Fragility and the Rate of Structural Ordering in a Supercooled Metallic Liquids

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imse

National Science Foundation
WHERE DISCOVERIES BEGIN

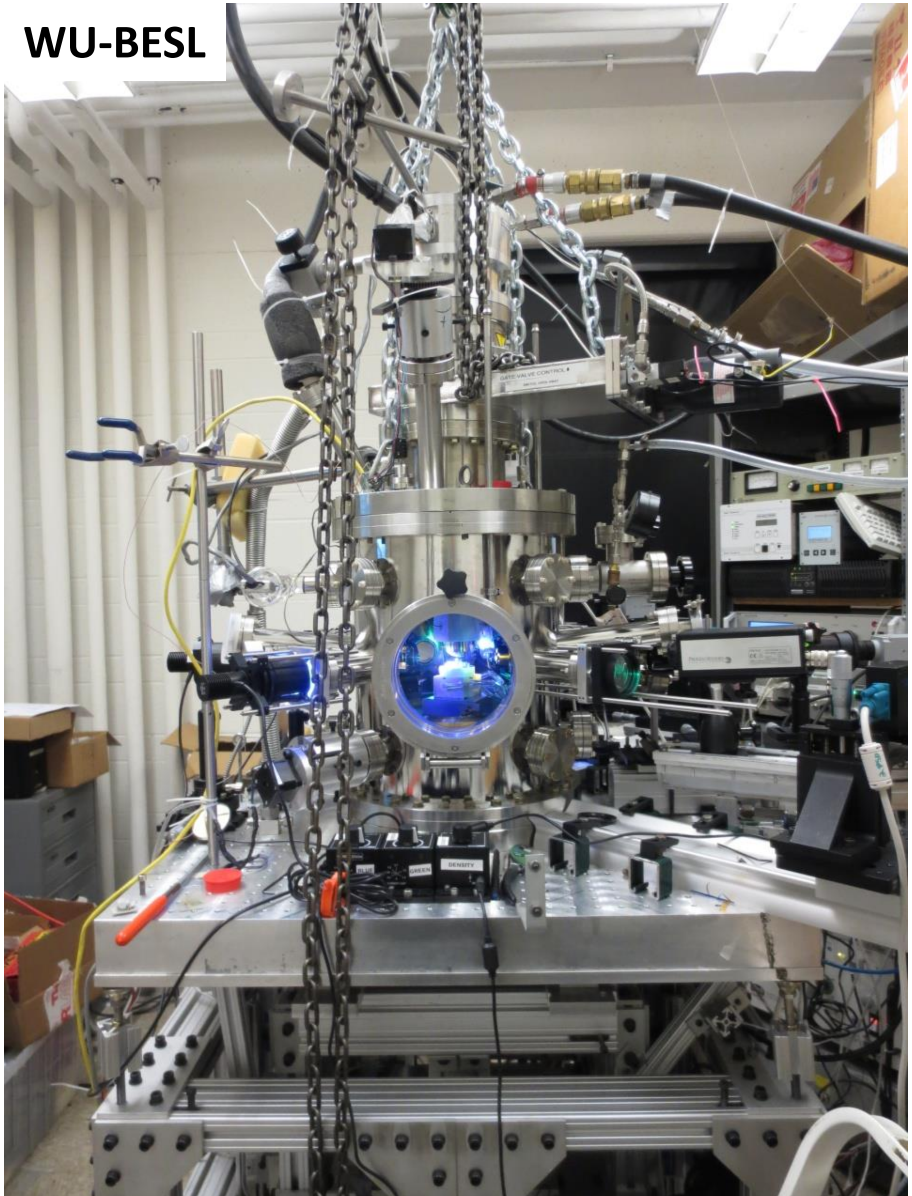
NASA

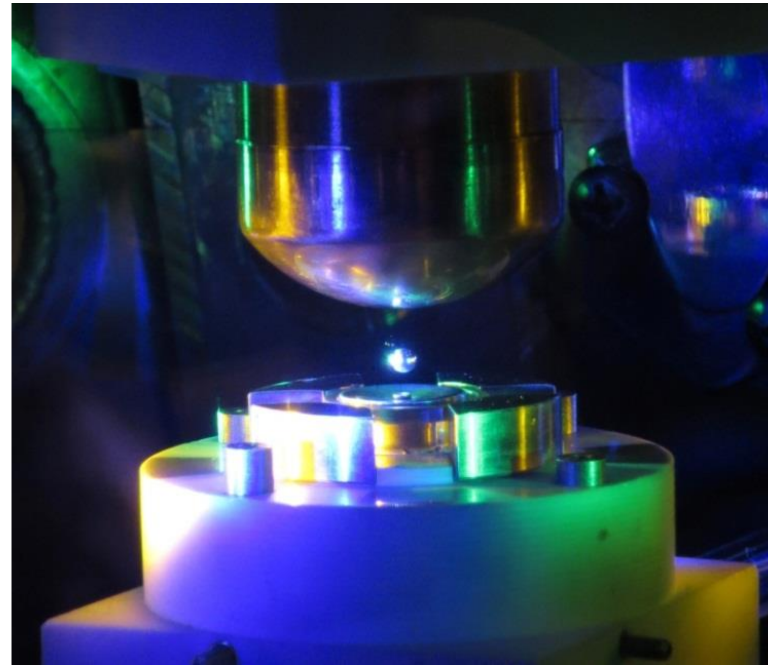
Metallic Glasses

Are There Clues for Good Glass Formation in the High Temperature Liquid?

Containerless Processing – ESL (Electrostatic Levitation)

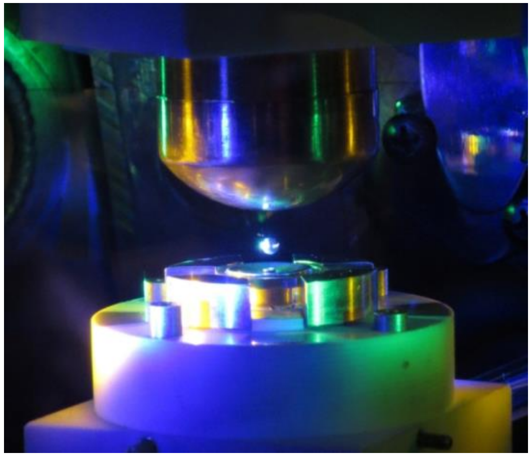
WU-BESL

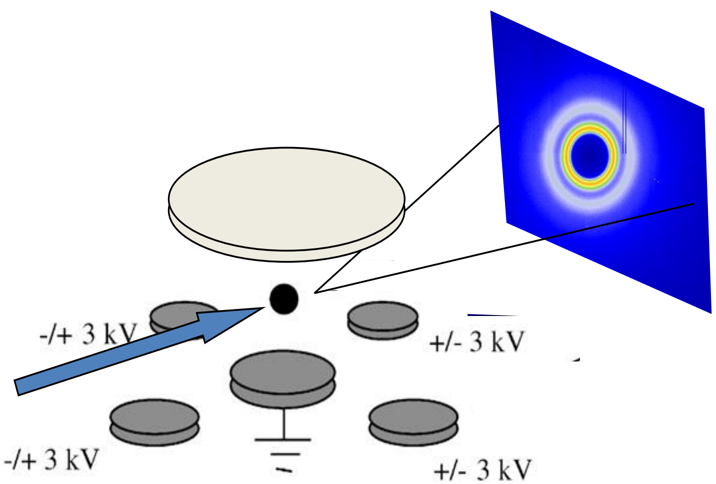


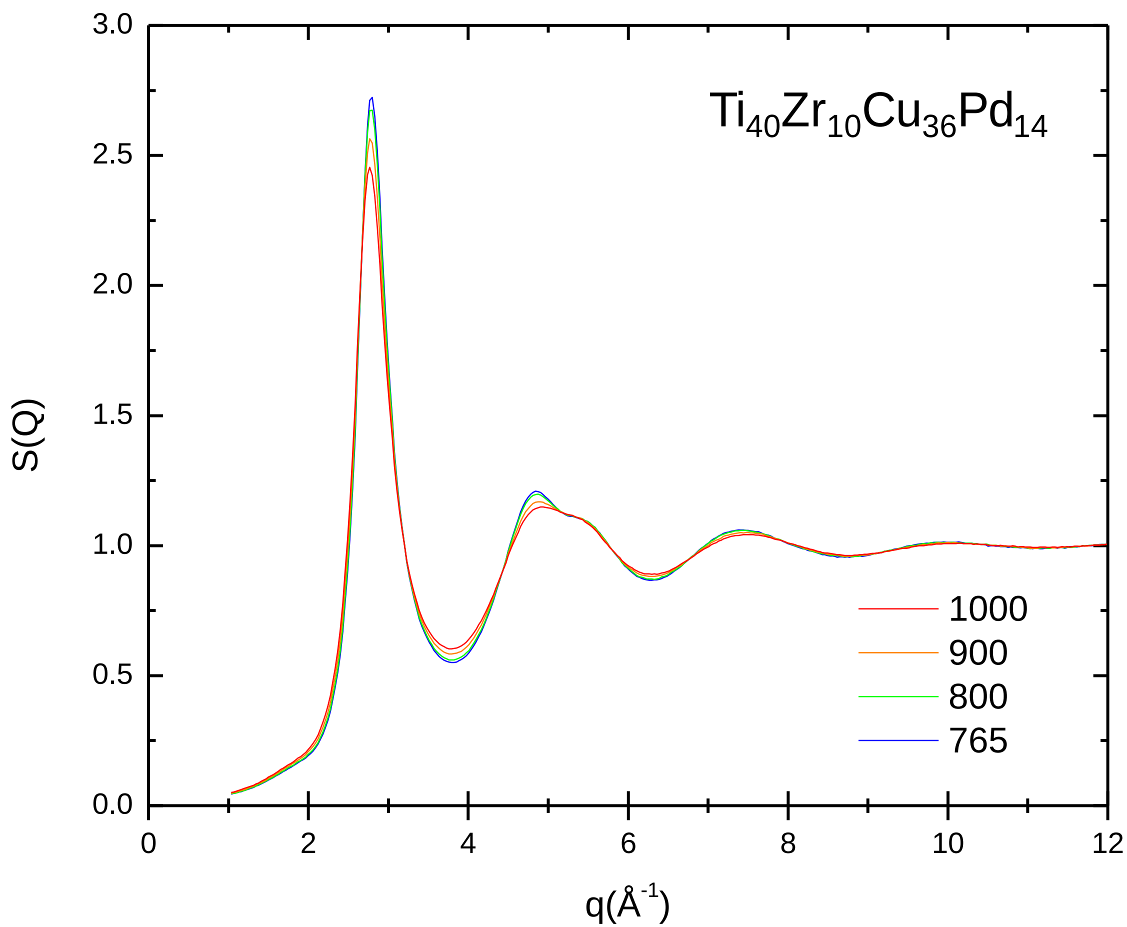


- Designed to be transportable
- Liquid measurements
    - Synchrotron X-ray scattering
    - Maximum undercooling
    - Specific heat
    - Density
    - Viscosity
    - Surface tension

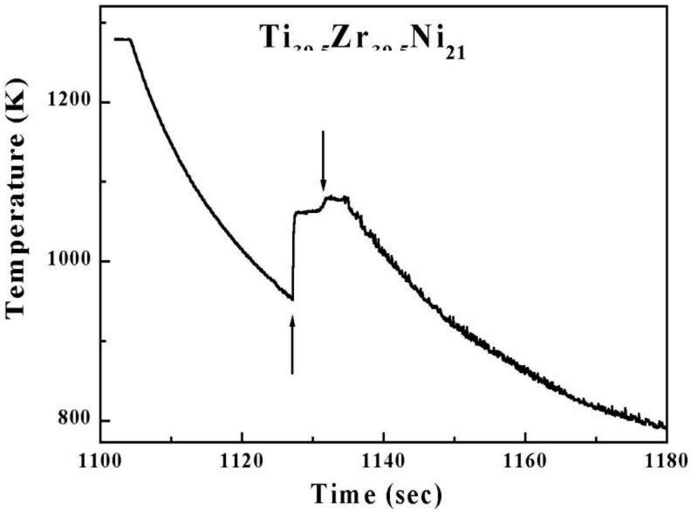
X-ray Scattering Studies with WU-BESL



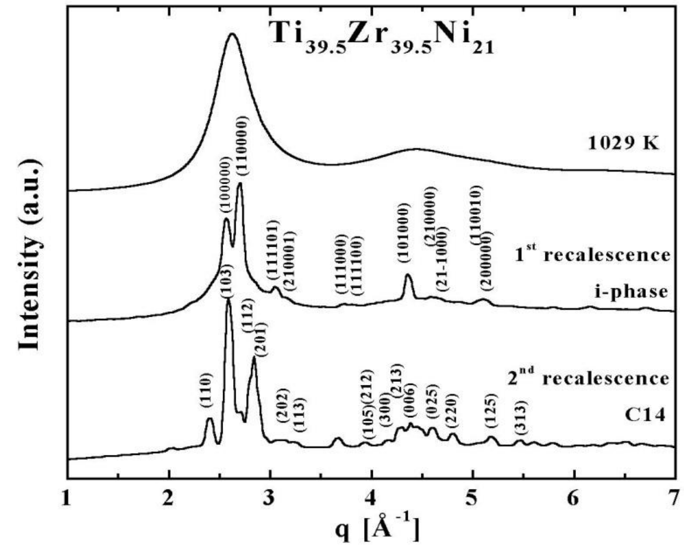


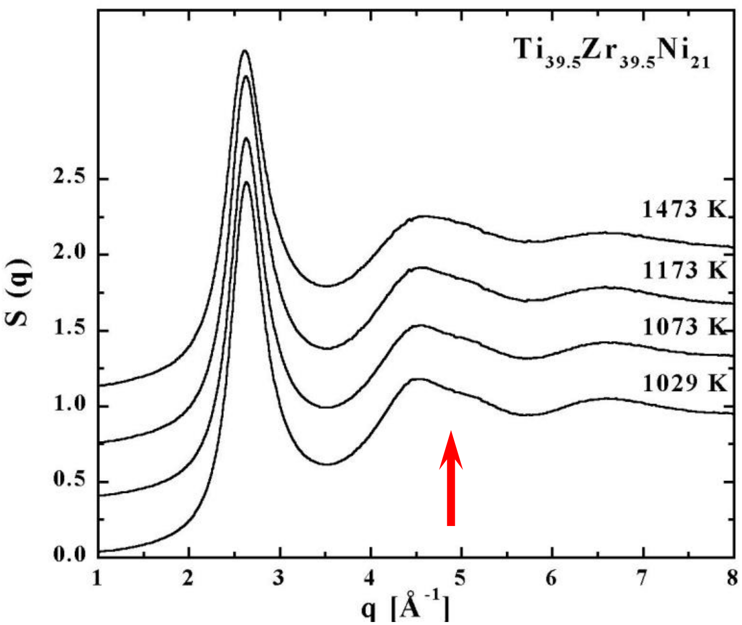


Icosahedral Ordering in a $Ti_{39.5}Zr_{39.5}Ni_{21}$ Liquid and Nucleation

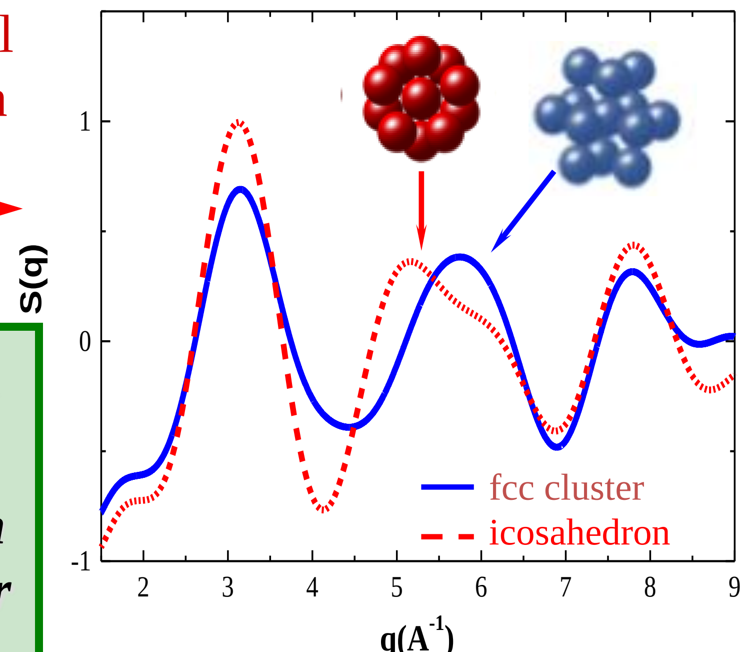


Recalescence to metastable quasicrystal





Icosahedral ordering in liquid



Ordering lowers nucleation barrier for i-phase

K. F.Kelton, et a. *Phys. Rev. Lett*, **90**, 195504 (2003)

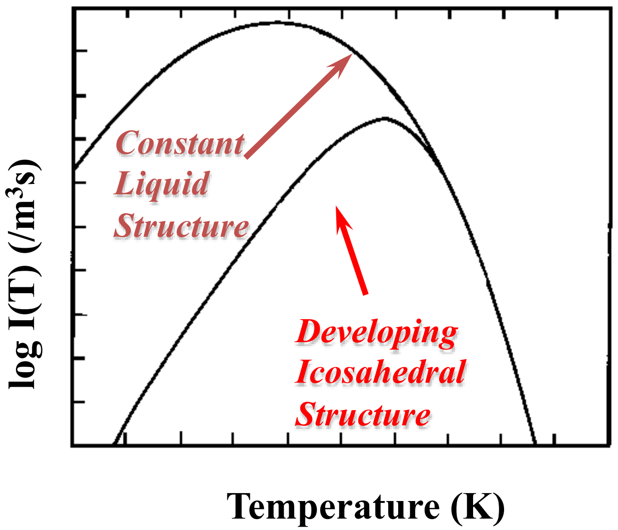
Consequences of ISRO

Crystal Nucleation Rate

$$I = \frac{A}{h}\exp\left(-\frac{B}{T}\frac{\sigma^3}{\Delta g^2}\right)$$

Based on Experiment and MD, ISRO:

- Increases σ
- Lowers energy of liquid, decreasing Δg
- Increases viscosity



- Decreases nucleation rate for crystal phases

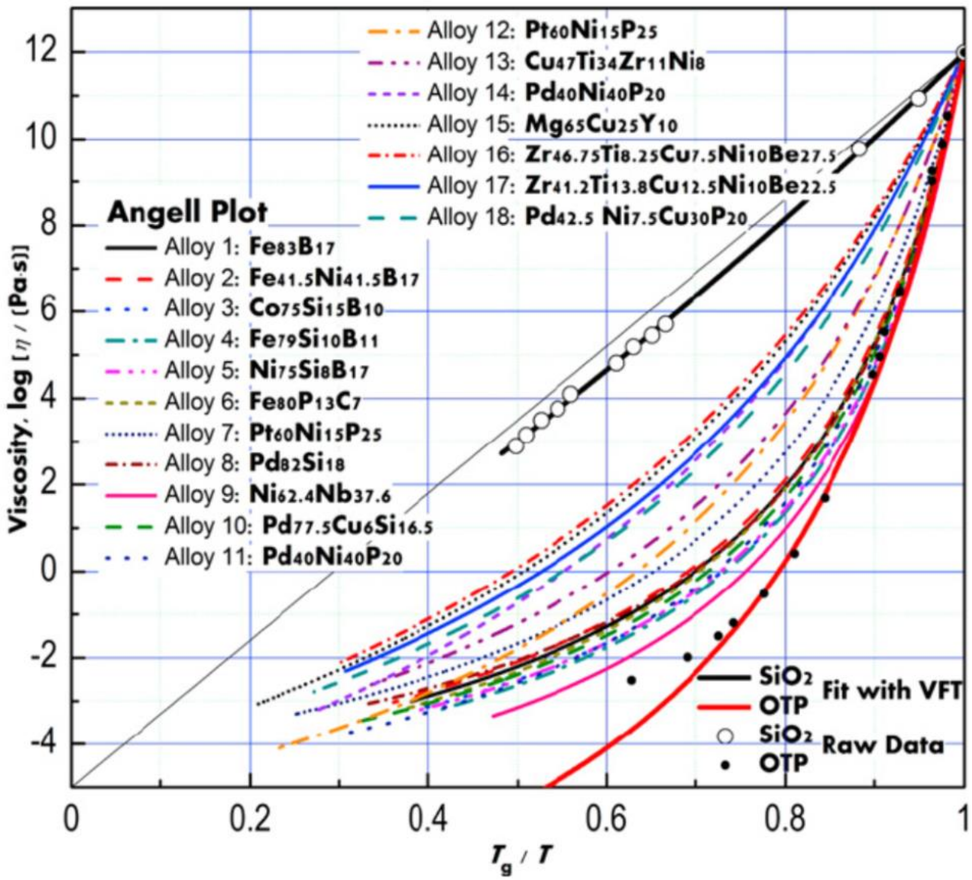
But:

a. ***While icosahedral ordering is very common in transition metal liquids, other alloy liquids likely have different local local ordering structures.***

b. ***Other types of local order in liquids, <u>if they lower the energy of the liquid and are incompatible with structures of potential crystal products</u>, will help glass formation in the same way as icosahedral ordering in transition metal liquids.***

c. ***Icosahedral ordering can actually HURT glass formation, increasing the chance for icosahedral phase formation.***

Liquid Fragility and Glass Formation



A. Takeuchi, H. Kato, A. Inoue, Intermetallics, **18**, 406-411 (2010)

Tg
1446
1112
713
670
550
370.5
yCl 275
332
300
85.2
bonate 152
239.7

- Fragility Index, m

$$m = \left. \frac{d(\log \eta)}{d(T_g / T)} \right|_{T=T_g}$$

- Larger m – fragile
- Smaller m – strong

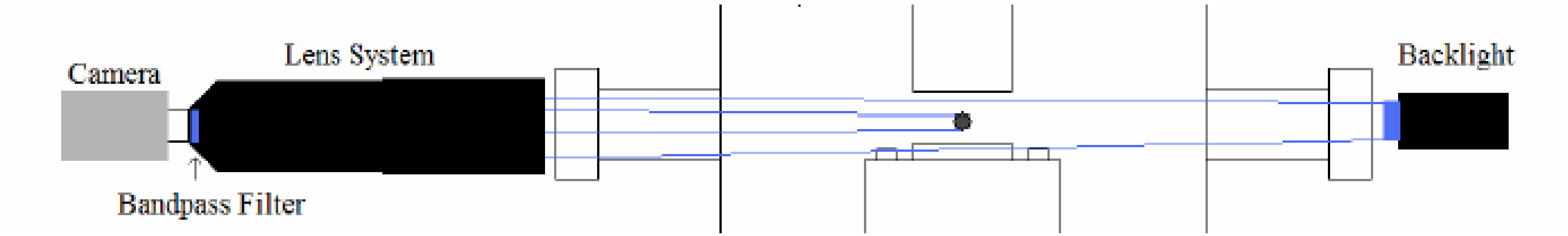
Stronger liquids argued to be better Metallic glass formers

R. Busch et al., Acta Mater. 46, 4725 (1998).
Sha et al, *JAP*, **105**, 043521 (2009)
Russew et al, *J. Phys.: Conf. Ser.*, **144,** 012094 (2009)
Jakse and Pasturel, *Phys. Rev. B*, **78**, 214204 (2008)

Is there a Structural Signature of Fragility?

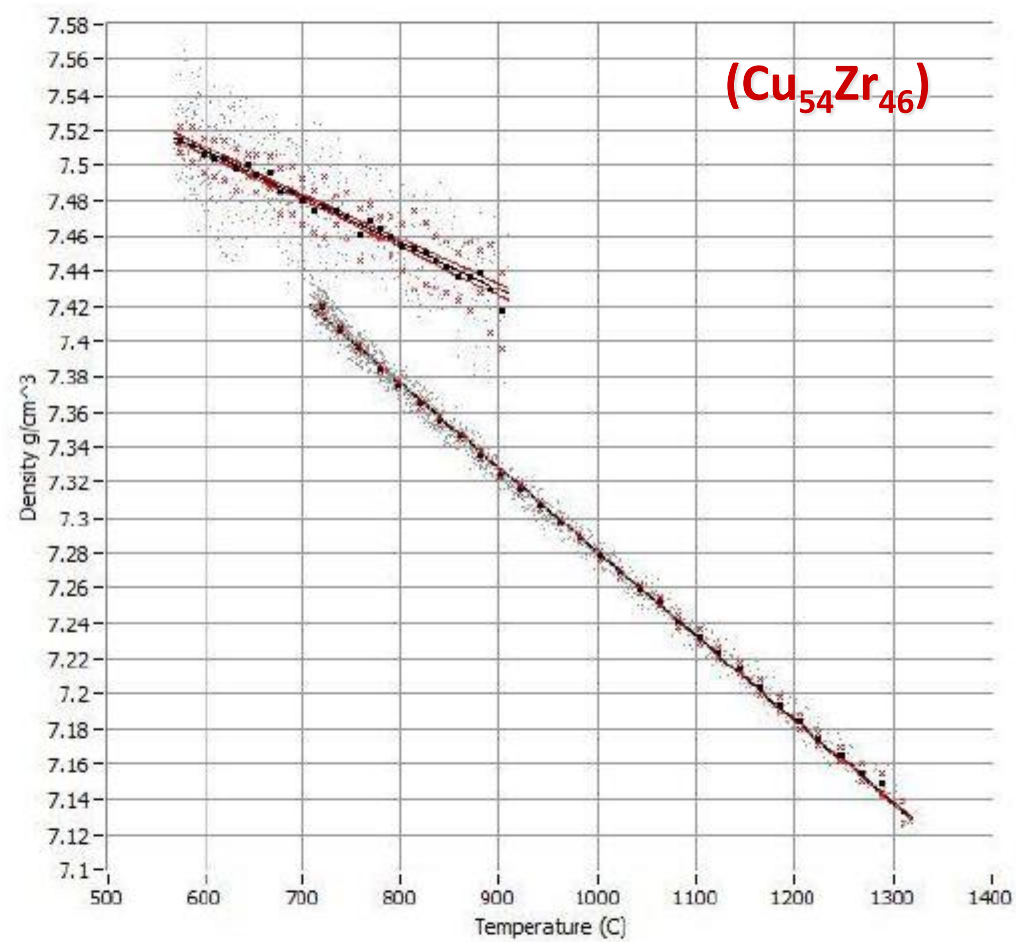
Temperature Dependence Of the Volume

Density Measurements in BESL

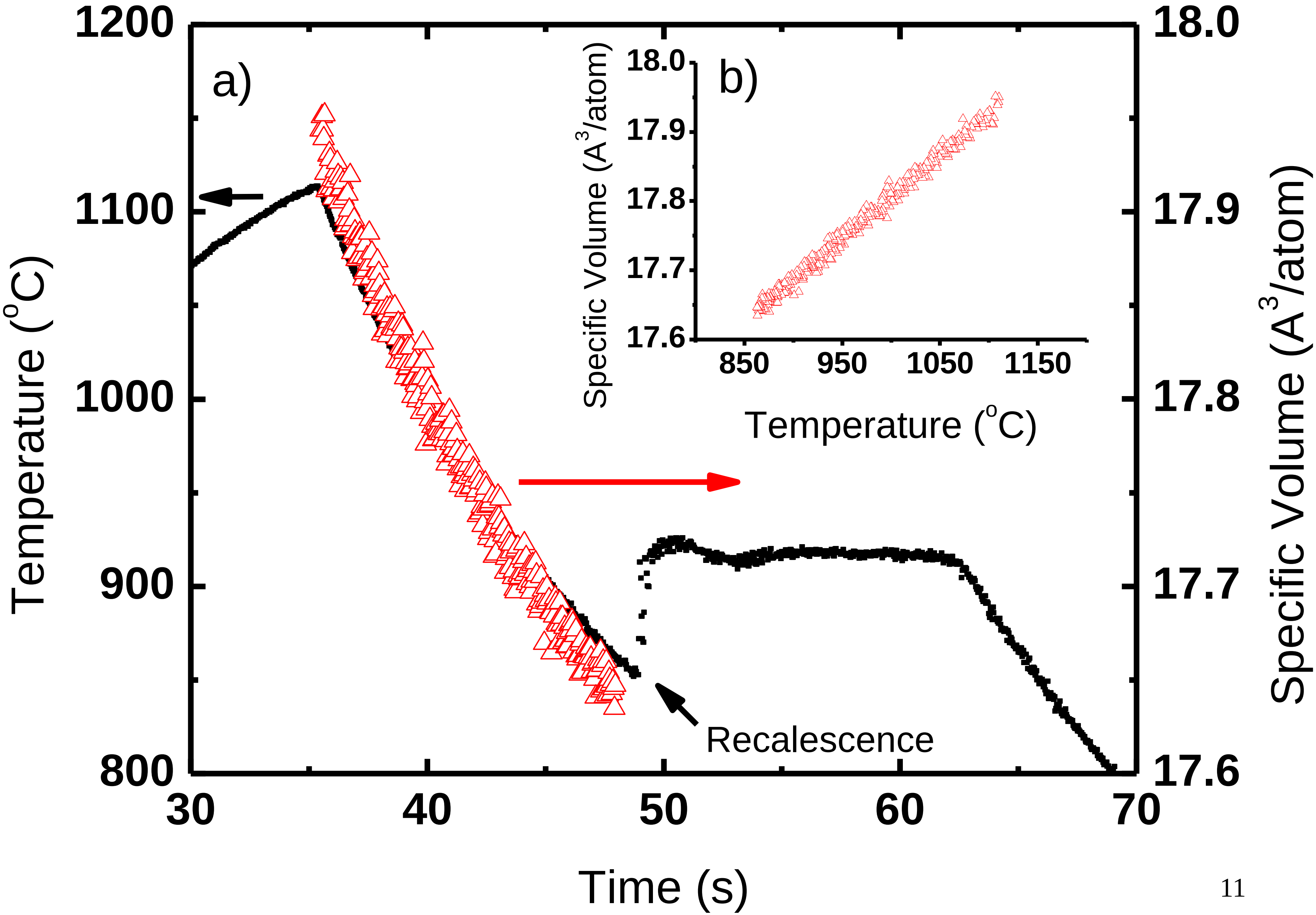


- Density measured from video of sample shadow
- Data processed to identify edges of 2D silhouette (sub-pixel resolution)
- Assume symmetry around vertical axis - calculate volume

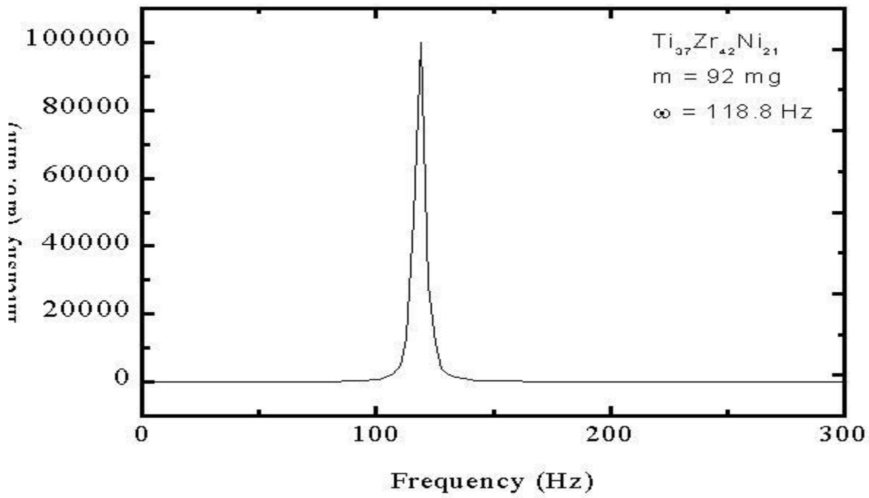
Developed from R. C. Bradshaw, D. P. Schmidt, J. R. Rogers, K. F. Kelton, R. W. Hyers , Rev. Sci. Instrum. 76: 12 125108 (2005).

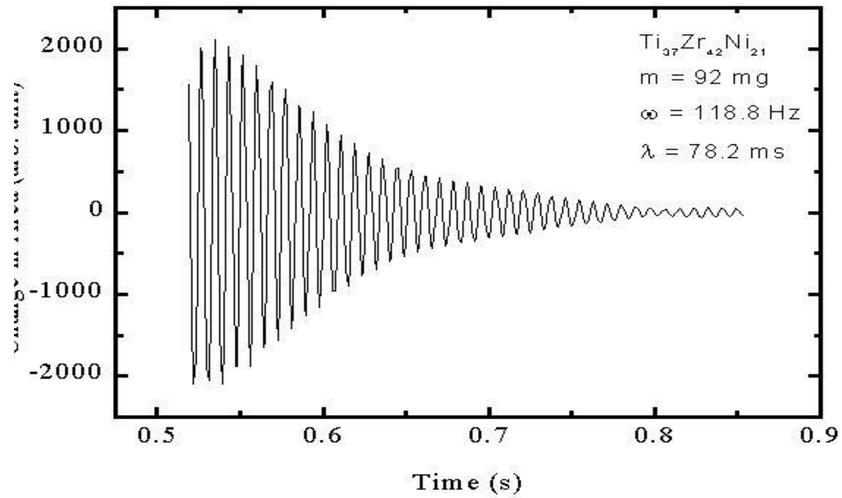


Characteristic Processing Cycle for $Cu_{54}Zr_{46}$



Viscosity Measurements





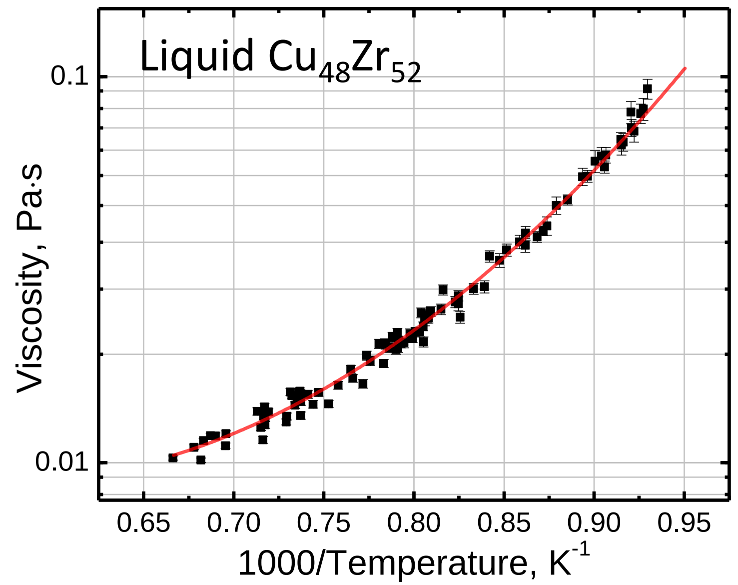
$$R = R_0\left(1+\delta\cos(\omega t)e^{-\lambda t}\right)$$

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

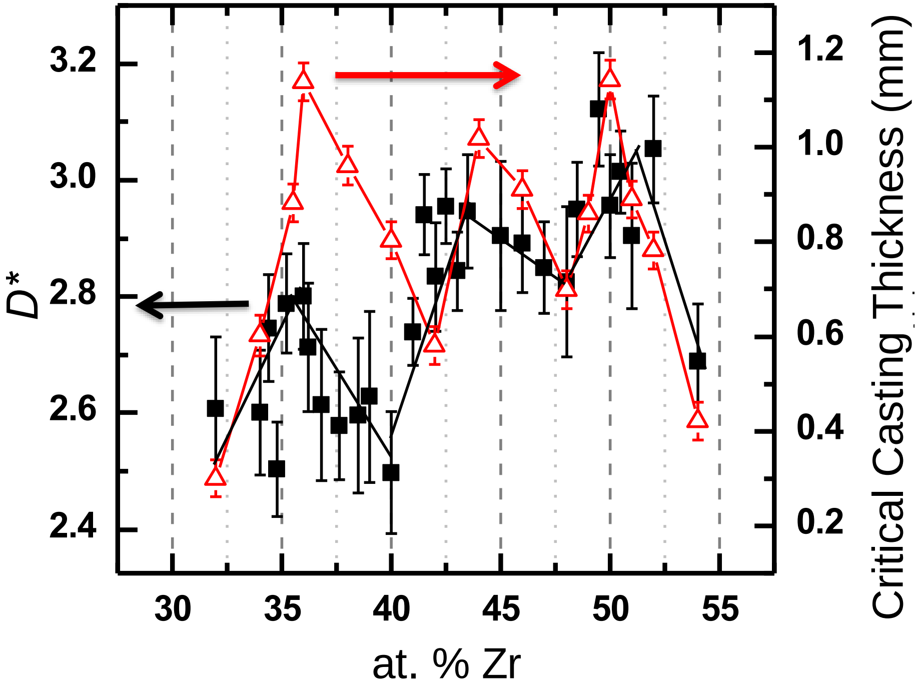
Rayleigh (1879)

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

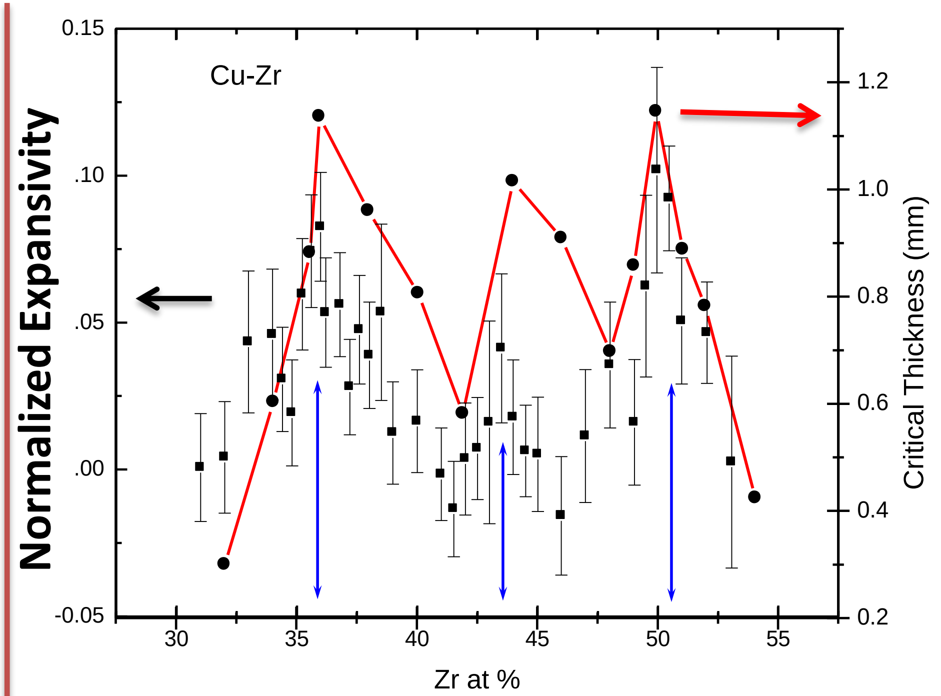
Lamb (1881)



Fragility and Glass Formabilty



J. C. Bendert and K. F. Kelton,
J. Non-Cryst. Solids, **376**, 205-208, (2013)

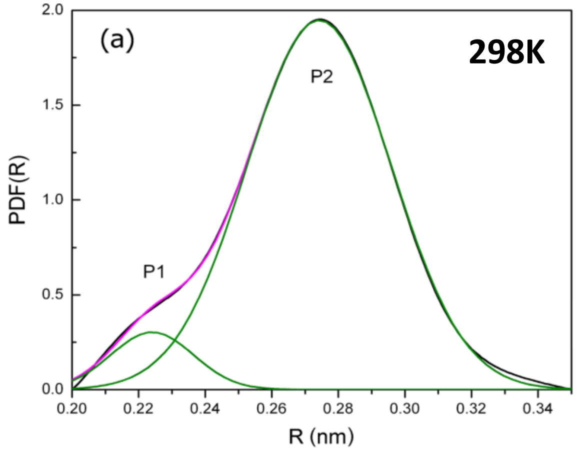


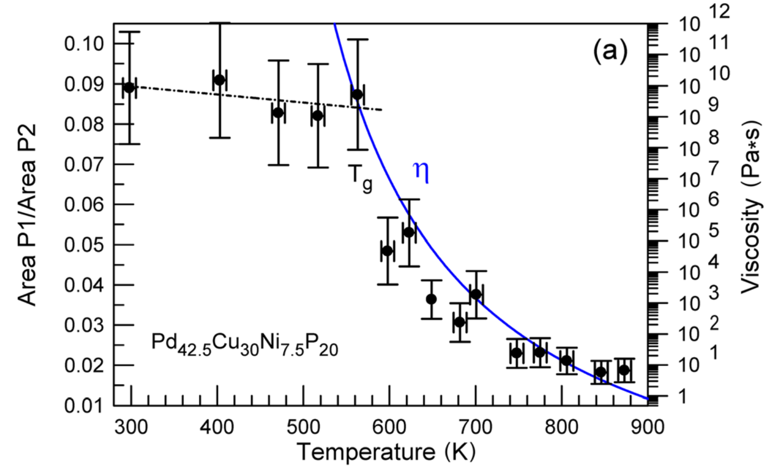
J. C. Bendert, A. K. Gangopadhyay, N. A. Mauro, and K. F. Kelton, PRL, **109** (18), 185901 (2012).

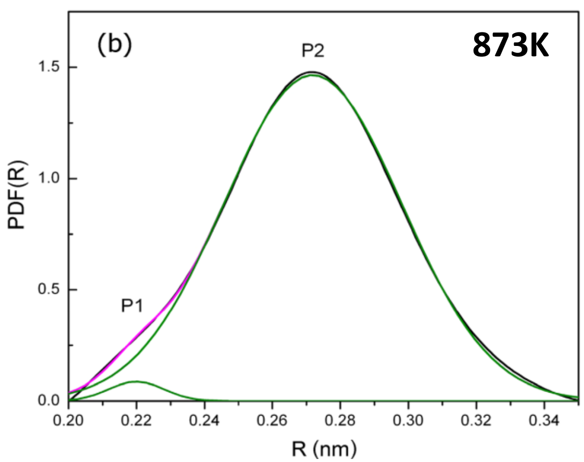
$$\eta = \eta_0 \exp\left[D^* T_0 / (T - T_0)\right]$$

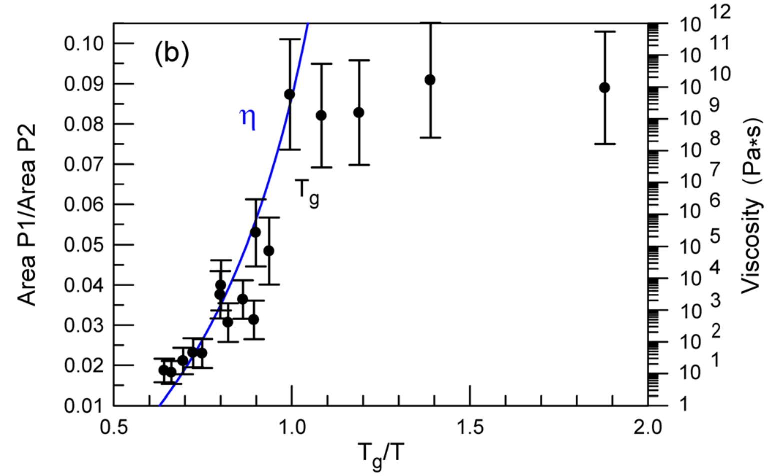
- Larger expansivity corresponds to larger D*…. stronger liquids
- Two components to expansivity in liquids
  - Anharmonic potential & Structural ordering
- Larger expansivity suggests faster ordering rate

Chemical Ordering in $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ BMG Liquid









- Chemical ordering around P (Ni-P and Cu-P bonds increase) on cooling to T_g (increased magnitude of P1 over P2
- Viscosity follows the P1/P2 area ratio with supercooling. Suggests -
  - Viscosity (and directly related to chemical ordering in the liquid (clusters)
  - Maybe a structural connection with fragility?

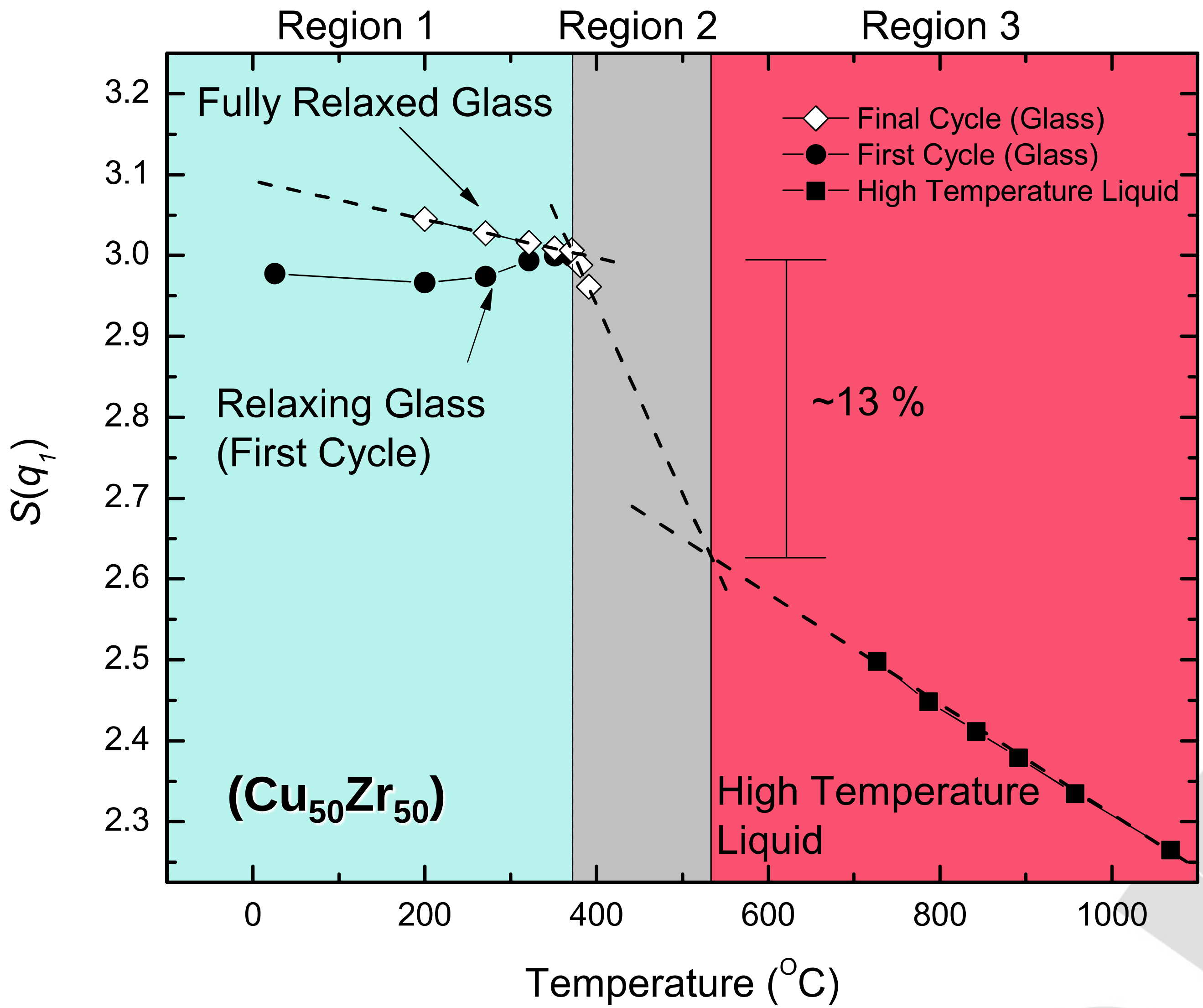
(from D. V. Louzguine-Luzgin *et. al*., J. Appl. Phys., **110**, 043519 (2011)

Thermal Expansivity is a Measure of Structural Ordering

-

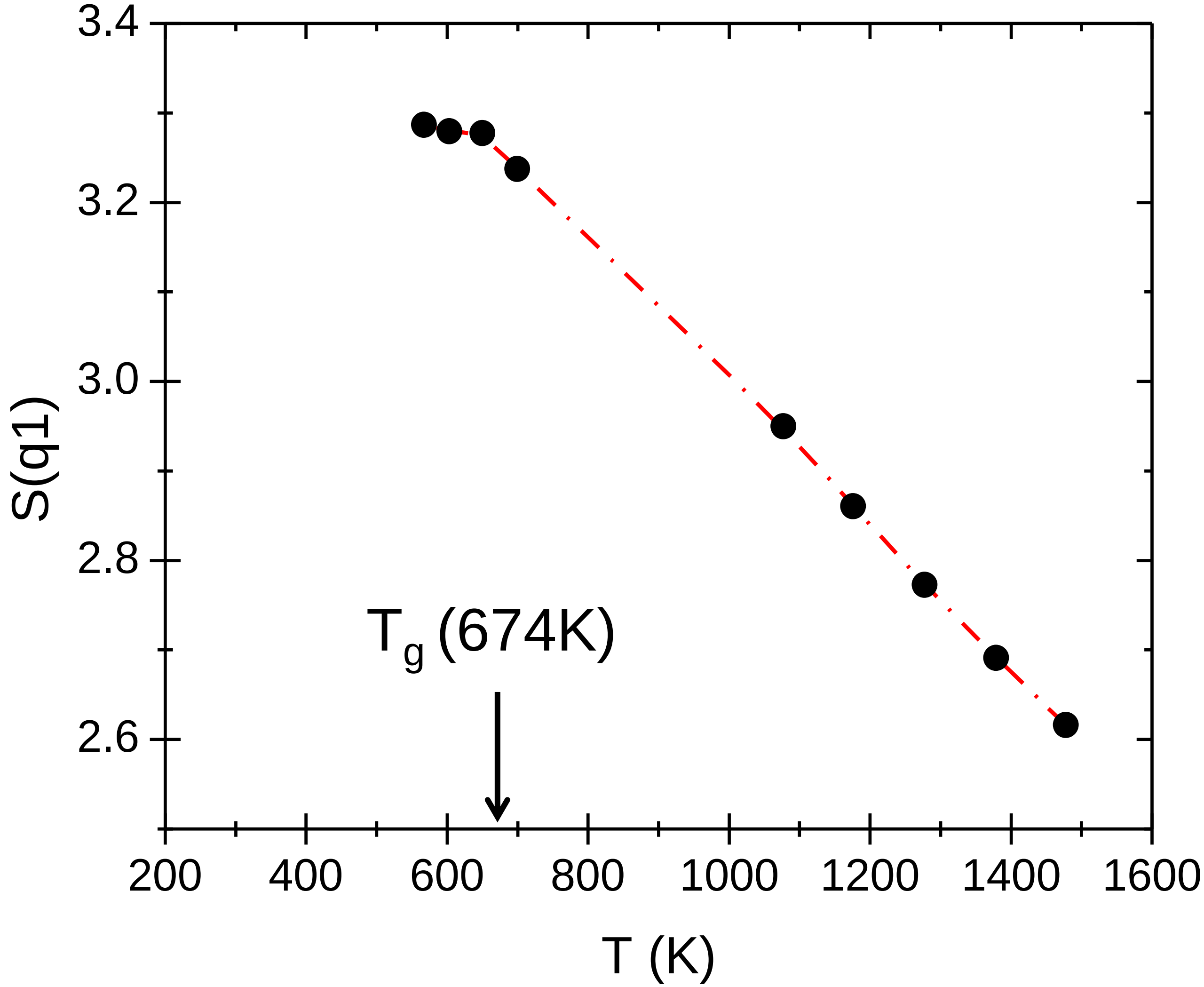
Should be Observable Directly In X-Ray Scattering Studies - S(q)

Structural Ordering
- Change in First Peak Height in S(q) -



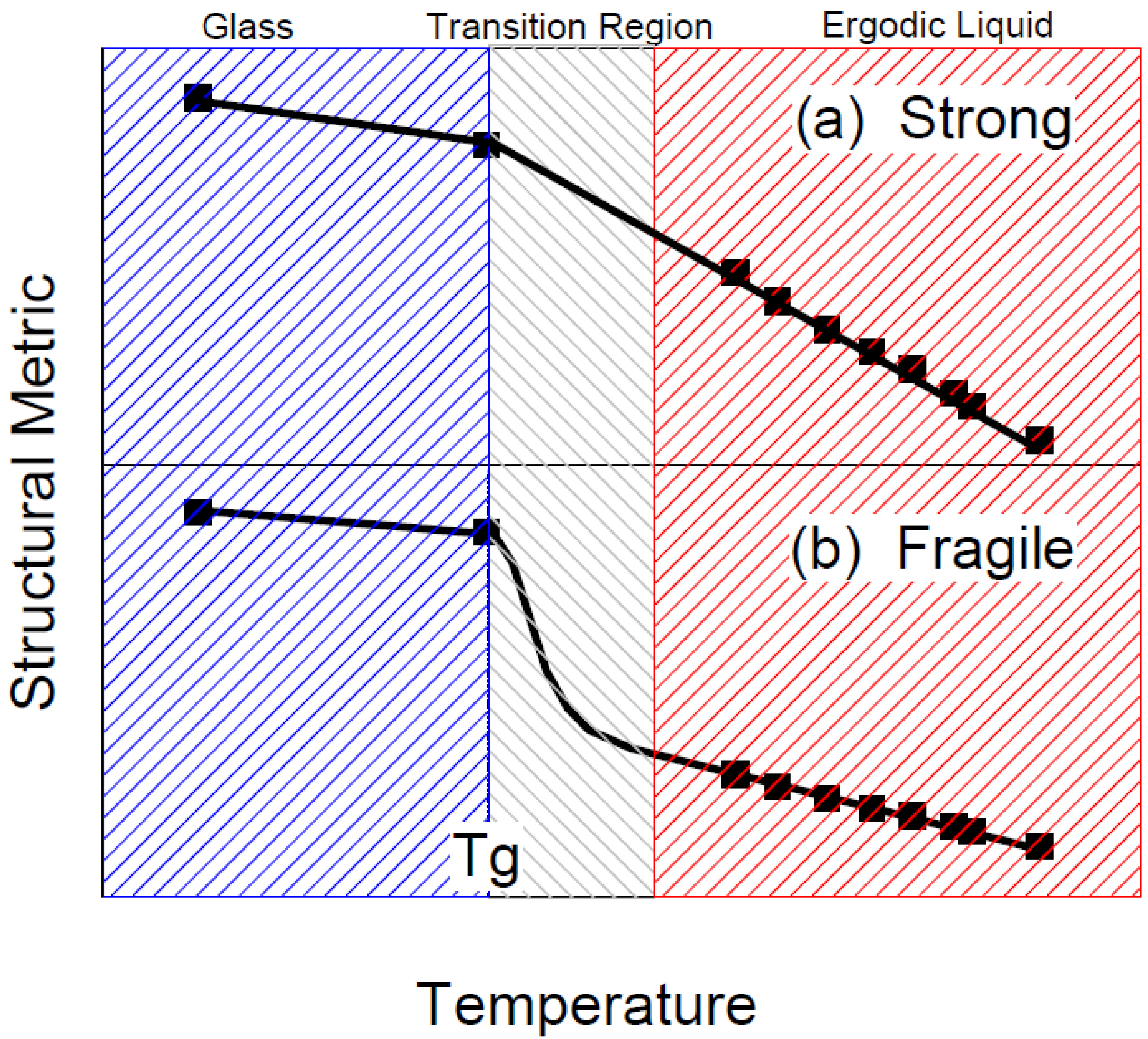
N. A. Mauro, et. al., Appl. Phys. Lett. **103**, 021904 (2013)

Vit 106a ($Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$) – strong liquid and good glass former



Continuous and gradual change with decreasing temperature

Fragility Inferred from Structural Data



Is Icosahedral Ordering Linked to Fragility?

Structural Information from S(q) Data

Reverse Monte Carlo (McGreevy) -- Topological analysis

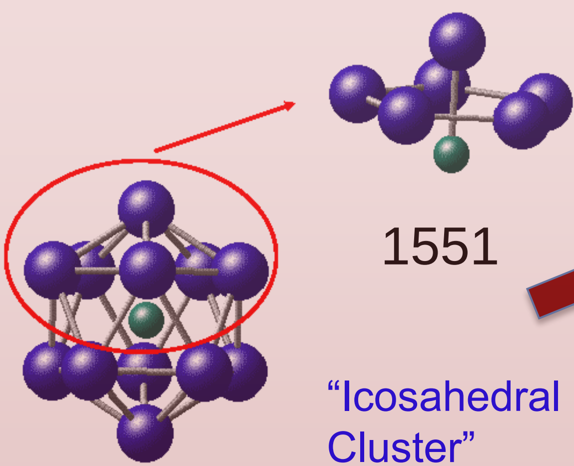
Bond Orienational Order Parameter Analysis (Steinhardt *et al.*)

- 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

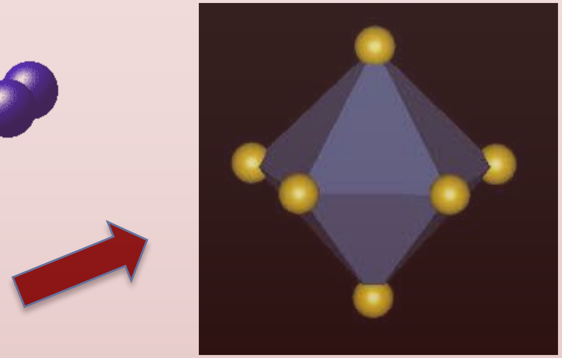
$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \overline{Q}_{lm} \right|^2 \right]^{1/2} \quad where \quad \overline{Q_{lm}} = \frac{1}{N_b} \sum_{bonds} Y_{lm}\left(\theta(\vec{r}), \varphi(\vec{r}) \right)$$

- Icosahedral order – Q_6

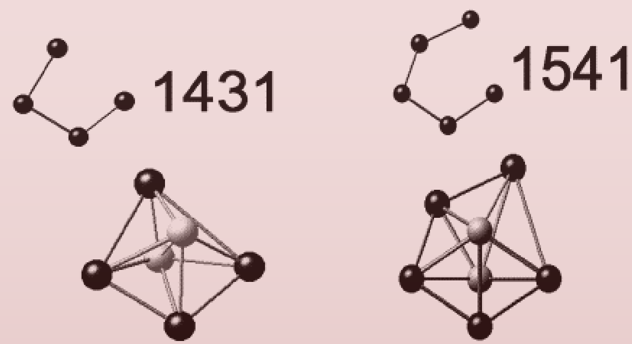
Honeycutt Andersen Indices (local topology in terms of 4 indices)



“Icosahedral Cluster”

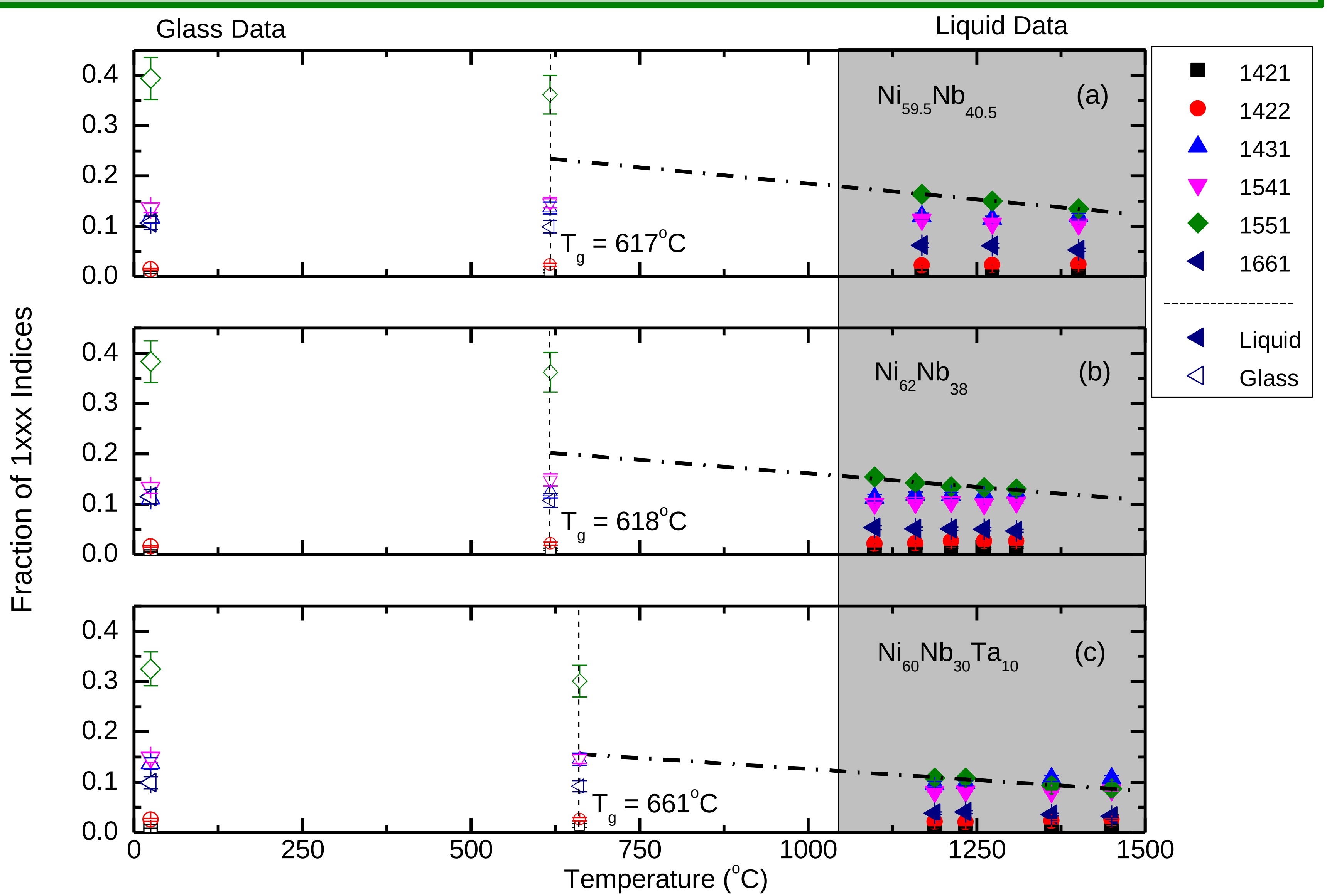


Pentagonal Bipyramid



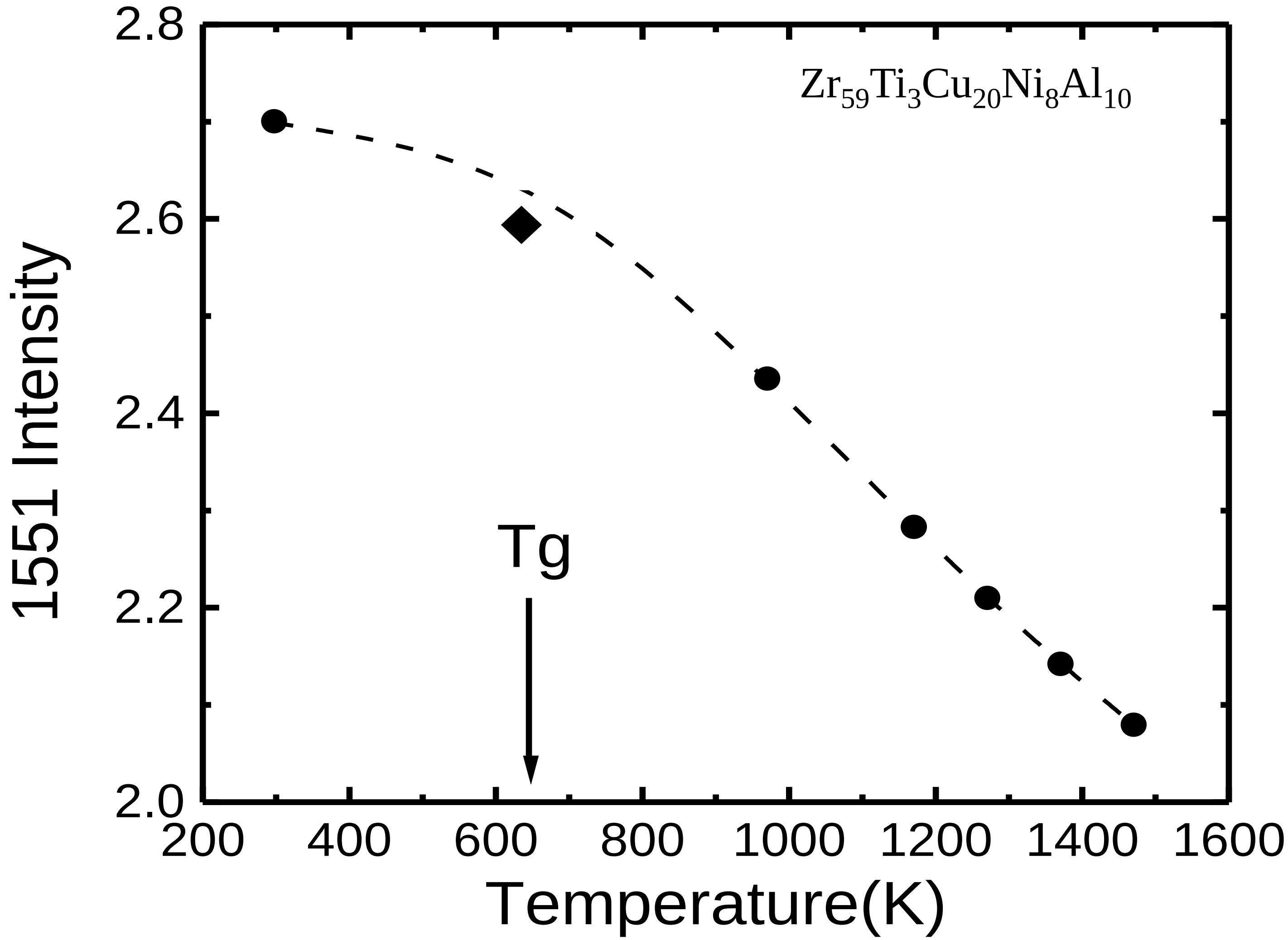
“Distorted Icosahedral Cluster”

HA 1551 Index for Ni-Nb Glass Forming Liquids



N. A. Mauro, M. L. Johnson, J. C. Bendert and K. F. Kelton, J. Non-Cryst. Solids **362**, 237-245 (2013).

Strong liquid – good glass former

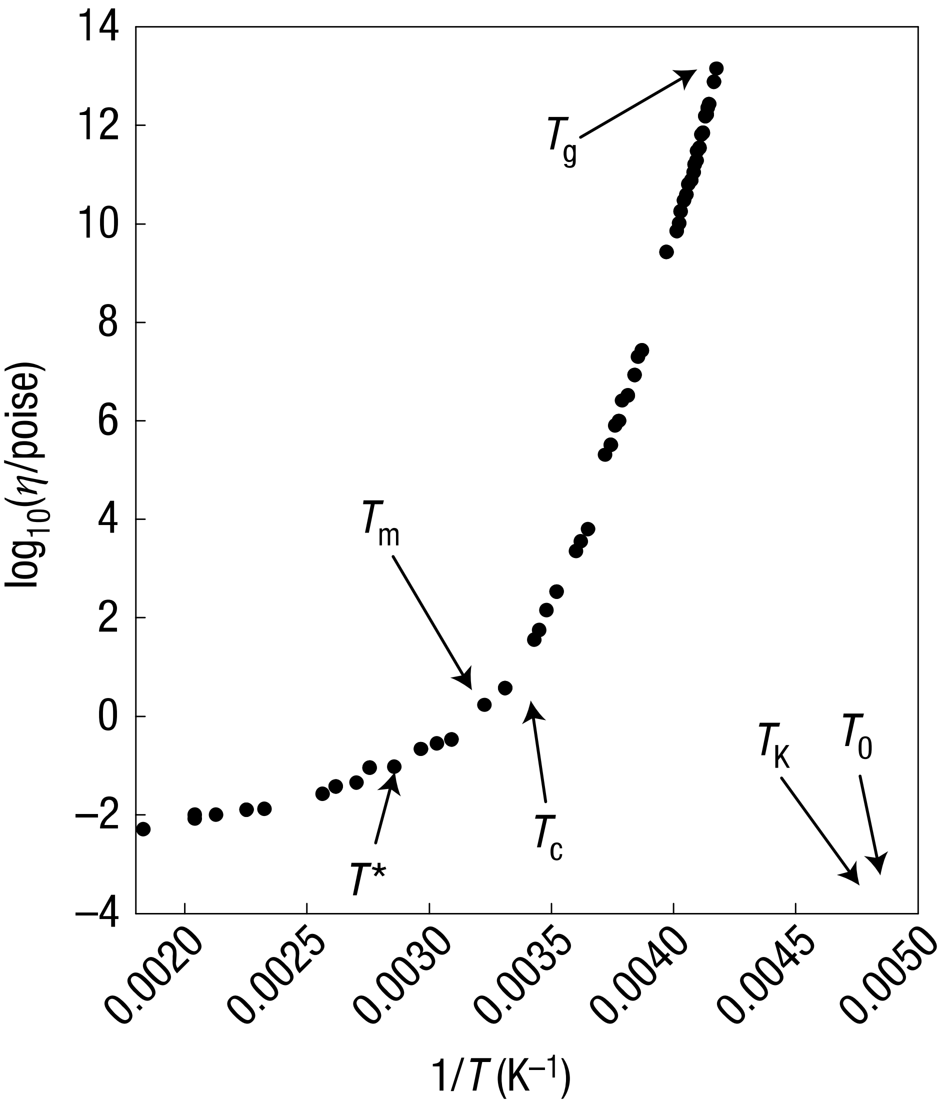


Y. Shen, T. H. Kim, K. F. Kelton, *Phys. Rev. Lett.*, **102** (2009) 057801

Scaling Temperature

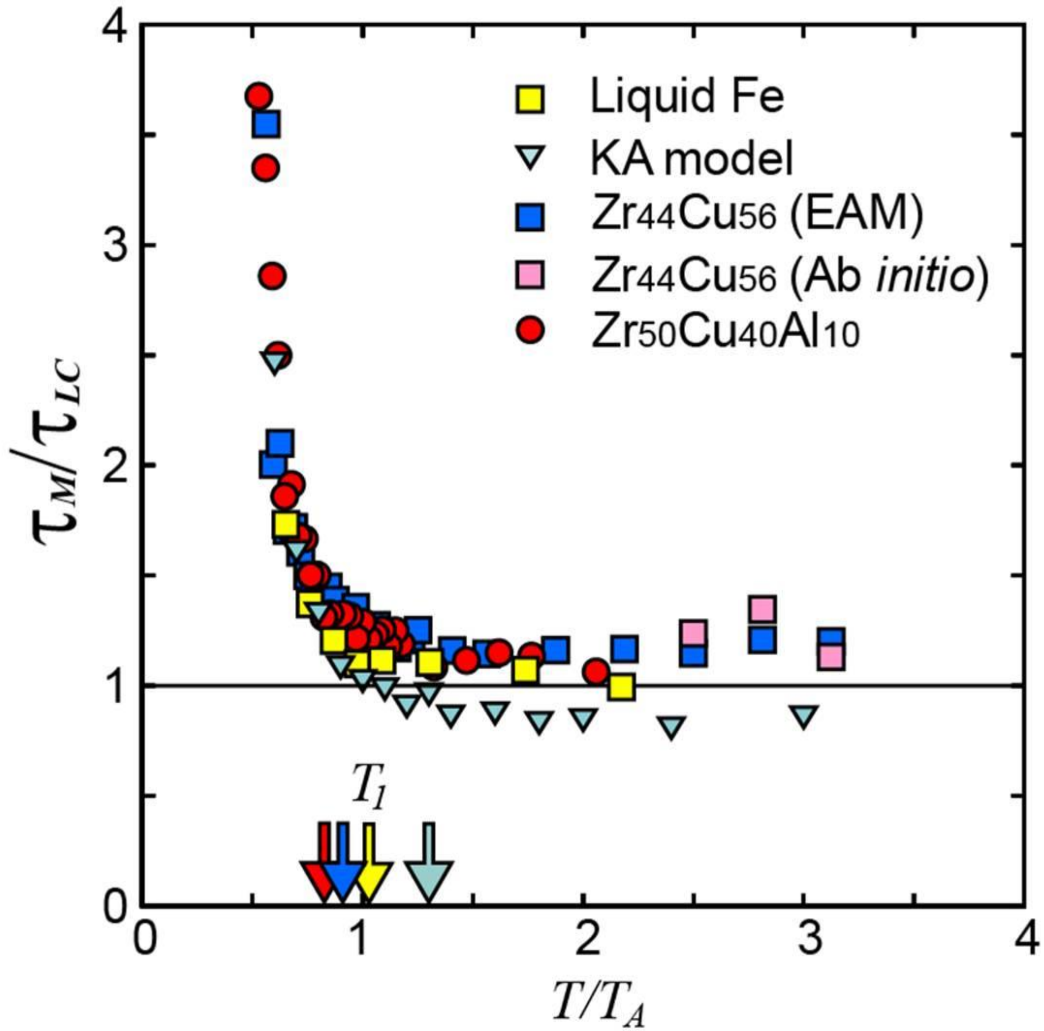
Possible Fundamental Temperatures

- T_m – Equilibrium melting temperature
- T^* - Crossover temperature for onset of collective behavior in supercooled liquid
- T_c – Mode coupling temperature
- T_g – Glass transition temperature
- T_K – Kauzmann temperature
- T_0 – Temperature of unobtainable phase transition



(from S. Kivelson and G. Tarjus, Nature Materials, **7**, 831 (2008))

T_A – Universal Scaling Temperature?



High temperature

$$t_M = t_{LC}$$

t_M - **Maxwell time (h/G$_{¥}$)**

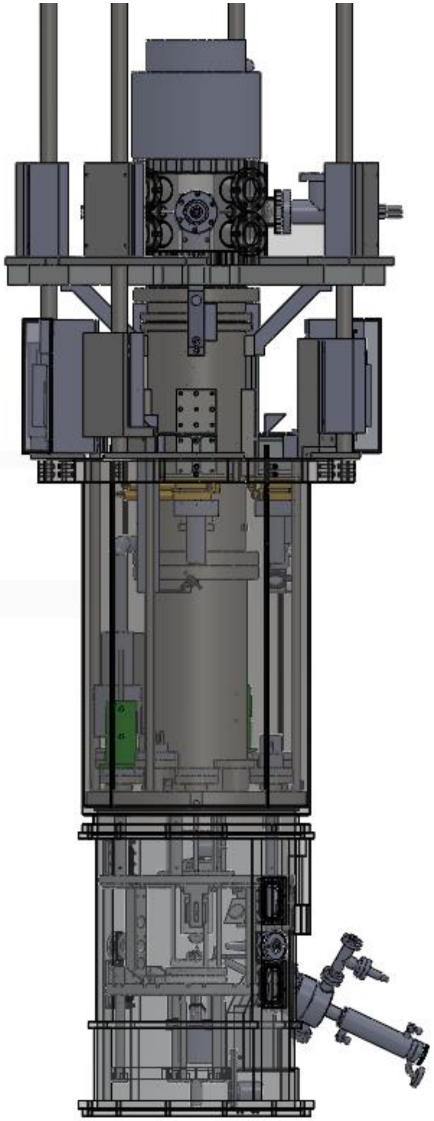
t_{LC} - **Time to break bond**

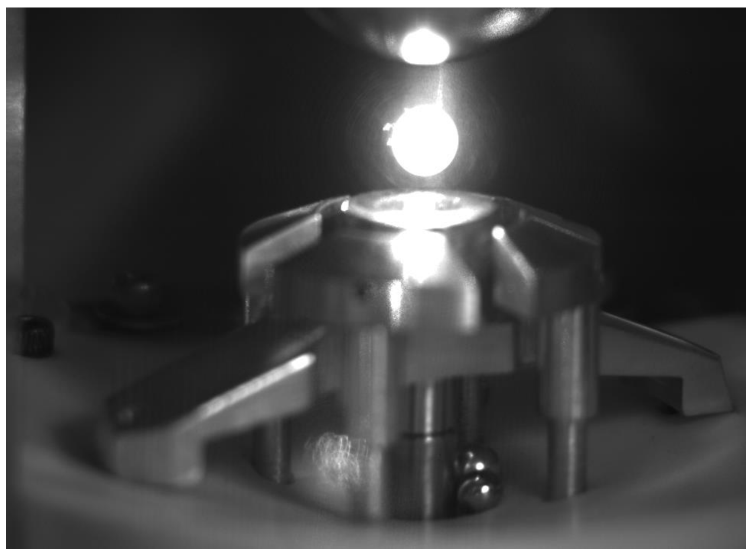
- **Fe: Johnson potential**
- **KA: Kob-Andersen potential ($Ni_{80}P_{20}$)**
- **$Cu_{56}Zr_{44}$: EAM**
- **$Zr_{50}Cu_{40}Al_{10}$: EAM**
- **$Cu_{56}Zr_{44}$: DFT-MD**

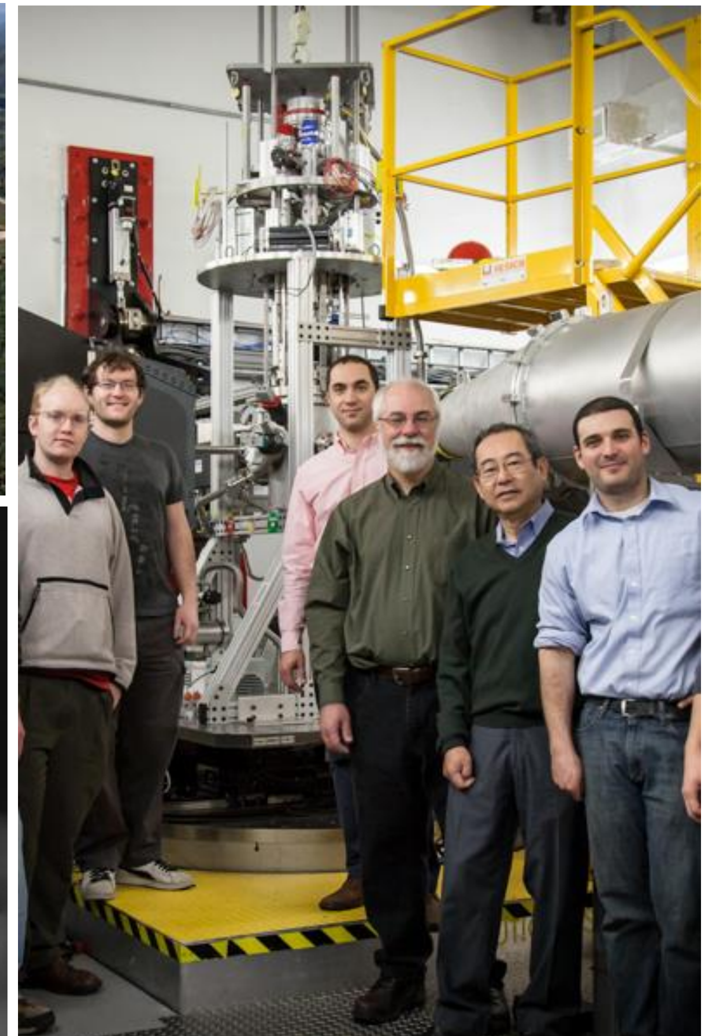
From T. Iwashita, D. M. Nicholson, T. Egami, Phys. Rev. Lett., **110**, 205504 (2013)

We see the same scaling in our high temperature viscosity data

Neutron Scattering – NESL (Electrostatic Levitation)







Conclusions

- Icosahedral short range ordering does not necessarily help glass formability – might enhance nucleation and growth of quasicrsytal phases.

- Fragility is correlated with liquid structure
  - Stronger liquids order gradually from high temperatures to the glass transition temperature,T_g.
  - Fragile liquids order slowly at high temperature, accelerate ordering near T_g.

- Universal scaling temperature for viscosity
  - Onset of cooperativity
  - Critical slowing down of glass transition anticipated in high temperature liquid

Acknowledgements

Washington University

- Nicholas Mauro – Structure Factor Measurements
- Matthew Blodgett – Viscosity Measurements
- Zohar Nussinov

University of Tennessee

- Takeshi Egami

Happy Birthday

Austen