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Title:	Solid-Solid Phase Transition Kinetics
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Intended for:	Energetic Materials Workshop Institute for Shock Physics Imperial College London, UK

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Solid – Solid Phase Transition Kinetics

Laura Smilowitz and Bryan Henson
Chemistry Division, Los Alamos National Laboratory

We will give a joint presentation by video teleconference to the Institute for Shock Physics, Imperial College, London. The presentation will cover experimental work unifying the kinetics of the beta-delta phase transition in HMX. We will also present theoretical work concerning the temperature dependence of the rate of transformation, which let to the publication of the virtual melt model of solid –solid phase transformation in 2004.

Solid-solid phase transition kinetics

Laura Smilowitz, Bryan Henson,

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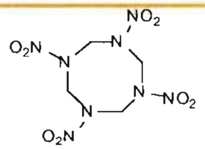
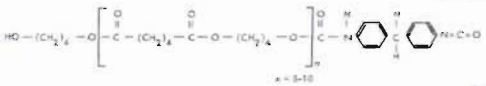
PBX 9501 - Plastic Bonded Explosive



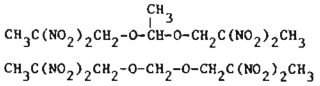
HMX (95%)

+



Estane (2.5%)

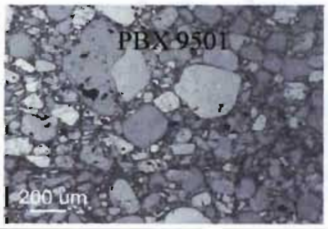
+



$$CH_3C(NO_2)_2CH_2\text{-}O\text{-}\overset{\displaystyle CH_3}{CH}\text{-}O\text{-}CH_2C(NO_2)_2CH_3$$

$$CH_3C(NO_2)_2CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2C(NO_2)_2CH_3$$

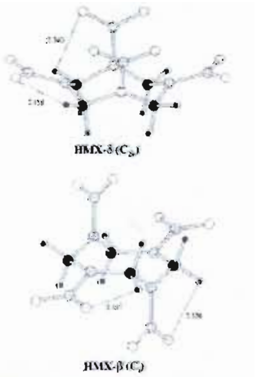
BDNPA/F (2.5%)



Outline

- Introduction to Thermal Explosion
  - Pre-ignition thermal decomposition
    - HMX Polymorphs
  - Transition to ignition
  - Ignition
  - Post-ignition burn propagation
- Experimental tools
  - SHG, Raman, DSC
  - comparison of observables
- Kinetics results
- Model of phase transition

HMX Polymorphs


HMX-δ (C_{2v})

HMX-β (C_i)

Optimized geometries of HMX in δ and β form.

Chakraborty et al. (2001) *J. Phys. Chem.* **A**

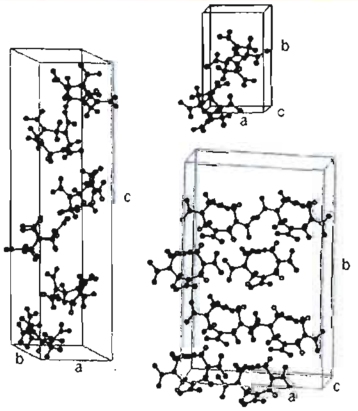


Figure 1. Unit cells for HMX polymorphs. Clockwise from top: β, α, and δ.

D. Bedrov et al. (2004) *Journal of Computer Aided Materials Design*, *8*, 77-85.

HMX Polymorphs: β,α,δ

Thermodynamics- which phase is stable, not how to get there
Kinetics- how to get there- needs to return thermodynamic phase diagram

Phase	β	α	δ
Sensitivity (drop hammer)	35cm	12cm	7cm
Volume change	0	β +4%	β +7%
Temperature stability	<105	103-160	>160

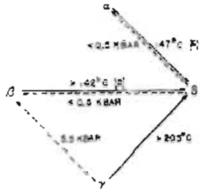


Figure 5. A summary of the temperature- and pressure-induced phase transitions of the α-, β-, γ-, and δ-polymorphs of HMX. The solid lines are transitions with slow heating (ref 1) and the dashed lines are transitions with pressure. (R) indicates reversibility with cooling.

Reference: LAMS-2652Studies on the polymorphs of HMX

Author: Cady, H.H., Smith, Louis C., LANL, Oct. 18, 1961.

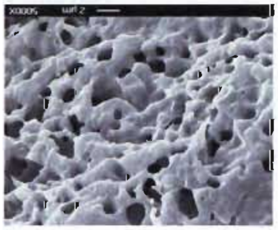
Reference: Brill, JCP 24 Aug 1978; vol.82, no.17, p.1912-1917

Chemical Kinetic Model for Decomposition of HMX

β-HMX $\longleftrightarrow$ δ-HMX
β-HMX + δ-HMX $\longleftrightarrow$ δ-HMX

L. Smilowitz (Los Alamos)

δ-HMX $\rightarrow$ $4CH_2O + 4N_2O$
δ-HMX $\rightarrow$ $4HCN + 2NO_2 + 2NO + 2H_2O$



R. Behrens (SNL)

$CH_2O + NO_2 \rightleftarrows HCO + HONO$

$HCO + NO_2 \longrightarrow CO + HONO$

$HCO + NO_2 \longrightarrow H + CO_2 + NO$

Focus on 1st step: solid-solid phase transition

- What we've done:
  - –Developed SHG probe as an instantaneous measure of the solid state fraction of beta and delta
  - –Used SHG in an imaging mode (SHG microscope) to make ansatz about mechanism of phase change: nucleation and growth
  - –Used integral SHG signal as measure of delta fraction
  - –Compare SHG observable to other observables: Raman, X-ray, DSC

- Results:

  A nucleation and growth model for the solid state phase transition with growth kinetics determined by thermodynamic properties of HMX and the nucleation kinetics empirically fit

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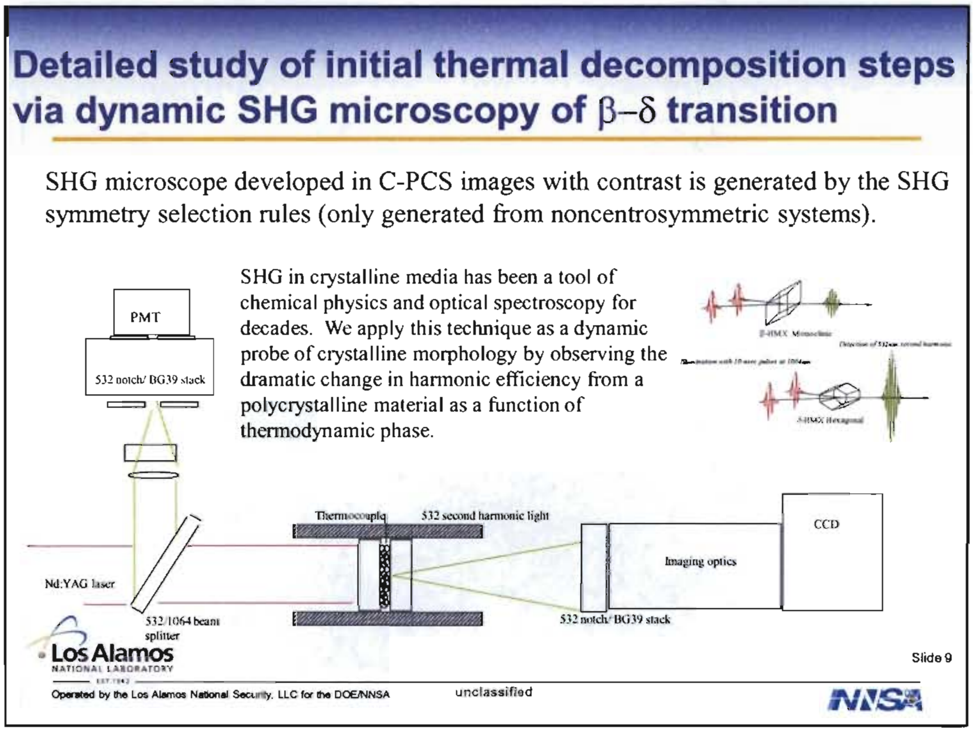
Experimental suite for solid-solid phase transition studies:

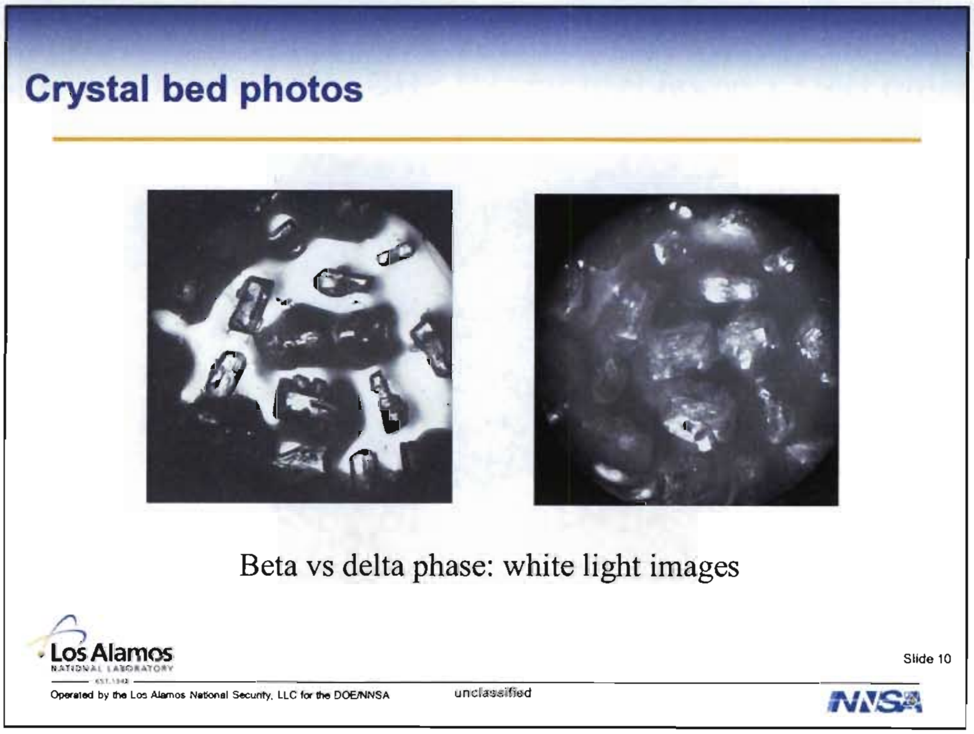
SHG microscope
Integrated SHG
Raman (in situ, post mortem)
FTIR (post mortem)
DSC (differential scanning calorimetry)
Temperature



Detailed study of initial thermal decomposition steps via dynamic SHG microscopy of β–δ transition

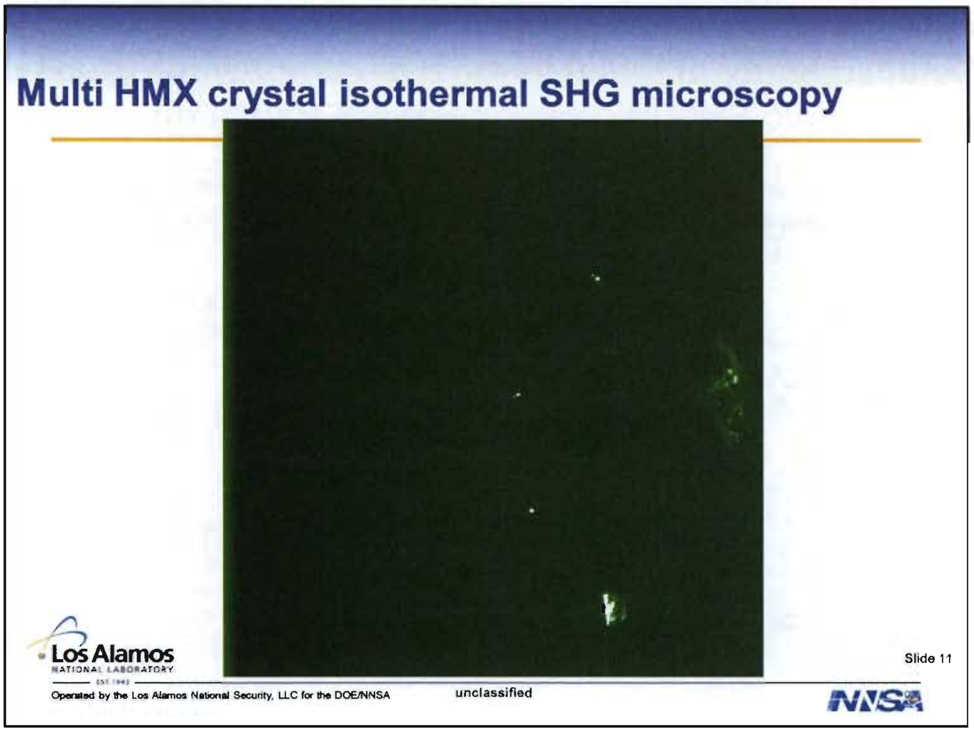
SHG microscope developed in C-PCS images with contrast is generated by the SHG symmetry selection rules (only generated from noncentrosymmetric systems).

SHG in crystalline media has been a tool of chemical physics and optical spectroscopy for decades. We apply this technique as a dynamic probe of crystalline morphology by observing the dramatic change in harmonic efficiency from a polycrystalline material as a function of thermodynamic phase.

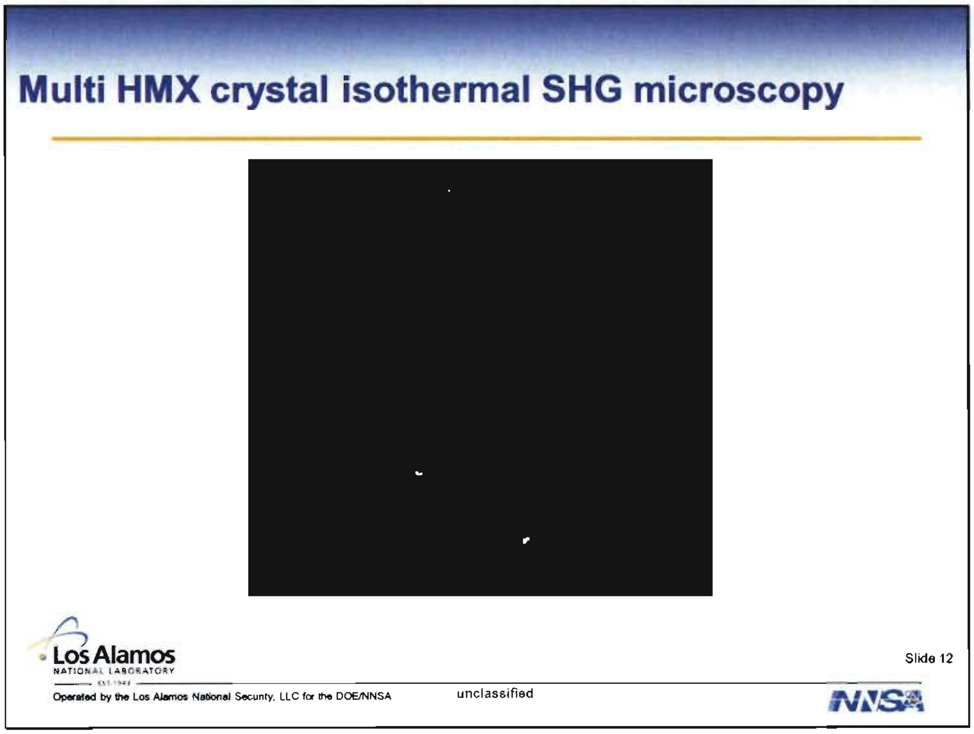


Crystal bed photos

Beta vs delta phase: white light images



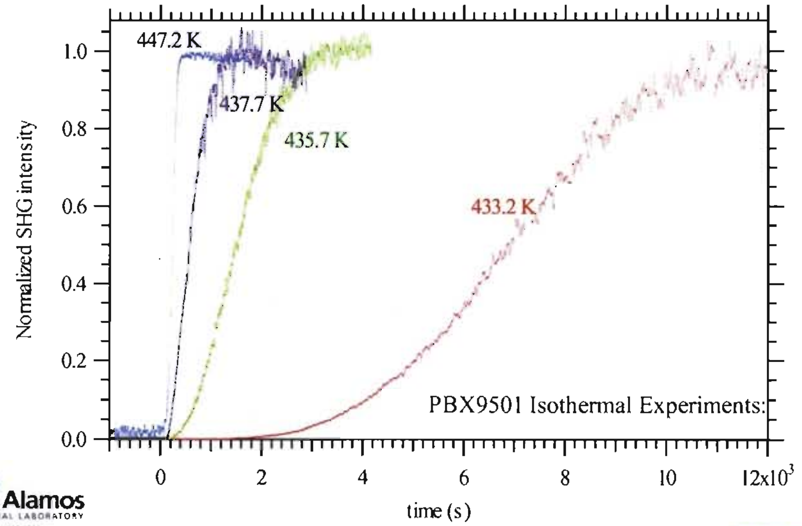
Multi HMX crystal isothermal SHG microscopy



Multi HMX crystal isothermal SHG microscopy

White light hot stage microscopy

Integrated SHG Results



Conclusions on comparison of observables

- All are in agreement, *assuming* that the observable probes a representative volume element
- Relative advantages/disadvantages of each:
  - SHG- sensitivity, but it's a relative measure
  - Raman- lose sensitivity when do spatial integration, but can distinguish non-centrosymmetric phases. Hard to use as an absolute measure (baseline flourescence, change in optical properties)
  - DSC- not an integral measure, so less sensitive and rate dependent, but best for use as an absolute measure. There is a minimum conversion rate needed for observation (dependent on baseline thermal stability)

Smilowitz, L.; Henson, B. F.; Romero, J. J., Intercomparison of Calorimetry, Raman Spectroscopy, and Second Harmonic Generation Applied to Solid-Solid Phase Transitions. *JOURNAL OF PHYSICAL CHEMISTRY A* **2009**, 113, (35), 9650-9657.

Kinetic Model Summary

Rate controlled by an activation energy which is equivalent to the heat of fusion.

Balance of forward and reverse growth rates defines equilibrium temperature (cusp in half-time curve)

2nd order kinetics- accelератory behavior due to dependence on interface between $\beta-\delta$

2^{nd} order kinetic component yields a 1^{st} order thermodynamic transition

virtual melt state- activation energy = heat of fusion,

but phase transition is occurring at $T < T_m$

Theory by V. Levitas based on the lowering of the melt temperature for a region of local tension at the interface – solves many previously reported conundra

Levitas, V. I.; Henson, B. F.; Smilowitz, L. B.; Asay, B. W., Solid-solid phase transformation via virtual melting significantly below the melting temperature. *Physical Review Letters* **2004**, 11, (92), 235702-1

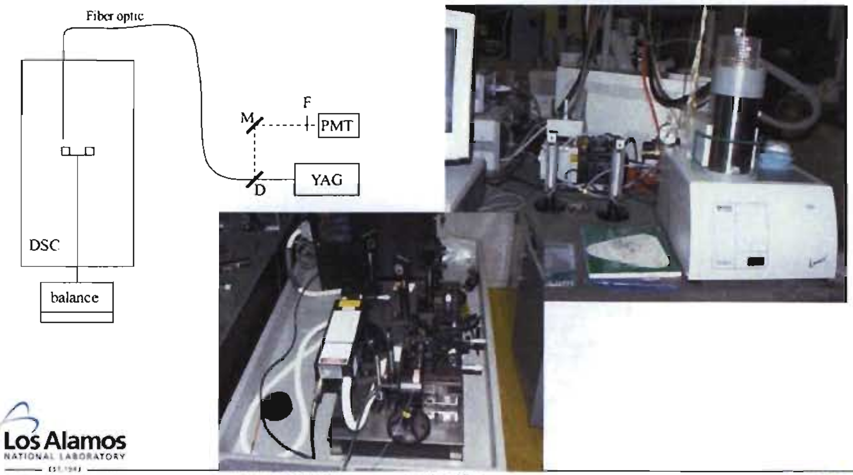
Levitas, V. I.; Smilowitz, L. B.; Henson, B. F.; Asay, B. W., Solid-solid phase transformation via internal stress-induced virtual melting: Additional confirmations. *Applied Physics Letters* **2005**, 87, (19), 1-3

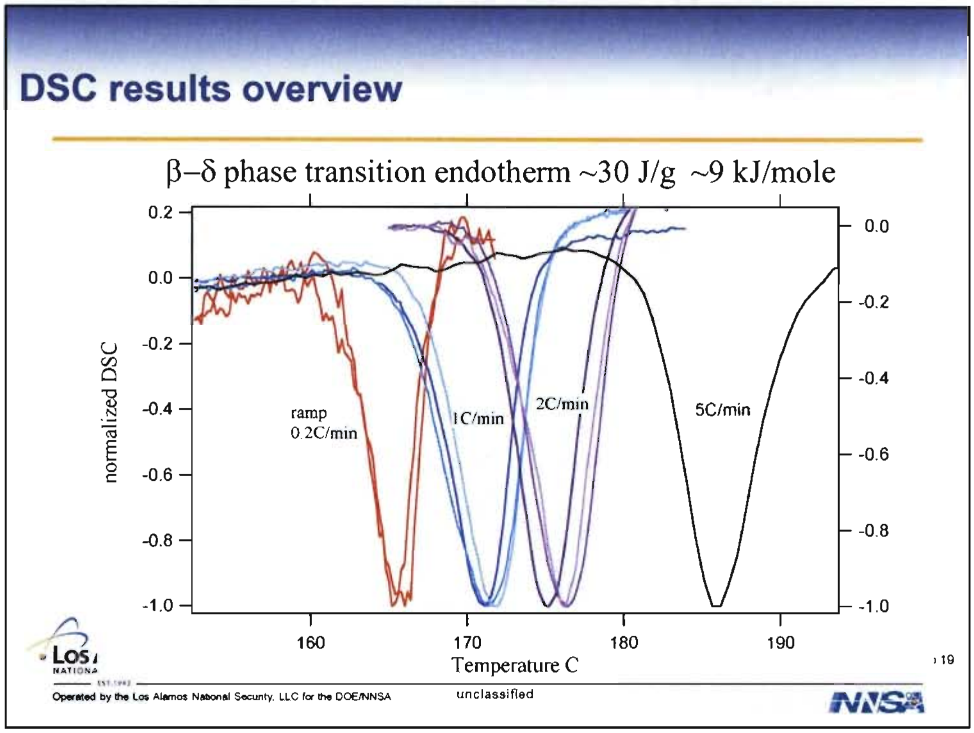
Comparison of observables

- There are inherent difficulties in observing solid to solid phase transitions- solids are heterogeneous and optically opaque, hindering observation.
- There have been confusing and contradictory reports with different kinetics reported depending on the observable- SHG vs Raman vs DSC vs X-ray vs dilatometry
- The goal of this study was to validate SHG as a probe of δ fraction, and understand the contradictions between observables

Experiment: DSC/TGA/MS: with SHG

Goal- couple existing diagnostics to probe solid state lattice, solid to gas dynamics, and gas phase products simultaneously





DSC results overview

β–δ phase transition endotherm ~30 J/g ~9 kJ/mole

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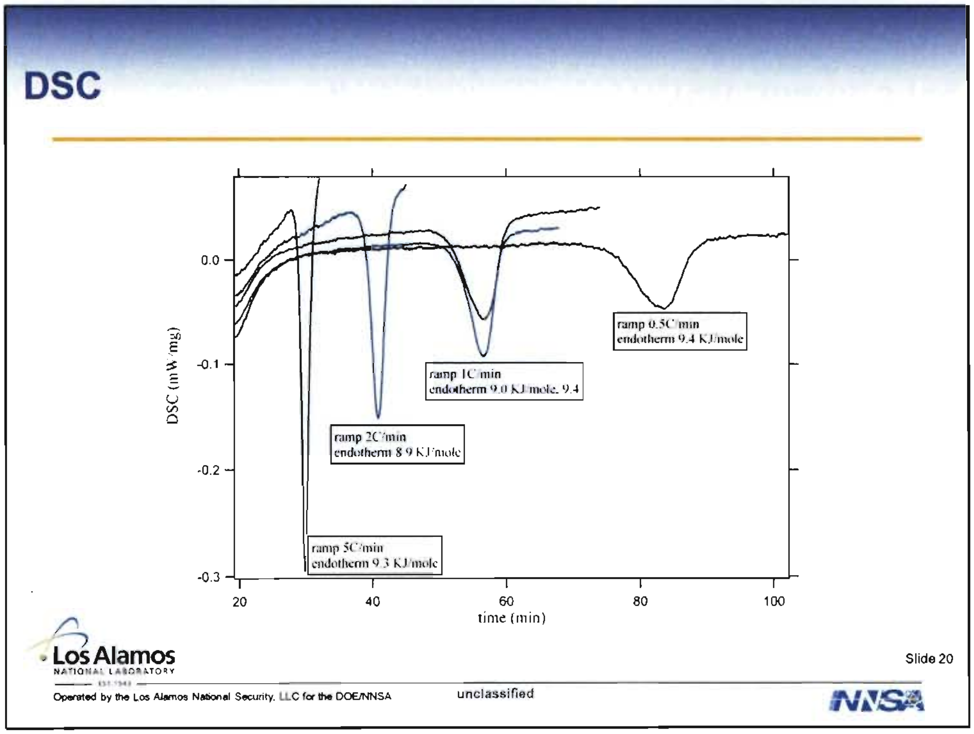

DSC

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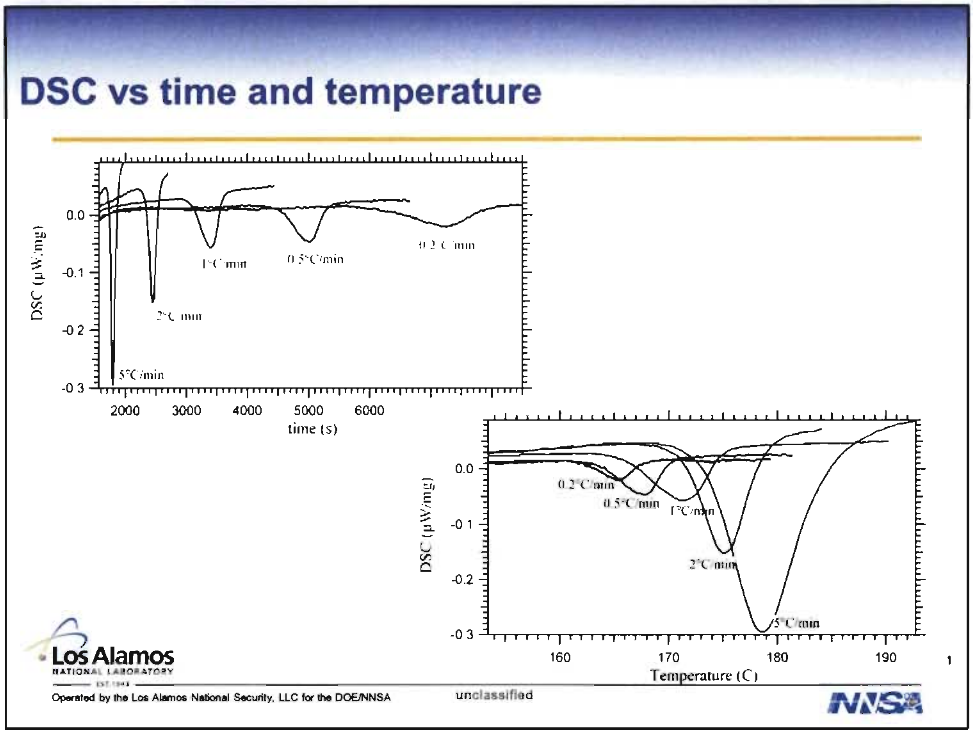

DSC vs time and temperature

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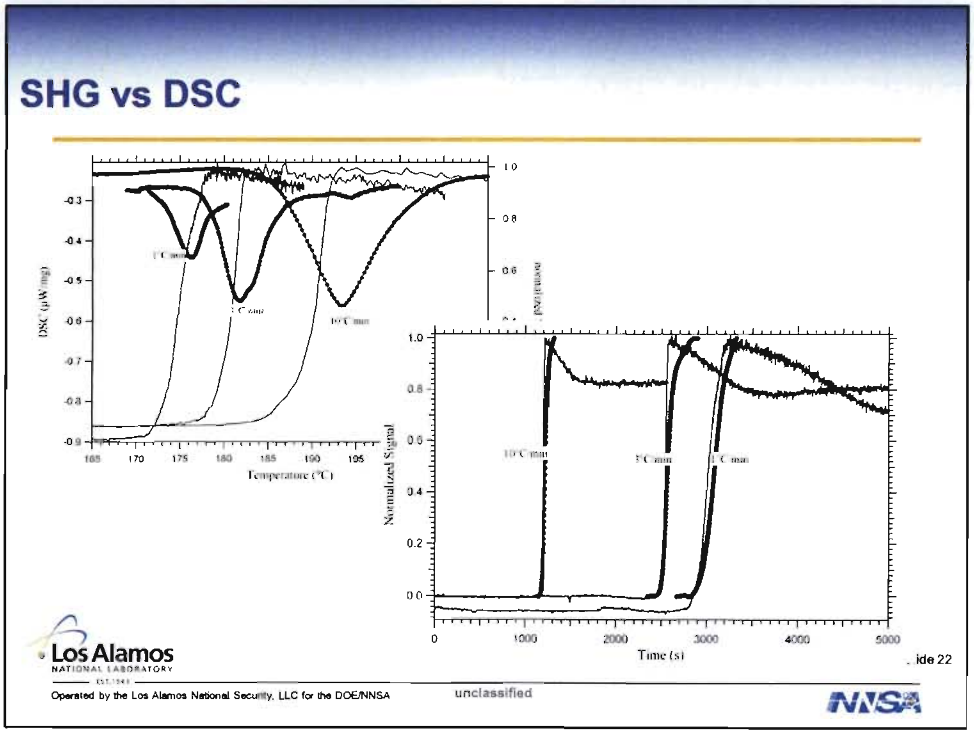

SHG vs DSC

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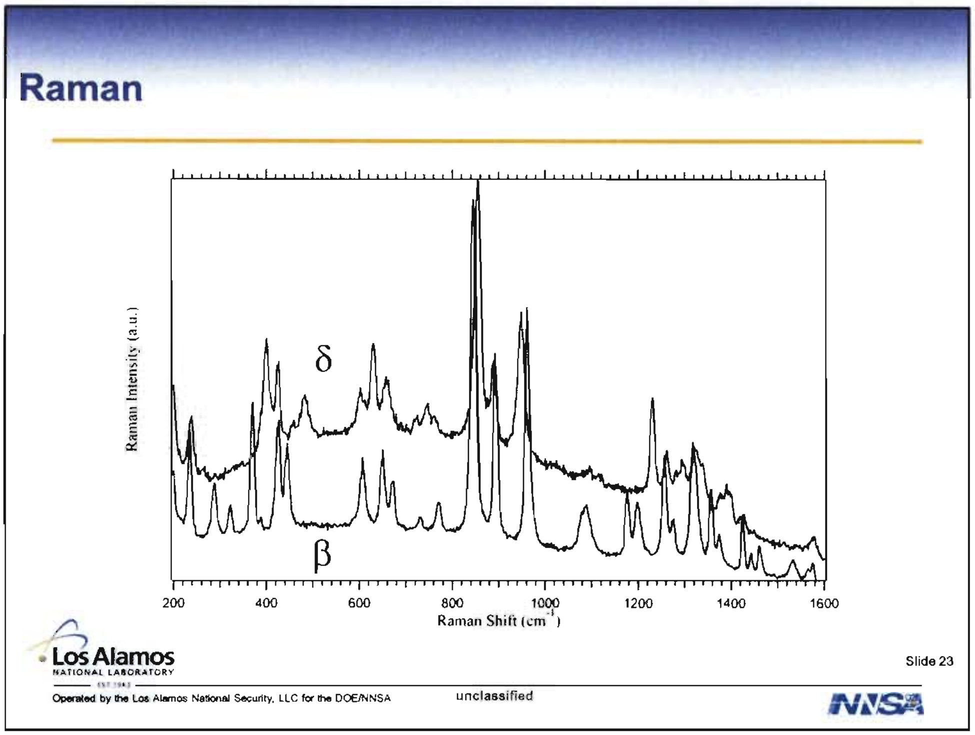

Raman

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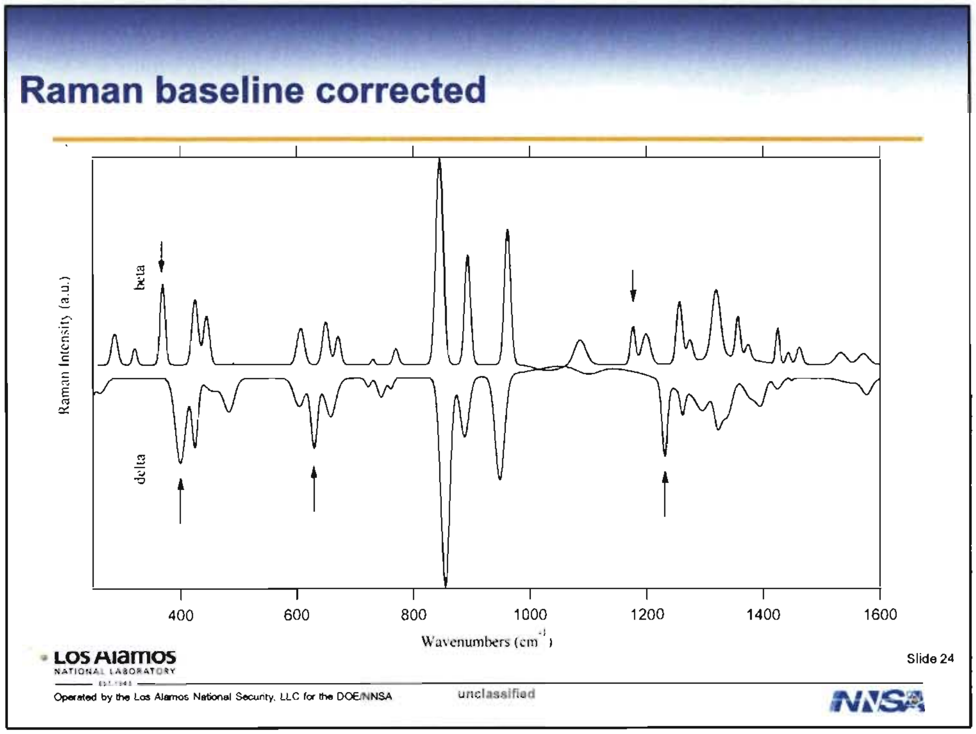

Raman baseline corrected

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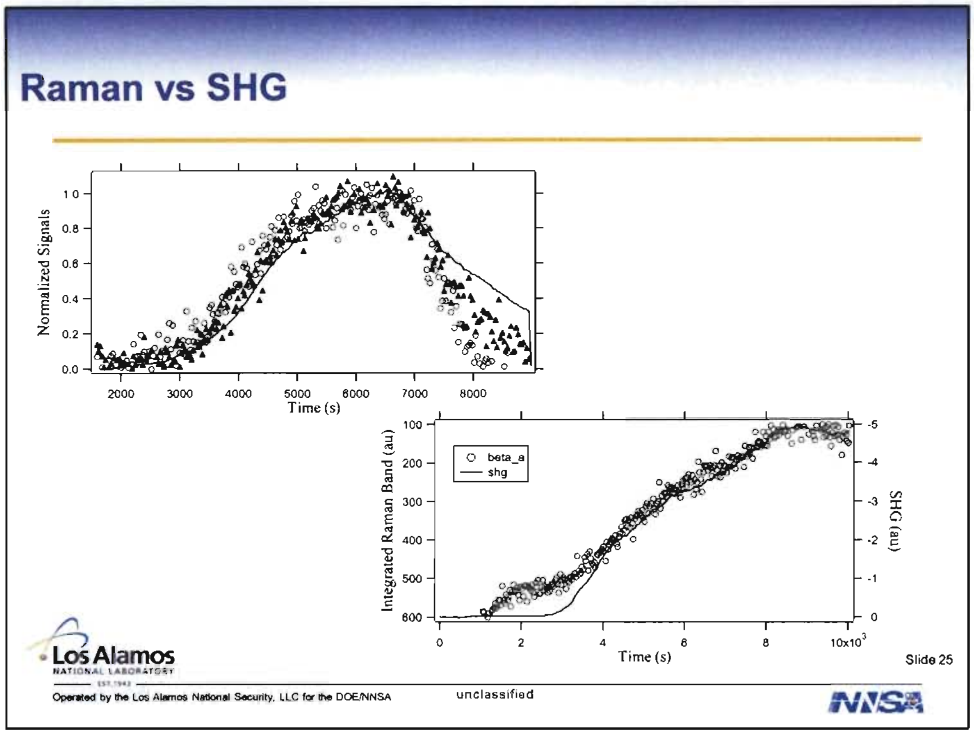

Raman vs SHG

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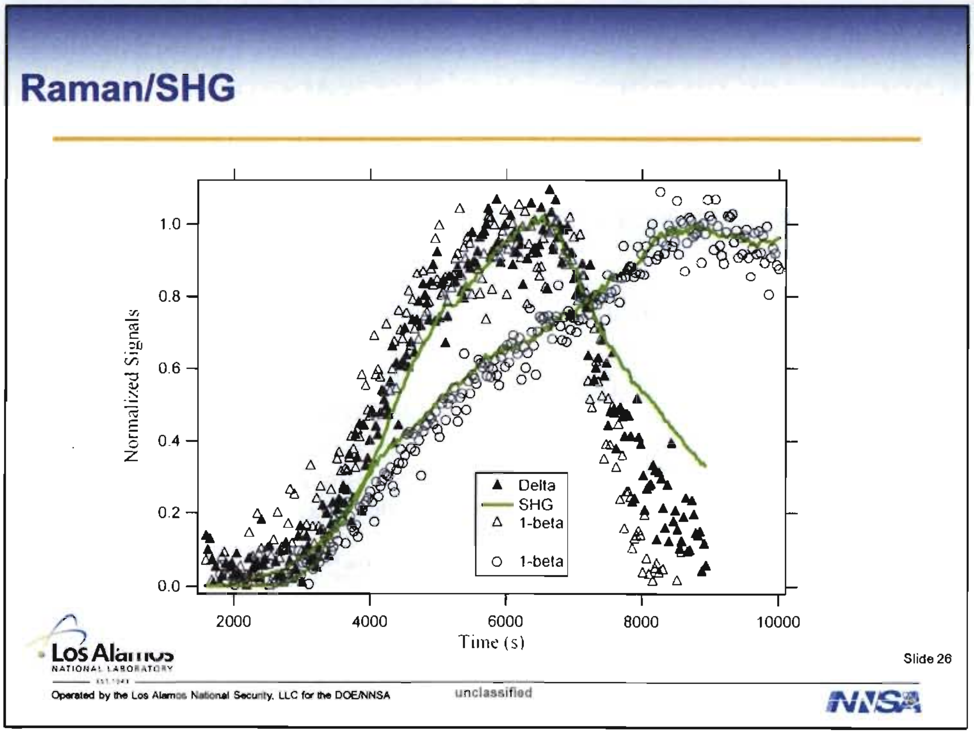

Raman/SHG

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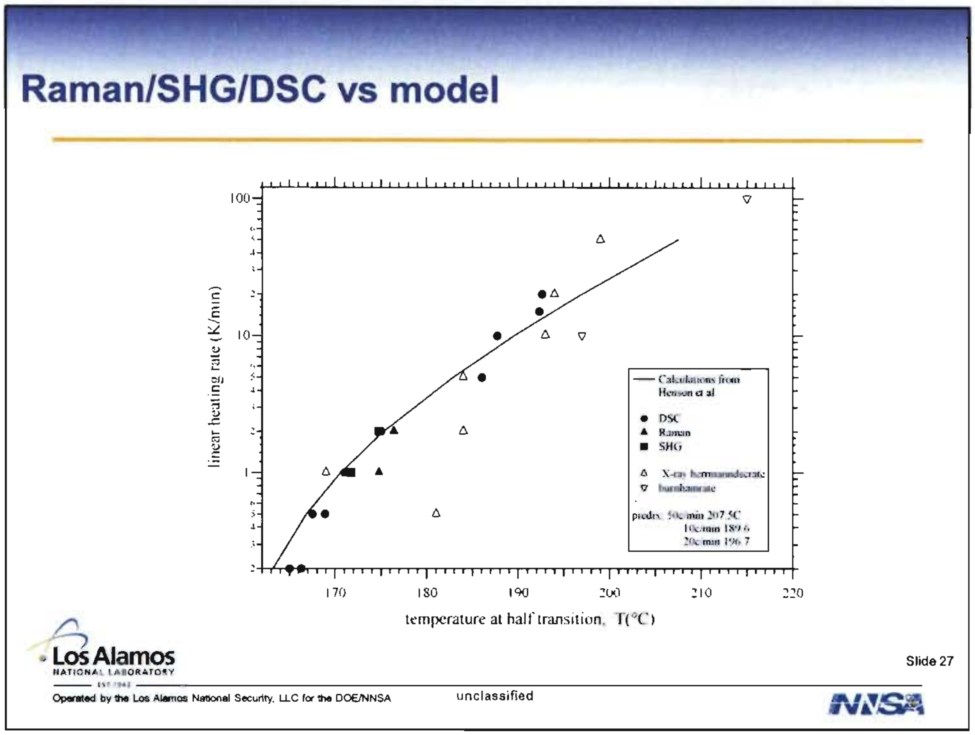

Raman/SHG/DSC vs model

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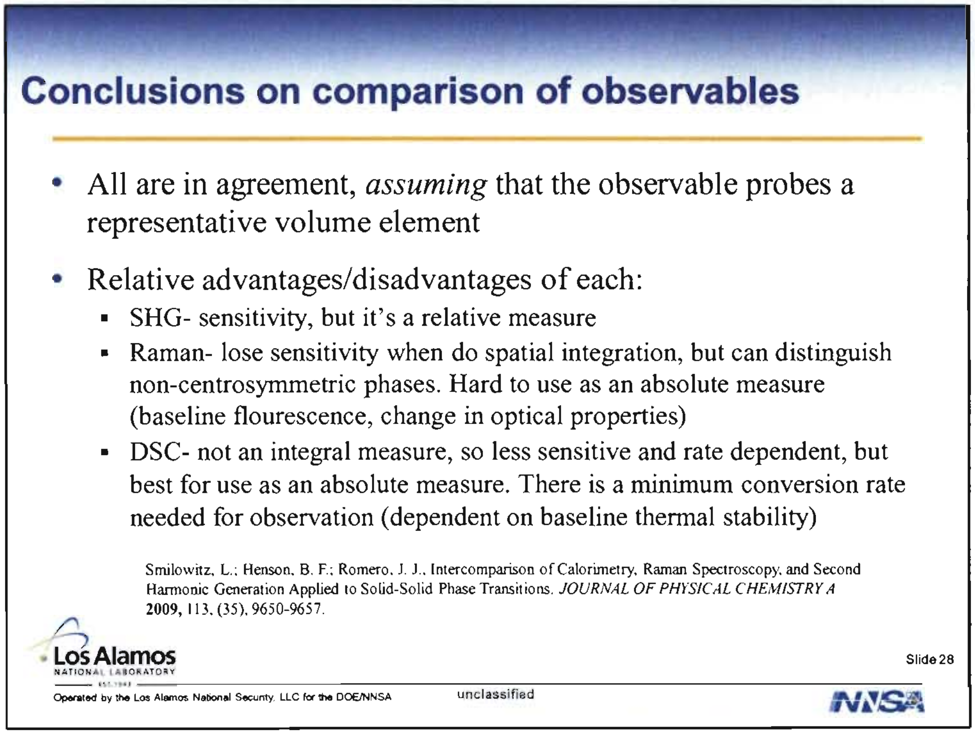

Conclusions on comparison of observables

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Smilowitz, L.; Henson, B. F.; Romero, J. J., Intercomparison of Calorimetry, Raman Spectroscopy, and Second Harmonic Generation Applied to Solid-Solid Phase Transitions. *JOURNAL OF PHYSICAL CHEMISTRY A* **2009,** 113, (35), 9650-9657.

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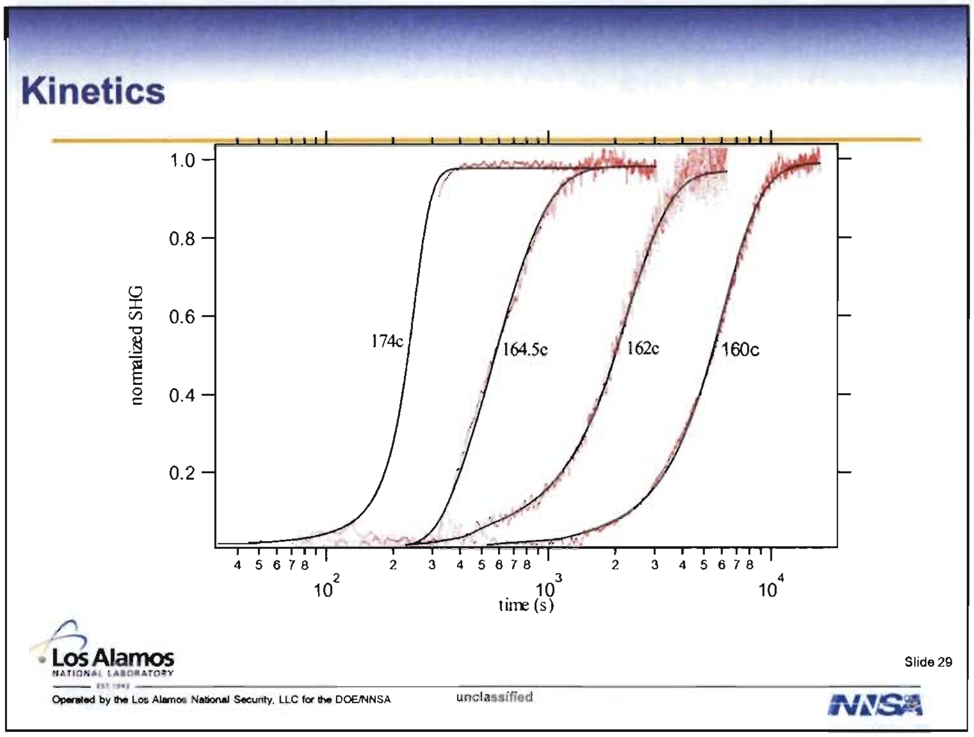

Kinetics

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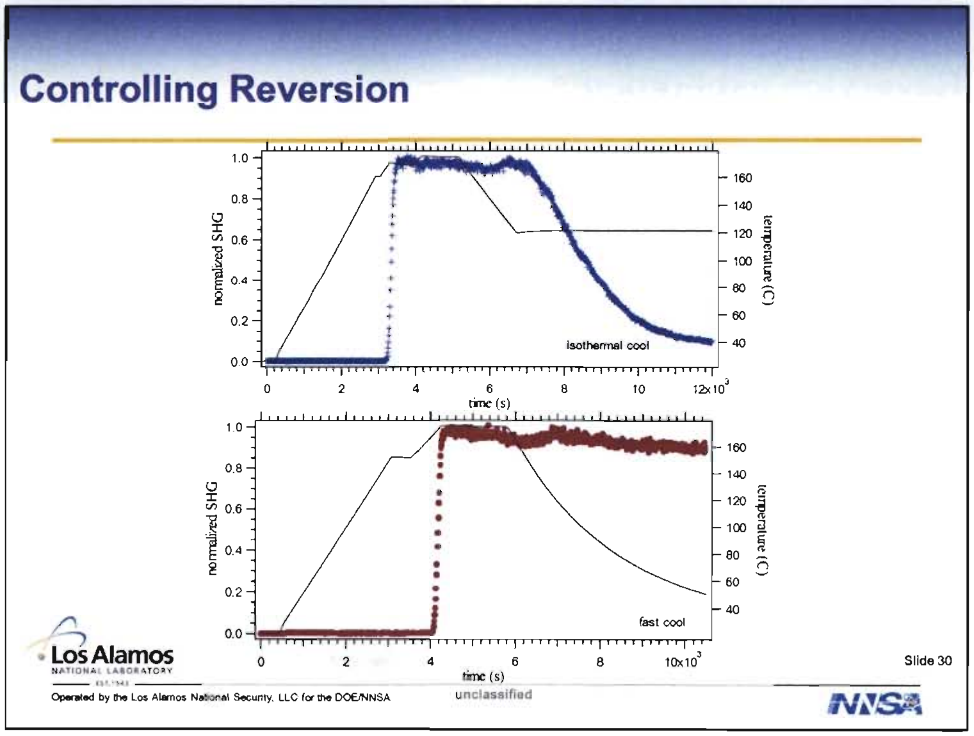

Controlling Reversion

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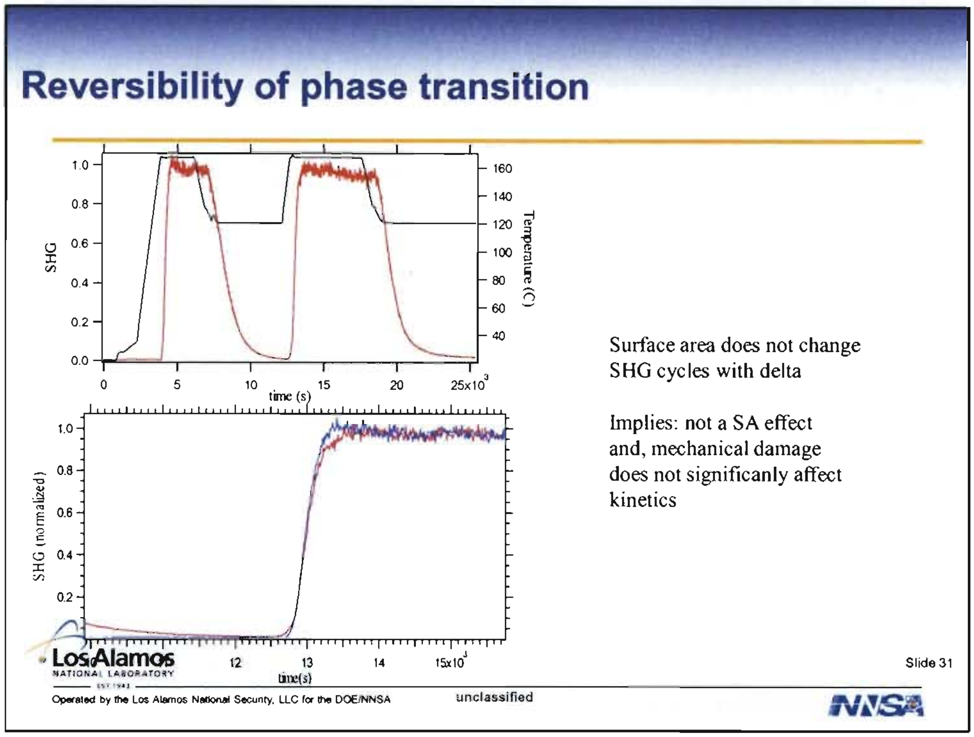

Reversibility of phase transition

Surface area does not change
SHG cycles with delta

Implies: not a SA effect
and, mechanical damage
does not significanly affect
kinetics

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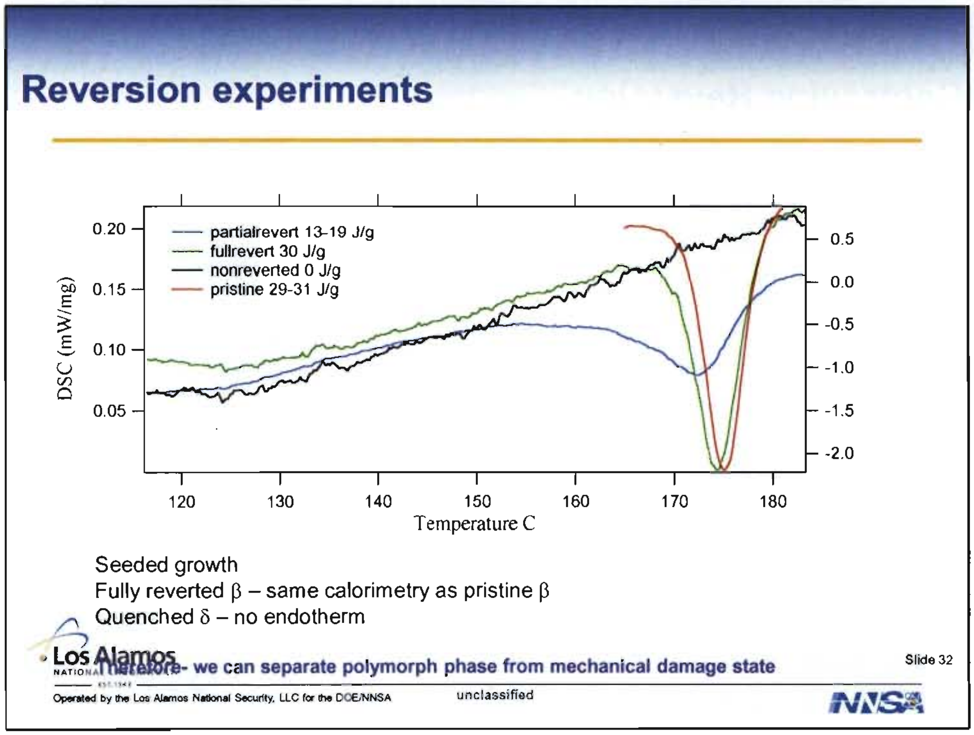

Reversion experiments

Seeded growth
Fully reverted β – same calorimetry as pristine β
Quenched δ – no endotherm

Therefore- we can separate polymorph phase from mechanical damage state

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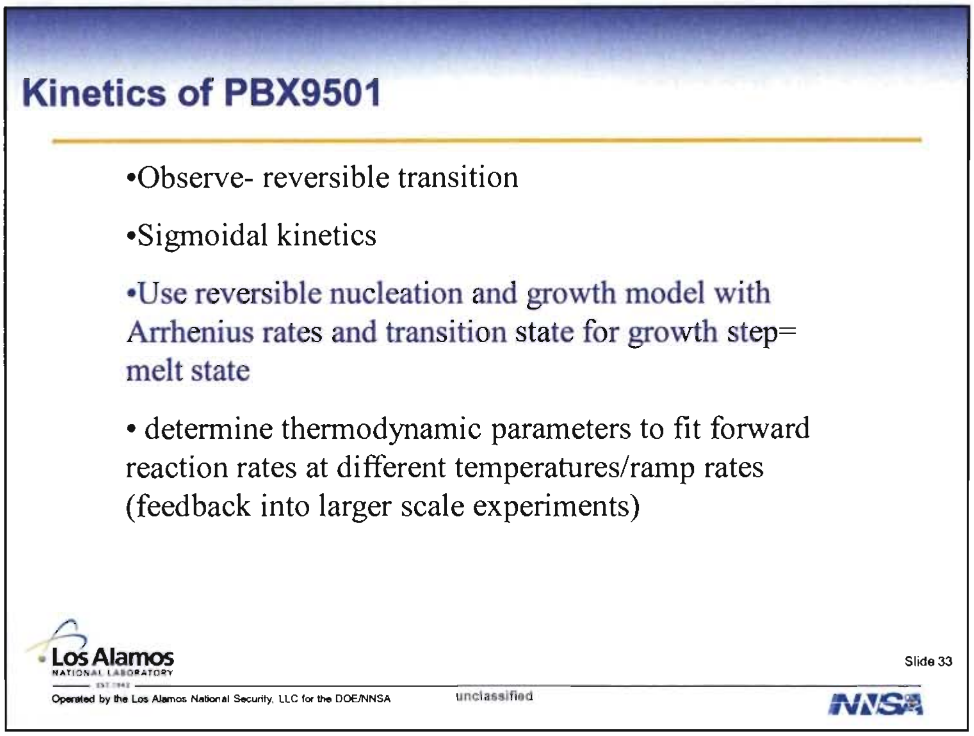

Kinetics of PBX9501

- Observe- reversible transition
- Sigmoidal kinetics
- Use reversible nucleation and growth model with Arrhenius rates and transition state for growth step= melt state
- determine thermodynamic parameters to fit forward reaction rates at different temperatures/ramp rates (feedback into larger scale experiments)

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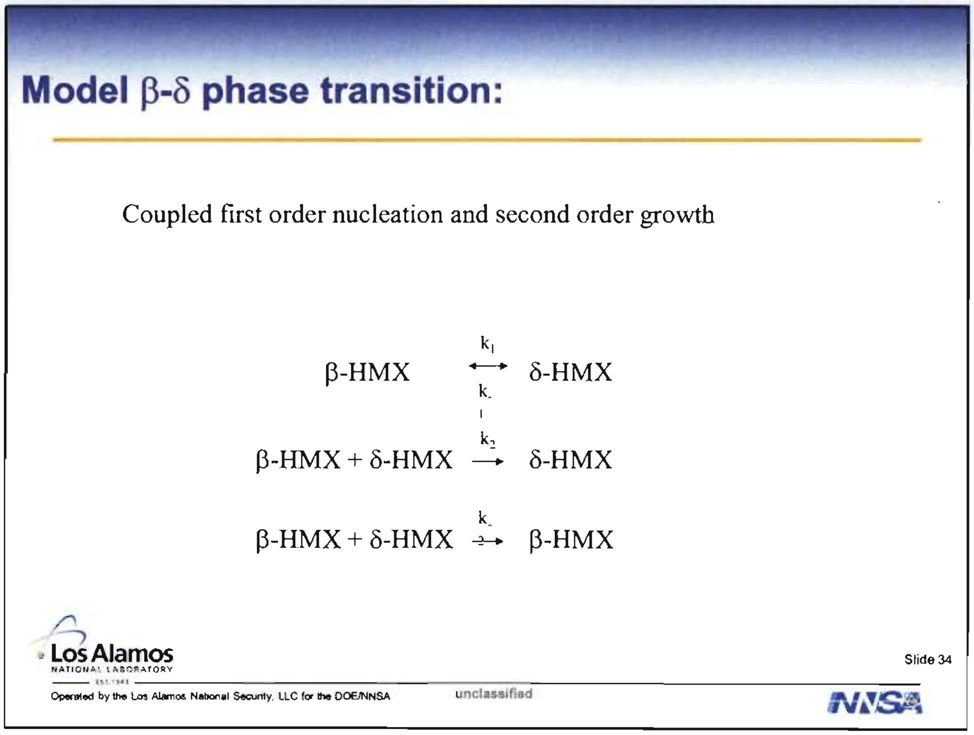

Model β-δ phase transition:

Coupled first order nucleation and second order growth

$$\beta\text{-HMX} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \xrightarrow{k_2} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \xrightarrow{k_{-2}} \beta\text{-HMX}$$

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Transition kinetics

$$\beta\text{-HMX} \overset{k_1}{\underset{k_{-1}}{\longleftrightarrow}} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \overset{k_2}{\underset{k_{-2}}{\longleftrightarrow}} \delta\text{-HMX}$$

Nucleation and growth rate law:

$$d\delta/dt = k_1\beta + k_2\,\beta{*}\delta - k_{-1}\,\delta - k_{-2}\,\beta{*}\delta$$

Where: $k_i(T) = kT/h \exp((T\Delta S^* - \Delta H^*)/RT)$

$= kT/h \exp(-\Delta G^*/RT)$

the rate is determined by the thermodynamic parameters of the transition state

Transition state= melt state

$\Delta G^* = \Delta G_{fusion}$

Virtual Melt

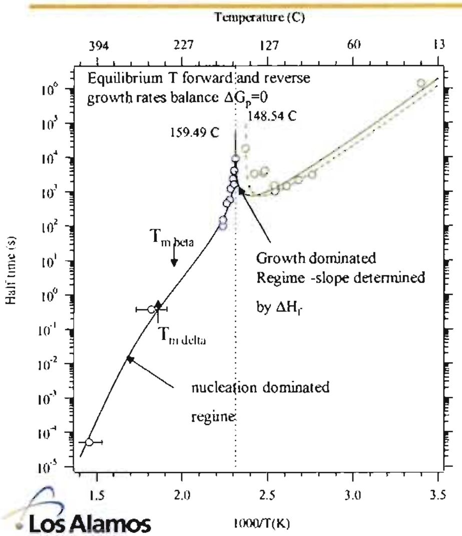
Valery I. Levitas,*,† Bryan F. Henson,‡ Laura B. Smilowitz,‡ and Blaine W. Asay‡

J. Phys. Chem. B **2006,** *110,* 10105-10119

We theoretically predict a new phenomenon, namely, that a solid-solid phase transformation (PT) with a large transformation strain can occur via internal stress-induced virtual melting along the interface at temperatures significantly (more than 100 K) below the melting temperature. We show that the energy of elastic stresses, induced by transformation strain, increases the driving force for melting and reduces the melting temperature. Immediately after melting, stresses relax and the unstable melt solidifies. Fast solidification in a thin layer leads to nanoscale cracking which does not affect the thermodynamics or kinetics of the solidsolid transformation. Thus, virtual melting represents a new mechanism of solid-solid PT, stress relaxation, and loss of coherence at a moving solid-solid interface. …**Sixteen theoretical predictions** are in qualitative and quantitative agreement with experiments conducted on the PTs in the energetic crystal HMX. In particular, (a) the energy of internal stresses is sufficient to reduce the melting temperature from 551 to 430 K for the ä phase during the *â* f ä PT and from 520 to 400 K for the *â* phase during the ä f *â* PT; (b) predicted activation energies for direct and reverse PTs coincide with corresponding melting energies of the *â* and ä phases and with the experimental values; (c) the temperaturendependence of the rate constant is determined by the heat of fusion, for both direct and reverse PTs; results b and c are obtained both for overall kinetics and for interface propagation; (d) considerable nanocracking, homogeneously distributed in the transformed material, accompanies the PT, as predicted by theory; (e) the nanocracking does not change the PT thermodynamics or kinetics appreciably for the first and the second PT*â* T ä cycles, as predicted by theory; (f) *â* T ä PTs start at a very small driving force (in contrast to all known solid-solid transformations with large transformation strain), that is, elastic energy and athermal interface friction must be negligible; (g) *â* f R and R f *â* PTs, which are thermodynamically possible in the temperature range 382.4 < *ô* < 430 K and below 382.4 K, respectively, do not occur.

- Levitas, V. I.; Henson, B. F.; Smilowitz, L. B.; Asay, B. W., Solid-solid phase transformation via virtual melting significantly below the melting temperature. *Physical Review Letters* **2004,** 11, (92), 235702-1
- Levitas, V. I.; Smilowitz, L. B.; Henson, B. F.; Asay, B. W., Solid-solid phase transformation via internal stress-induced virtual melting: Additional confirmations. *Applied Physics Letters* **2005,** 87, (19), 1-3

β-δ phase transition: Temperature extrapolation



Detailed study of phase transition kinetics involving SHG probe yielded "virtual melt" phase transition model

Ref- Levitas, Smilowitz, Henson, Asay, **PRL, JUN 11 2004**

$$t = \frac{2\left(Arctan\left(\frac{-(k_1+k_{-1})}{\sqrt{B}}\right) \pm Arctan\left(\frac{((k_1+k_{-1})+\beta_a(k_{-2}-k_2))}{\sqrt{B}}\right)\right)}{\sqrt{B}}$$

Plot of the transition 'half life' as a function of temperature

Kinetic data show slowing near the stability temperature of delta HMX and reflect regimes of temperature where the growth or nucleation process dominate the conversion rate.

β- δ phase transition: Parameters

Nucleation

Use temperature dependence to constrain first order component of mechanism due to lack of a known activation state

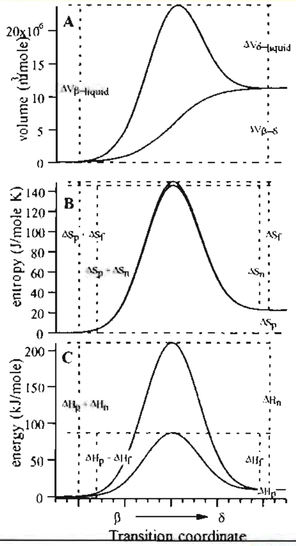
Data sets in agreement with literature values

(fit 2 parameters: E1, S1, V1)

Growth

Based on observations of Cady et al. and theoretical prediction: Assume that the growth mechanism is via melt and recrystallization. Therefore, energy of activation for growth step based on heat of fusion and β–δ energy difference

(thermodynamics determine E2, S2, V2, E-2, S-2, V-2, E-1, S-1)



$$\frac{\partial x}{\partial t} = k_1(1-x) - k_{-1}x + \beta_o(k_2 - k_{-2})x(1-x)$$

First order kinetics

$$\frac{\partial x}{\partial t} = k_1(1-x) - k_{-1}x$$

$$x_e = \frac{k_1}{k_1 + k_{-1}}$$

$$\frac{k_1}{k_1 + k_{-1}} = \frac{\exp\left(\frac{-\Delta G_{phase}}{RT}\right)}{\left(1 + \exp\left(\frac{-\Delta G_{phase}}{RT}\right)\right)}$$

$$x_e = \frac{\exp\left(\frac{-G_\delta}{RT}\right)}{\exp\left(\frac{-G_\delta}{RT}\right) + \exp\left(\frac{-G_\beta}{RT}\right)}$$

Second order thermodynamics

Second order kinetics

$$\frac{\partial x}{\partial t} = \beta_o(k_2 - k_{-2})x(1-x)$$

$$\beta_o(k_2 - k_{-2}) = 0$$

$$k_2(T) - k_{-2}(T) = \frac{k_B T}{h} Q \exp\left(\frac{-\Delta G_{fusion}}{RT}\right)\left(1 - \exp\left(\frac{-\Delta G_{phase}}{RT}\right)\right)$$

$$\Delta G_{phase} = \Delta H_{phase} - T\Delta S_{phase} = 0$$

$$T = T_{phase}$$

First order thermodynamics

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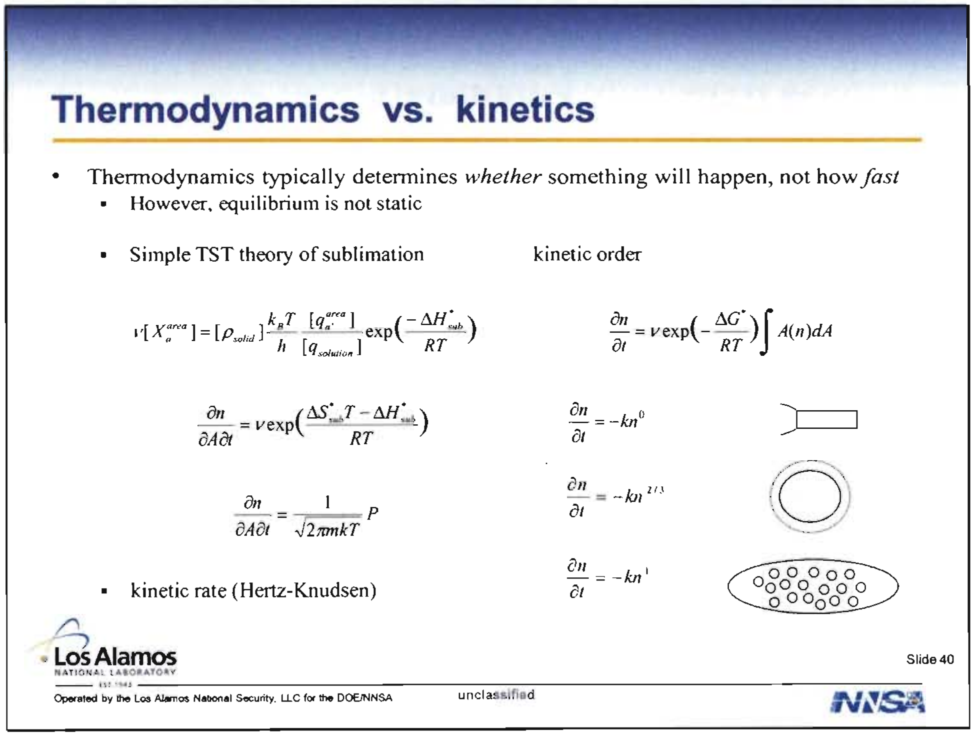

Thermodynamics vs. kinetics

- Thermodynamics typically determines *whether* something will happen, not how *fast*
  - However, equilibrium is not static
  - Simple TST theory of sublimation

kinetic order

$$\nu[X_a^{area}] = [\rho_{solid}]\frac{k_B T}{h}\frac{[q_{a^*}^{area}]}{[q_{solution}]}\exp\left(\frac{-\Delta H^*_{sub}}{RT}\right)$$

$$\frac{\partial n}{\partial A \partial t} = \nu \exp\left(\frac{\Delta S^*_{sub} T - \Delta H^*_{sub}}{RT}\right)$$

$$\frac{\partial n}{\partial A \partial t} = \frac{1}{\sqrt{2\pi m k T}} P$$

  - kinetic rate (Hertz-Knudsen)

$$\frac{\partial n}{\partial t} = \nu \exp\left(-\frac{\Delta G^*}{RT}\right)\int A(n)dA$$

$$\frac{\partial n}{\partial t} = -kn^0$$

$$\frac{\partial n}{\partial t} = -kn^{2/3}$$

$$\frac{\partial n}{\partial t} = -kn^1$$

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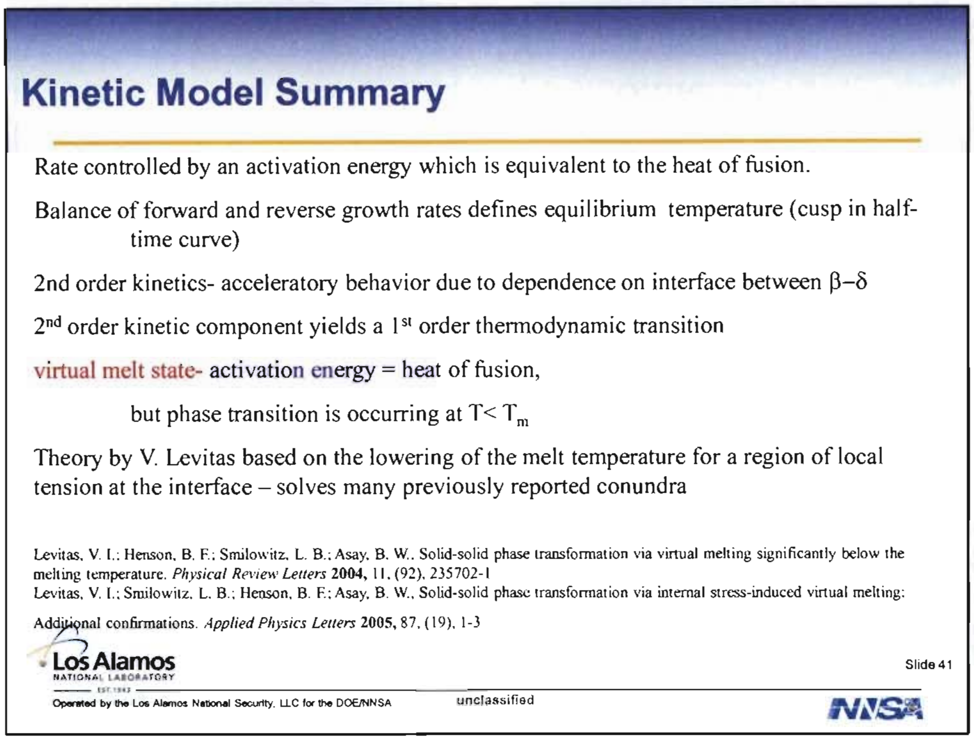


Kinetic Model Summary

Rate controlled by an activation energy which is equivalent to the heat of fusion.

Balance of forward and reverse growth rates defines equilibrium temperature (cusp in half-time curve)

2nd order kinetics- acceleratory behavior due to dependence on interface between β–δ

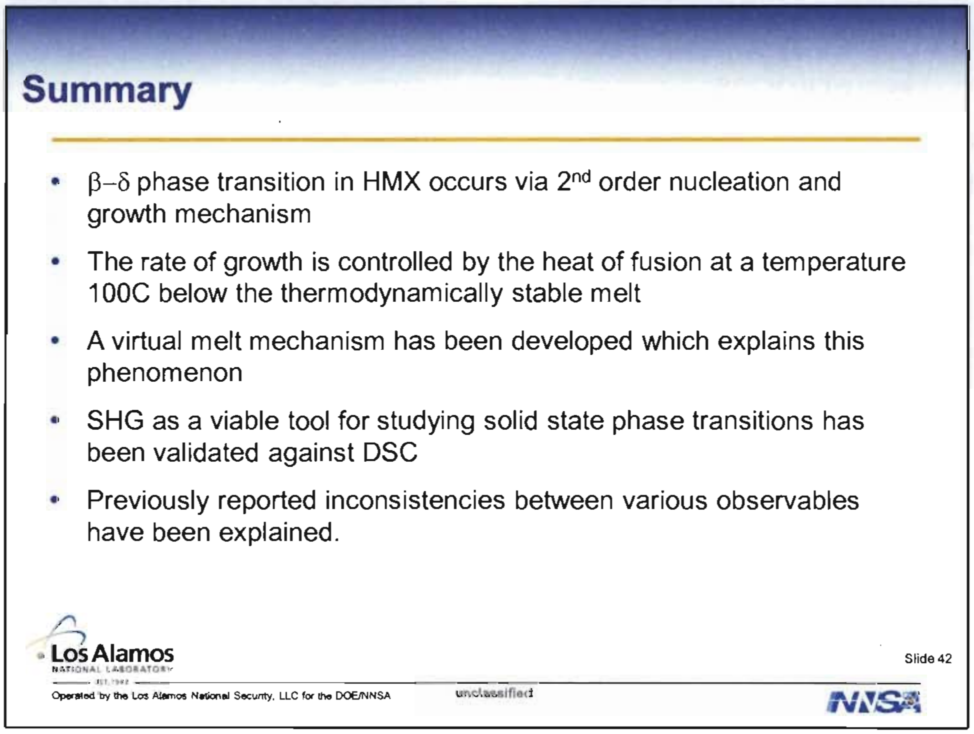
2nd order kinetic component yields a 1st order thermodynamic transition

virtual melt state- activation energy = heat of fusion,

but phase transition is occurring at $T < T_m$

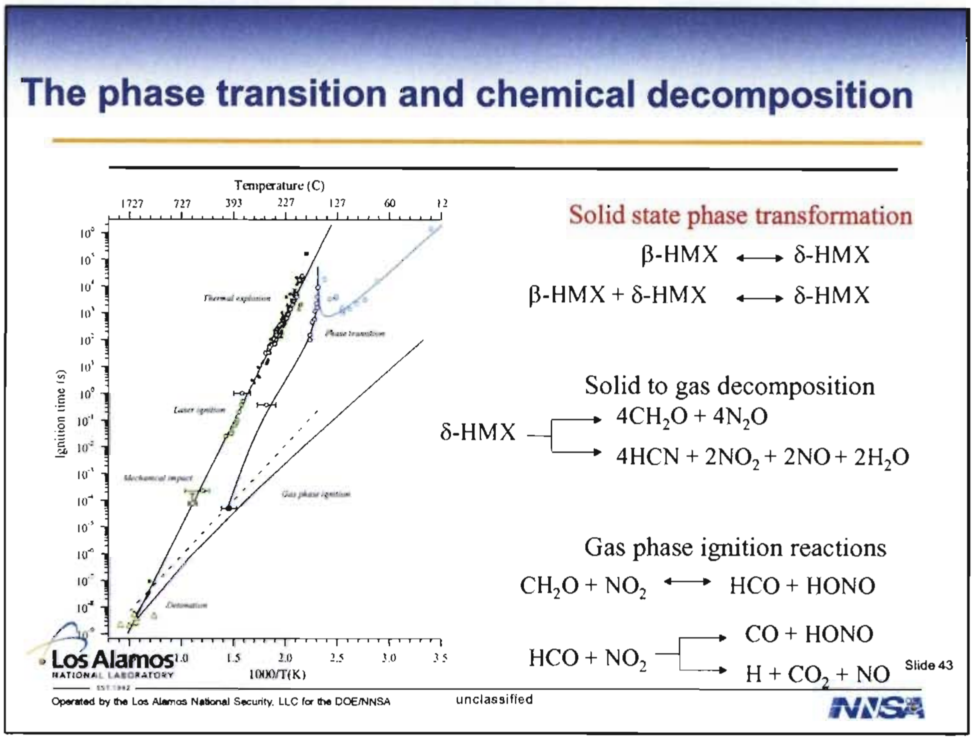
Theory by V. Levitas based on the lowering of the melt temperature for a region of local tension at the interface – solves many previously reported conundra

Levitas, V. I.; Henson, B. F.; Smilowitz, L. B.; Asay, B. W., Solid-solid phase transformation via virtual melting significantly below the melting temperature. *Physical Review Letters* **2004**, 11, (92), 235702-1
Levitas, V. I.; Smilowitz, L. B.; Henson, B. F.; Asay, B. W., Solid-solid phase transformation via internal stress-induced virtual melting: Additional confirmations. *Applied Physics Letters* **2005**, 87, (19), 1-3



Summary

- β–δ phase transition in HMX occurs via 2nd order nucleation and growth mechanism
- The rate of growth is controlled by the heat of fusion at a temperature 100C below the thermodynamically stable melt
- A virtual melt mechanism has been developed which explains this phenomenon
- SHG as a viable tool for studying solid state phase transitions has been validated against DSC
- Previously reported inconsistencies between various observables have been explained.



The phase transition and chemical decomposition

Solid state phase transformation

β-HMX ⟷ δ-HMX

β-HMX + δ-HMX ⟷ δ-HMX

Solid to gas decomposition

$\delta\text{-HMX} \rightarrow 4CH_2O + 4N_2O$

$\delta\text{-HMX} \rightarrow 4HCN + 2NO_2 + 2NO + 2H_2O$

Gas phase ignition reactions

$CH_2O + NO_2 \leftrightarrow HCO + HONO$

$HCO + NO_2 \rightarrow CO + HONO$

$HCO + NO_2 \rightarrow H + CO_2 + NO$

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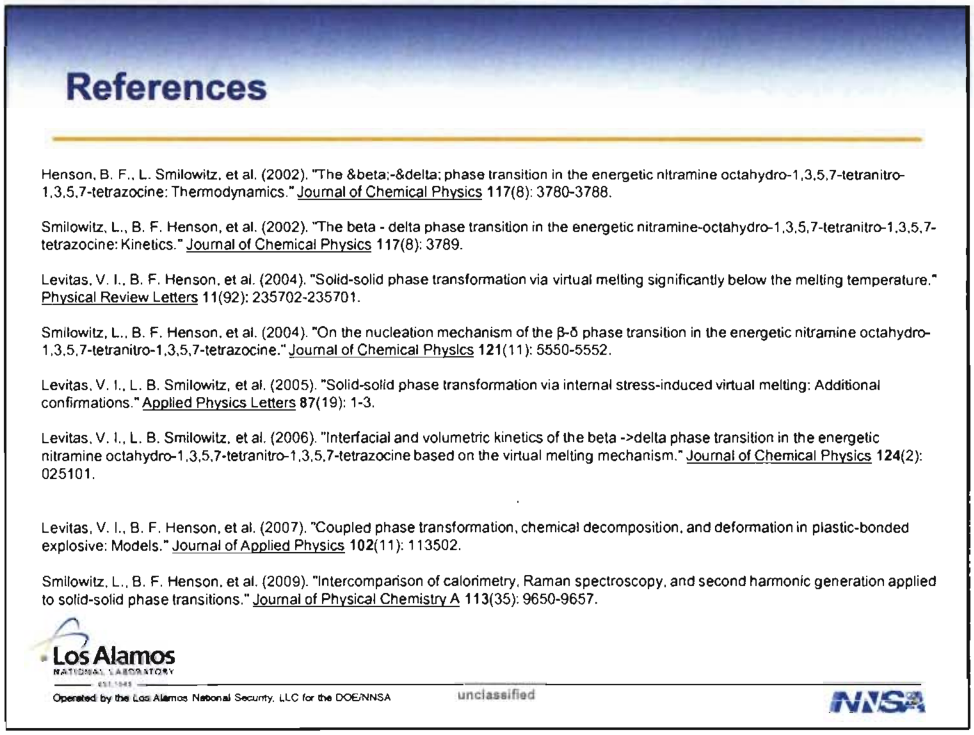

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