

A low-angle photograph looking up into a dense tropical forest. Sunlight filters through the thick canopy of green leaves and palm fronds, creating a dappled light effect. The image serves as a background for the text.

Liquid and Glass Structures and Physical Properties

Nucleation Processes in Liquids and Glasses



# ***Liquid and Glasses - Structures and Properties -***



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**Department of Physics &  
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**Funding**



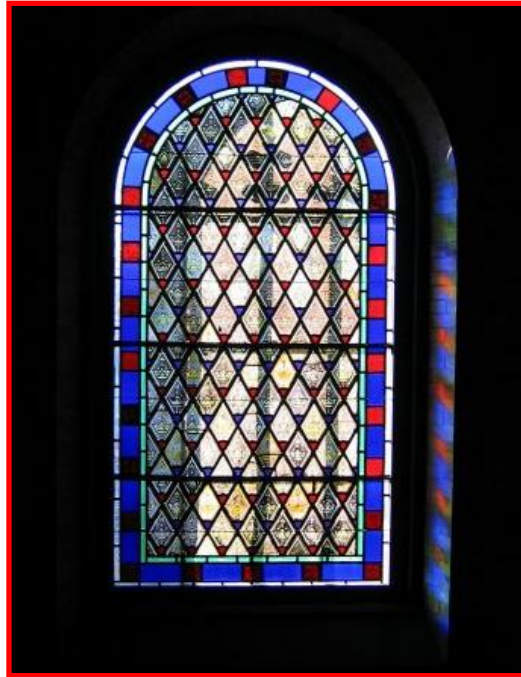
**National Science Foundation**  
WHERE DISCOVERIES BEGIN



# ***Outline of Talk***

- Introduction
- Containerless processing for liquids
  - Experimental techniques
  - Thermophysical property measurements
  - Diffraction studies
- Selected Case Studies
  - Liquid/liquid phase transition in silicon?
  - Ordering in amorphous metals
    - In glasses
    - In liquids
    - Icosahedral ordering and the glass transition
  - Anomalies in thermophysical properties of transition metal liquids - possible liquid phase transition
- Conclusions

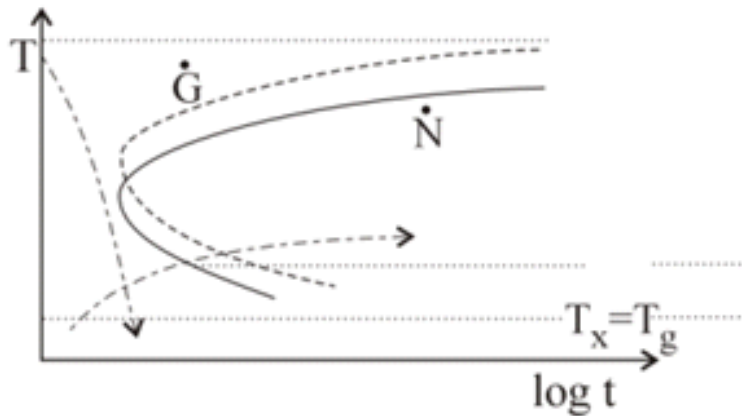
# *Examples of Glasses*



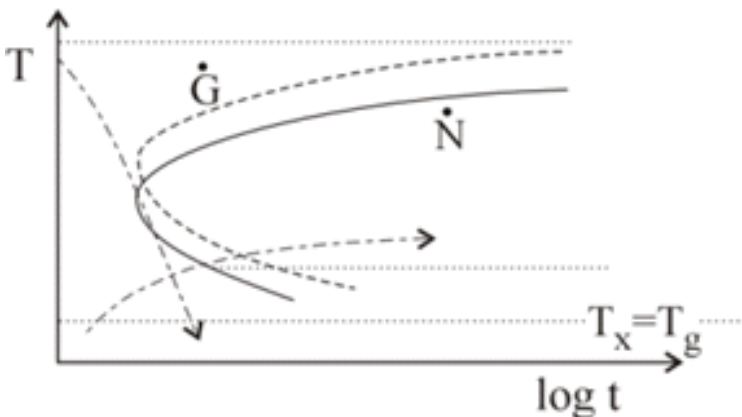


# Glass Formation

Nucleation Control:

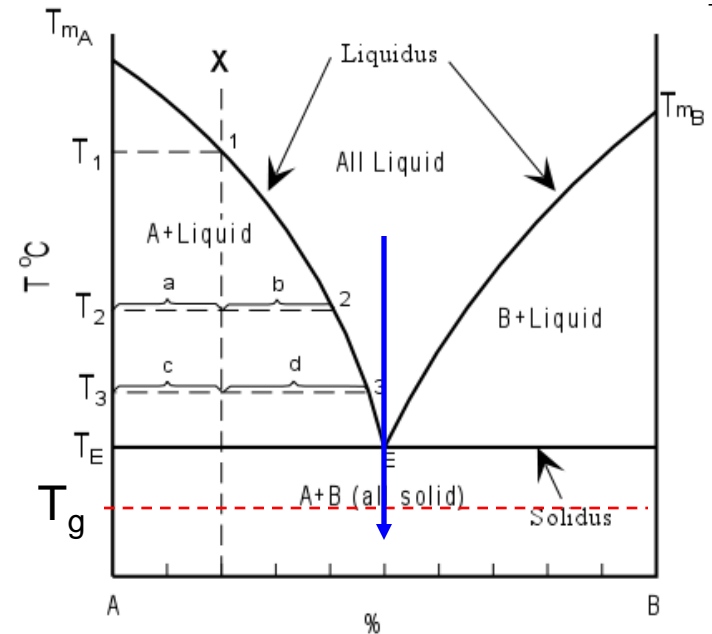


Growth Control:



J. H. Perepezko and R. J. Herbert,  
JOM, TMS (March, 2002)

**Deep Eutectic (Turnbull, 1969)**



$$I = A^* \exp \left( - \frac{16\pi}{3k_B T} \frac{\sigma^3}{\Delta g^2} \right)$$

- $A^*$  is function of atomic mobility, very low below  $T_g$
- Minimize temperature range between  $T_e$  and  $T_g$  – minimize driving free energy ( $\Delta g$ )

**Other Criteria - None Perfect  
Liquid Structure Important**

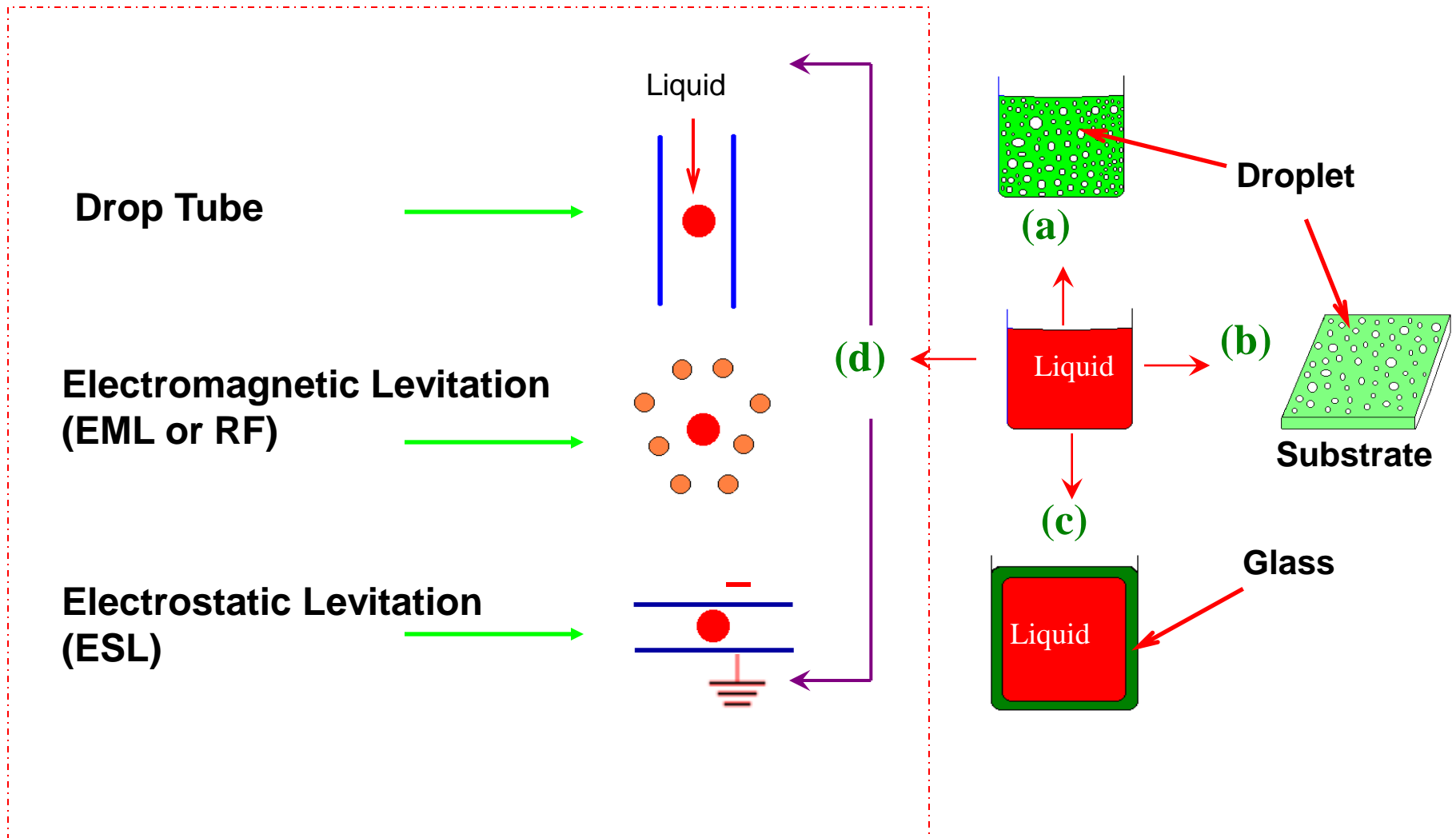
# ***Studies of Liquids***

## ***(Mostly Metallic)***

- Glasses traditionally formed when liquid is cooled sufficiently fast to avoid **significant** crystallization
- Studies of liquid structures and physical properties yield information on crystallization and other phase transitions
- Containers tend to limit amount of “supercooling”
  - heterogeneous nucleation (second lecture)
- Containerless processing for liquids
  - Experimental techniques
  - Thermophysical property measurements
  - Diffraction studies

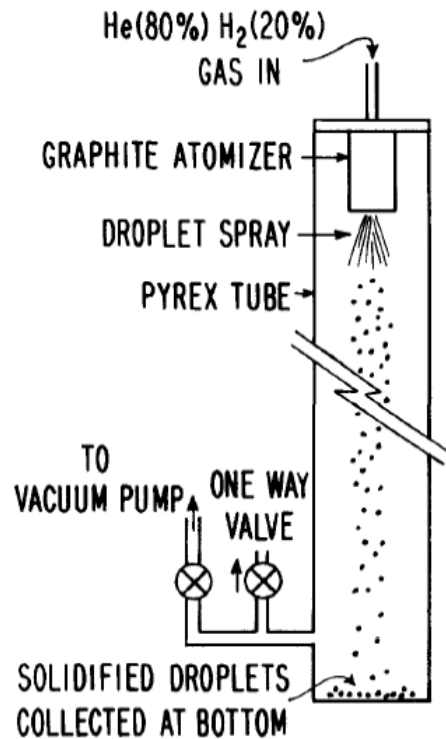


# Supercooling Techniques

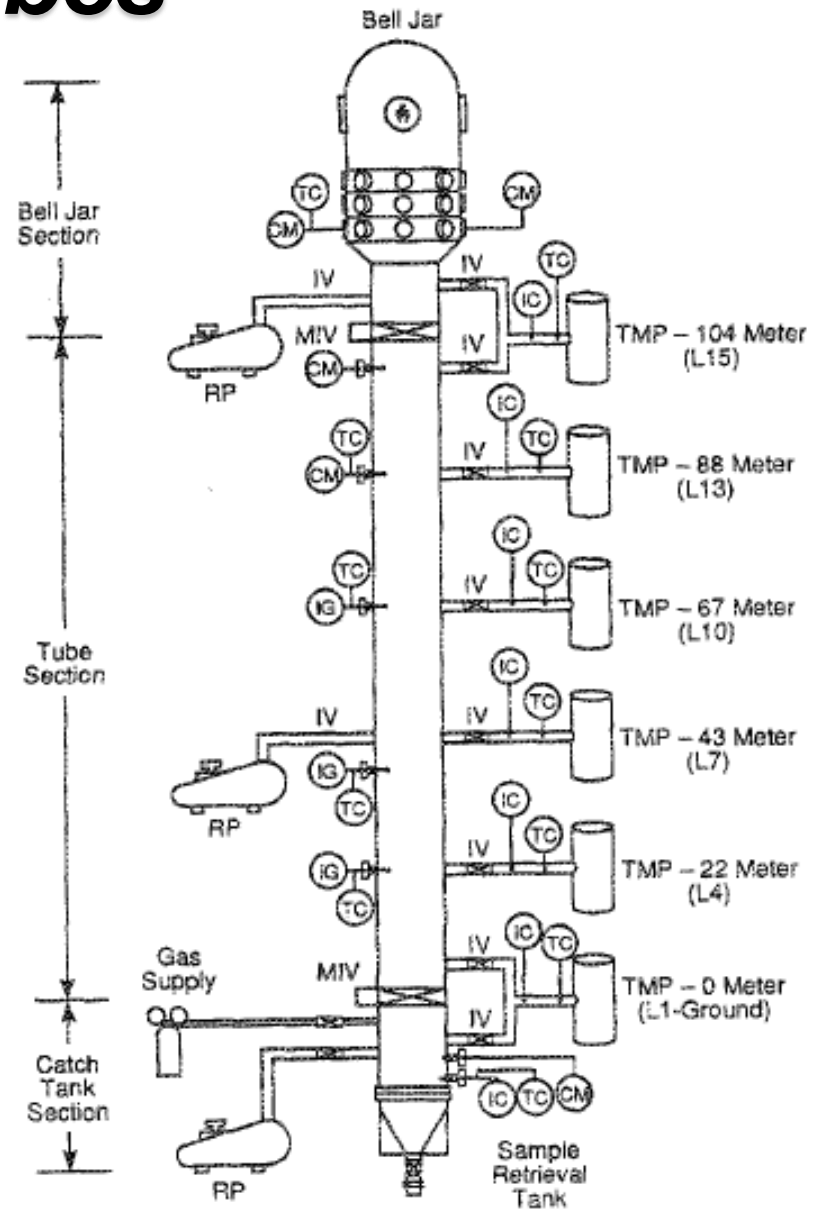


**Containerless Solidification**

# Drop-Tubes

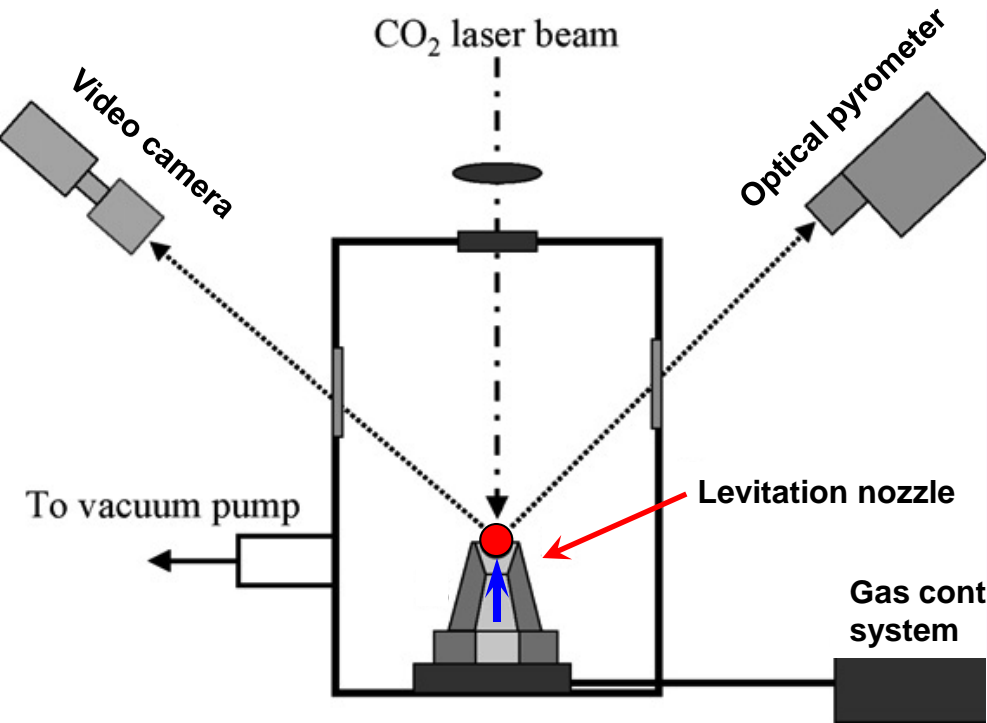


- Samples are melted and allowed to solidify while in free fall in vacuum or inert gas
- Lab-scale – atomized droplet (above, from [2])
- Marshall Space Flight Center (right, from [3])
- Allowed some temperature measurements during free fall



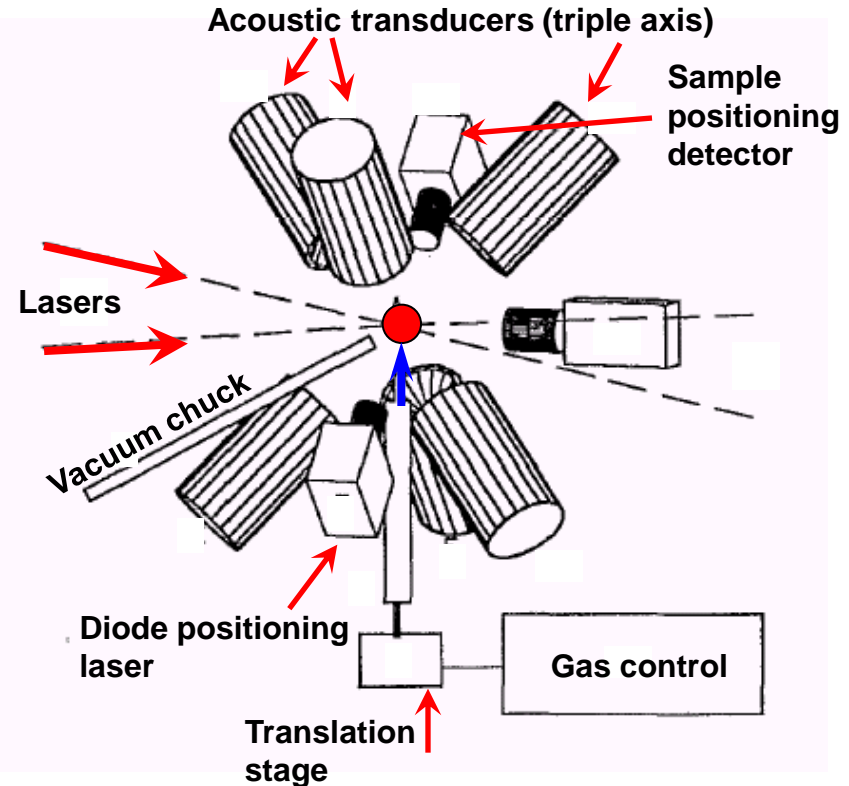


# Aerodynamic and Acoustic Levitation



**Aerodynamic Levitation** (from[4])

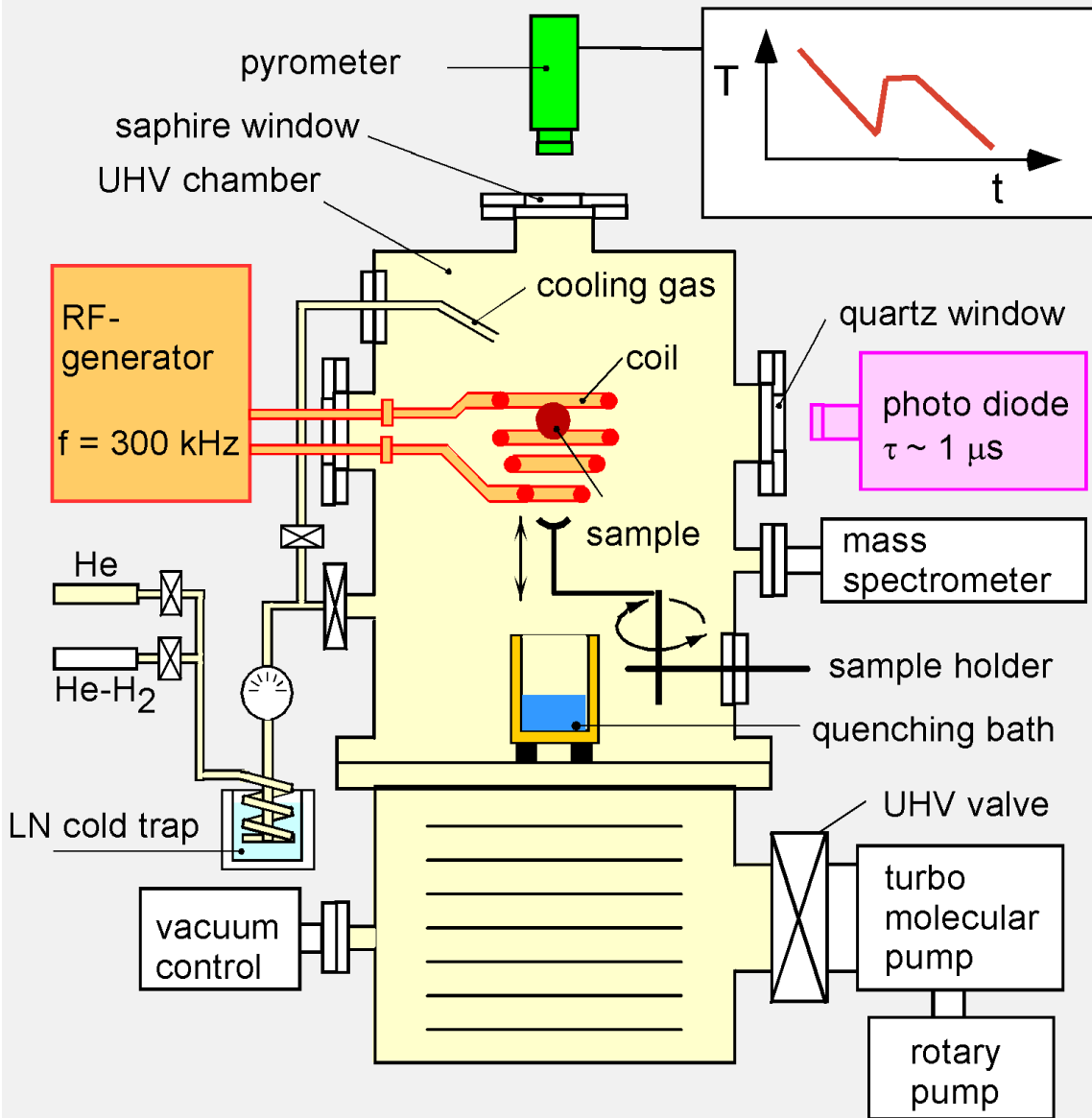
- Liquid oxides and reactive metals
- Levitation in controlled gas flow through nozzles designed for sample size and density
- Samples heated up to 2700K using high-power lasers
- Sample temperature measured with optical pyrometer
- The flowing gas makes temperature and positioning control difficult & gas impurities may limit supercooling



**Aeroacoustic Levitation** (from[5])

- Combines aerodynamic and acoustic forces
- Additional positioning control (diode laser and detector)
- Gas flow provides stable quiescent boundary layer around sample – suppresses oscillation from acoustic forces
- Sample positioning and containment better than aerodynamic levitation alone

# Advanced EML (TEMPUS)



- More stable control than aerodynamic levitation
- Can be used to measure a variety of thermophysical and electrical properties and liquid structures

**BUT**

- Requires conducting sample
- Dense samples with low melting temperatures require cooling gas for undercooling studies

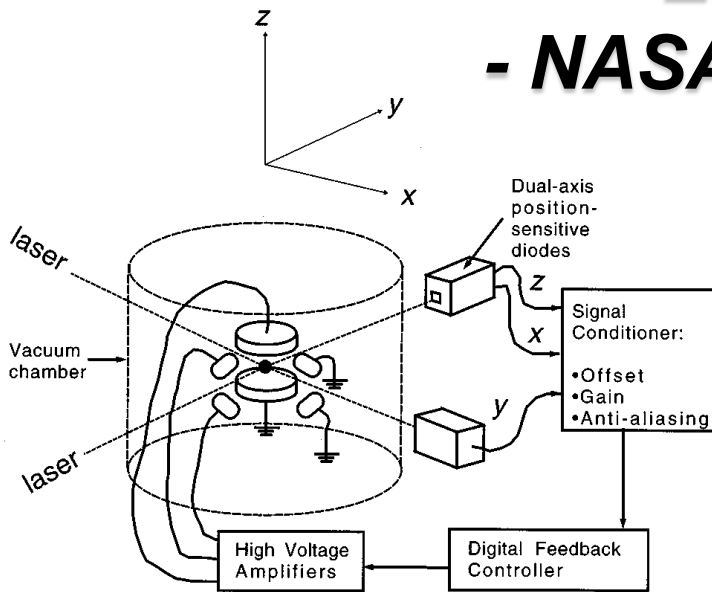
**TEMPUS** – Microgravity experiments on space shuttle (MSL-1)

**ISS – MSL-EML** facility under construction; planned to be flown in 2011

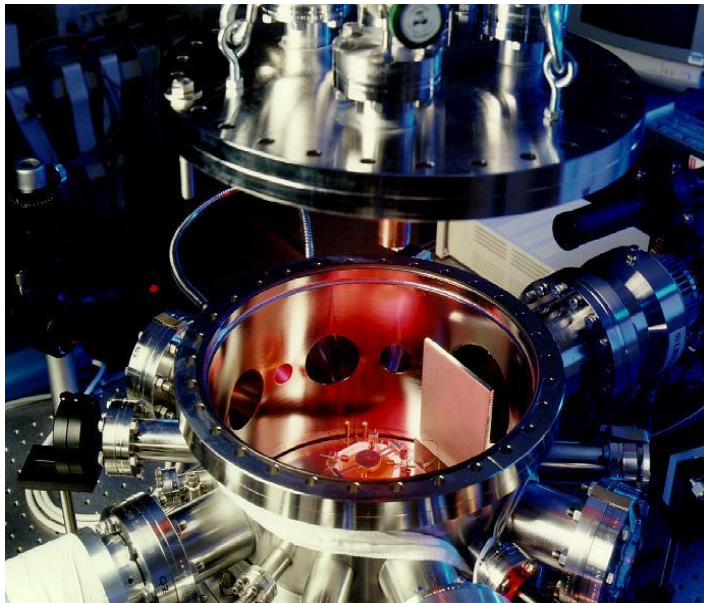
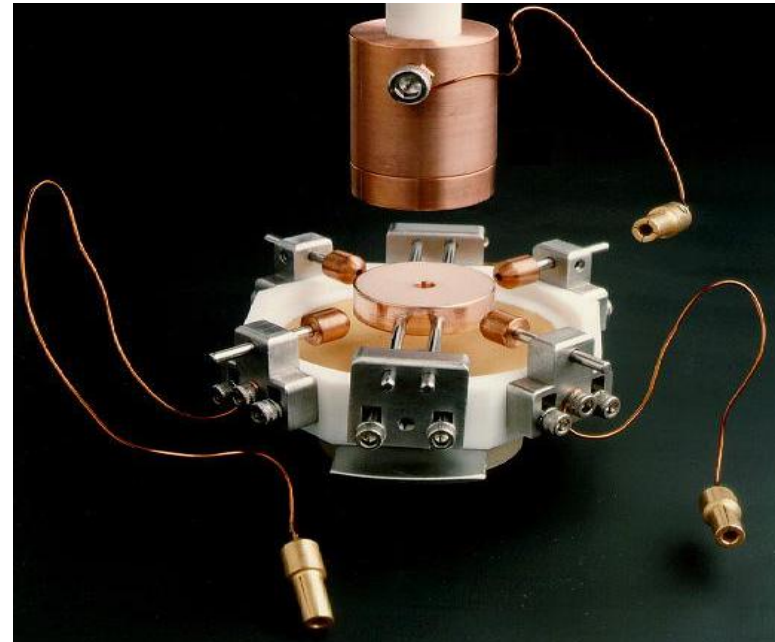


# ***Electrostatic levitation (ESL)***

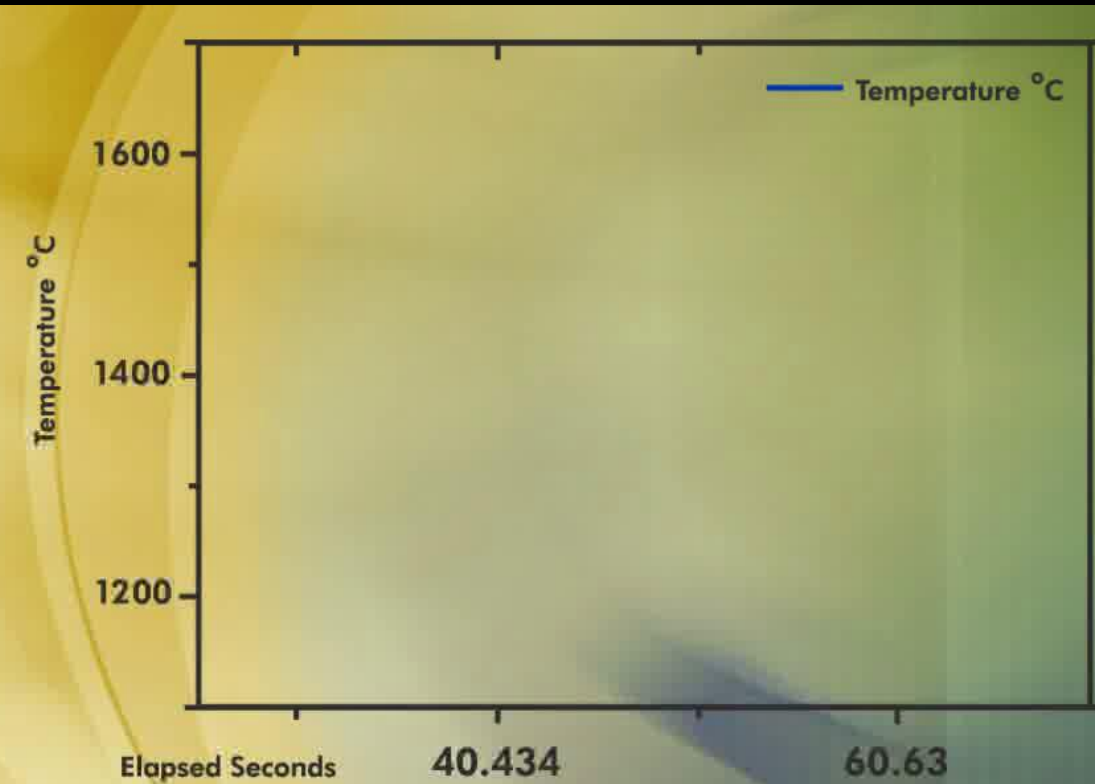
## ***- NASA Marshall Space Flight Center -***



From [7]

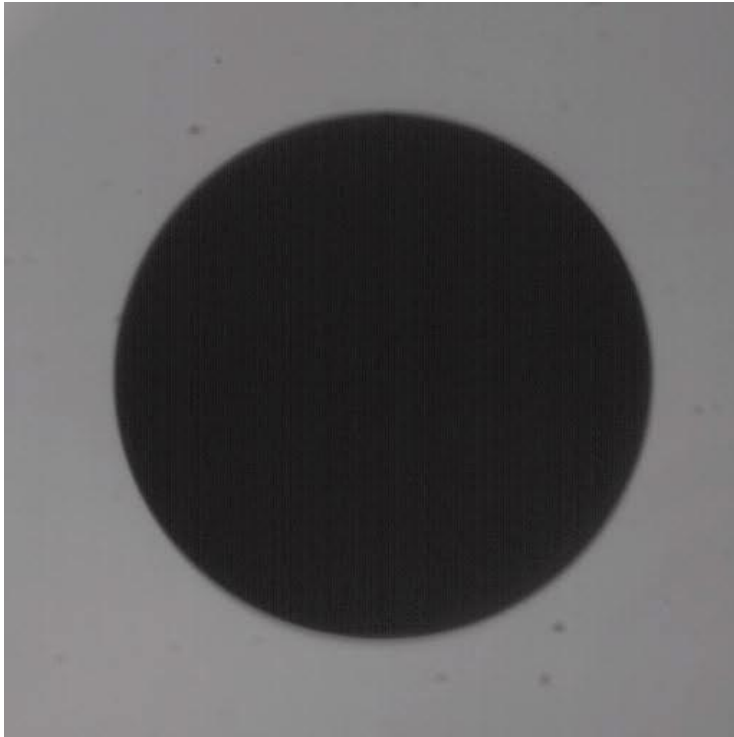


- Sample levitated in high vacuum ( $\approx 10^{-7}$  -  $10^{-8}$  torr)
- Add surface charge on sample by induction
- Maintain surface charge with ultraviolet lamp
- Apply large dc-field to generate sufficient force to counter gravity
- Fast feed-back mechanism to stabilize sample position (three independent sets of electrodes for x, y, and z positioning)
- Position stability to better than 50 micrometers
- Lasers used to heat the sample

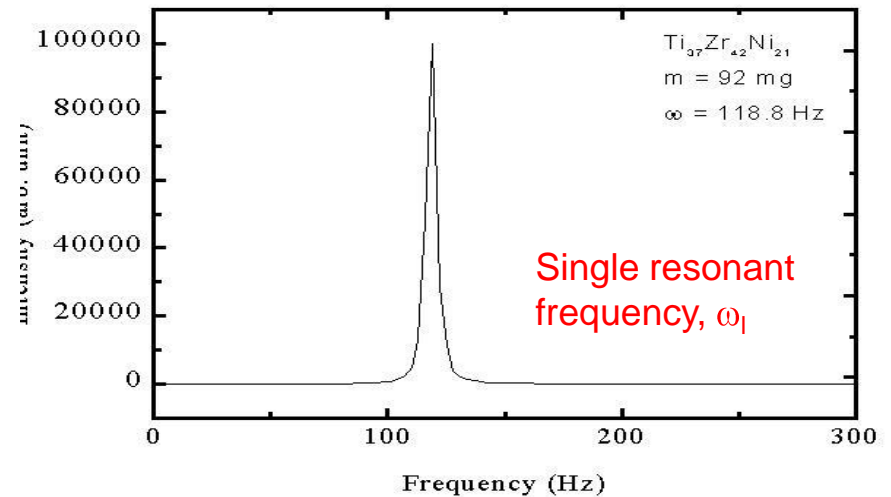


J. R. Rogers,  
NASA

# Oscillating Droplet Measurements



- Modulate ESL field near sample resonant frequency
- Damped Oscillations  $\text{Ti}_{37}\text{Zr}_{42}\text{Ni}_{21}$  at 1048 K
- Recorded at 1000 Hz, played at 10 Hz



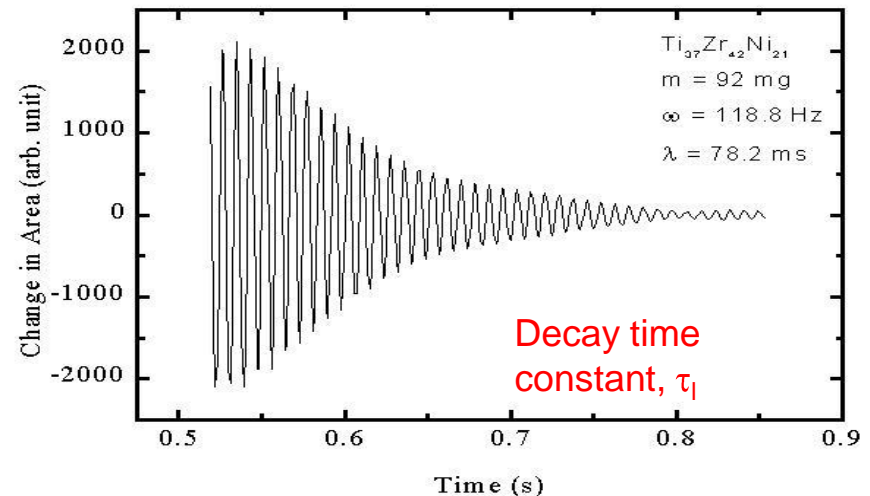
$$R = R_0(1 + \delta \cos(\omega t) e^{-\lambda t})$$

$$\omega_l = \sqrt{\frac{l(l-1)(l+2)\sigma}{\rho R_o^3}}$$

Rayleigh  
(1879)

$$\tau_l = \frac{\rho R_o^2}{l(l-1)(2l+1)\eta}$$

Lamb  
(1881)



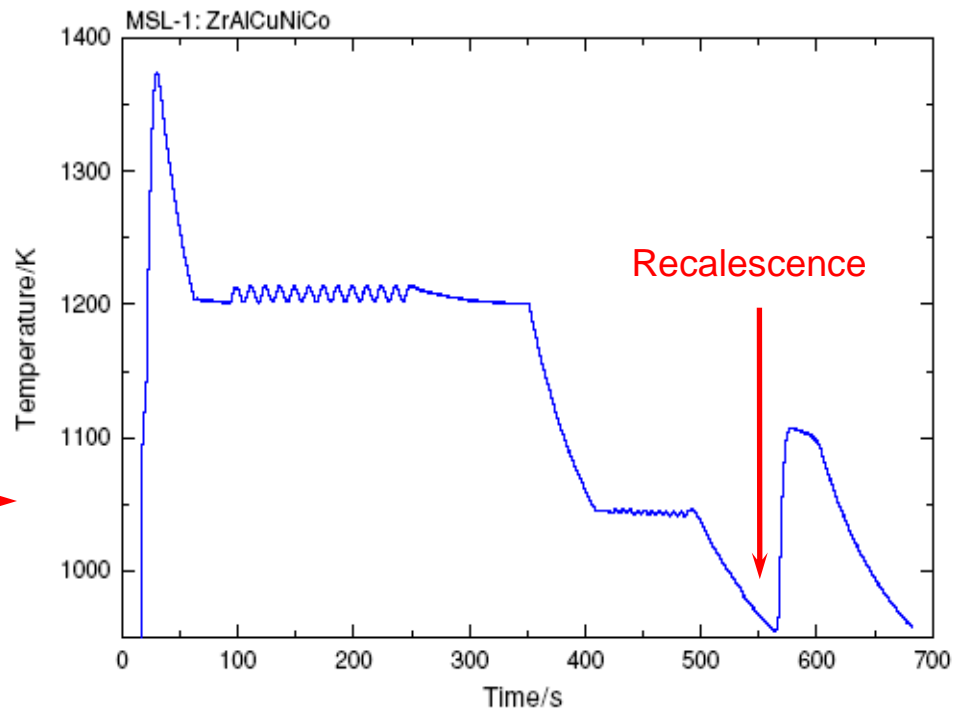
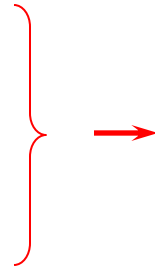
# Other Property Measurements

## Specific Heat ( $C_p/\epsilon$ )

- Radiation Cooling  $mC_p(T)\frac{dT}{dt} = \sigma_B A \epsilon_T (T^4 - T_r^4)$

- Modulation Calorimetry
  - Modulate power
  - Measure response in sample temperature

MSL-1 Spacelab mission.  
Experimental study of  
 $\text{Zr}_{60}\text{Al}_{10}\text{Cu}_{18}\text{Ni}_9\text{Co}_3$  liquid  
using modulation  
calorimetry

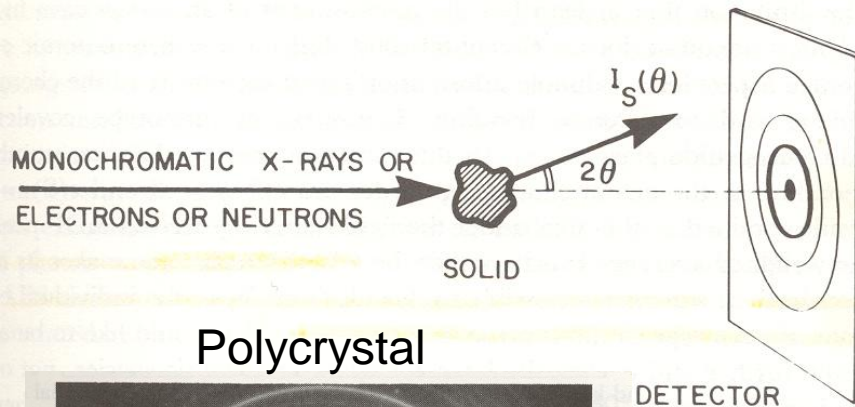


## Density

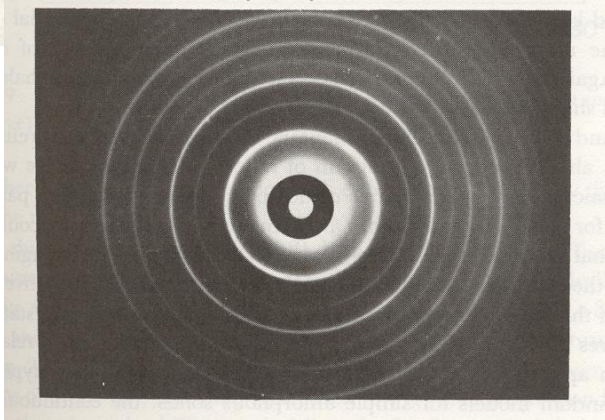
High resolution image of sample (perpendicular to axis)  
Sub-pixel resolution edge fitting



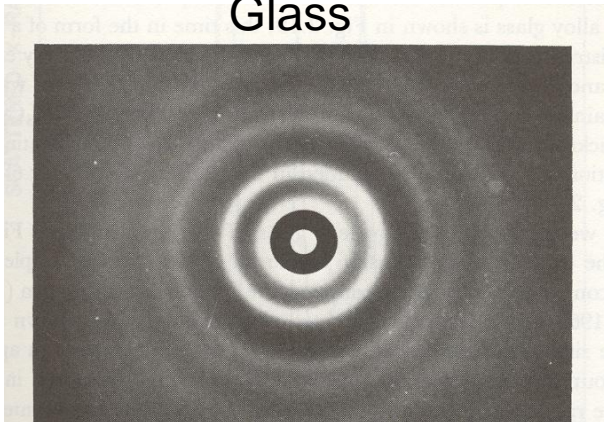
# Amorphous Phase Structure



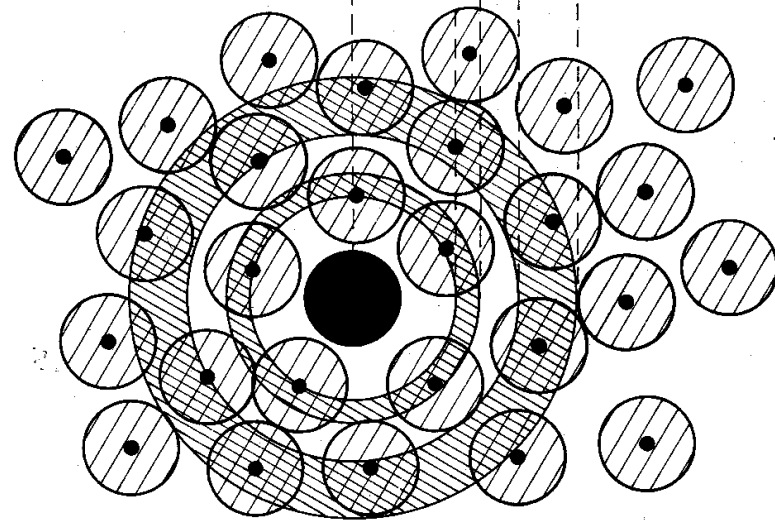
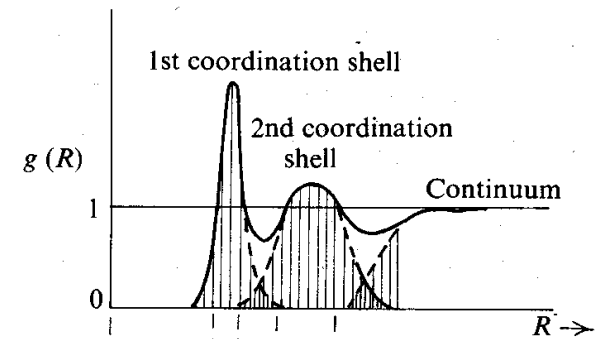
Polycrystal



Glass



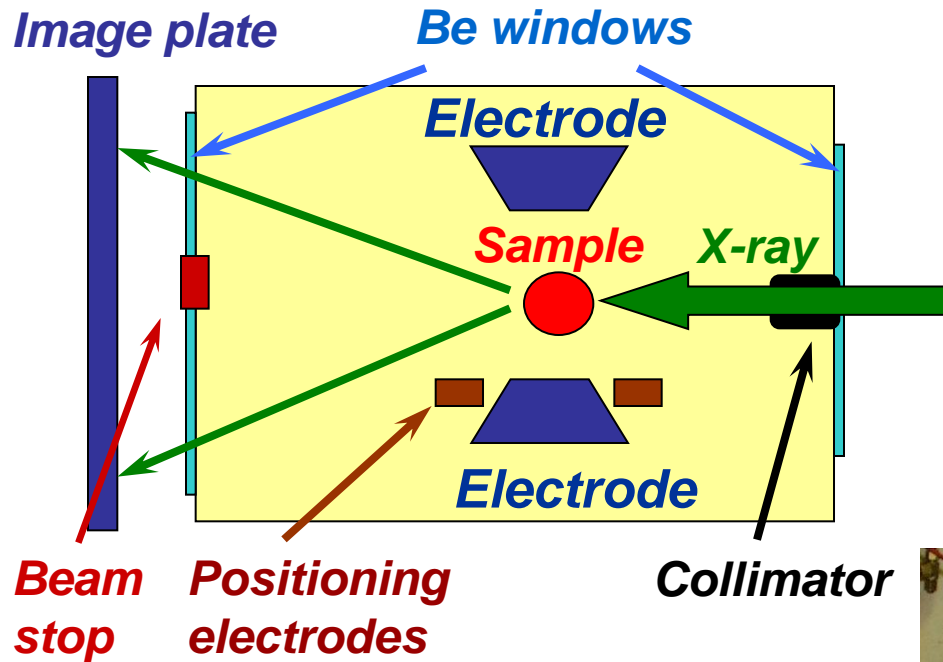
Radial Distribution Function



**Glasses (and liquids\*) have significant nearest-neighbor order**

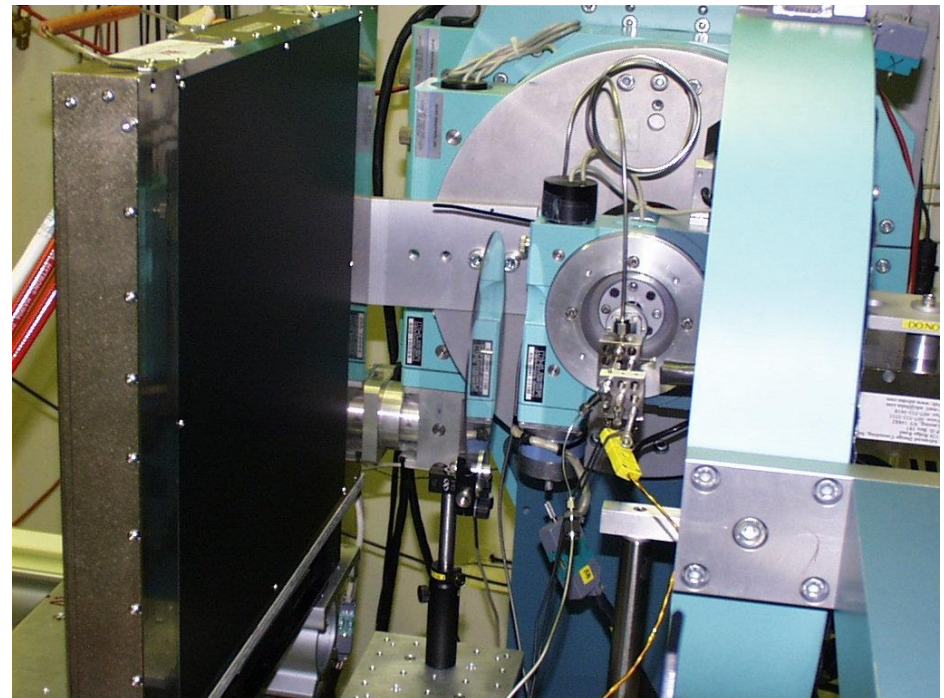
(See, for example, papers by Y. Waseda et al.)

# Beamline ESL (BESL)



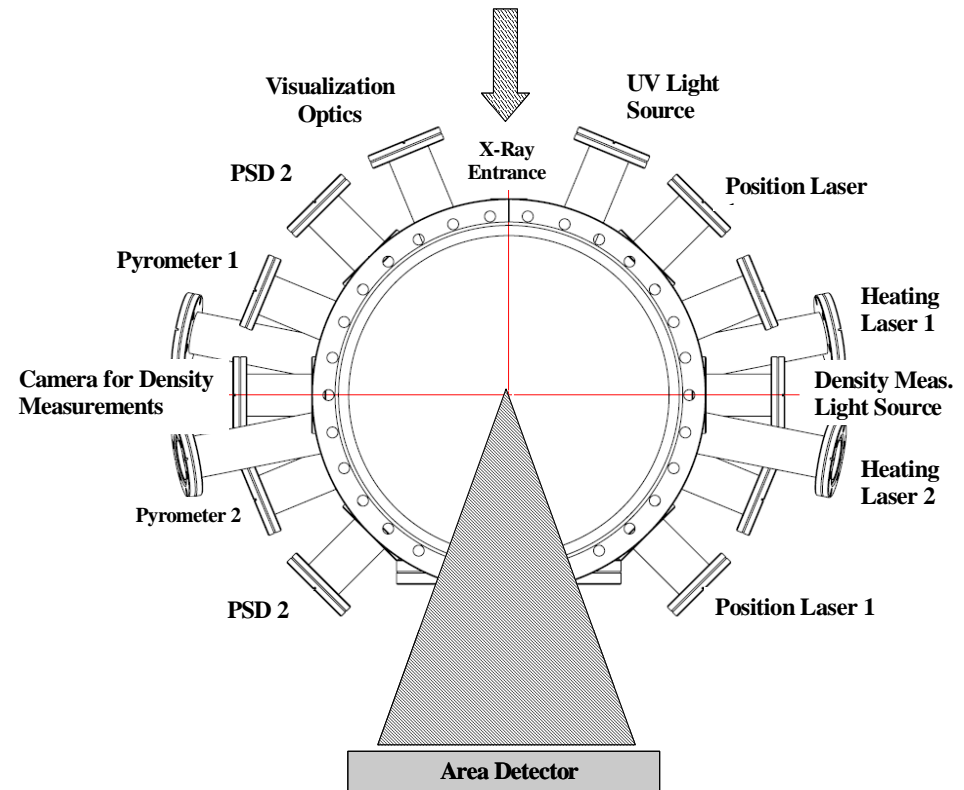
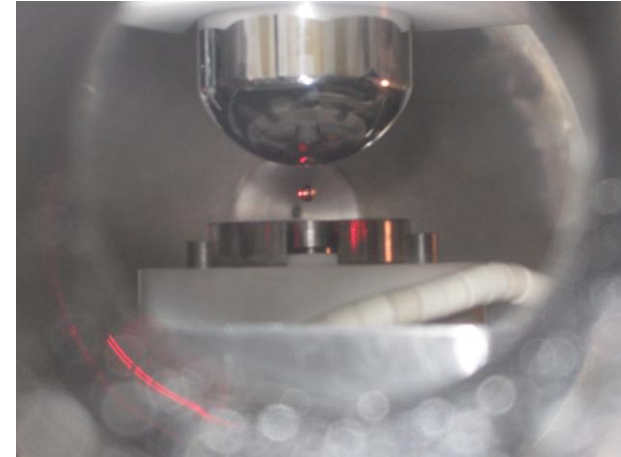
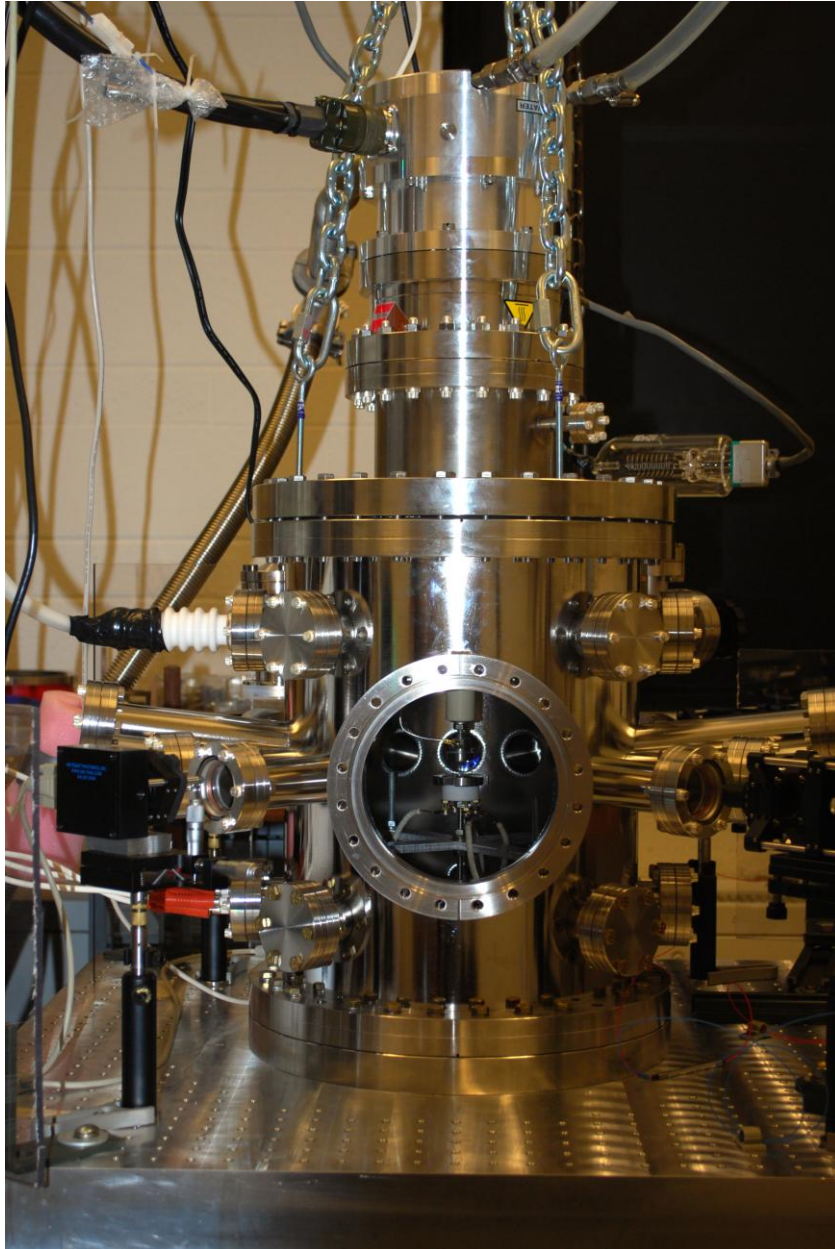
- First measurements made using ESL at Marshall Space Flight Center
- Washington University, Marshall Space Flight Center, Iowa State University
- Ref. [8,9]
- **First experimental confirmation of Frank's hypothesis (second lecture – Nucleation)**

GE - Image Plate Detector

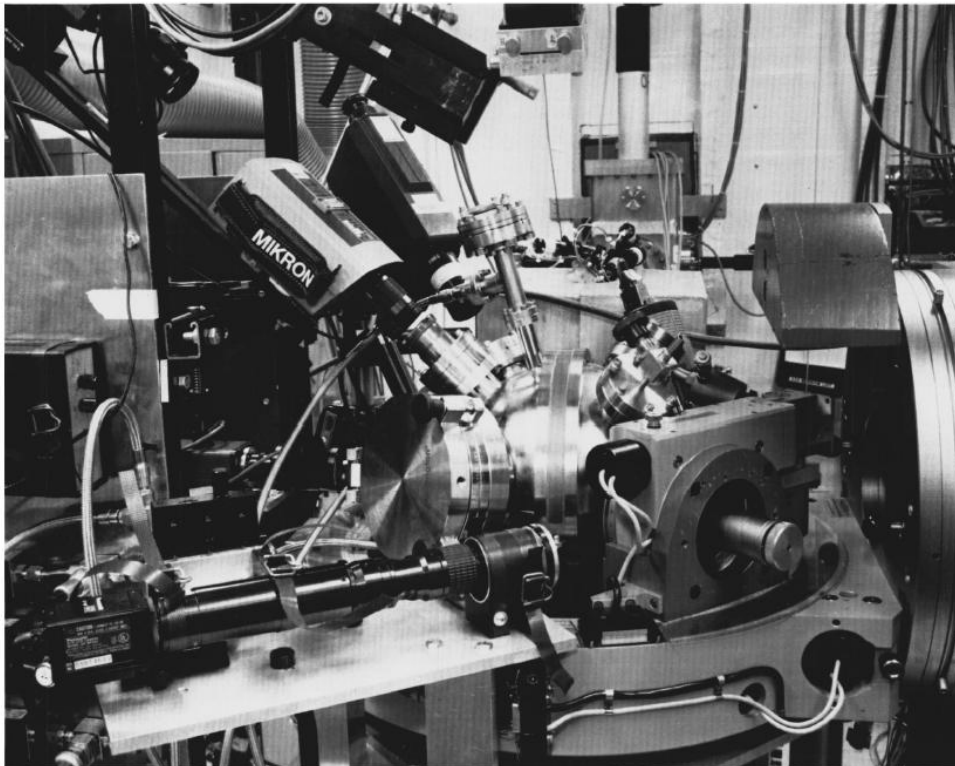
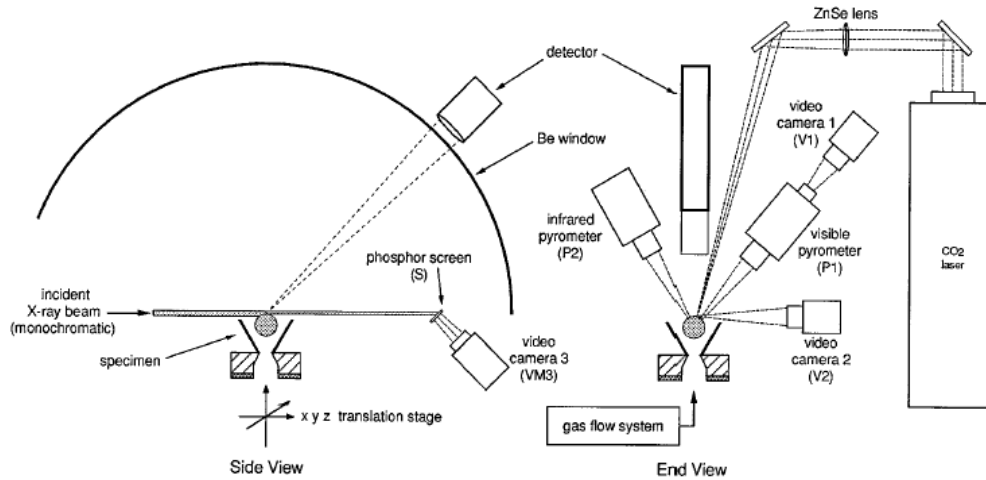




# WU-BESL (Washington University Beamline ESL)



# Aerodynamic Levitation Diffraction Apparatus



- Based on  $\theta$ -2  $\theta$  geometry
- Heating with one or two CO<sub>2</sub> lasers
- Capable of studying very high temperature liquids

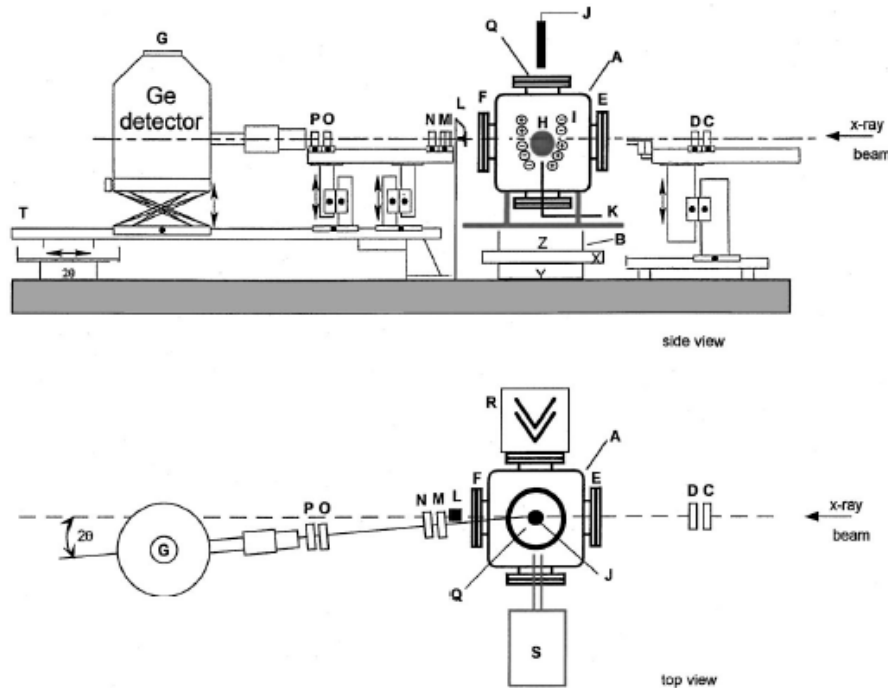
## But

- Sample stability not as good as EML or ESL
- Large temperature gradients in poorly conducting samples
- Diffraction geometry not suited for studies of phase transitions or structure evolution in deeply undercooled liquids

From [10]

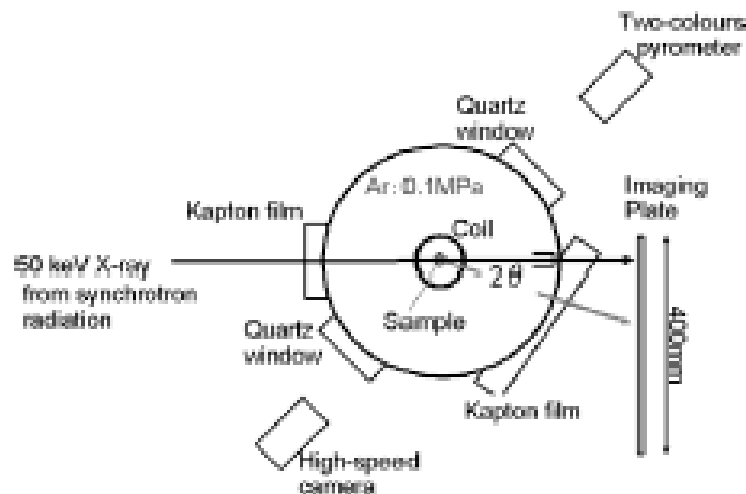


# Other Levitation Diffraction Approaches



## EML levitation chamber (Germany)

- Energy dispersive x-ray diffraction using white beam synchrotron radiation
- Diffracted beam is by energy dispersive germanium detector at a constant angle  $2\theta$ . From [11]



## ESL levitation chamber (Japan)

- Fixed energy (50 kV) x-rays
  - Imaging plate detection
  - **Laboratory-based x-ray diffraction**
- From [12]
- From [13]

# References for Levitation Apparatus

1. *Nucleation in Condensed Matter – Applications in Materials and Biology*, K. F. Kelton and A. L. Greer, Elsevier (to be published, Spring, 2010).
2. A. J. Drehman and D. Turnbull, "Solidification behavior of undercooled Pd<sub>83</sub>Si<sub>17</sub> and Pd<sub>82</sub>Si<sub>18</sub> liquid droplets," *Scripta Metall*, **15** (1981) 543.
3. T. J. Rathz, M. B. Robinson, W. M. Hofmeister and R. J. Bayuzick, "The Marshall Space Flight Center drop tube facility," *Rev. Sci. Instrum.* **61** (1990) 3846.
4. J. J. Wall, R. Weber, J. Kim, P. K. Liaw, H. Choo, "Aerodynamic levitation processing of a Zr-based bulk metallic glass," *Mat. Sci. Eng.*, **A445-446** (2007) 219.
5. J. R. Weber, D. S. Hampton, D. R. Merkley, C. A. Rey, M. M. Zatarski, P. C. Nordine, "Aero-acoustic levitation: a method for containerless liquid-phase processing at high temperatures," *Rev. Sci. Instrum.* **65** (1994) 456.
6. D. M. Herlach, R. F. Cochrane, I. Egry, H. J. Fecht, A. L. Greer, "Containerless processing in the study of metallic melts and their solidification," *Int. Mater. Rev.*, **38** (1993) 273.
7. A. J. Rulison, J. L. Watkins, B. Zambrano, "Electrostatic containerless processing system," *Rev. Sci. Instrum.* **68** (1997) 2856.
8. K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, D. S. Robinson, "First X-ray scattering studies on electrostatically-levitated metallic liquids – demonstrated influence of local icosahedral order on the nucleation barrier," *Phys. Rev. Lett.*, **90** (2003) 195504.
9. A. K. Gangopadhyay, G. W. Lee, K. F. Kelton, J. R. Rogers, A. I. Goldman, D. S. Robinson, T. J. Rathz, R. W. Hyers, "Beamline electrostatic levitator for in situ high energy x-ray diffraction studies of levitated solids and liquids," *Rev. Sci. Instrum.* **76**(2005) 073901.
10. S. Krishnan, J. J. Felton, J. E. Rix, J. K. R. Weber, P. C. NOrdine, M. A. Beno, S. Ansell and D. L. Price, "Levitation apparatus for structural studies of high temperature liquids using synchrotron radiation," *Rev. Sci. Instrum.*, **68** (1997) 3512.
11. C. Notthof, H. Franz, M. Hanfland, D. M. Herlach, D. Holland-Moritz, W. Petry, "Electromagnetic levitation apparatus for investigations of the phase selection in undercooled melts by energy-dispersive x-ray diffraction" *Rev. Sci. Instrum.* **71** (2000) 3791.
12. K. Higuchi, K. Kimura, A. Mizuno, M. Watanabe, Y. Katayana and K. Kuribayashi, *Meas. Sci. Technol.*, **16** (2005) 381.
13. T. Masaki, T. Ishikawa, P.-F. Paradis, S. Yoda, "Compact electrostatic levitator for diffraction measurements with a two axis diffractometer and a laboratory x-ray source," *Rev. Sci. Instrum.*, **78** (2007) 026102.

# ***A Few Selected Case Studies***

- Liquid/liquid phase transition in silicon?
- Possible chemical ordering in liquid Cu-Zr
- Ordering in amorphous metals
  - In glasses
  - In liquids
  - Icosahedral ordering and the glass transition
  - Alloying and glass formation
- Anomalies in thermophysical properties of transition metal liquids - possible phase transitions associated with ordering?

# Liquid-Liquid Phase Transition in Supercooled Silicon?

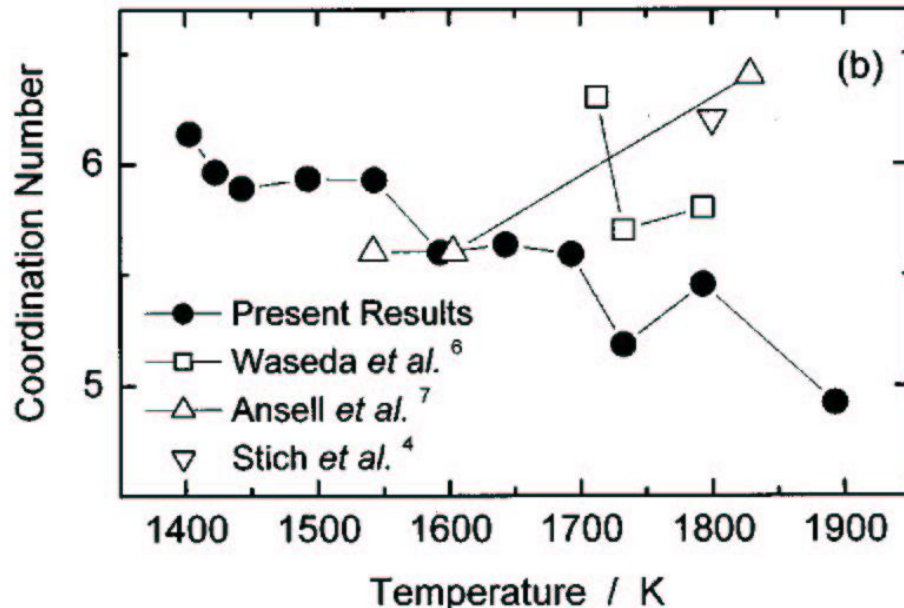
Predicted high-density – low-density liquid phase

- L. I. Aptekar, Sov. Phys. Dokl. **24**, 993 (1979).
- P. H. Poole et al., Science, 275, 322 (1997)
- S. Sastry and C. A. Angell, Nature Materials **2**, 739 (2003)
- C. R. Miranda and A. Antonelli, J. Chem. Phys. **120**, 11672 (2004).

## Coordination Number Change ?

### Electromagnetic Levitation

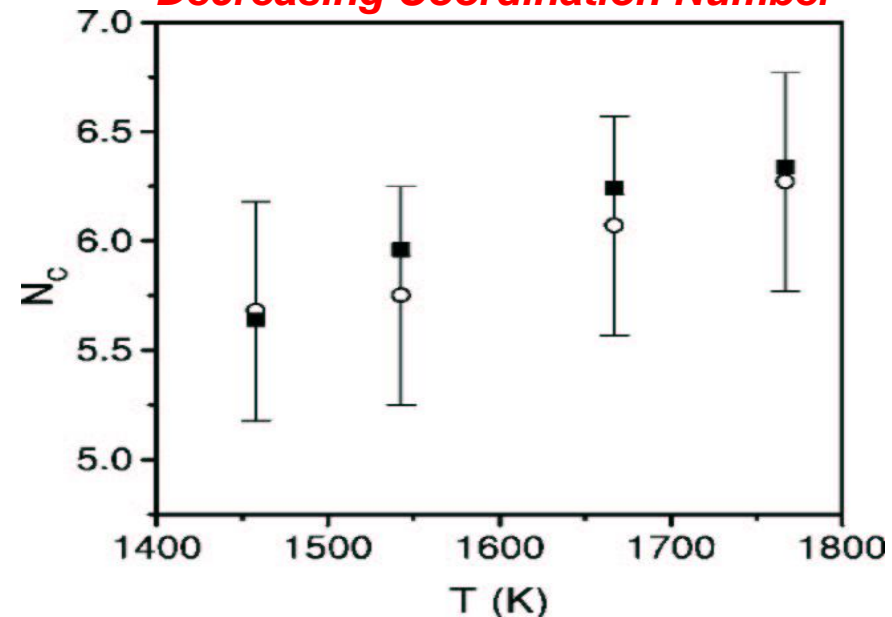
Increasing Coordination Number



H. Kimura, M. Watanabe, K. Izumi, et al.,  
App. Phys. Lett. **78**, 604 (2001).

### Aerodynamic Levitation

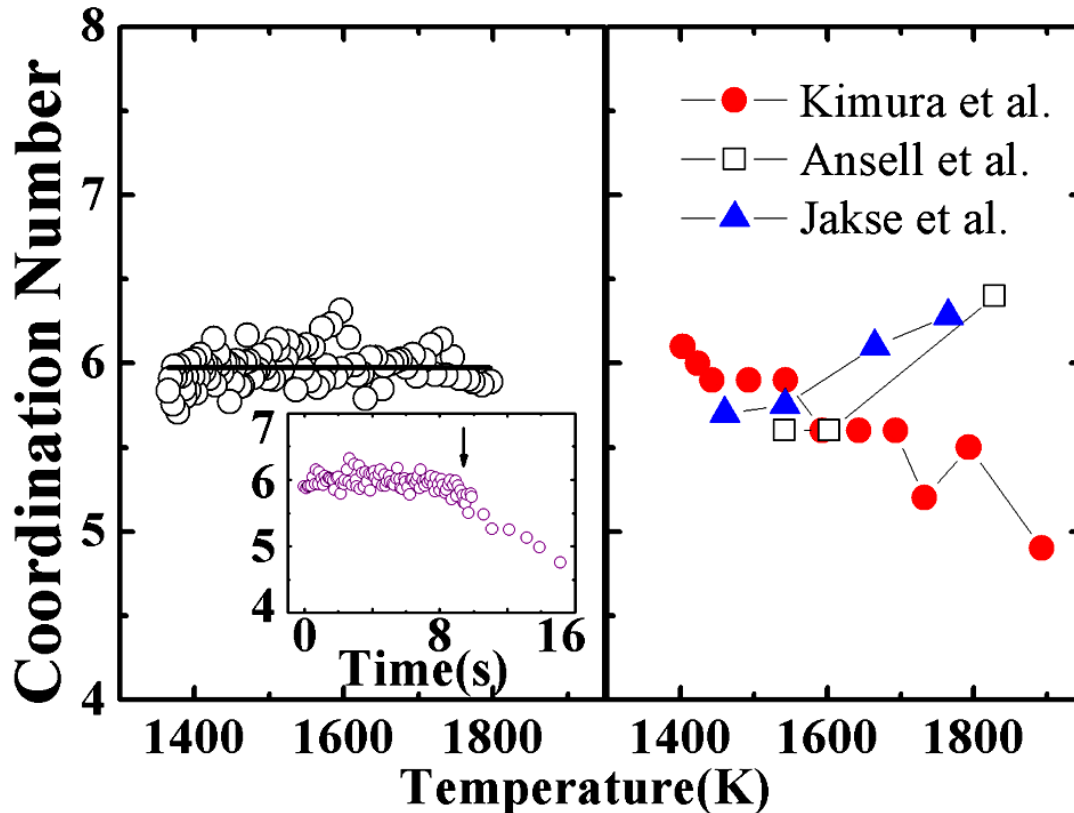
Decreasing Coordination Number



N. Jakse, L. Hennet, D. L. Price, et al.,  
App. Phys. Lett. **83**, 4734 (2003)

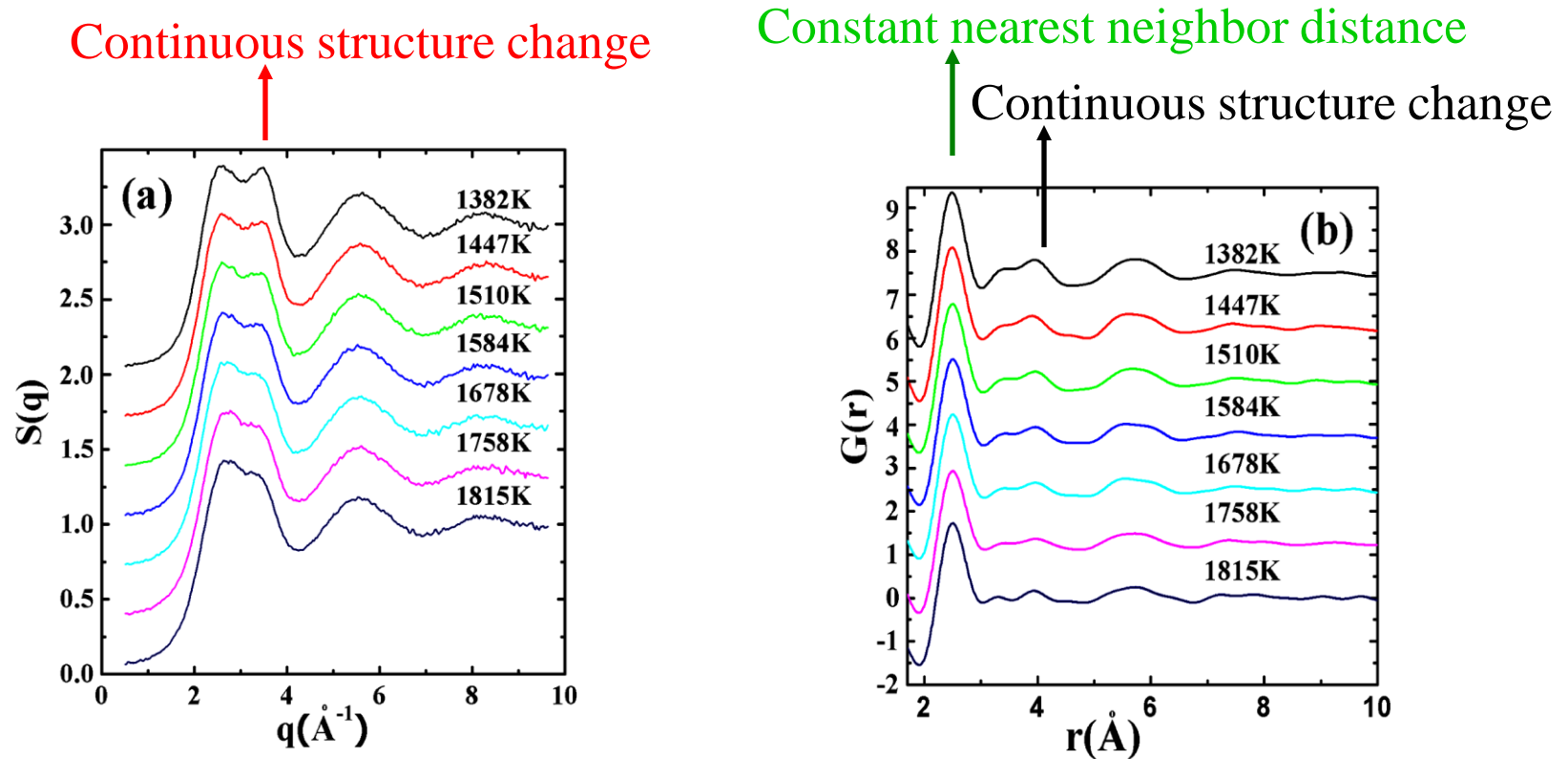


# ***Constant Coordination Number of supercooled liquid Si (10 Hz)***



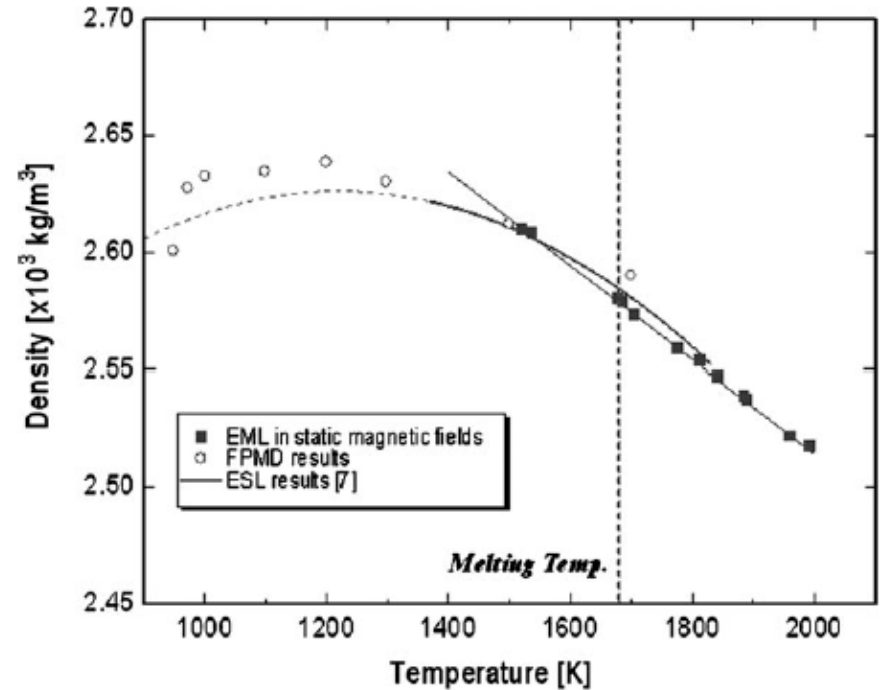
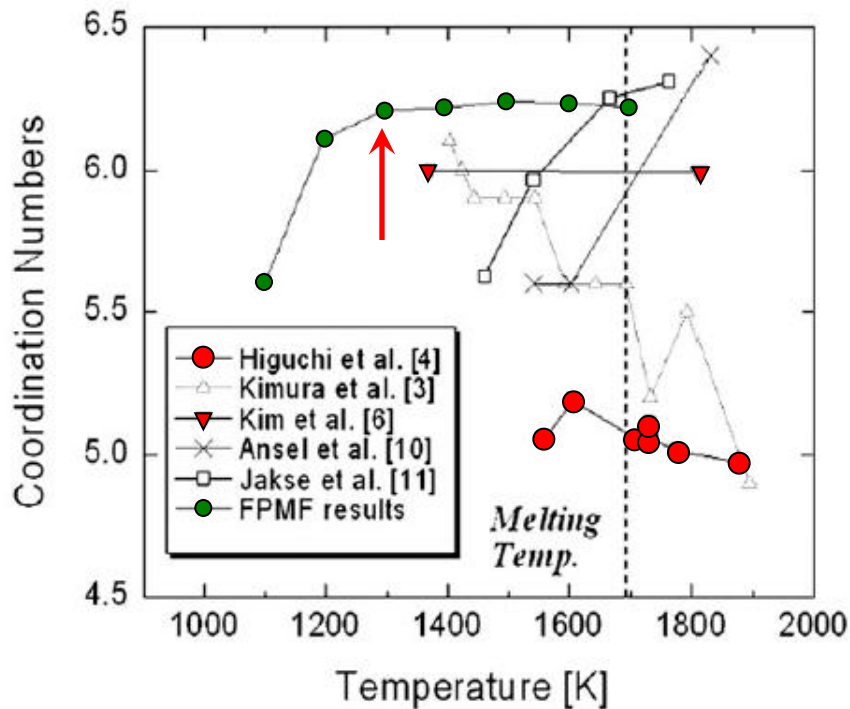
- **Constant CN of  $6.0 \pm 0.5$  over the entire temperature range**
- In conflict with previous experimental reports (right figure).
- No signal of a LL phase transition in CN down to 1382K

# Structure factor $S(q)$ & reduced pair correlation function $G(r)$ of supercooled liquid Silicon (1 Hz data)



- A primary peak in  $S(q)$  is observed at approximately  $2.6$  ( $\text{\AA}^{-1}$ ) with a shoulder on the high- $q$  side that becomes better resolved as temperature is lowered.
- The second peak in  $G(r)$  is composed of two sub-peaks increasing in intensity, signaling a change in the **medium-range** order of the liquid upon cooling.

# More Recent Studies



- **First Principles Molecular Dynamics (FPMF)**
- **Predicts constant coordination number from melting temperature to approximately 1300K** (consistent with data from T. H. Kim et al., Phys. Rev. Lett., **95**, 085501 (2005)).
- **Predicted decrease below 1200K correlates with predicted density maximum**
- **See no change in short-range order above 1200K** (agrees with analysis of T. H. Kim et al. Phil. Mag., **88**, 171-179 (2008))

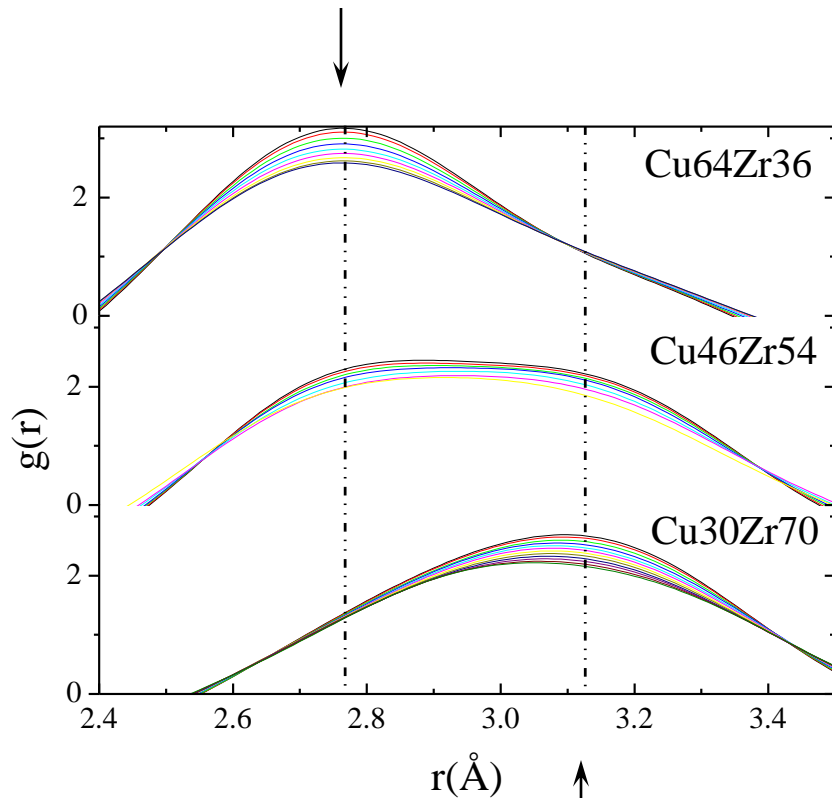
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# First peak in Pair Correlation for Cu-Zr

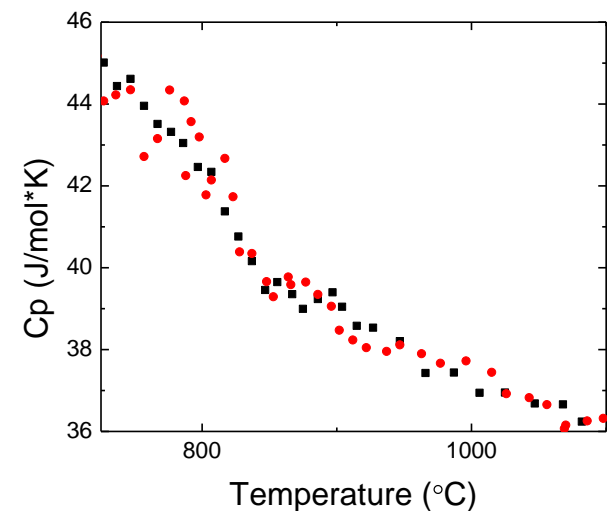
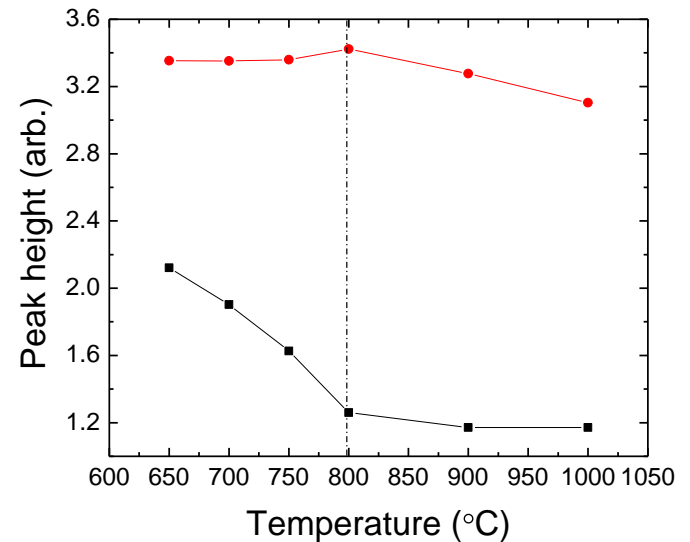
Cu-Cu and Cu-Zr separation distance



Zr-Zr separation distance

A. Sadoc et Al. J. Non-Cryst. Solids,  
B. 1984. **65**(1): p. 109-129

Cu<sub>46</sub>Zr<sub>54</sub>



**Chemical Ordering in the Liquid**

# ***A Few Selected Case Studies***

- Liquid/liquid phase transition in silicon?
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## Dense Random Packing

J. D. Bernal, *Nature*, **185**, 68 (1960)

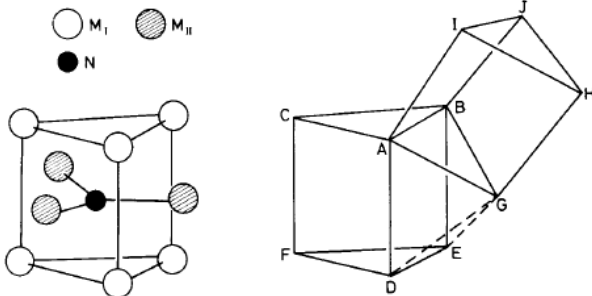


- Dominant polyhedra
- Reasonable model for
  - monatomic systems
  - alloys with atoms of similar size, no chemical short-range order

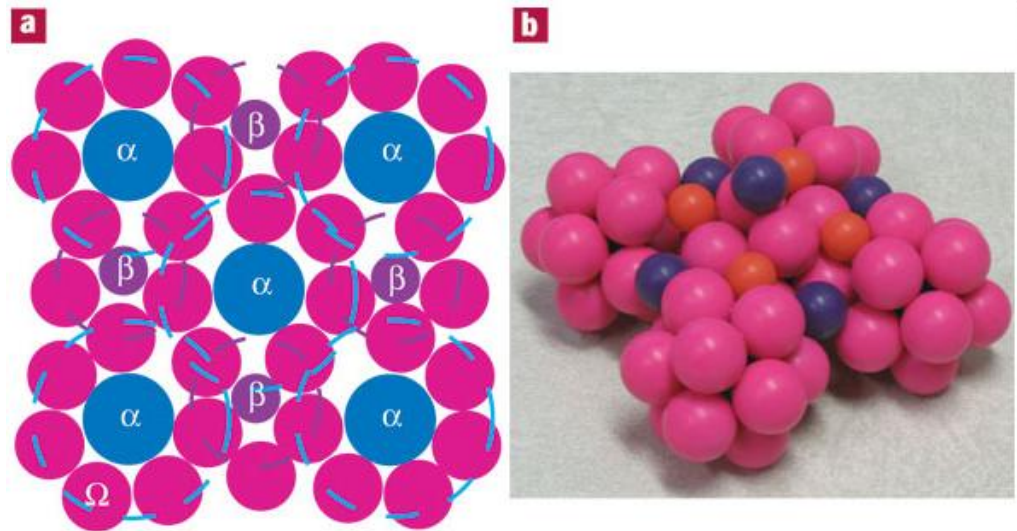
## Stereochemical Model

P. H. Gaskell, *Nature*, **276**, 484 (1978)

- Metal/metalloid glasses
- Local units have same structures as in crystal counterparts
- Regular prismatic polyhedra



## Packing Models for Glasses



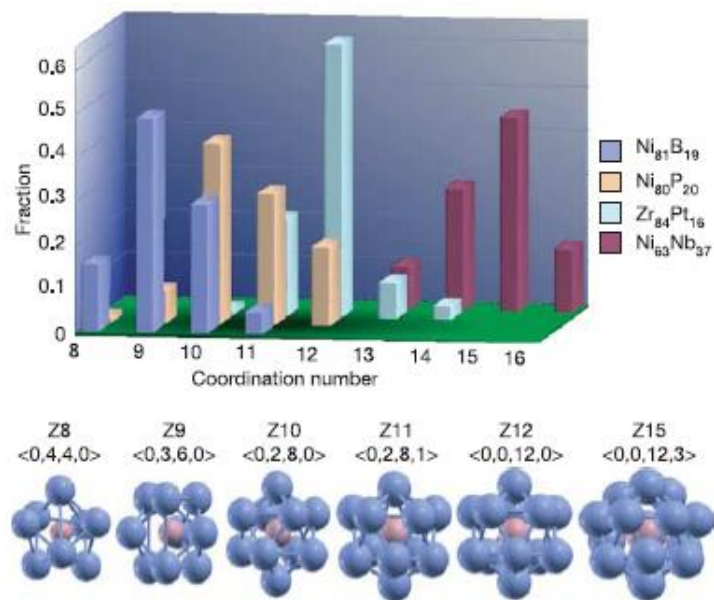
D. B. Miracle, *Nature Materials*, **3**, 697 (2004)

- Interpenetrating Clusters
- $\Omega$  - solvent atoms
- Solutes (in order of size)
  - $\alpha$  - primary cluster-forming solute
  - $\beta$  - secondary solute (cluster-octahedral sites)
  - $\gamma$  - secondary solute (cluster-tetrahedral sites)
- Preferred sizes of  $\alpha$  relative to  $\Omega$  give efficient packing in solute-centered clusters ( $R\alpha = D\alpha/D\Omega$ )
- Solute sizes for  $\beta$  and  $\gamma$  enable efficient packing in the first coordination shell
- Clusters packed into fcc/hcp packing – short coherence length due to strain effects

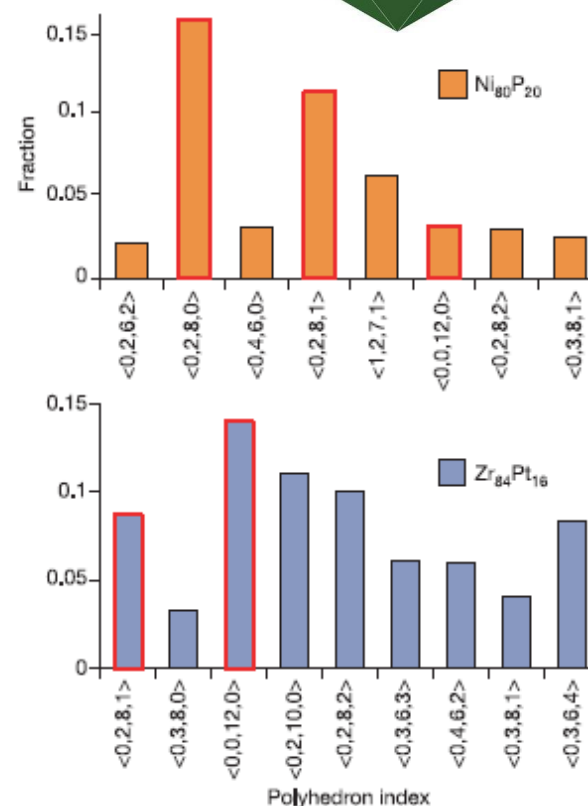
# Determining the Structure – Rather than Assuming One

H. W. Shen *et al.*, Nature, **439**, 419 (2006)

- Experimental Studies
  - X-ray and EXAFS
  - Reverse Monte Carlo Analysis
  - Voronoi tessellation
- Computational Studies - ab-initio MD
- Found distinct polyhedron types
- Solute centered (chemical SRO)
- Supports cluster packing



- Significant icosahedral order in some glasses

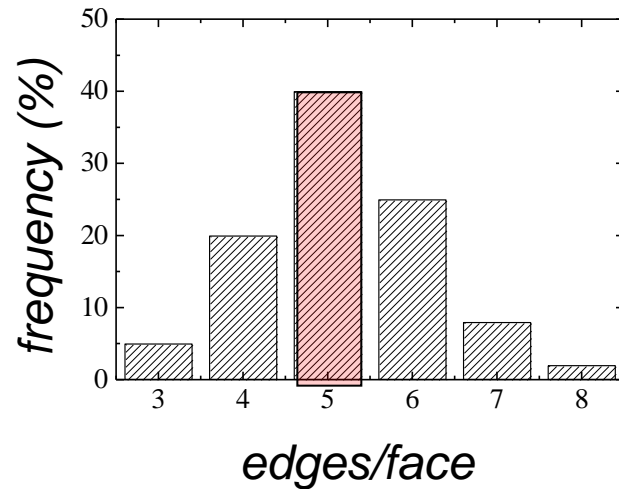


- Solute-centered icosahedral connected to form strings

# Evidence for Icosahedral Order in Liquids and Glasses

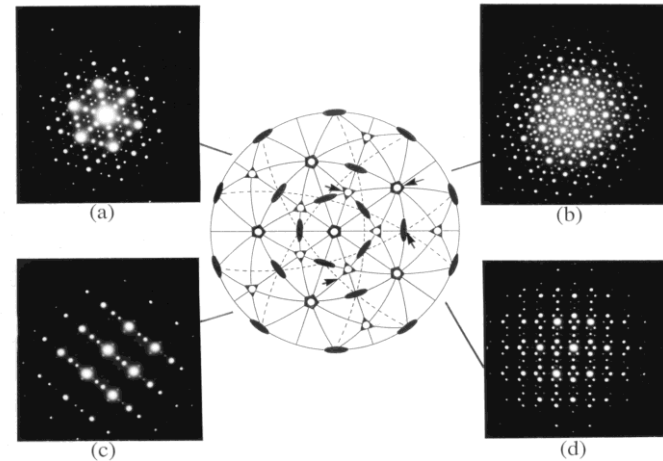
Computer Calculations of DRP

**Bernal and Finney**



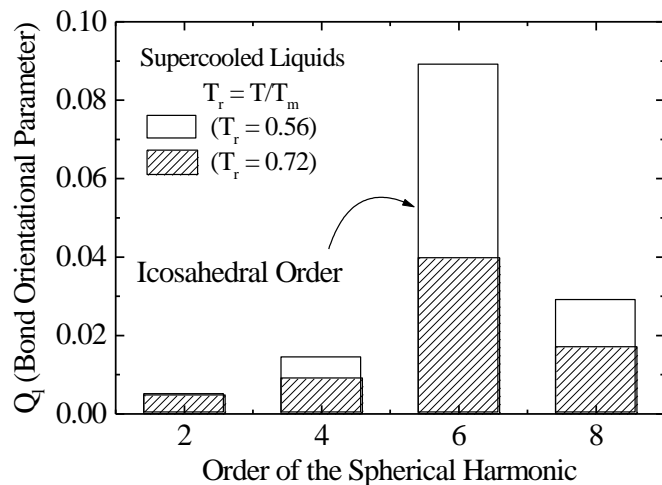
Icosahedral Quasicrystal

(D. Shechtman et al, PRL, 1984)



Molecular Dynamics (Lennard-Jones Potential)

**Steinhardt, Nelson, Ronchetti (1981, 1983)**



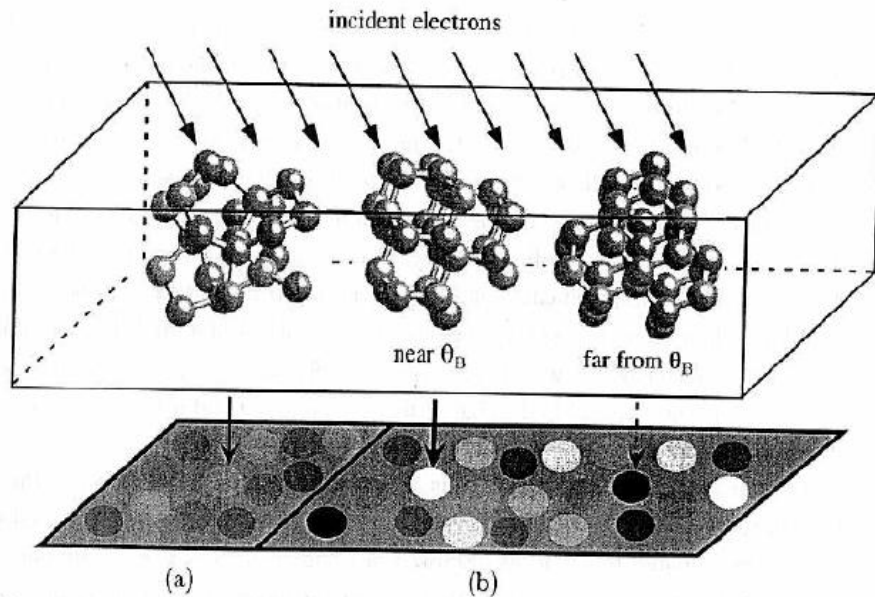
*i(HoMgZn)* - I. R. Fisher and P. C. Canfield

**Metallic glass diffraction peaks related to those from quasicrystal** (S. Sachdev and D.R. Nelson, PRL (1984))



# Fluctuation Transmission Electron Microscopy

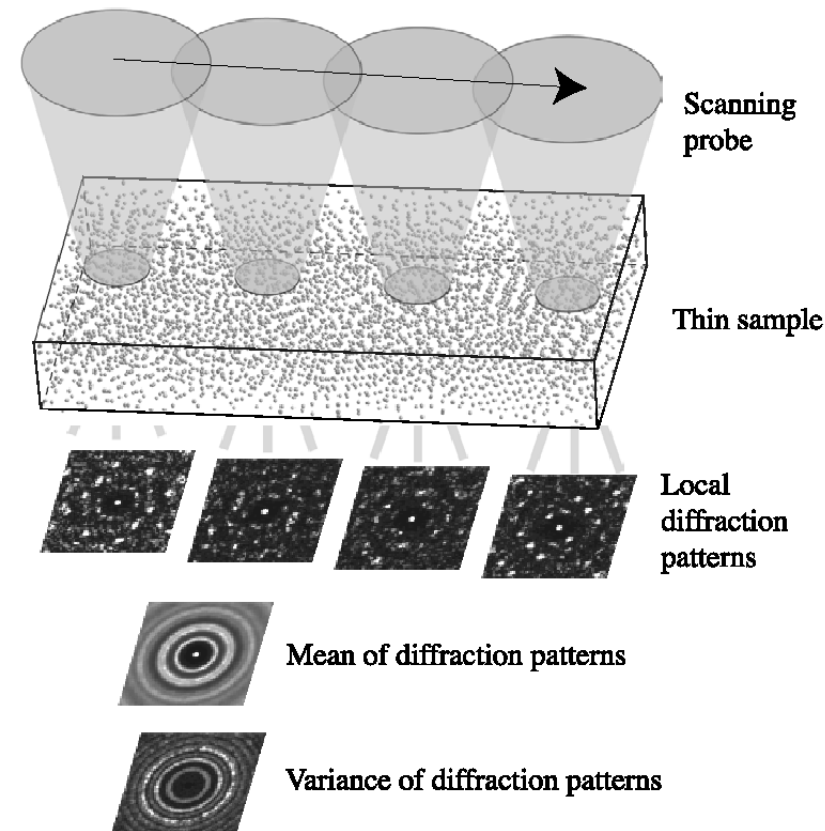
*M. Gibson, M. Treacy, P. Voyles*



Local diffraction from  
(a) Random Structure  
(b) Oriented Clusters

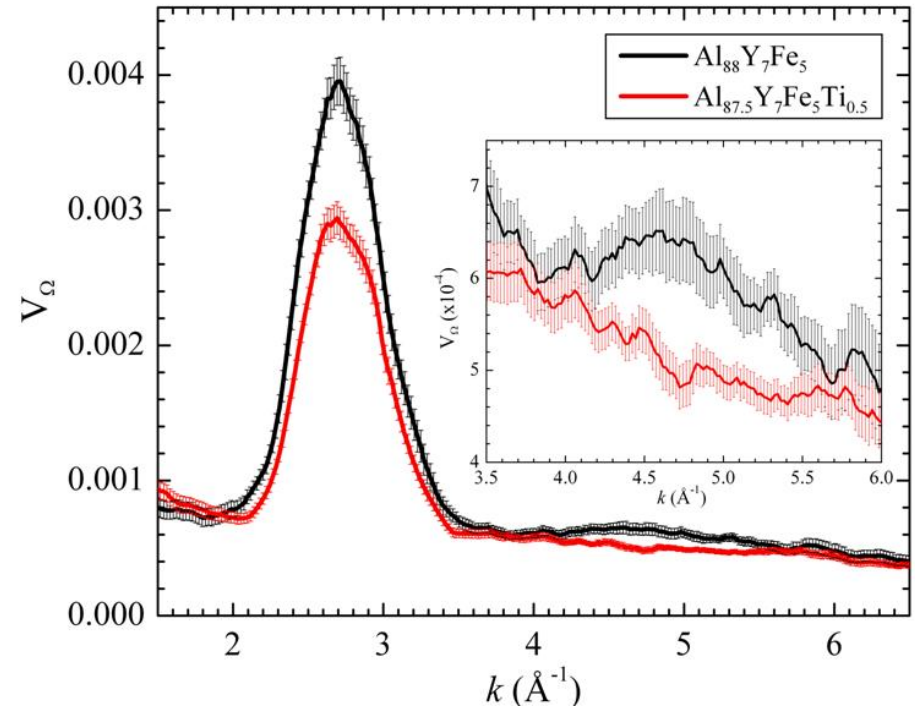
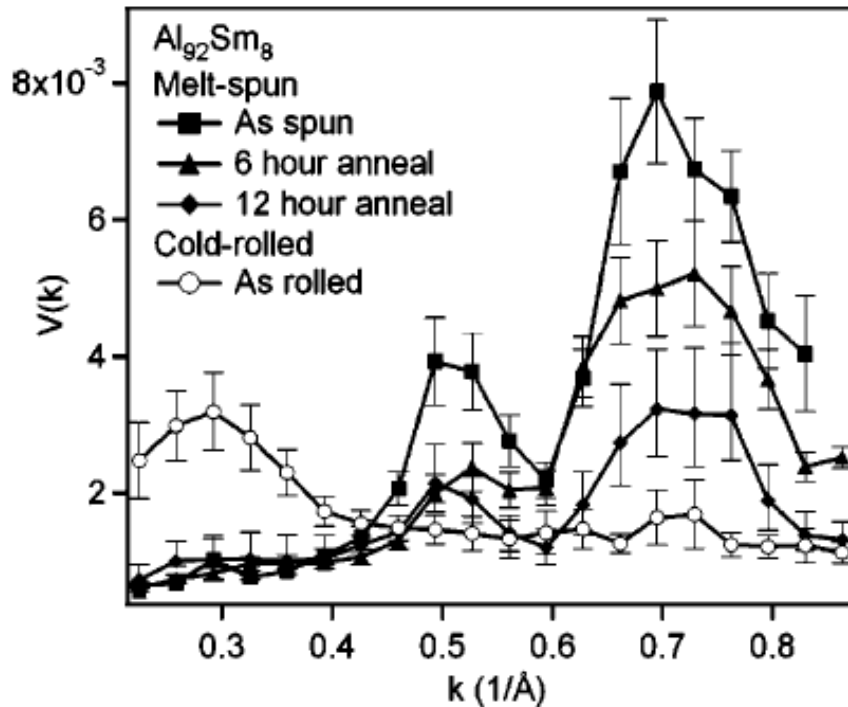
- Determination of Speckle in Image
- Measure dark-field image as function of  $k$
- Calculate the variance,  $V$  as a function of  $k$

## Rastered Nanoprobe diffraction



**FEM provides information on medium-range order  
- and 3 and 4 body correlation functions -**

# Sample FEM Results



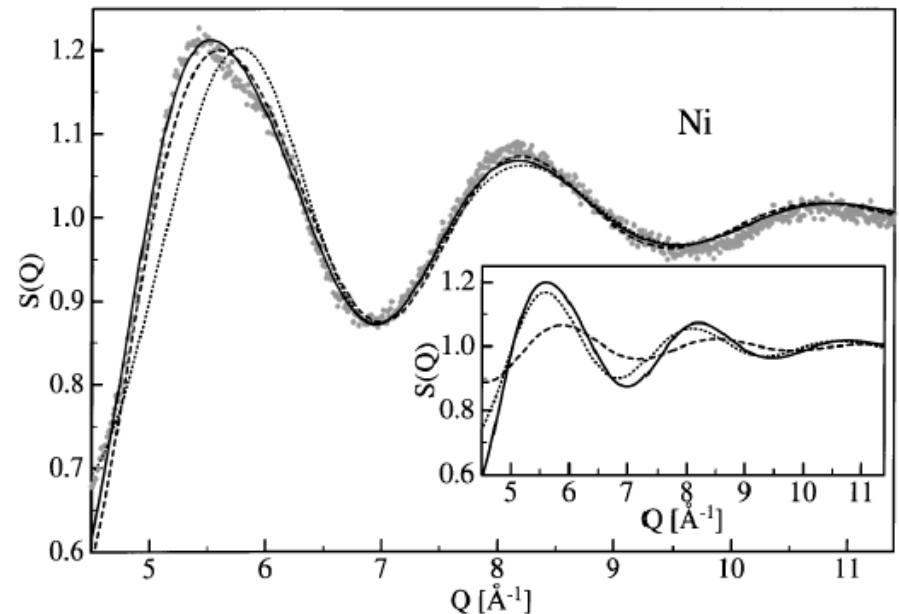
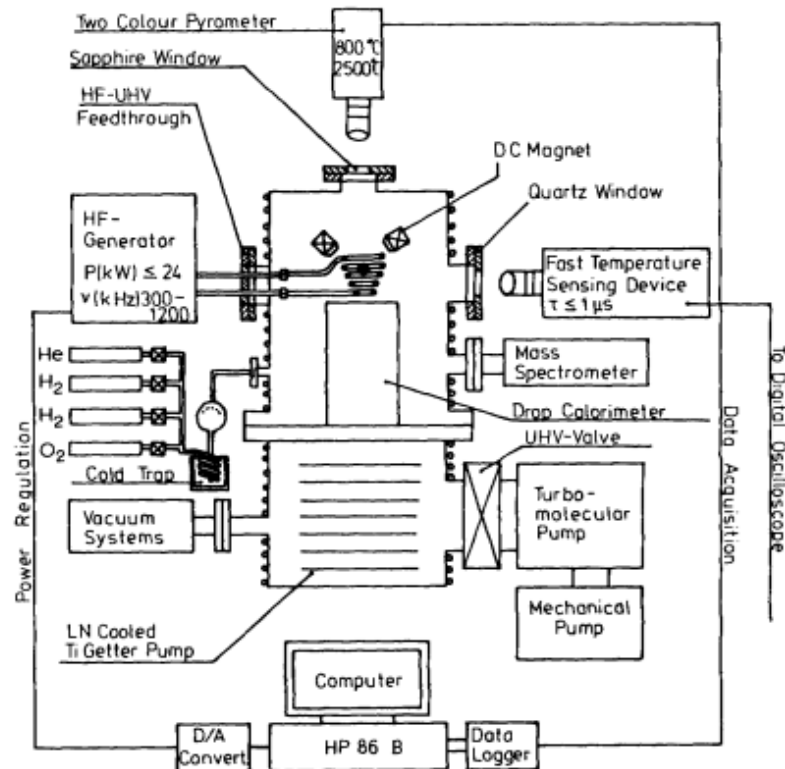
- Nanoscale (of order 1 nm diameter) Al-like ordering in melt-spun glass ribbons
- Suggests quenched-in clusters of order
- W. G. Stratton et al., APL, **86**, 141910 (2005)
- Microaddition of Ti changes medium range order
- AlYFeTi more ordered on range of probe size (1.5 nm)
- Increased medium range Al order
- Consistent with Ti-induced suppression of nanoscale phase separation (3D atom probe tomography)

# ***A Few Selected Case Studies***

- Liquid/liquid phase transition in silicon?
- Possible chemical ordering in liquid Cu-Zr
- Ordering in amorphous metals
  - In glasses
  - In liquids
  - Icosahedral ordering and the glass transition
  - Alloying and glass formation
- Anomalies in thermophysical properties of transition metal liquids - possible phase transitions associated with ordering?

# Experimental Scattering Evidence for Icosahedral Order

## Electromagnetic Levitation



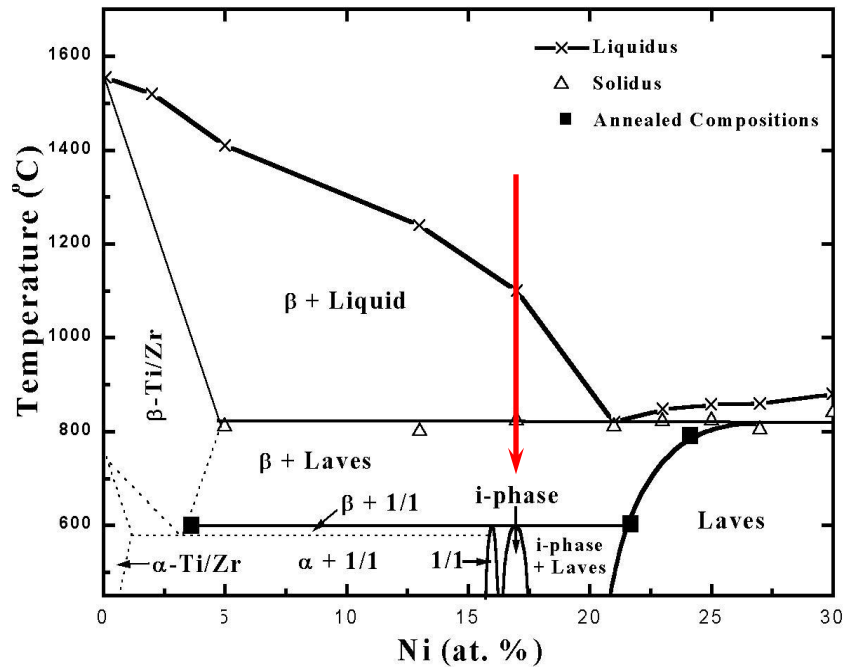
- Neutron diffraction
- Fits to single shell icosahedra
- Icosahedral cluster (dashed line); dodecahedra, (solid line); fcc (dotted line)

T. Schenk, D. Holland-Moritz, V. Simonet, R. Bellissent, and D. M. Herlach,  
Phys. Rev. Lett., 89, 075507 (2002)

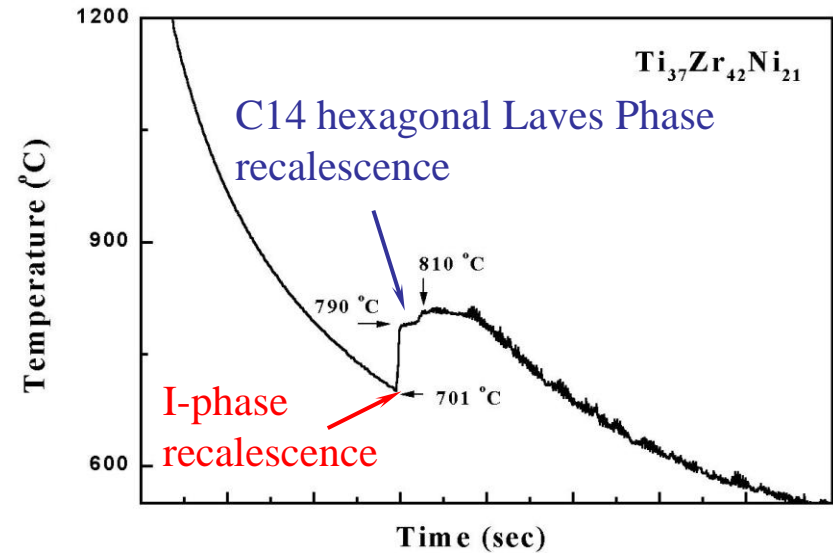


# Nucleation of Metastable Ti-Zr-Ni Quasicrystals

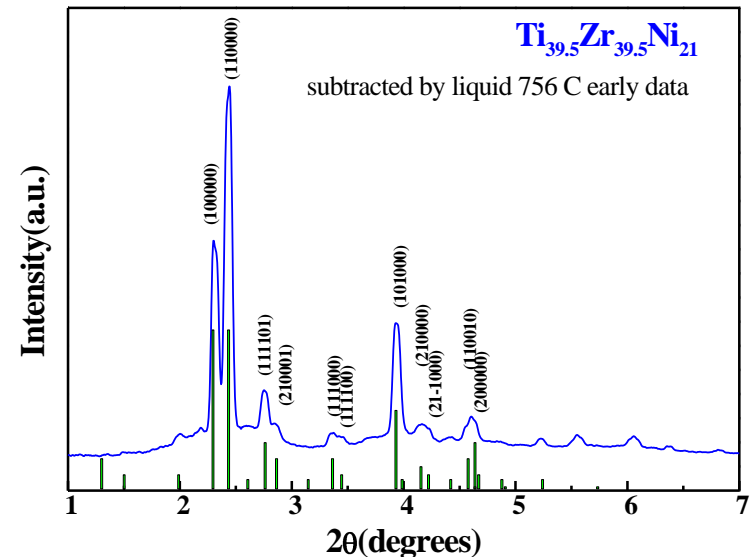
**Pseudo-binary Phase Diagram  
for [Ti]/[Zr] = 1**



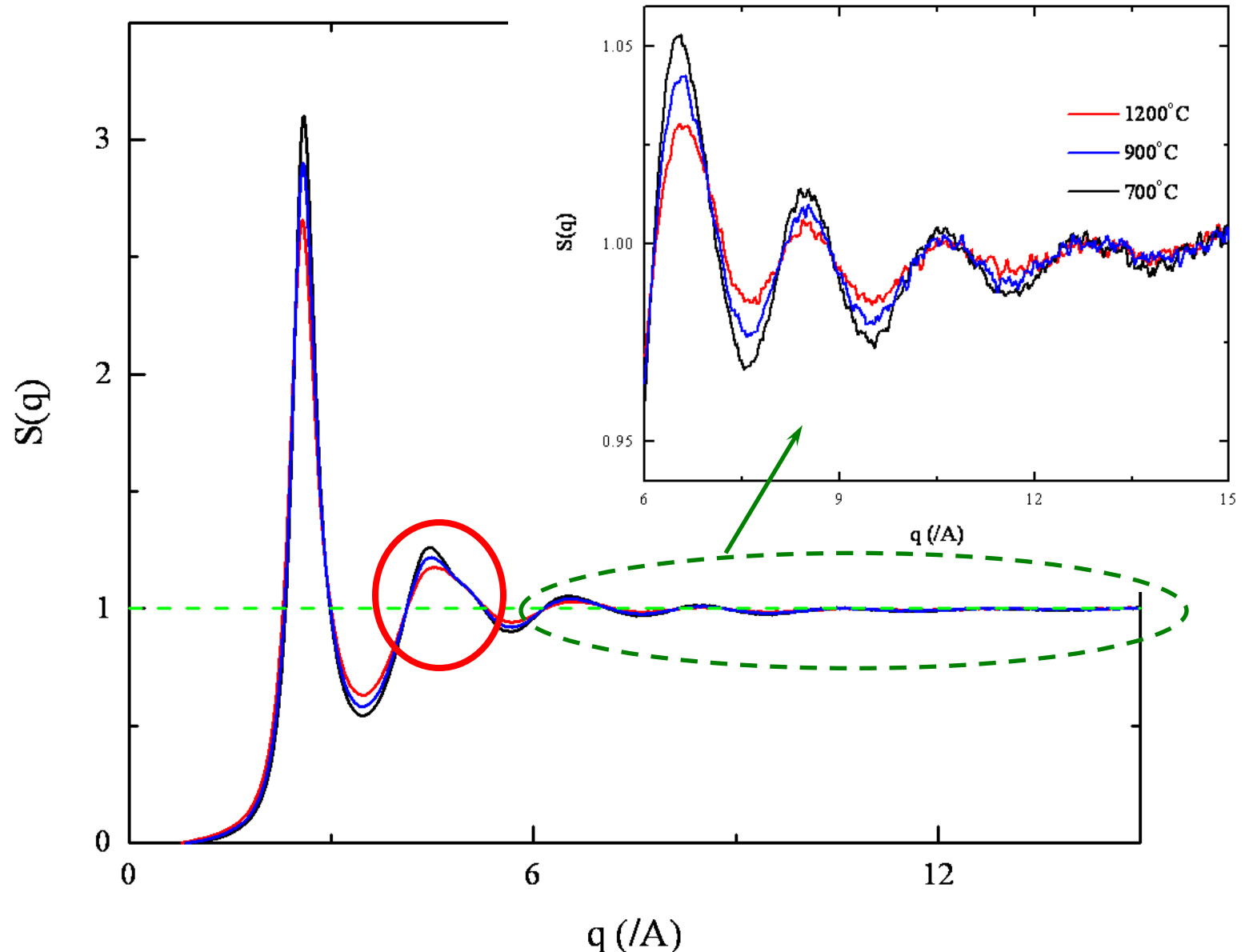
- I-phase forms reversibly from  $\beta$  (Ti/Zr) and C14 Laves phase over 600°C below the liquidus
- Quasicrystal is possible ground-state



**ESL of Liquid During Recalescence**

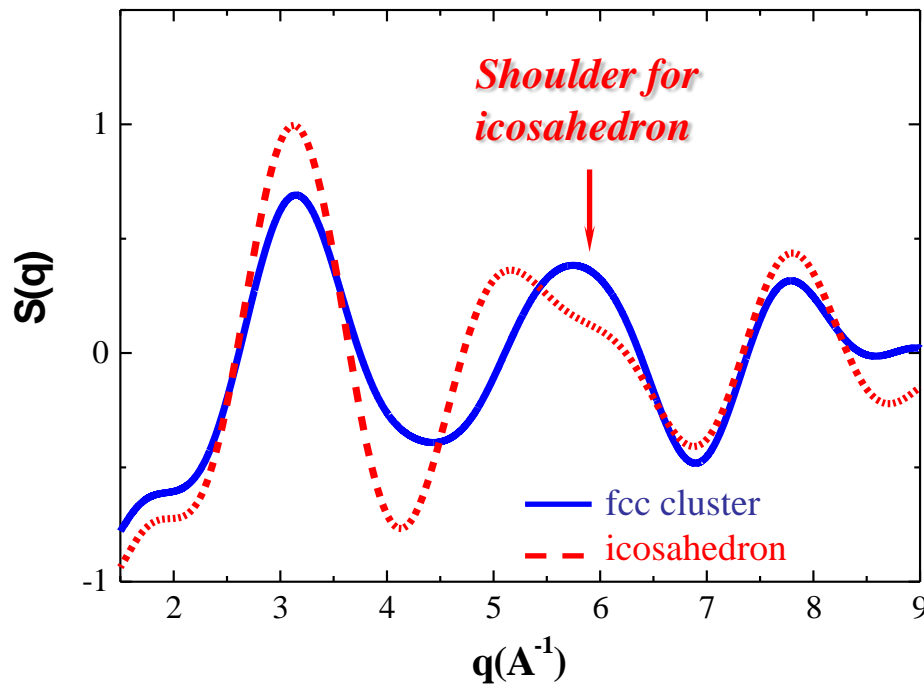
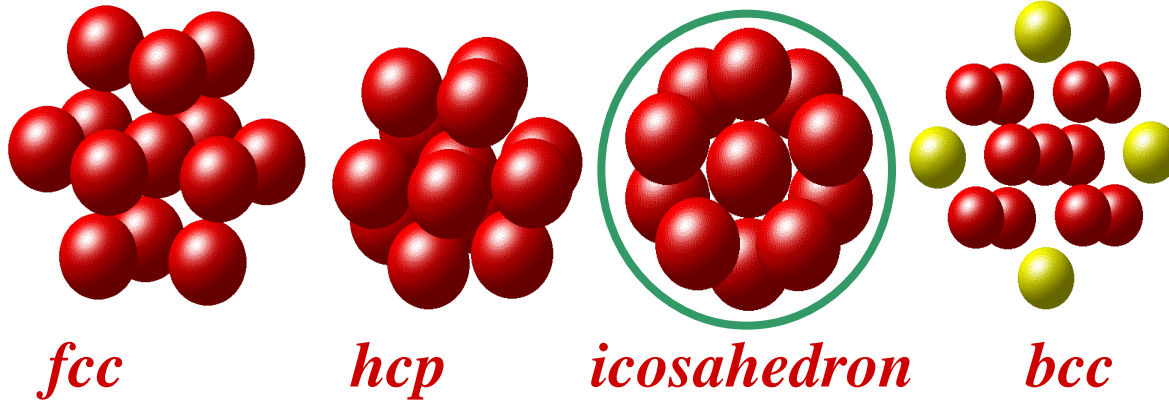


# ESL Diffraction Measure



K. F. Kelton, A. K. Gangopadhyay, G. W. Lee, R. W. Hyers, R. J. Rathz, J. Rogers, M. B. Robinson, D. Robinson, *Phys. Rev. Lett.*, **90**, 195504 (2003).

# Assuming a Dominant Cluster $\Rightarrow$ Icosahedral Ordering in the Liquid



Ratios of  $S(q)$  peak positions:

$$q(2\text{nd})/q(1\text{st}) = 1.74 \pm 0.01$$

$$q(\text{shoulder})/q(1\text{st}) = 1.95 \pm 0.01$$

Perfect icosahedron\*:

(\*S. Sachdev and D. R. Nelson, *PRL* **53**, 1947 (1984).)

$$q(2\text{nd})/q(1\text{st}) = 1.71$$

$$q(\text{shoulder})/q(1\text{st}) = 2.04$$







# Going Beyond the Single Cluster Model

## Reverse Monte Carlo (McGreevy)

- Iteratively refines 3-d structural model of system from structural measurements
- Can combine results from x-ray and neutron diffraction, EXAFS, NMR, etc.

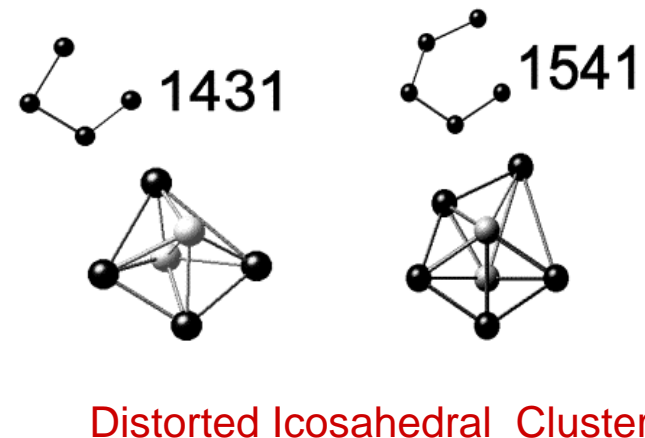
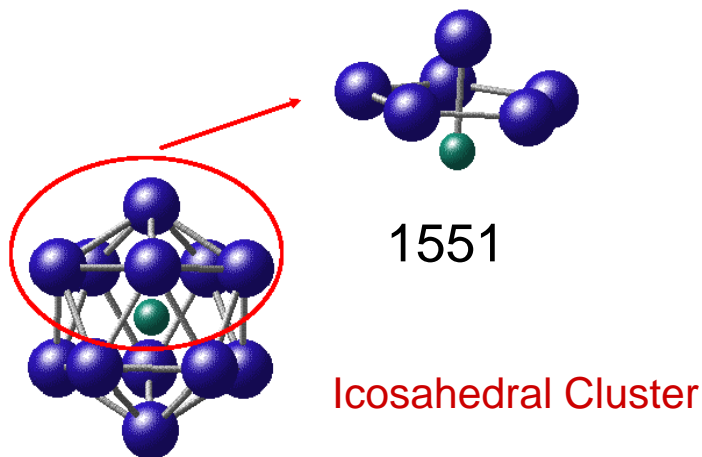
## Bond Orientational Order Parameter Analysis (Steinhardt *et al.*)

- Calculate bond angles ( $\theta$  and  $\phi$ ) between atom at center of cluster and vertex atoms
- Express as average order parameter in terms of spherical harmonics

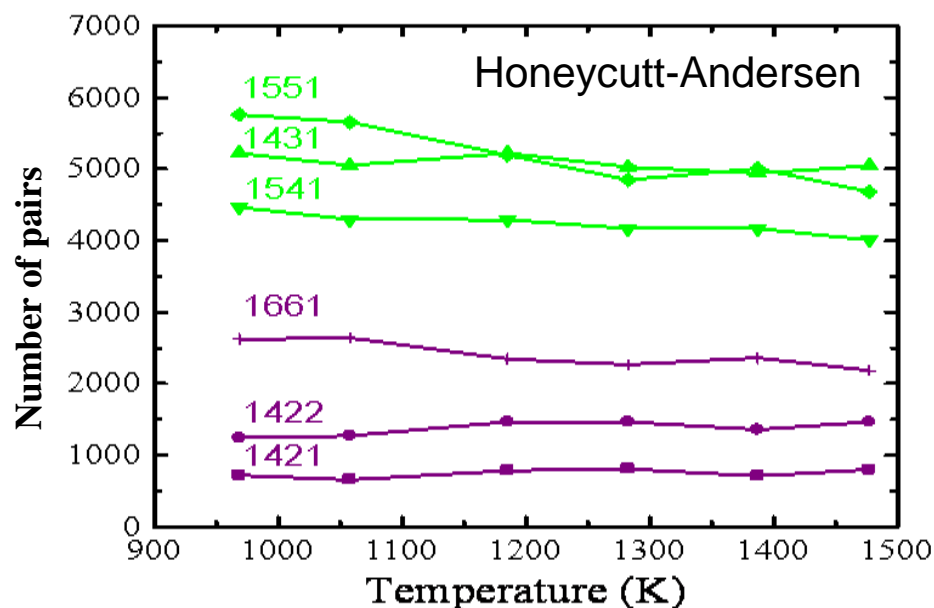
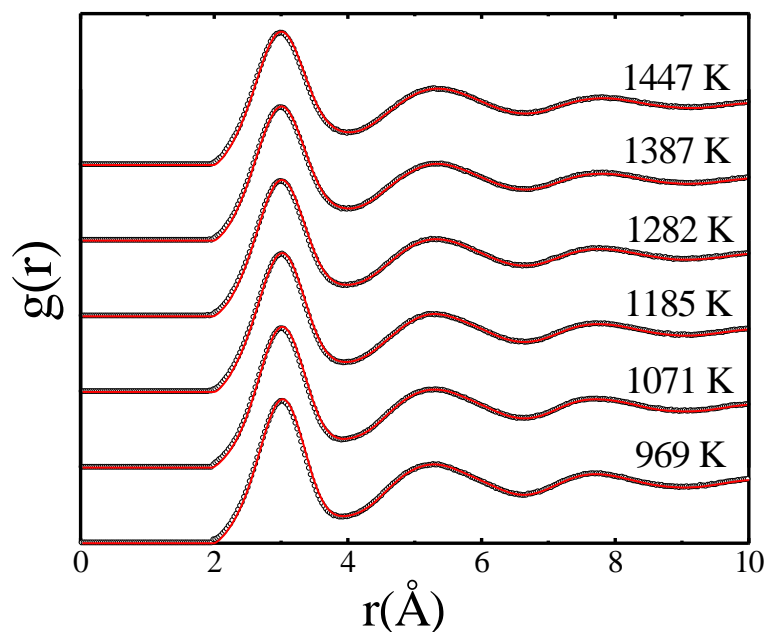
$$Q_l = \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^l |\overline{Q}_{lm}|^2 \right]^{1/2} \quad \text{where} \quad \overline{Q}_{lm} = \frac{1}{N_b} \sum_{\text{bonds}} Y_{lm} \left( \theta(\vec{r}), \phi(\vec{r}) \right)$$

- Icosahedral order –  $Q_6$

## Honeycutt Andersen Indices (local topology in terms of 4 indices)



# Results from RMC Fits

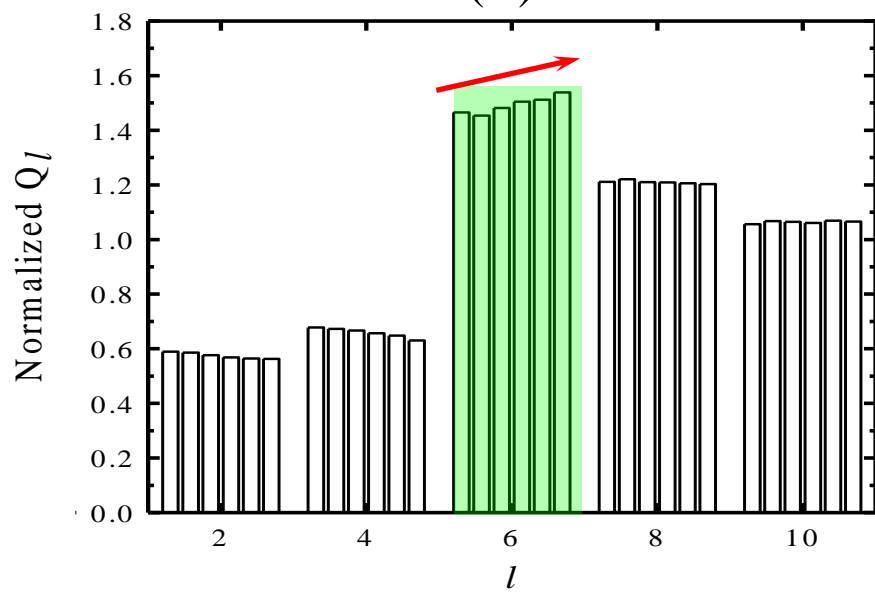


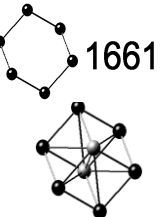
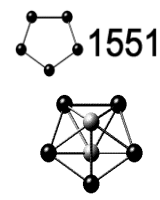
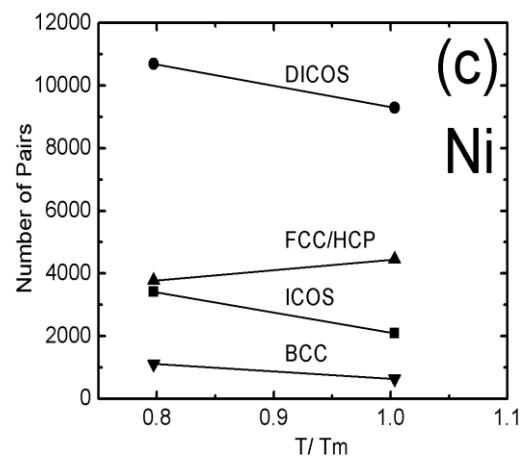
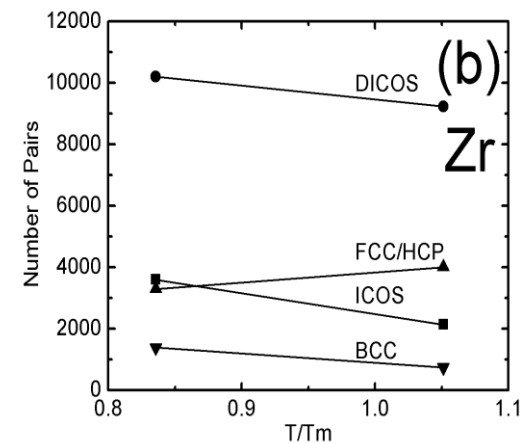
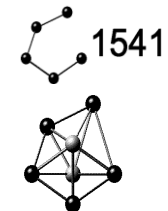
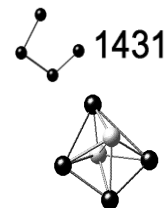
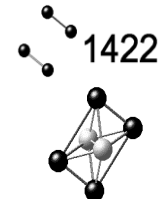
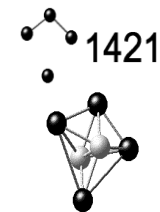
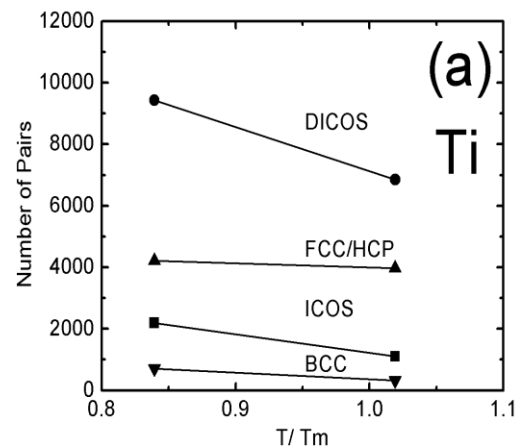
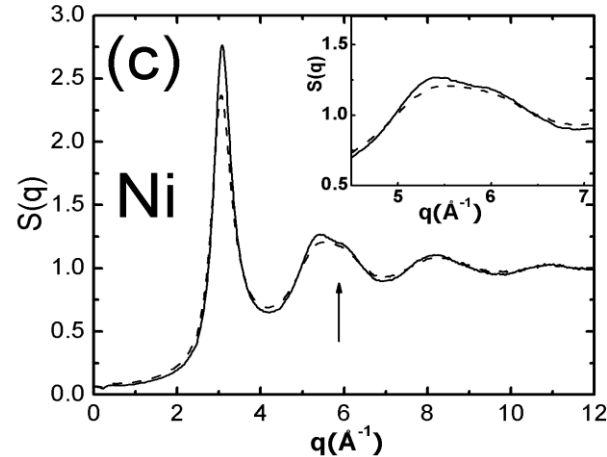
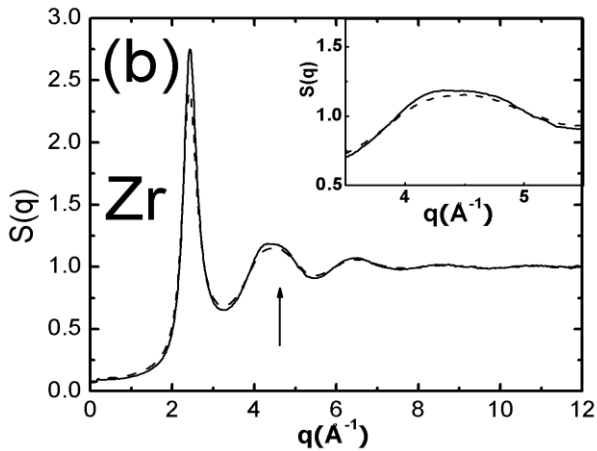
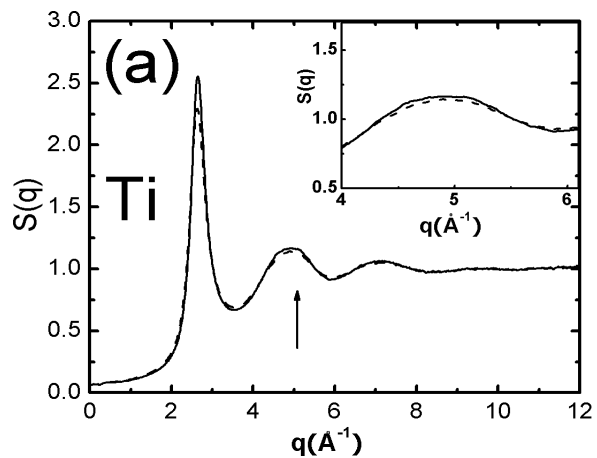
## Honeycutt Andersen Indices

- Icosahedral order is greatest
  - 1551 (pure)
  - 1431 and 1541 (distorted)
- Icosahedral order increases with supercooling
- Significant fraction of crystal order (bcc)

## Bond Orientational Order

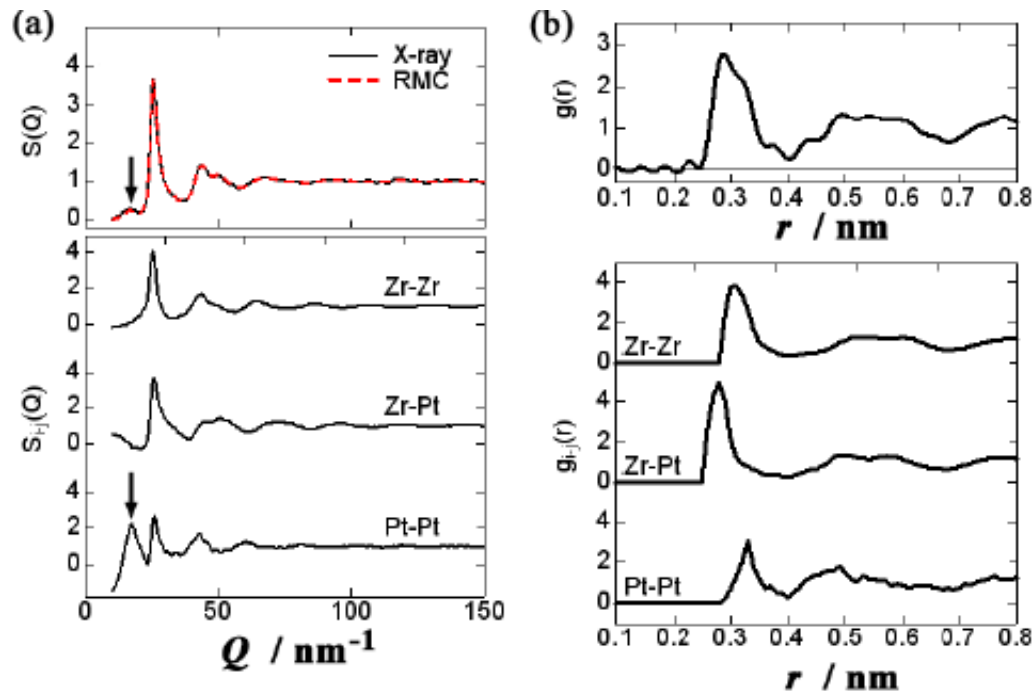
- Q6 – measure of icosahedral order
- Q6 increases with supercooling
- All others decrease





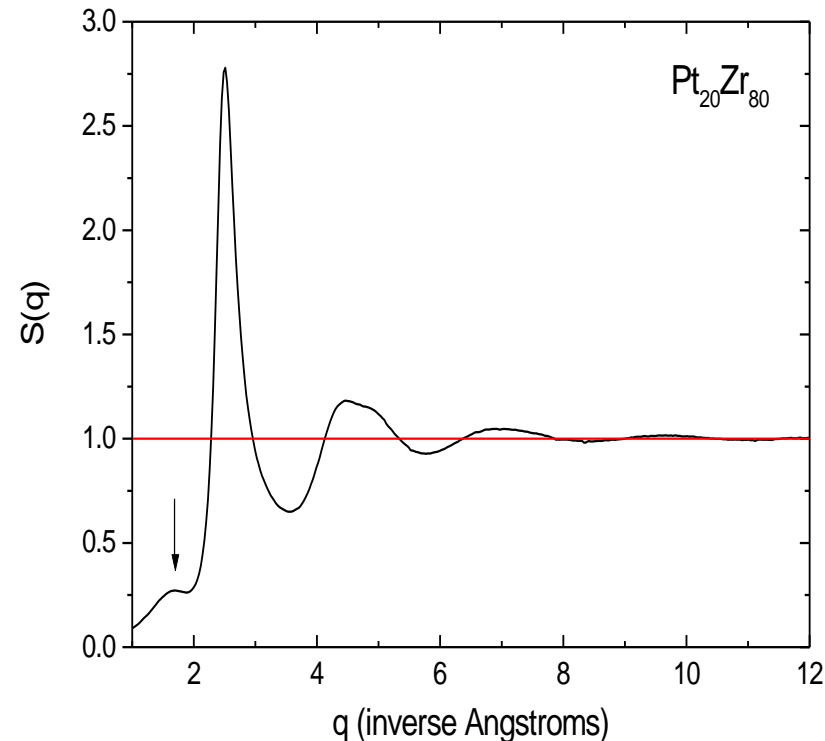
# Prepeak in $S(q)$ – Medium-Range Order

Zr<sub>80</sub>Pt<sub>20</sub> Metallic Glass



- Prepeak at 17 nm<sup>-1</sup> - medium-range ordering
- Pt-Pt Ordering
- Icosahedral Ordering (Voronoi polyhedron analysis)

Zr<sub>80</sub>Pt<sub>20</sub> Liquid



- Same prepeak in liquid
- RMC analysis also indicates Pt-Pt ordering and HA analysis indicates icosahedral ordering
- Due to very strong negative heat of mixing between Zr and Pt

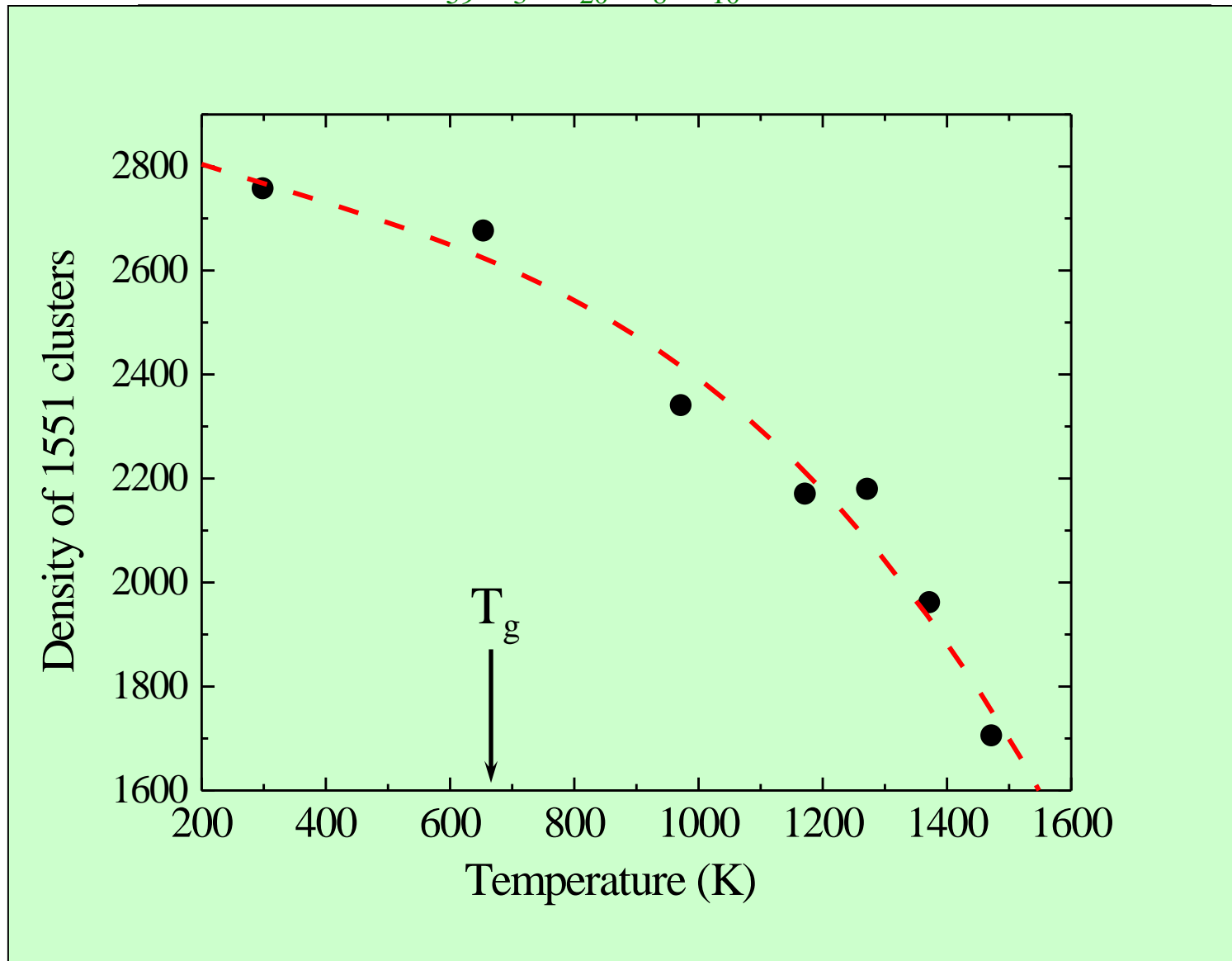
N. Mauro and K. F. Kelton private comm.



# ***A Few Selected Case Studies***

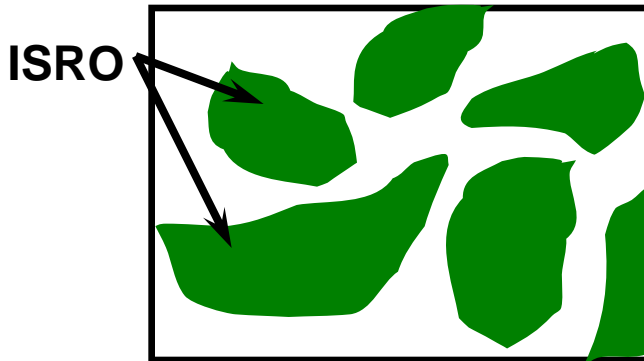
- Liquid/liquid phase transition in silicon?
- Possible chemical ordering in liquid Cu-Zr
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  - In glasses
  - In liquids
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  - Alloying and glass formation
- Anomalies in thermophysical properties of transition metal liquids - possible phase transitions associated with ordering?

# *Synchrotron High Energy X-Ray Diffraction Studies*

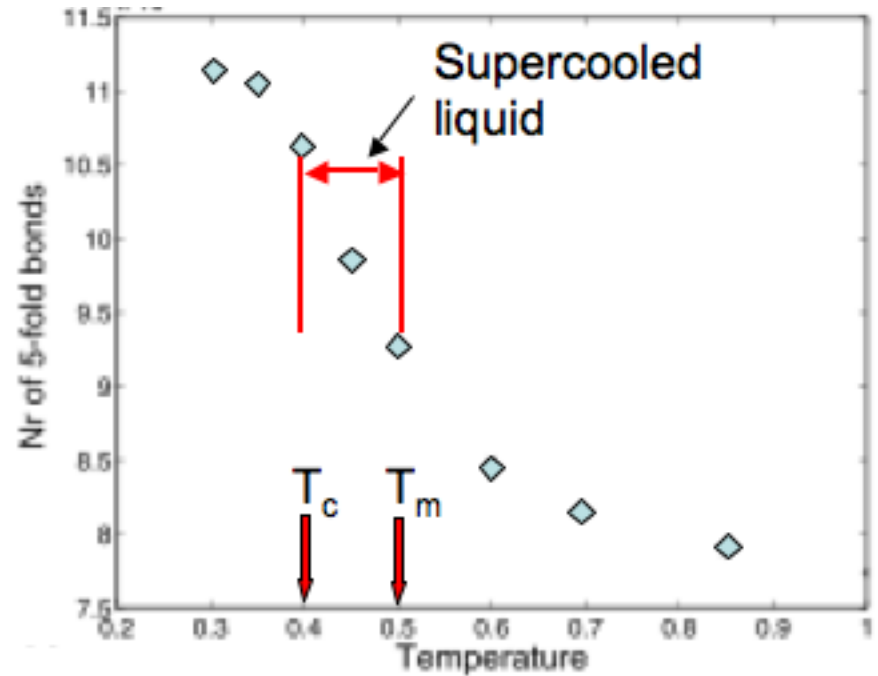


# The Glass Transition

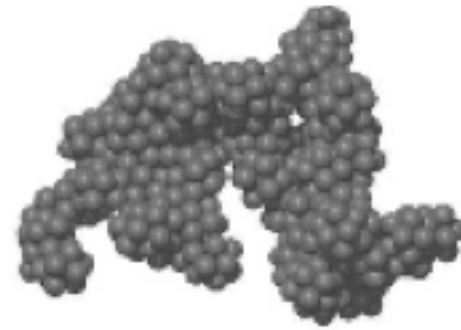
- Geometrical frustration



- ISRO - geometrical fluctuation



$T = T_m$



$T \sim T_c$

- MD Calculations - LJ potential
- Cluster extent  $>$  container as  $T \rightarrow T_c$
- Resembles percolating bond network

# ***A Few Selected Case Studies***

- Liquid/liquid phase transition in silicon?
- Possible chemical ordering in liquid Cu-Zr
- Ordering in amorphous metals
  - In glasses
  - In liquids
  - Icosahedral ordering and the glass transition
  - Alloying and glass formation
- Anomalies in thermophysical properties of transition metal liquids - possible phase transitions associated with ordering?

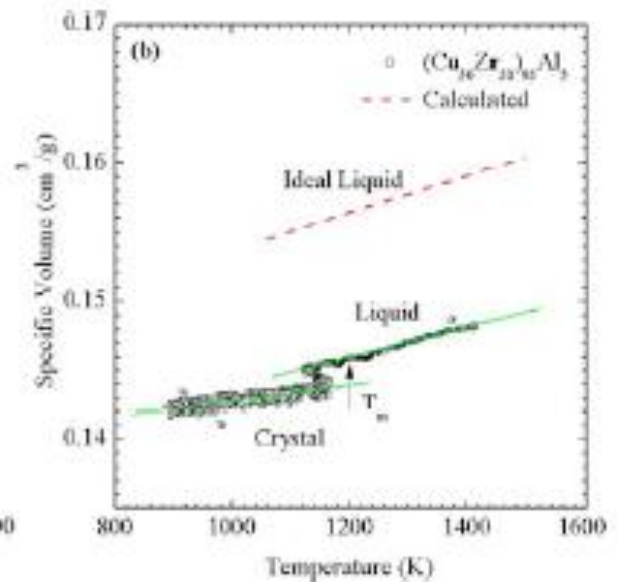
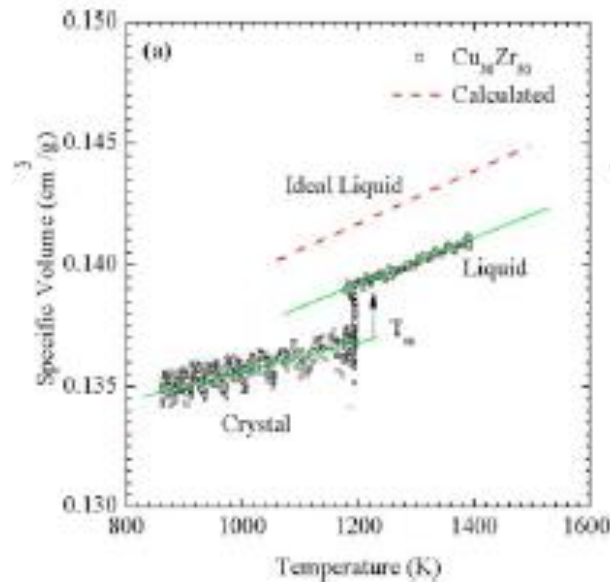
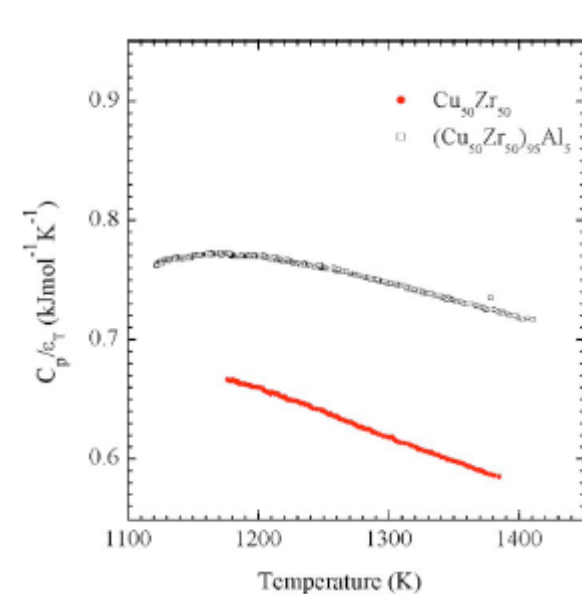
# Addition of Al to Cu-Zr

Fan et al, APL, **89**, 241917 (2006)

- Addition of 5 at.% Al for Cu/Zr improves glass formation

Increases  $C_p/\varepsilon$

Decreases volume from rule of mixtures AND difference between crystal and liquid phases



- And increases viscosity

**Addition of Al causes structural modifications in the liquid – stabilizing the liquid and improving glass formability**



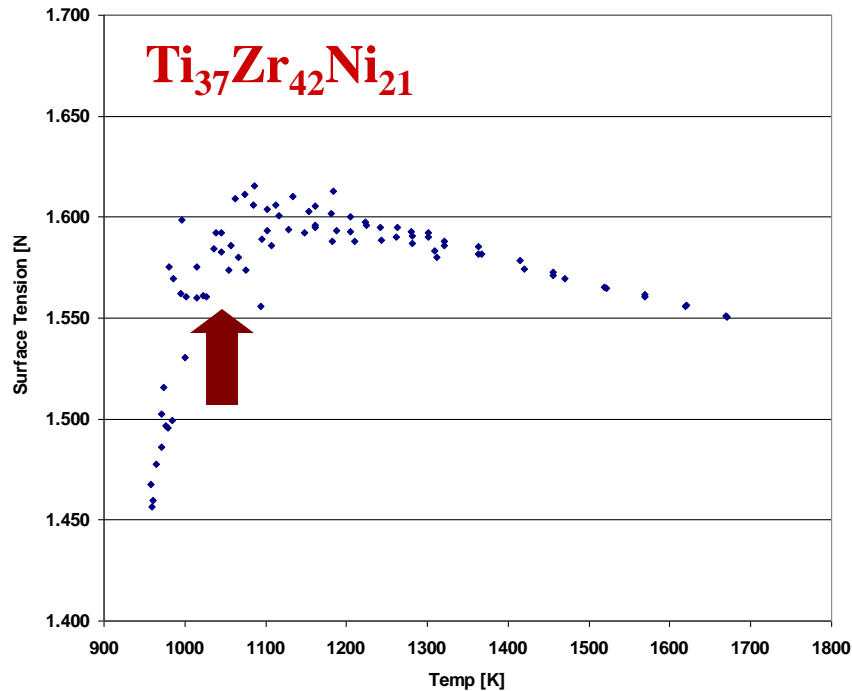
# ***A Few Selected Case Studies***

- Liquid/liquid phase transition in silicon?
- Possible chemical ordering in liquid Cu-Zr
- Ordering in amorphous metals
  - In glasses
  - In liquids
  - Icosahedral ordering and the glass transition
  - Structure and Glass Formation
- Anomalies in thermophysical properties of transition metal liquids - possible phase transitions associated with ordering?

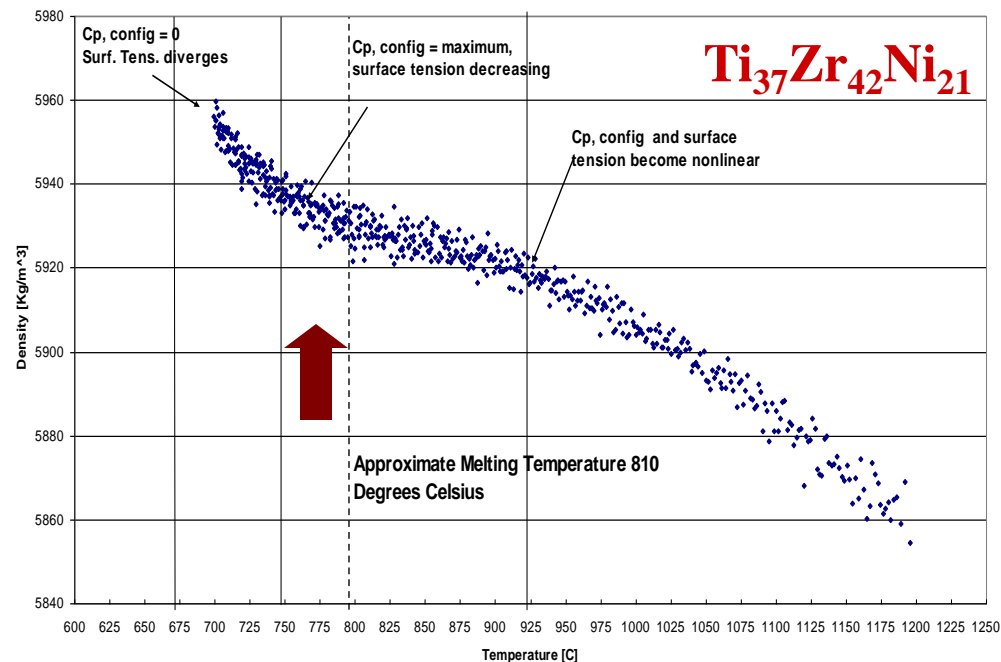
# Thermo-physical Properties of Supercooled Liquid

R. W. Hyers, R. Bradshaw,  
U. Mass

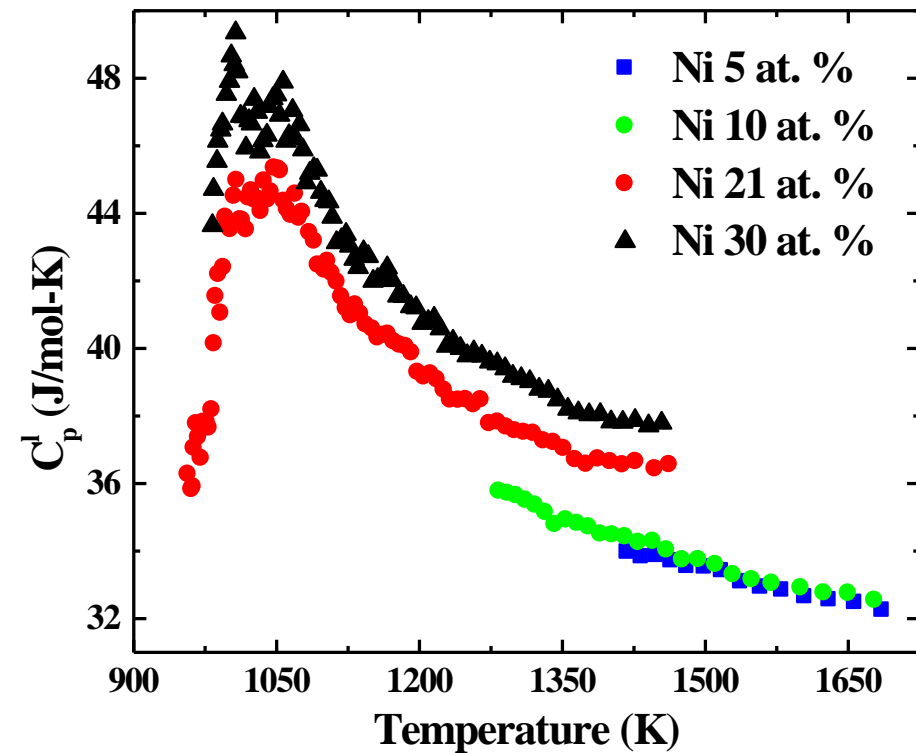
**Dramatic decrease in  
surface tension – indicates  
chemical surface segregation**



**Density Inflection** →



# Thermo-physical Properties of Supercooled Liquid

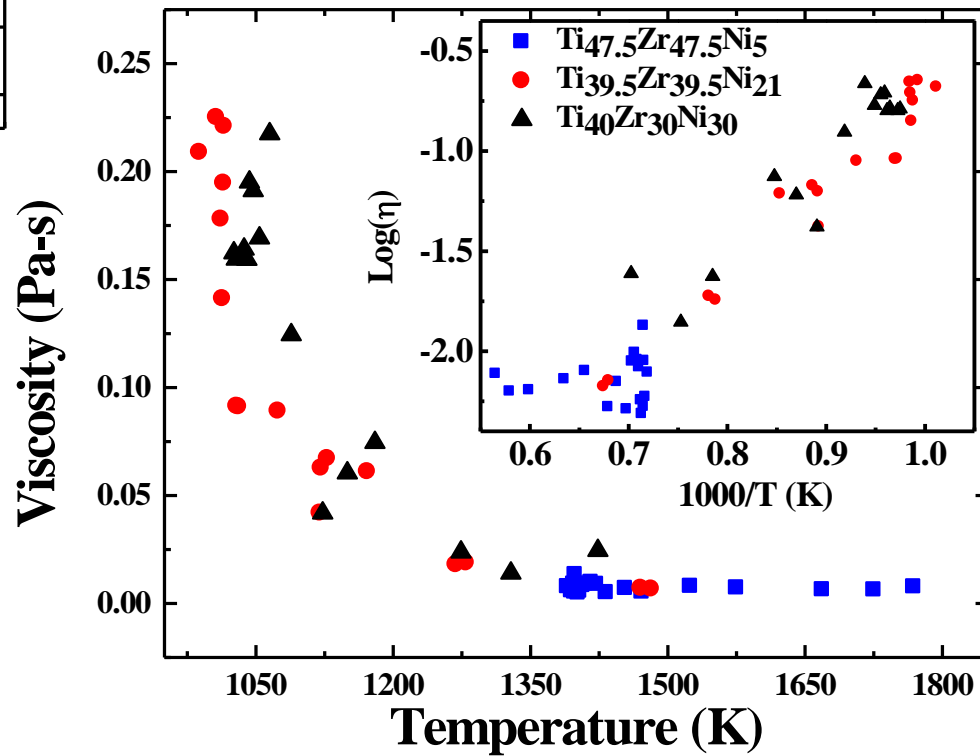


*Specific heat maximum*

*Issues with noise, emissivity - under investigation ...*

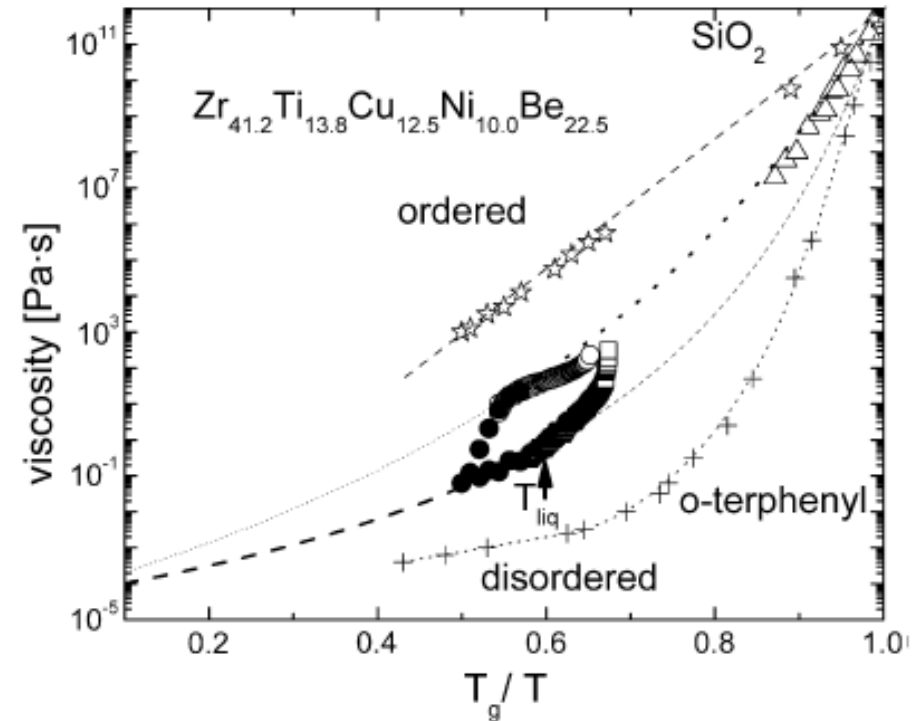
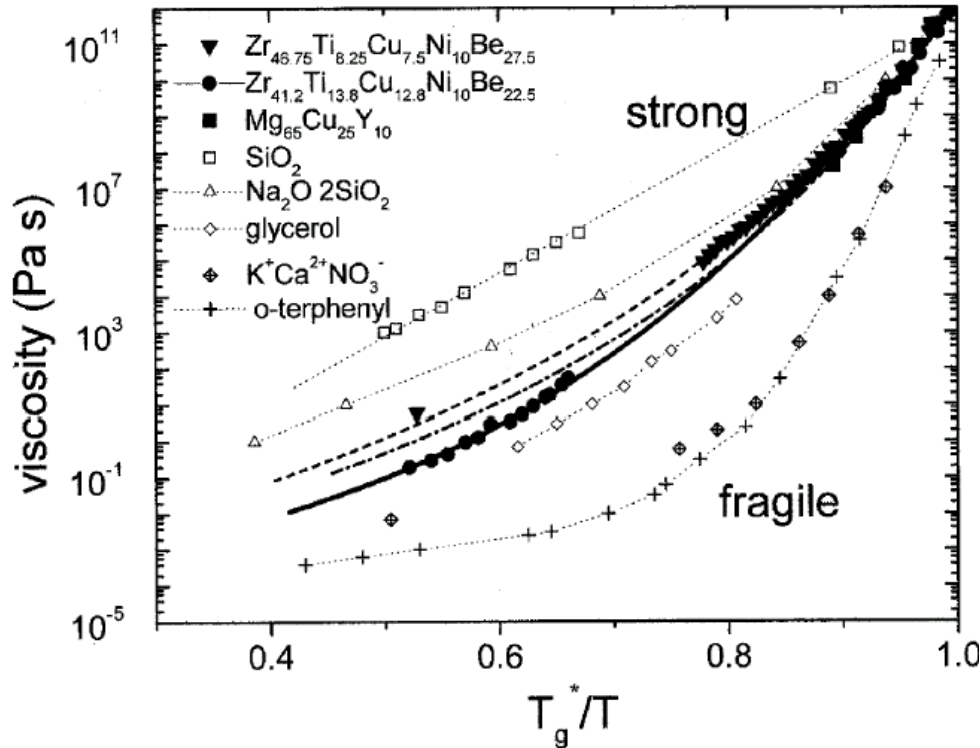


*Rise in viscosity*



*R. W. Hyers, R. Bradshaw, G. W. Lee,  
A. Gangopadhyay, J. Rogers, K. F. Kelton.*

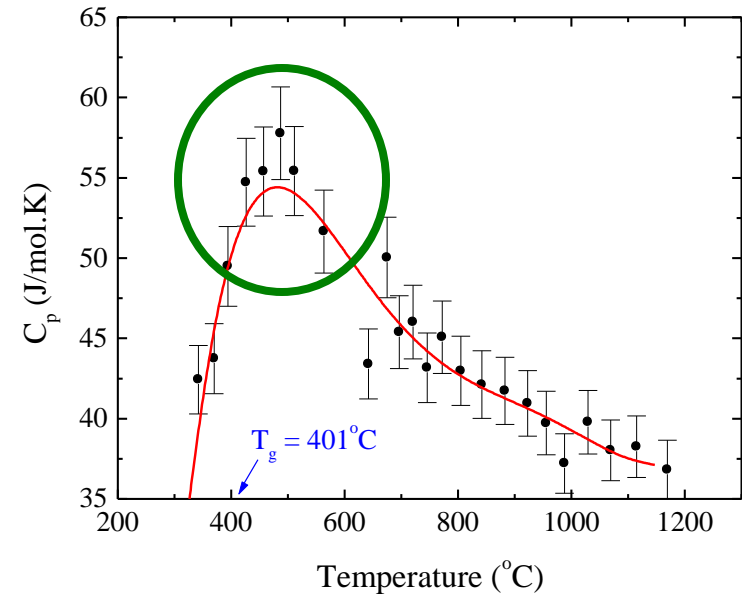
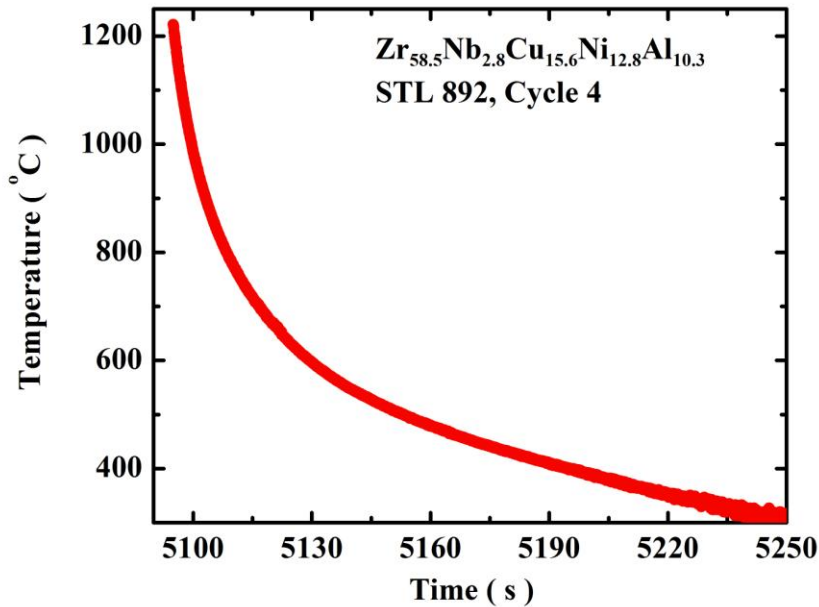
# Strong - Fragile Transition in Vit106a



- Fragility proposed by Angell (C. A. Angell, "Relaxation in Complex Systems" US Dept of Commerce, Springfield (1985)).
- Viscosity
  - strong glasses - Arrhenius behavior
  - fragile glasses – non-Arrhenius more collective process
- Metallic glasses fall in between

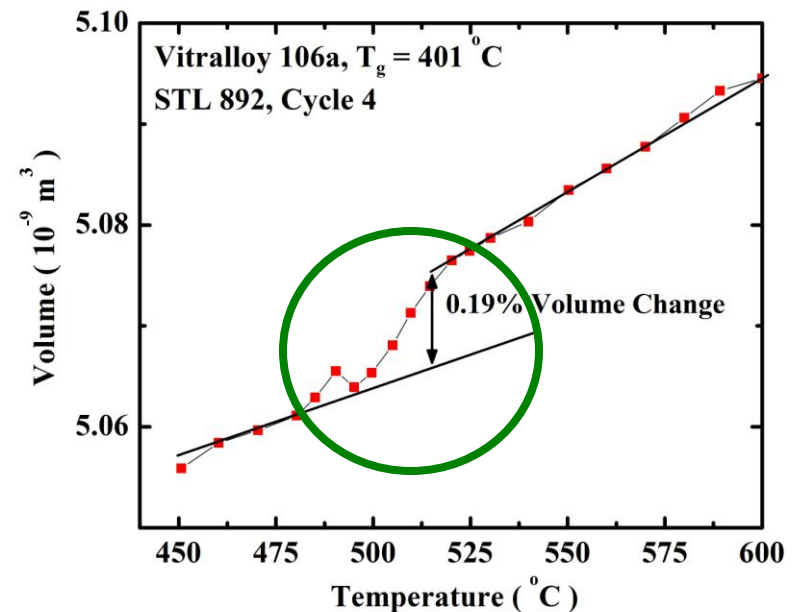
- In Vit106a observe hysteresis
- Strong behavior on initial heating from glassy state
- Transforms to more fragile state on further heating (completed above 1225K)
- Speculated that strong to fragile transition due to destruction of local order

# Thermo- physical Properties of Supercooled Vit 106a



- No evidence for recalescence in time-temperature plot (formed glass)
- Broad specific heat maximum -  

$$mC_p(dT/dt) = 4\pi r^2 \sigma \epsilon (T^4 - T_o^4)$$
- Volume/density anomaly near specific heat maximum





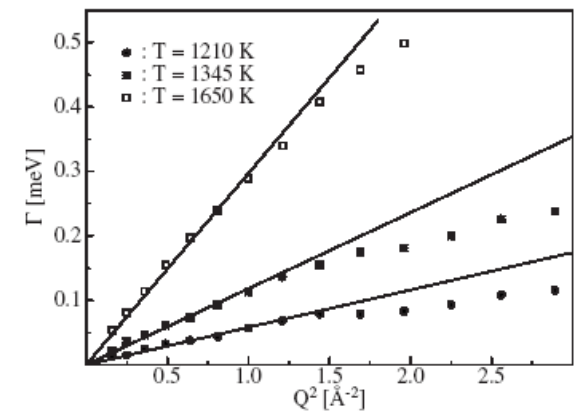
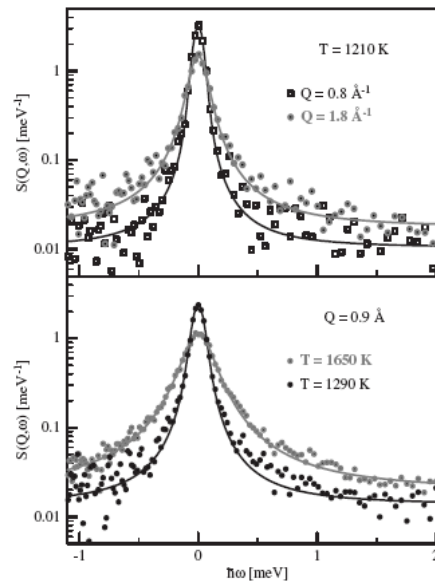
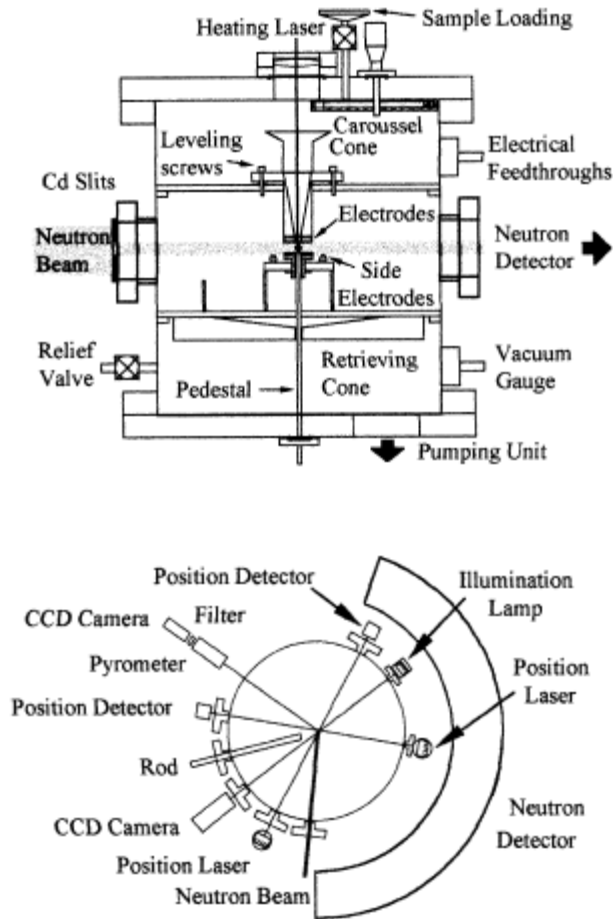
# ***Summary and Conclusions***

- New experimental techniques are allowing deeper investigations of amorphous structures
- Both liquids and glasses show distinct short-range order and in some cases even medium range order
- Evidence for novel liquid/liquid phase transitions
- Neutron studies of liquids - an emerging area

# Coming - Neutron Diffraction Studies of Liquids

## Example\*

- Obtain partial structure factors (isotopic substitution)
- Quasielastic and inelastic scattering studies (information on dynamical effects and diffusion)



Small momentum transfer –

$$\Gamma = 2\hbar D_{\text{Ni}} Q^2$$

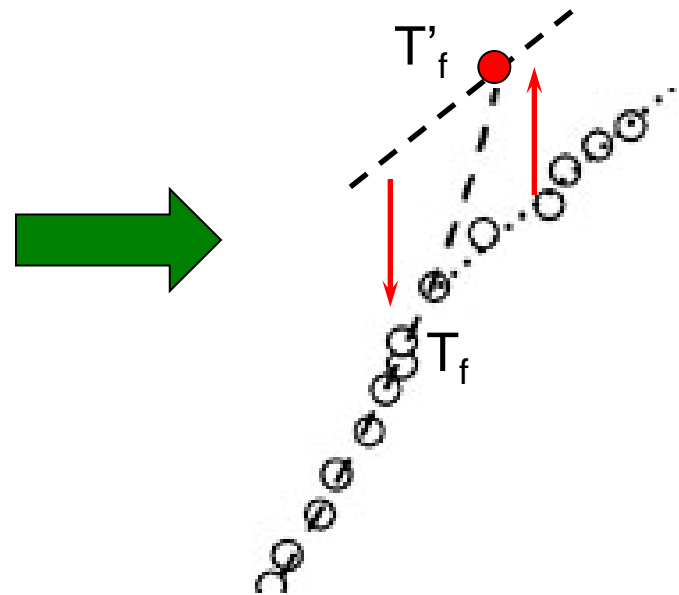
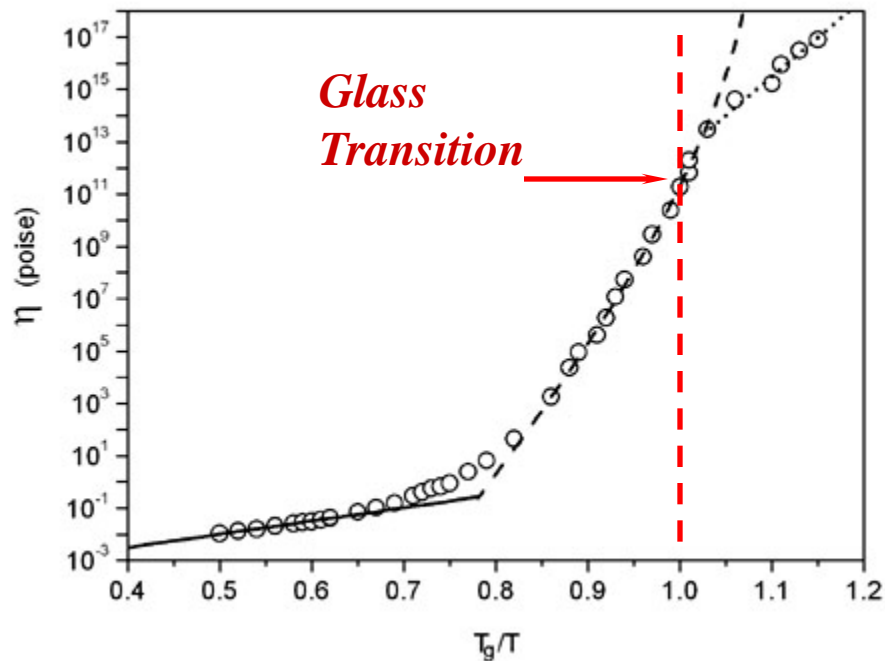
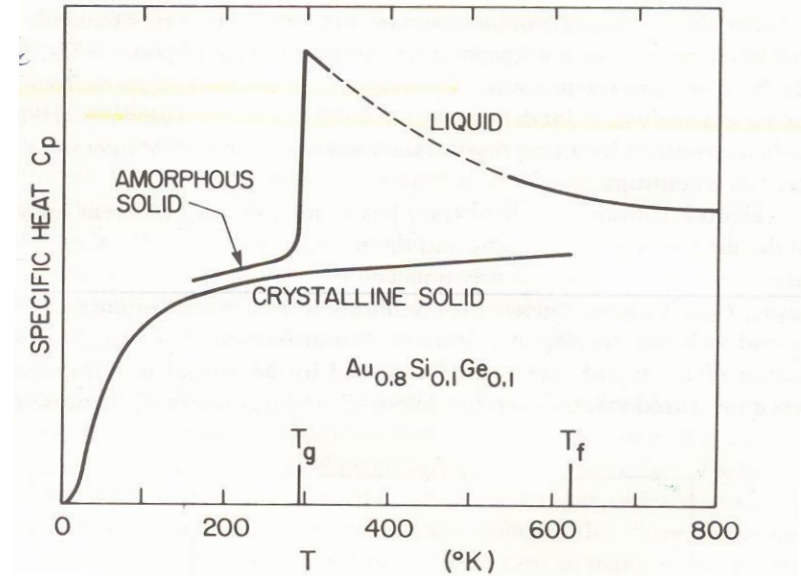
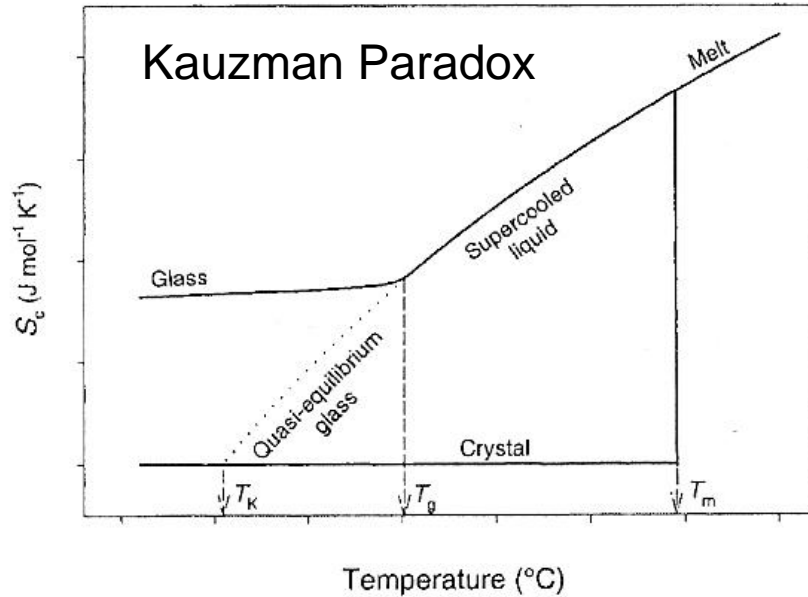
- $D \propto T - T_c$  - agrees with prediction from mode coupling
- Large activation energy for Ni diffusion reflects chemical short range ordering (not icosahedral)

\*D. Holland-Moritz, Phys. Rev. B., **79**, 064204 (2009)

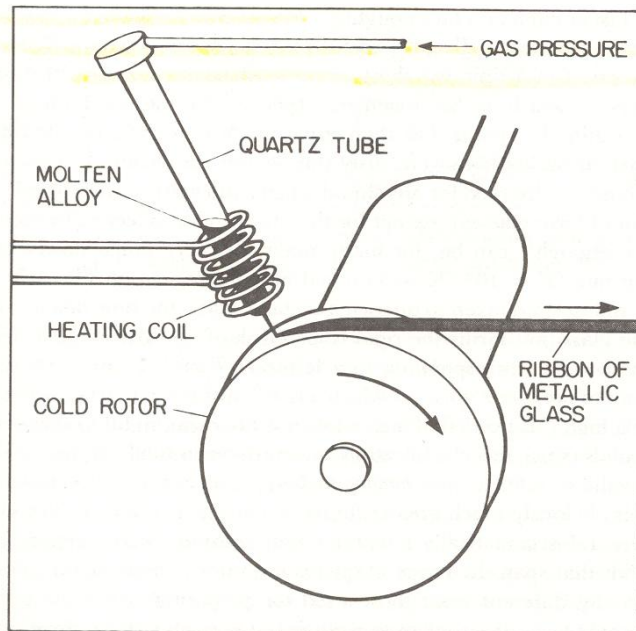
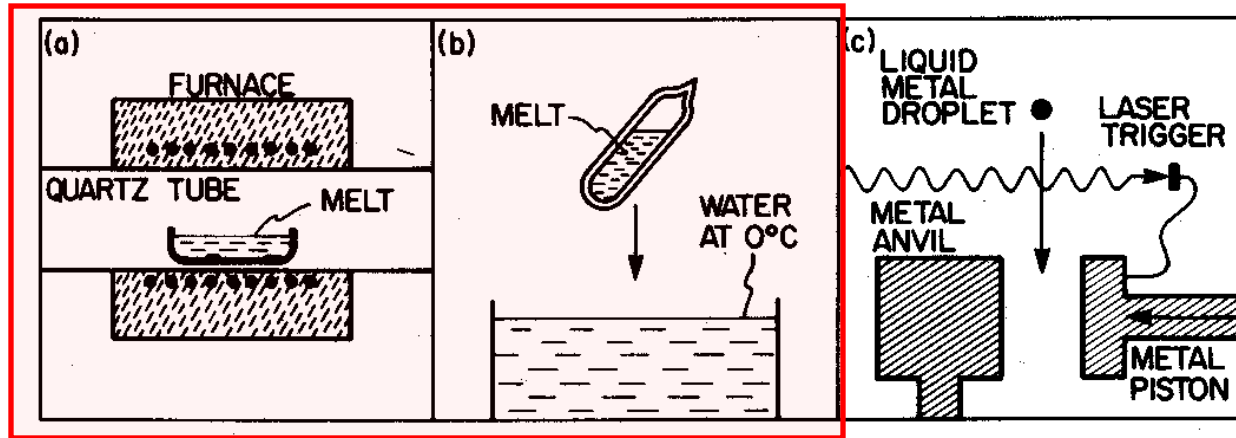
P.-F. Paradis et al., J. Non-Cryst. Solids, **312-314**, 309-313 (2002)



# The Glass Transition



# Glass Formation - Cool the Liquid Quickly



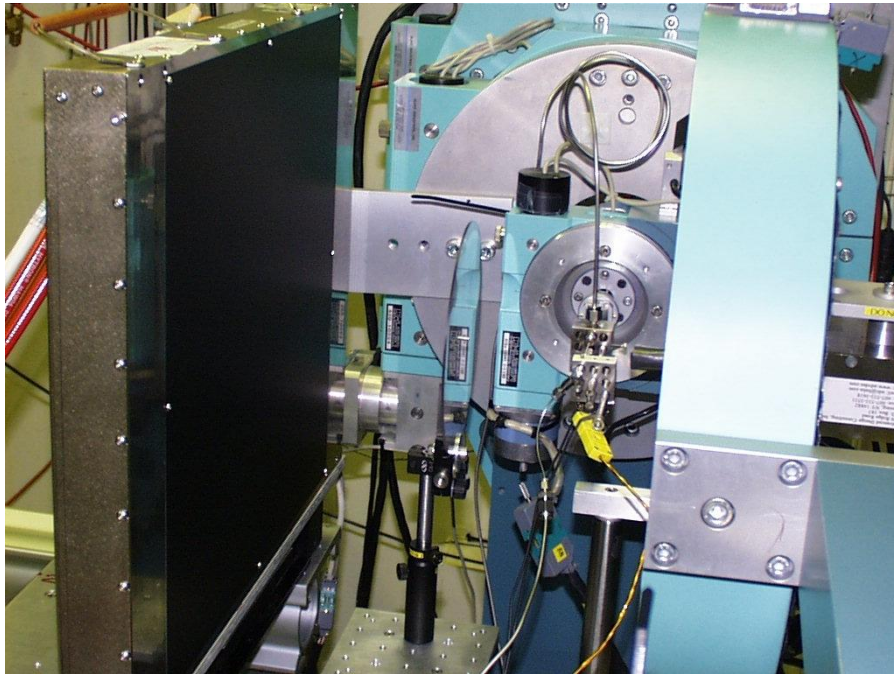
**Melt Spinning – Most common for formation of early metallic glasses**  
**Now Bulk Metallic Glasses (BMG)– cooling rates like traditional silicate glasses**



# *Area Detectors*

- Image Plate (IP) allows rapid acquisition of diffraction patterns
- Example - MAR3450

## *General Electric Medical Systems Radiography Detector*



- **Faster than IP – up to 30 patterns per second**
- Smaller dynamic range than IP
- Higher background (dark current) than IP.

