Liquid and Glass Structures & Their Influence on Phase Transitions

K. F. Kelton

Department of Physics &
Center for Materials Innovation
Washington University
St. Louis, MO 63131

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WHERE DISCOVERIES BEGIN

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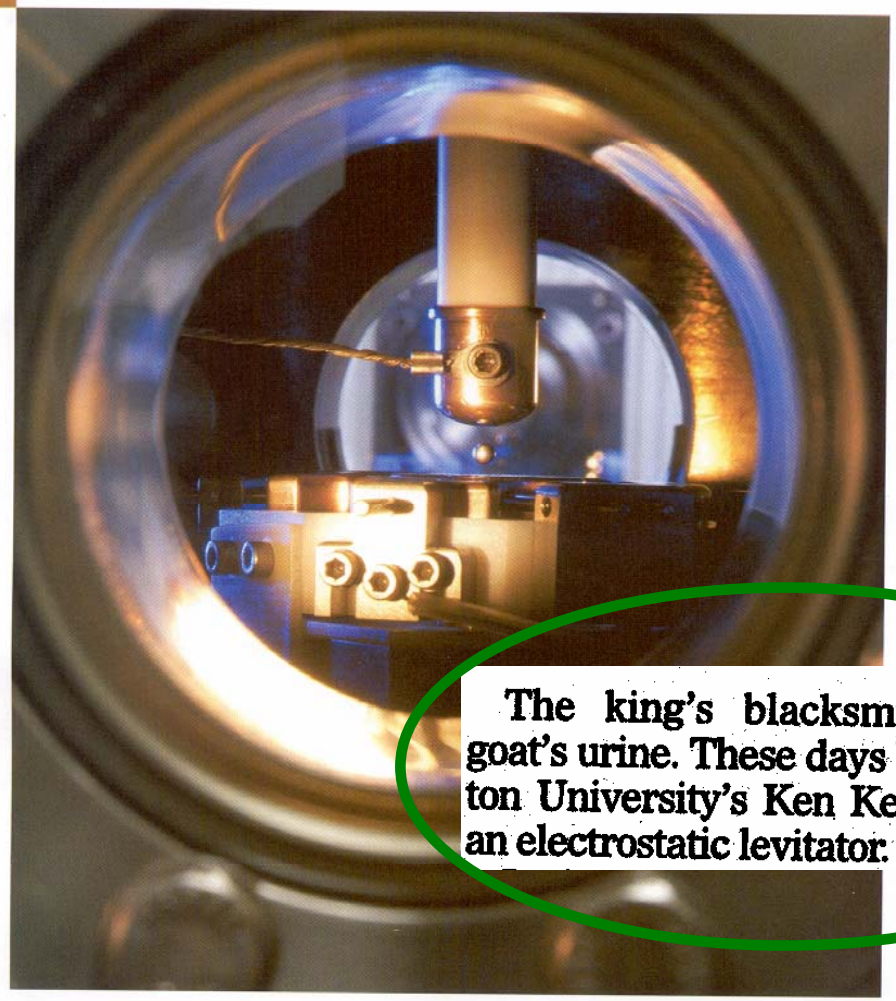
JULY 2003

PHYSICS TODAY



Targeting molten metals

The king's blacksmith used goat's urine. These days Washington University's Ken Kelton uses an electrostatic levitator.

WU team's quasicrystal research gets notice nationally

Findings could help with fuel cells in cars, prolong artificial joints

BY ANGELA VIERLING
Of the Post-Dispatch

The king's blacksmith used goat's urine. These days Washington University's Ken Kelton uses an electrostatic levitator.

In both cases, the two were trying to control a process called crystallization to make a better product. The smithies wanted to make better swords. Kelton's research could have an impact on matters as diverse as energy consumption and the manufacture of artificial joints. It's featured on the cover of the July issue of Physics Today

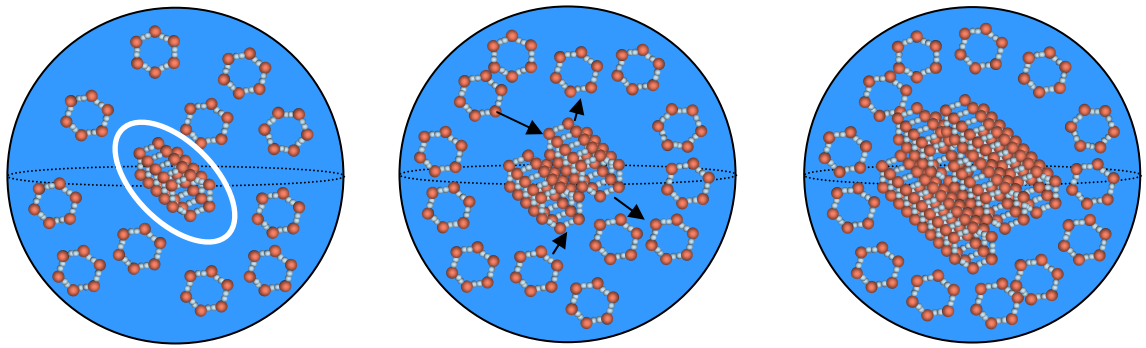
St. Louis, Post Dispatch, July, 2003

Outline

- Nucleation background
- Ordering in metallic liquids
- Coupling processes in nucleation
- Ordering and the glass transition
- Future directions
- Conclusion

It Starts with Nucleation

- First step in most first-order phase transitions
- Homogeneous nucleation – random in time and space

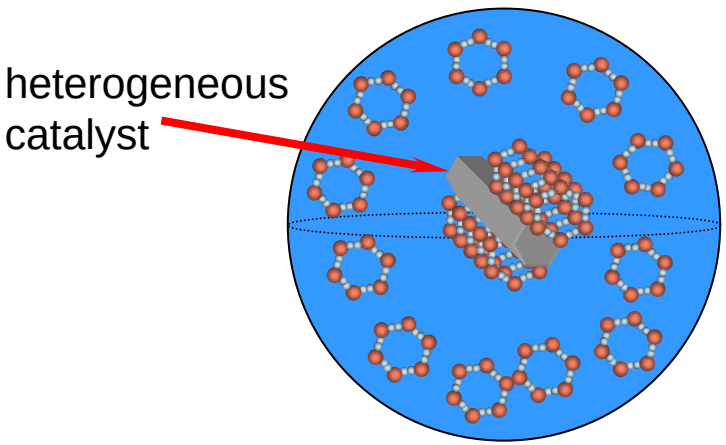


Crystal nuclei form by chance aggregation

Crystal nuclei grow and shrink (stochastic)

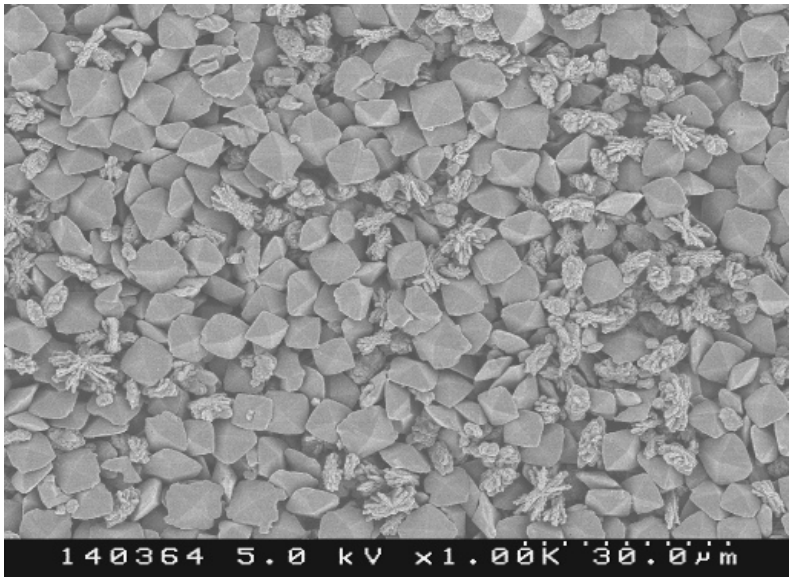
Critical size – then quickly grows

- Heterogeneous nucleation – random in time but not space



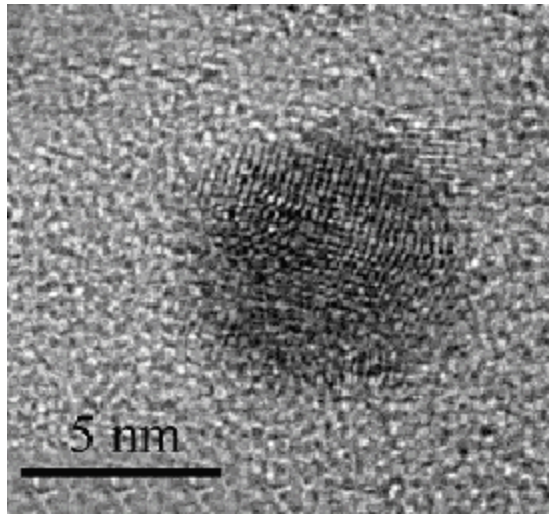
- *Nucleation catalyzed by foreign substances*
- *Lower nucleation barrier*
- *Most common type of nucleation*
- *Practical uses*
  - *Seeding of clouds*
  - *Grain refinement (smaller grain sizes)*
  - *Corning ware – fine grained ceramic*

Nucleation in Medicine



urinary stones

Nanobiotechnology



Au Nanoparticles Alfalfa plants
J. L. Gardea-Torresdey et al.
Nano Letters, ***2***, 397 (2002)

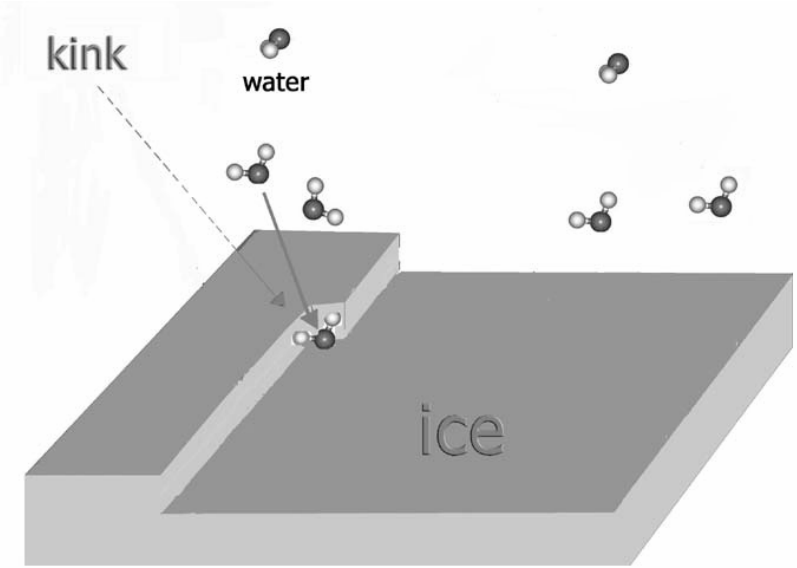
Nucleation in Cosmology

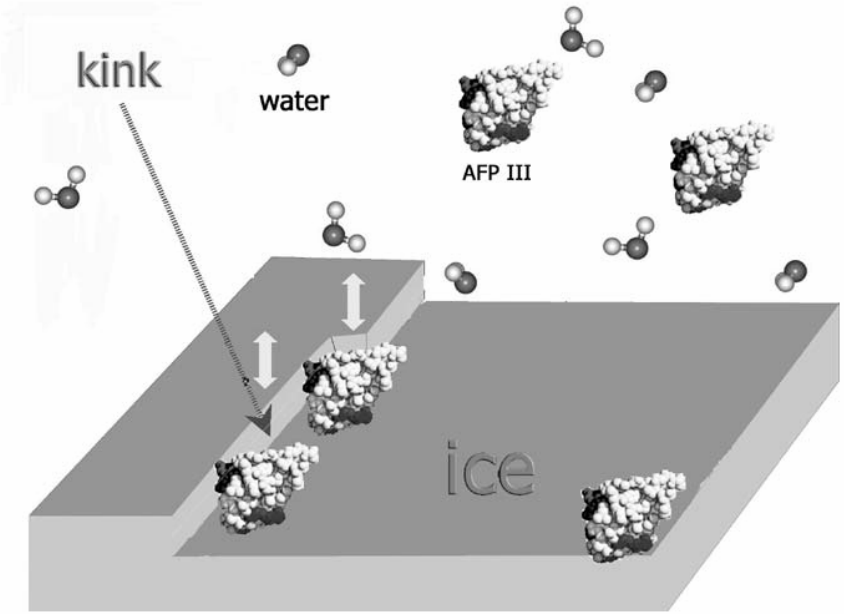
A First Order Phase Transition from Inflationary to Big Bang Universe
GERALD HORWITZ
Annals of the New York Academy of Sciences
Volume 470, Issue Twelfth , Pages380 - 380
1986 The New York Academy of Sciences

Anti-Nucleation/Growth Agents

Dissostichus mawsoni
the Antarctic toothfish

- Melting temperature of blood = - 0.8^{o}C
- Water temperature = -1.9^{o}C
- Antifreeze glycoproteins
- Poison growth sites



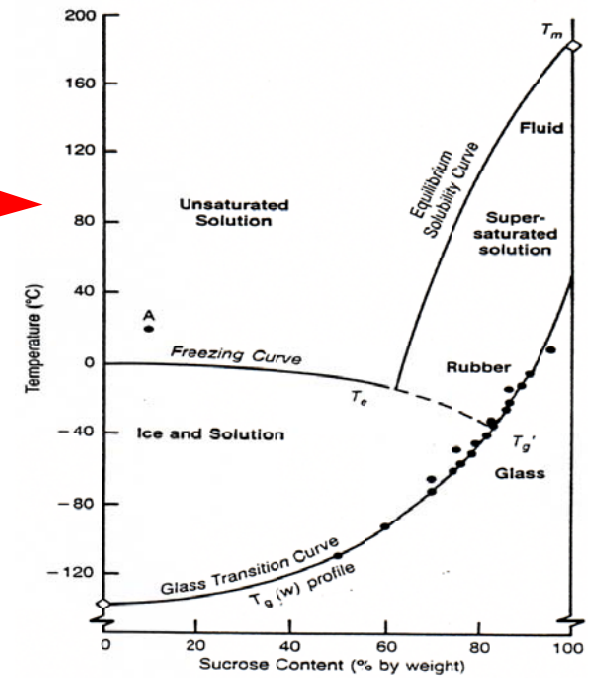


Promotion of the Nucleation of Ice

Northern Wood Frog

Rana sylvatica

- only frog north of Artic Circle
- in winter completely solid, 65% ice
- Ice nucleating agent
  - promotes freezing outside cell
  - draws water from cells by osmosis
  - cells congeal into glass



Gabriel Fahrenheit (1686 – 1736)

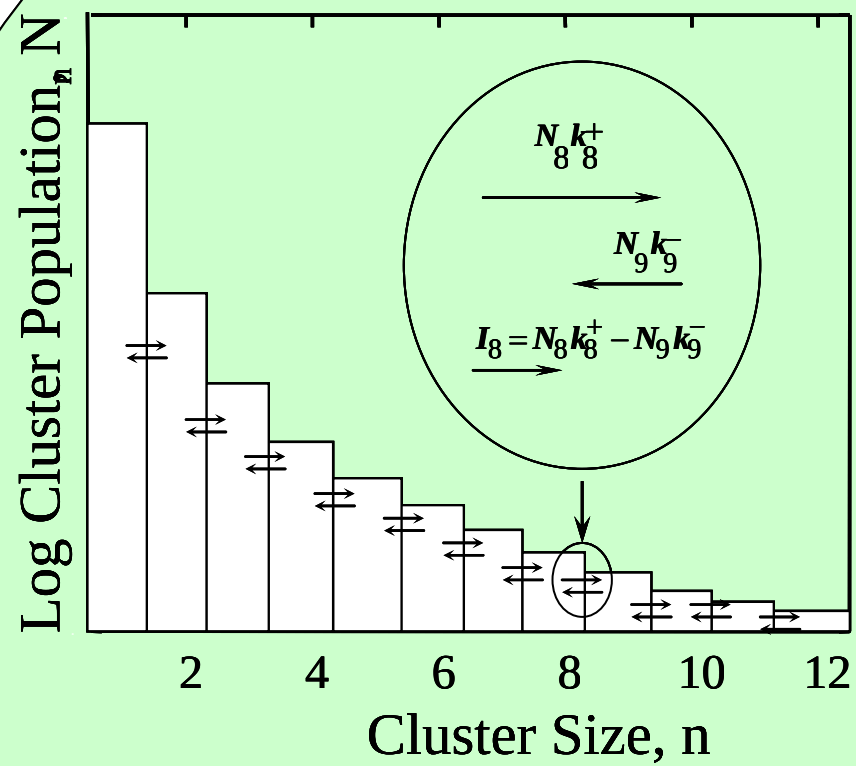
1721 – discovered ***supercooling*** *of water,* ***i.e. water is liquid below 32°F***

D.G. Fahrenheit, Proc. Roy. Soc. London **33**, 78 (1724)

VIII. *Experimenta & Obſervationes de Congelat aquæ in vacuo factæ a* D. G. Fahrenh R. S. S.

INter plurima admiranda Naturæ Phœnomena aq rum congelationem non minoris momenti eſſe ſe per judicavi; hinc ſæpe experiundi cupidus fui, qu nam effectus frigoris futuri eſſent, ſi aqua in ſpatio a aere vacuo clauderetur. Et quoniam dies ſecundus, tertius & quartus *Martii*, (Styli V.) Anni 1721. ejuſmodi experimentis favebat, hinc ſequentes obſervationes & experimenta a me ſunt factæ.

Volmer and Weber



$$I_{n,t} = k_n^+ N_{n,t} - k_{n+1}^- N_{n+1,t}$$

$\kappa\, n^{2/3} \sigma$

Energy

er

I … $_{n*}\, k_{n*}^+$

Barrier to Crystallization

Outline

- Nucleation background
- Ordering in metallic liquids
- Coupling processes in nucleation
- Ordering and the glass transition
- Future directions
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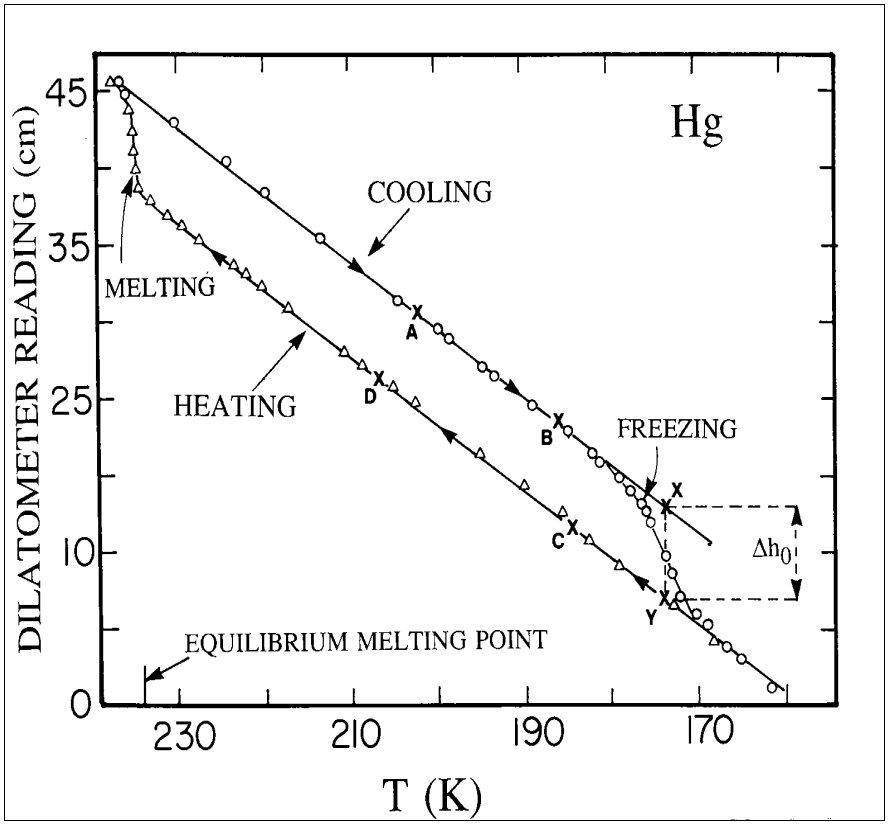
Supercooling of Liquid Metals (1952)

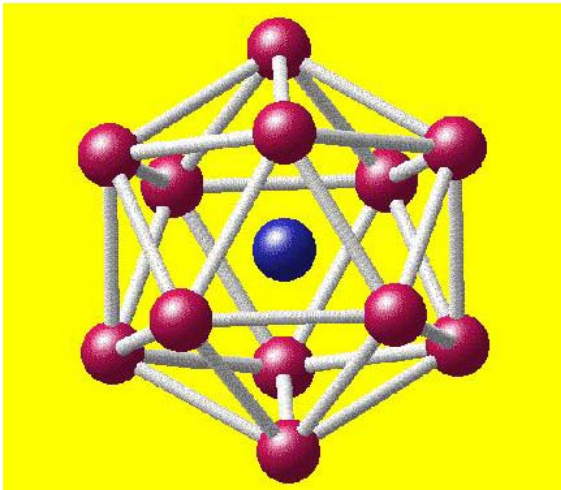
Turnbull Experiment



- All metals supercool to ≈ 80% of Tm
- Surprising since it was thought that liquid/crystal strucures are similar

Frank's hypothesis

The atoms in a metallic liquid are arranged in the form of an icosahedron

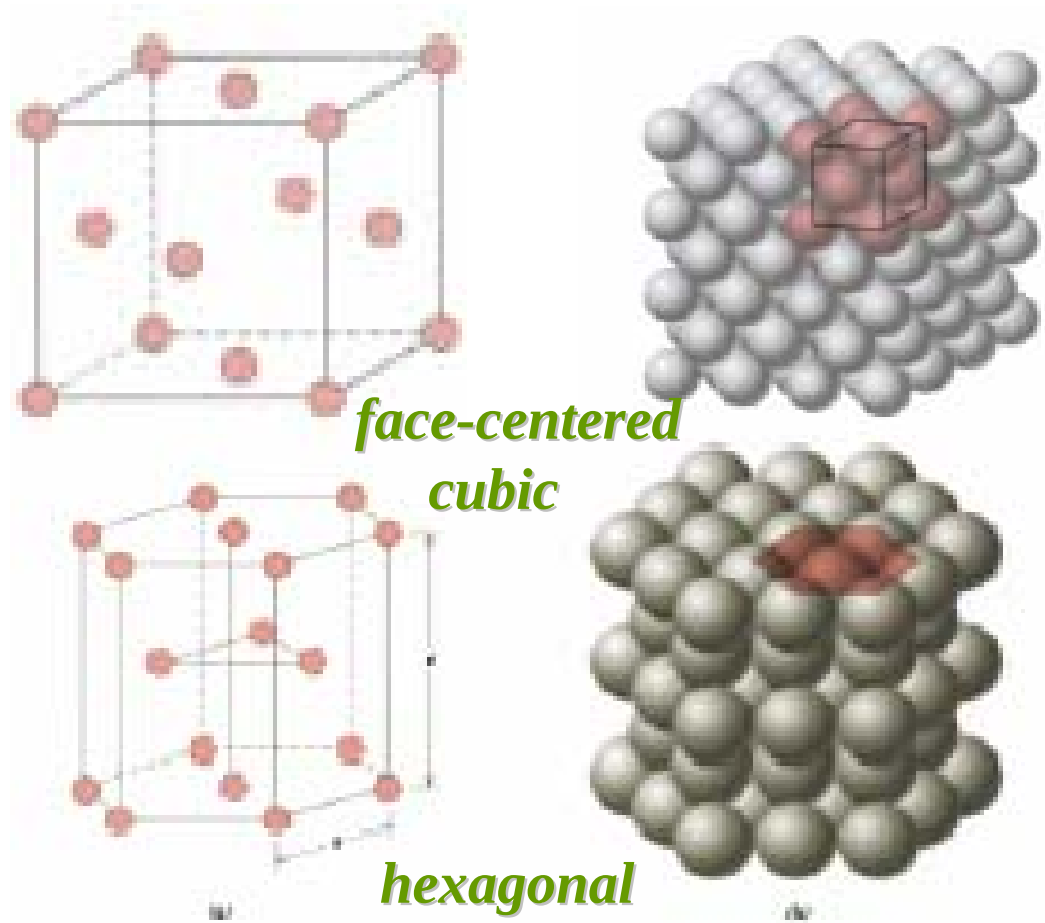


Nucleation of an ordered crystal requires that the icosahedral order be destroyed

Crystals
Periodic Arrangement of Atoms

FeS_2 (Pyrite)

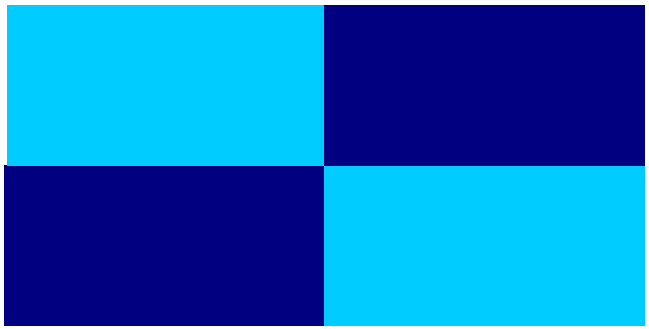
$Al_2(SiO_4)(FOH)_2$
(Topaz)



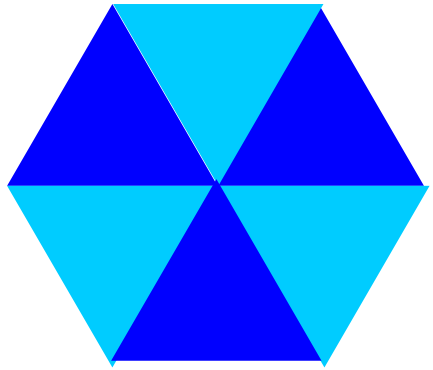
Metallic Crystals

Atoms packed like hard spheres

Allowed Symmetries for Tilings



2-fold



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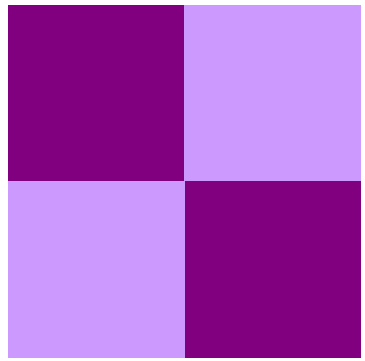
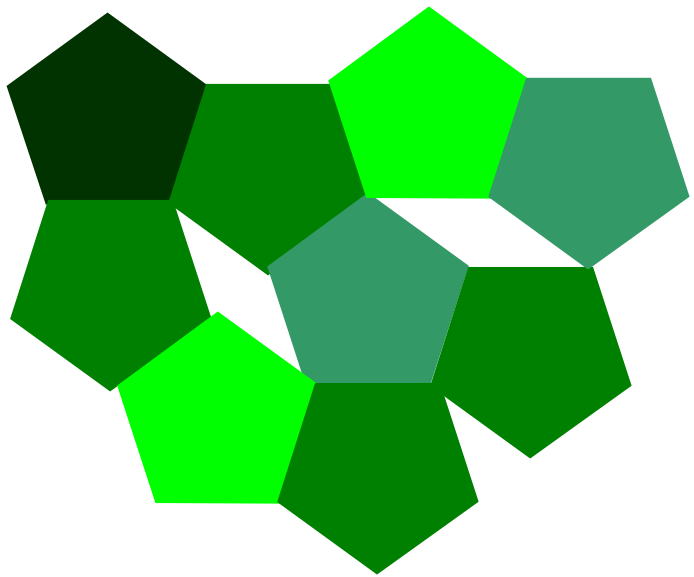


4-fold

6-fold

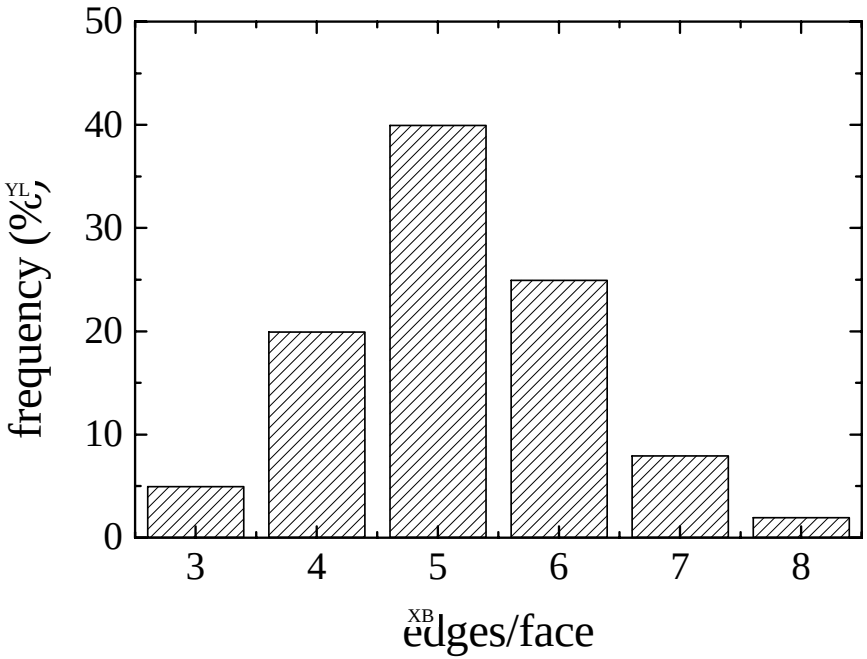


5-fold

Theoretical Evidence for Icosahedral Order

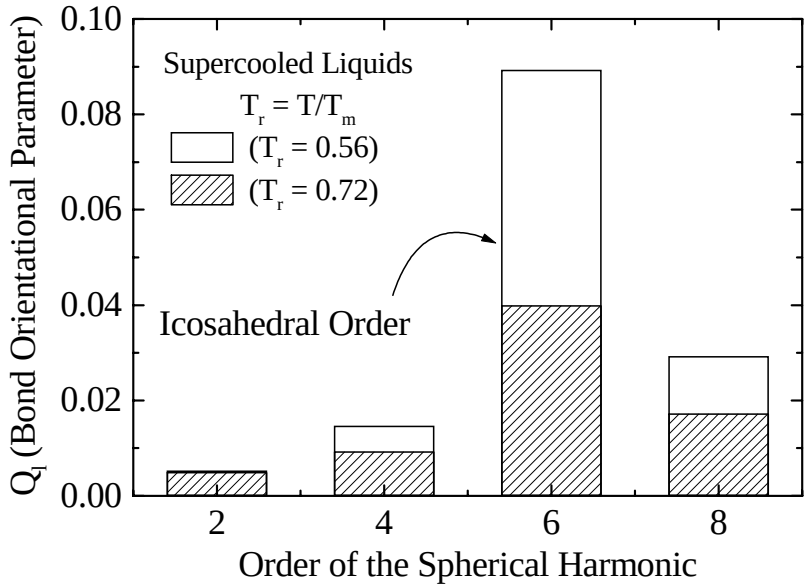
Computer Calculations of DRP

Bernal and Finey



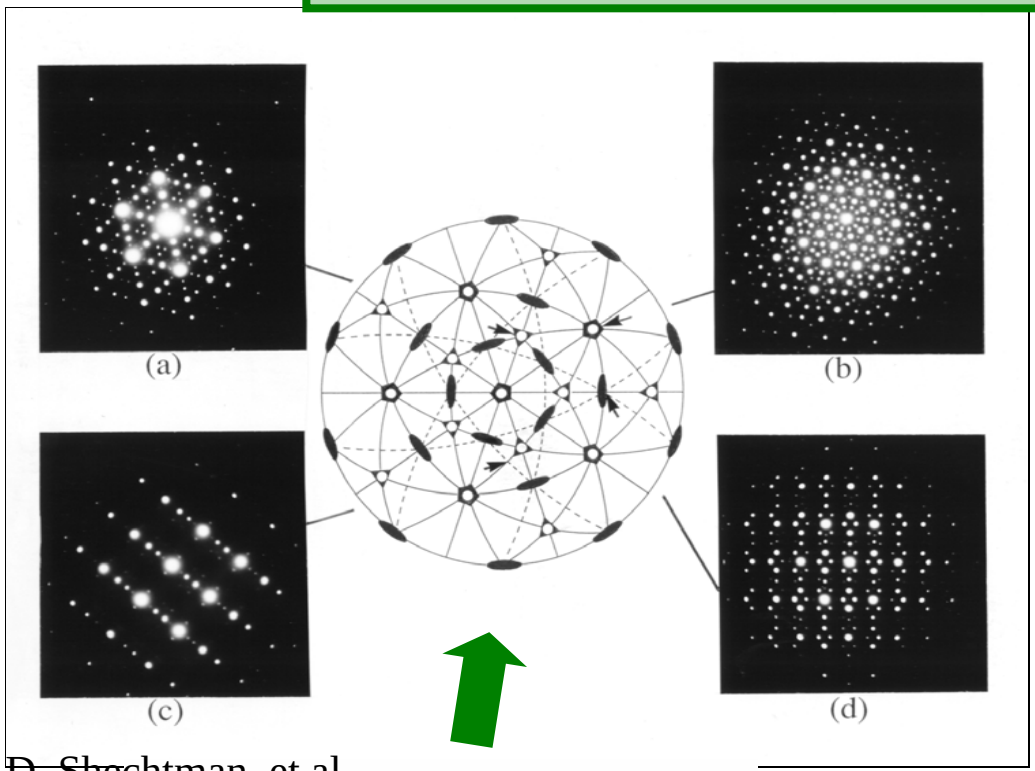
Molecular Dynamics

(Lennard-Jones Potential)

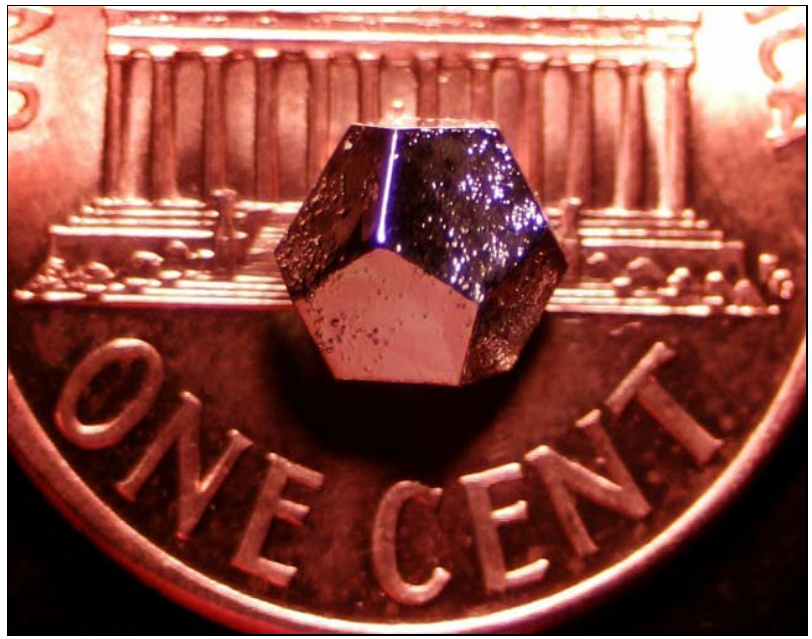


Steinhardt, Nelson, Ronchetti (1981, 1983)

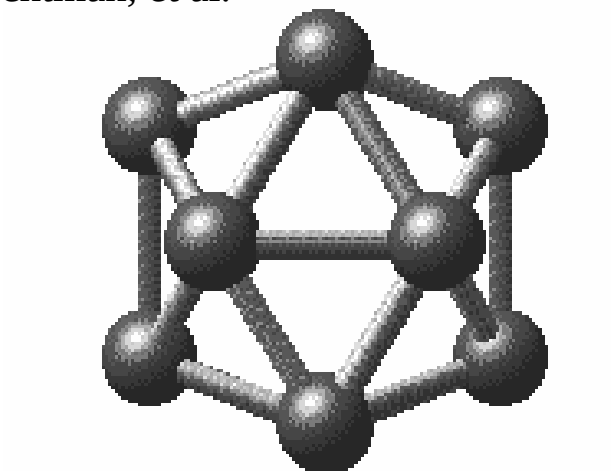
Icosahedral Quasicrystals (I-phase)



D. Shechtman, et al. 1984

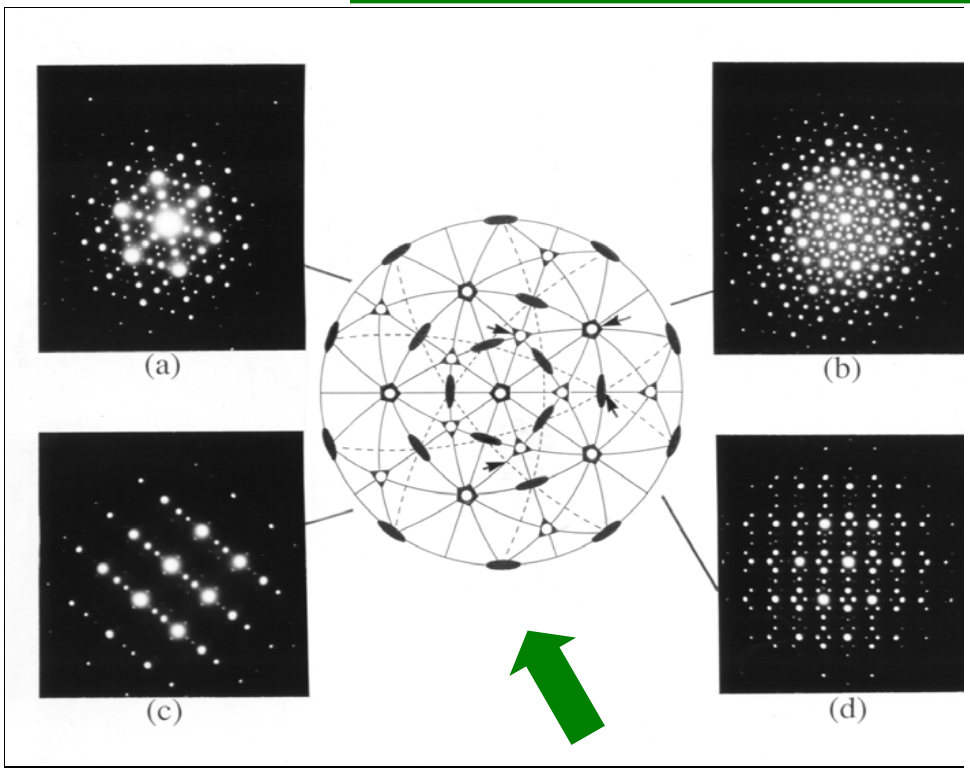


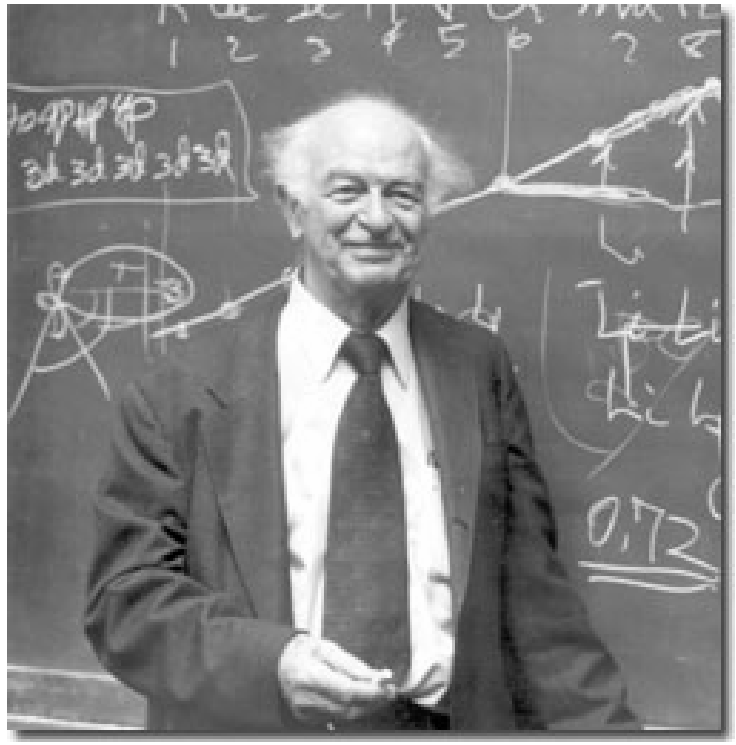
i(HoMgZn) - I. R. Fisher and P. C. Canfield

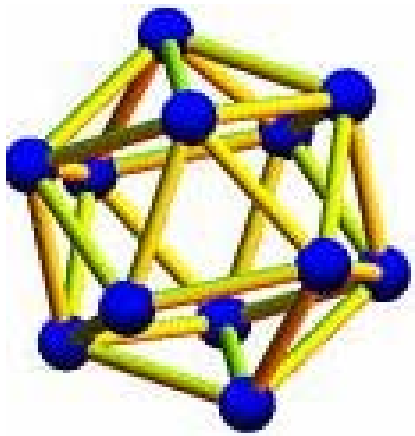


- Non-crystallographic symmetry
- Quasiperiodic translational order
- Local and extended icosahedral symmetry

Icosahedral Quasicrystal (i-phase)





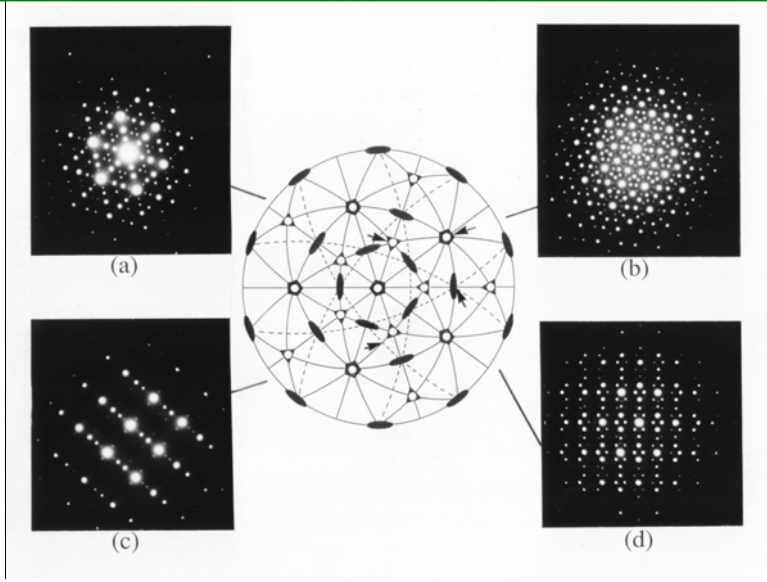


Linus Pauling

"Quasi[illegible]ls are wha[illegible]ppen when physicis[illegible] do crystallography" (APS Meeti[illegible]1985)

D. Shechtman, et al. 1984

Nucleation of the icosahedral phase (i-phase) from AlCuV Metallic Glass



- I-phase – extended icosahedral order
- Fit to classical theory of nucleation
- Very small interfacial free energy

$$\sigma_{i/g} < 0.1\ \sigma_{xtl/l}(Al)$$

- Local structures of i-phase and glass are very similar

J. C. Holzer & K. F. Kelton, Acta. Metall., **39**, 1883-43 (1991)

Nucleation of i-phase in Undercooled Liquid

D. Holland-Moritz, Int. J. Non-Eq. Processing, **11**, 169-199 (1998).

- rf-levitation studies of i-phase and related phases (crystal approximants)

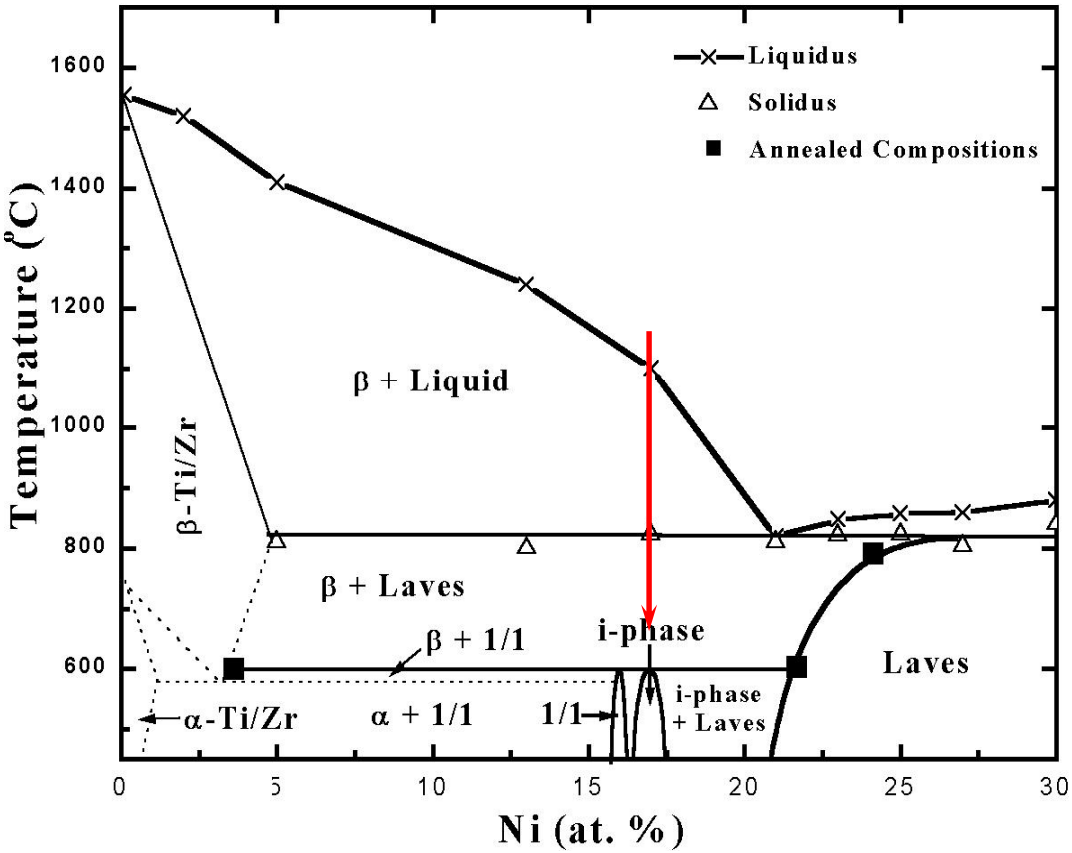
- **Icosahedral Phase**
  - $Al_{60}Cu_{34}Fe_6$
    $\Delta T^I \approx 100K \Rightarrow \Delta T^I/T_L \approx 0.1$
  - $Al_{58}Cu_{34}Fe_8$
  - Al- Pd - Mn
    $\Delta T^I \approx 125K \Rightarrow \Delta T^I/T_L \approx 0.11$

- **Crystal Approximants**
  - λ - $Al_{13}Fe_4$ $\Rightarrow \Delta T^\lambda/T_L \approx 0.12$
  - μ - Al_5Fe_2 $\Rightarrow \Delta T^\mu/T_L \approx 0.15$

- **Crystal Phases**
  - β(AlCuCo) - (CsCl Structure)
    $\Rightarrow \Delta T^\beta/T_L \approx 0.25$

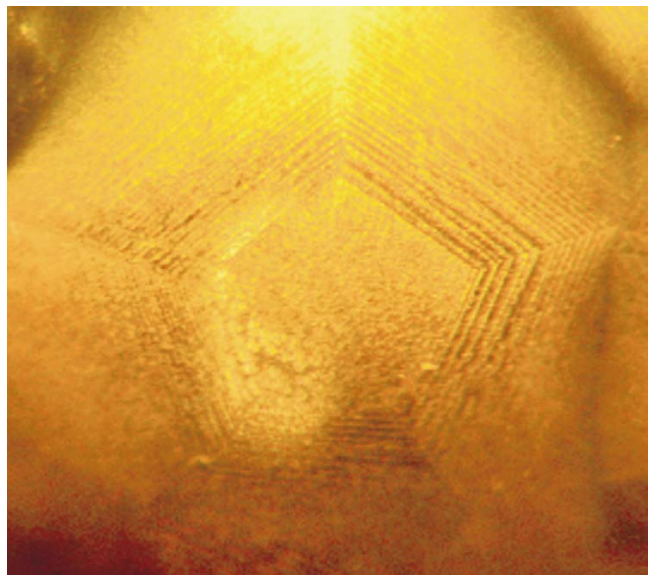
Ti-Zr-Ni Quasicrystals

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



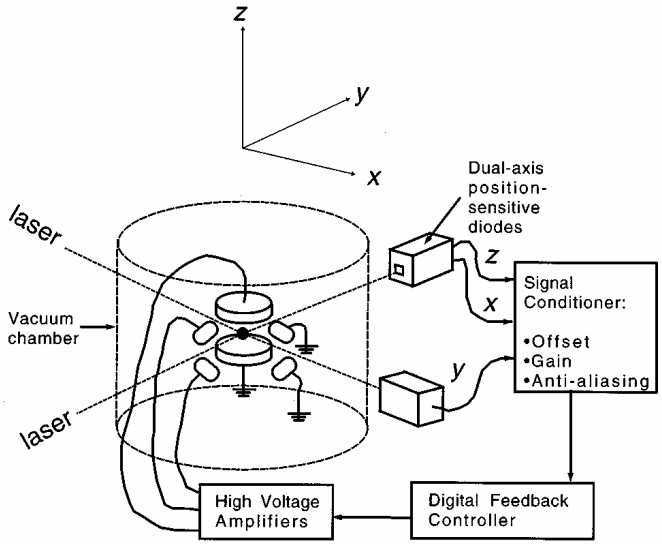
I-phase forms by solid-solid phase transformation

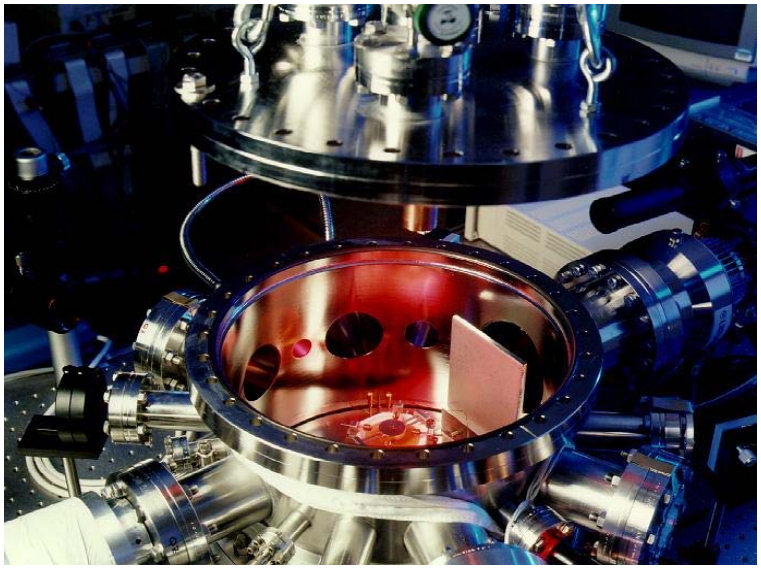
But …. small as-cast droplets sometimes contain the i-phase



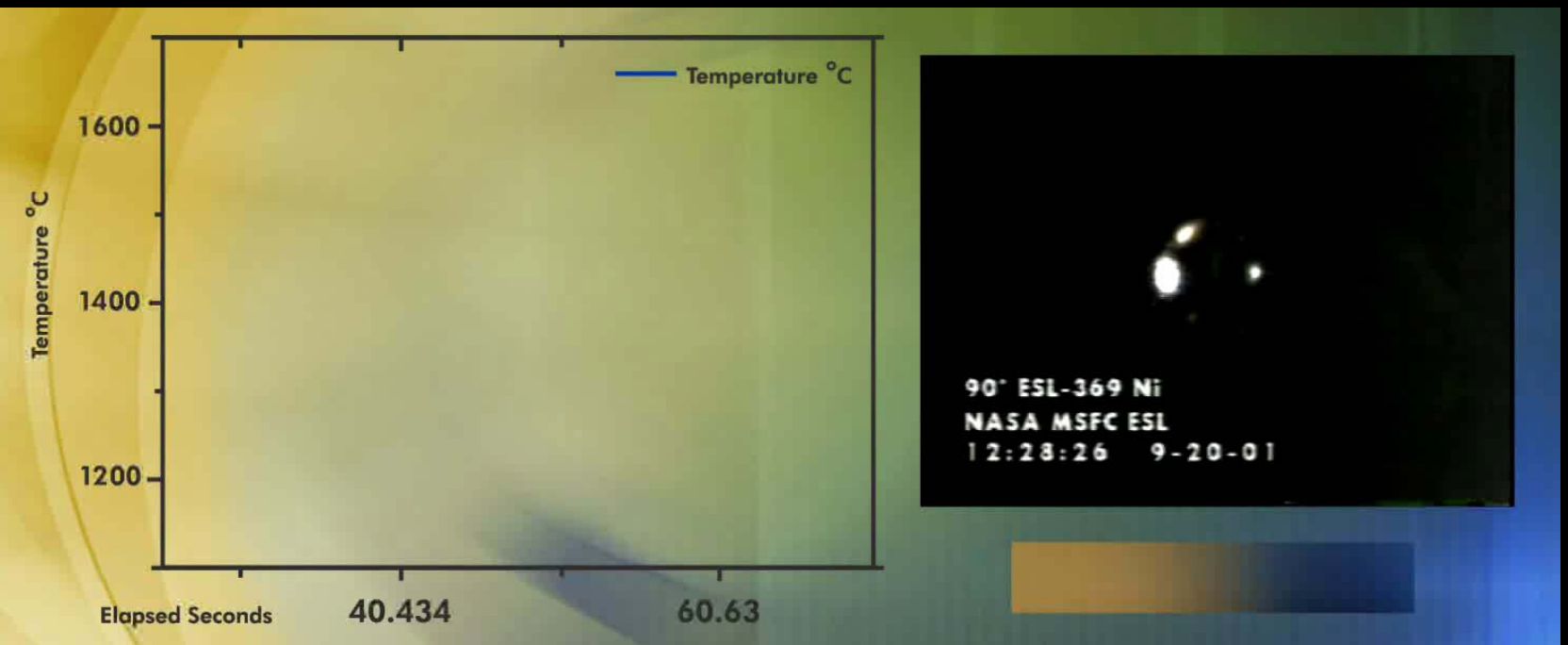
Growth rings indicate i-phase grew from the liquid

Electrostatic levitation (ESL)



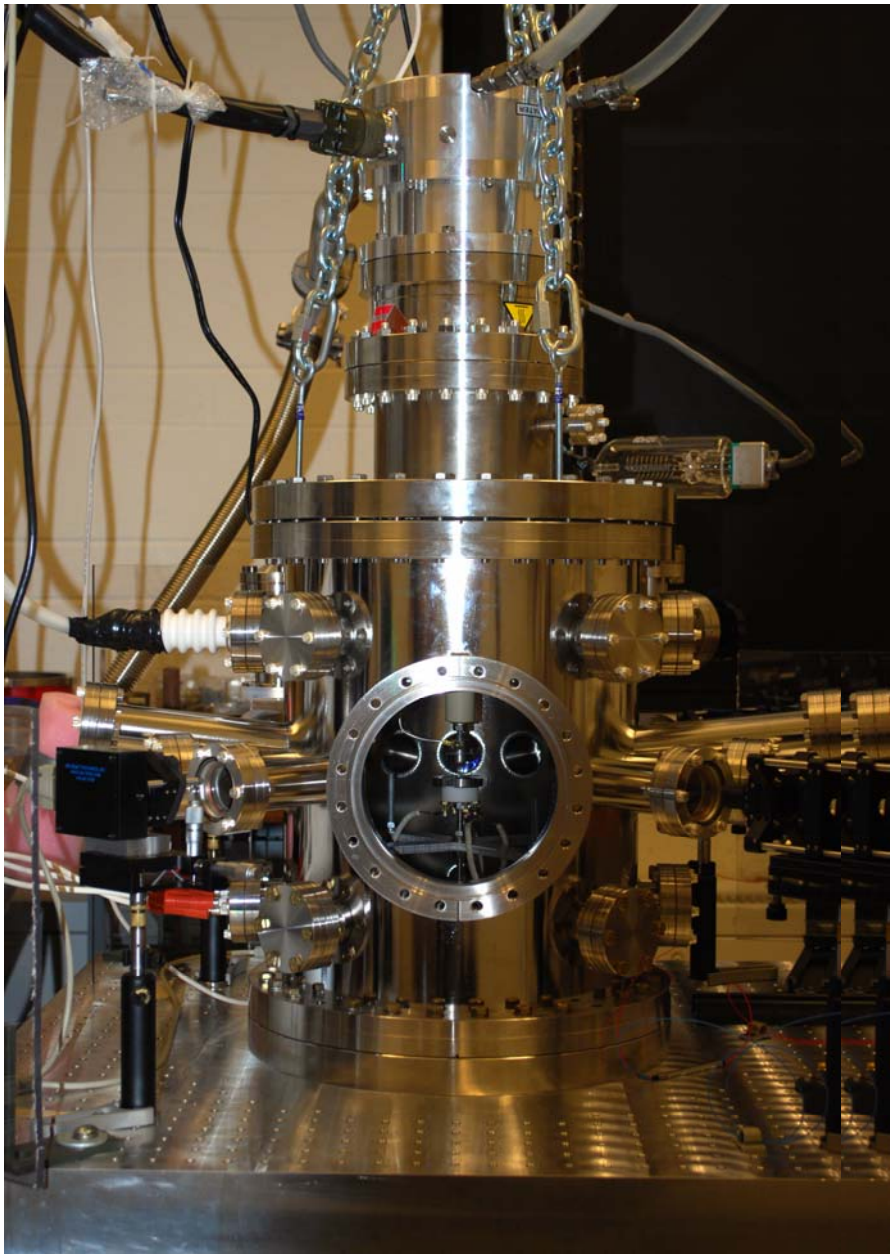


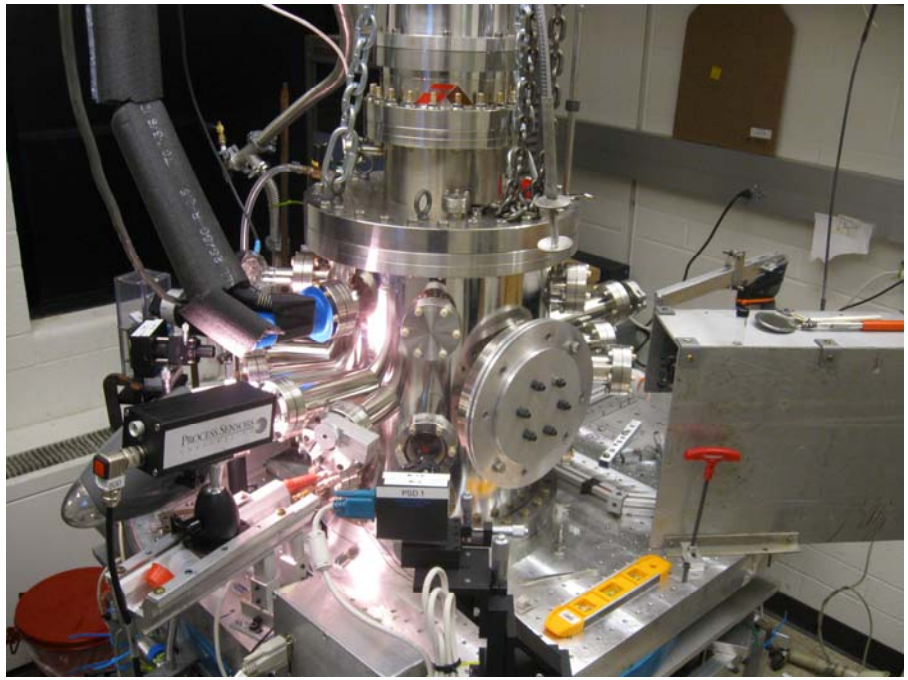
- ~ 10^{-8} torr
- Heating & positioning decoupled
- Stable within 50-100 μm

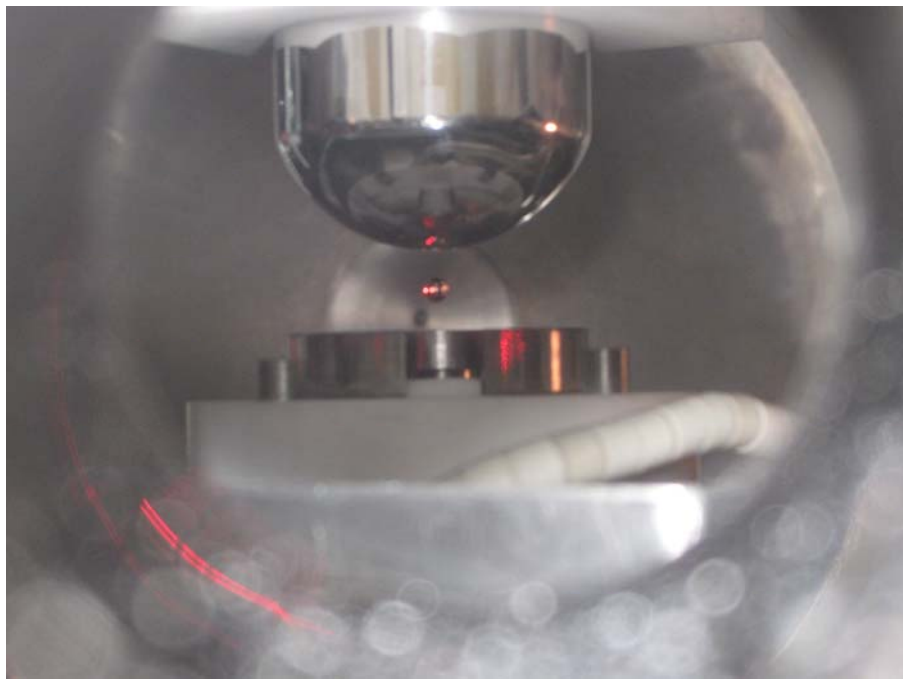


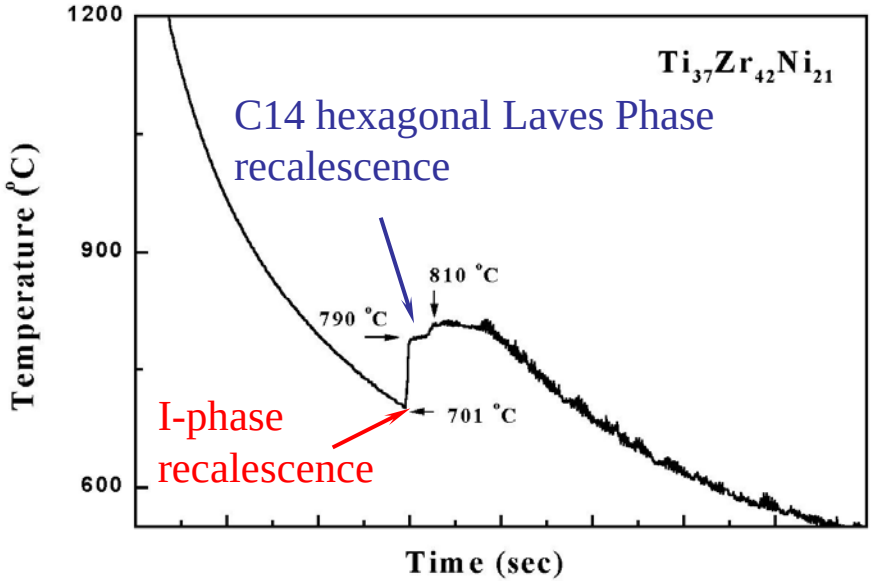
J. R. Rogers, NASA

WU-ESL

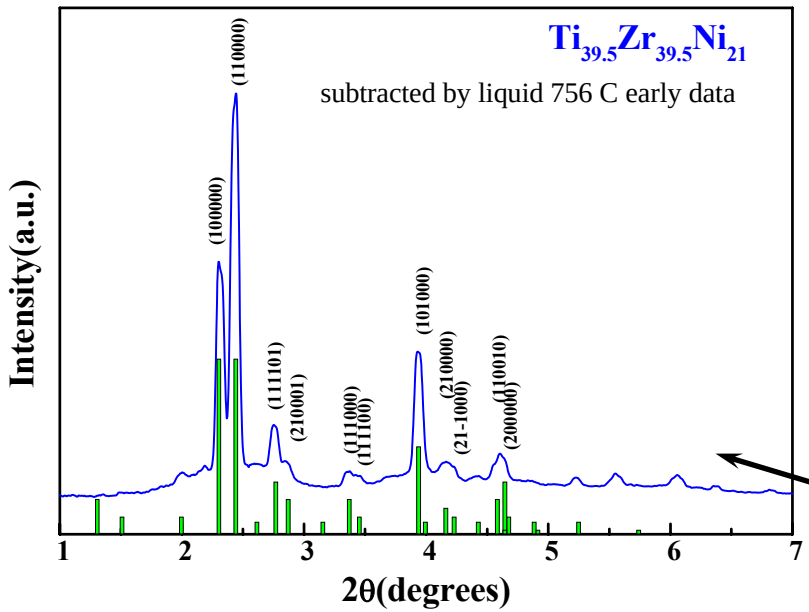




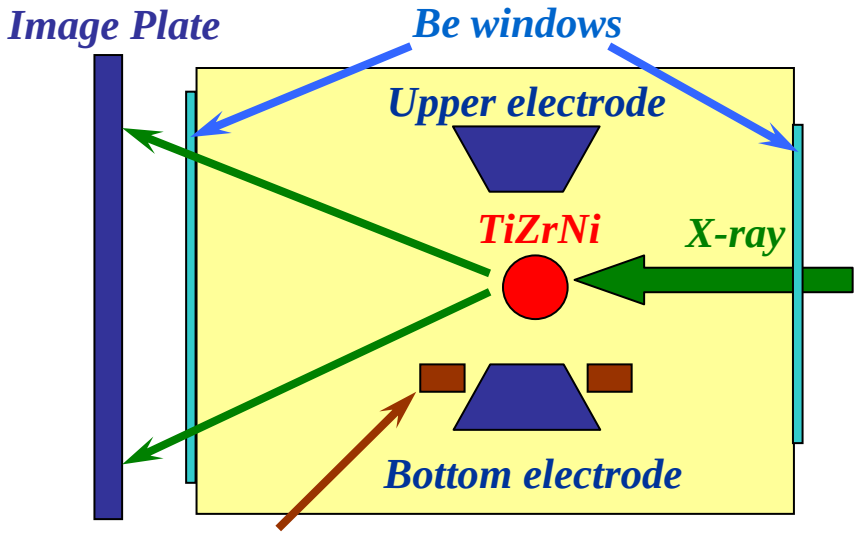




ESL of Liquid During Recalescence



Beamline Electrostatic levitation (BESL)



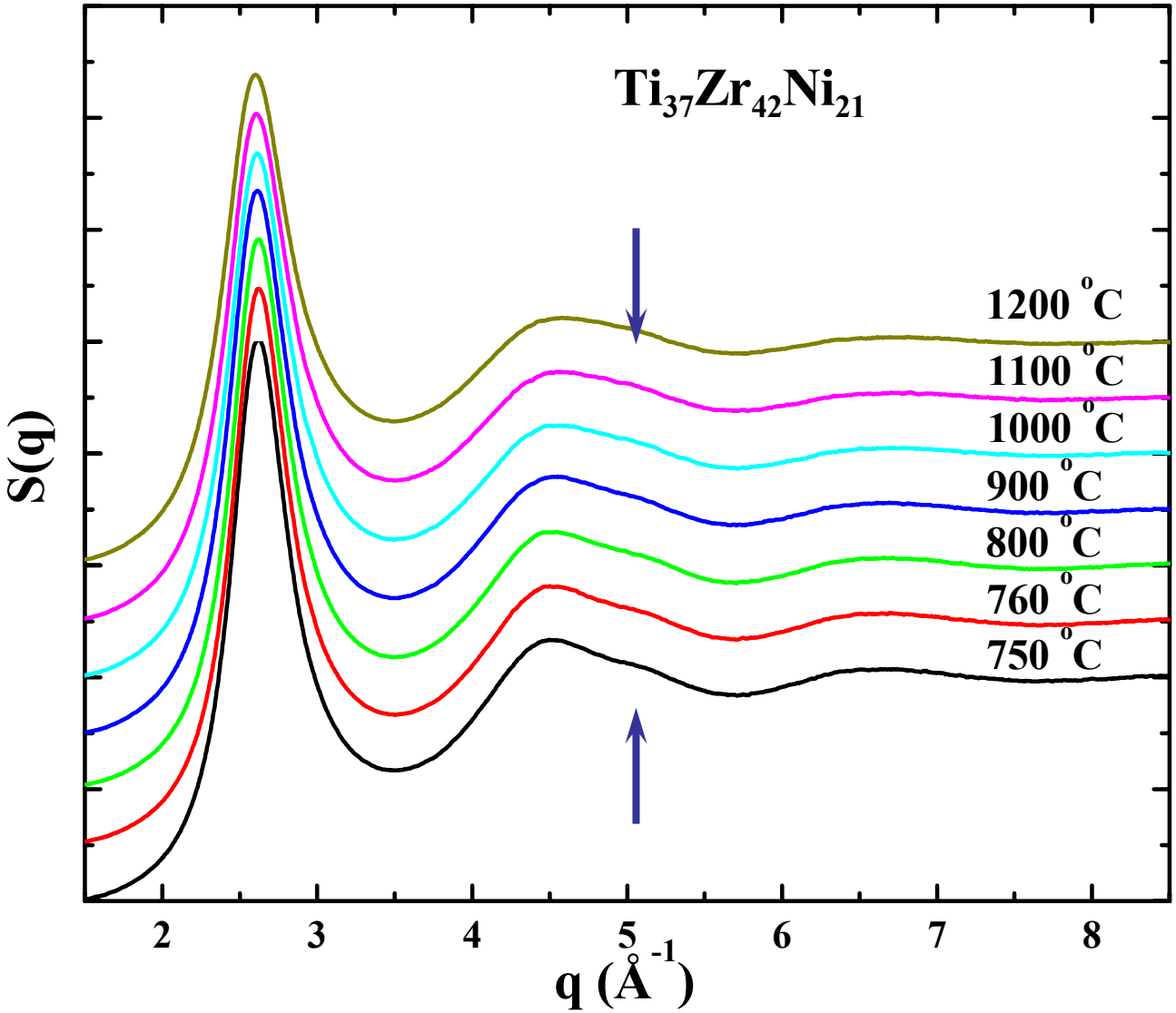
Positioning electrode

Wash. U., NASA, Ames Lab

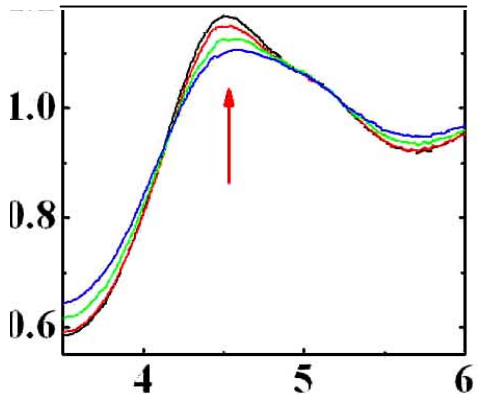
K. F. Kelton, A. K. Gangopadhyay, G.W. Lee, J.R. Rogers, M. B. Robinson, R. W. Hyers, T. J. Rathz, A.. I. Goldman, D. S. Robinson

Icosahedral quasicrystal is primary crystallizing phase

BESL Measurements of S(q) for $Ti_{37}Ni_{42}Ni_{21}$

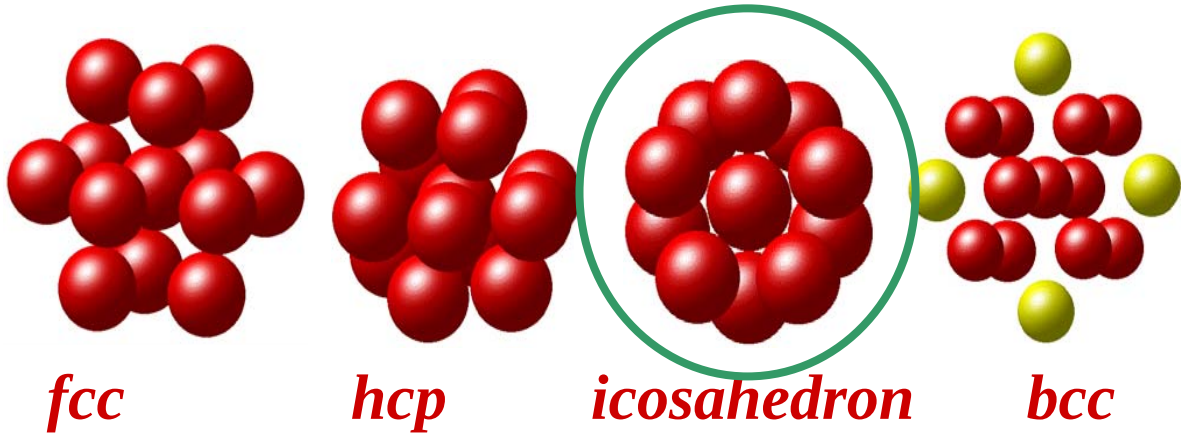


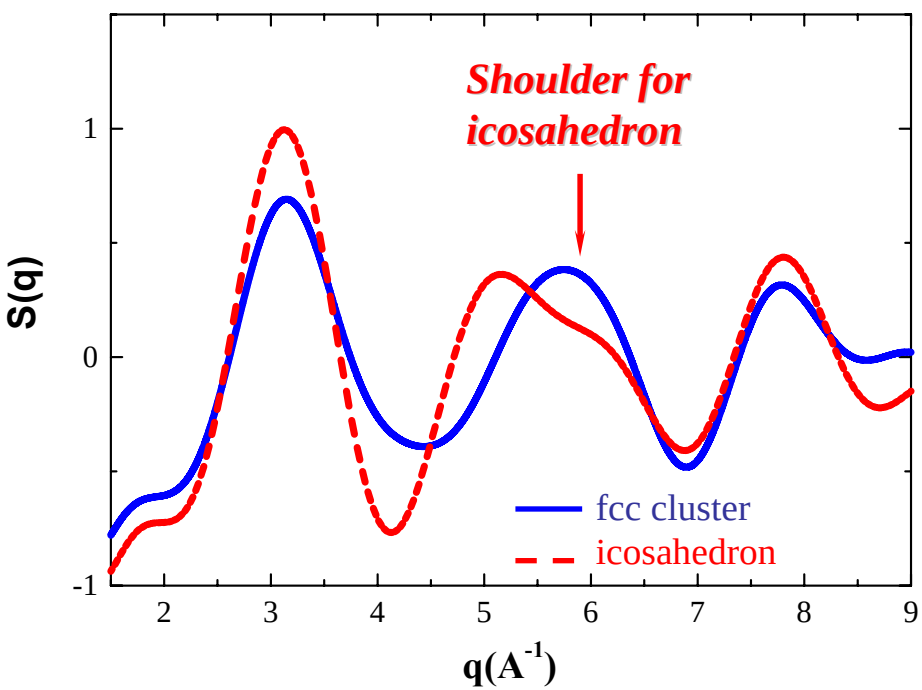
Increased short-range order with decreasing temperature



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).*

Icosahedral Ordering in the Liquid





Ratios of S(q) peak positions:

q(2nd)/q(1st) = 1.74 ± 0.01

q(shoulder)/q(1st) =1.95 ±0.01

Perfect icosahedron:*

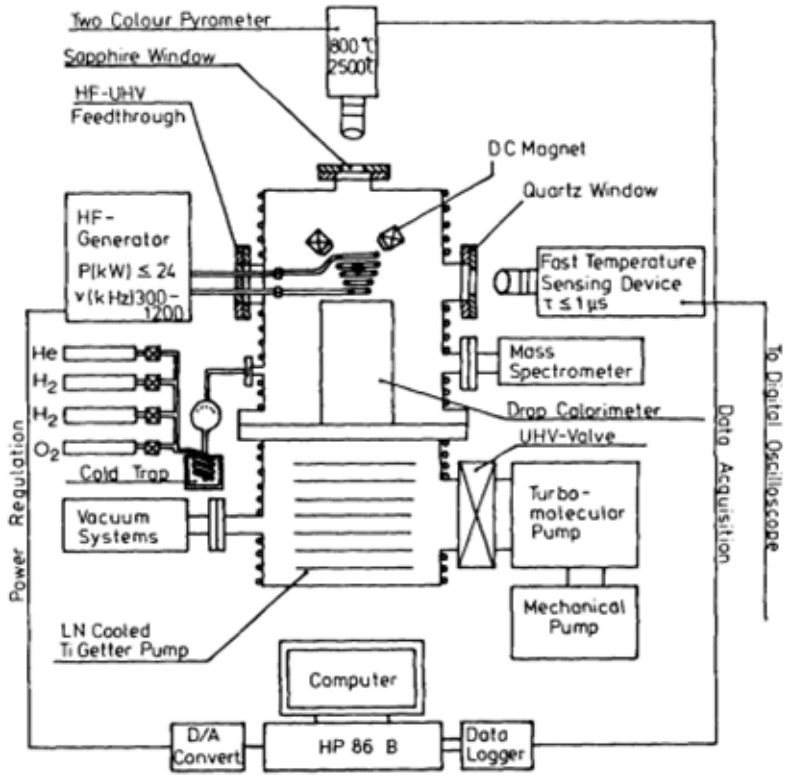
*(*S. Sachdev and D. R. Nelson, PRL* ***53*** *, 1947 (1984).)*

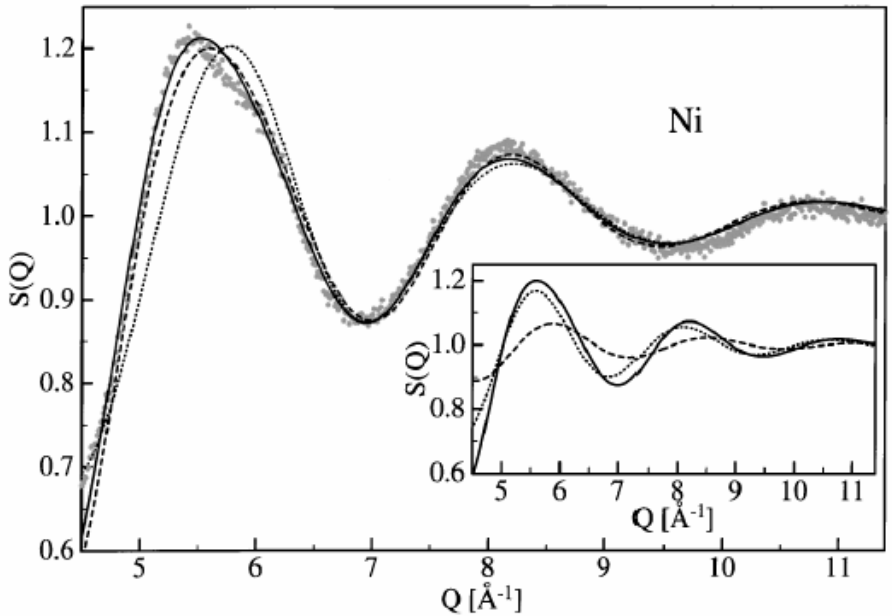
q(2nd)/q(1st) = 1.71

q(shoulder)/q(1st) =2.04

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)

Going Beyond the Single Cluster Model

Reverse Monte Carlo (McGreevy)

- Statistical fit to S(q) or g(r) data to obtain atomic structure
- No energies involved – worry about uniqueness of structure

Topological analysis

Bond Orienational Order Parameter Analysis (Steinhardt *et al.*)

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

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

- Icosahedral order – Q_6

Honeycutt Andersen Indices (uses root pairs)

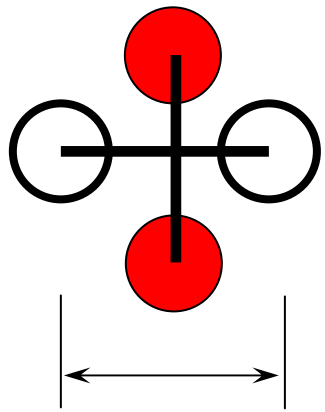
1st index – the peak in g(r) to which the pair belongs

2nd index – number of atoms counted as nearest-neighbors of the root pair

3rd index - the number of pairs of nearest-neighbors that form a bond

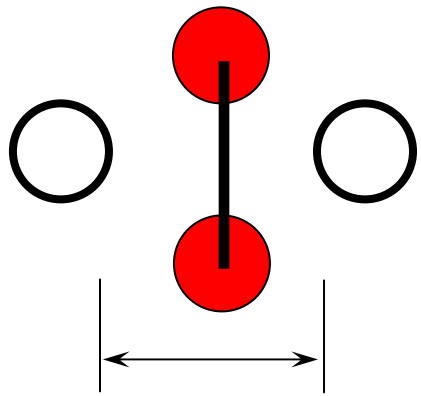
4th index - classification for clusters with identical sets of the first three indices but with different bond arrangements

HA Indices – Some Examples



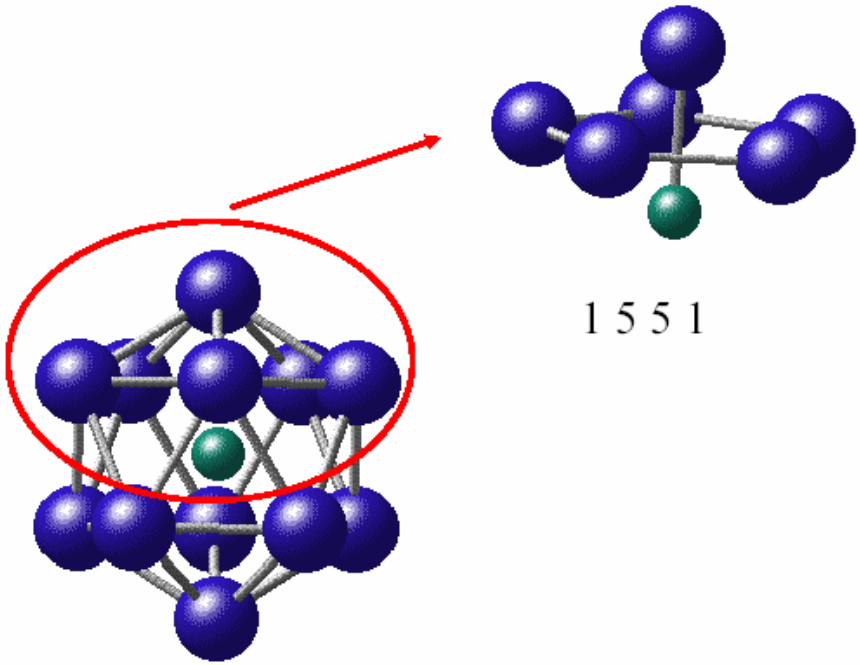
cutoff distance

(1 2 1 1)



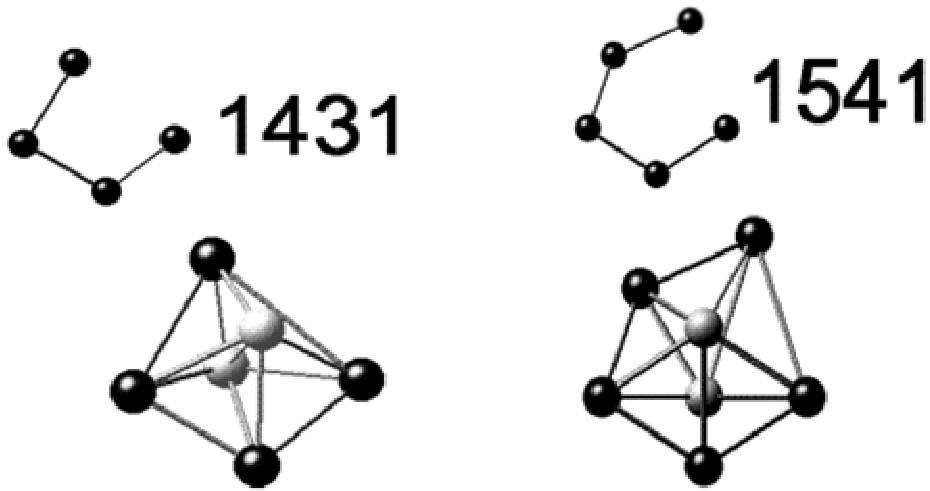
cutoff distance

(1 2 0 1)



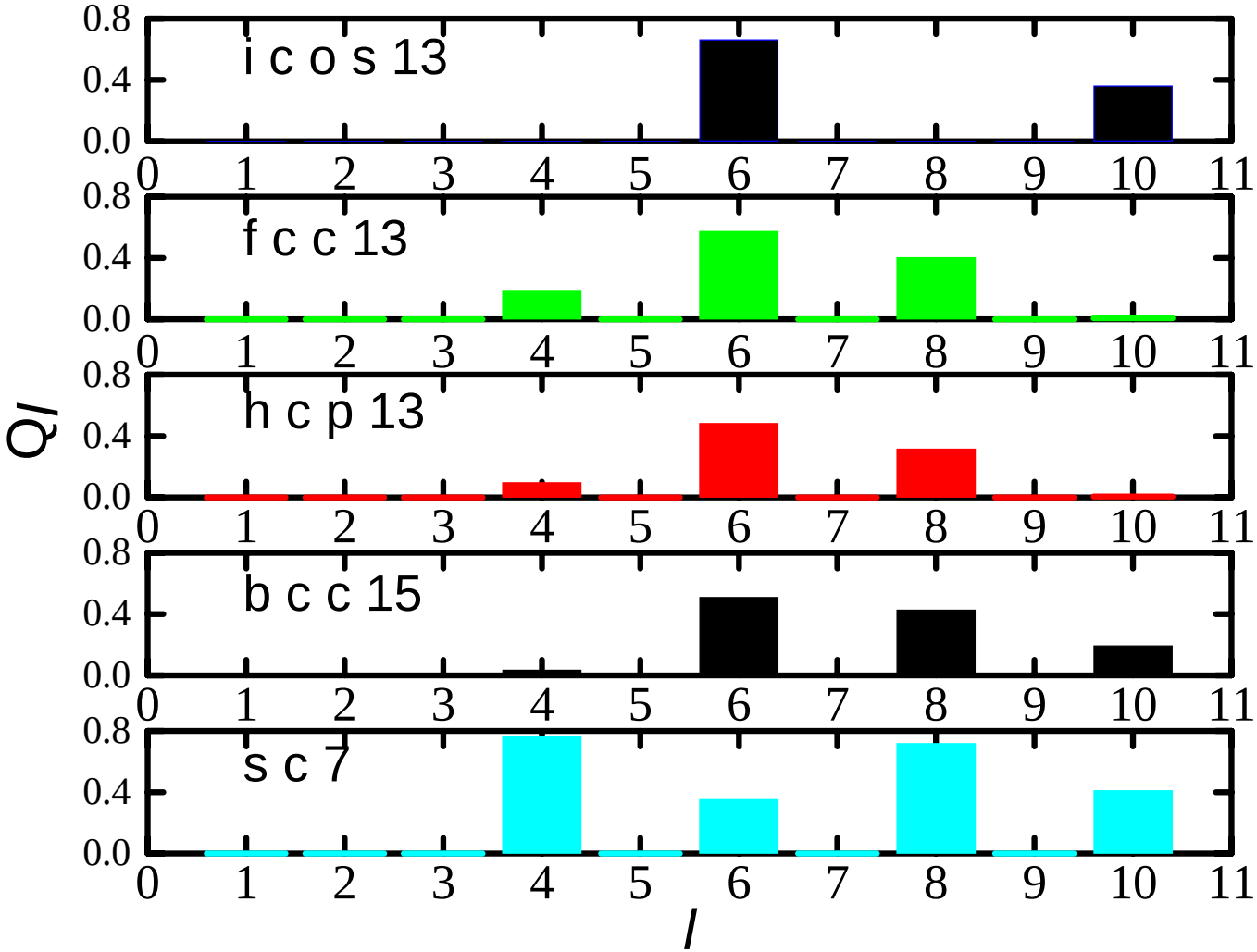
1 5 5 1

Icosahedral Cluster

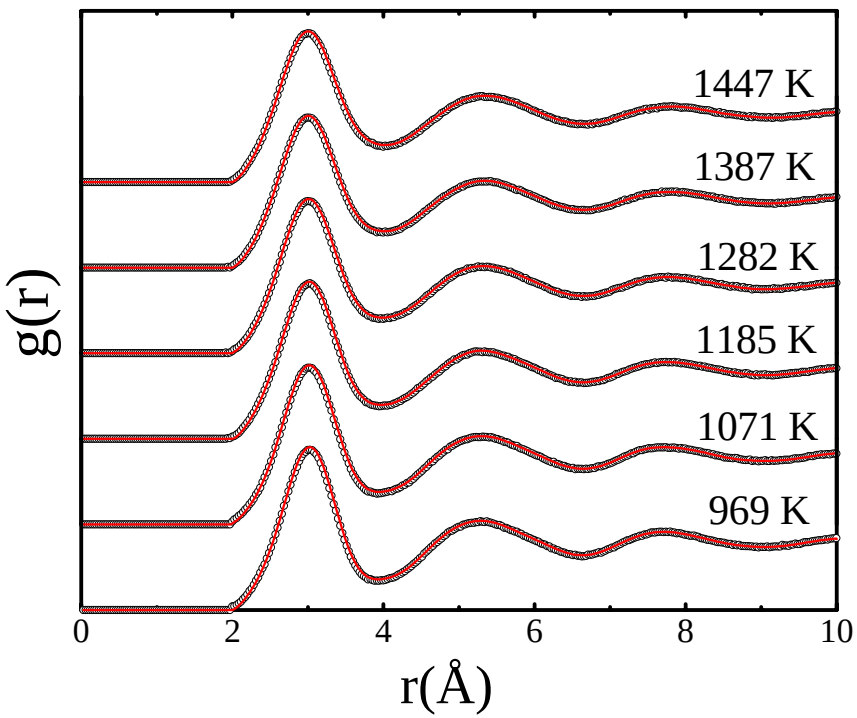


Distorted Icosahedral Cluster

- Bond Orientational Indices - Examples



Results from RMC Fits

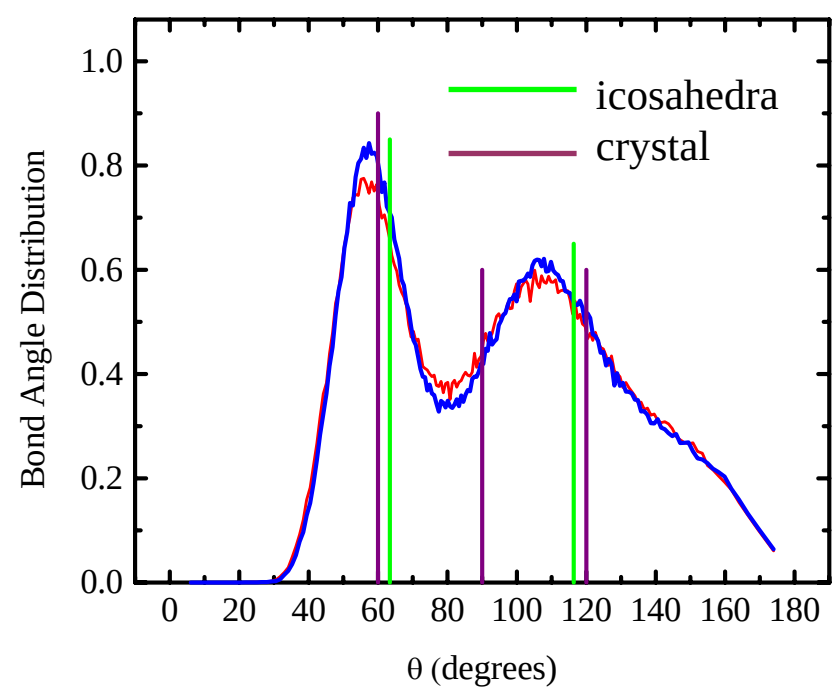


RMC Results

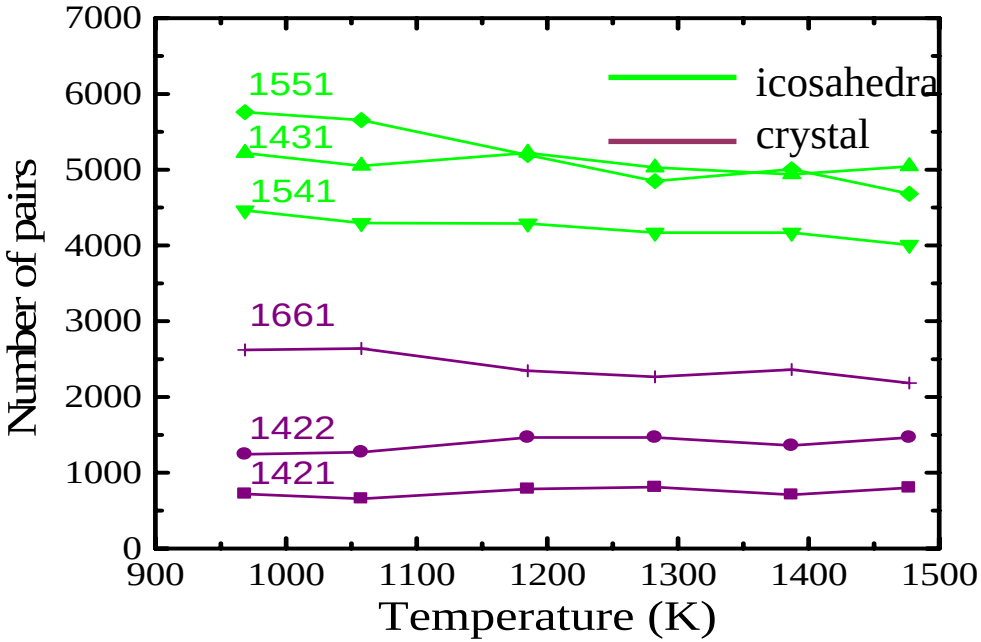
- Excellent fits to all data
- Good for different starting configurations
- Reasonable average structure

Bond angle distribution

- Slightly better fit to icosahedral
- Indicates mixture of order



Analysis of RMC Results

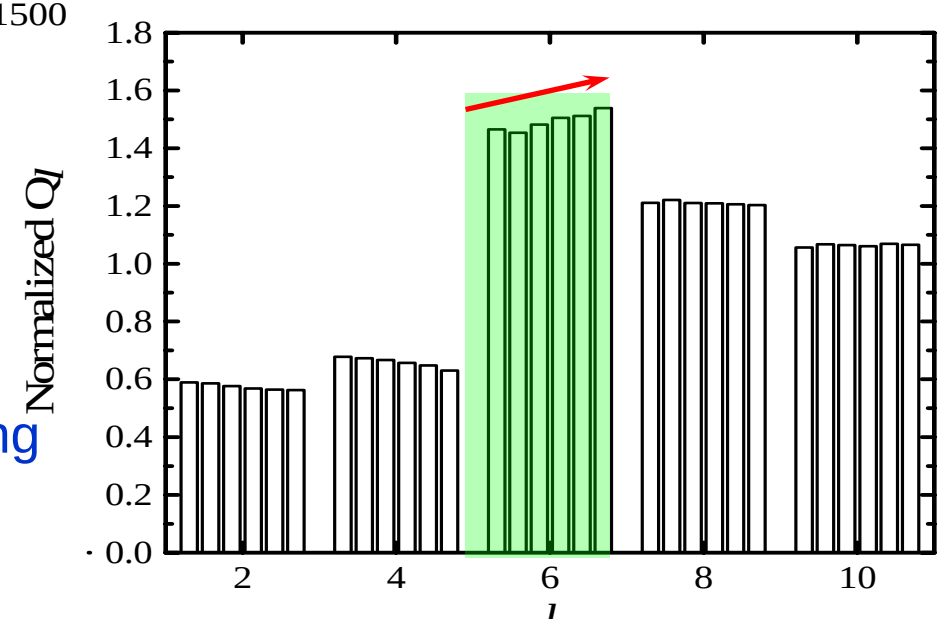


Honeycutt Andersen Indices

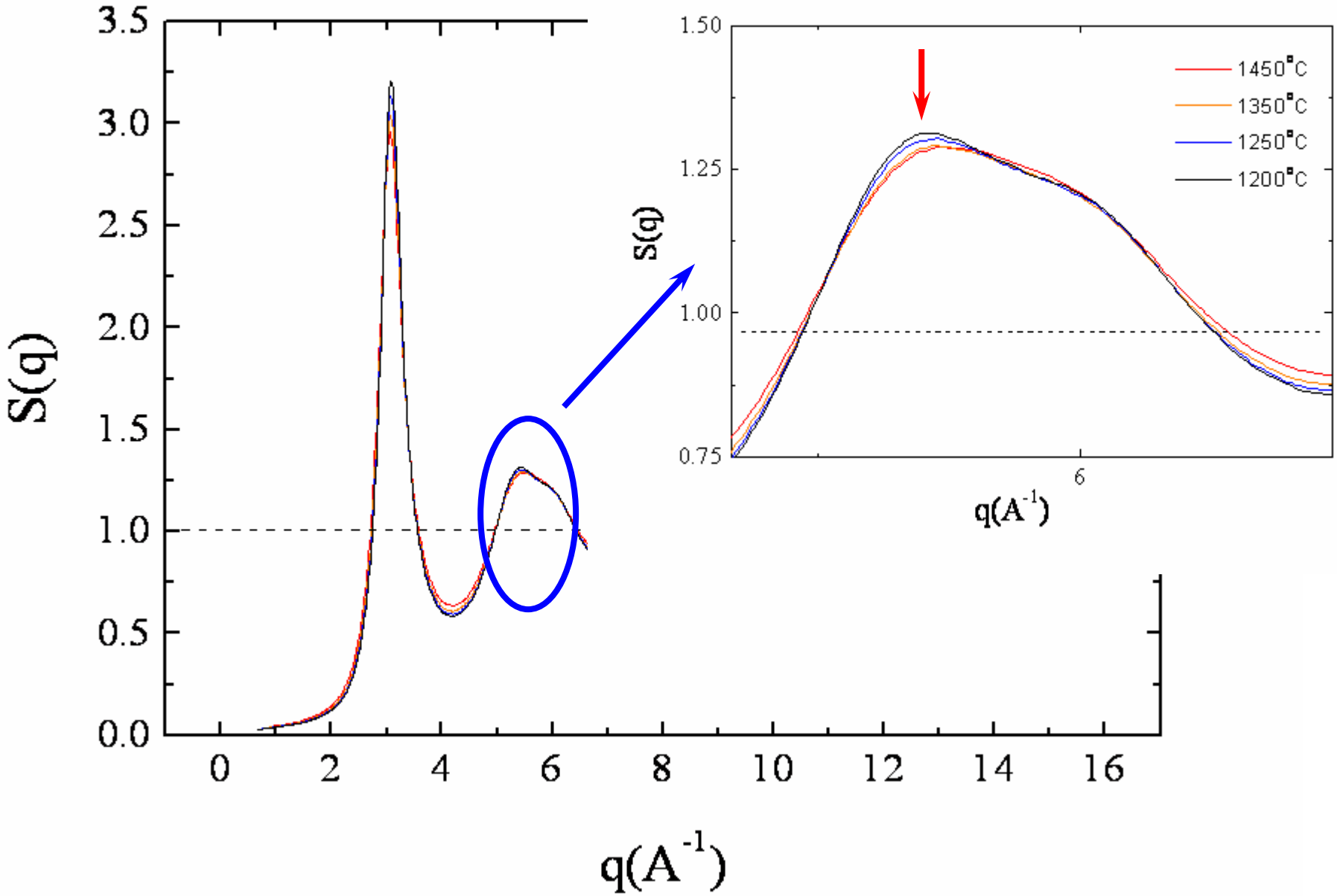
- Icosahedral order is greatest
  - 1551 (pure)
  - 1431 and 1541 (distorted)
- Icosahedral order increases with supercooling
- Significant fraction of crystal order (bcc)

Bond Orientational Order

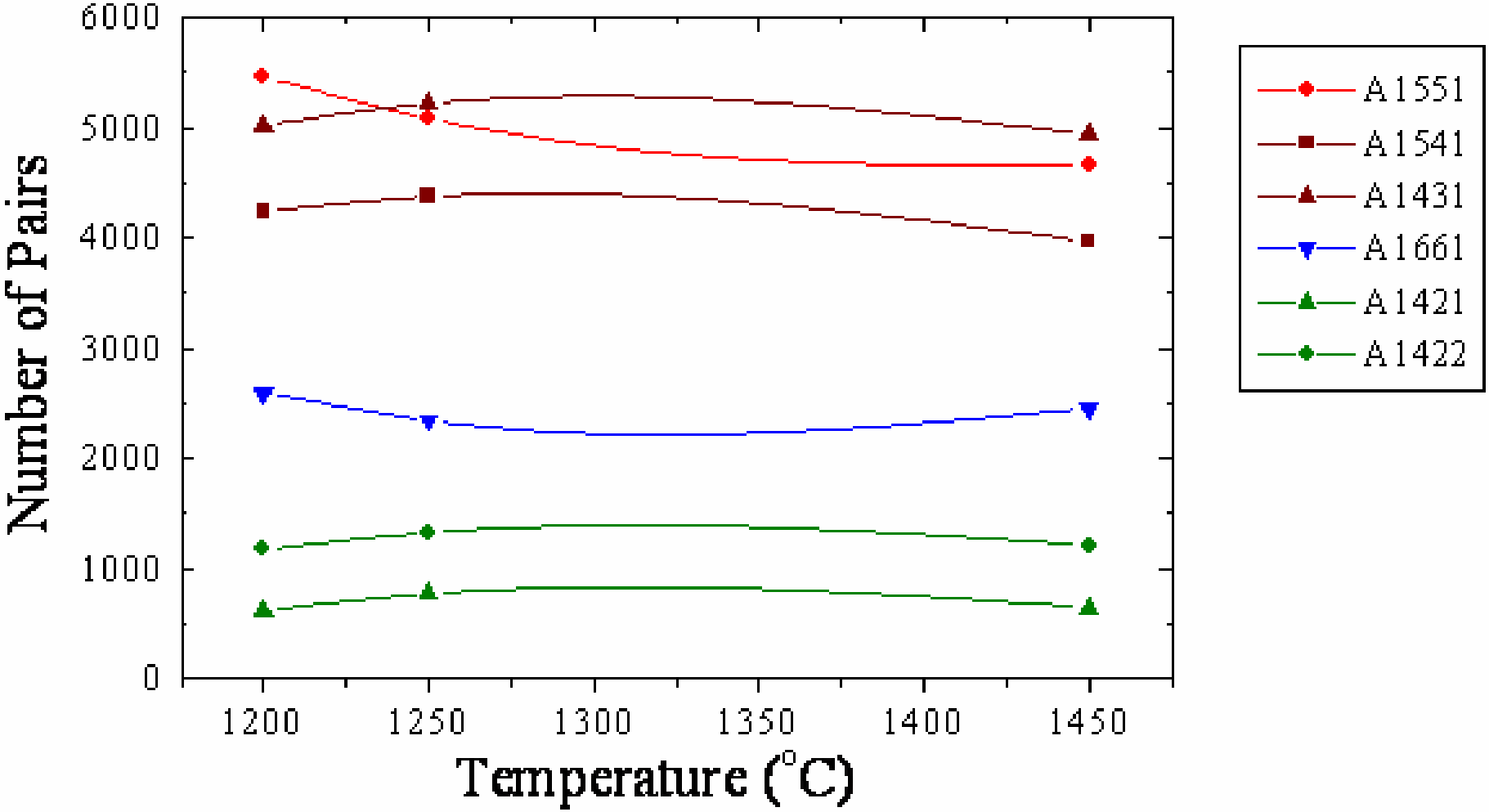
- Q6 – measure of icoshaedral order
- Q6 increases with supercooling
- All others decrease

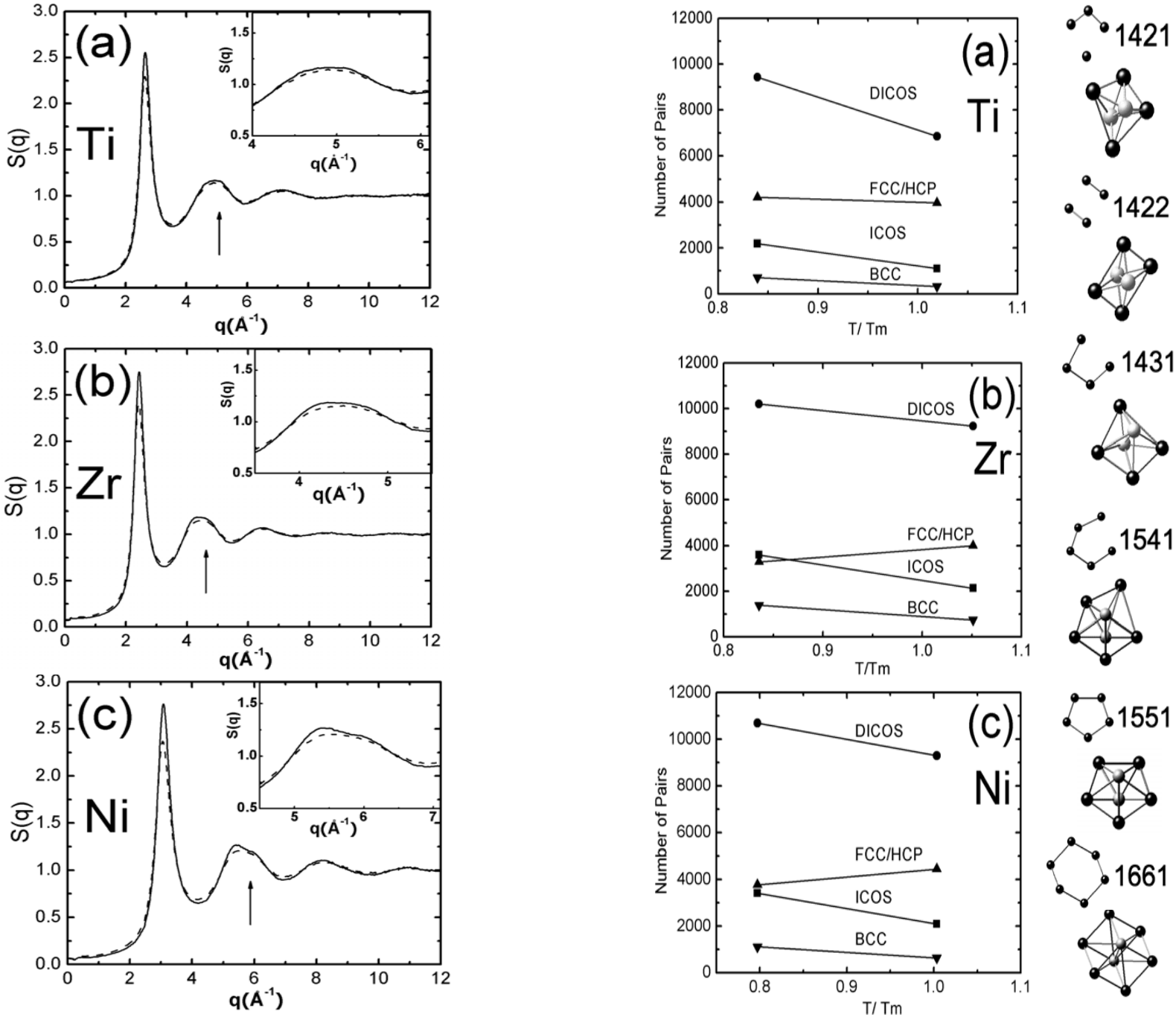


Supercooled Ni Liquid



Ordering in Supercooled Liquid Ni





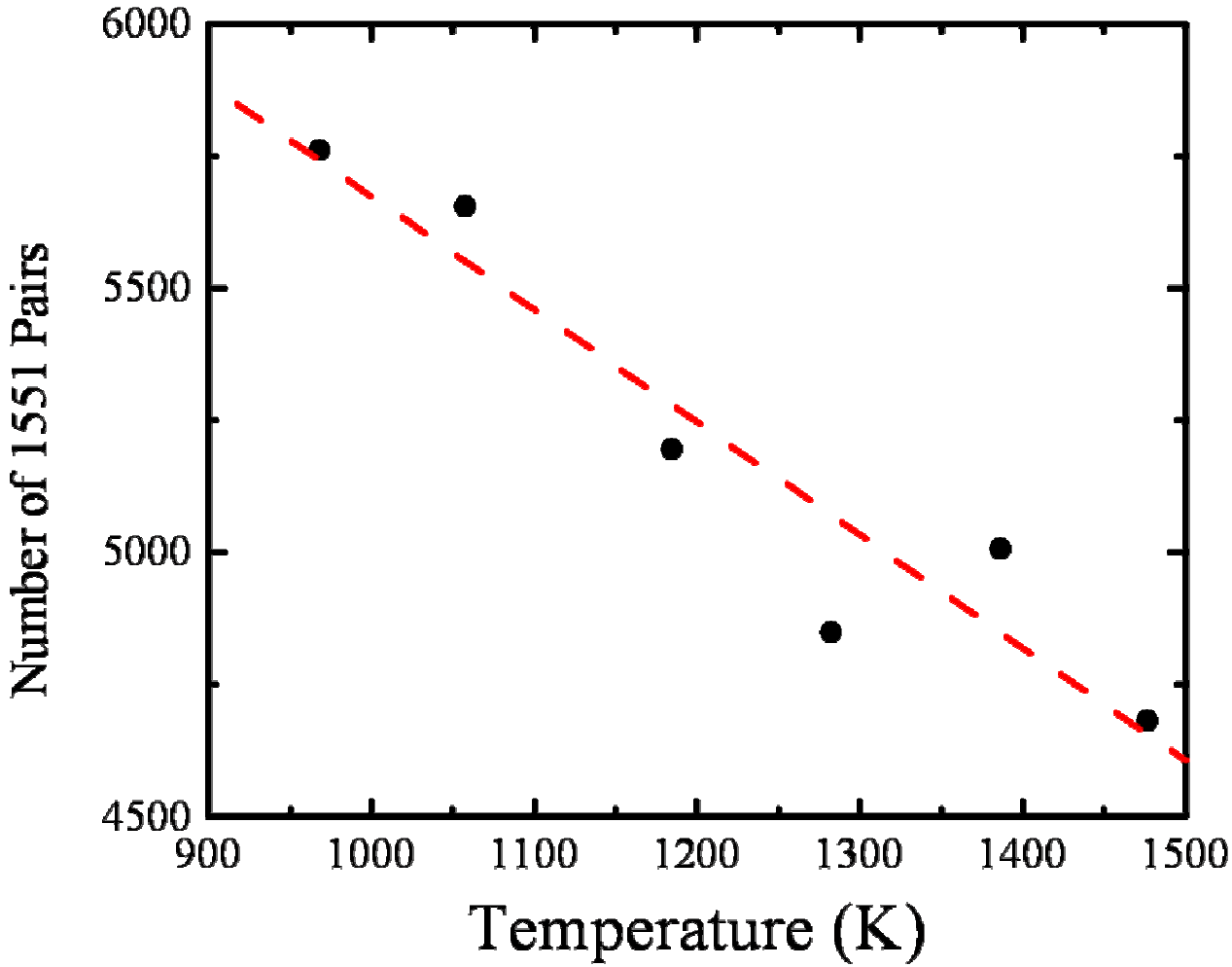
T. H. Kim and K. F. Kelton, J. Chem. Phys. 126, 54513 (2007)

Key Conclusions from RMC Results

- These transition metal liquids are characterized by icosahedral order that increases in quantity and coherence length (from narrowing peak widths) with supercooling
- Supports key conclusions from previous dominant cluster analysis
- ***But – significant types of other local environments, some with crystal character***

- ***Icosahedral order even found in pure transition metals***

Liquid Structure Template for Nucleation



Critical cluster diameter for nucleation - 3.5 nm

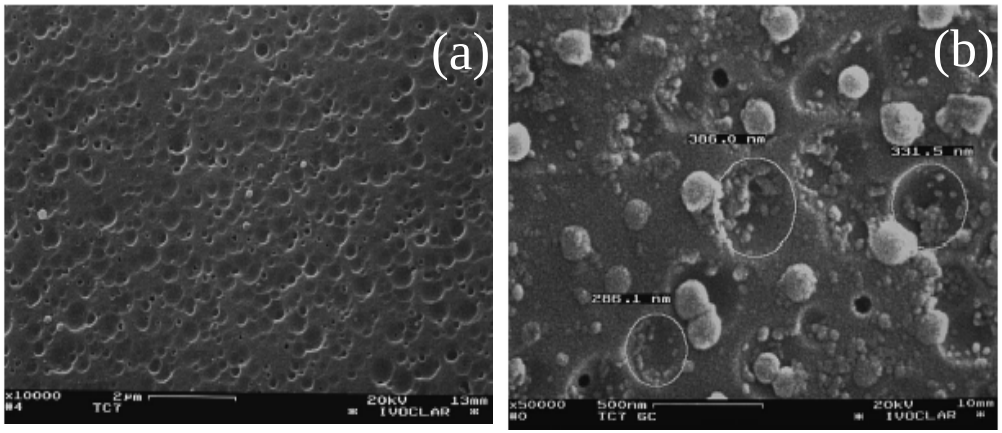
Coherence length of icosahedral order - 2.1 nm

T. H. Kim and K. F. Kelton (2007)

Outline

- Nucleation background
- Ordering in metallic liquids
- Coupling processes in nucleation
- Ordering and the glass transition
- Future directions
- Conclusion

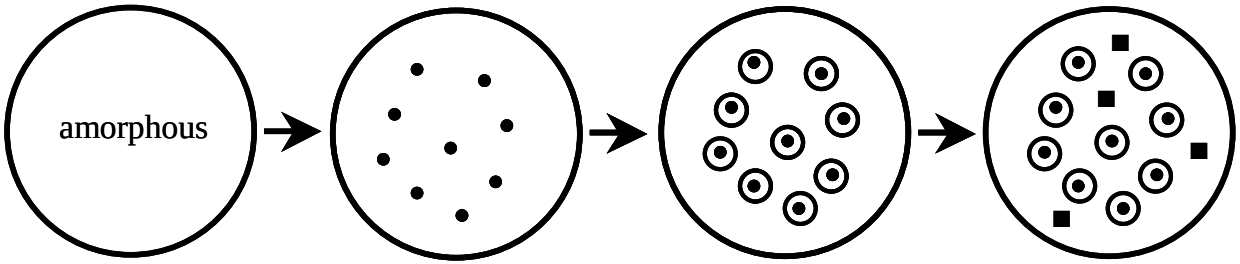
Phase Separation Catalyzes Nucleation



- Phase separation into $CaO.P_2O_5$ rich regions
- Catalyzes crystallization

SEM of phase separated $(SiO_2)_{61.5}(Al_2O_3)_{9.4}(Na_2O)_{9.2}(K_2O)_{7.7}$-$(CaO)_6(ZrO_2)_{0.5}(TiO_2)_{0.2}(P_2O_5)_{1.9}(CeO_2)_{0.3}(Li_2O)_{0.5}(B_2O_3)_{0.3}F_{2.5}$ glass

Nano-precipitation Catalyzes Nucleation



As-quenched (1)

Precipitation of Cu clusters (2)

Heterogeneous Nucleation of α-Fe(Si) on Cu (3)

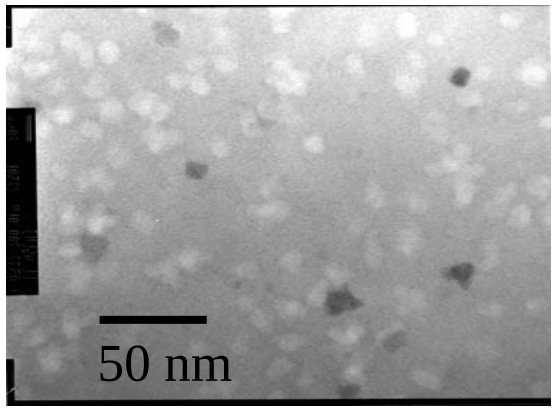
α-Fe(Si), Cu-rich precipitate (■), Nb&B enriched glass (4)

Increasing anneal time →

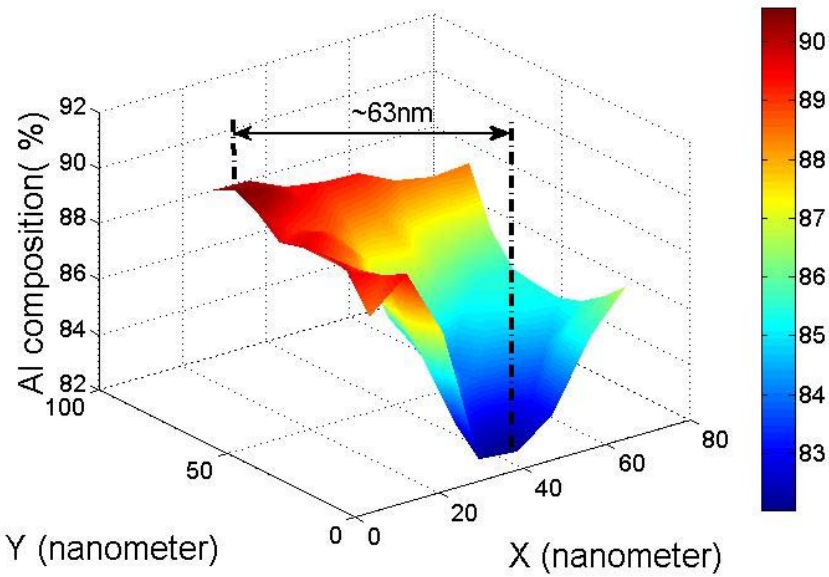
FINEMET Metallic Glasses

Y. Q. Wu, T. Bitoh, K. Hono, A. Makino, A. Inoue, Acta Mater. ***49*** *(2001) 4069*

Extremely high nucleation rate
Diffusion-limited growth



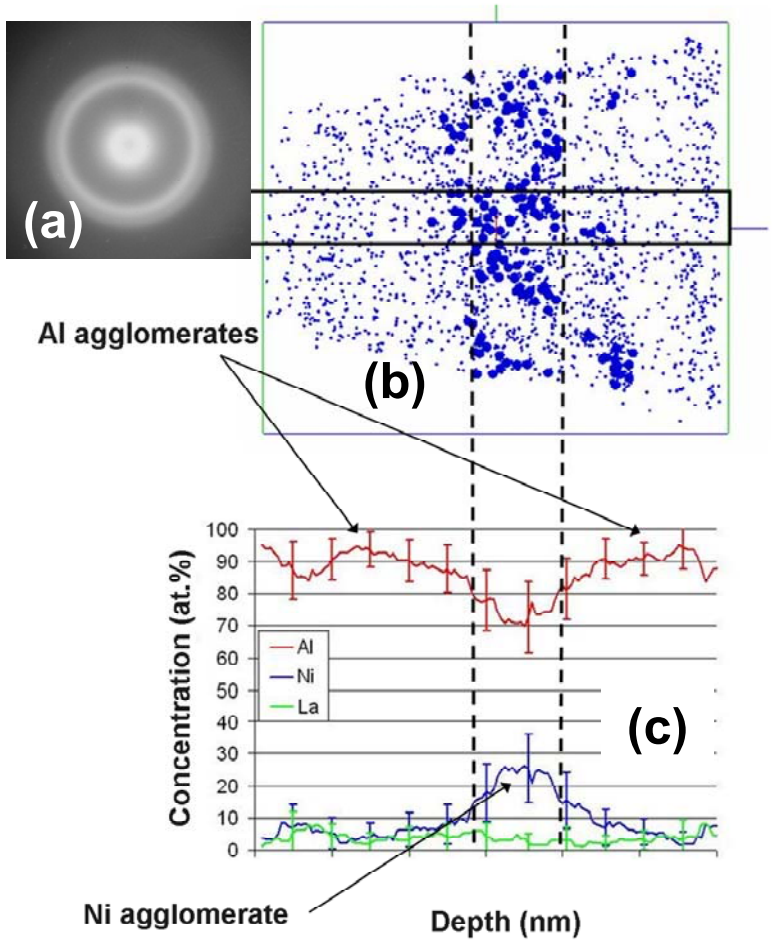
Nanoscale Phase Separation



N. Mauro, L. Longstreeth-Spoor, K. Sahu, M. Miller, K. F. Kelton, Acta Mater. (submitted).

Common in Al-based glasses

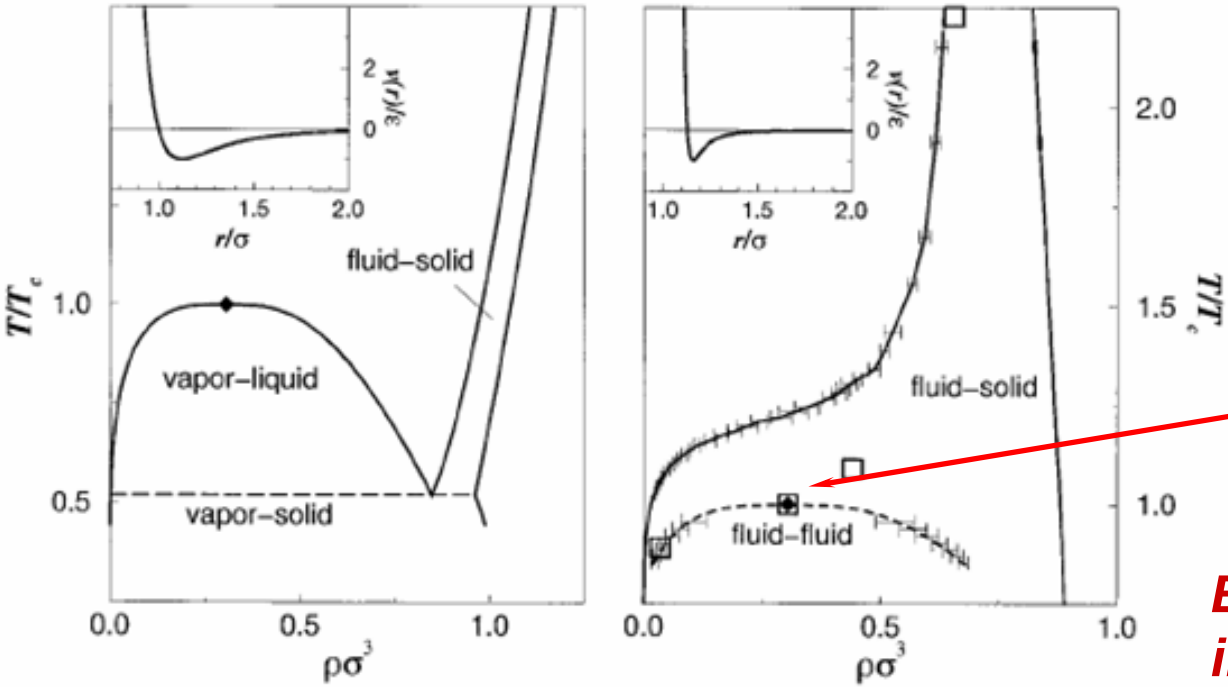
$Al_{89}Ni_6La_5$ - another example



B. Radiguet, APL, **92**, 103126 (2008)

Molecular Dynamics Calculations for Colloidal Suspension

Long-Range *Short-Range*

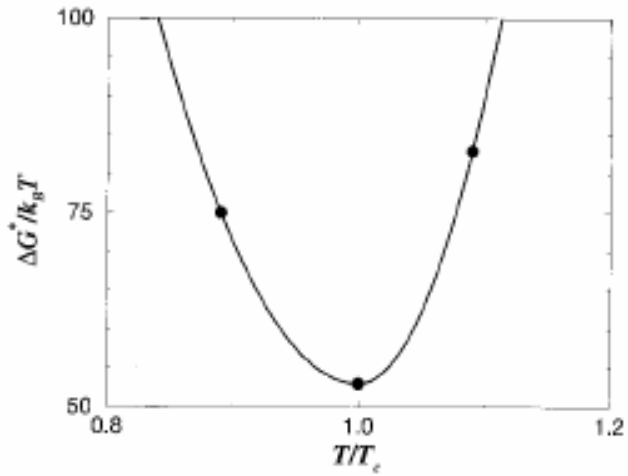


Pieter Rein ten Wolde & Daan Frenkel, Science, Vol. 277, 1975-78 (1997)

Metastable Critical Point

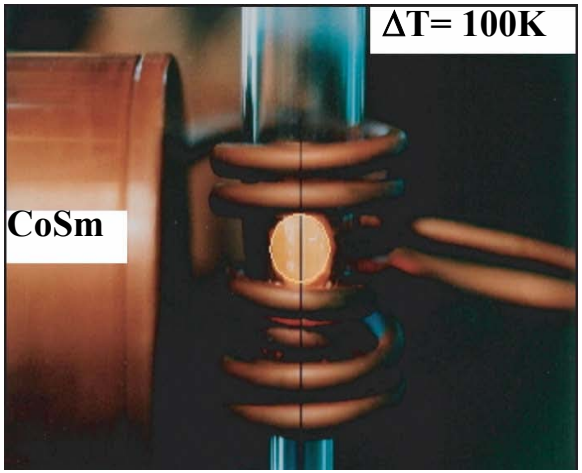
Enormous decrease in nucleation barrier !

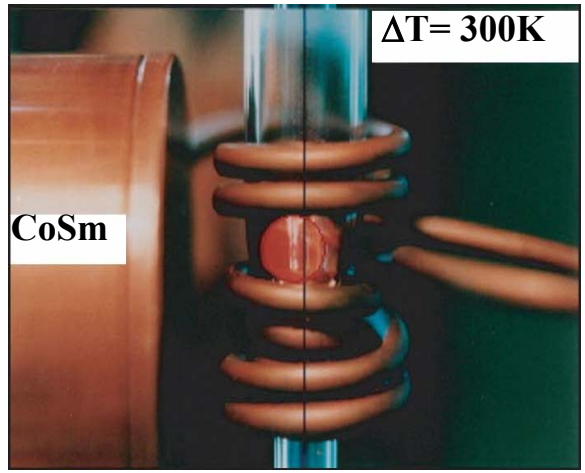
- dilute colloidal liquid (analogous to vapor phase)
- dense colloidal fluid (analogous to liquid)
- colloidal crystal phase



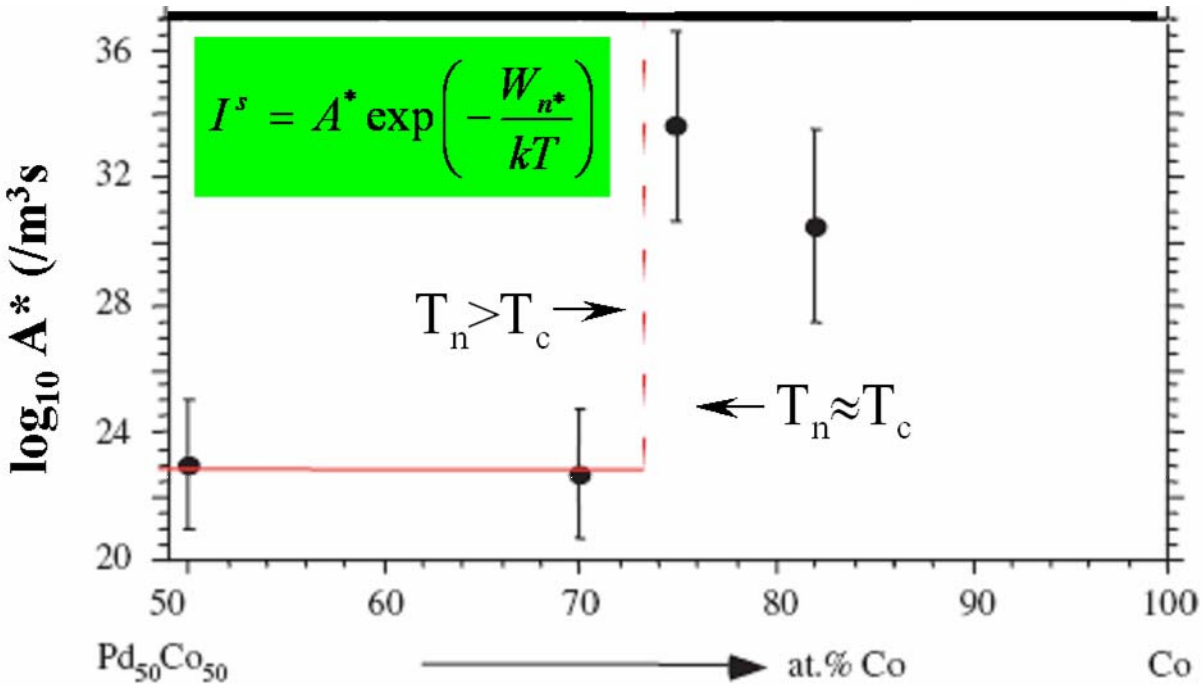
Coupling with Magnetic Ordering

D. Herlach *et al.* - Phil. Trans. Roy. Soc. **361**, 497 (2003)

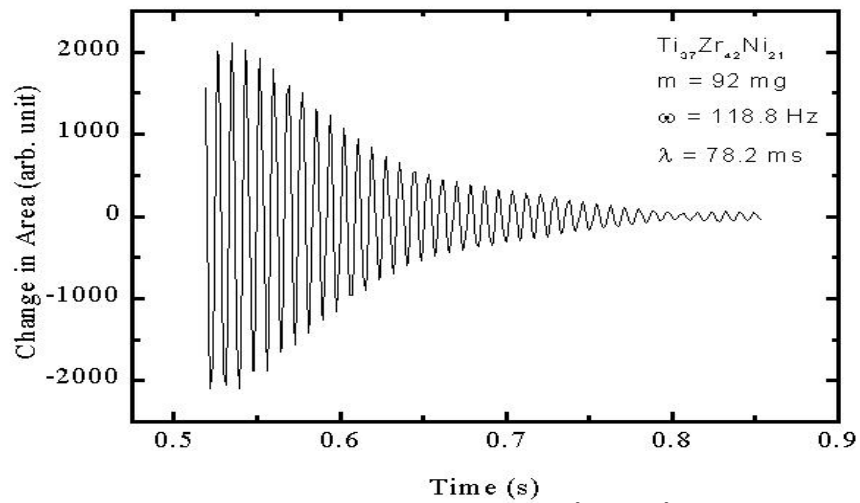




Undercooling is limited by onset of magnetic ordering, just above T_c in undercooled Co-based liquids

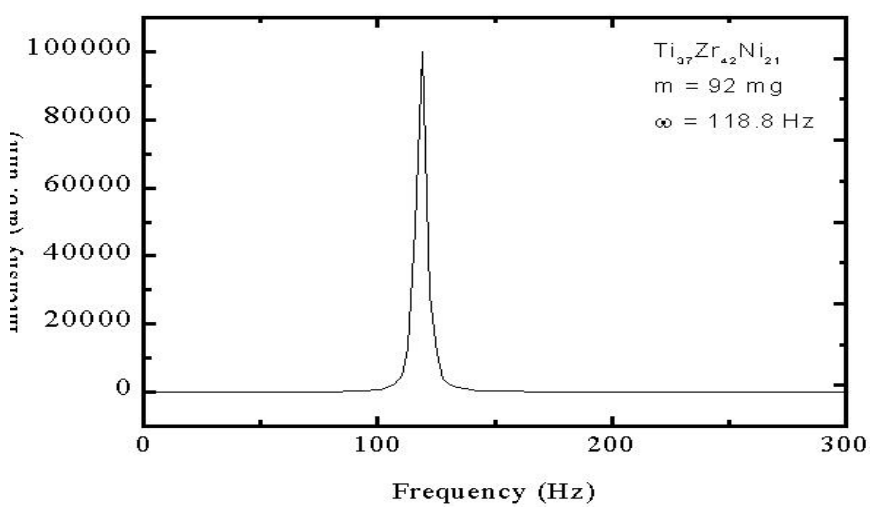


Oscillating Droplet Measurements



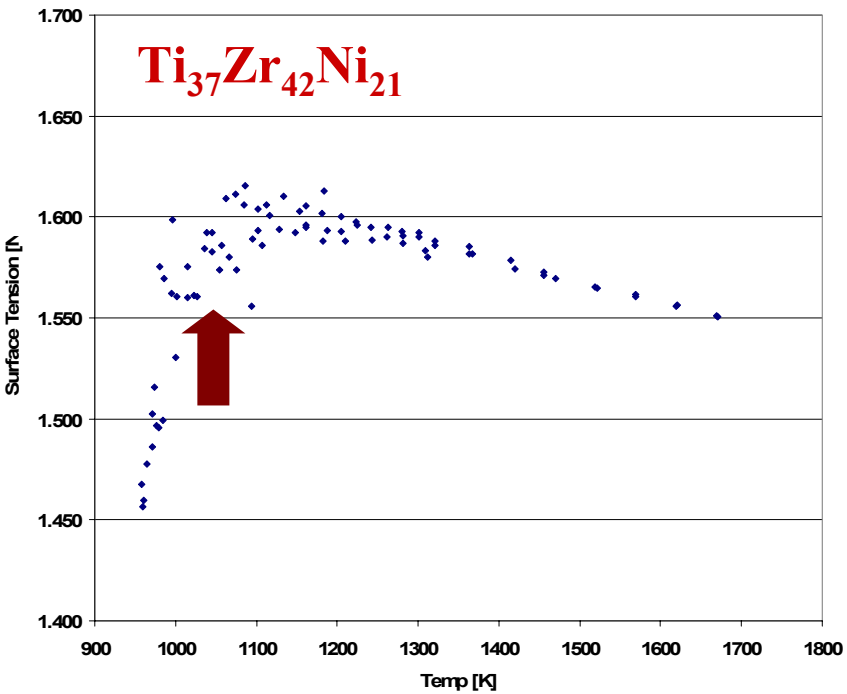
Damped oscillations

Exponential decay of amplitude



Single Frequency

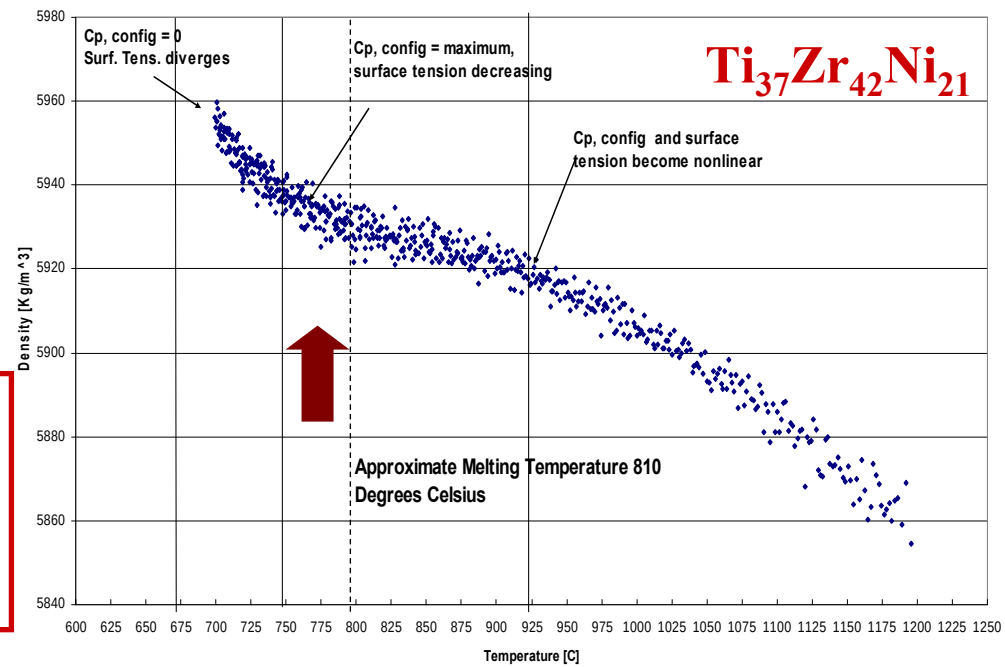
Thermo- physical Properties of Supercooled $Ti_{37}Zr_{42}Ni_{21}$



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

Dramatic decrease in surface tension

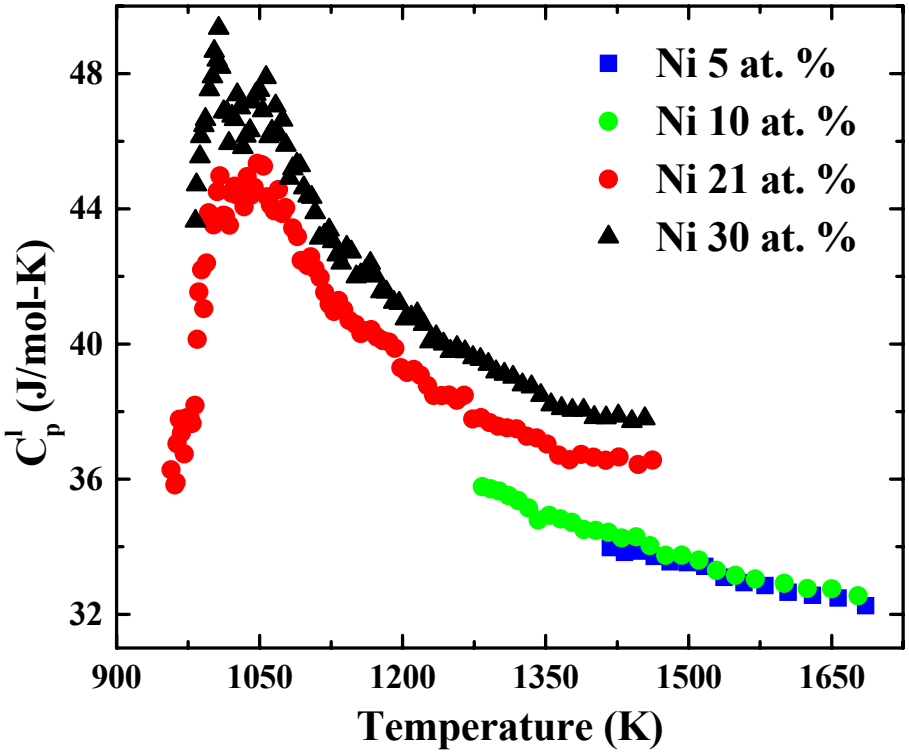
Density Inflection



Critical point ? – liquid/liquid phase transition associated with icosahedral ordering

Mode Coupling ?

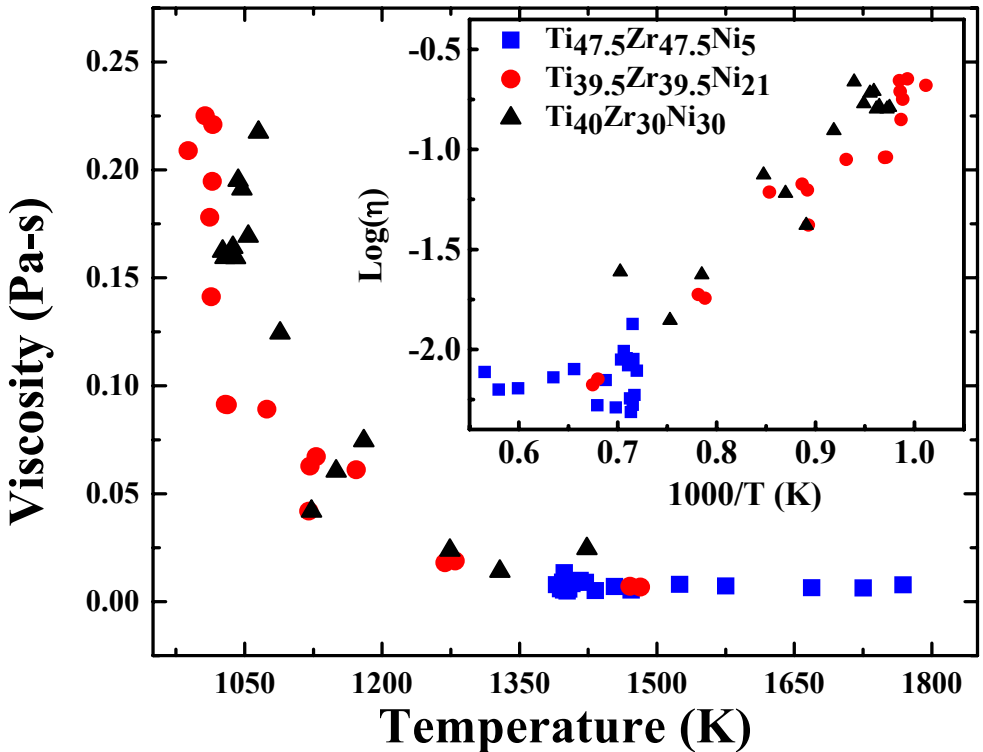
Thermo- physical Properties of Supercooled Liquid



Specific heat maximum ?

Issues with noise, emissivity - these are under investigation …

Rise in viscosity



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

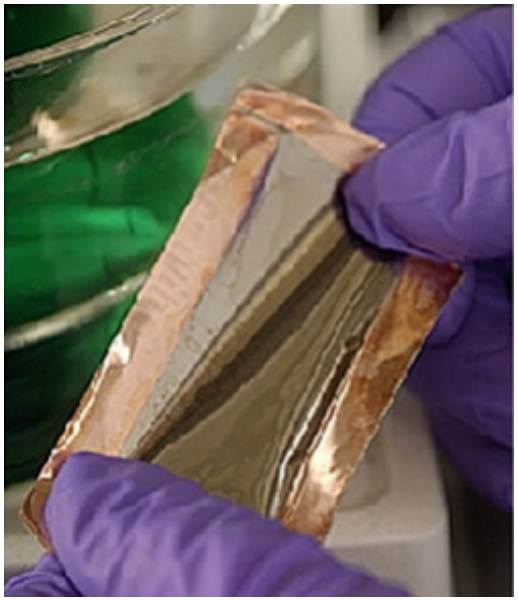
Outline

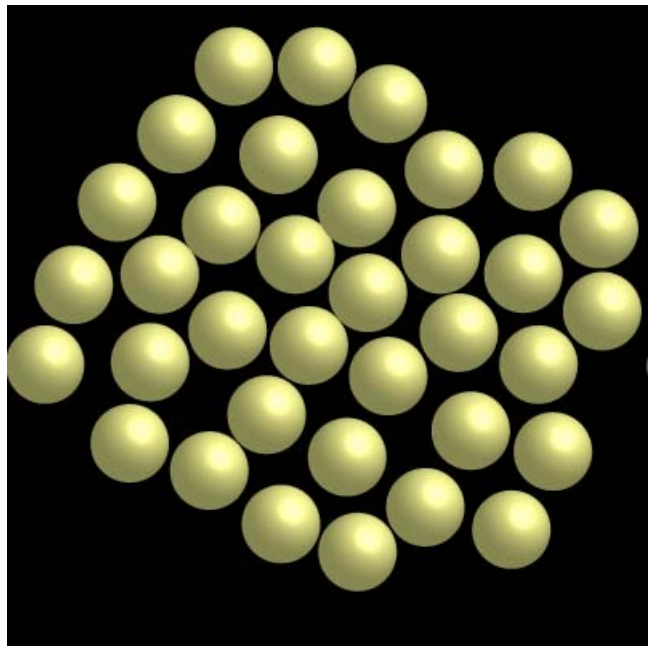
- Nucleation background
- Ordering in metallic liquids
- Coupling processes in nucleation
- Ordering and the glass transition
- Future directions
- Conclusion

Local Probe of Icosahedral Order in a Glass

Time-Dependent Nucleation Studies

Metallic Glasses

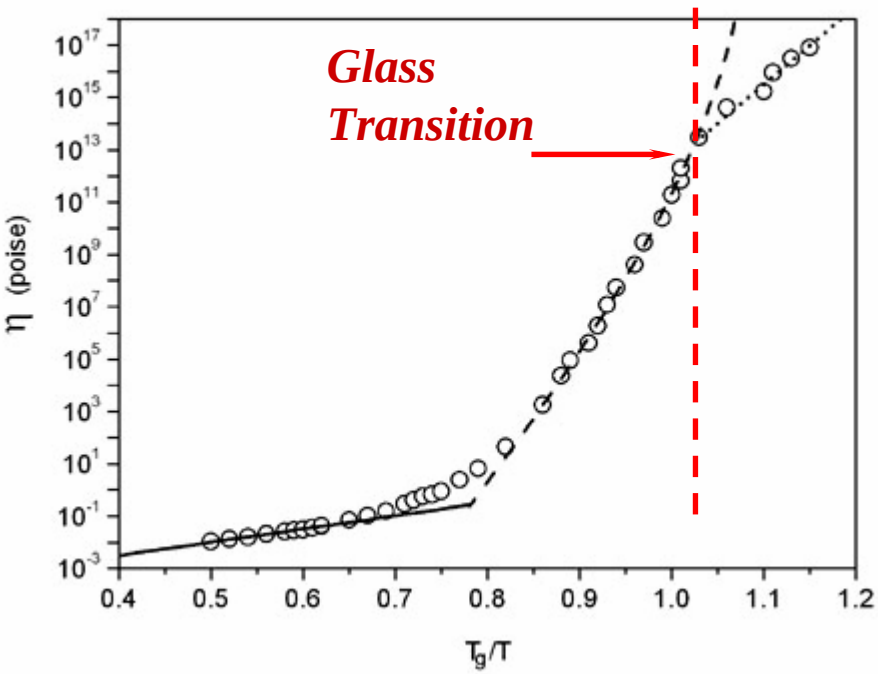


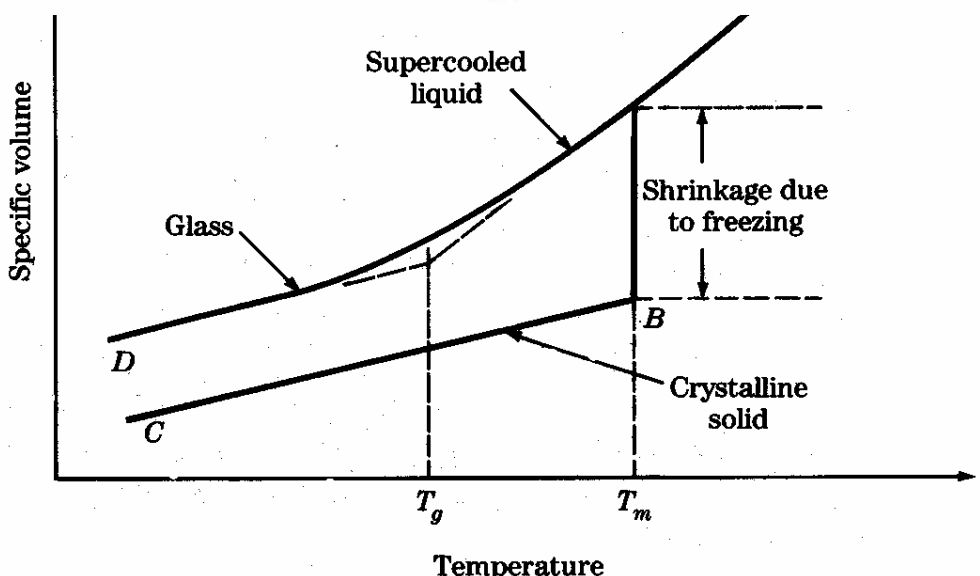


LIQUIDMETAL TECHNOLOGIES

- Rapidly cooled from liquid
- Dense packing but local structures are less ordered than crystals
- Similar to dense random packing structure
- Icosahedral short range order is prominent

Glasses and the Glass Transition

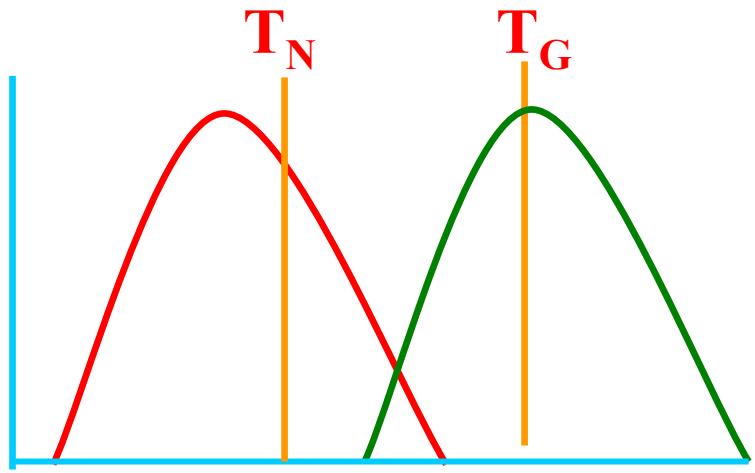


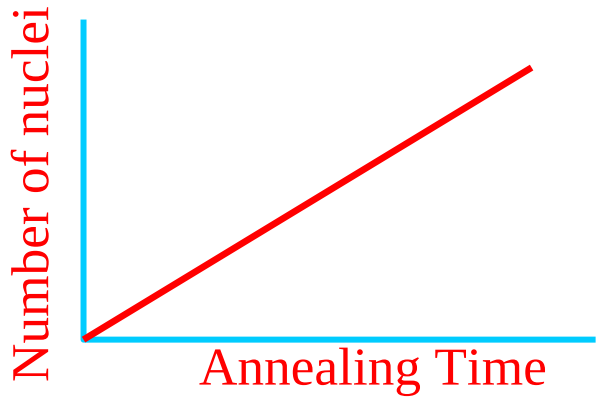


Quantitative Nucleation Rate Measurements

- Two-step annealing treatments
  - Nucleation Rate
  - Growth Velocity
- Count nuclei directly
  - Optical microscopy
  - SEM or TEM

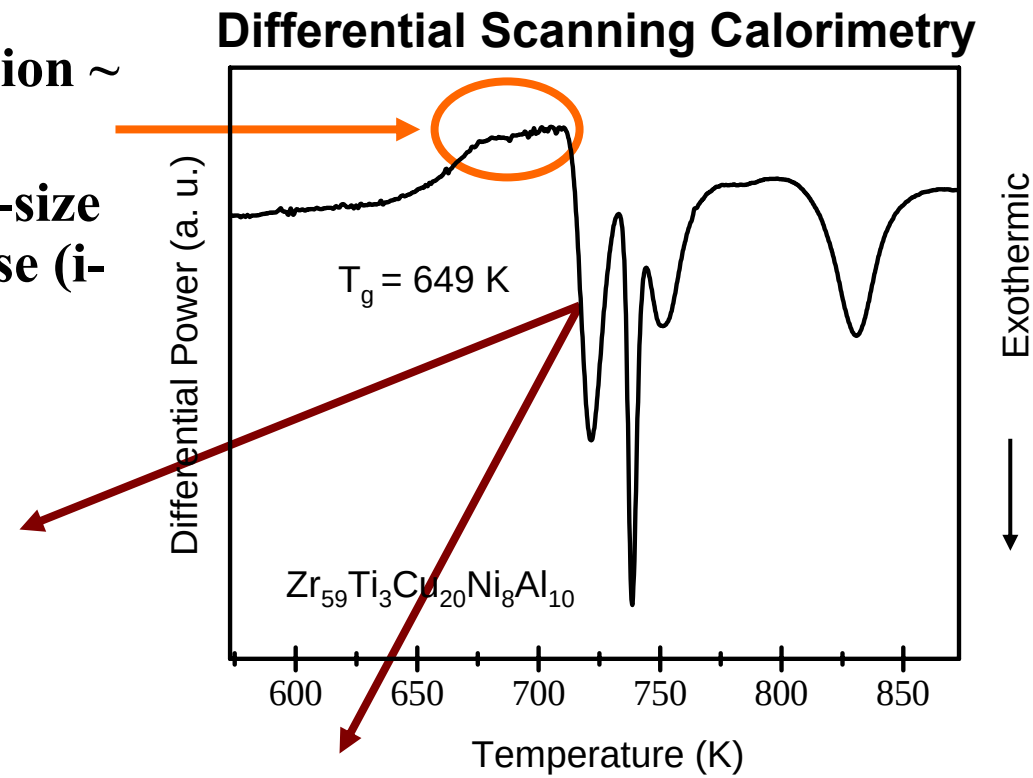
$$N = \int_0^t I(t)\,dt = I^S t$$

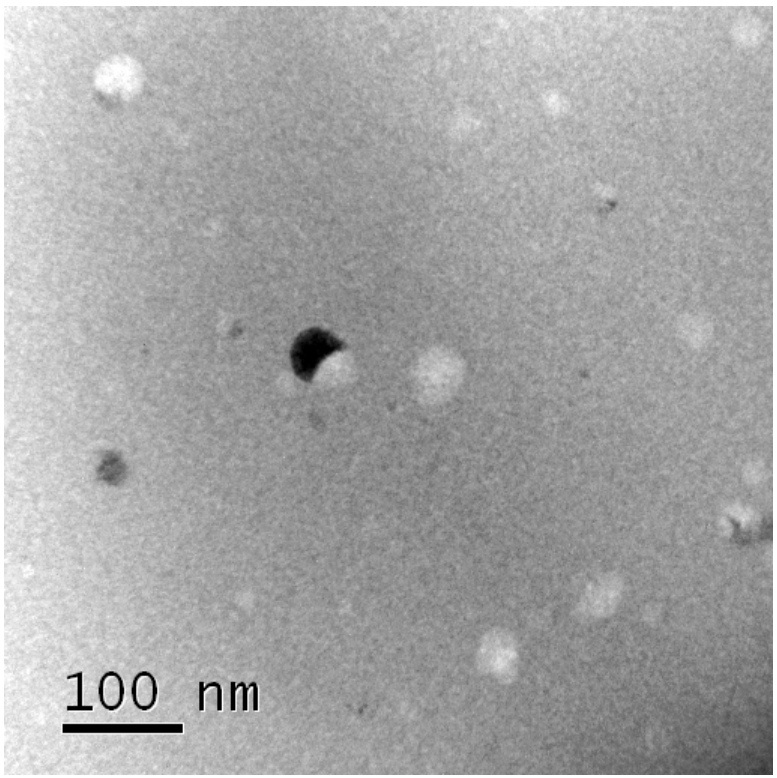


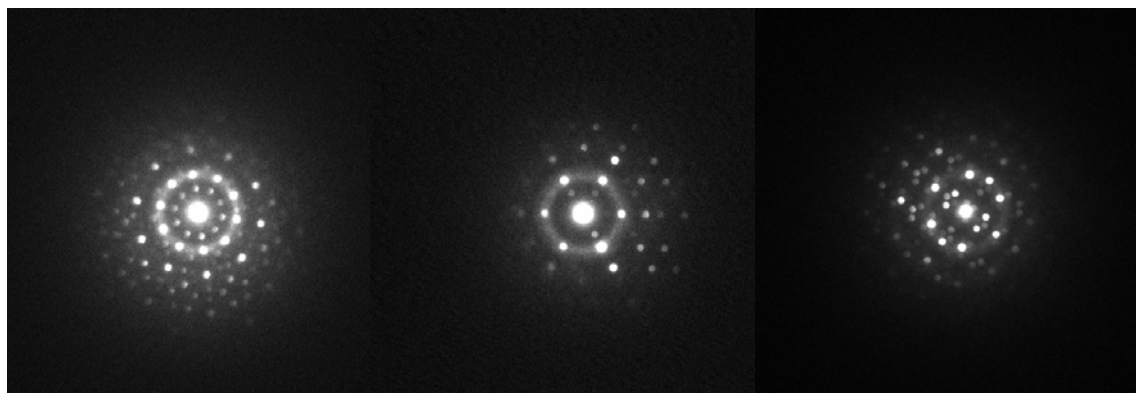


$Zr_{59}Ti_3Cu_{20}Ni_8Al_{10}$ Glass

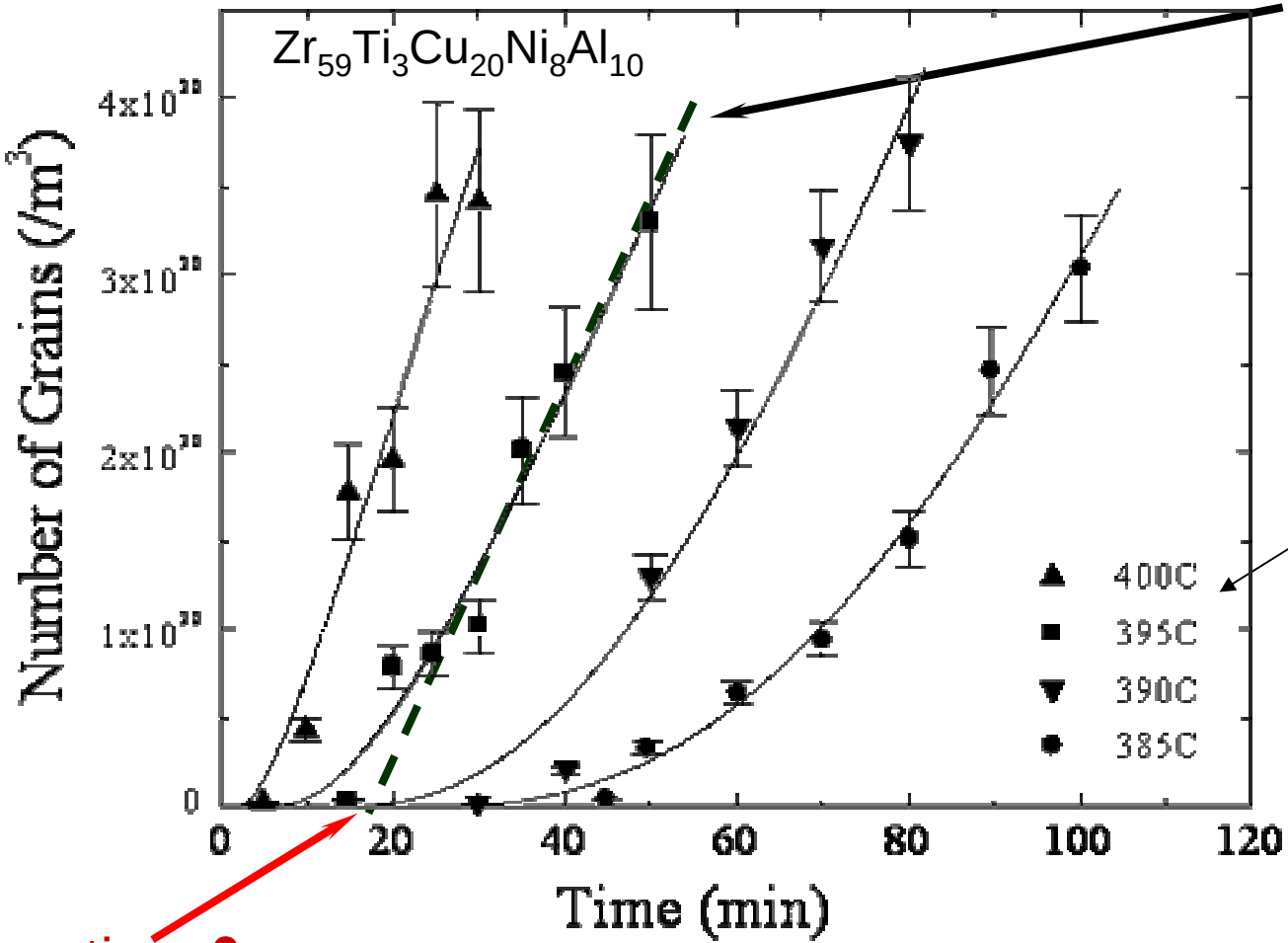
- **Bulk metallic glass former**
- **Large supercooled liquid region ~ 60 K**
- **Primarily crystallize to nano-size icosahedral quasicrystal phase (i-phase)**







Time-Dependent Nucleation of i-Phase



Steady State Nucleation Rate, I^s

Nucleation Temperatures

Induction time, **θ**

Growth (430°C)

T. Shen, T. H. Kim, A. K. Gangopadhyay, and K. F. Kelton, Phys. Rev. Lett., **102**, 05780 (2009)

From the Classical Theory of Nucleation

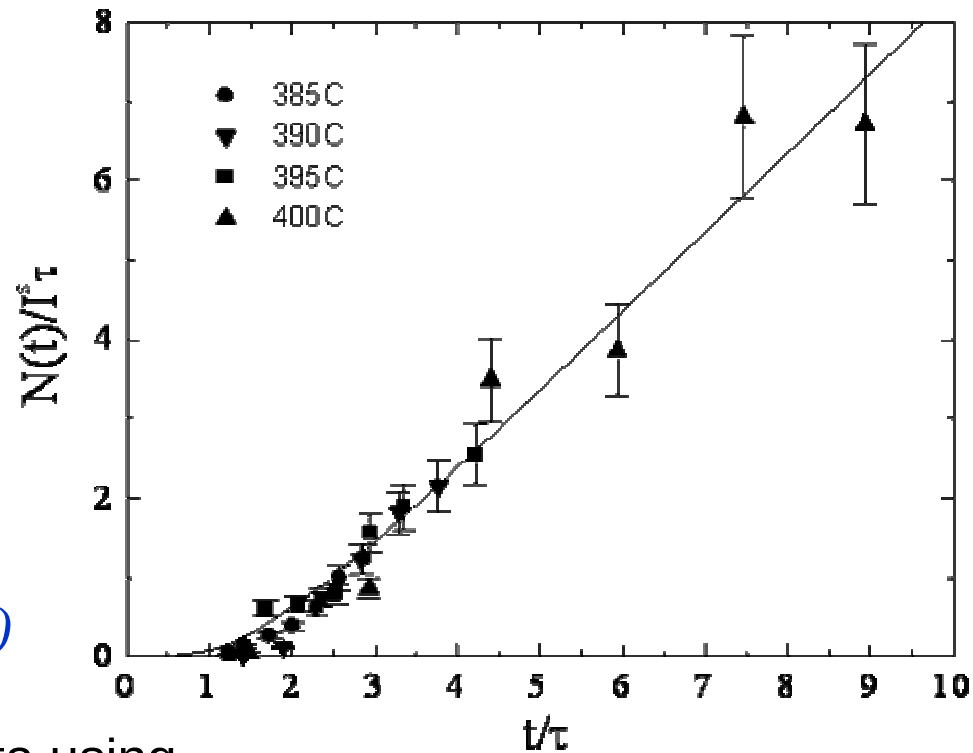
Transient time:

$$\tau = \frac{6}{\pi^2} \cdot \theta$$

Kashchiev scaling expression*:

$$\frac{N(t)}{I^s \tau} = \frac{t}{\tau} - \frac{\pi^2}{6} - 2\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{n^2 t}{\tau}\right)$$

D. Kashchiev, Surf. Sci. 14, 209 (1969)



Fit to time-dependent nucleation data using

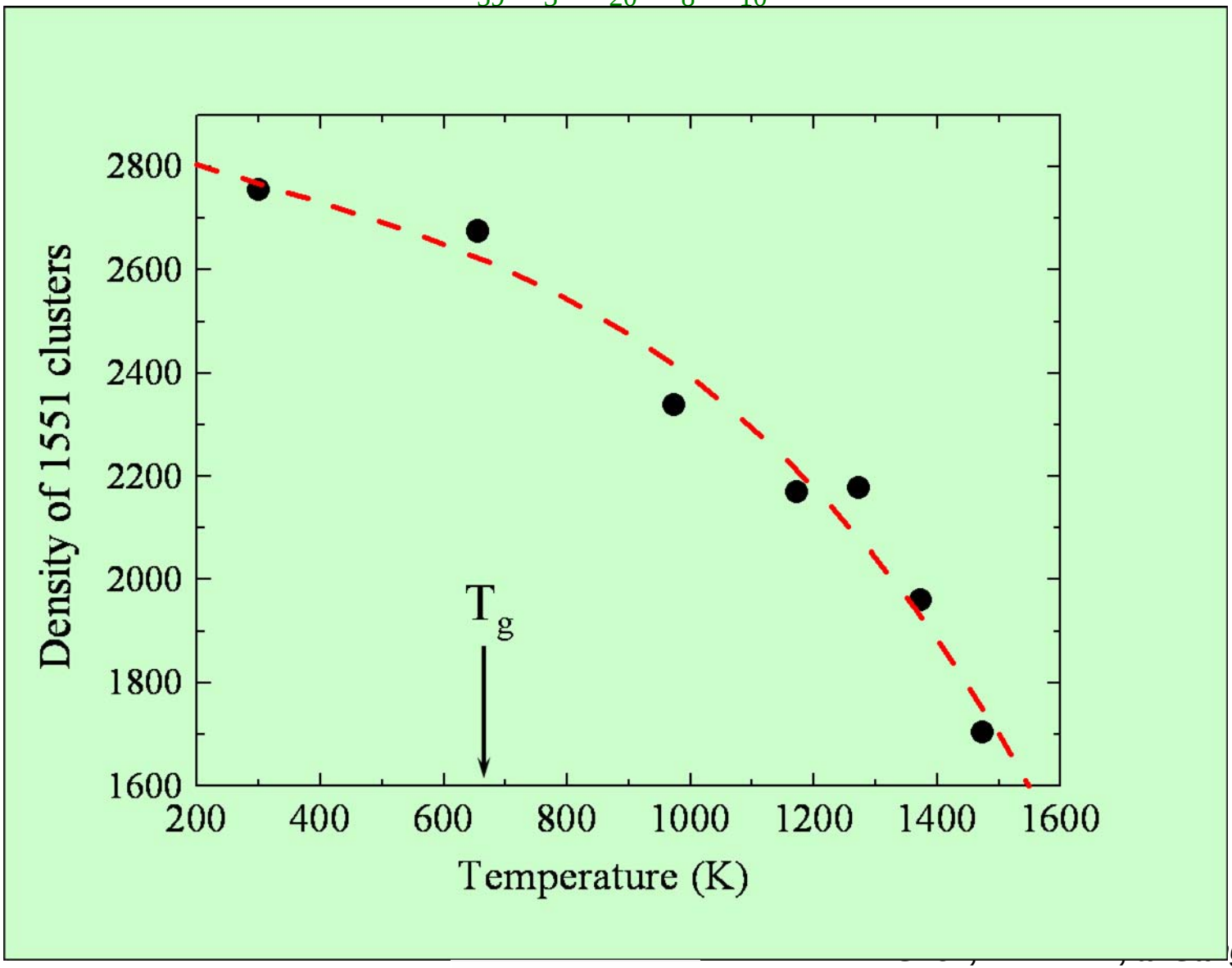
- measured viscosity
- calculated driving free energy from enthalpy and measured specific heats

$\sigma = 0.01 \pm 0.004\ \mathrm{J/m^2}$

$\Rightarrow$ glass has significant short- and medium-range icosahedral order

Synchrotron High Energy X-Ray Diffraction Studies

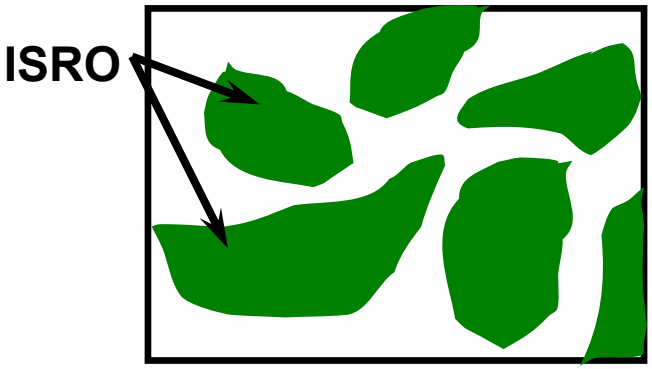
$Zr_{59}Ti_3Cu_{20}Ni_8Al_{10}$



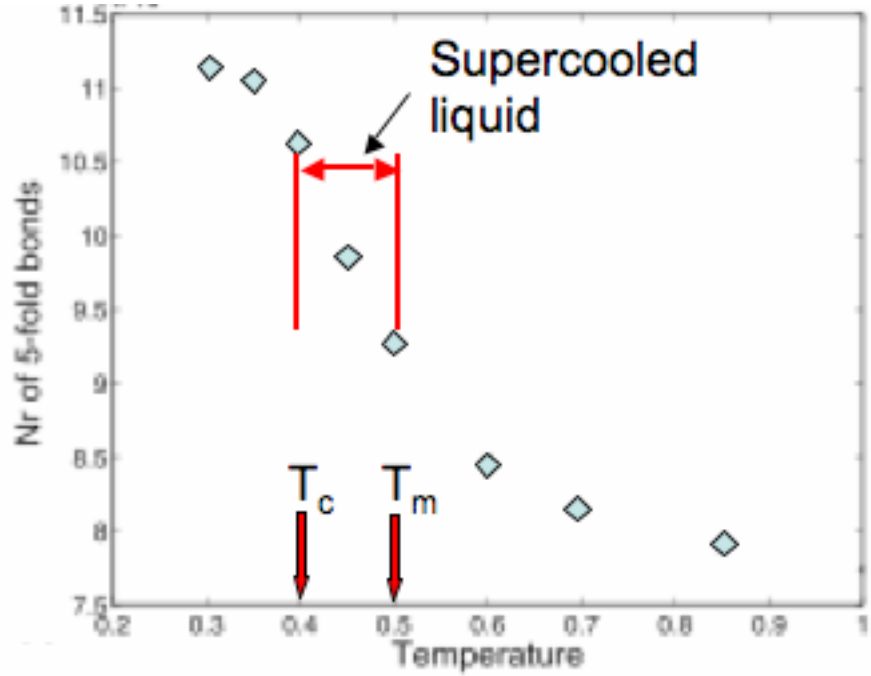
gopadhyay,
K. F. Kelton (2007)

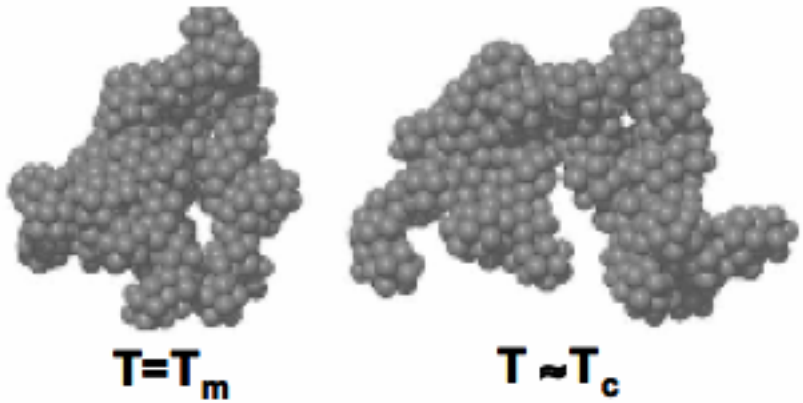
The Glass Transition

- Growth of ISRO



- Geometrical frustration





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

Zetterling et al, JNCS, **293-295**, 39 (2001)

Outline

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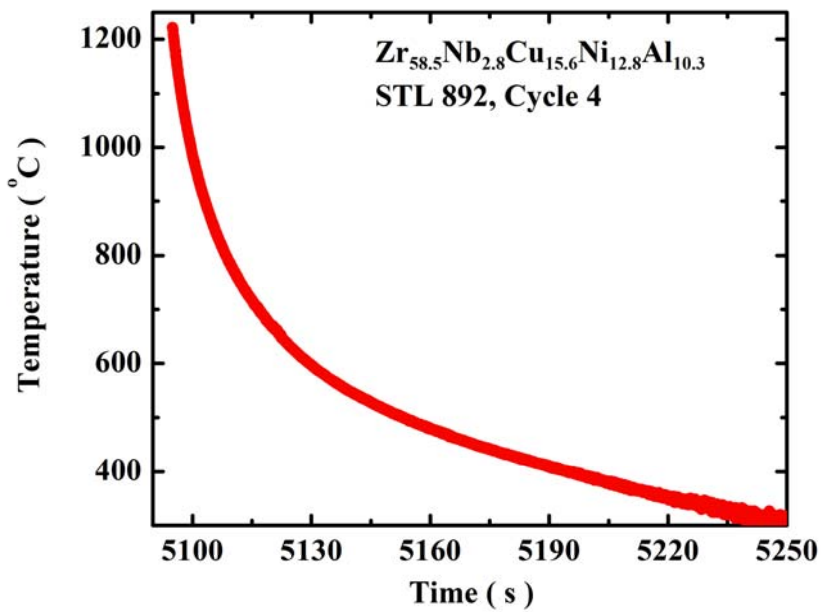
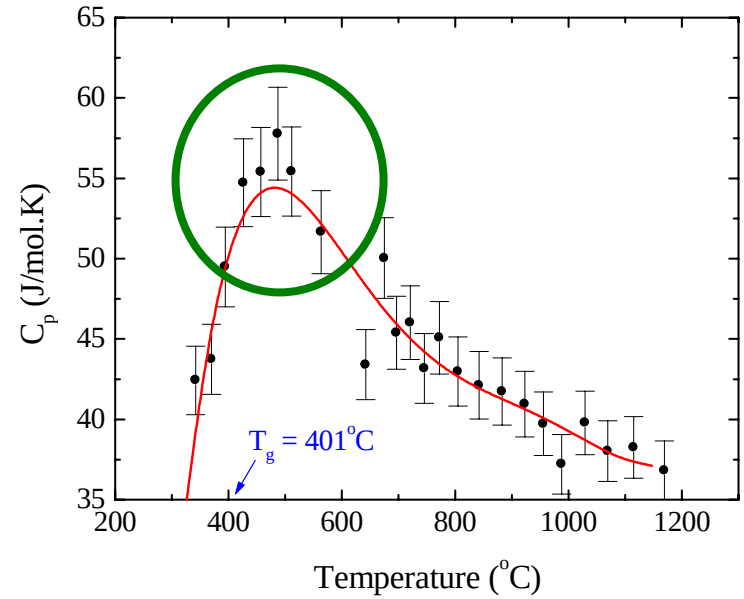
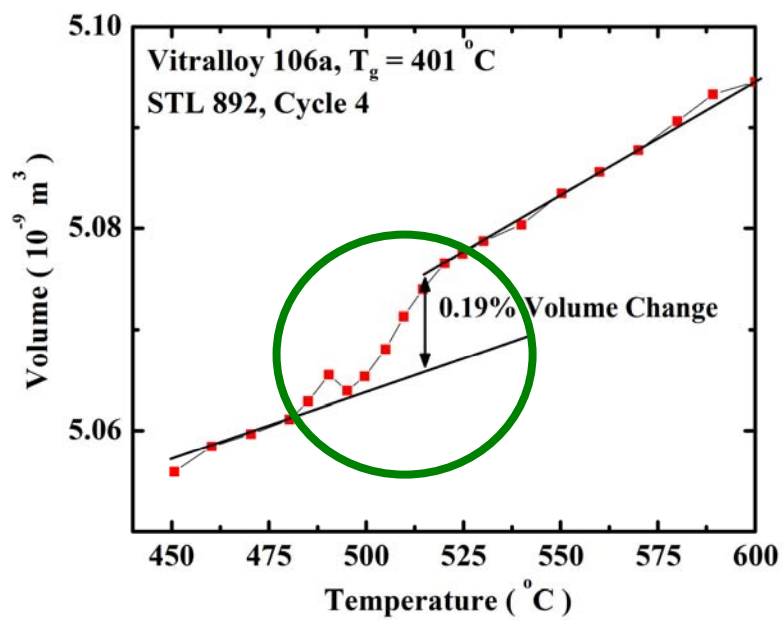
Thermo- physical Properties of Supercooled Vit 106a



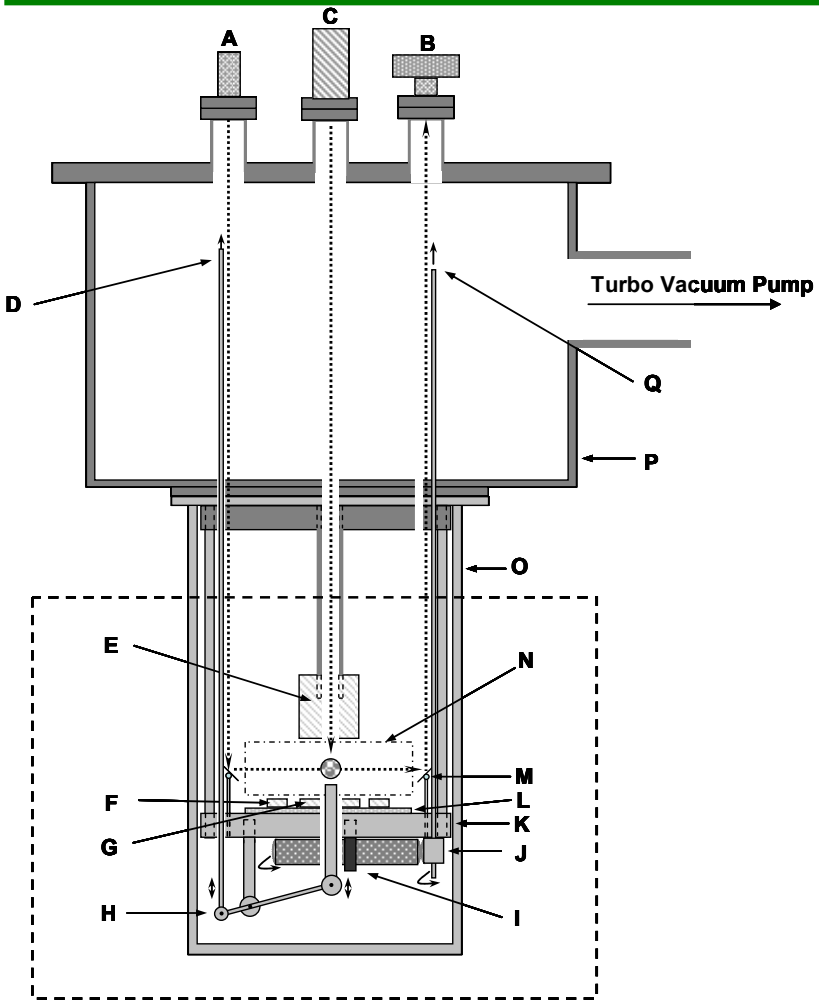


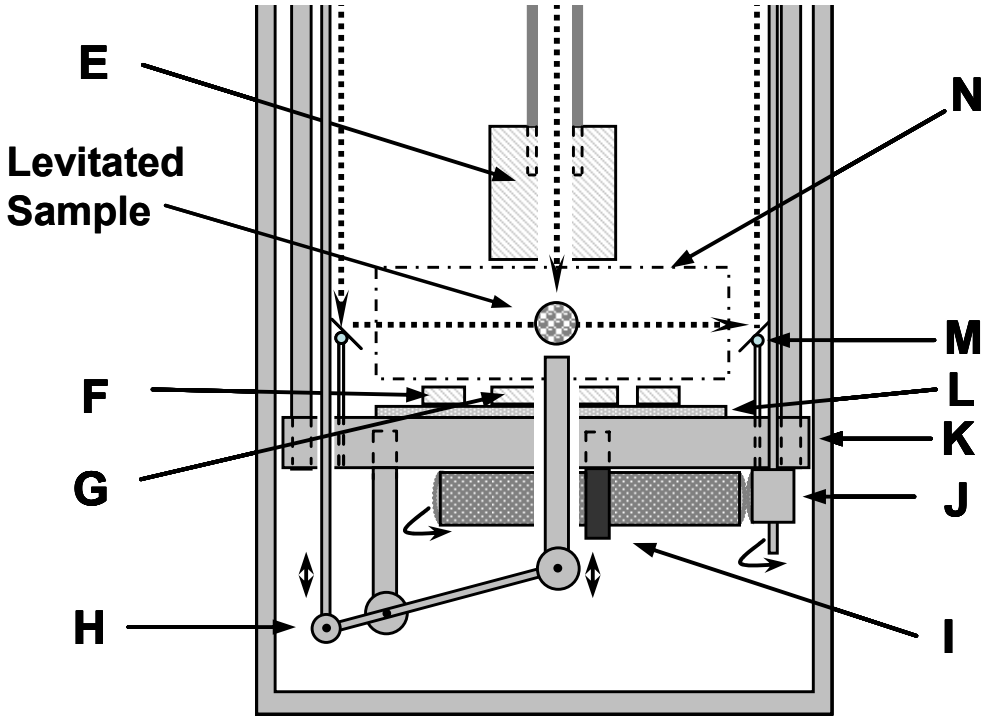
- No evidence for recalescence in time-temperature plot (formed glass)
- Broad specific heat maximum -

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



NESL – Neutron ESL





- MRI^2 Proposal Pending (submitted August, 2009)
- Elastic, inelastic and quasi-elastic studies on SNS (Oak Ridge)

Outline

- Nucleation background
- Ordering in metallic liquids
- Coupling processes in nucleation
- Ordering and the glass transition
- Future directions
- Conclusion

Conclusions

Local structure of supercooled transition metal liquids and glasses

- Icosahedral short-range order is significant in many cases, but
- The amorphous structures also contain many other types of local environments, including some with crystal character
- Some liquids show medium-range order
- An increase in icosahedral order is associated with the glass transition

Amorphous structure is important for phase formation and stability

- Directly couples with nucleation barrier
- Likely important for glass formation (crystal nucleation is difficult)

Possible new types of nucleation where other phase transitions (not Necessarily of the same order couple with the nucleation barrier

Studies of dynamical properties of liquids needed

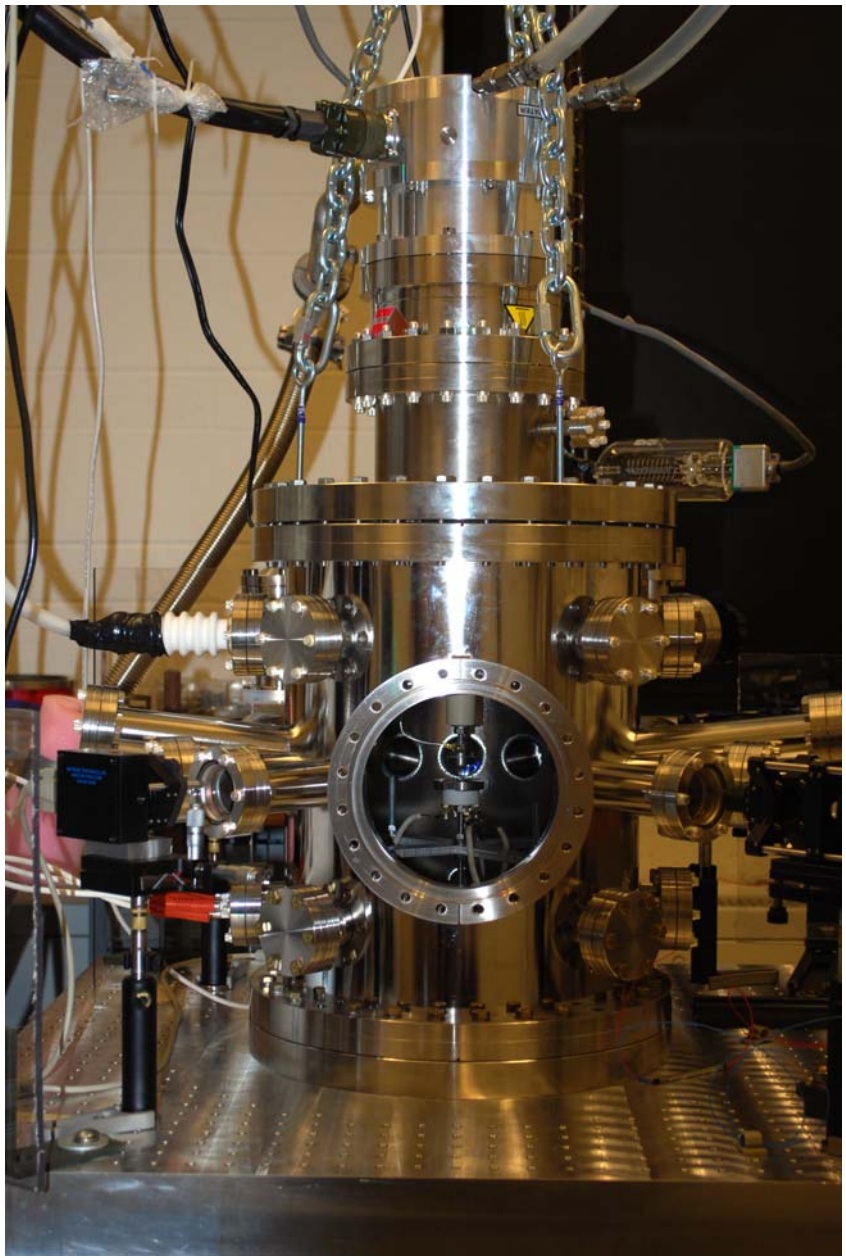
Postdoctoral and Graduate Student Openings

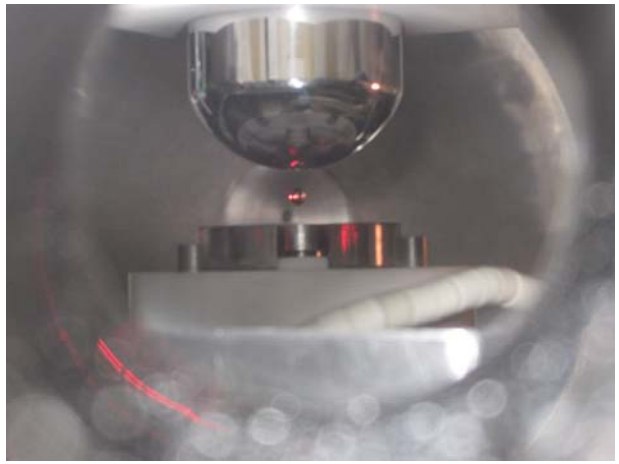
Oh, Yea – What about the goat urine?

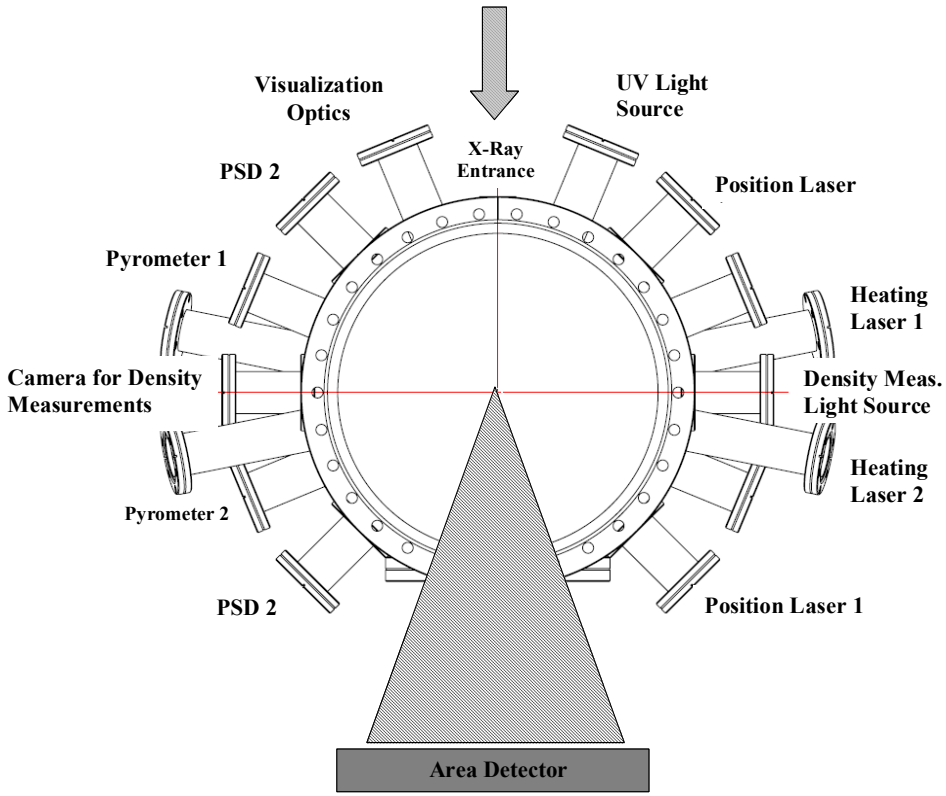
- *Forms martensite (tetragonal) from austenite (fcc)*
- *Precipitation of carbides and nitrides at the surface*
- *Surface hardening treatments*

Case Hardened Steel

WU-BESL






Visualization Optics
UV Light Source
X-Ray Entrance
PSD 2
Position Laser
Pyrometer 1
Heating Laser 1
Camera for Density Measurements
Density Meas. Light Source
Heating Laser 2
Pyrometer 2
PSD 2
Position Laser 1
Area Detector