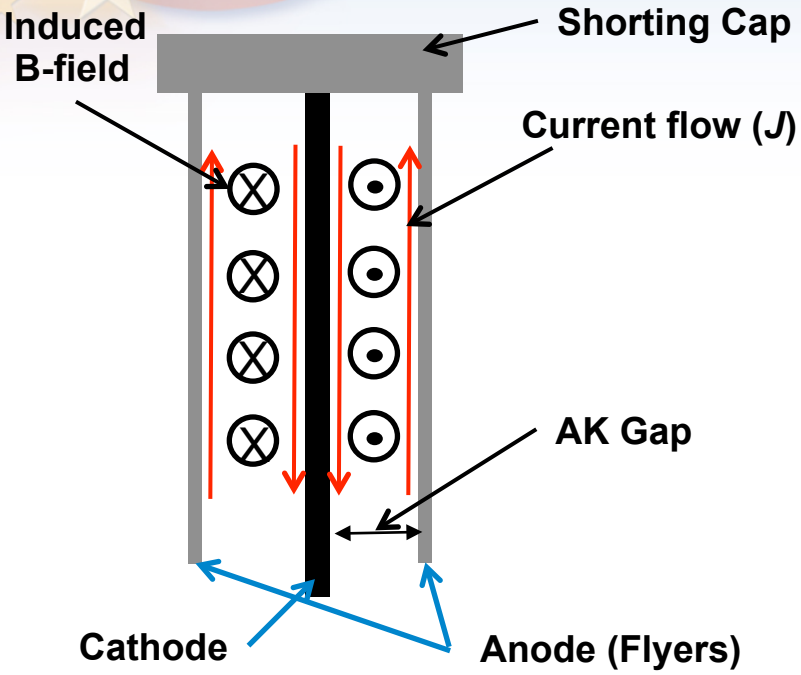
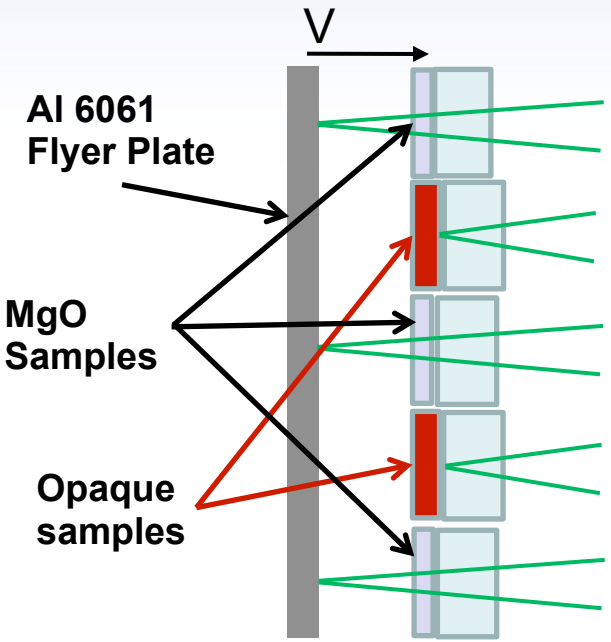
Experimental Approach





- Current pulse loops through shorting cap inducing a *B* – field.
- Resulting *J x B* force accelerates anodes (flyers) outward up to 40 km/s
- Asymmetric AK Gaps result in two different flyer velocities (two Hugoniot points per experiment

- Multiple samples per experiment
- MgO windows are initially transparent and are backed by quartz, TPX plastic, or aerogel windows
- VISAR used to measure flyer velocity
- Multiple VPFs per sample – reduces uncertainty

Method produces steady shock state in the MgO

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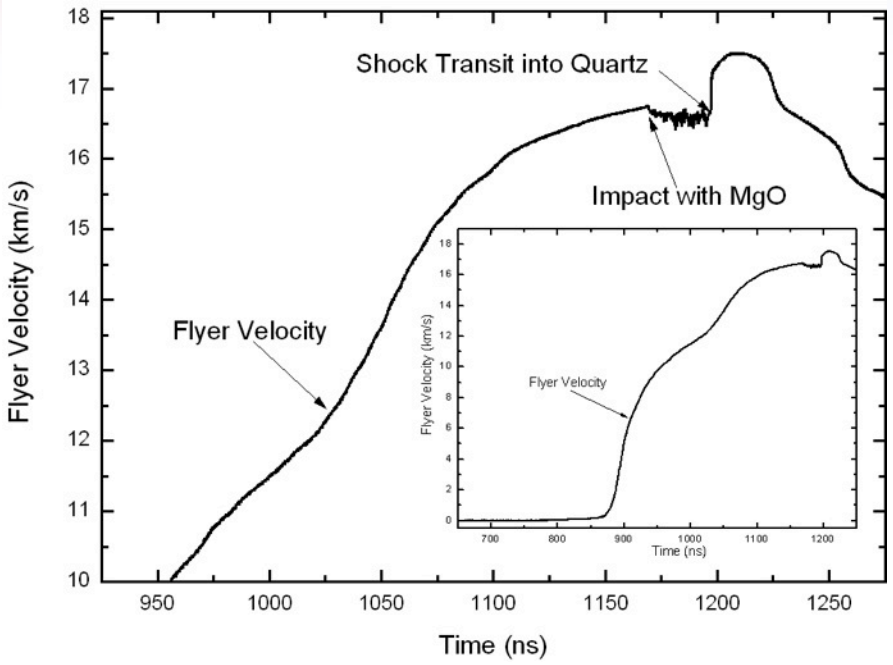
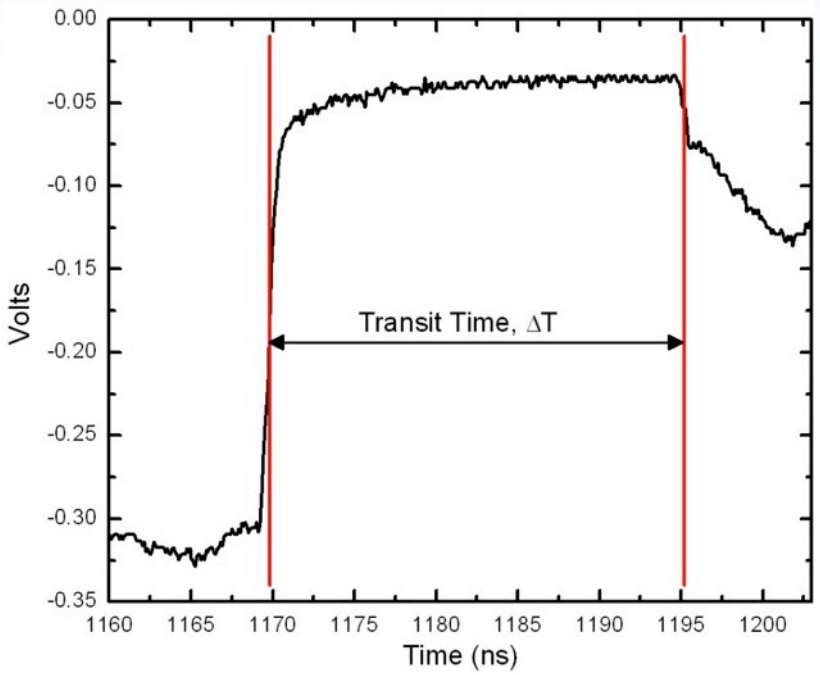
Experimental Measurements





- **VISAR tracks flyer plate velocity up to impact**
- **Shock front in MgO not reflective – Loss of contrast in VISAR signal**
- **Clear impact and shock transit fiducials – transit time analysis**
- **At higher pressures, MgO shock front reflective and shock velocity measured directly**
- **Shock front in back window is reflective – release state for MgO is determined (not discussed here)**

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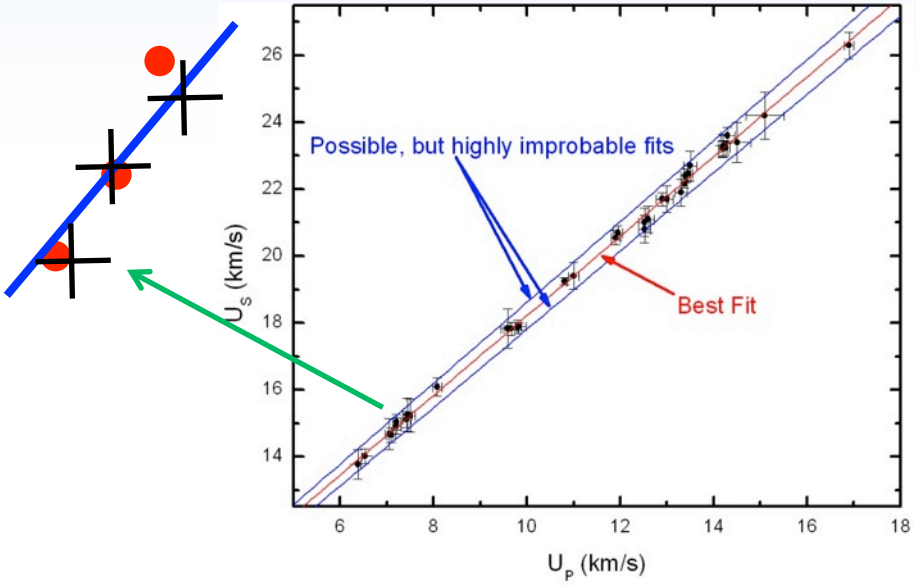
Monte Carlo (MC) Impedance Matching

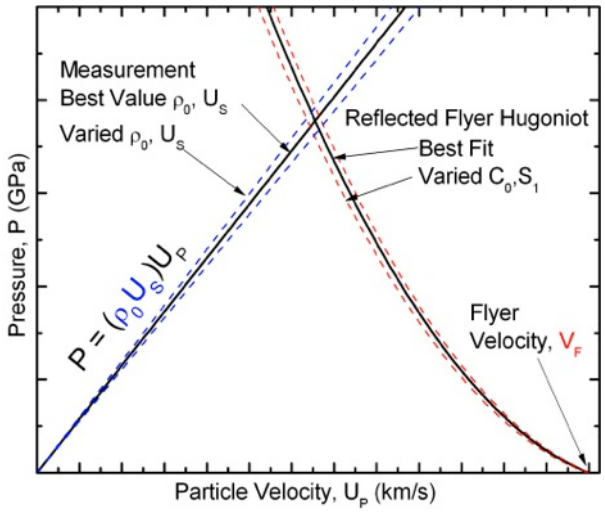
Aluminum

- Uncertainty in experimental data (Knudson *et al.*, JAP 2003)
- Vary each U_S-U_P point by an uncorrelated random number with σ = expt. Uncertainty
- Solve for linear fit parameters
- Determine mean, σ, and correlation of fit parameters



MgO

- Vary measured parameters (V_F, U_S, ρ_0) with uncorrelated random numbers, σ = experimental uncertainty
- Vary Al fit parameters using correlated random numbers
- Calculate U_P, P, and ρ
- Determine mean and σ



Monte Carlo **technique accounts for all experimental uncertainty and propagates the Al standard error into the MgO data.**

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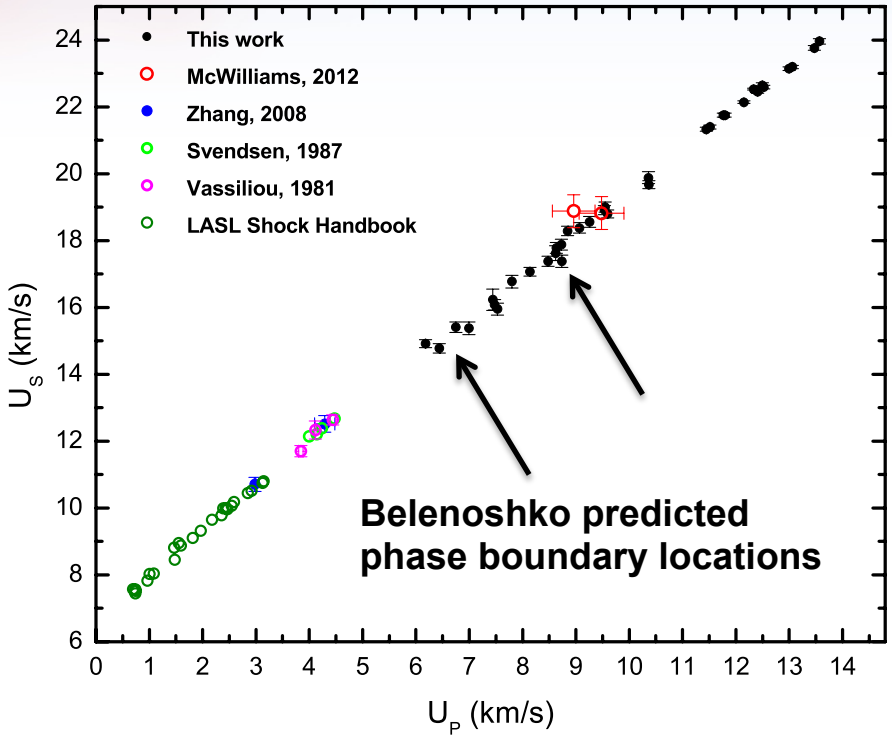
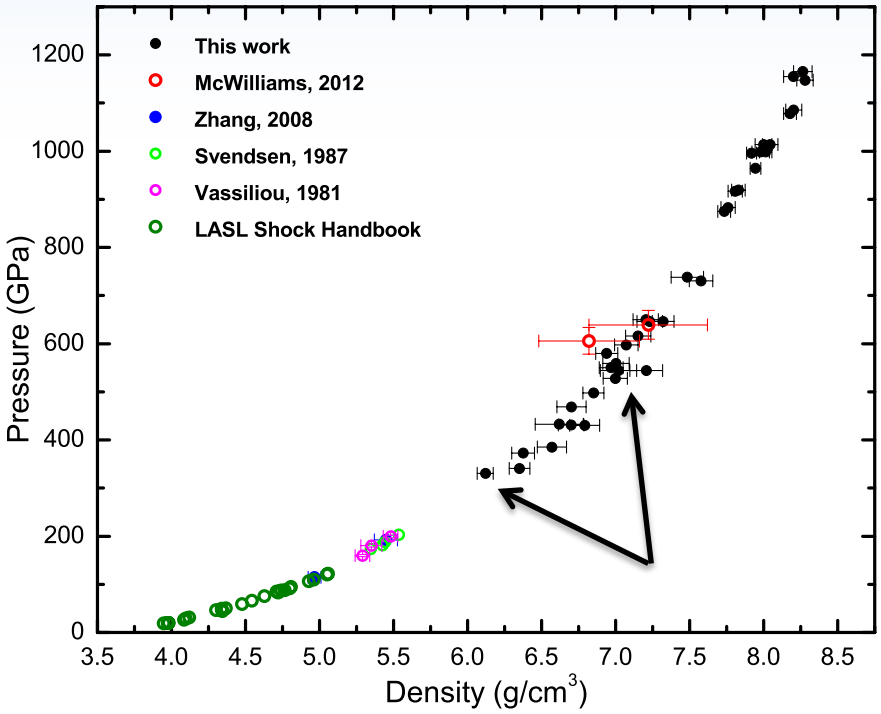
Experimental Results





- **Total of 37 Hugoniot measurements**
- **Highest pressure Hugoniot measurement - 11.6 Mbar**
- **Lowest pressure Hugoniot measurement – 330 Gpa**
- **No reflective shock front below 7 Mbar**
- **Data spans the B1-B2 transition and the B2 - melt transition**

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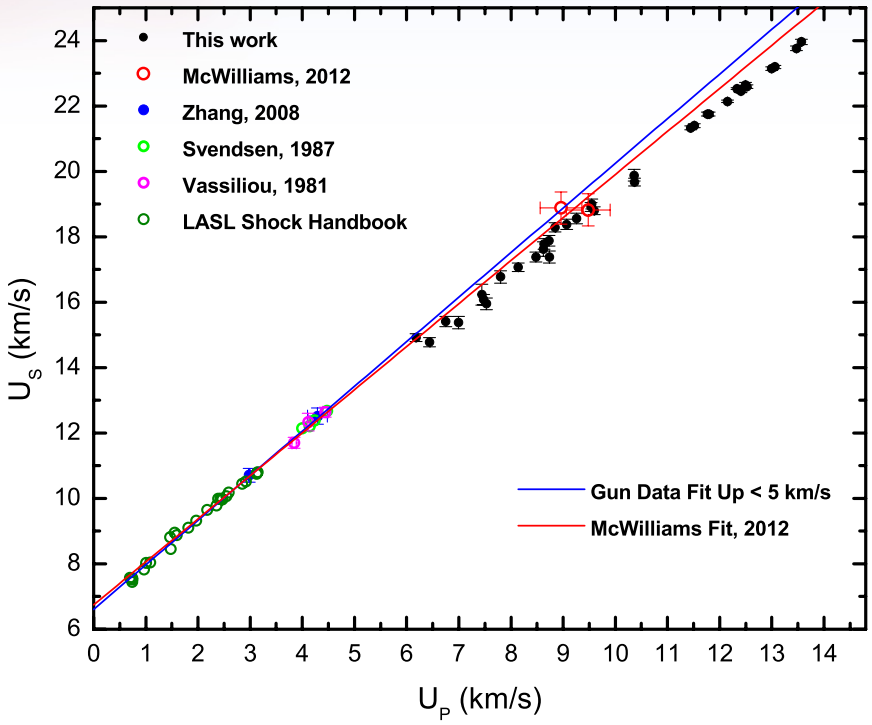
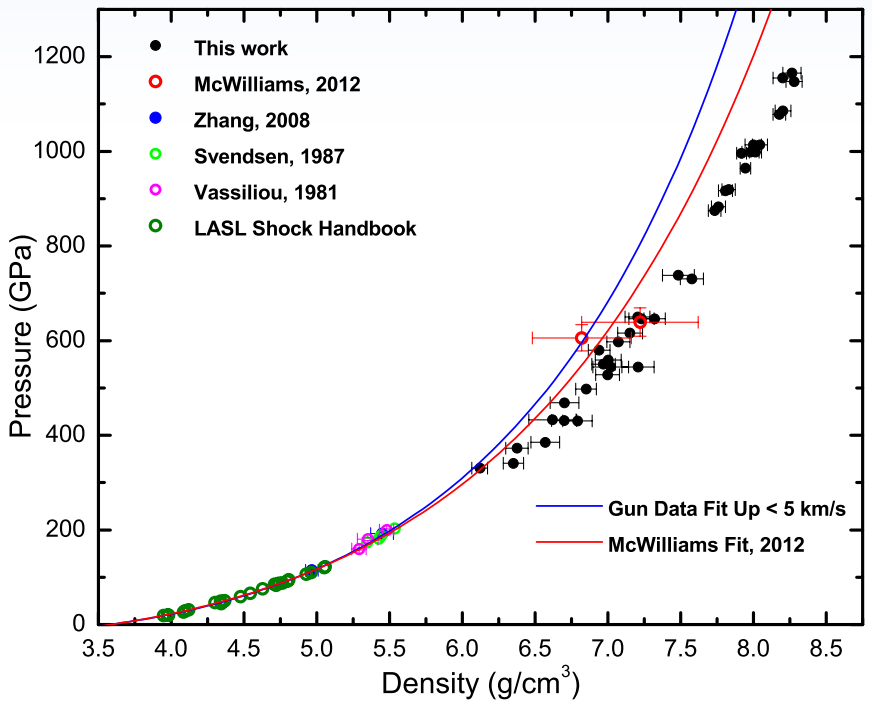
Comparison To B1 Solid Fit





- **Z data deviate from the extrapolated gun data fit at 330 Gpa**
- **Z data also deviate from the McWilliams *et al* fit near 330 Gpa**
- **Suggests the B1-B2 solid phase transition starts around 330 Gpa**
- **No obvious change in Hugoniot as MgO transitions from B2 - Liquid**

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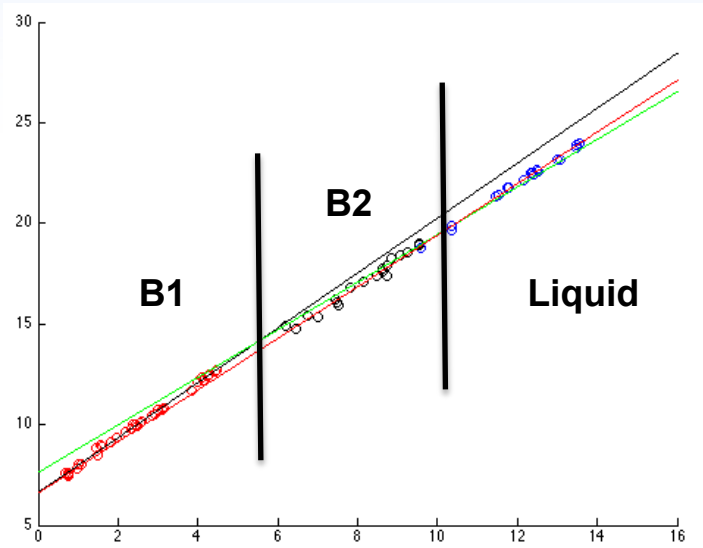
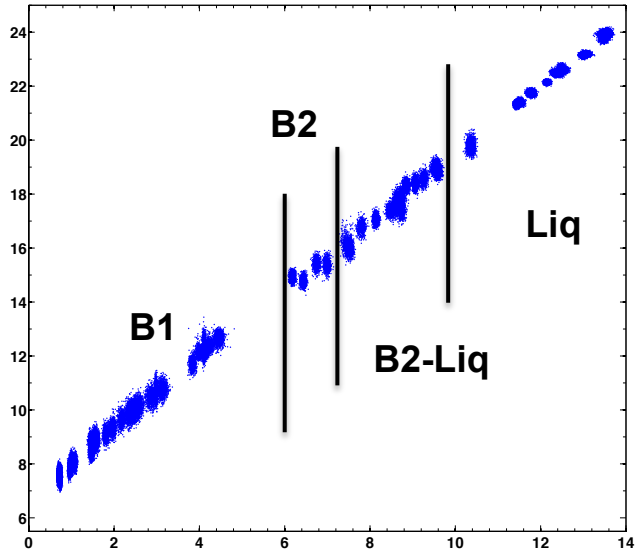
Optimization for Phase Boundaries

- Use Genetic Algorithm (GA) methods to optimize a 3 and 4 piece linear fit.
- 3 – Piece uses B1, B2, Liquid regions
- 4 – Piece uses B1, B2, Coexistence region, and liquid region
- Similar method applied to diamond (Knudson et al, Science 322, 1822 (2008).
- GA method optimizes ‘break points’ for a multi-piece linear fit using linear regression
- Several optimization runs performed to estimate uncertainty in break points
- 3-piece linear fit suggests a large B2 region inconsistent with previous phase diagrams and has a larger χ^2 than a 4-piece fit





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Optimization Results

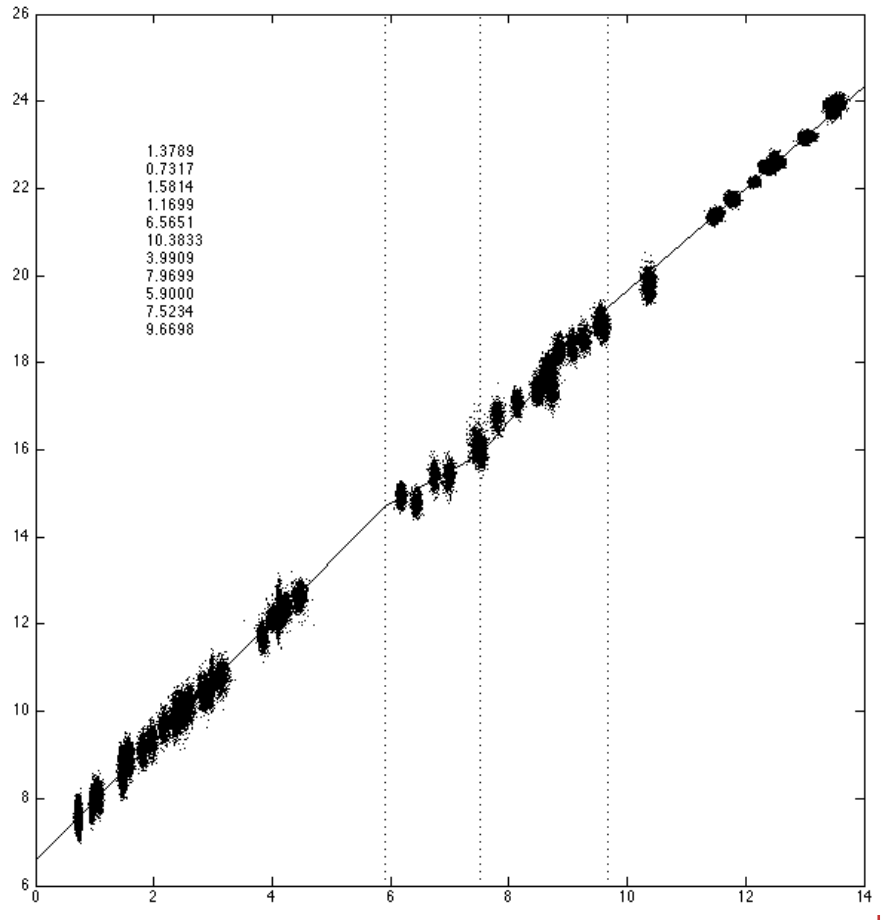
B1 – B2 Boundary
Up = 6.00 ± 0.20 km/s
P = 330 – 355 Gpa

B2 – Liquid Coexistence Region
Up = 7.5 ± 0.3 km/s
P = 412 – 466 Gpa

Coexistence Region – Liquid Boundary
Up = 9.7 ± 0.1 km/s
P = 660 – 683 GPa

Largest uncertainty in the B2 – coexistence region

More data will improve the result statistics



Use DFT methods to further elucidate the phase diagram

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Density Functional Theory

- **Use DFT-MD to assess the state of MgO at high pressures**

- **DFT-MD simulations performed using VASP 5.2.12***
- **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:**

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

- **Simulations start from the B1 and the B2 phase**
- **216 atoms per simulation (B1 phase); 250 atoms (B2 phase)**
- **AM05 (Armiento-Mattsson) exchange correlation functional**
- **VASP PAW potentials: Mg($3s^2$) and O($2s^2p^4$) for low temp (< 1eV)**
  Mg($2s^22p^63s^2$) and O($2s^2p^4$) for (> 1eV)

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

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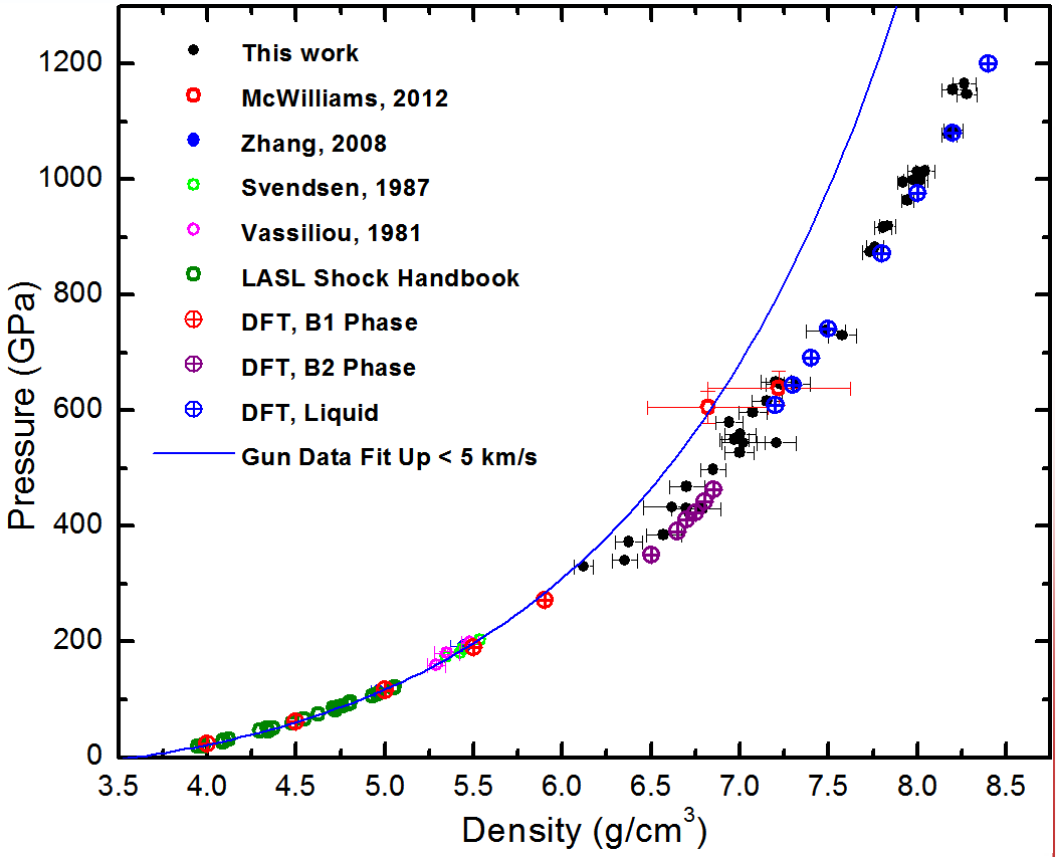
DFT Hugoniot Results

- DFT simulations to 12 Mbar
- Simulations start from B1, B2, or liquid phase
- Excellent agreement with the experimental data over the entire range
- DFT data suggest a large region for B2 – Melt coexistence on the Hugoniot



- Examine the phase boundaries

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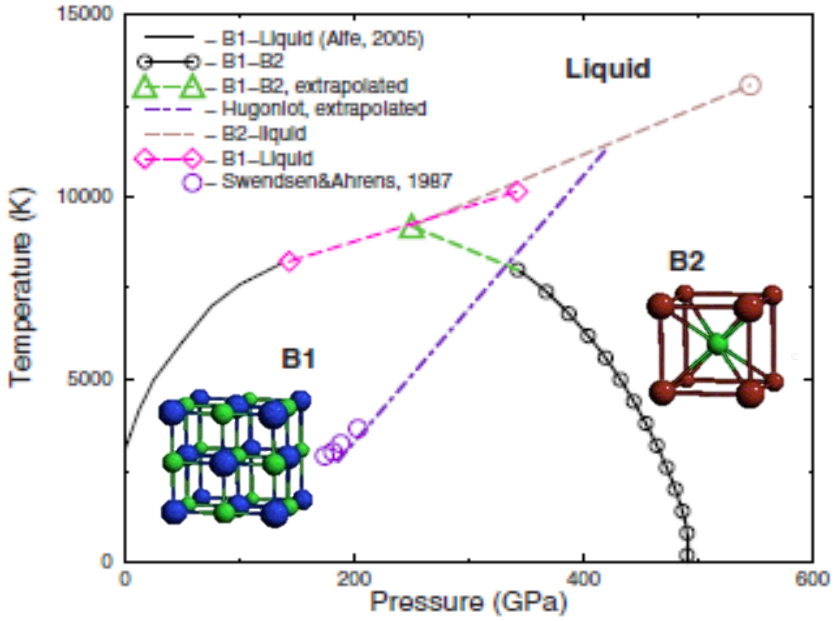
Calculation of Solid-Solid Phase Boundary

- **Pressure and Energy are directly calculated in DFT-MD**
- **For finite temperature phase transitions entropy is necessary**
- **At low temperatures, harmonic phonon approximation provides solution**
- **Use finite displacements in a supercell following the approach of the Phon code**
  (Alfe, Computer Physics Communications. 180, 2622 (2009))
- **Entropy can be calculated directly using analogy to finite temperature quantum harmonic oscillator**
- **Approximation breaks down for moderate temperatures**



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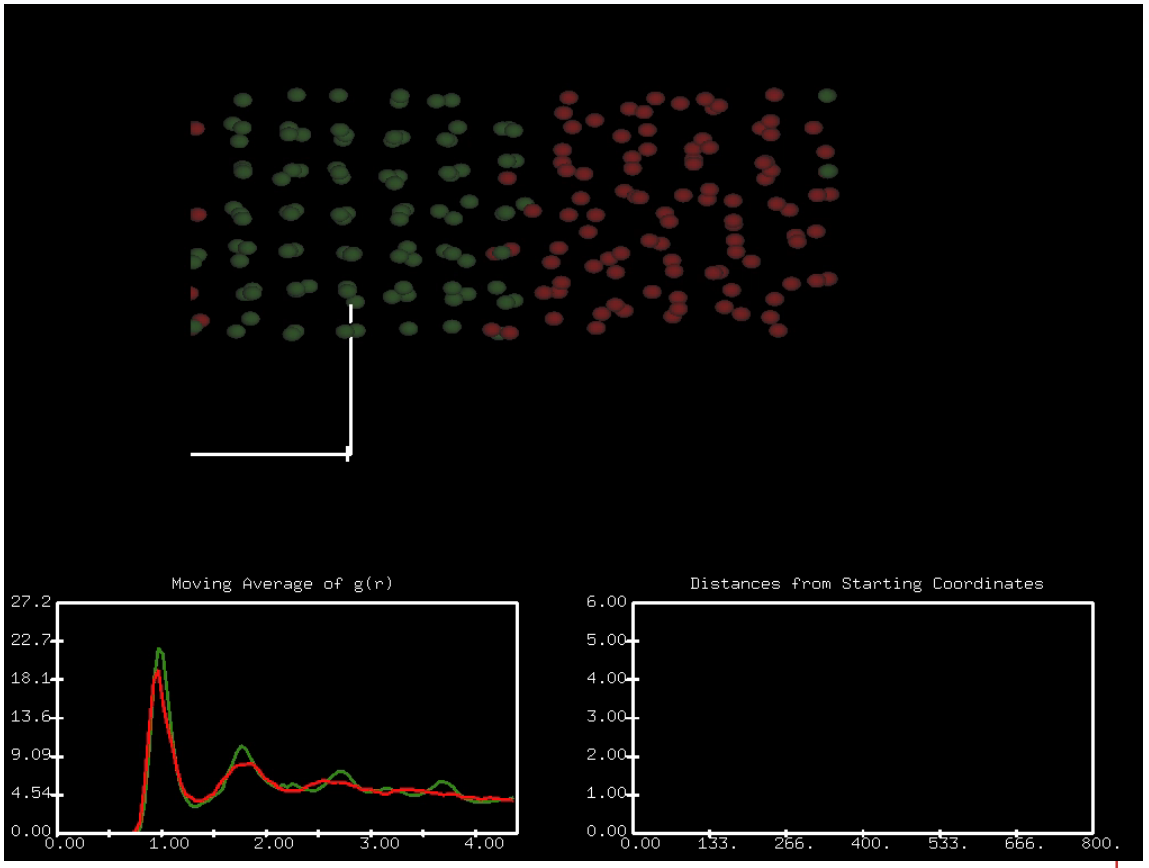
Solid – Melt Boundaries

- For melting boundary use two phase coexistence simulations
- Place solid and liquid in contact with each other
- Run at different temperatures or starting energies 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



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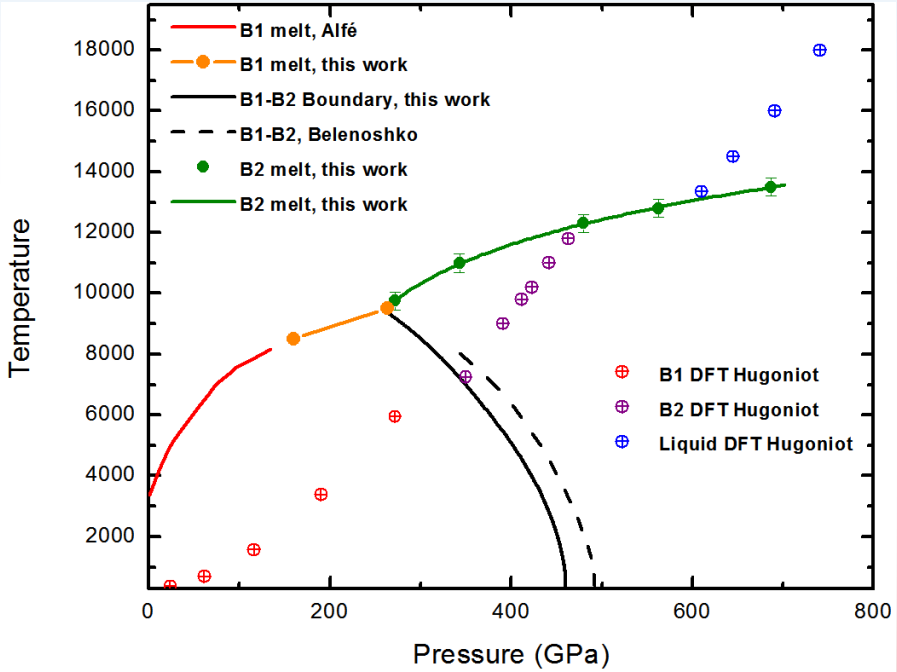
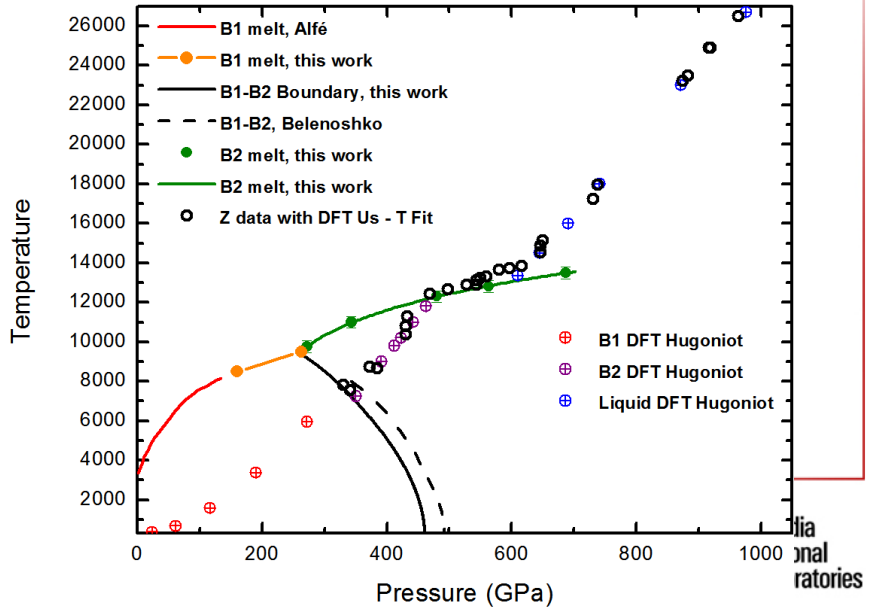
MgO Phase Diagram

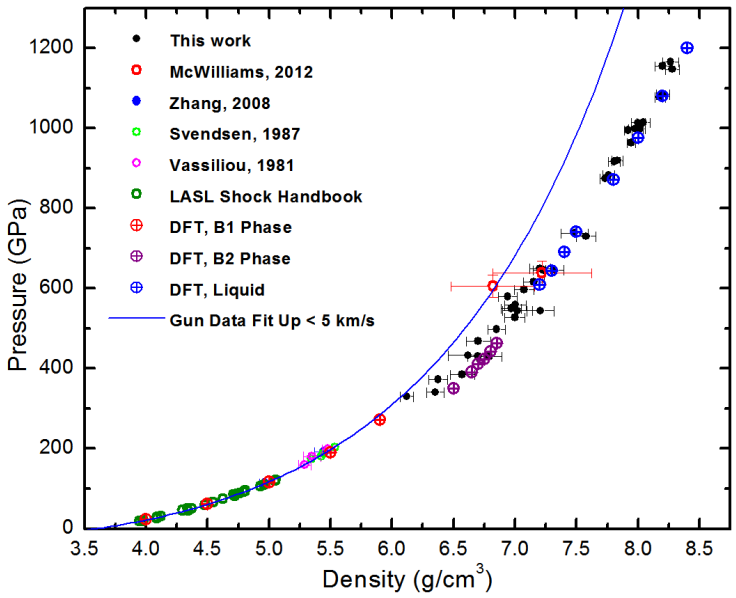
- B1 – B2 phase boundary occurs lower than predicted by Belenoshko
- B1 – melt boundary consistent with Alfe
- DFT Hugoniot shows a large region of coexistence on the B2 – melt boundary
- US – Temperature Fit applied to experimental data
- Region of B1 – B2 coexistence from DFT ranges from 330 – 350 GPa
- Region of B2 – melt coexistence ranges from 430 – 660 GPa

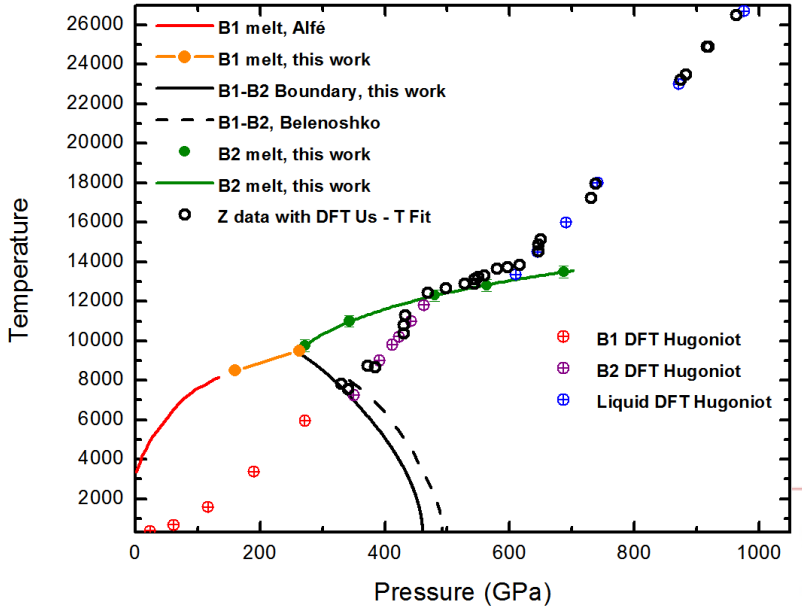




Summary

- Accurately measured the MgO Hugoniot from 330 GPa to 1160 Gpa
- Determine the phase boundary regions for the B1, B2, and Liquid phases of MgO along the Hugoniot
- Show MgO has a large coexistence region along the Hugoniot between B2 and liquid
  - Significant importance to planetary and moon formation
  - Shock pressures of ~7 Mbar or greater needed to completely melt MgO
- Developed an updated phase diagram for MgO





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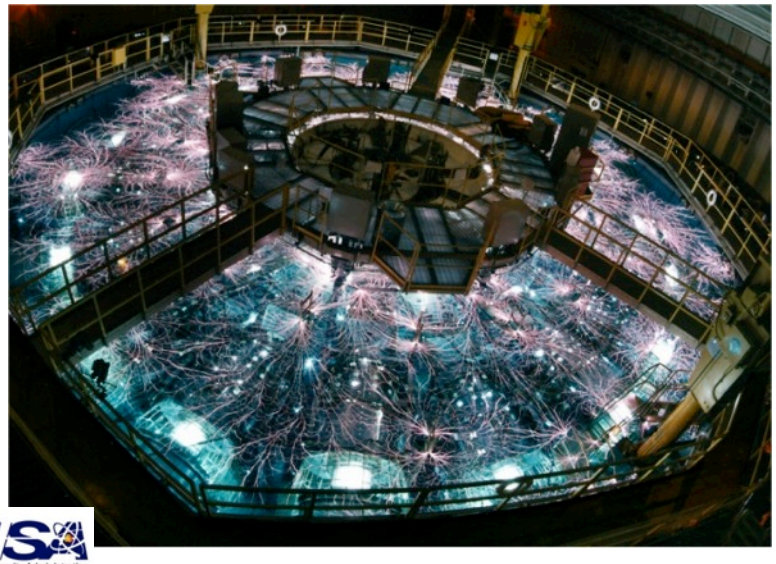
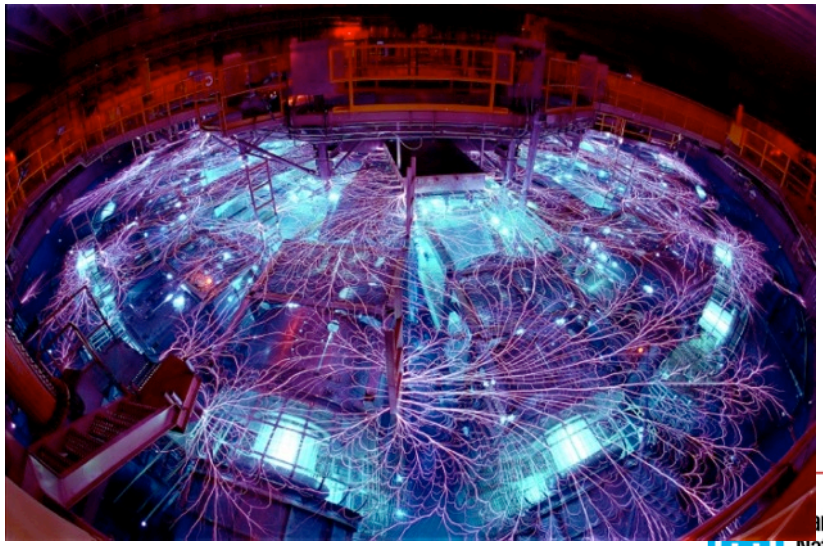
Acknowledgements

Dan Dolan for the Optimization routine

Mike Desjarlais and Marcus Knudson

All members of the Sandia Z-Operations Team and Target Fab./Metrology Team





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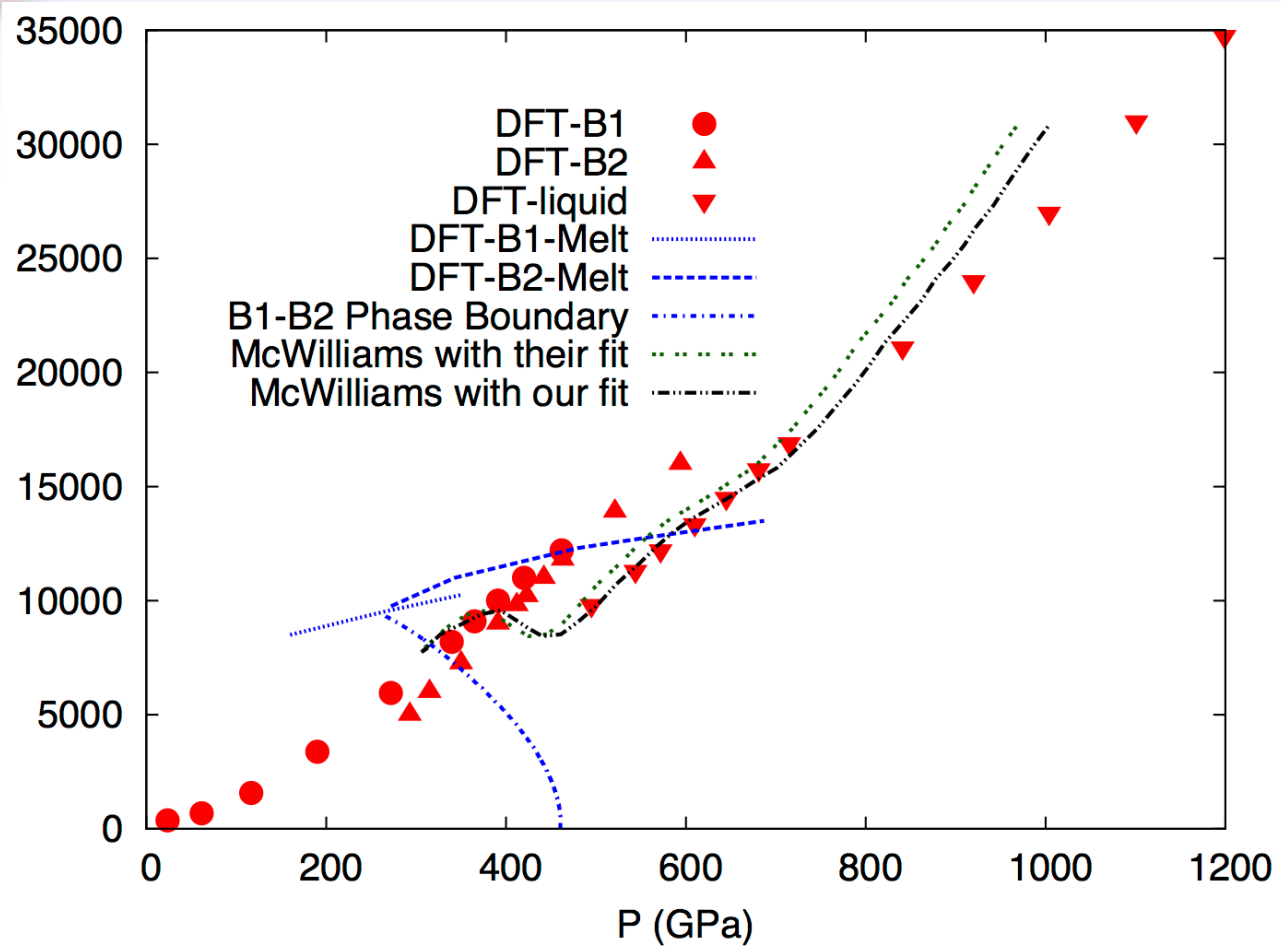
Extra Slides

Comparison to McWilliams



- **The B1-B2 transition occurs at lower pressure**
- **Larger B2 – Liquid coexistence region**
- **DFT temperatures lower than measured temperatures in the liquid state**

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