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Title: Influence of Impurities on the Solid-Solid Phase Transitions in Zirconium

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Influence of Impurities on the Solid-Solid Phase Transitions in Zirconium

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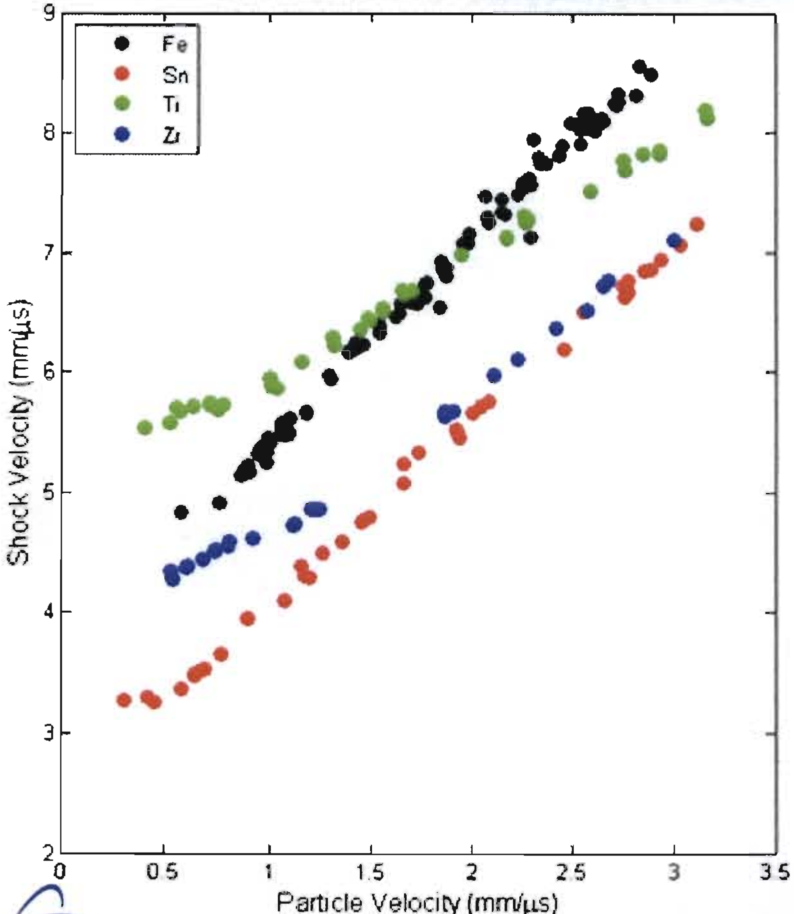
Sandia Z-Machine Team, many others...

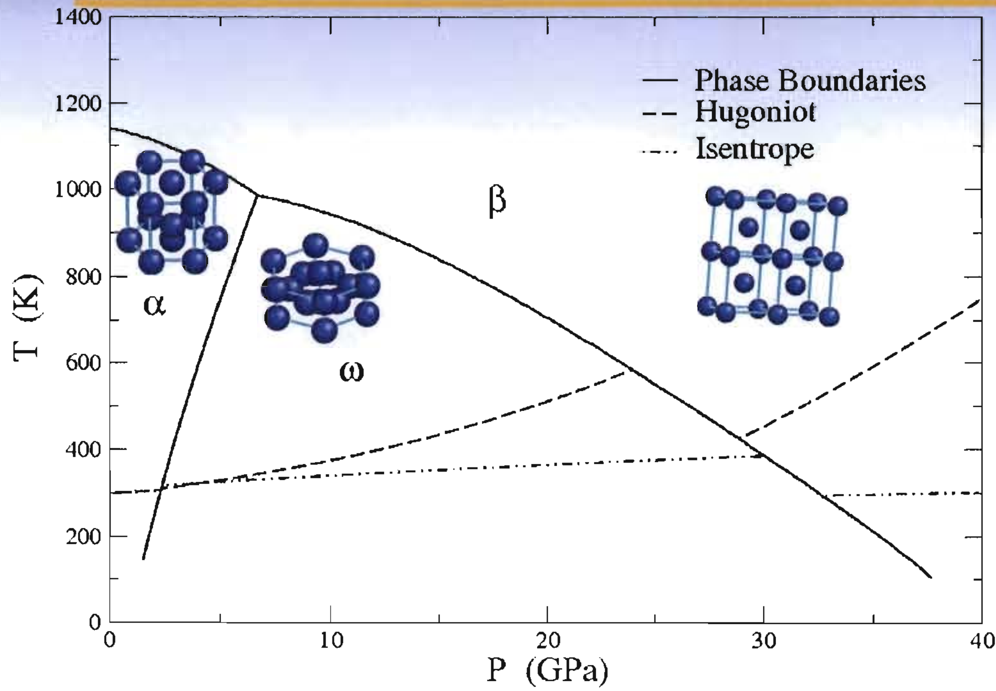
Many materials of interest to the weapons program exhibit solid-solid phase transformations

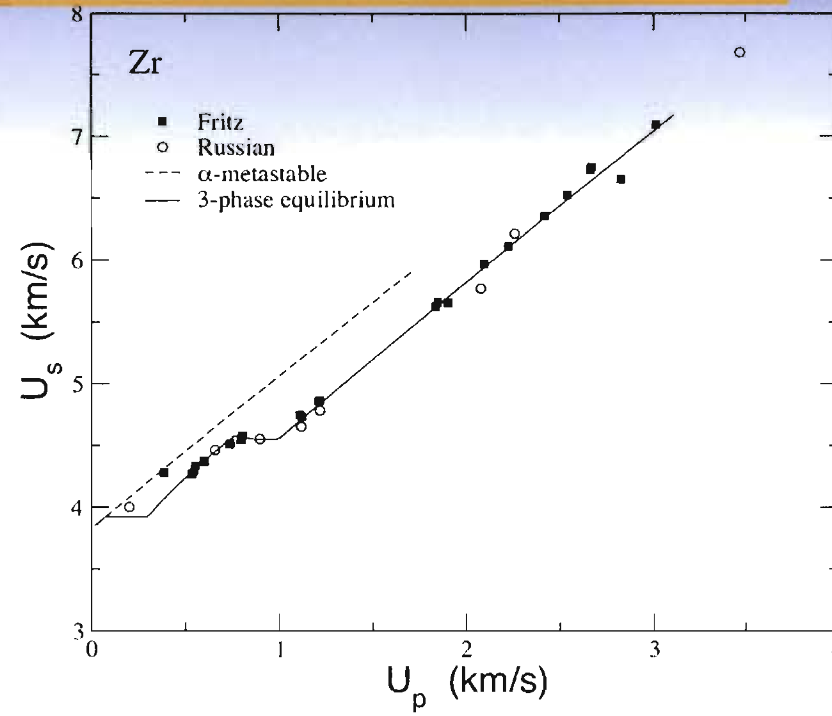
U_s - U_p Data for Several Metals with Known Phase Transformations



- Decades of shock compression experiments have provided Hugoniot data on a large number of materials.
- A kink in the U_S – U_P curve can indicate the presence of a solid-solid phase transition.
- These data tell us nothing about the kinetics and underlying atomic level mechanisms responsible for the phase change
- Developing accurate, physics-based multi-phase equations of state to describe these materials is of vital importance to our stewardship mission
- Data obtained using advanced diagnostics are needed to compliment existing data sets
- Zirconium is well suited for such studies

Zirconium is well suited for investigating solid-solid phase transitions under dynamic loading conditions

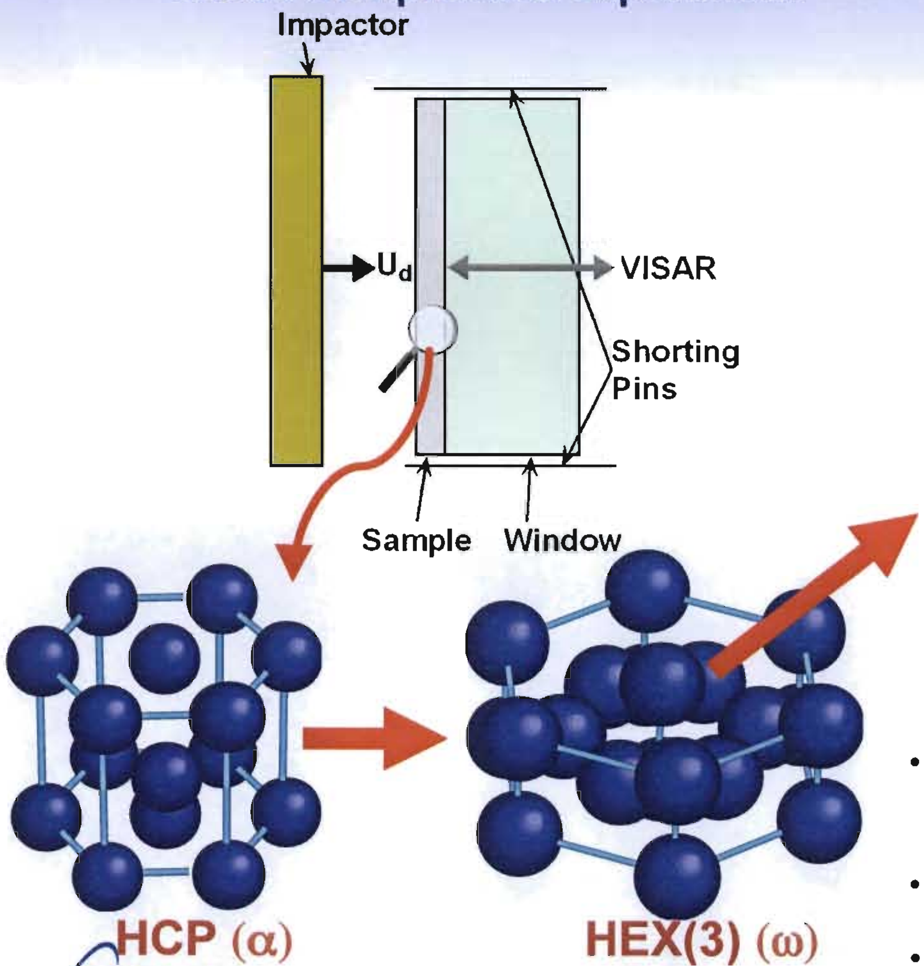




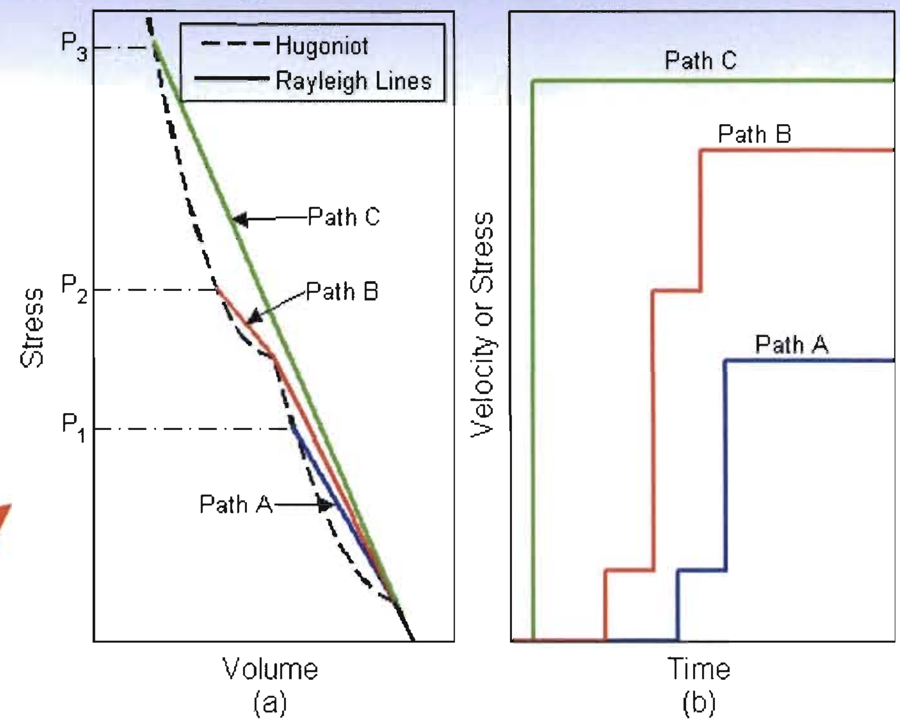
- Three solid phases exist in Zr in pressure regimes easily accessible through shock and isentropic loading.
- Kinks in legacy $U_S - U_P$ data indicate that transitions should be observable in shock compression experiments

Velocimetry is used in shock compression experiments to detect phase transitions in real time

Shock Compression Experiment

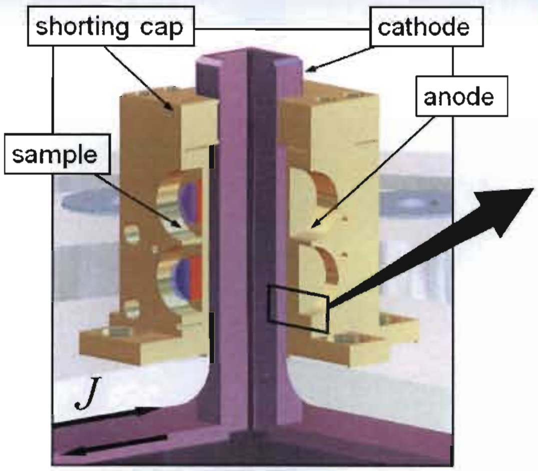


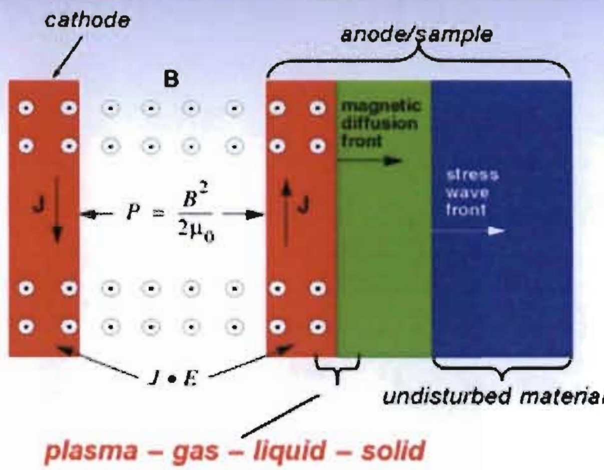
Loading Paths and Ideal Wave Profiles



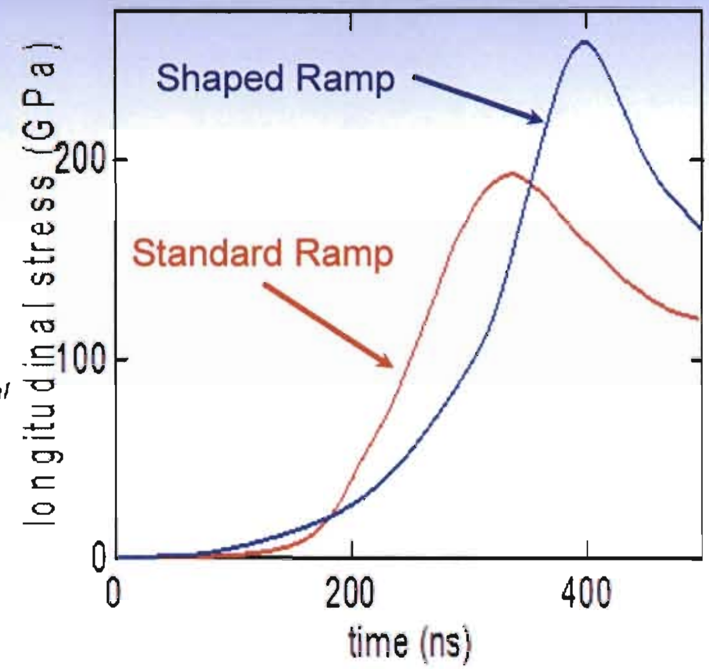
- A kink in the Hugoniot indicates a change in the material:
  - Elastic-plastic deformation
  - Phase transition
- When the Rayleigh line intersects these kinks, multiple shock waves are formed (Paths A & B).
- **Path C:** Changes still occur, but with no wave profile signature – **changes are "overdriven".**

Isentropic compression data can provide additional information about the kinetics of phase transformations





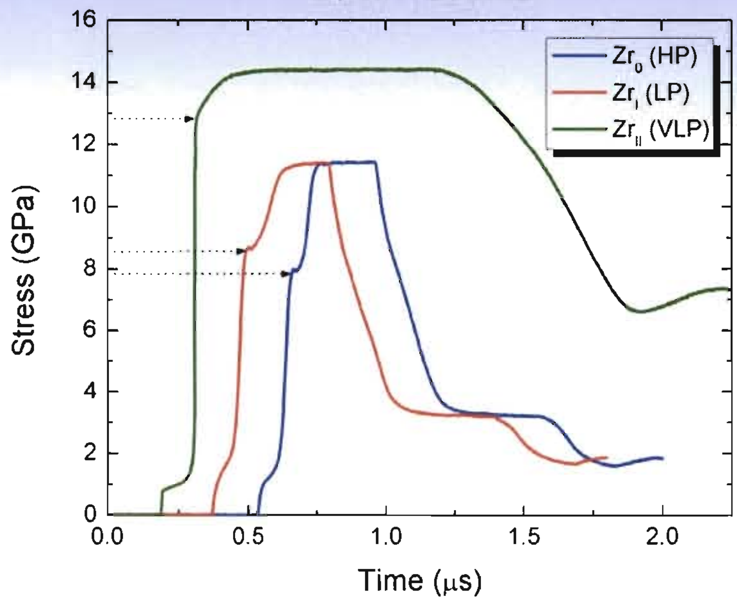
22 MJ stored energy
~25 MA peak current
~200-600 ns rise time



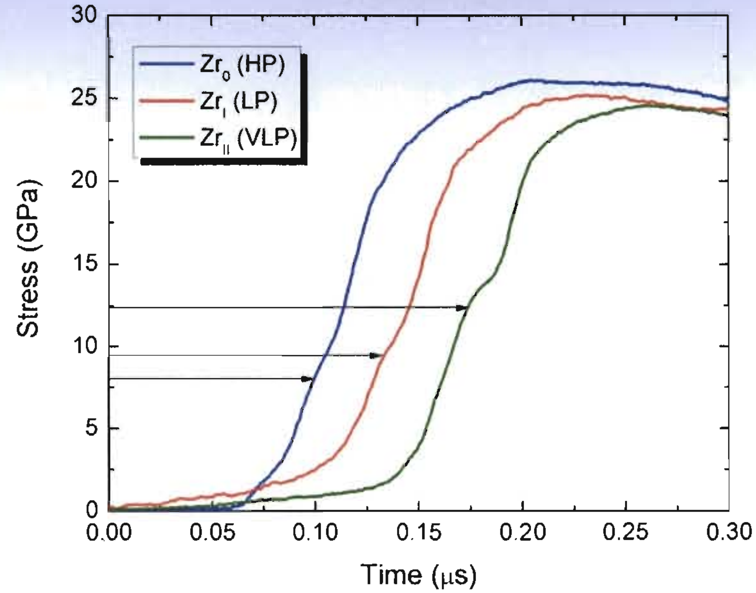
- Magnetic field between anode/cathode induces pressure on the sample.
- Pressure pulse temporally follows current
  - This can be tailored by dumping capacitors sequentially
- Materials closely follow isentrope when ramp loaded.
- Isentrope will follow Hugoniot very closely for several hundred kbar.
- Same phase boundaries are accessible through shock and isentropic loading.
- Phase transition cannot be "overdriven".
- Lower strain-rates allow investigation of strain-rate effects on phase transitions.

The presence of oxygen in Zr dramatically increases the stress at which the α – ω phase transition occurs

Gun Results

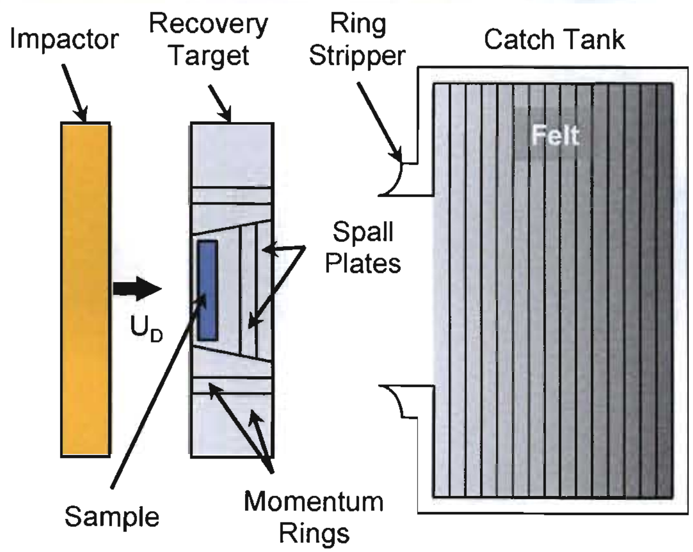


Z Results



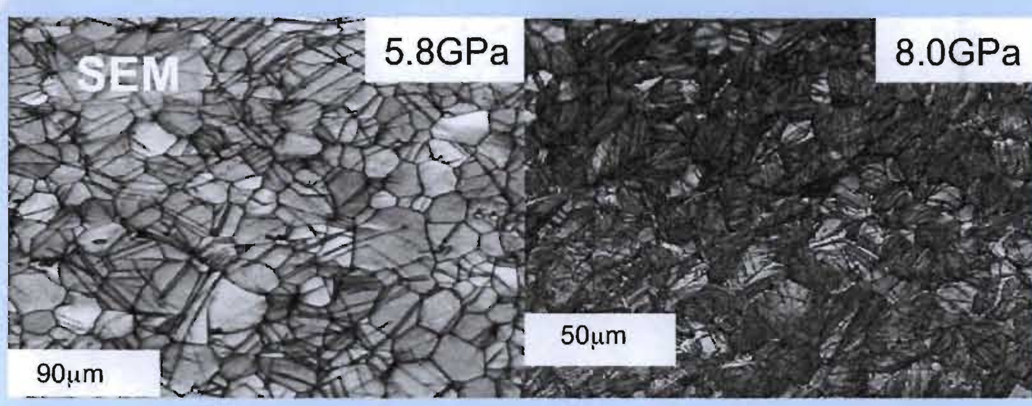
- Oxygen levels are < 50ppm for Zr_0, 390ppm for Zr_I, and 1200ppm for Zr_{II}.
- The phase transition signature is very subtle in the shocked impure sample and is overdriven just a few GPa higher.
- In contrast, the signature is more pronounced for the isentropically loaded impure sample indicating that strain rate is important.
- No rarefaction shock indicating ω phase is retained upon release.

Shock recovery experiments can provide further insight into mechanisms responsible for phase transitions



- Samples were subjected to shock loading and soft-recovered in felt
- Samples are subjected to 1-d loading/ unloading only
  - Samples are encapsulated to reduce damage during recovery
  - Momentum rings prevent edge wave from reaching the sample
  - Spall plates prevent tension waves from reaching the sample
- Recovered samples were investigated using several techniques:
  - X-ray Diffraction, Electron Back Scattered Diffraction, and Neutron Diffraction
  - Transmission Electron Microscopy, Scanning Electron Microscopy, and Optical Microscopy

A suite of metallurgical analysis techniques are used to provide insight into micro- and meso-scopic shock-induced changes in Zr

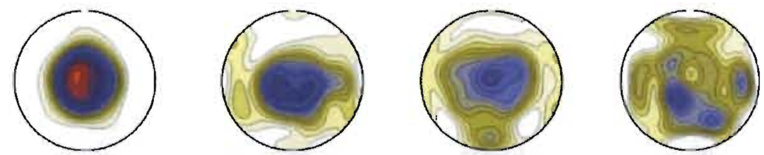


Scanning Electron Microscopy (SEM) shows increased twinning and dislocation production with increasing stress

Neutron Diffraction

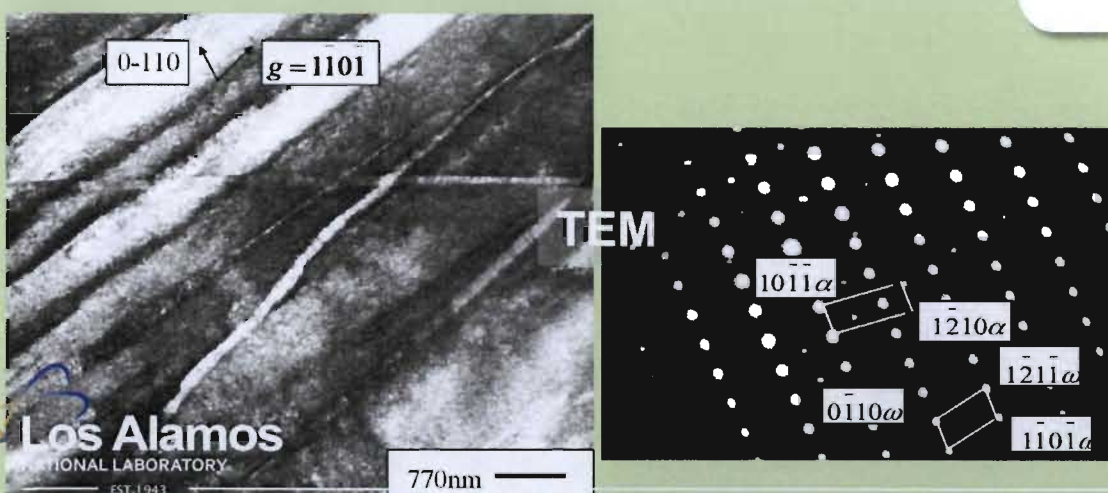
(0002) Poles

0 MRD 5.5



Annealed, α — 5.8 GPa, α — 8.0 GPa, α — 8.0 GPa, ω

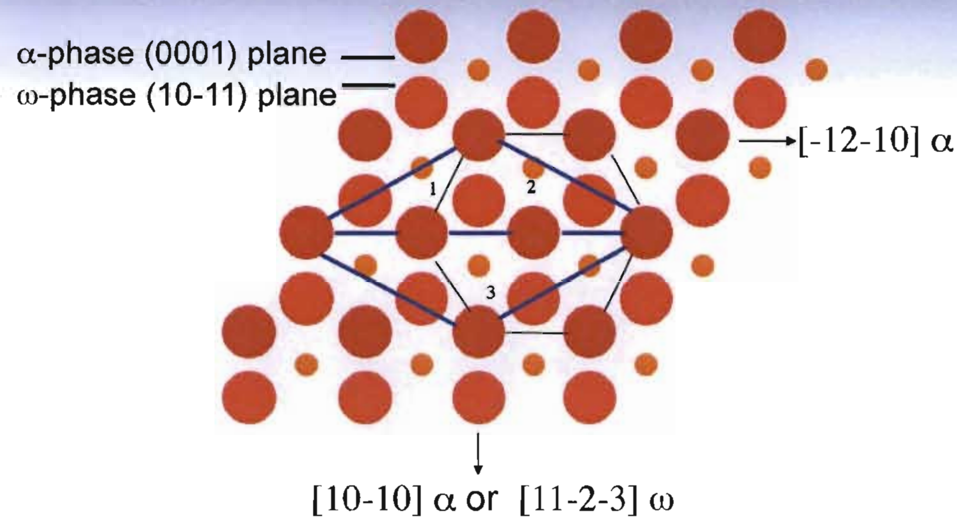
Neutron diffraction shows increasing reorientation of the microstructure with increasing stress and ~35% of the w phase is retained at 8 GPa

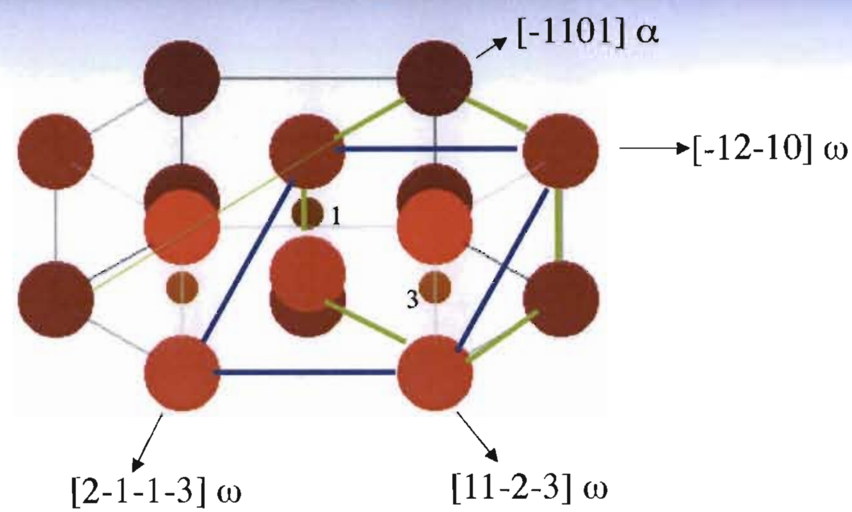


Transmission Electron Microscopy (TEM) was used to determine the relative orientation between the a and w phases.

There is also evidence of a high strain substructure with a high density of dislocations

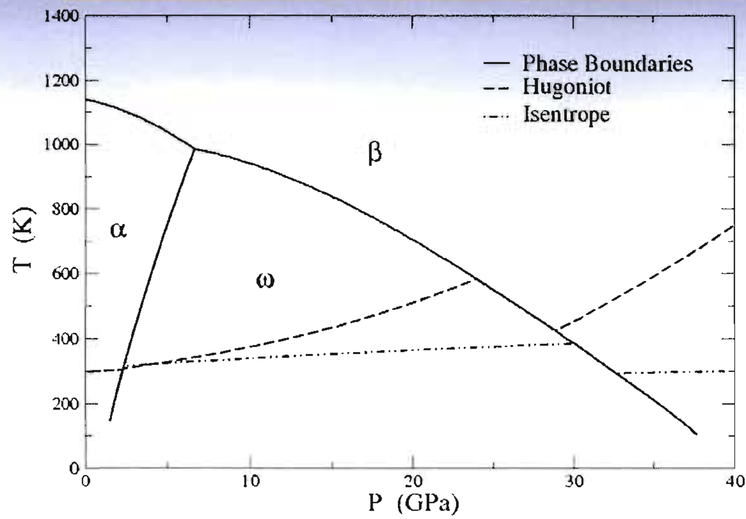
The combination of all data help us develop a story for the mechanisms responsible for the α – ω phase transition in Zr

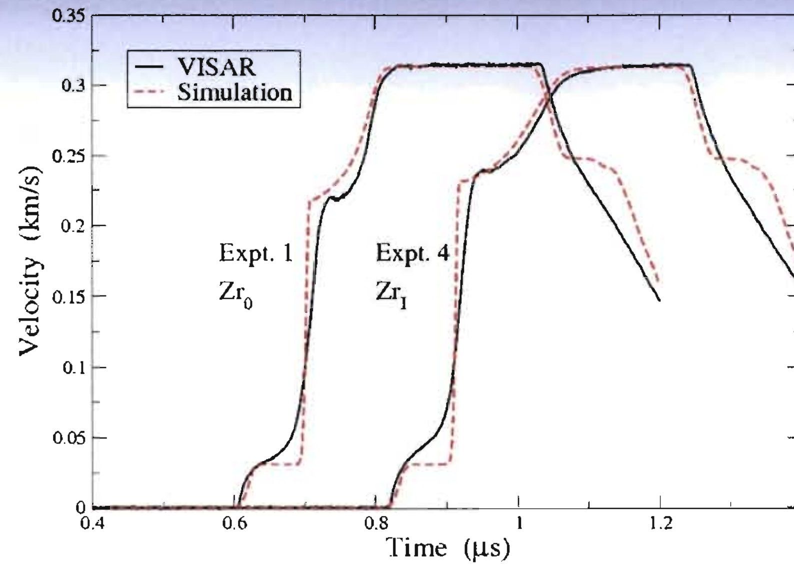


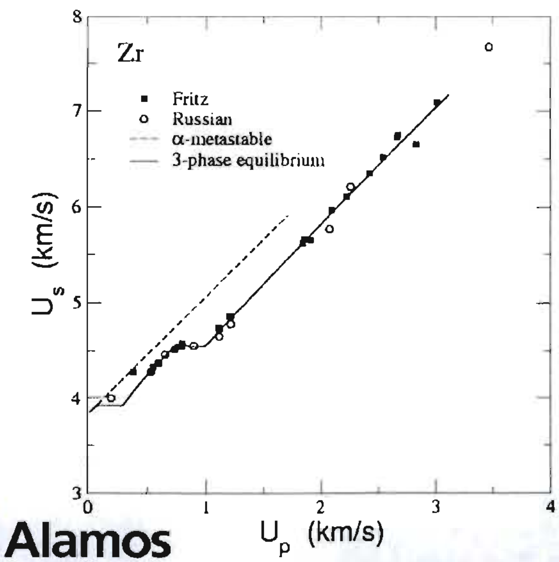


- The proposed mechanism is a two step process: The first is a translation along the [-1 2 -1 0]α direction; the second is a subtler atom shift to collapse closely spaced (0 1 1 -0) planes
- Oxygen occupies interstitial sites in the α lattice which inhibits the first step of this process, thus the effective transition stress increases with increased oxygen content.
- The lower strain rate in the isentropic compression experiments may allow the transition more time to complete in the $Zr_{||}$ material making the signature more pronounced in these data

Finally, all available data are used to develop a multi-phase equation of state to describe Zr

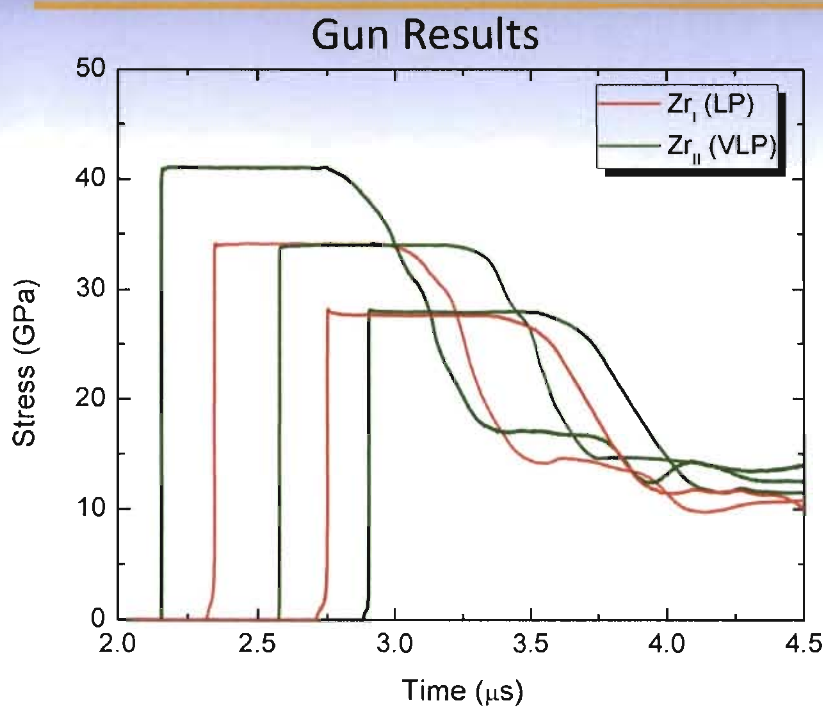


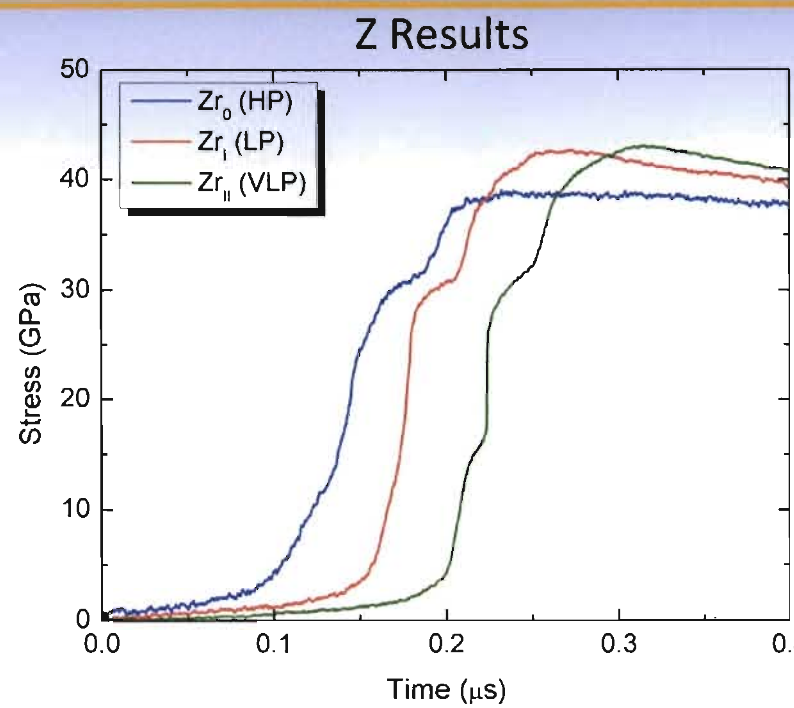




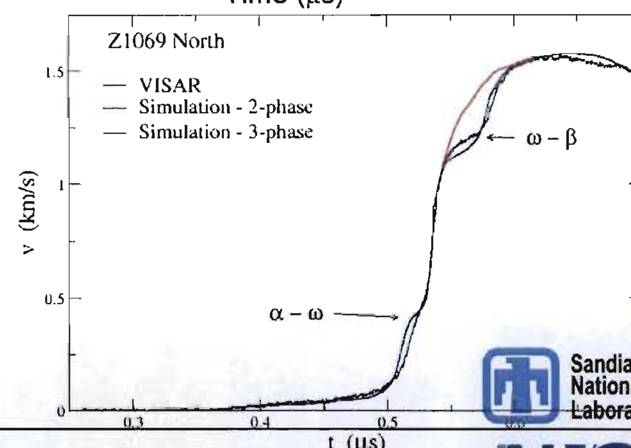
- Carl Greeff (T-1) has used all available data to develop and evaluate a multi-phase EOS for Zr.
- Reasonable agreement is obtained between experimental data and simulations for Zr_0 and Zr_I.
- More work is needed in order to describe the least pure material, Zr_{II}.
- This work is helping us understand the influence of impurities and the mechanisms responsible for phase transformations.
- This, and similar work, is helping to develop more accurate equations of state for use in today's hydrocodes.

Further experiments conducted to look for ω – β transition



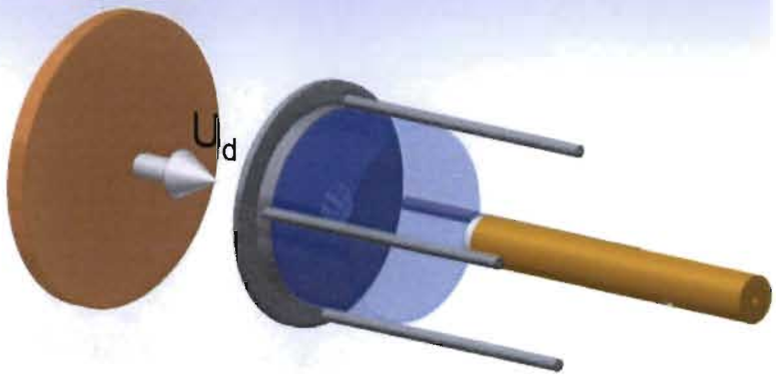


- 3-wave structure not observed in gun experiments.
- Oxygen content does not affect ω – β transition stress in Z experiments.
- Model matches Z data well. Shock data not modeled



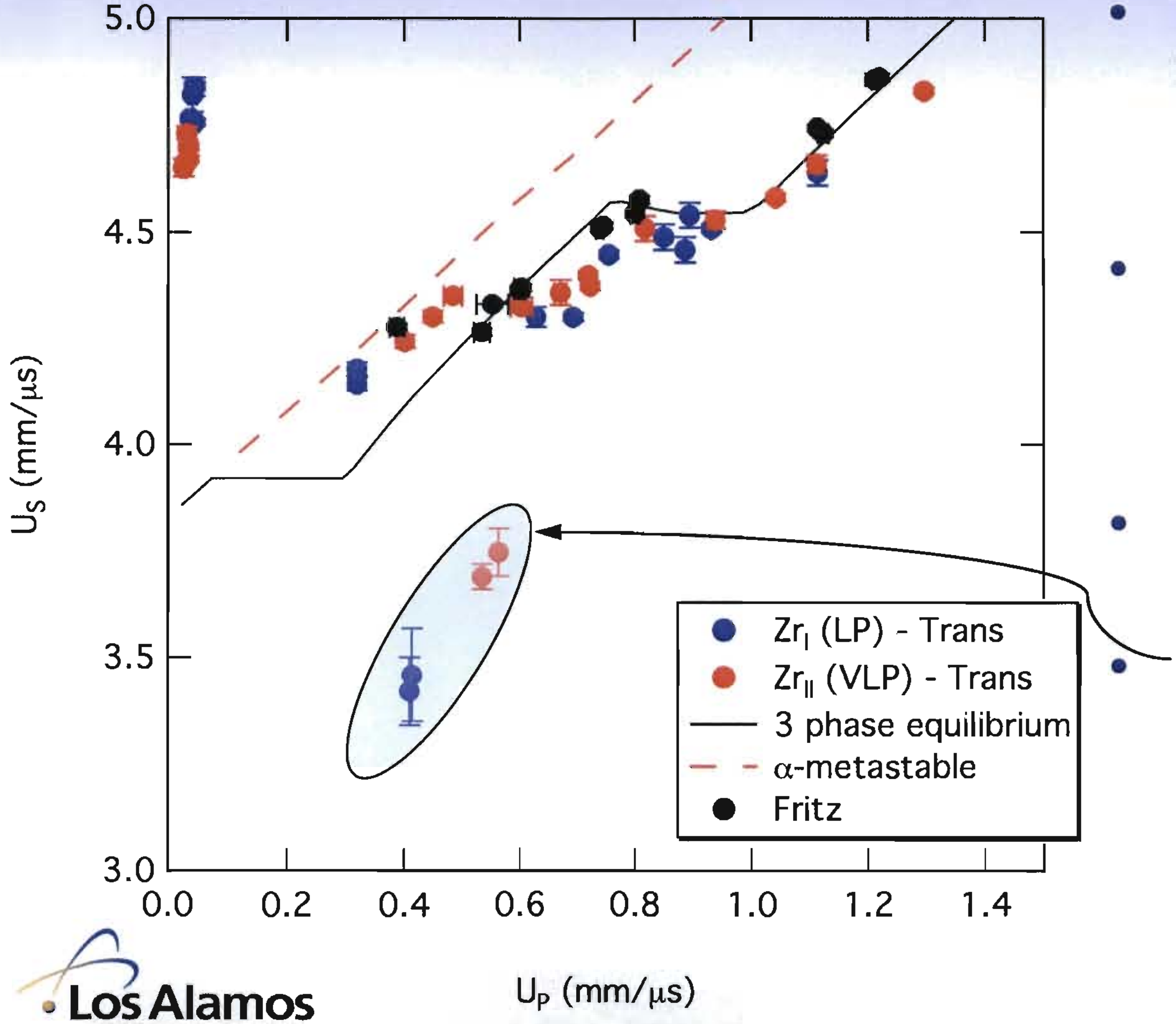
Obtaining Hugoniot data from transmission experiments

- Standard impedance matching technique used:
  - Projectile velocity measured to 0.1% (using PDV) in most cases.
  - Shock velocity in the sample measured using multi-point VISAR, multi-point PDV, and/or with impact pins/VISAR.



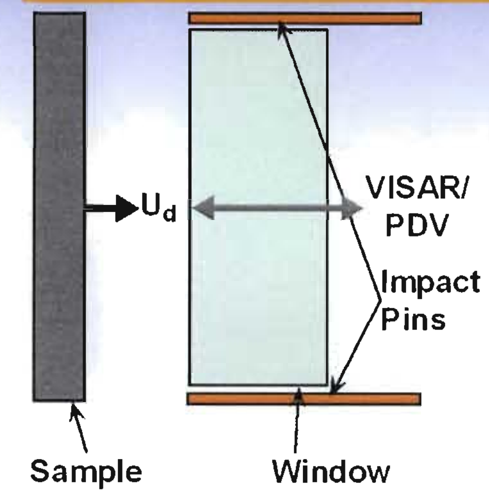
- Presence of multiple waves accounted for in analysis.
- Impedance matching does not properly account for wave interactions when precursor states are large with respect to final state:
  - Large impedance mismatch between sample/window can lead to large errors.
  - Zr impedance is between that of LiF and Sapphire (both used in experiments described here).

$U_S - U_P$ data obtained using transmission geometry

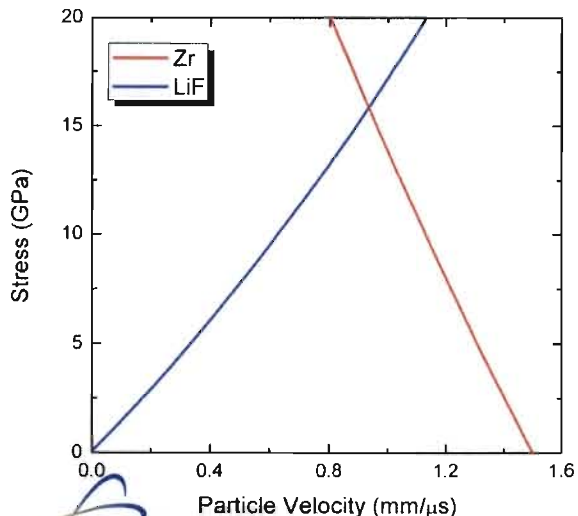


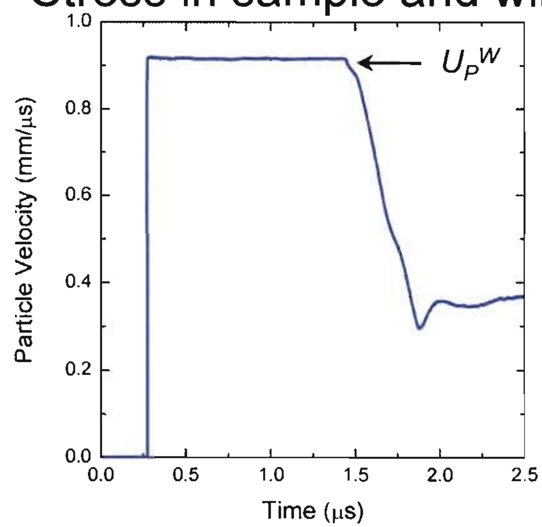
- The solid-solid phase transformations can be identified by kinks in U_S-U_P data.
- Legacy data analyzed using single wave analysis resulting in artificially high U_S.
- α and ω phases may need to be shifted in Greeff EOS.
- Wave interactions not properly accounted for in extracting U_S from 3-wave profiles.

Front surface impact (FSI) experiments eliminate wave interactions due to multi-wave structure



- Sample is impacted on window directly.
- Measurement of projectile velocity, U_d, and particle velocity, U_P^W, needed to determine Hugoniot point:
  - Projectile velocity measured using shorting pins or PDV to 0.1%.
  - Particle velocity measured at impact using VISAR and PDV to ~0.5 - 1%.
- Stress in sample and window defined by window Hugoniot



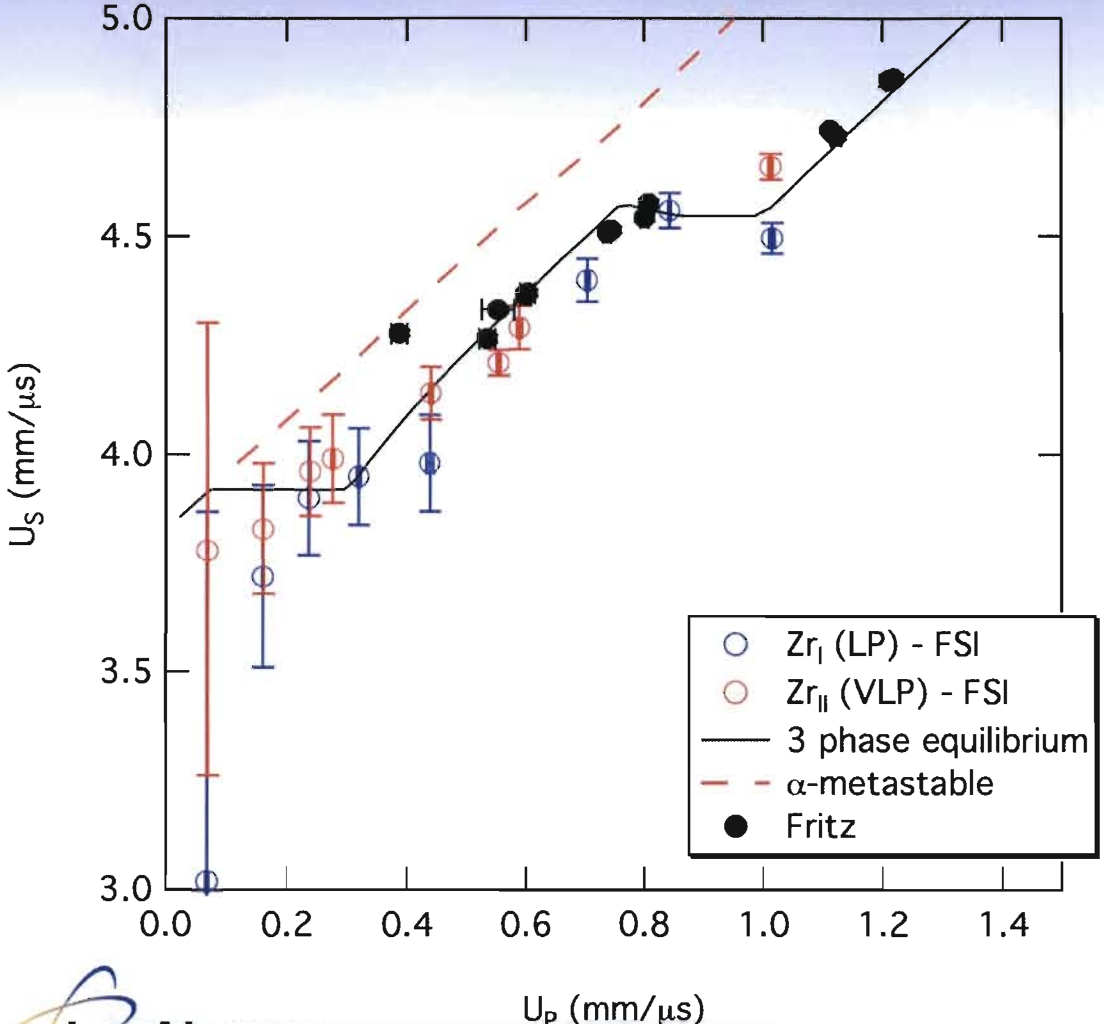


- Shock Velocity determined from R-H Jump Conditions:

$$U_S^S = \frac{P - P_1}{\rho_1 (U_d - U_P^W - U_{P1})}$$

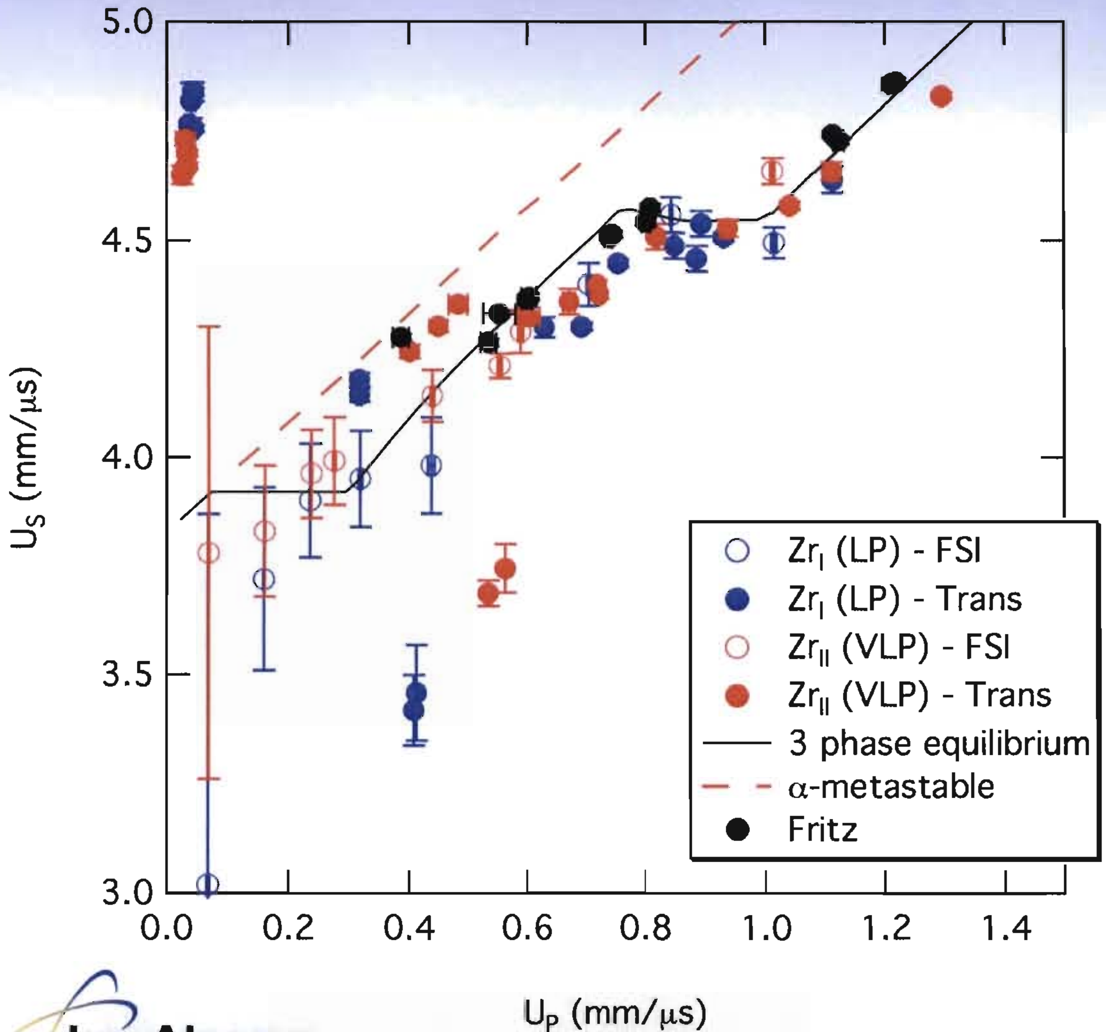
- Must know initial conditions!

Calculated Hugoniot is in very good agreement with data from front surface impact experiments



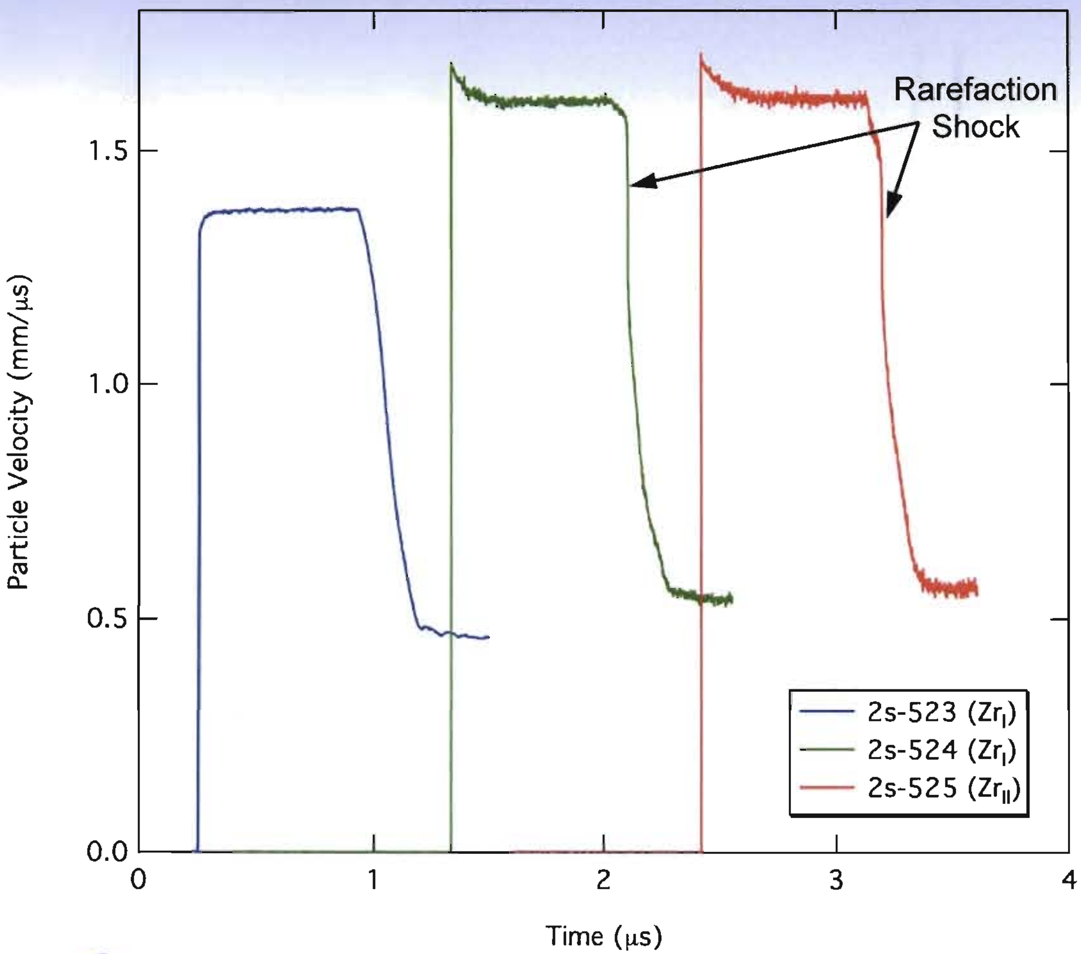
- Errors are large at low stresses due to uncertainties in initial state parameters.
- Results near the $\alpha - \omega$ transition are more consistent with the calculated Hugoniot
  - Better measurement of equilibrium at transition??

Calculated Hugoniot is in very good agreement with data from front surface impact experiments



- Errors are large at low stresses due to uncertainties in initial state parameters.
- Results near the $\alpha - \omega$ transition are more consistent with the calculated Hugoniot
  - Better measurement of equilibrium at transition??
- Transmission experiments seem to be better for determining the $\omega - \beta$ transition stress, but…

FSI experiments reveal β to ω transition on release



- Experiments conducted at 25 and 31 GPa on Zr_I and 31 GPa on Zr_{II} samples.
- At 25 GPa and below – Flat-top shock with ramped release
- At 31 GPa – Overshoot and relaxation at the front followed by shock formation on release
  - ω – β boundary crossed on shock
  - Kinetics of transition observed at shock front
  - Material reverts to ω phase upon release

Summary

- Both front surface impact and transmission experiments were performed to investigate the influence of impurities on the solid-solid phase transitions in three purities of Zr.
- Presence of interstitial O_2 dramatically changes kinetics of $\alpha - \omega$ phase transformation, but not the $\omega - \beta$ transformation.
- Differences between shock- and isentropically loaded experiments shows kinetics are also influenced by the initial loading conditions.
- Greeff Equation of State includes kinetic model which successfully captures much of the phenomena observed experimentally.
- More work needed to successfully model Zr_{II} material and simulation of gun experiments around $\omega - \beta$ transition still needs to be done.
- Combination of several experimental techniques and theory are leading to a better understanding of phase transition kinetics.