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Title: MultiphaseProperties of Cerium

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Los Alamos NATIONAL LABORATORY

EST. 1943

Multiphase Properties of Cerium

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There is a scientific need to obtain dynamic data to develop and validate multiphase equation-of-state (EOS) models for metals. Experiments are needed to examine the relevant pure phases, transition kinetics, phase boundaries, and other material properties such as strength. Cerium is an ideal material for such work because it exhibits a complex multi phase diagram at relatively moderate pressures readily accessible using standard shock wave methods. In the current work, plate impact experiments were performed to examine the dynamic phase diagram for cerium including the shock melting transition, the low-pressure $\gamma-\alpha$ transition, and higher pressure solid phases below melt. Consequently, information regarding strength and EOS data for the α, γ, and liquid phases were obtained. Experiments included standard plate impact experiments to generate shock-release load profiles, preheat experiments to map boundaries by varying initial sample temperature, and double-shock loading. Details of the experimental methods and recent experimental results will be presented along with a discussion on how these results will inform a recently developed multiphase EOS for cerium.

Multiphase Properties of Cerium

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Contributors/Acknowledgments

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N. Velisavljevic (WX-9), D. Holtkamp (P-23), B. Carrow (NSTech), J. Stone (P-23),

J.Cooley (MST-LANL), and many more.

Funding: R. Martineau and R. Olson (C2, DOE)

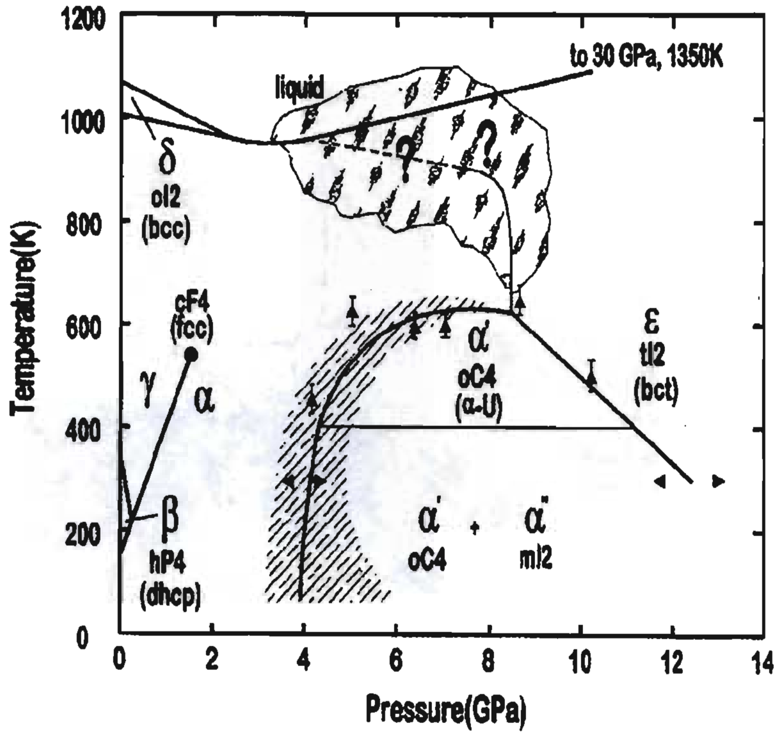
Outline

- Introduction – Traditional shock wave experiments
- Multiphase properties of metals: Cerium as an ideal material
- Experiments to examine multiphase properties of cerium
  - Sound speed and Hugoniot experiments to determine melt boundary
  - Pre-heat experiments to map the low-pressure g-a region
  - Multiple-shock loading and DAC to examine the a-e region
- Summary and Conclusions
  - On-going efforts
    - Pyrometry measurements on Hugoniot
    - Multiple shock loading to examine the liquid-solid boundary
    - Advanced diagnostics (reflectivity, pyrometry, dynamic Laue diffraction)
- Current picture of dynamic properties of cerium

Cerium – a material with a rich multiphase diagram

- There are four solid phases known at zero pressure, with at least three more phases at high pressure.
- The only pure element known with a solid-solid critical point
- γ-Phase has negative dK/dP as it approaches the low pressure phase transition (γ→α).
- Anomalous melting at low pressure though dynamic melt boundary uncertain
- Phase diagram uncertain above 3 GPa.
- Existence, location, and slope (and sign) of α-α′ phase boundary uncertain
- Location of the ε-phase uncertain especially at higher temperatures below melt
- Much of the uncertainty is a consequence of the details of DAC experiments including complications with grain-growth
- The multiphase region exists at low-pressures (including melt) less than 25 GPa

An Example Phase Diagram for Cerium



Zhao & Holzapfel; J. Alloys and Compounds (1997)

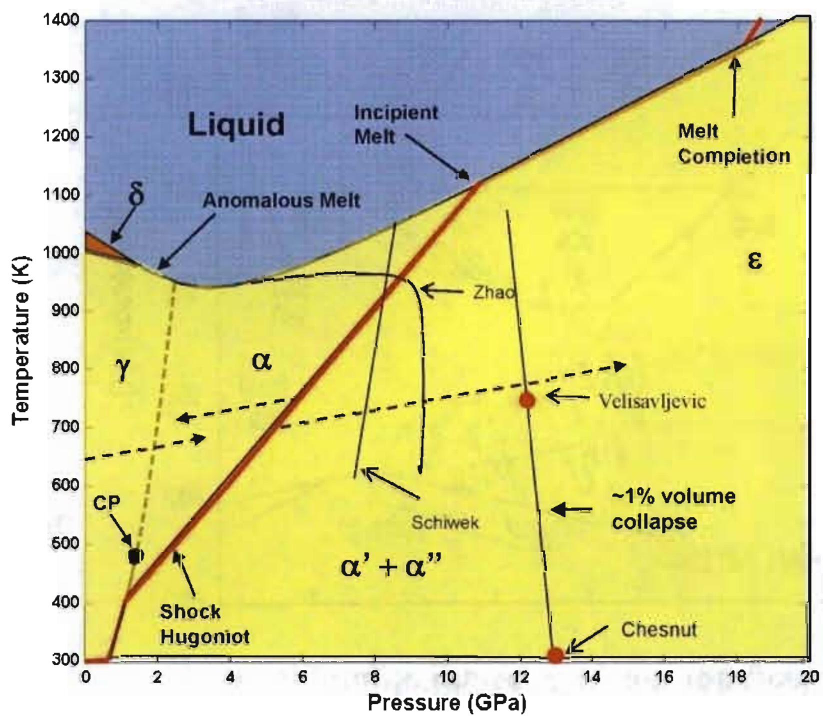
There is a scientific need to obtain new data to describe multiphase properties of metals

- Experiments are needed to:
  - Locate phase boundaries
  - Obtain EOS data in each phase
  - Obtain information on kinetics, strength, etc.

- Cerium chosen for this work because
  - Large-body of static data
  - Complex phase diagram in moderate stress range
  - Multiphase EOS available for experimental design/analysis
  - Limited dynamic data available

- The overall objective was to develop an experimentally validated dynamic multiphase equation-of-state for cerium

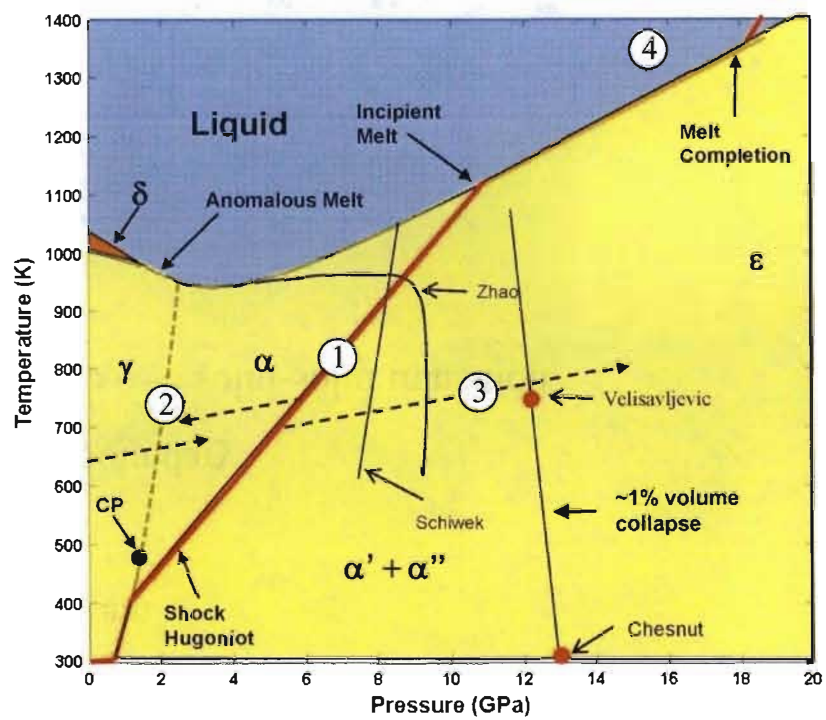
Schematic Ce phase diagram



Systematic Experimental Approach to Examine the Multiphase EOS of Cerium

- **Region 1**: Principle shock melting using plate impact experiments to obtain Hugoniot and sound speed data that span the melt transition.
- **Region 2**: Mapping of low-pressure γ–α phase transition as a function of initial temperature
- **Region 3**: Multiple shock loading to examine the high pressure, low-temperature solid region of the phase diagram which includes the α–ε region
- **Region 4**: High-temperature liquid EOS and liquid-solid transition
- **Current and Future Work:**
  - Continued EOS including kinetics
  - Strength along the Hugoniot
  - Temperature measurements on Hugoniot

Schematic Ce phase diagram

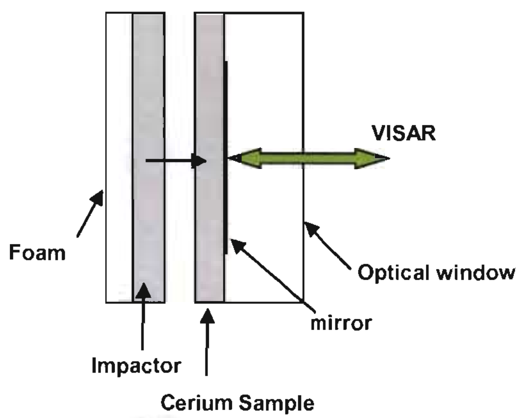


Outline

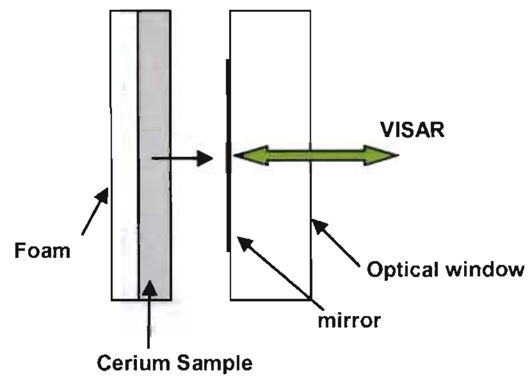
- Motivation
- Cerium: a complex material with a rich phase diagram
- **Shock melting**
- Mapping the low-pressure solid-solid ($\gamma-\alpha$) phase boundary
- Double-shock and DAC experiments to examine the $\alpha-\varepsilon$ solid-solid transition
- Summary and conclusions
- Path Forward

Traditional shock-wave experiments to measure impact stress, shock velocity, sound speed at pressure, etc.

Transmission Configuration



Front-Surface impact Configuration

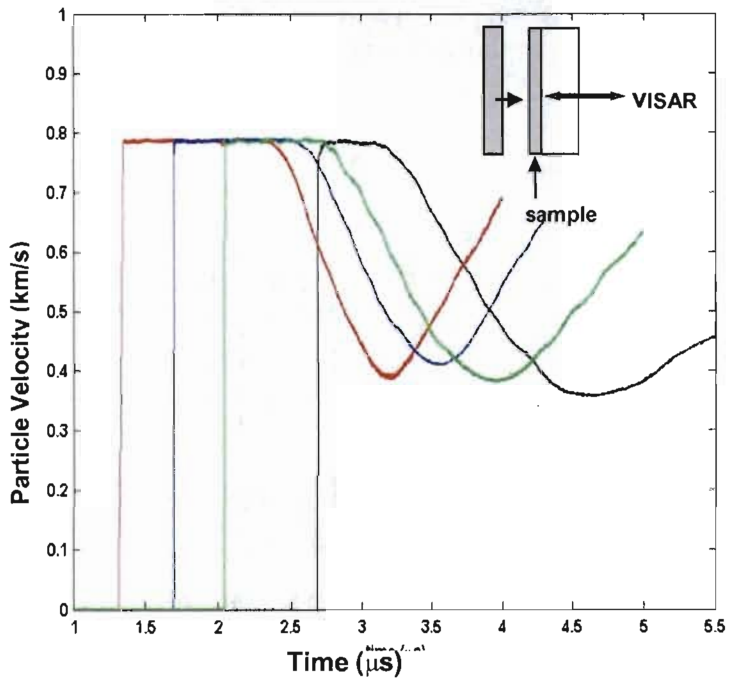


- Traditional overtake method uses multiple samples to monitor release arrival time (sound speed at pressure) (Rev. Sc. Instr., 53(2) 1982)
- Measure shock speed directly
- Px and up obtained from impedence matching method
- Kinetics convolved with wave propagation

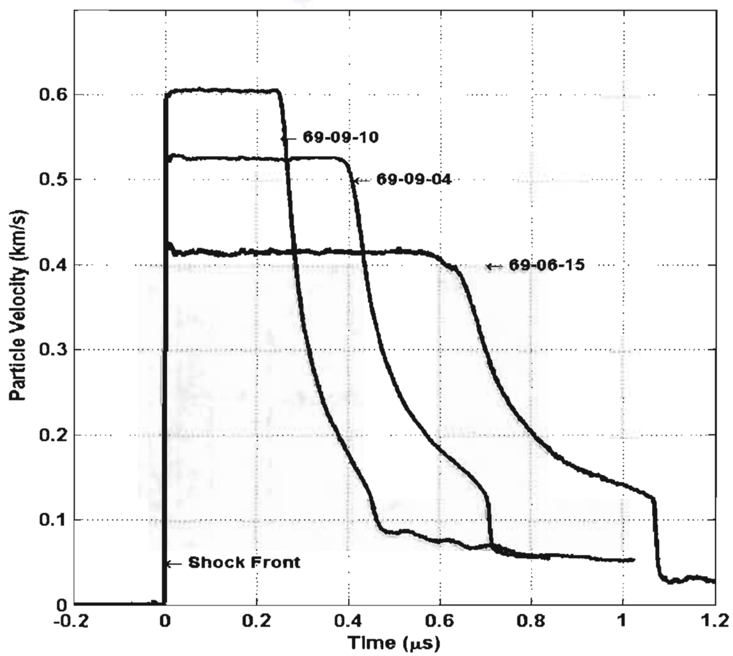
- Direct measurements of the Px, transition kinetics, sound speed (longitudinal and bulk)
- Strength information contained in release behavior
- Release arrival time depends only on characteristics of sample material

Examples of wave profile data using transmission and front-surface configurations

Example shock wave profiles
(Transmission Configuration)



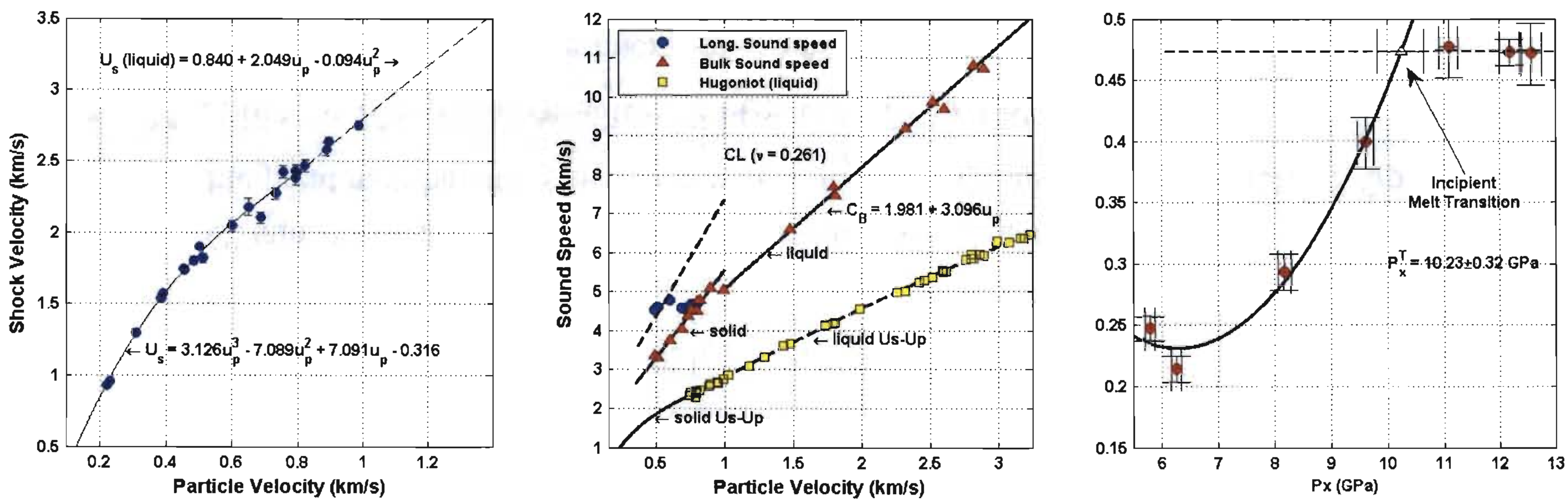
Example shock wave profiles
(Front-Surface impact Configuration)



Summary of Hugoniot and Sound Speed Data: Shock-Melting Transition of Cerium (Rev. B, 81, 214109 (2010))

- Low-pressure Hugoniot data obtained for stresses that span the melt transition
- Longitudinal and Bulk sound speed data obtained
- Incipient melt estimated to occur at 10.2 GPa with complete melting at 18 GPa

Us vs. up (low-P) **Us and C vs. up** **Poisson's Ratio vs. Px**



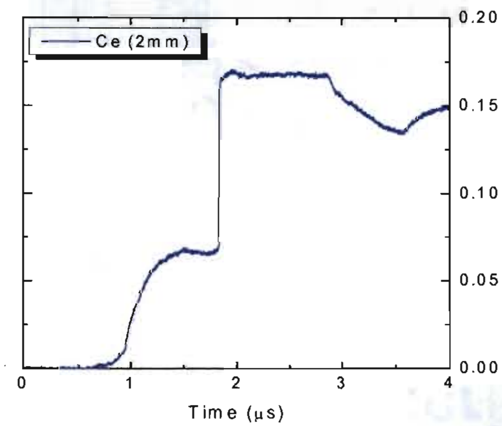
Outline

- Motivation
- Why cerium: a complex material with a rich phase diagram
- Shock melting
  - Obtained low-pressure Hugoniot and sound speed data through the melt transition
  - Incipient melt begins at 10.2 GPa with complete melting at approximately 18 Gpa
- **Mapping the low-pressure solid-solid (γ–α) phase boundary**
- Double-shock and DAC experiments to examine the a-e solid-solid transition
- Summary and conclusions
- Path Forward

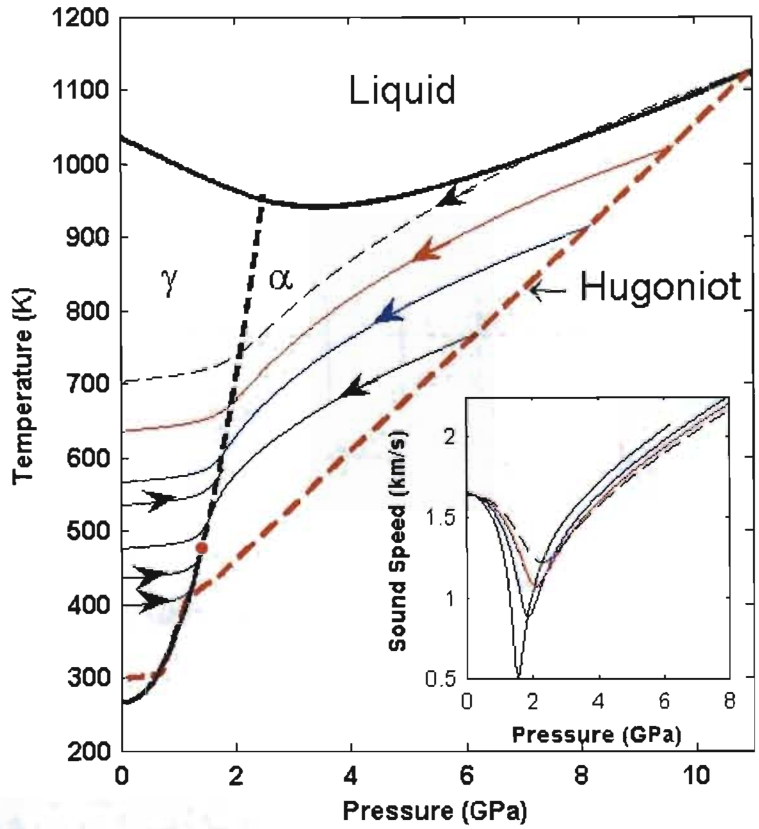
Mapping the low-pressure ($\gamma-\alpha$) phase boundary

- Preliminary shock data show ramp-shock profile likely due to anomalous behavior for C_B, K_S, etc.
- Use preheat capability to shock across the $\gamma-\alpha$ boundary for different T_o
- Use front-surface impact data to probe the $\gamma-\alpha$ boundary on release
- Reasonable model need for design/analysis

Low-pressure Wave Profile for Ce

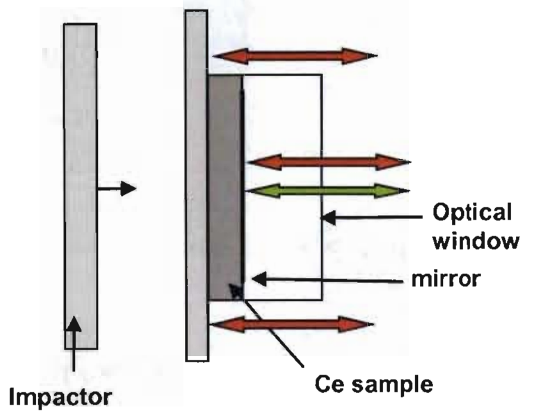


Calculated Ce phase diagram Illustrating possible loading paths



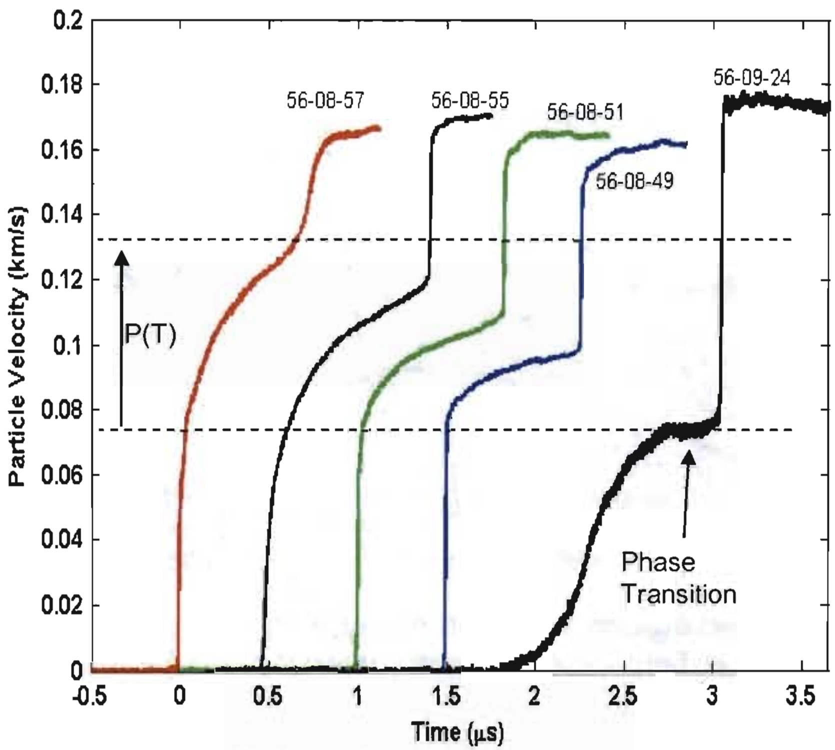
Pre-Heat Experiments to map the low-pressure solid-solid boundary for cerium ($\gamma - \alpha$ transition)

Pre-heat Transmission Experiments

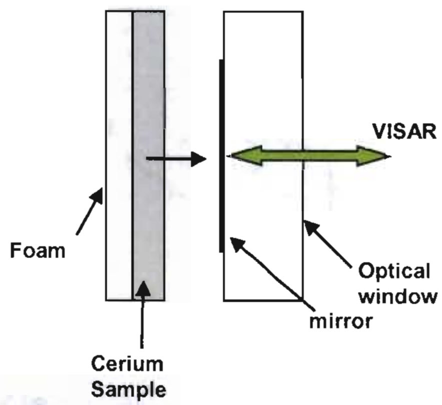


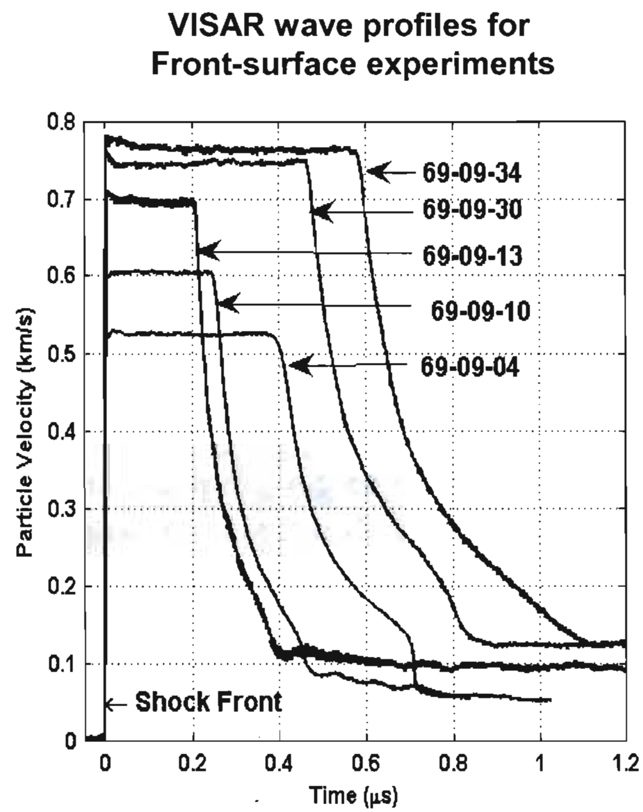
- Experiments performed up to 535 K
- Approximately constant impact stress
- Transition stress observed to increase with T
- Unlike DAC data, wave profile exhibits structure even above the critical point due to anomalies in the K_T, C_L, etc.

VISAR wave profiles for heated Ce experiments



Front-surface impact experiments to map the low-pressure solid-solid boundary for cerium ($\gamma-\alpha$ transition)



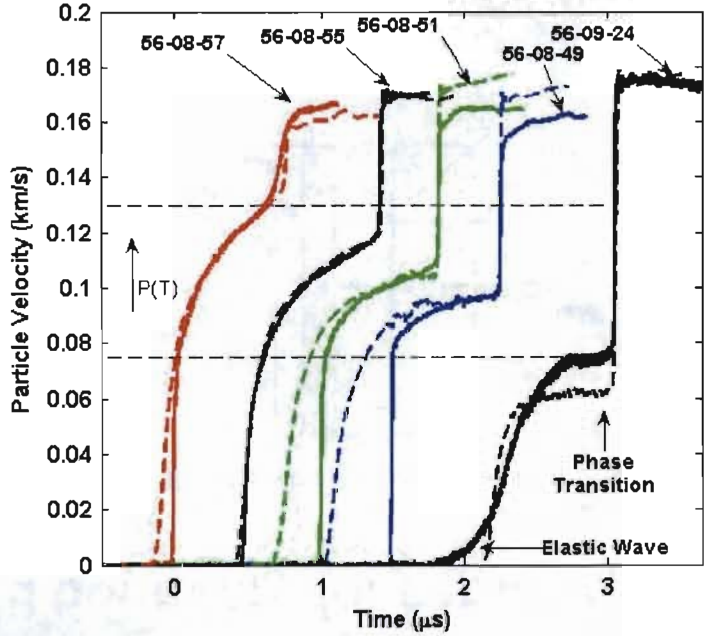


- Experiments performed up to the melt transition
- Rarefaction shock observed during unloading corresponding to the $\alpha-\gamma$ transition
- This feature observed for temperatures above and below the critical point similar to the heated experiments
- Transition observed to increase with increasing impact stress and is not observed for impact stresses greater than 13 Gpa
- Implication: $\gamma-\alpha$ boundary extends to melt as a 2nd order transition – does not extend into the melt region

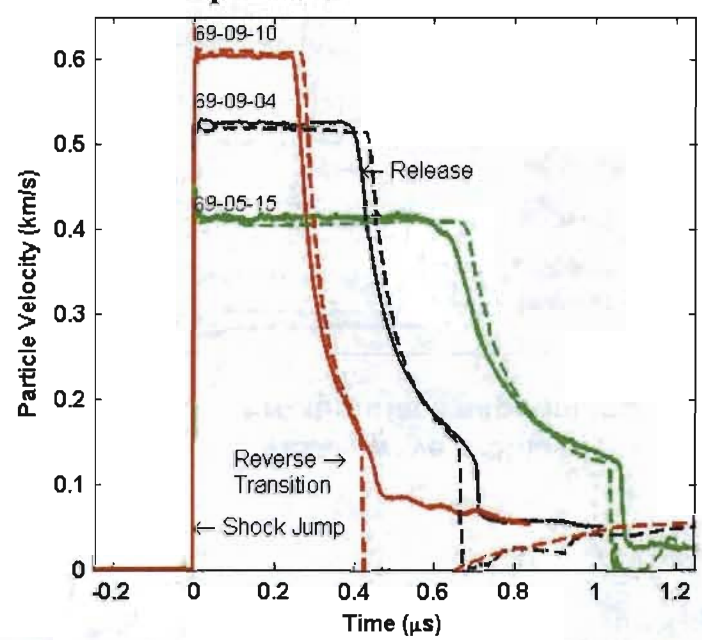
Model calculations using the MEOS show good agreement

- Good agreement observed between calculation and experimental profiles although there are some differences
- Transition pressure increases with initial T; shock-jump decreases
- Similar behavior observed for the shock-release data

Pre-heat data compared to EOS calculations



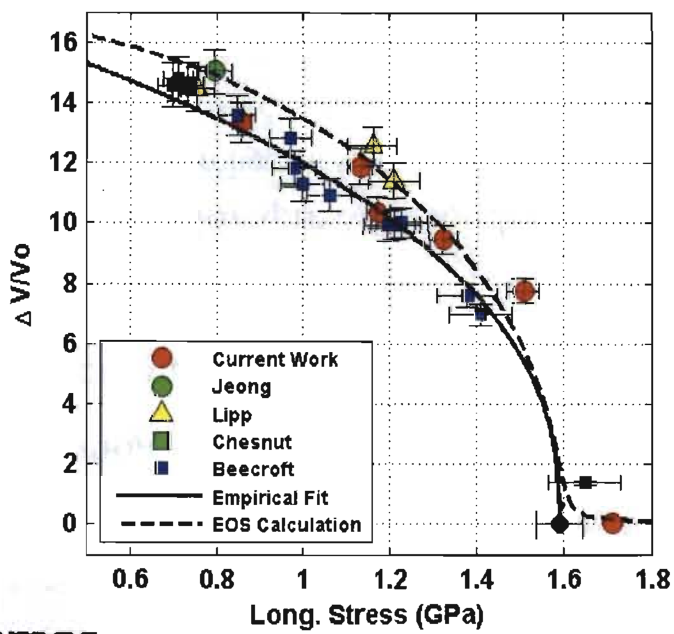
Front-surface impact data compared to EOS calculations



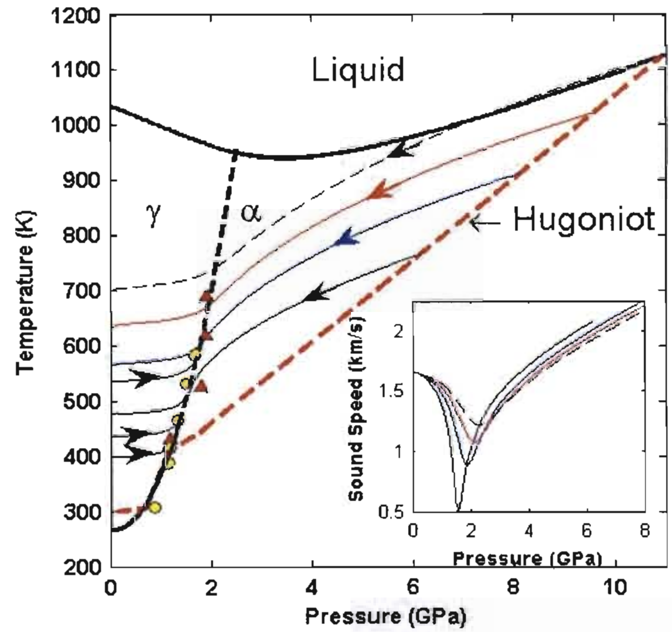
Summary of Experimental Results for Preheated Experiments

- Volume compression data for static, dynamic, and model prediction all in agreement
- Volume compression function used to constrain multiphase EOS
- Critical point estimated from dynamic data (1.6 GPa)
- Above critical point where the volume change is continuous, wave structure persists

Volume compression vs. Pressure



Calculated Temperatures vs. Measured Transition Stress

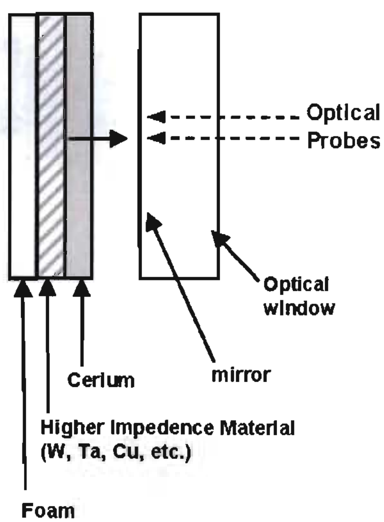


Outline

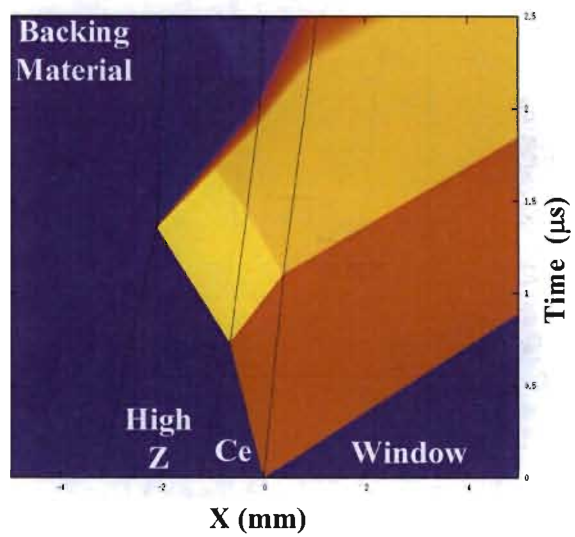
- Motivation
- Why cerium: a complex material with a rich phase diagram
- Shock melting
- Mapping the low-pressure solid-solid (g-a) phase boundary
  - Obtained preheated sample data and shock-release data for the g-a region of the phase diagram
  - Volume compression data point to a critical point at 1.6 GPa
  - Wave profile data shows a two-wave structure even above the critical point
  - The $\gamma-\alpha$ boundary continues beyond the critical point to the melt line likely as a 2^{nd} order transition
  - Transition stress in good agreement with model predictions and static data
- **Double-shock and DAC experiments to examine the $\alpha-\varepsilon$ solid-solid transition**
- Summary and conclusions
- Path Forward

Double-shock and DAC experiments to examine the $\alpha-\varepsilon$ region

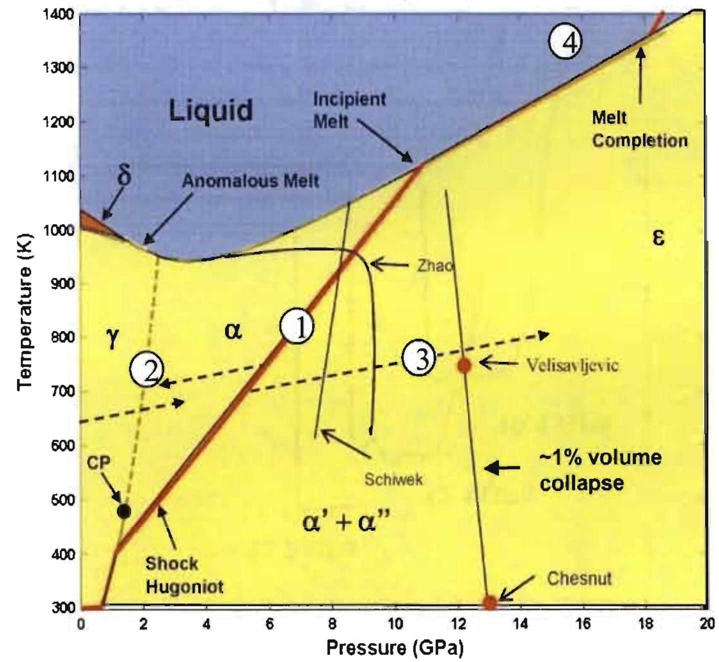
Double-Shock Experiment



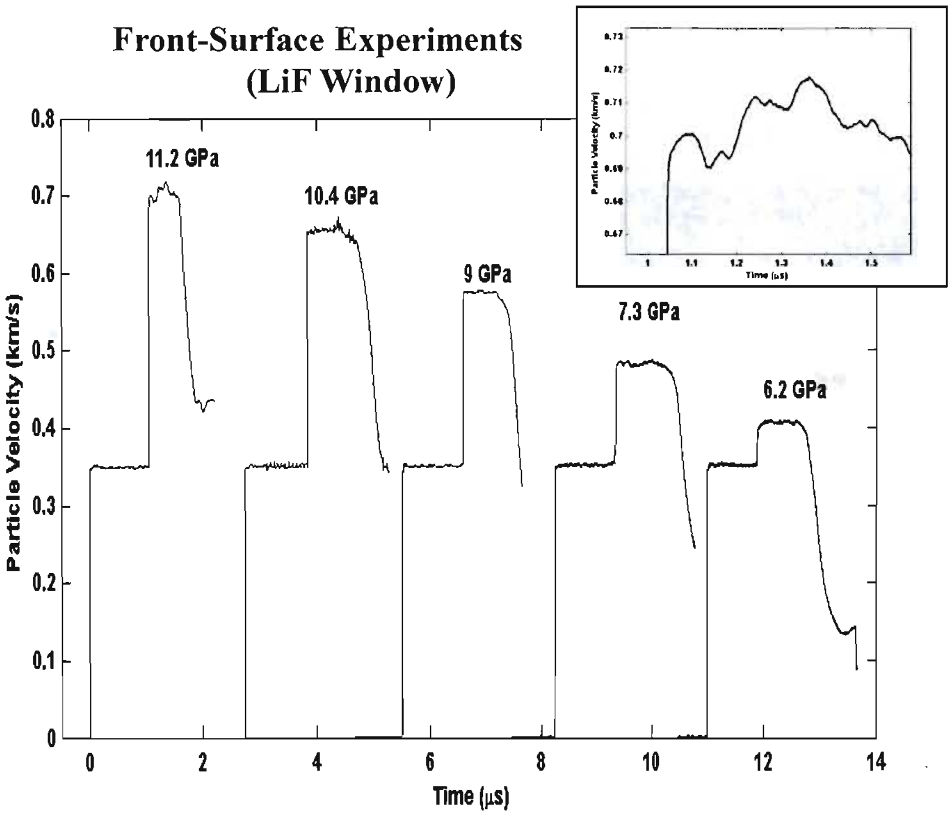
X-T Diagram

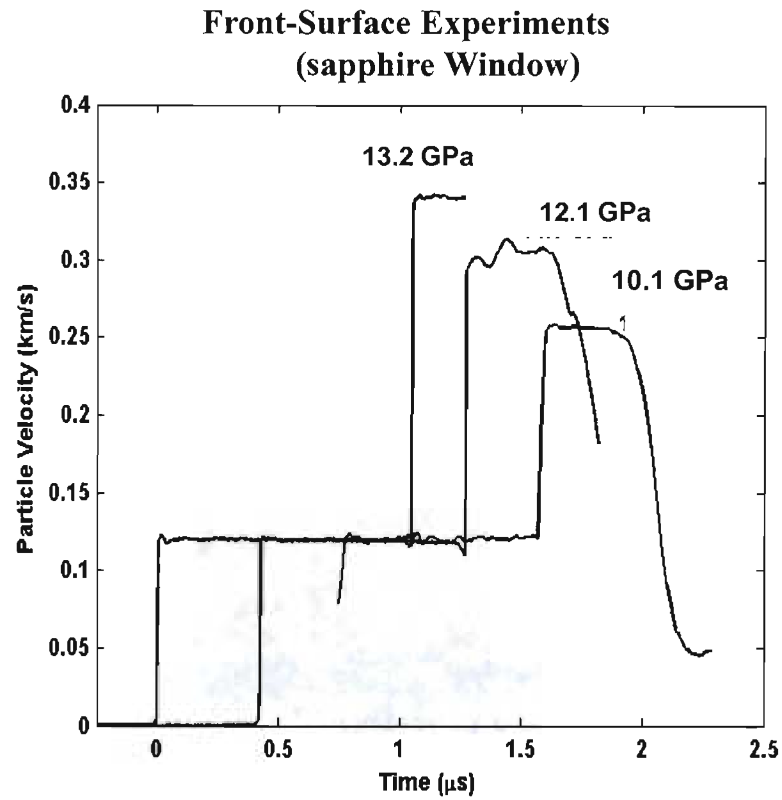


Schematic Ce phase diagram



Experimental Results (2nd shock stress states 6-13 GPa)





- Wave profiles show well-defined double-shock
- No wave structure observed through the expected region for ε-phase
- Features observed in the peak state between 10 and 13 GPa

EOS for α-Cerium using a Keane Isentrope

- Developed a Mie-Gruneisen Keane equation-of-state for α-cerium
- Keane formulation allows for curved Hugoniots in Us-up
- Hugoniot data spans α-phase and liquid showing significant curvature
- No strength or phase boundaries are included in the model
- More complete analysis will use our current multiphase EOS

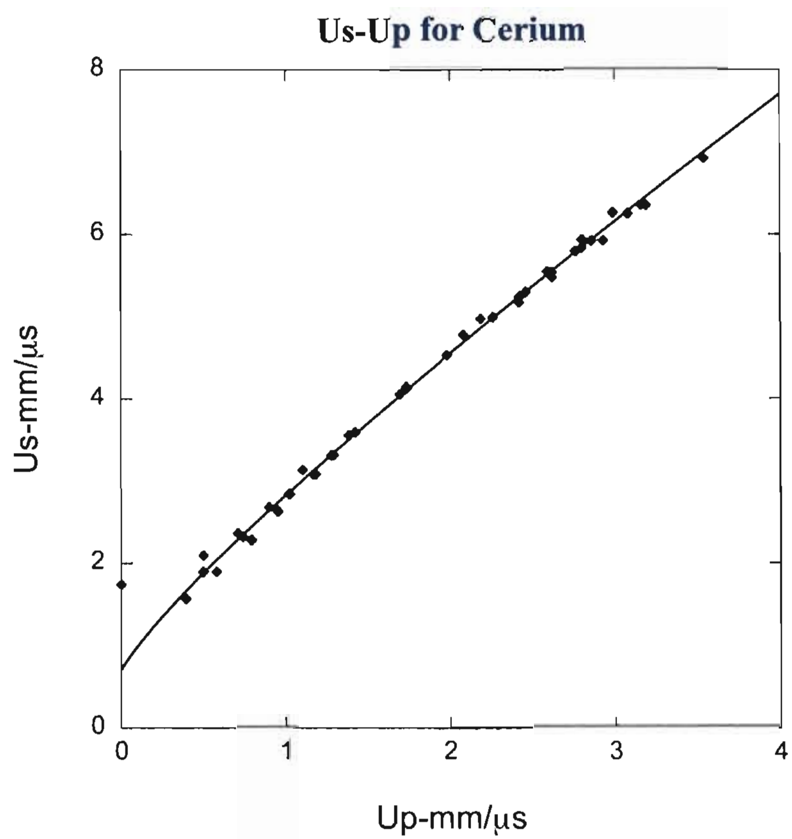
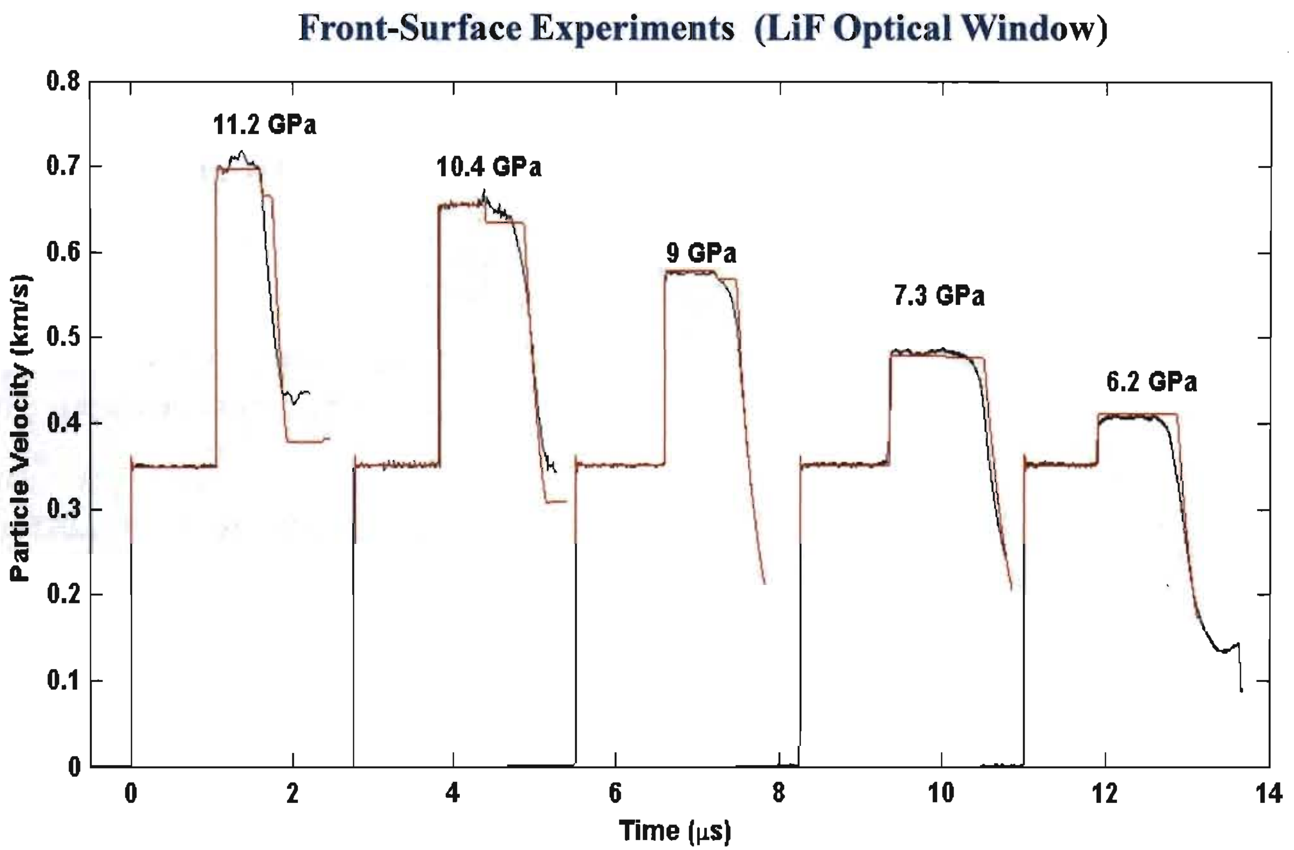
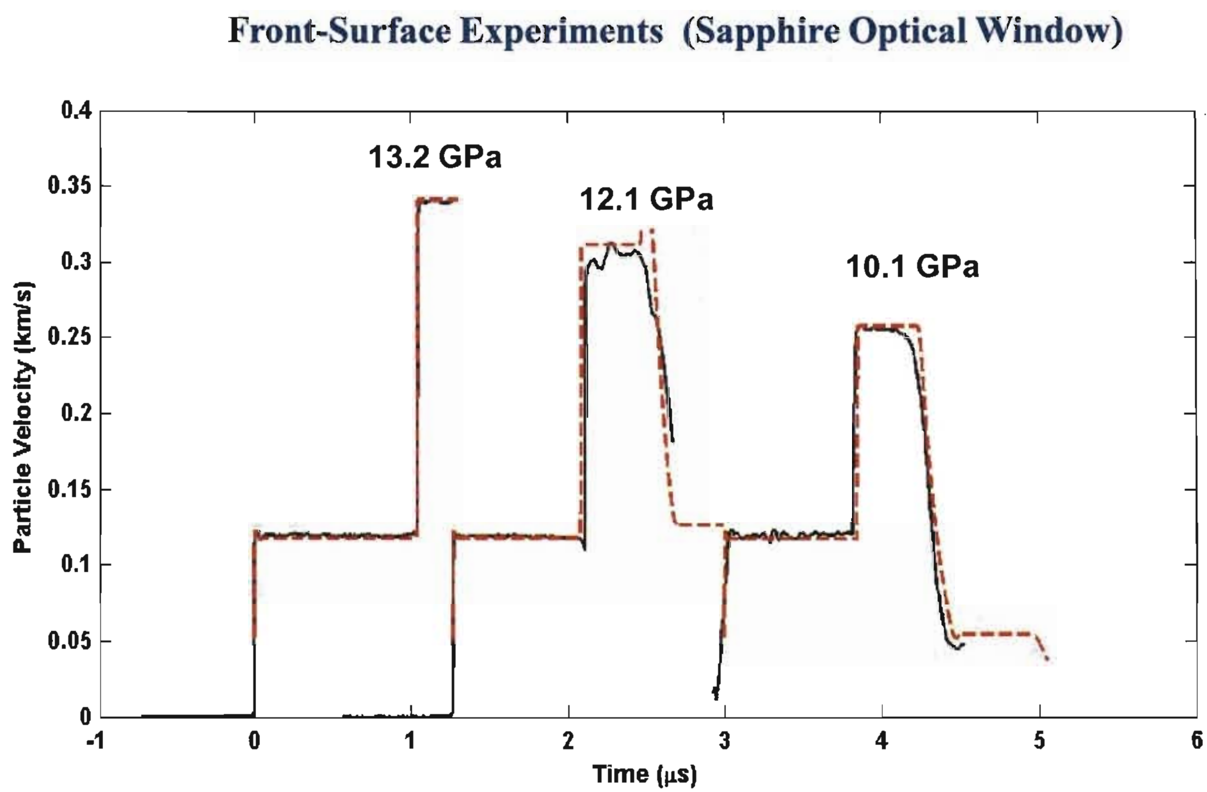


Figure 3: Ce Hugoniot data and Mie-Gruneisen Keane Hugoniot.

Comparison between experimental profiles and calculated wave profiles

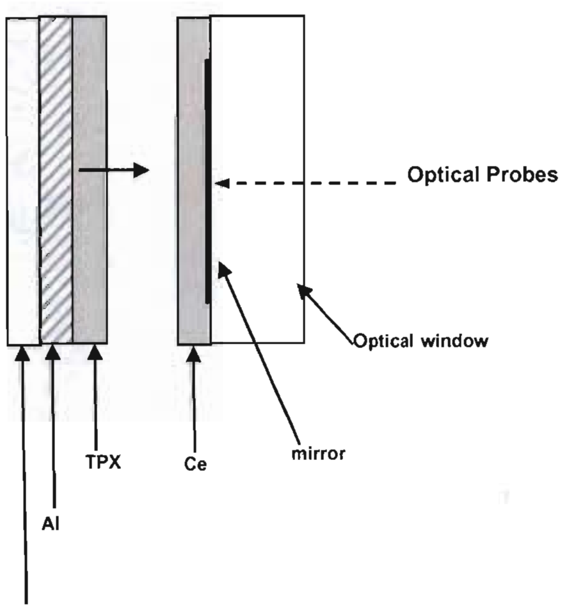


Comparison between experimental profiles and calculated wave profiles

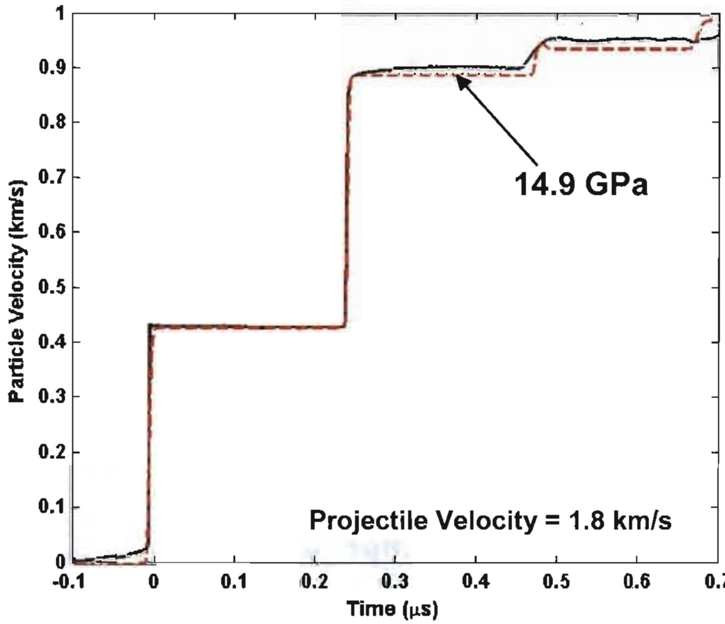


Transmission experiments to obtain higher pressure second shock states

Double-Shock Transmission



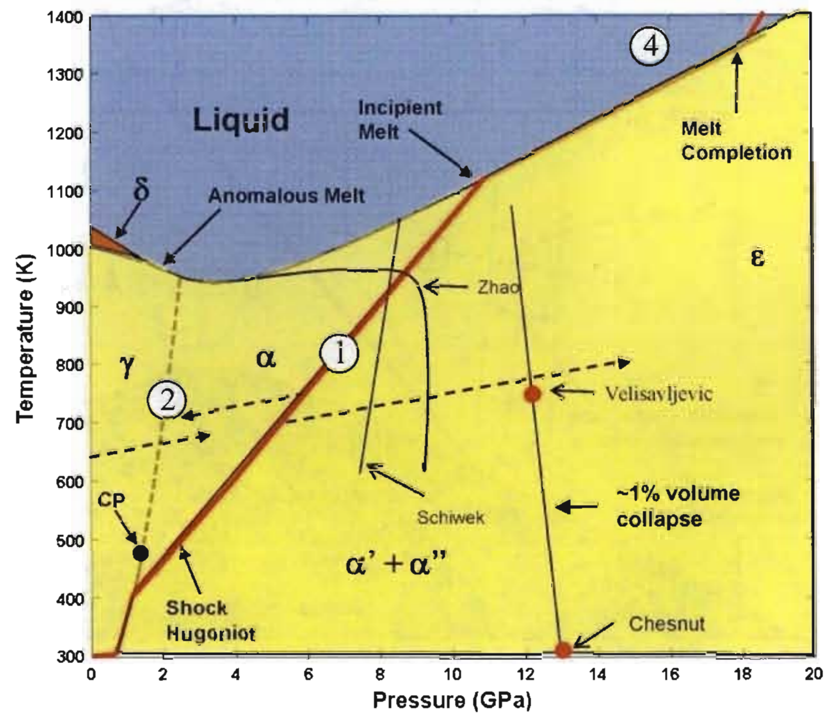
Transmission Experiment (LiF Optical Window)



Summary and Conclusions: Region 1 and 2

- Hugonot and sound speed data obtained to define the shock Hugoniot and determine the melt transition stress (10.2 GPa – 18 GPa)
  - Low-pressure Hugoniot and sound speed data obtained for impact stresses that span the melt transition
  - Incipient melt begins at 10.2 GPa and is complete by 18 GPa
- Preheated and shock-release experiments completed to examine the γ–α region of the phase diagram
  - The γ–α boundary was mapped in compression and during release
  - Volume compression estimated through the critical point – provides model constraint
  - Wave structure above the critical point indicates that the γ–α boundary extends to the melt line as a 2nd order transition – does not extend into the liquid
  - EOS data obtained – Elevated T Hugoniot data and compression/release data

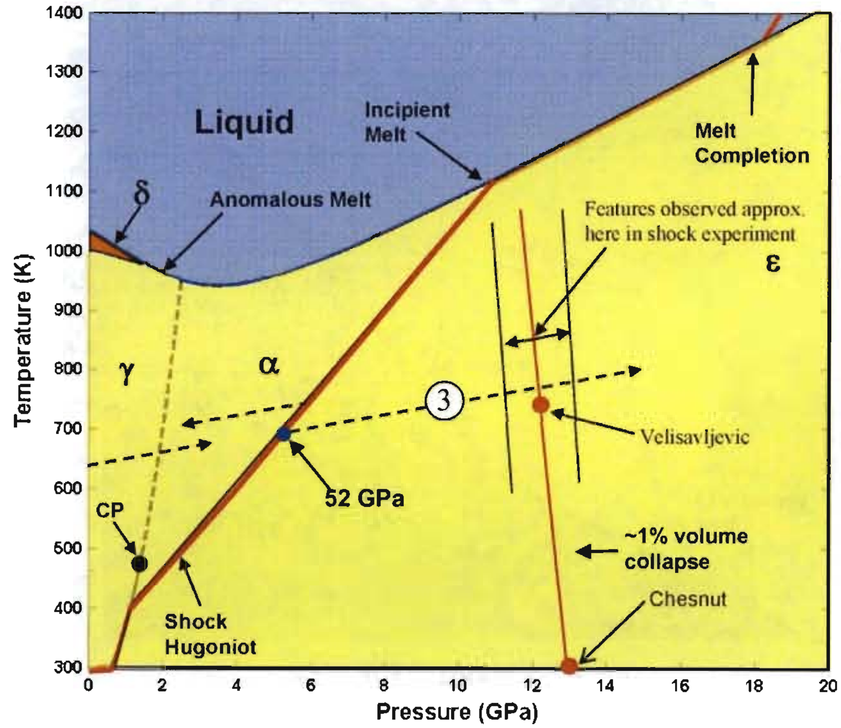
Schematic Ce phase diagram



Summary and Conclusions: Region 3

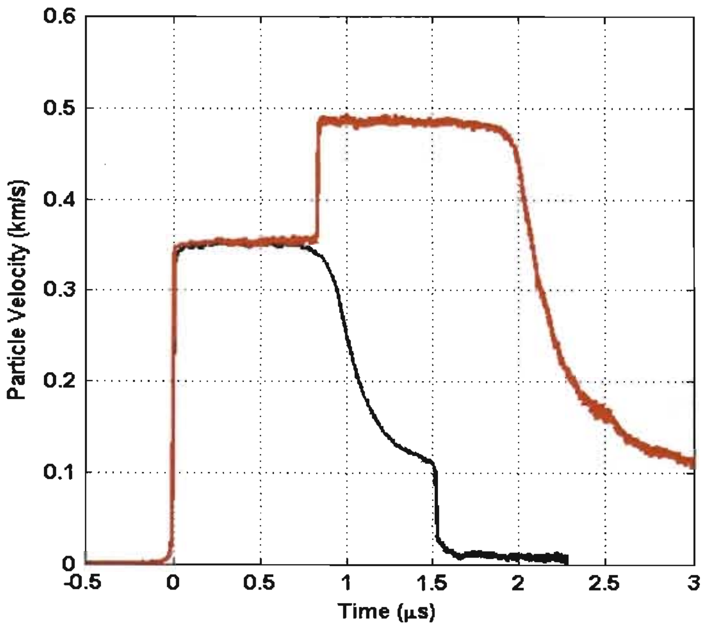
- Double shock experiments were performed to examine the α-ε region of the phase diagram: 1st shock ~5.2 GPa, 2nd shock 6-16 Gpa
- No wave structure observed for loading near the static phase boundary
- Features in the peak shocked state were observed in the 11-13 GPa range consistent with location of the ε-boundary (DAC)
- Calculations using an α-Ce model (no strength or phase boundaries) agree well with the experimental profiles
- Work underway to analyze these data using a multiphase EOS which includes the ε-phase boundary
- Work on-going to use these data to examine strength in the α-phase up to melt

Schematic Ce phase diagram

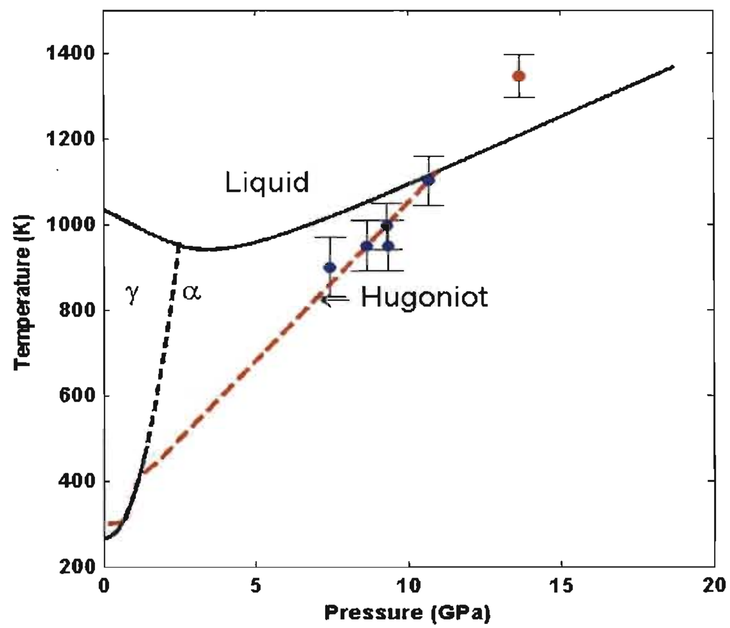


On-going and Future work

Shock-release and Double-shock (Strength)



Hugoniot Temperatures (T vs. Px)



- Shock-release and double shock to examine strength on Hugoniot up to melt
- Temperature measurements (pyrometry) on Hugoniot through the melt transition
- Multiple shock loading to examine the liquid and liquid-solid transition

Questions?

Contributors/Acknowledgments

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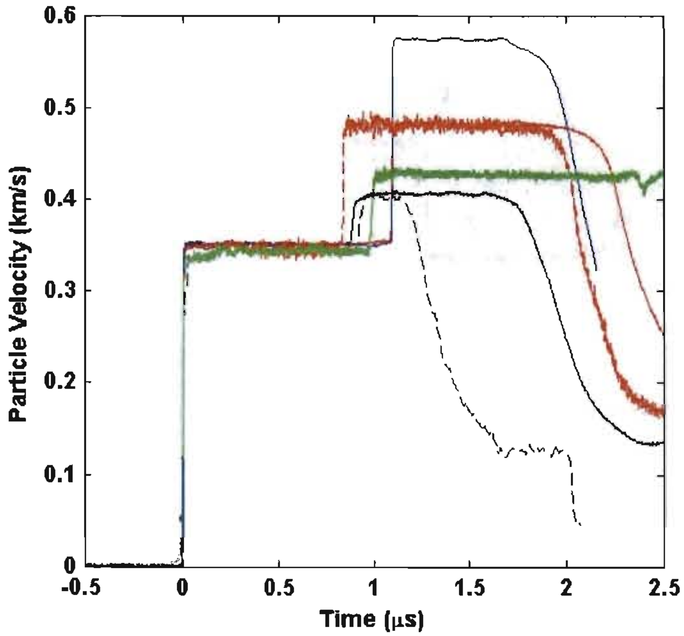
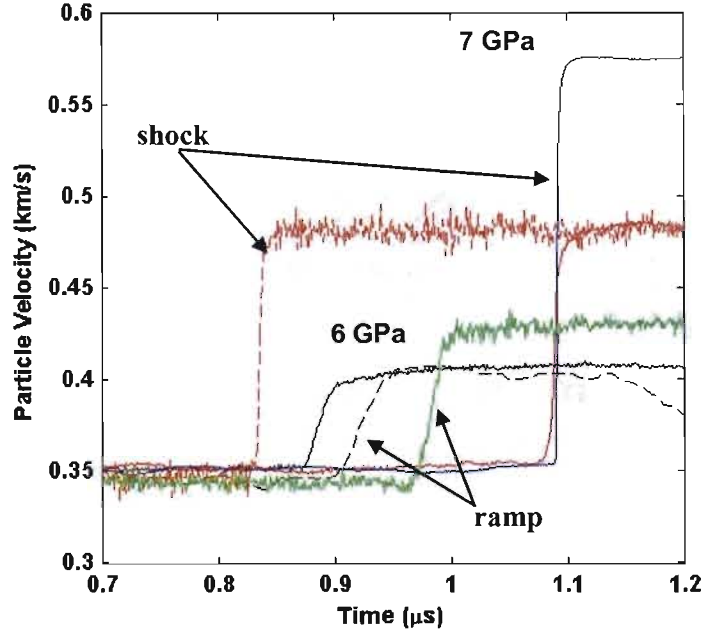
Funding: R. Martineau and R. Olson (C2, DOE)

Re-shock experiment to examine strength (Low-pressure 2nd-shocks data)

Wave profiles for several double-shock (5.2 – 7 GPa)



Wave profiles for several double-shock (5.2 – 7 GPa) - Closeup View

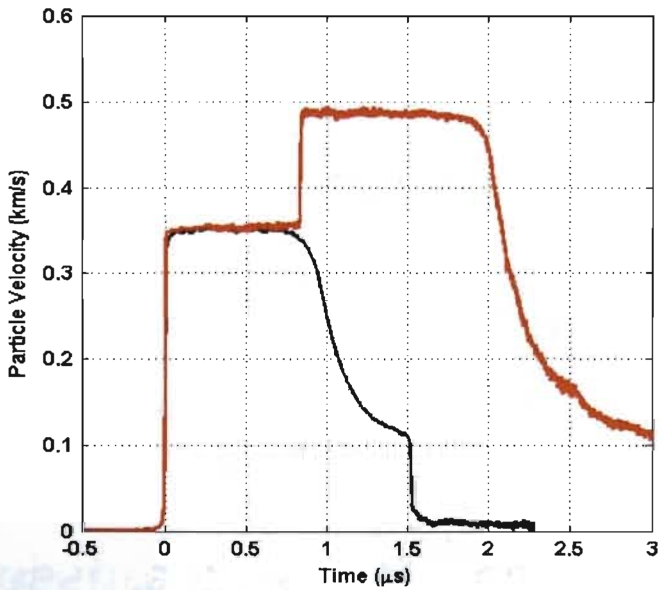


- Low-pressure 2nd shock data show ramp-waves at ~6 Gpa which forms a shock by ~7 GPa
- No distinct elastic wave observed in 2nd shock
- Existing shock-release data being analyzed to estimate during release (not shown)

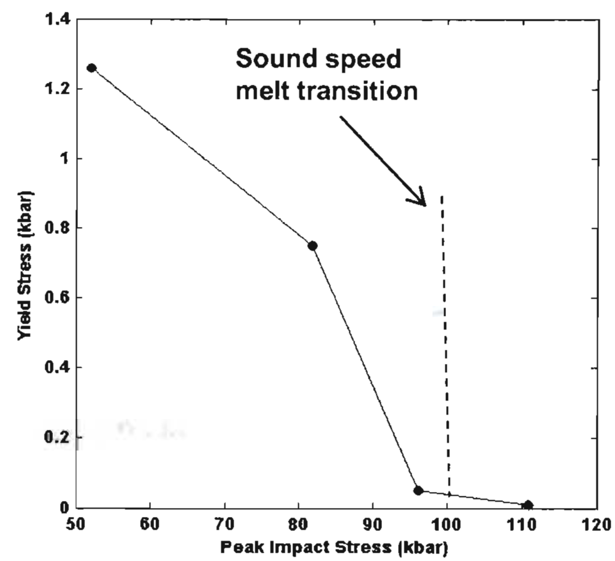
Work *In-Progress* to examine the multiphase properties of Ce: Properties of α-phase cerium: strength

- Shock-release experiments are being re-analyzed to obtain estimates of strength during release (Asay method)
- Double-shock data also expected to provide strength information
- Additional experiments underway to fill in the data set and to approach the $\gamma-\alpha$ boundary

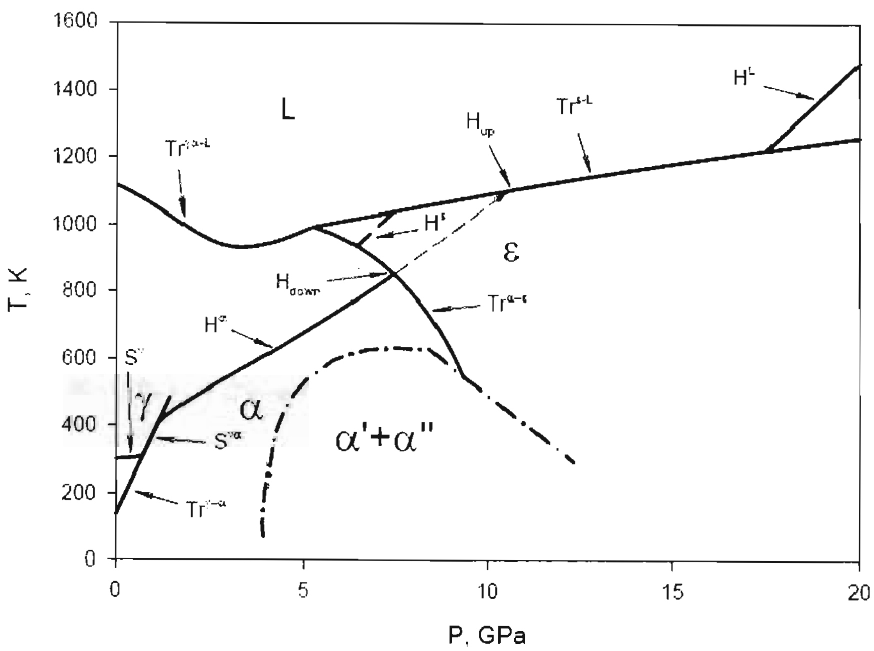
Shock-release and Double-shock



Yield Stress vs. Peak Stress



VNIITF has constructed a multi-phase EOS for Ce



Construct a Helmholtz potential as a sum of three terms:

$$F(V,T) = F_C(V) + F_H(V,T) + F_{AE}(V,T) - S_m T\,.$$

The cold energy curve

The quasi-harmonic free energy

An energy term characterizing the anharmonic lattice vibrations and thermally excited electrons

- G-a region treated as a binary alloy which provides a convenient method for including the anomalous behavior of the bulk modulus, sound speed, specific heat

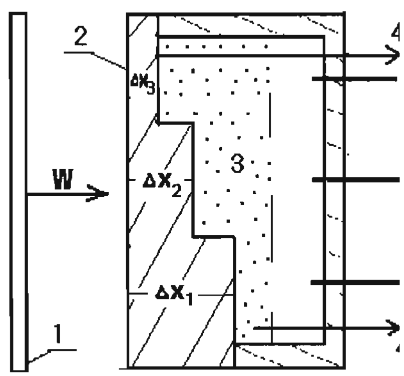
- Volume collase along g-a used as a constraint with an adjustable critical point and dv/vo function

Traditional Sound Speed Measurements at Pressure

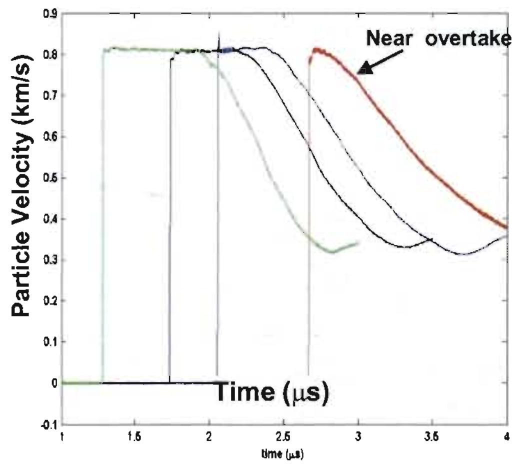
(McQueen, Marsh, Fritz, et al, Rev. Sc. Instr., 53(2) 1982)

- Technique uses multiple samples to monitor release arrival time as a function of thickness
- Sample thickness vs. steady state time duration provides the overtake distance
- Sound speed is directly related to the overtake distance

Experimental Configuration



VISAR profiles for Cerium (Vp = 1.158 km/s)



Peak State Time Duration vs. Thickness

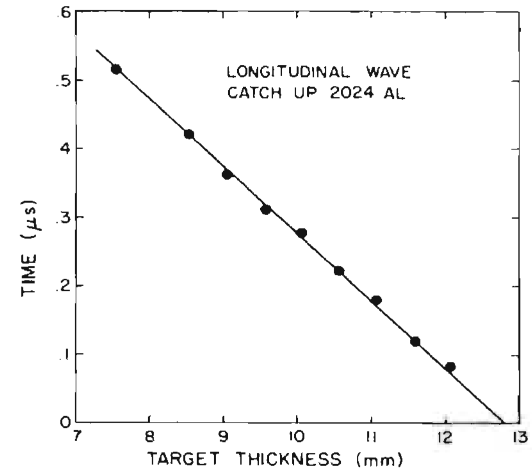
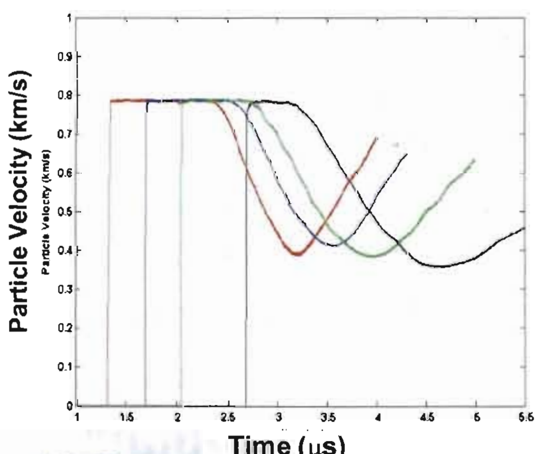


FIG. 7. The results of a high quality experiment to measure the longitudinal catch-up velocity. Nine out of ten records are plotted. The tenth at $X = 12.6$ mm had some cable ring which obscured what should have been ~30 ns flat top.

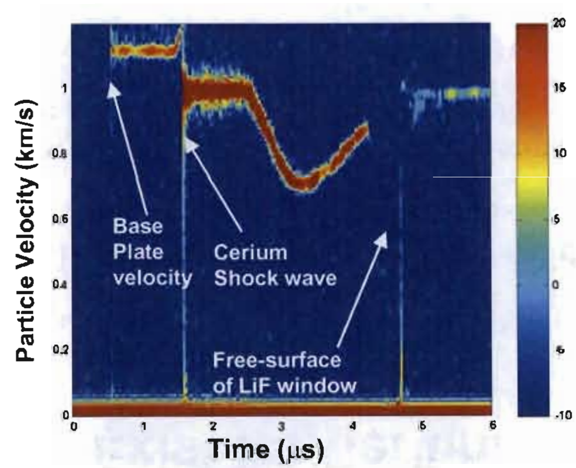
Multi-sample Experiments on Cerium using the Traditional Overtake Method

- Photonic Doppler Velocimetry (PDV) used to obtain:
  - Shock velocity
  - Wave profile at sample/window interface
  - Shock wave tilt and base plate measurements
  - Some probes multiplexed to minimize digitizer channels
- VISAR used to obtain accurate wave profile measurement

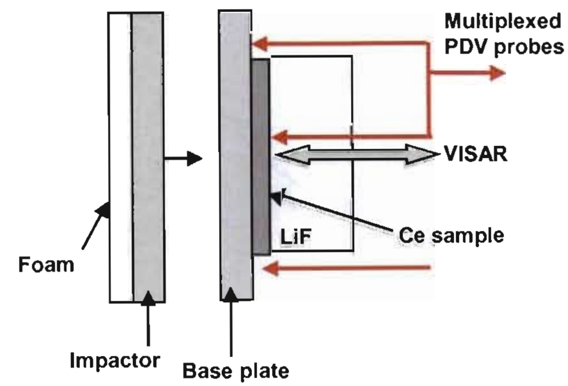
VISAR Wave Profiles



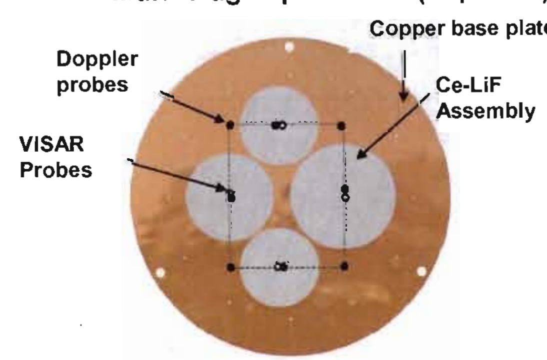
Analyzed PDV Data



Multi-Slug Experiments (Side-view)

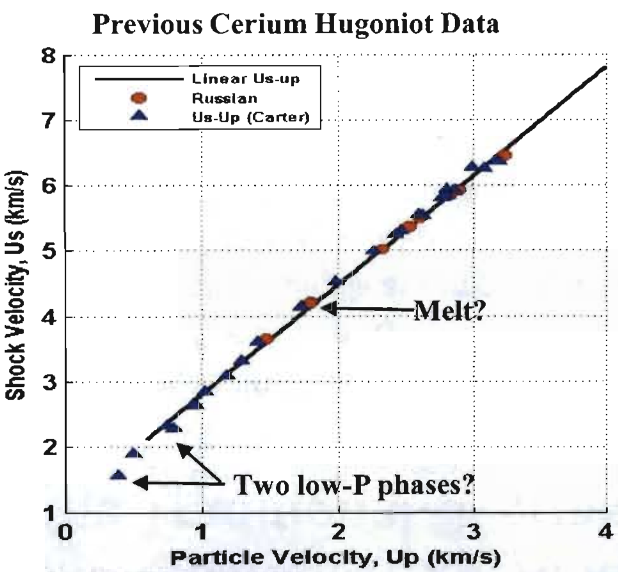


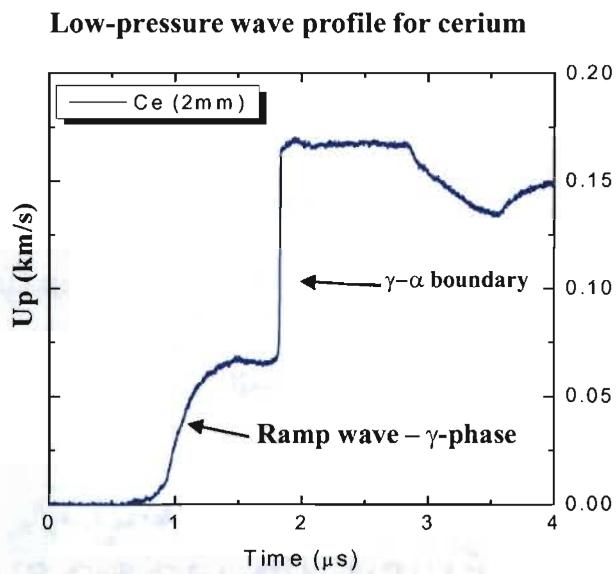
Multi-Slug Experiments (Top-view)

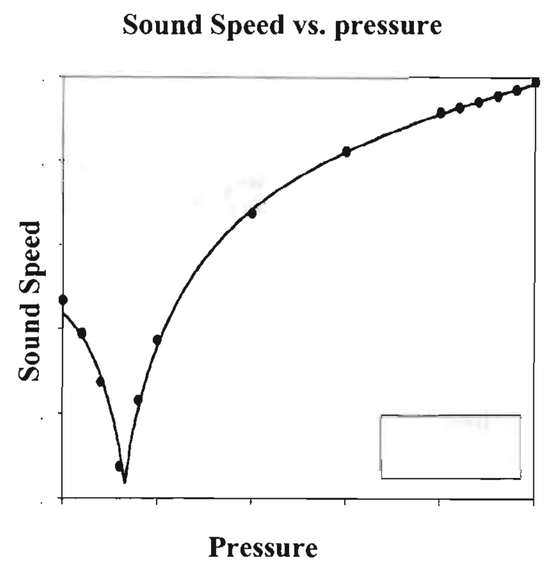


Limited Dynamic Data Exist for Cerium

- Wave profile data showed anomalous low-pressure behavior (Pavlovskii)
- High-pressure data (Carter 1970s) interpreted as revealing two solid phases and a 48 GPa melt. Zhernokletov reproduced high-pressure data but did not observe the high-pressure melt
- Preliminary low-pressure shock wave data obtain in 2001 (Hixson et al.) along with efforts to develop consistent manufacturing process for samples (Lashely, Cooley)
- Some spall and shock wave data obtained between 2004-2006 (Cherne)

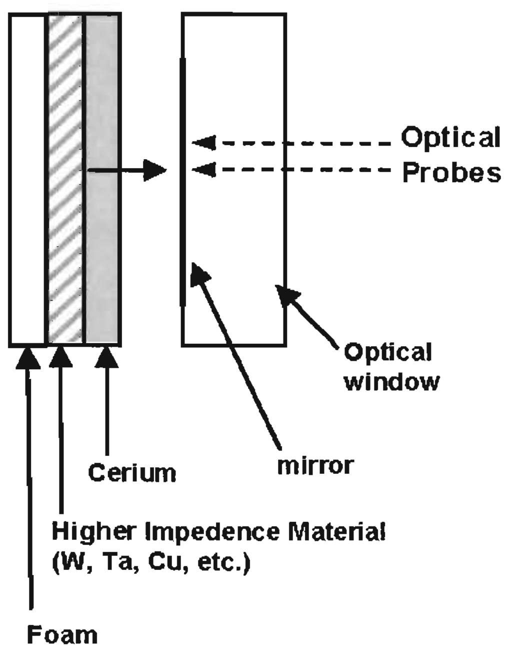






Experimental configuration: double-shock

Double-Shock Experiment



X-T Diagram