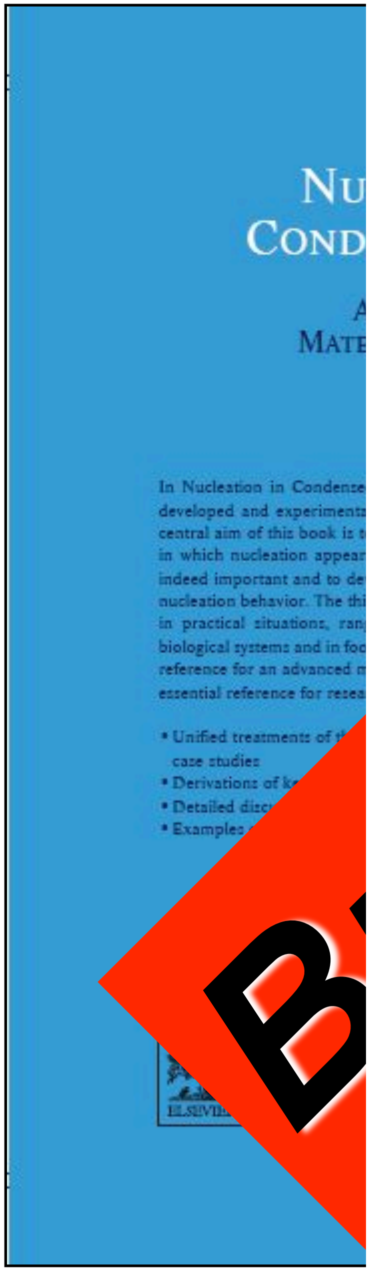


ELSEVIER

Special 30% Discount

To receive 30% off order from ElsevierDirect.com with code **NCMTMS97**. Offer expires 1 September 2010.

Nucleation in Condensed Matter

Applications in Materials and Biology

By K. F. Kelton and A. L. Greer
Washington University in St. Louis, USA and University of Cambridge, UK

KEY FEATURES:

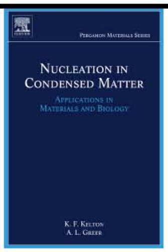
- Unified treatment of key theories, experimental evaluations and case studies
- Complete derivation of key models
- Detailed discussion of experimental measurements
- Examples of nucleation in diverse systems

DESCRIPTION

In *Nucleation in Condensed Matter*, key theoretical models for nucleation are developed and experimental data are used to discuss their range of validity. A central aim of this book is to enable the reader, when faced with a phenomenon in which nucleation appears to play a role, to determine whether nucleation is indeed important and to develop a quantitative and predictive description of the nucleation behavior. The third section of the book examines nucleation processes in practical situations, ranging from solid state precipitation to nucleation in biological systems to nucleation in food and drink. *Nucleation in Condensed Matter* is a key reference for an advanced materials course in phase transformations. It is also an essential reference for researchers in the field.

TABLE OF CONTENTS:

ELSEVIER



ISBN: 978-0-08-0421476

PUB DATE: March 2010

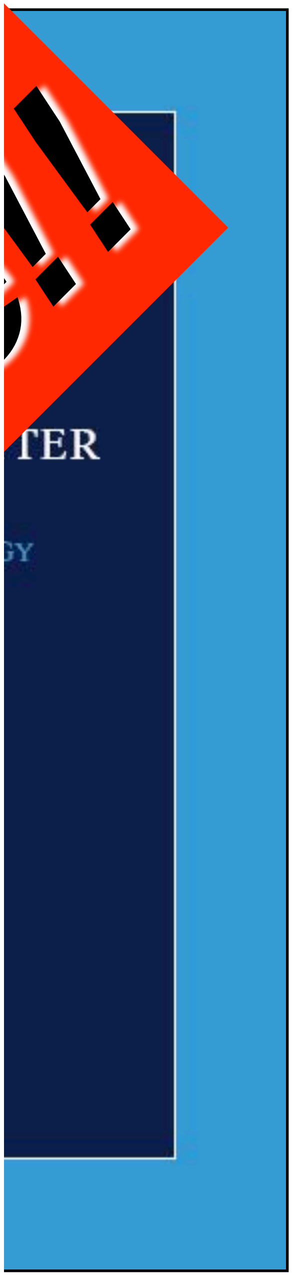
LIST PRICE:
EUR 137 / GBP 105 / USD 175

30% OFF PRICE: EUR 95.95 / GBP 73.50 / USD 122.50

FORMAT: Hardback

PAGES: 630

AUDIENCE: Scientists in condensed matter physics and anyone interested in phase transformations.



ELSEVIER

Nucleation in Metallic Liquids and Glasses

Ken Kelton

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

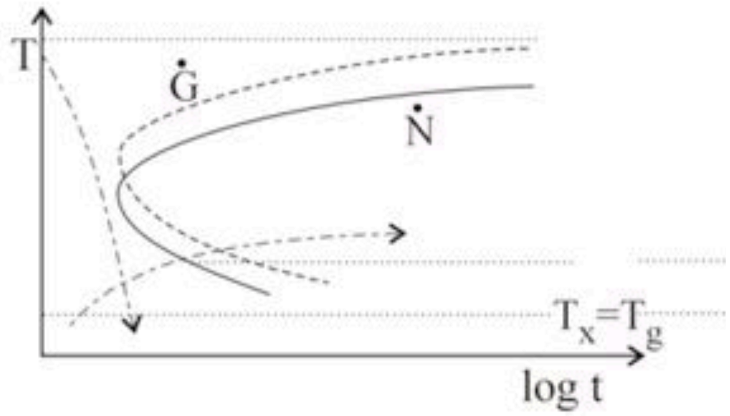
National Science Foundation
WHERE DISCOVERIES BEGIN

NASA

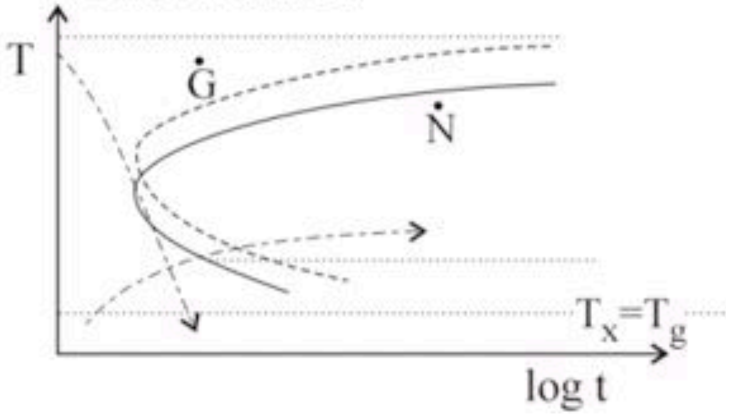
Metallic Glasses

Formation

Nucleation Control:

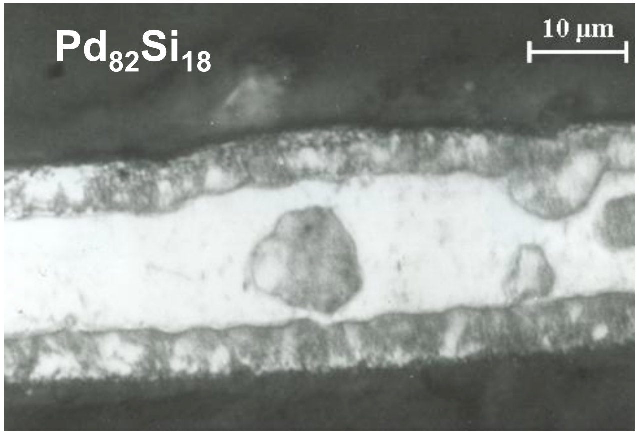


Growth Control:

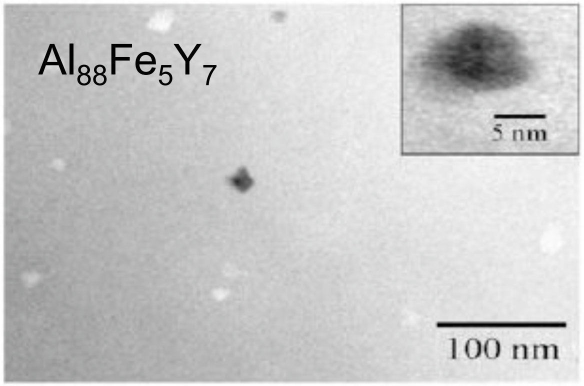


J. H. Perepezko and R. J. Hebert,
JOM (2002)

Crystallization



K. F. Kelton and F. Spaepen, Acta Metall., **33**, 455-464 (1985).



J. H. Perepezko, Prog. Mater. Sci. **49** 263 (2004)

Common Nucleation Rate Measurement Techniques in Liquids and Glasses

- Liquids – maximum undercooling
- Metallic glasses
  - JMAK transformation kinetics (volume fraction transformed)

$$x = 1 - \exp\left(-\frac{4\pi}{3}\int_0^t I(t')\left(\int_{t'}^{t} u(t'')\,dt''\right)^3 dt'\right)$$

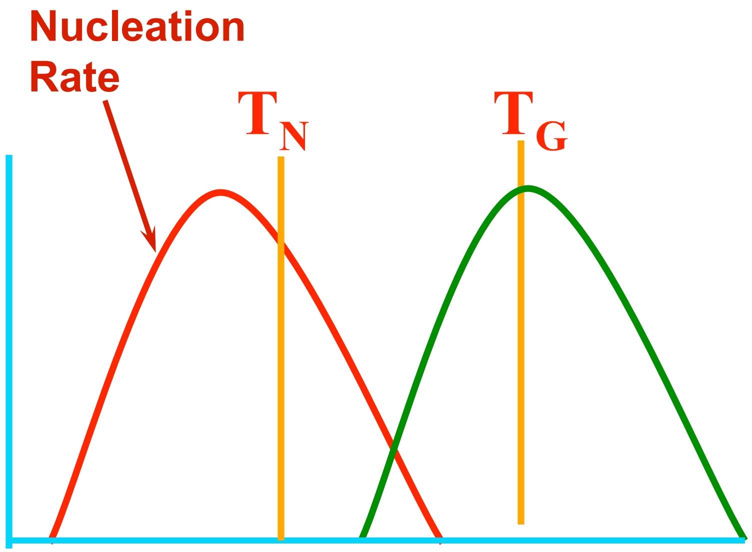
  - Single Temperature Annealing
  - Nucleation and growth convoluted in both
- Two-temperature annealing treatment – common in silicate glasses, recently applied to metallic glasses

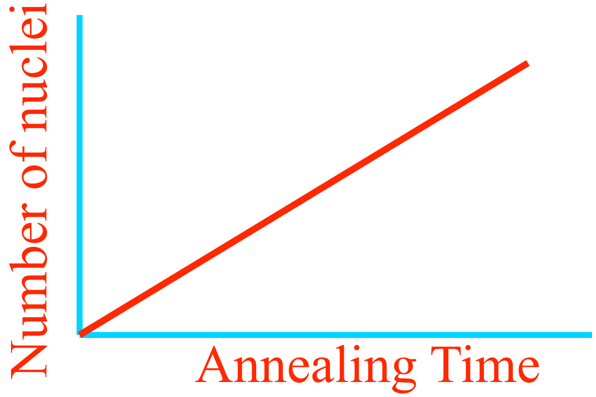
- Two-step annealing treatments

  — Nucleation Rate
  — Growth Velocity

- Count nuclei directly
  - Optical microscopy
  - SEM or TEM

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

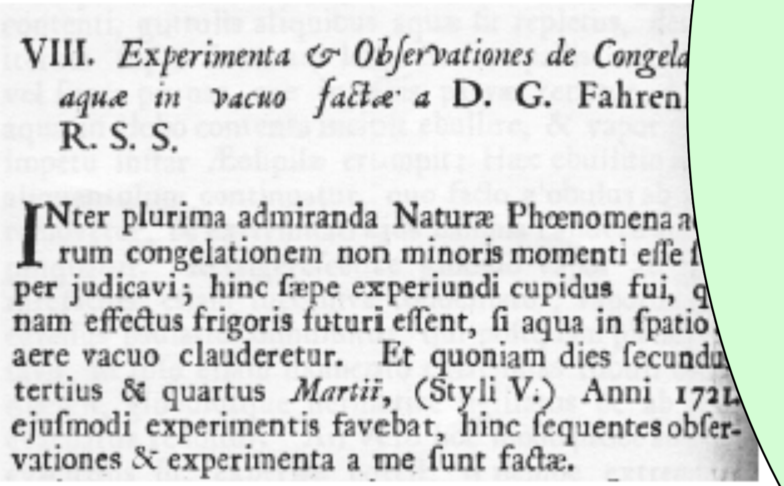




The Classical Theory Of Nucleation

Gabriel Fahrenheit (1686 – 1736) In 1721 – discovered <u>supercooling</u> of water, i.e. water is liquid below 32°F

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



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

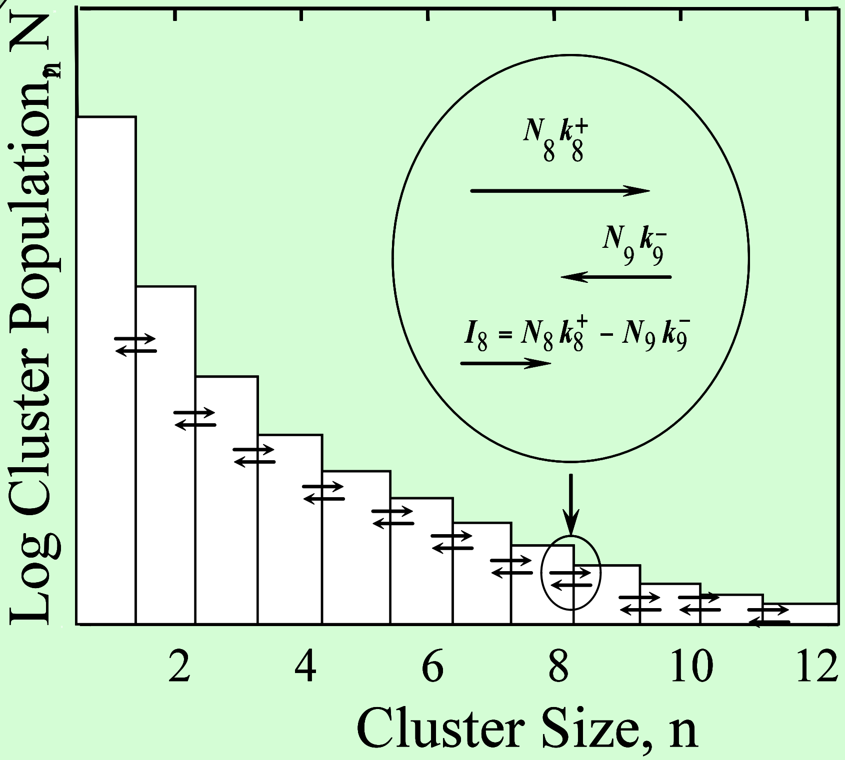
INter plurima admiranda Naturæ Phœnomena a
rum congelationem non minoris momenti eſſe
per judicavi; hinc ſæpe experiundi cupidus fui, q
nam effectus frigoris futuri eſſent, ſi aqua in ſpatio
aere vacuo clauderetur. Et quoniam dies ſecundu
tertius & quartus *Martii*, (Styli V.) Anni 172
ejuſmodi experimentis favebat, hinc ſequentes obſer-
vationes & experimenta a me ſunt factæ.

Barrier to Crystallization

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

e Energy
ier

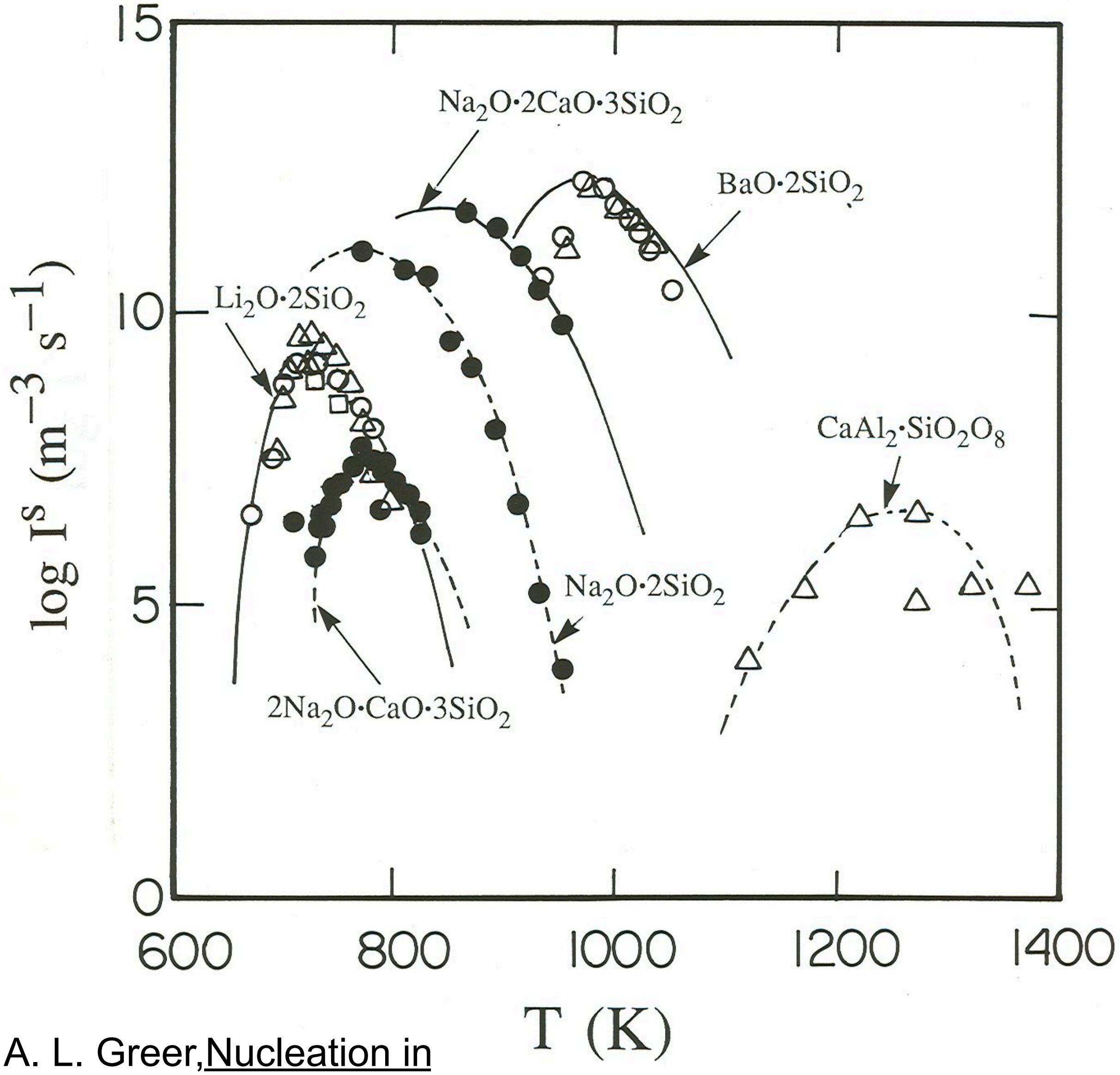
Volmer and Weber



IkNkN +−
nt,,nt,nt
++

I
+
nn*

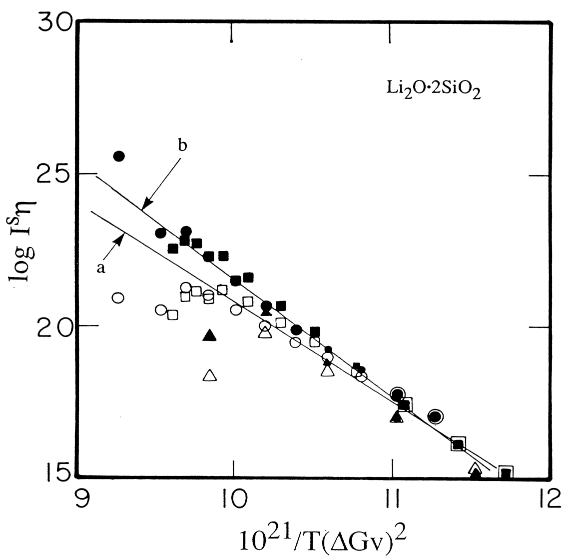
Good fit to nucleation in silicate glasses that form crystals of the same composition



K. F. Kelton and A. L. Greer, Nucleation in Condensed Matter, Elsevier, 2010.

Fits to Glass Crystallization Data

$$I = \frac{A}{\eta}\exp\left[-\frac{16\pi\sigma^3}{3k_BT\Delta G_v^2}\right] \Rightarrow \ln(\eta I) = \ln A - \frac{16\pi\sigma^3}{3k_BT\Delta G_v^2}$$



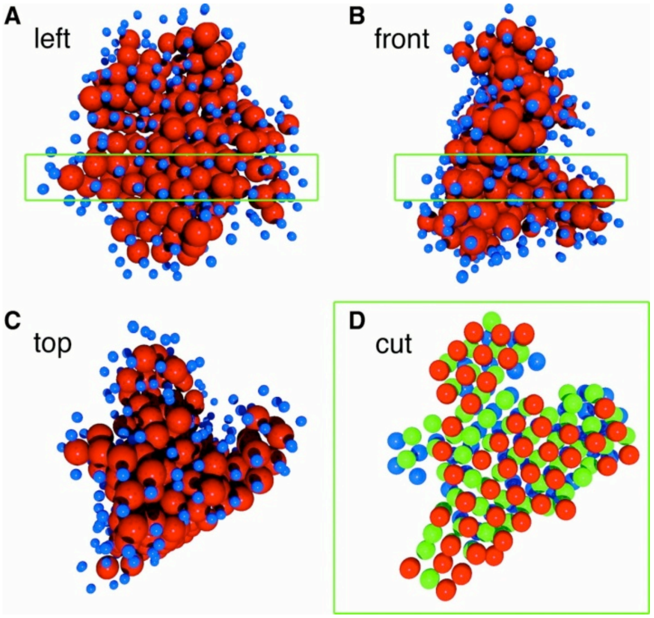
K. F. Kelton
Solid State Physics **45** (1991)

THEORETICAL		CALCULATED					
				$\sigma = \sigma_o + \sigma_1 T$		$\sigma(T_{max})$	(J/m^{2}K)
Glass	▯ (Pa/m^3)	▯ (Pa/m^3)	σ(J/m^2)	σ_o(J/m^2)	σ_1(J/m^2)	Kelton	James
$Li_2O.2SiO_2$	$10^{33.0}$	$10^{53.2}$	0.139	0.138	2.1×10^{-5}	0.153	0.143
		$10^{60.1}$	0.147	0.125	3.7×10^{-5}	0.152	0.147
$Na_2O.2CaO.3SiO_2$	$10^{32.6}$	$10^{60.8}$	0.131	0.103	3.1×10^{-5}	0.130	0.108
$BaO.2SiO_2$	$10^{32.9}$	$10^{55.3}$	0.100	0.077	2.8×10^{-5}	0.104	0.101

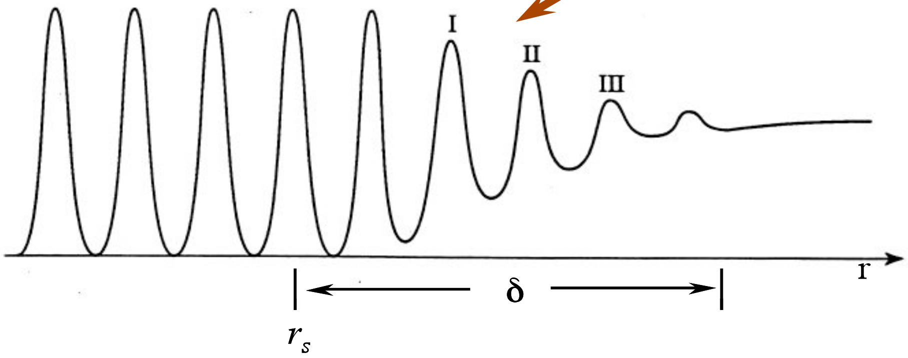
Diffuse Interface

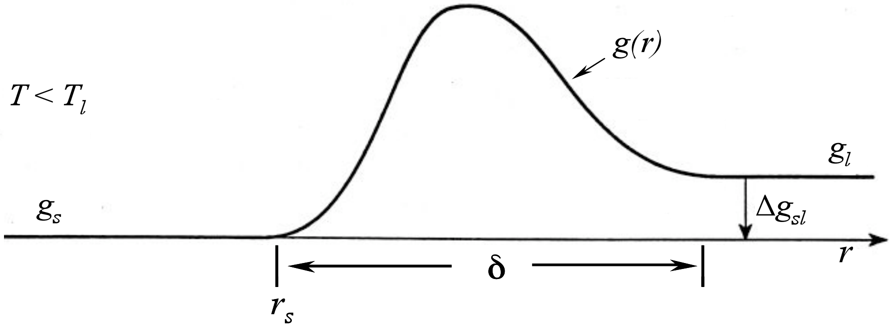
Ordered near interace

Crystallization in Colloidal Suspensions
Diffuse Interface – Not Compact



U. Gasser et al. *Science,* **292**, 258–262 (2001).





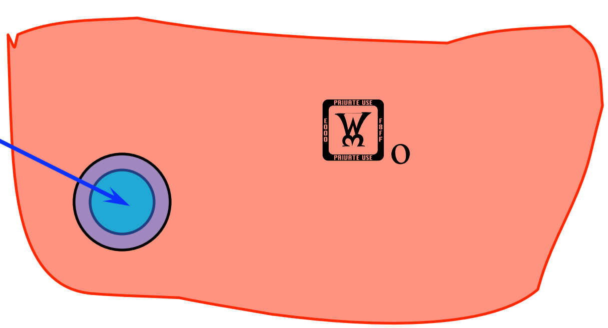
$$W(r_s) = \int_0^\infty 4\pi r^2 \Delta g(r)\, dr$$

$$\left.\frac{\mathrm{d}W(r_s)}{\mathrm{d}r_s}\right|_{r_s = r^*}$$

L. Granasy, J. Non-Cryst. Solids, **162**, 301 (1993)
F. Spaepen, Solid State Physics, Academic Press (1994), pp. 1-32

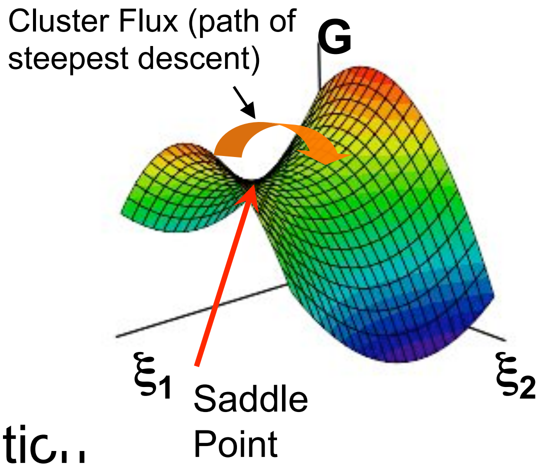
Density Functional Theory (DFT)

$$G[\rho(\mathbf{r})] = \int_V g(\rho(\mathbf{r}))\,d\mathbf{r}$$



Work of cluster formation

$$W[\rho(\mathbf{r})] = \int_V \{(g(\rho(\mathbf{r})) - g(\rho_o))\}\,d\mathbf{r}$$



- Does not rely on any assumed dividing surface
- Does not require introduction of interfacial energy
- Determine critical size

$$\left(\delta W[\rho(\mathbf{r})]/\delta\rho\right)_{\rho(\mathbf{r})=\rho^*(\mathbf{r})} = 0$$

- Analogous to dG/dr = 0 for r=r*
- Solve for density profile ($\rho^*(\mathbf{r})$) using Euler's equati
- Determine W* from

$$W^* = \int_V \{(g(\rho^*(\mathbf{r})) - g(\rho_o))\}\,d\mathbf{r}$$

D. Oxtoby, Liquids, Freezing and the Glass Transition, Elsevier (1991), pp. 145-161

Fits of Data to Non-Classical Theories

$$I^s T = 2A^{*3}\exp\left(\cup\,\frac{W^*_{CNT}}{kT}\right) \Longrightarrow \ln\left(\frac{I^s}{A^{*2}kT}\right) = 2\,\cup^3\,T\,\frac{16}{3}\,\frac{MO^3_{CNT}}{\int I}$$

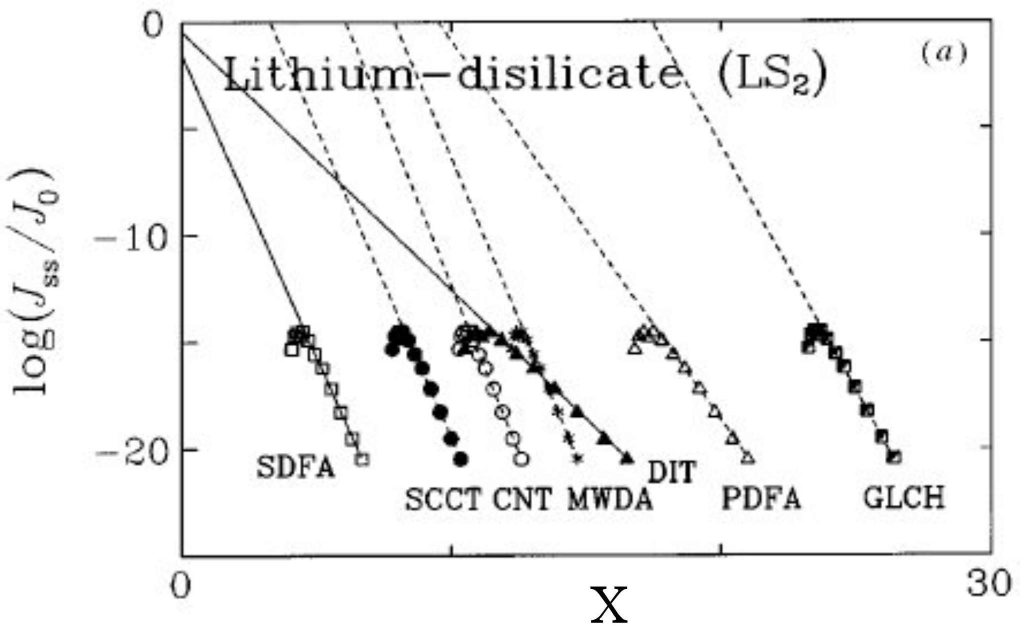
$$\text{where}\ \cup(T) = \left(W^{*}_{NC}\,W^{*}_{CNT}\right)^{1/3}$$

Fitting Procedure

- Assume expected value for □*
- Plot ln(I^s/□*), where I^s are the measured values for the steady-state nucleation rate, as a function of X=□^{3}(T) □□$^{-2}$T^{-1}
- Expect
  - straight line with slope proportional to σ^3
  - intercept at origin
- Use measured intercept to differentiate between predictions of models

Model	Acronym
Self-consistent CNT	SCCT
Phenomenological diffuse interface theory	DIT
Perturbative DF	PDFA
Semi-empirical DF	SDFA
Modified-weighted DF	MWDA
Ginzburg-Landau free energy used in Cahn-Hilliard model	GLCH

Fits to Glass Crystallization Data



L. Granasy, P.F. James, Proc. Roy. Soc. Lond. A 454 (1998) 1745–1766.

Intercept Values and Errors Obtained by Fitting Experimental Nucleation Data*

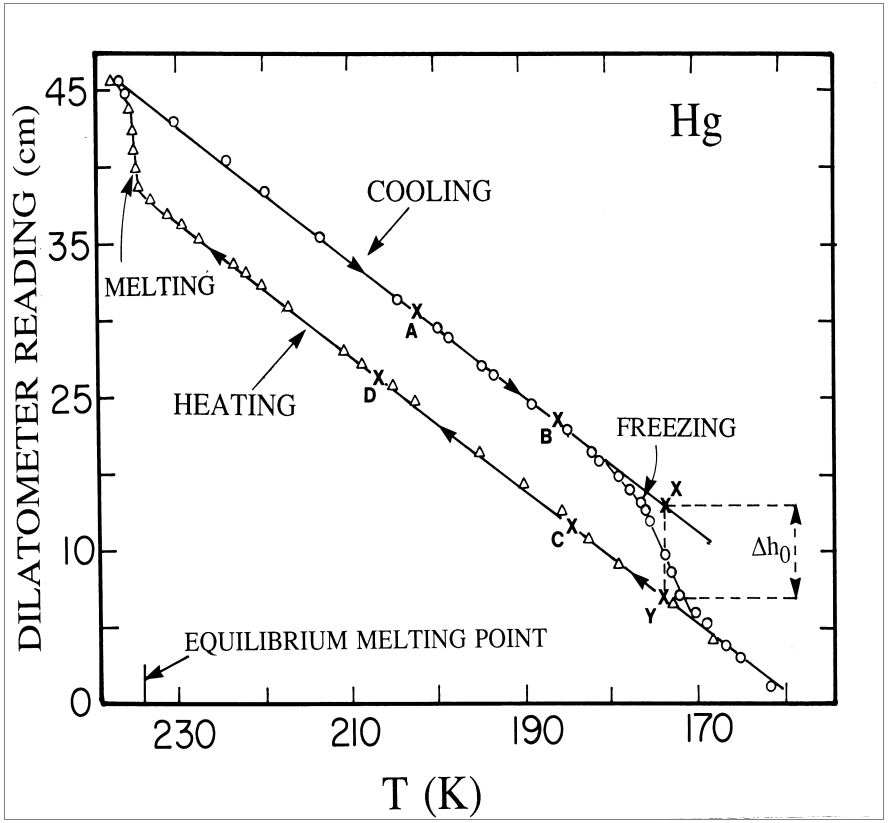
Glass	CNT	SCCT	DIF	SDFA	PDFA	MWDA	GLCH	log x_c
LS_2	19 ± 4	10 ± 4	-0.5 ± 2.0	-1.5 ± 1.9	15 ± 4	24 ± 5	40 ± 8	
BS_2	24 ± 5	28 ± 5	-0.7 ± 2.3	-4.9 ± 1.9	22 ± 5	30 ± 7	49 ± 10	-12.2
N_2CS_3	125 ± 66	92 ± 52	-0.5 ± 3.1	0.8 ± 2.6	71 ± 27	180 ± 92	-410 ± 328	
NC_2S_3	56 ± 18	40 ± 19	-2.9 ± 5.5	-9.2 ± 1.8	49 ± 15	72 ± 25	156 ± 94	-12.5
CS	178 ± 64	157 ± 59	-3.6 ± 4.8	-13 ± 2	165 ± 57	263 ± 123	1837	-17.2
NS	257	194 ± 165	-10 ± 3	-13 ± 2	92 ± 67	138 ± 104	-108 ± 65	
LB_2	581	472	-13± 3	-17 ± 2	-336	202	-96 ± 81	-16.6
CAS_2	-15± 4	-18± 3	-17± 2	-17± 2	15±4	-14±4	-13±6	

*From [Granasy, 1998 #1430]. Glasses: $Li_2O.2SiO_2$ (LS_2), $BaO.2SiO_2$ (BS_2), $2Na_2O.CaO.3SiO_2$ (N_2CS_3), $Na_2O.2CaO.3SiO_2$ (NC_2S_3), $CaO.SiO_2$ (CS), $Na_2O.SiO_2$ (NS), $Li_2O.2B_2O_3$ (LB_2) and $CaO.Al_2O_3.2SiO_2$ (CAS_2).

Metallic Liquids and Glasses

Supercooling of Liquid Metals (1952)

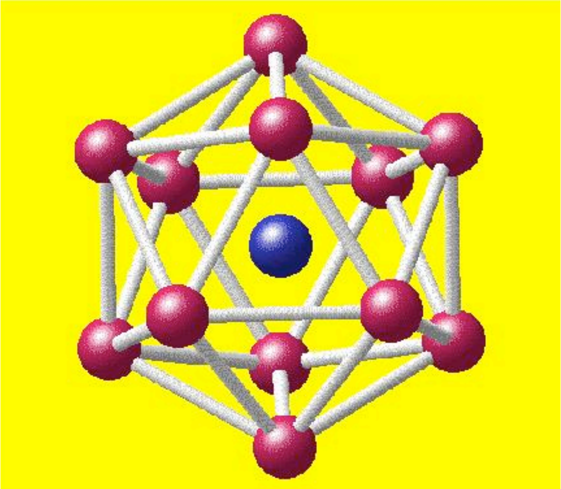
Turnbull Experiment



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

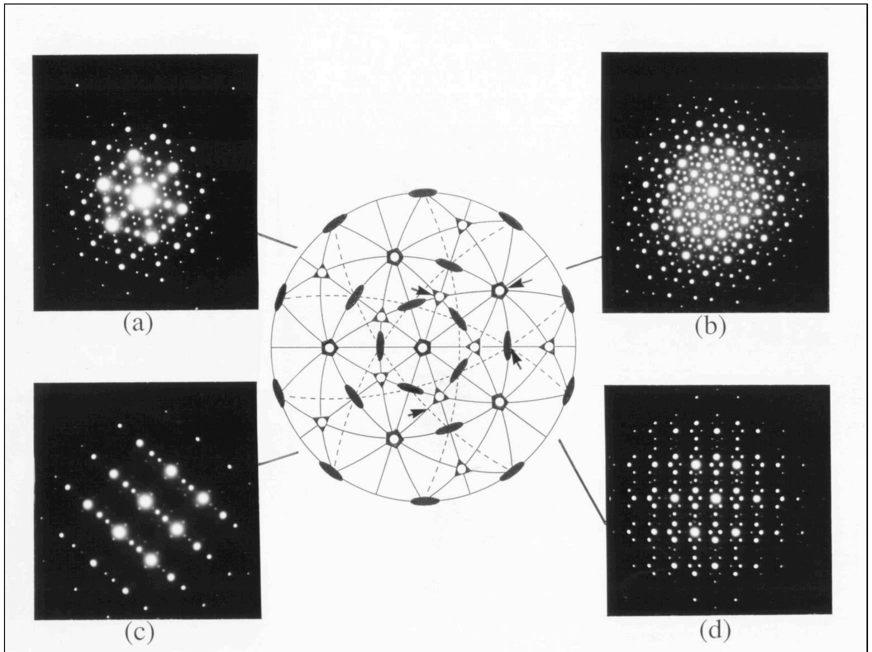
Frank's hypothesis

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

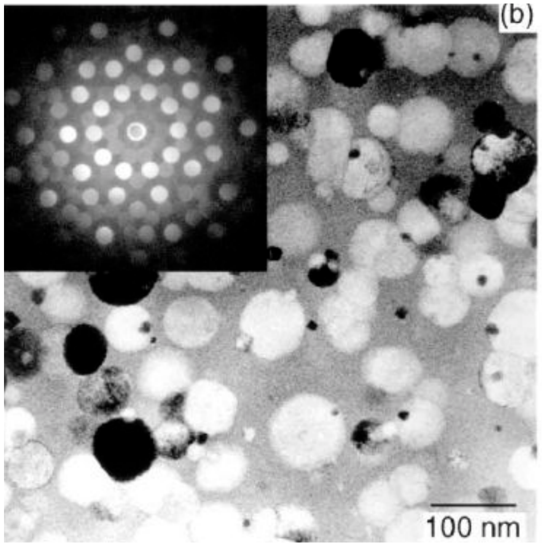


Nucleation of an ordered crystal requires that the icosahedral order be destroyed

Nucleation of the icosahedral quasicrystal in metallic glasses



D. Shechtman et al., PRL (1984)

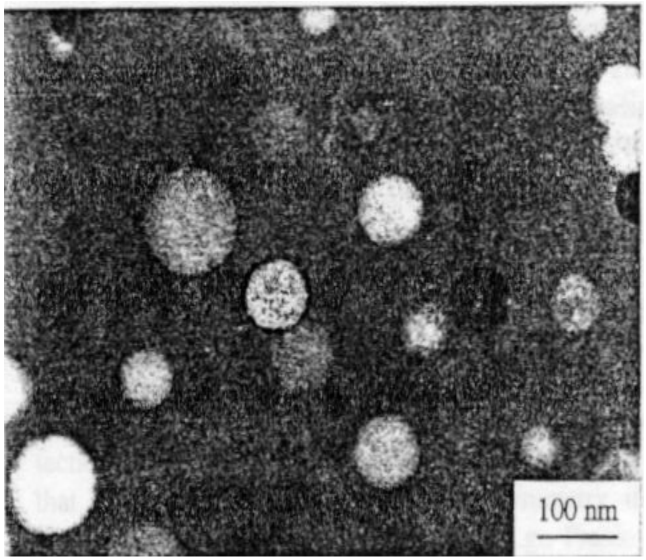


$Zr_{64.9}Cu_{27.5}Al_{7.5}O_{0.1}$

B. S. Murty & K. Hono, Mat. Sci. Eng., **A312**, 253 (2001)

- **Common in Ti/Zr/Hf based glasses**
  - $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$
  - $Zr_{70}Fe_{20}Ni_{10}$
  - $Zr_{62-x}Ti_xCu_{20}Ni_8Al_{10}$ $(3 \leq x \leq 5)$
  - $Zr_{80}Pt_{20}$
  - $Hf_{59}Ni_8Cu_{20}Al_{10}Ti_3$
  - $Zr_{55}Cu_{35}Al_{10}$
  - …
- **Also observed in other glasses**
  - $Pd_{60}U_{20}Si_{20}$
  - $Al_{95}Cr_3Co_2$
  - $Al_{75}Cu_{15}V_{10}$
- **Often nanocrystals ⇒ high nucleation rate (low barrier) & slow growth (often diffusion-controlled)**

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



- Fit to classical theory of nucleation
- Very small interfacial free energy

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

- 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**
  - $Al_{60}Cu_{34}Fe_6$

    $\Delta T^{I} \approx 100K ⇨ \Delta T^{I}/T_L \approx 0.1$
  - $Al_{58}Cu_{34}Fe_8$
  - Al- Pd - Mn

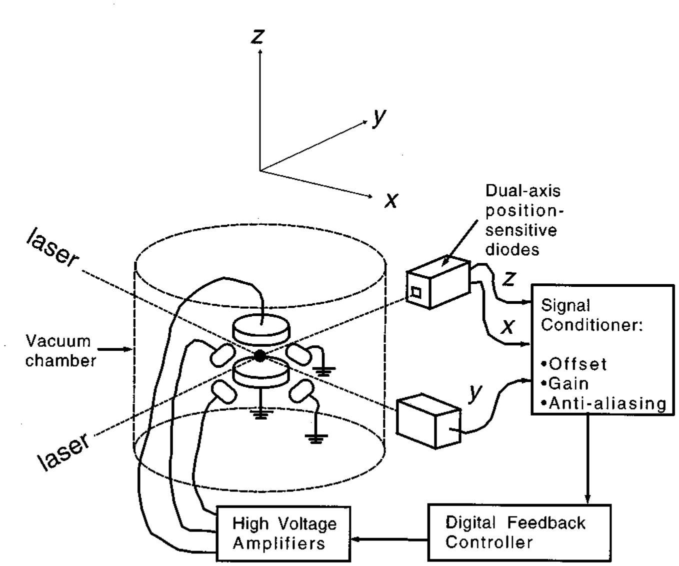
    $\Delta T^{I} \approx 125K ⇨ \Delta T^{I}/T_L \approx 0.11$

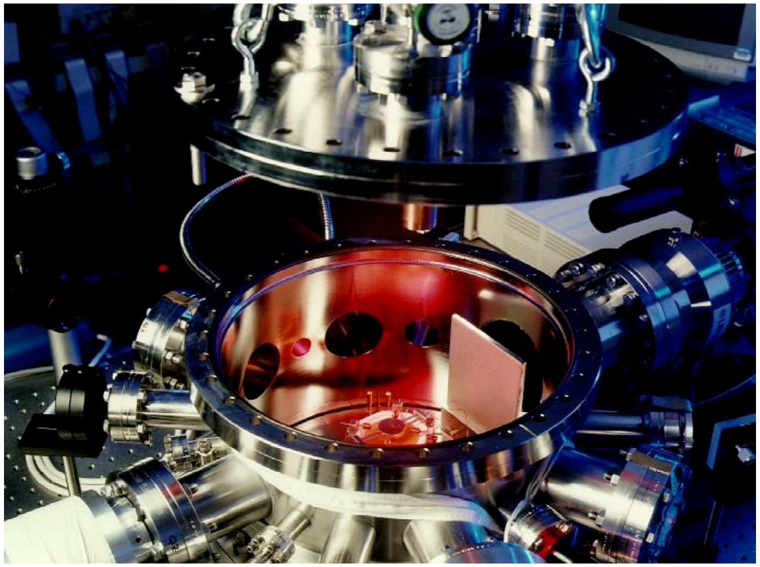
- **Crystal Approximants**
  - □ - $Al_{13}Fe_4$ ⇨ $\Delta T^{□}/T_L \approx$ 0.12
  - □ - Al_5Fe_2 ⇨ $\Delta T^{□}/T_L \approx$ 0.15

- **Crystal Phases**
  - β(AlCuCo) - (CsCl Structure)

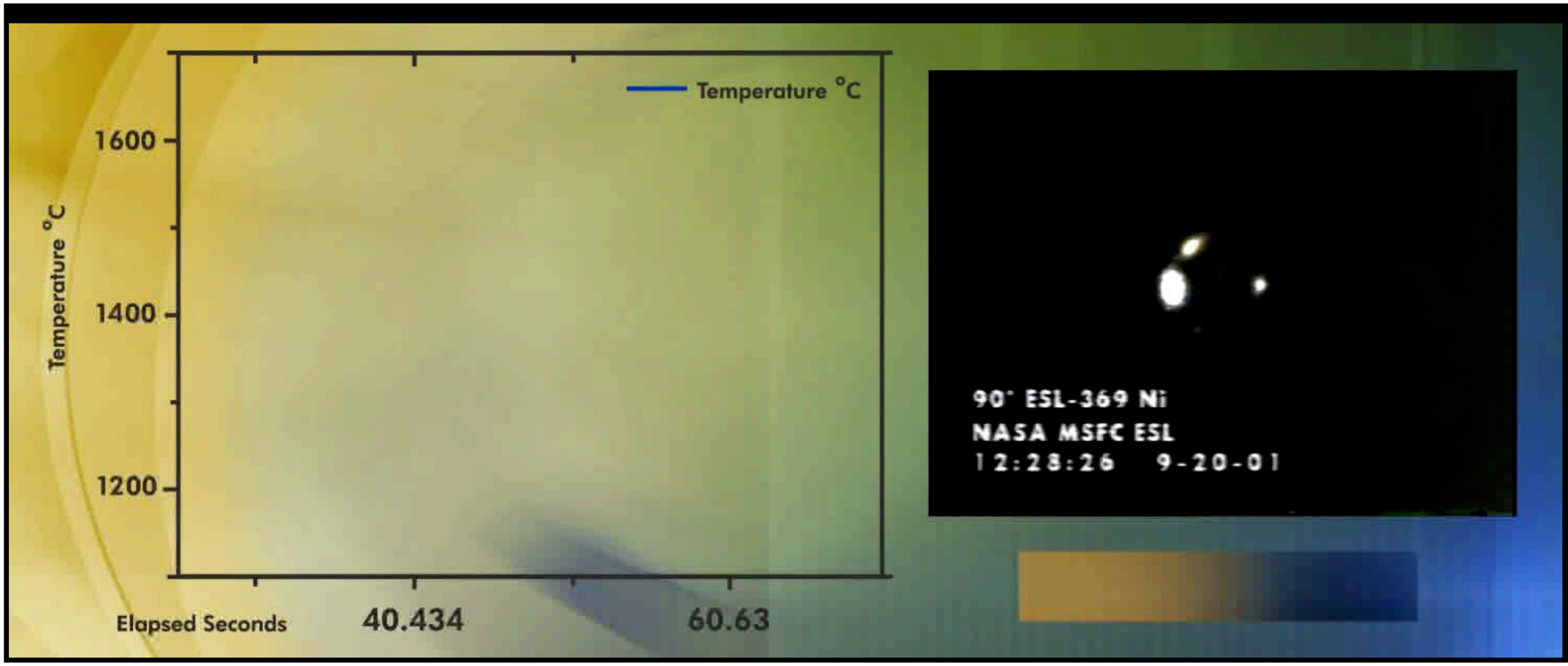
    ⇨ $\Delta T^{\beta}/T_L \approx 0.25$

Electrostatic levitation (ESL)



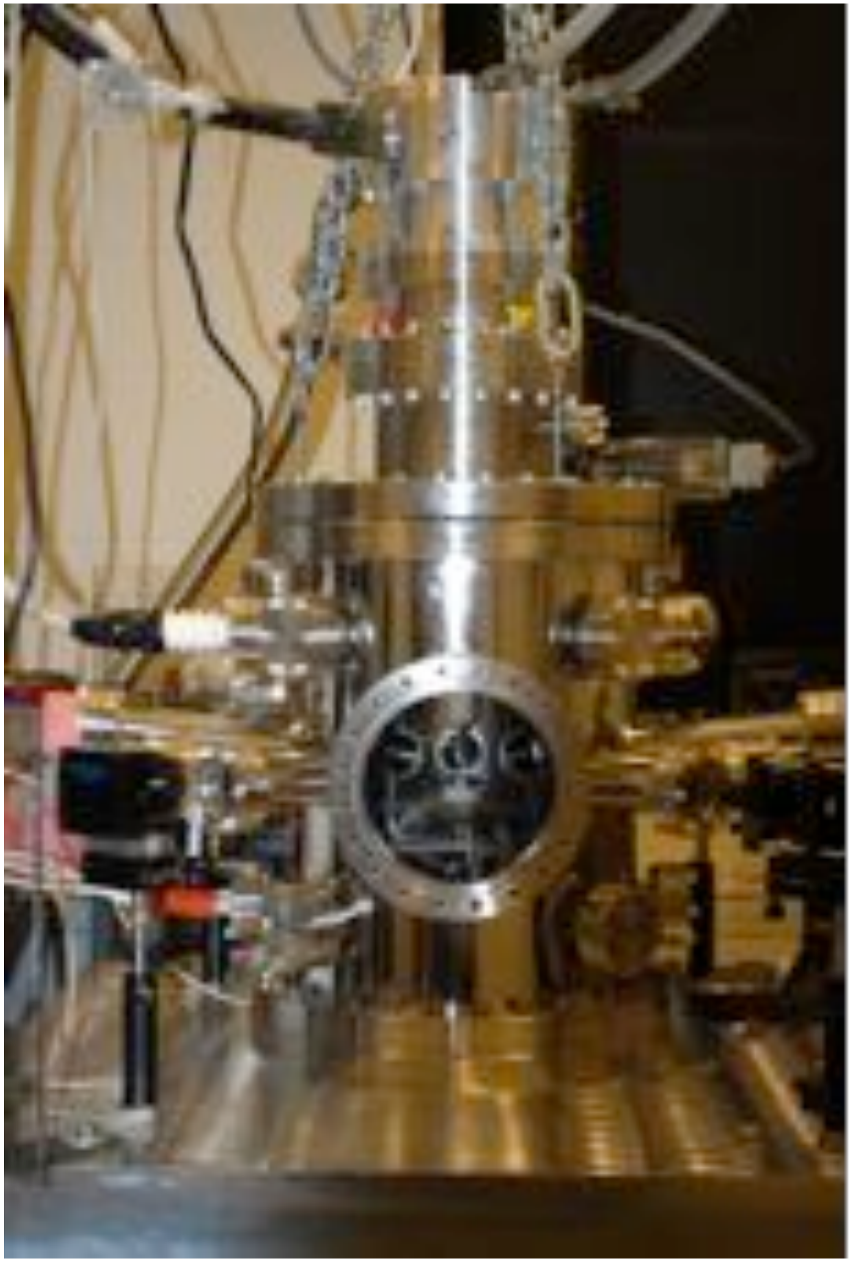


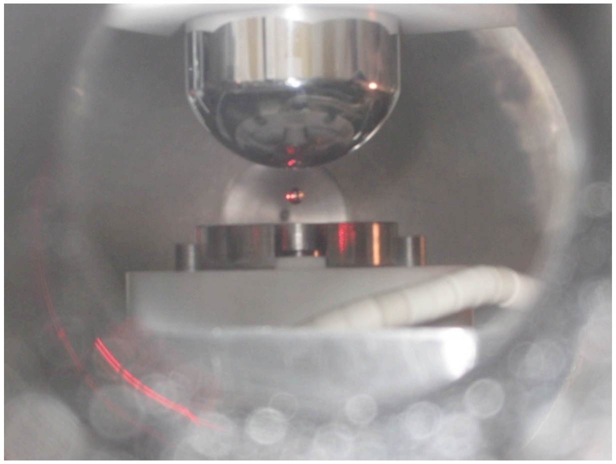
- $\sim 10^{-8}$ torr
- Heating & positioning decoupled
- Stable within 50-100 μm

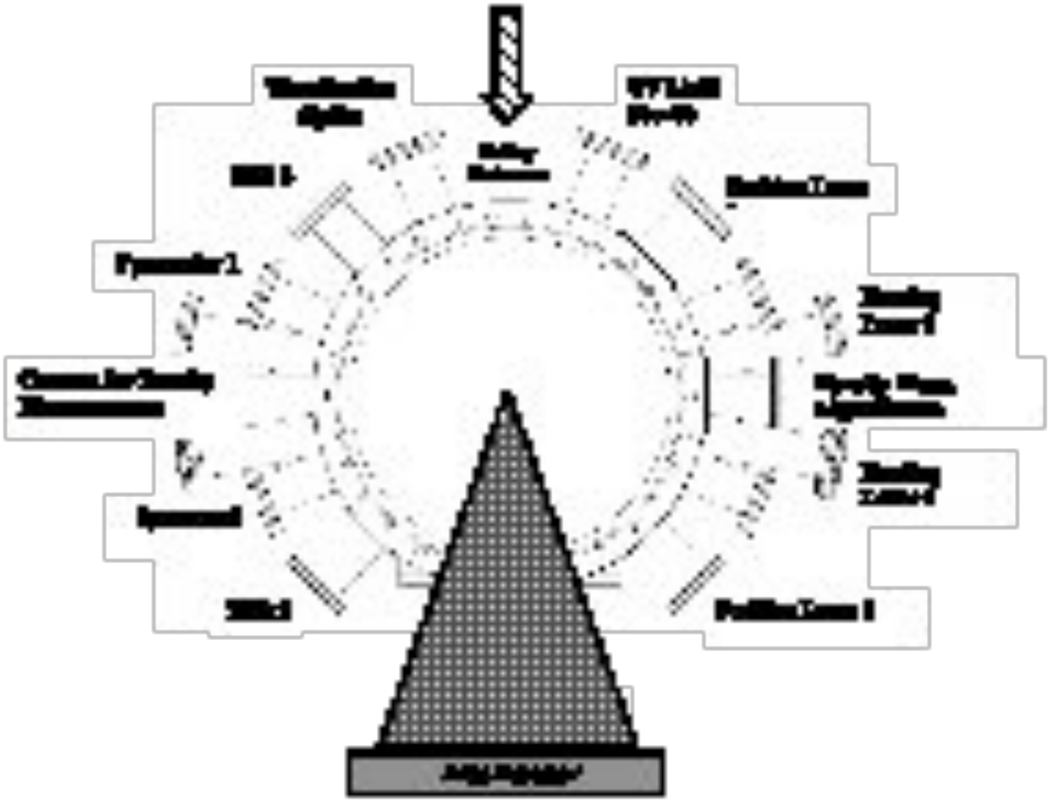


J. R. Rogers, NASA

WU-BESL (Washington University Beamline ESL

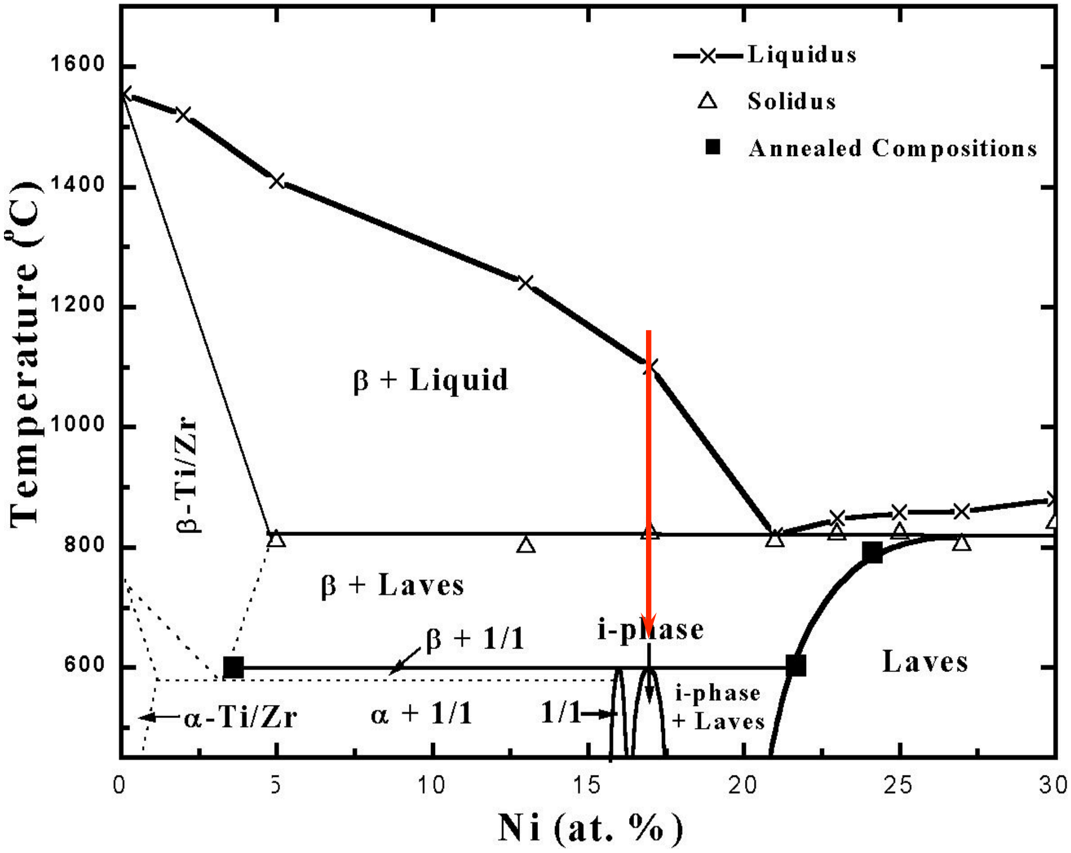






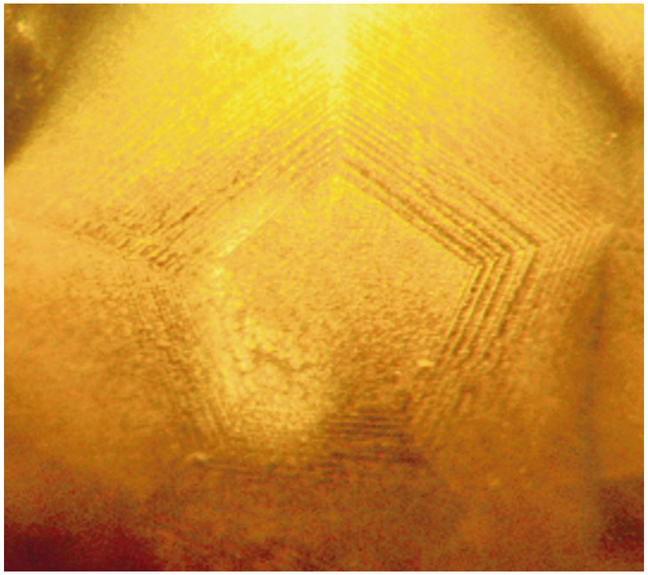
Ti-Zr-Ni Quasicrystals

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



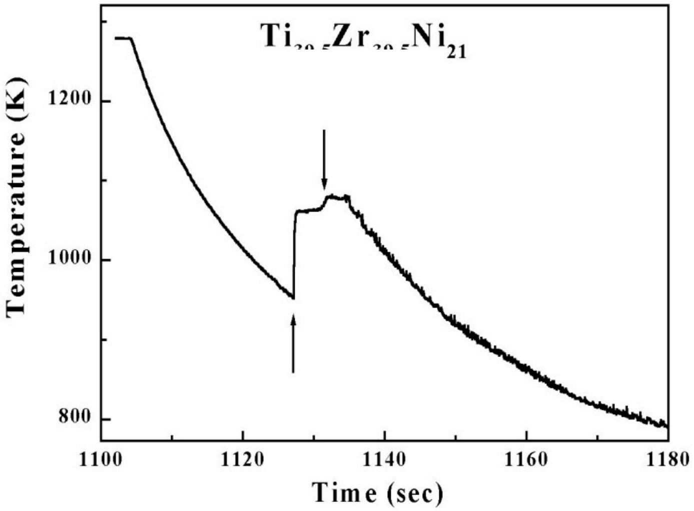
I-phase forms by solid-solid phase transformation

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

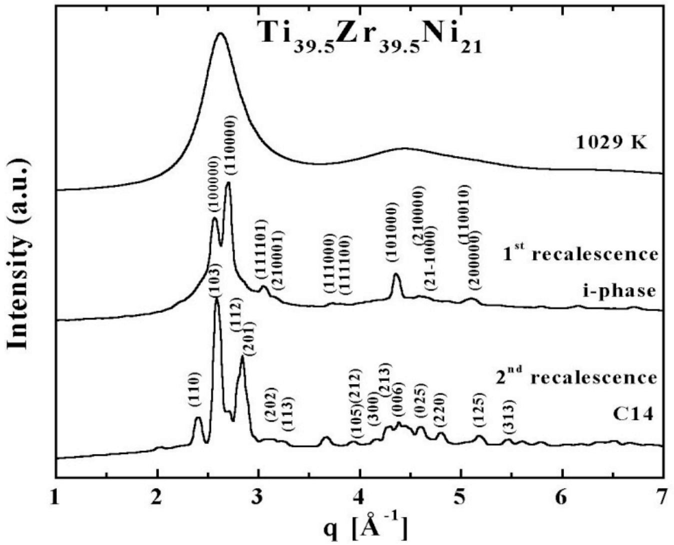


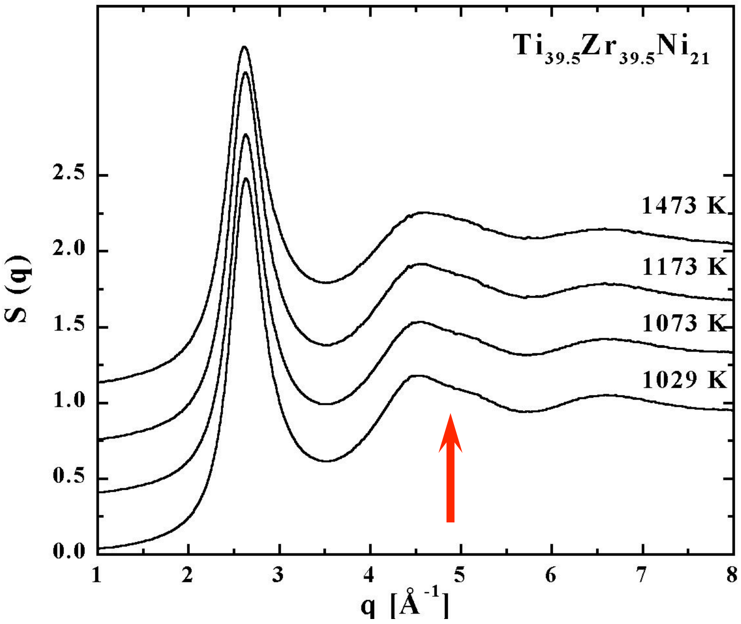
The growth rings indicated that it grew from the liquid

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

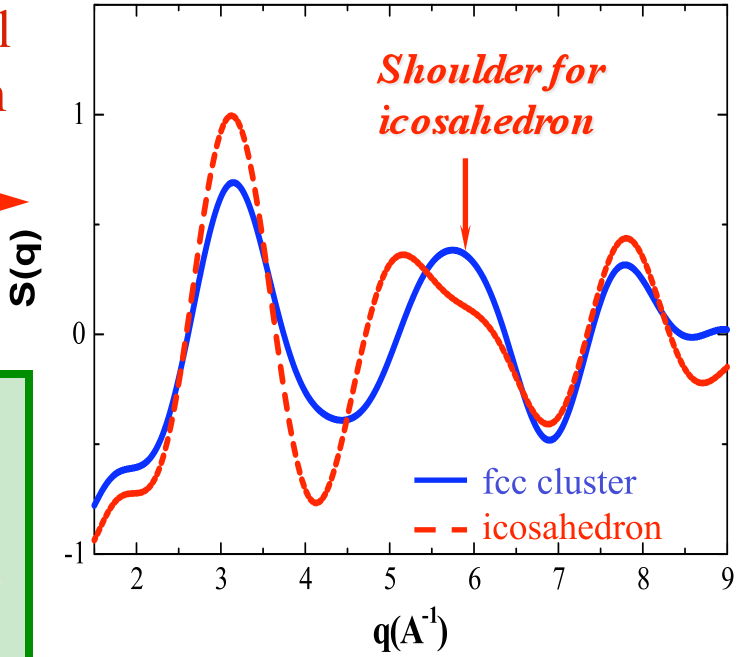


Recalescence to metastable quasicrystal





Icosahedral ordering in liquid



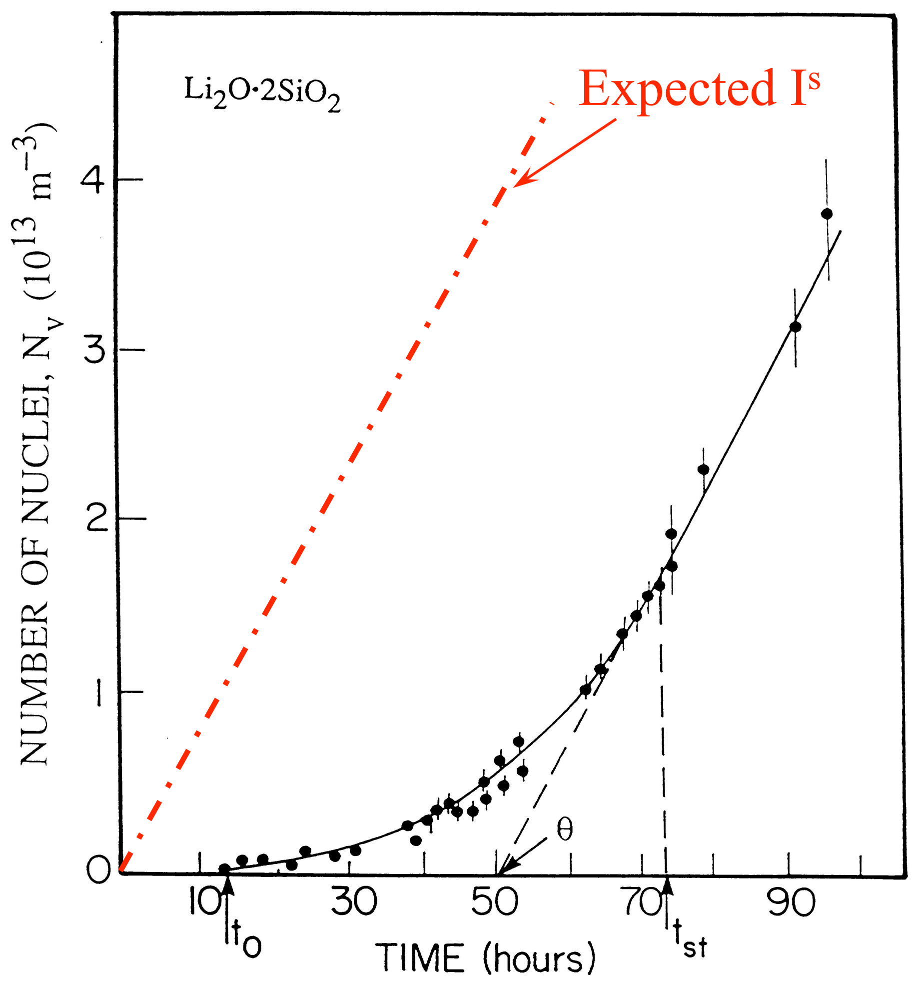
Ordering lowers nucleation barrier

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

Time-Dependent Nucleation

Time-dependent nucleation

- In the quenched cluster distribution, the cluster population at the critical size is too small (can’t maintain steady-state distribution during the quench)
- The quenched distribution evolves toward the steady-state distribution with annealing



$$N_v = I^s (t-\theta)\ , \qquad for\ \ t >> \theta$$

V. M. Fokin, A. M. Kalinina and V. N. Filipovich, J. Cryst. Growth, **52**, 115 (1981)

Fits to Transient Data

Zeldovich-Frenkel equation

¶NN n,tn,t ¶t¶n¶nN = ¶¶ éù êú kN ëû êú ëû n e æö ç ÷ ç ÷ è ø e n ÷

Diffusion equation in size space

æ¶¶¶¶ ç è ø¶t¶x¶x = éù ëû ÷ ø

Fick's law

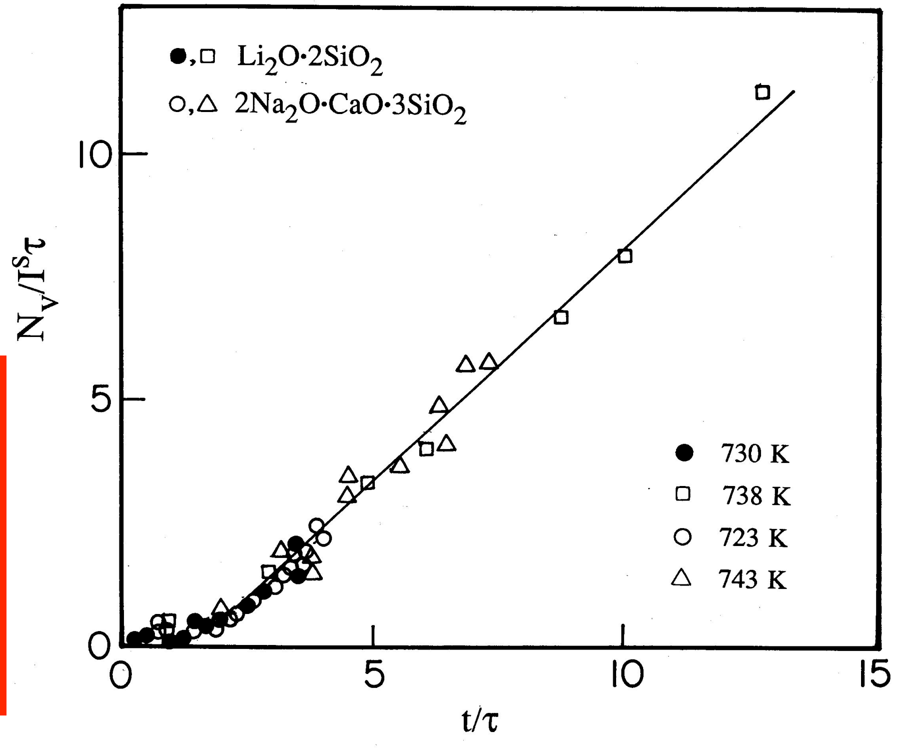
Kashchiev's solution - I(t)

1.kk ++ nn* ®

2.WW(nn*) nn* +- 1 W¶ 2 2n¶ 2 n | nn* 2

$I_{n^*,t}$ = 1 + 2 χ∋ υ⊕ ψ⊗ (-1 -)^m exp φ τ÷ φε $m^2 t$ / Π_K , m=1

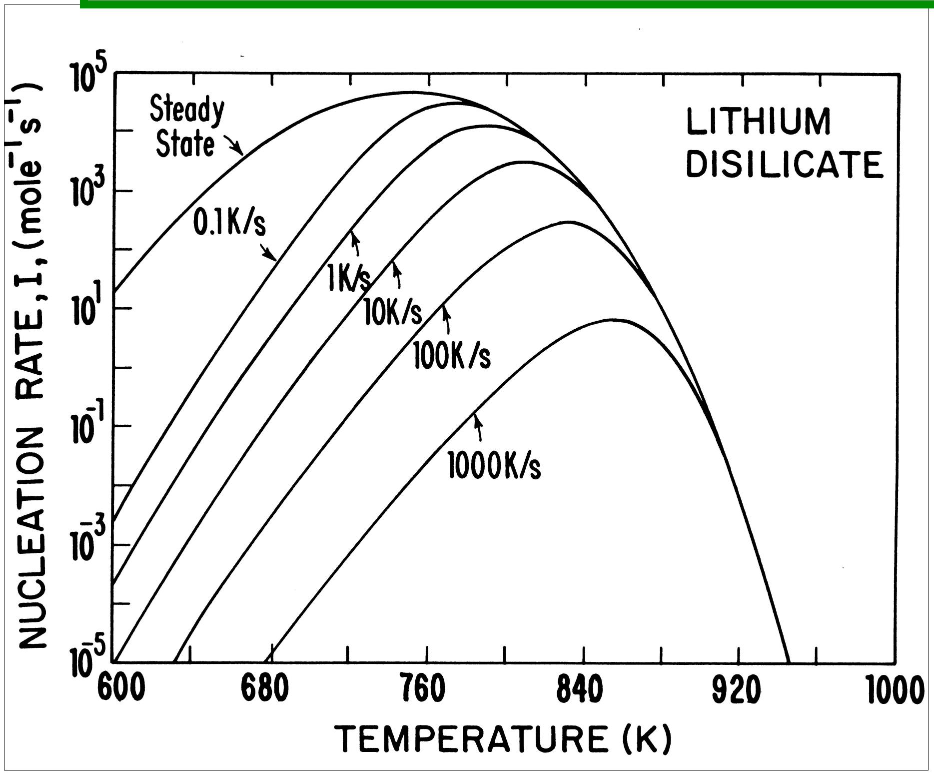
Π_K = - 24Tkn*4 / MNk$^{2+3}_{n^*n}$∞I ———— *$^+$Z^2 $N = \frac{M\Pi^2}{6}$

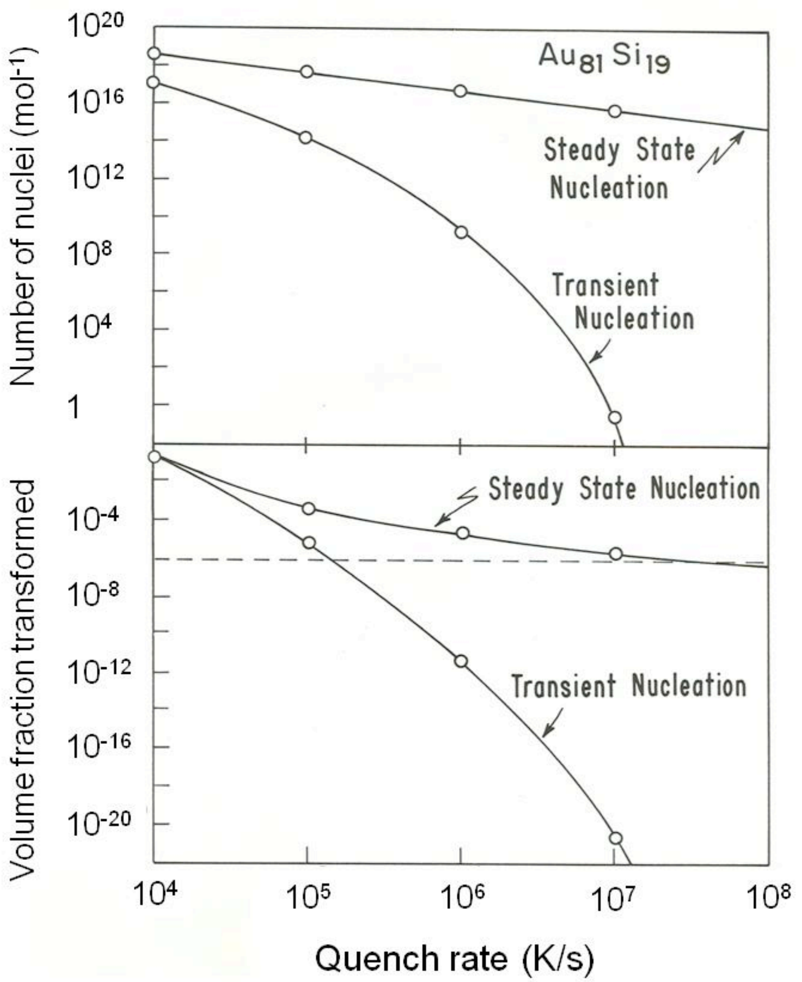


Scaling

D. Kashchiev, *Surface Science* **14**, 209–220 (1969)

Nucleation rate during a rapid quench

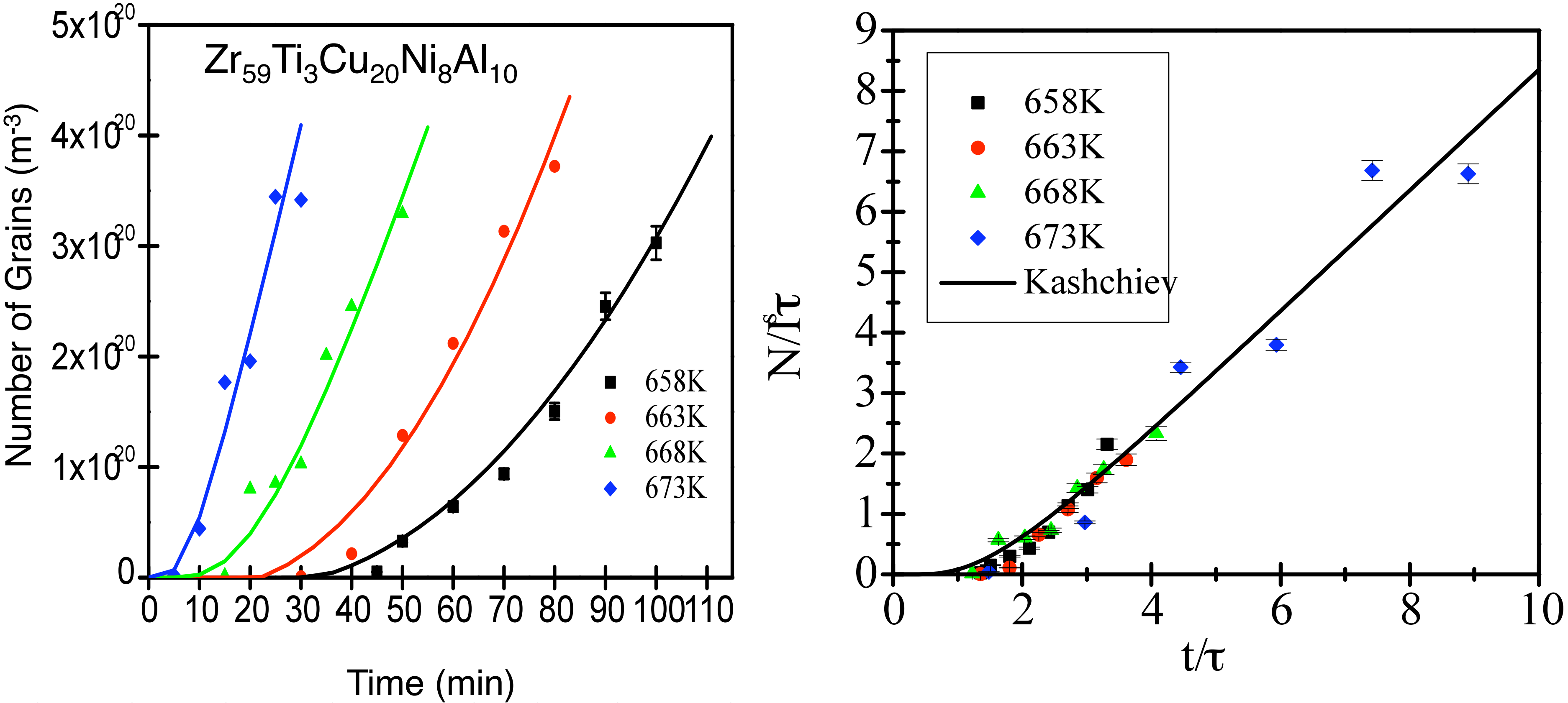




- Nucleation rate decreases far below the steady-state rate
- Temperature of departure from steady state rate increases with quench rate
- Due to inability for cluster distribution to relax during quench (frozen distribution - more typical of high-temperature distribution)

Can dramatically Influence glass formation in marginal glasses

Two Step – Quasicrystal Nucleation in Metallic Glasse



Fit to time-dependent nucleation data using

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

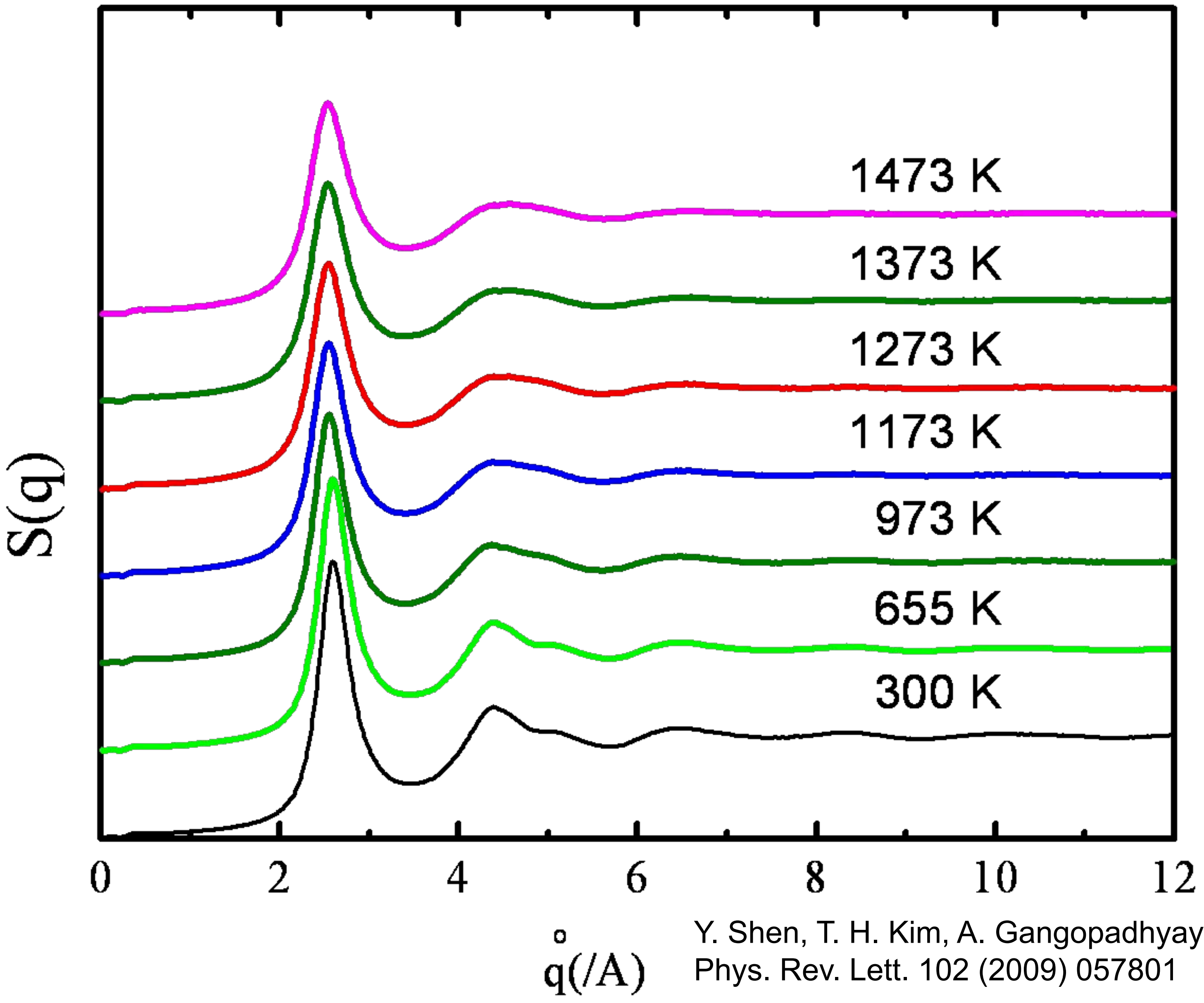
$\sigma = 0.01 \pm 0.004$ J/m^2

Evidence for significant short-range icosahedral order in glass

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

Synchrotron High Energy X-Ray Diffraction Studies

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



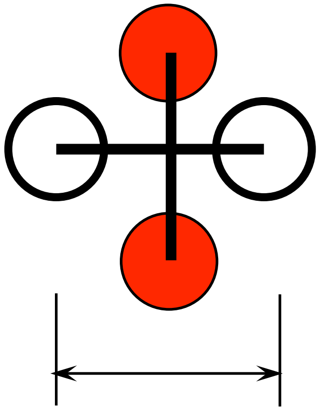
Y. Shen, T. H. Kim, A. Gangopadhyay, K. F. Kelton
Phys. Rev. Lett. 102 (2009) 057801

Reverse Monte Carlo (McGreevy)

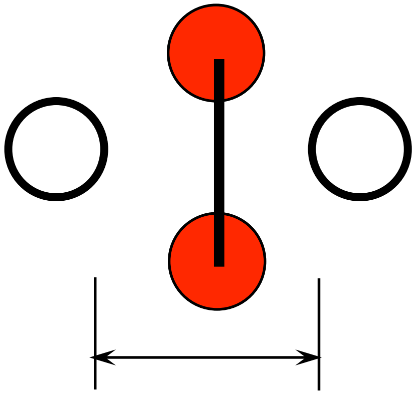
Statistical fit to S(q) or g(r) data to obtain atomic structure

No energies involved – worry about uniqueness of structure

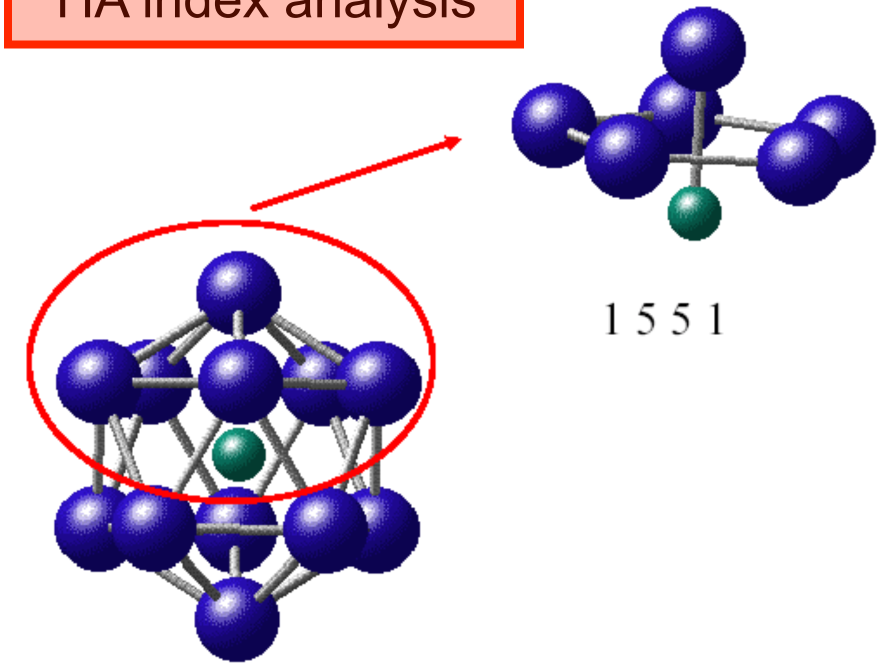
HA index analysis


cutoff distance

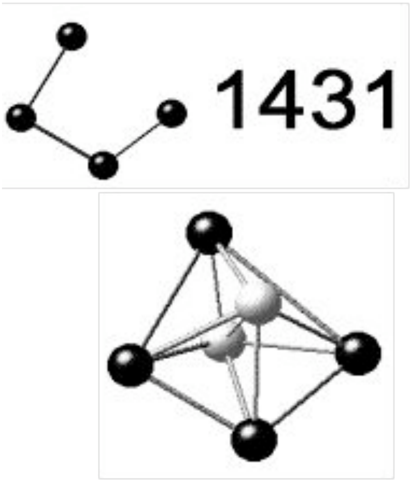
(1 2 1 1)

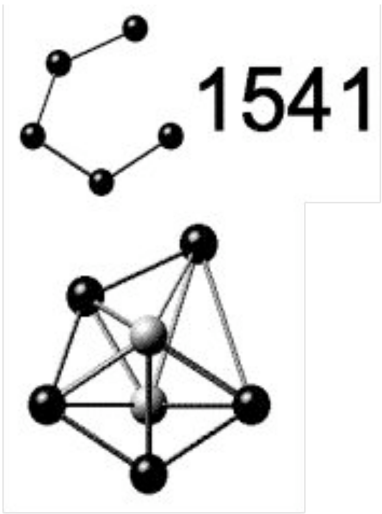

cutoff distance

(1 2 0 1)


1 5 5 1

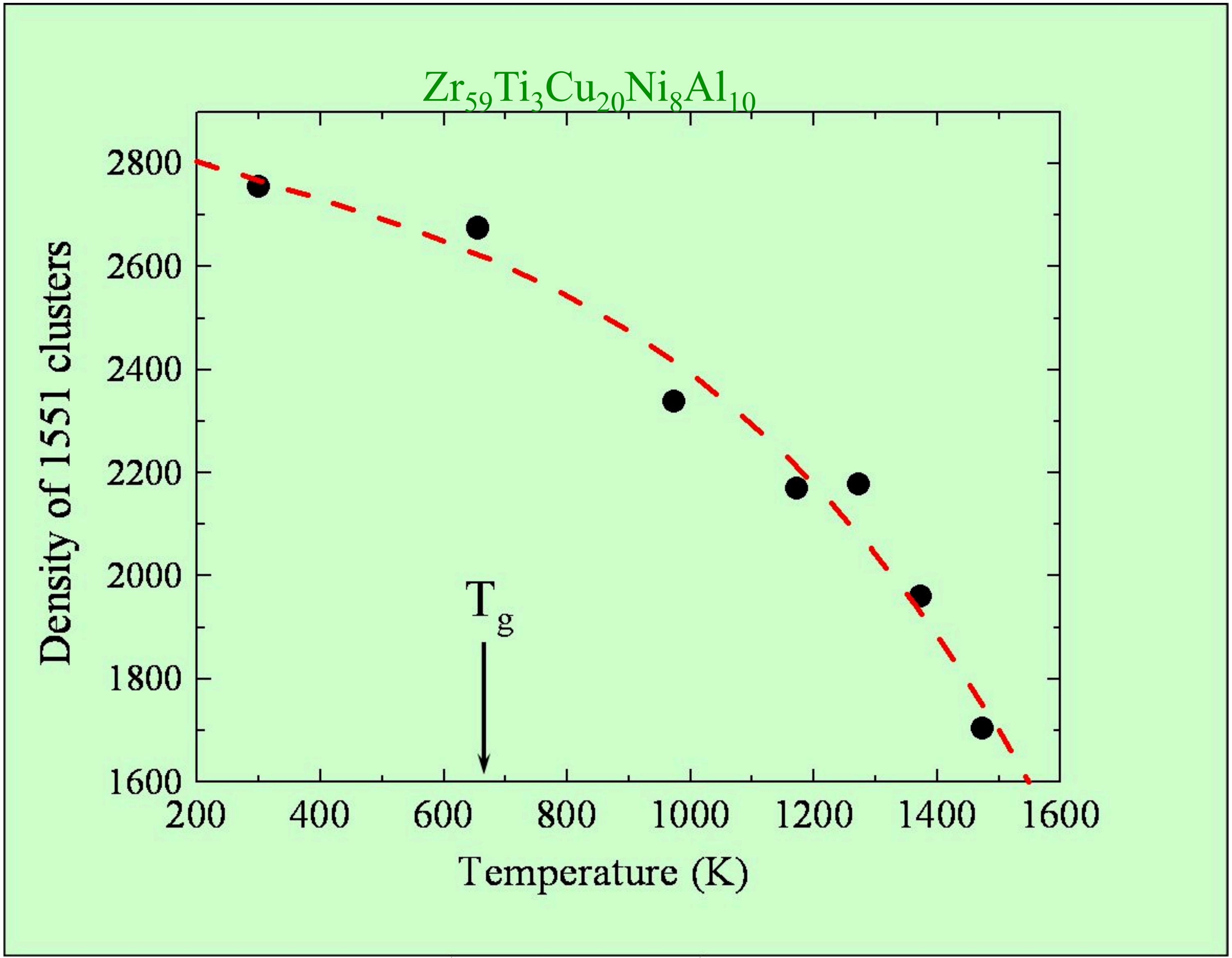
Icosahedral Cluster





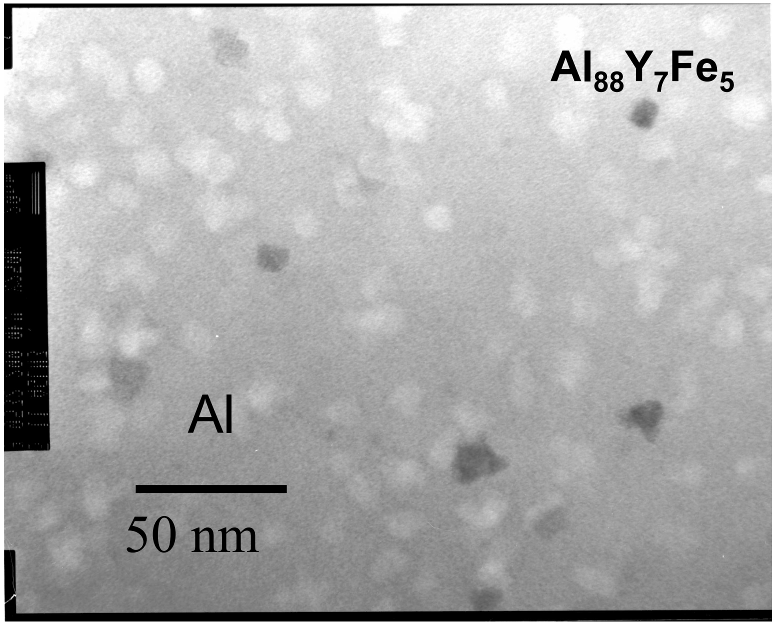
Distorted Icosahedral Cluster

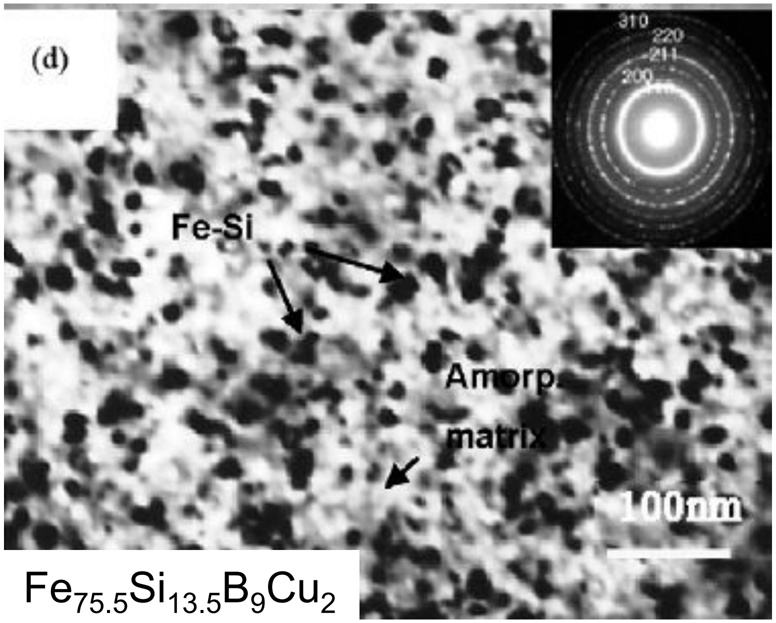
Significant Growth of Icosahedral Order



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

But High Nucleation Rates are also Found in GlassesThat Don’t Have Strong Icosahedral Order





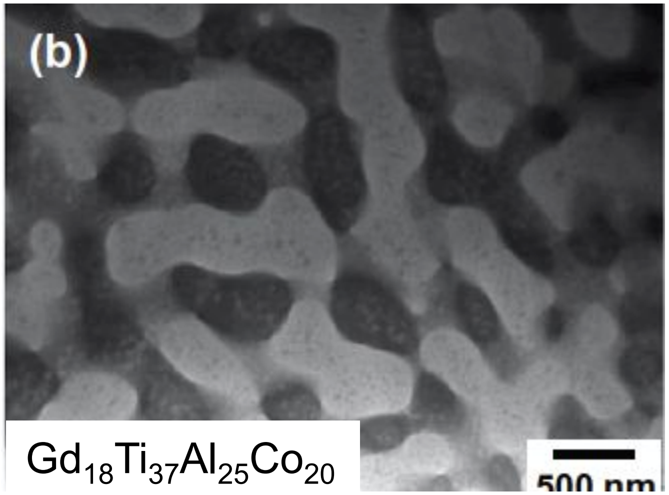
$Fe_{75.5}Si_{13.5}B_9Cu_2$

– Perepezko et. al.
– Kelton et. al.

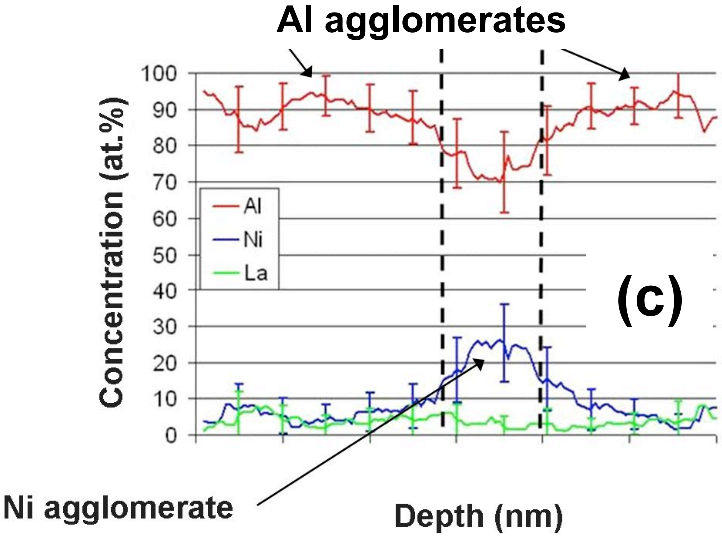
H. T. Zhou, J. Alloy. Comp., **475**, 706, 2009

Coupling between first order phase transitions

Phase Separation



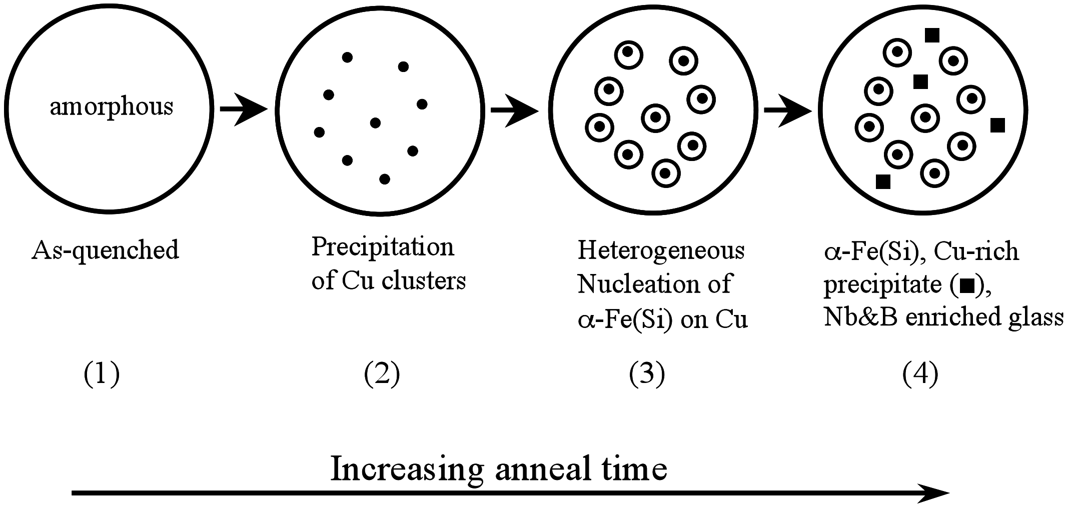
H. J. Chang et al., Acta Mater., **58**, 2483 (2010)



$Al_{89}Ni_6La_5$

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

Precipitation



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)

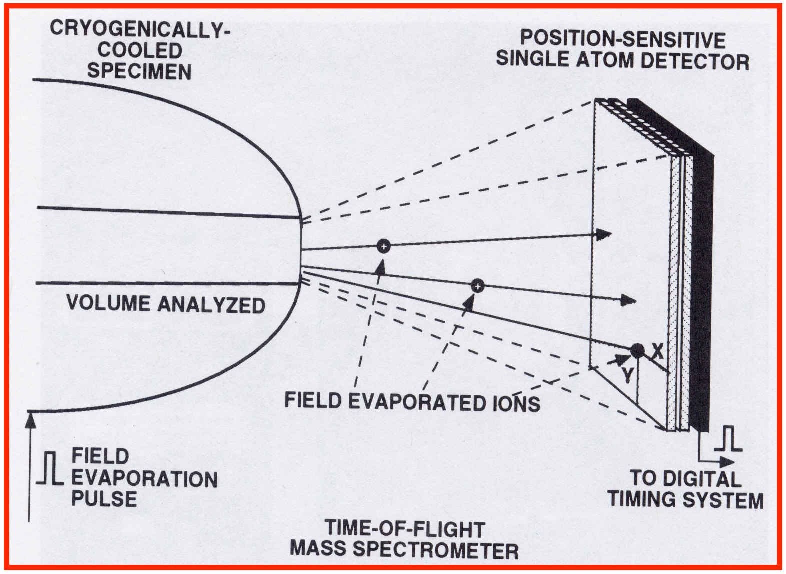
Increasing anneal time

FINEMET Metallic Glasses

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

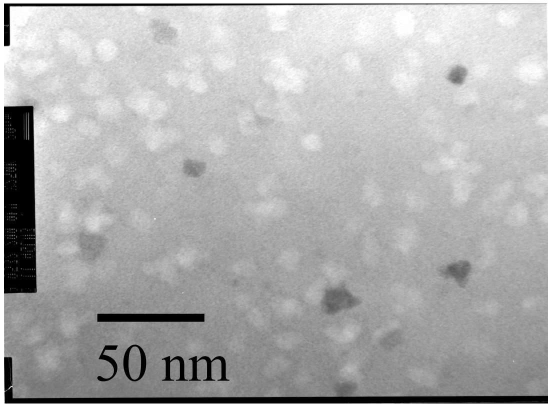
Atom Probe Tomography

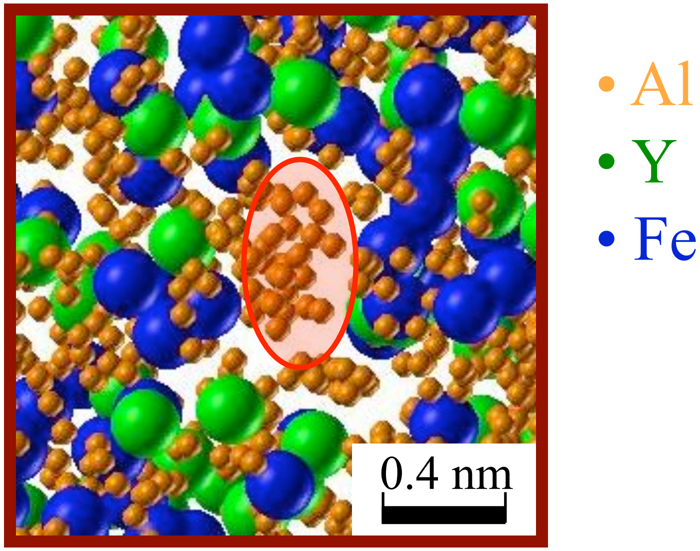
LEAP Si™ Metrology System
Imago Scientific Instruments



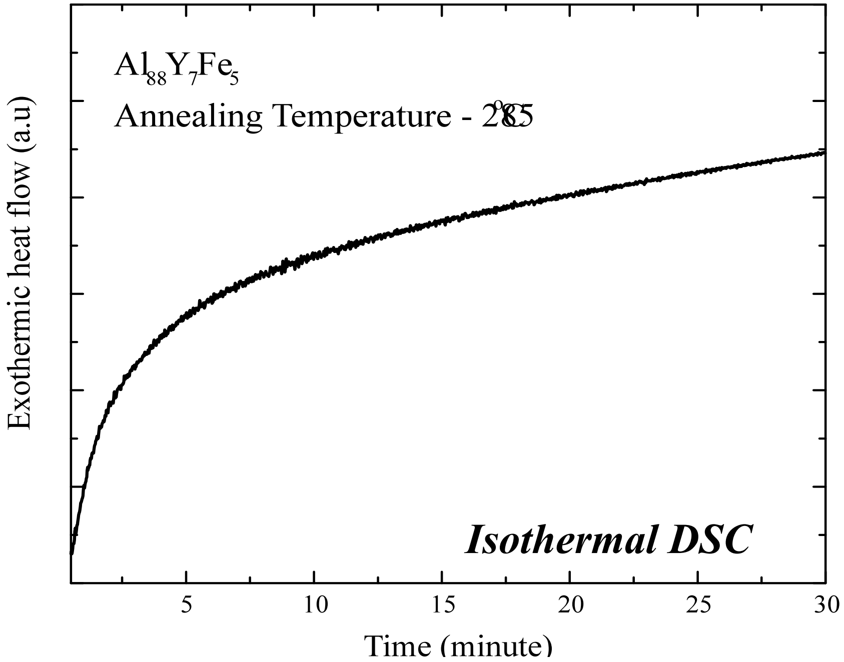
- **Ideally**
  - Remove atoms one at time from sample
  - Record atom type and original position

$Al_{88}Y_7Fe_5$

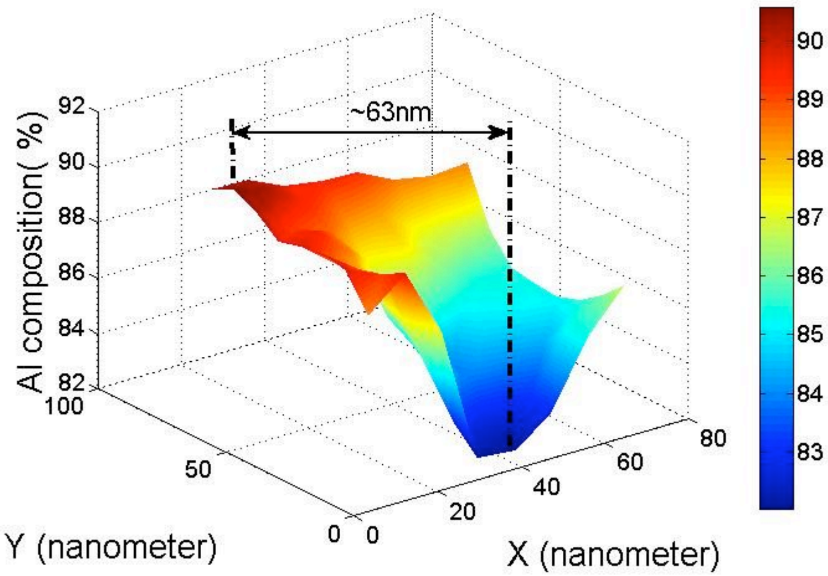




Nanoscale Phase Separation



Extremely high nucleation rate
Diffusion-limited growth

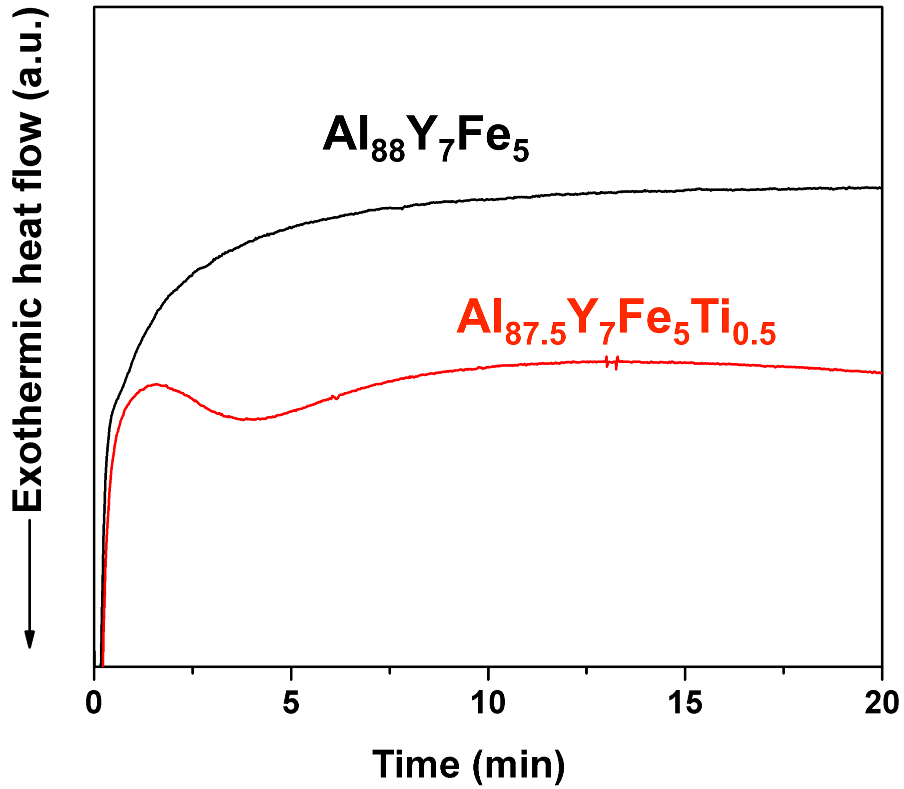


K. Sahu et al, Acta Mater. (2010).

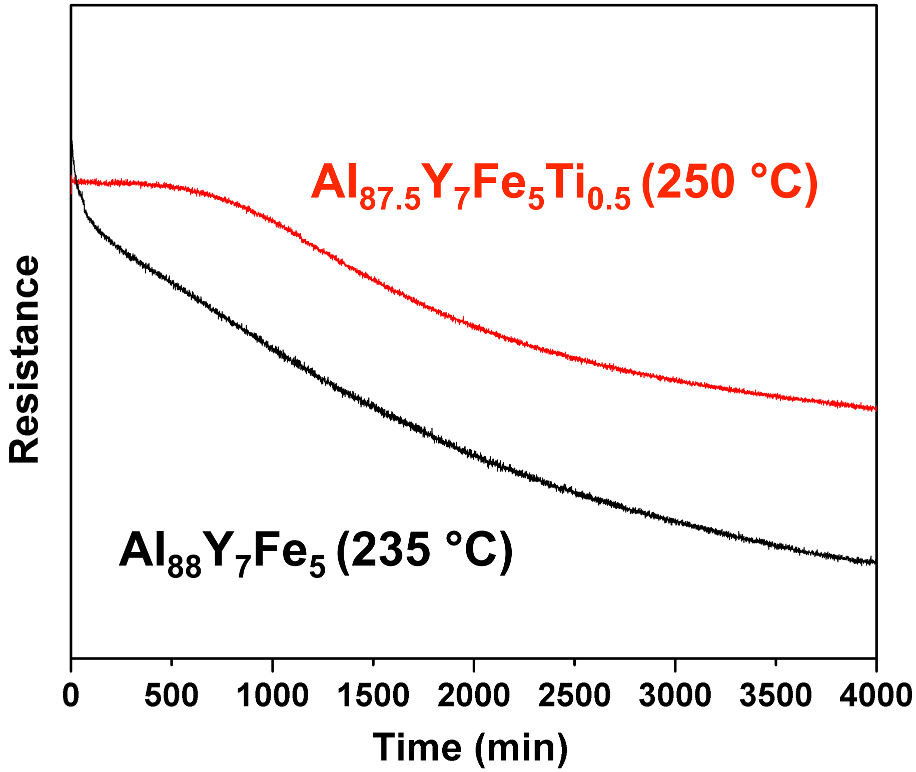
Microalloying

Ti, Zr, V microadditions improve glass formation in $Al_{88}Y_7Fe_5$

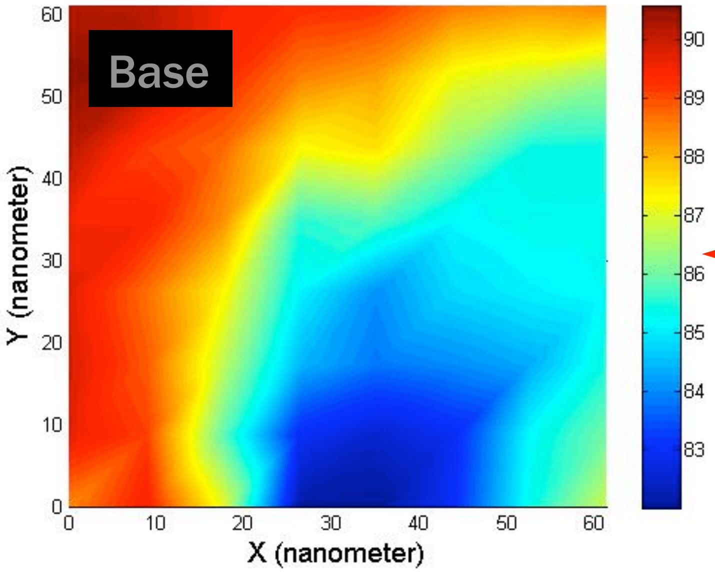
Isothermal DSC scan



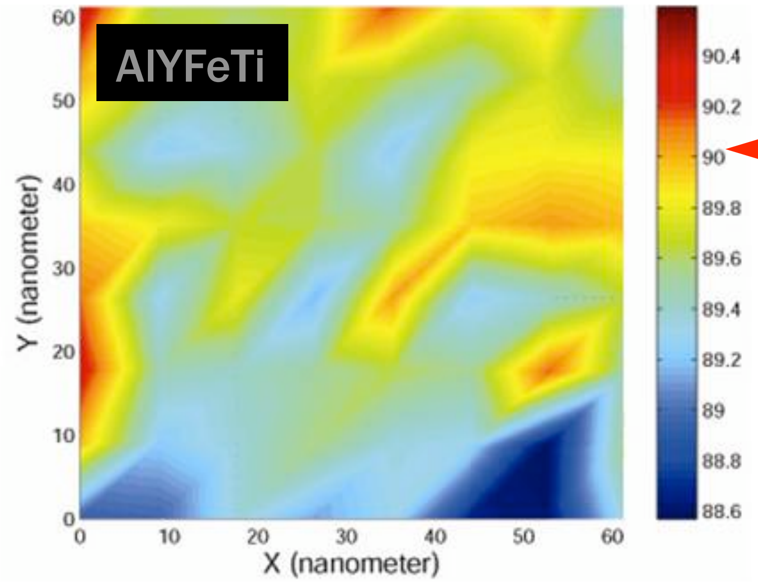
Resistance vs. annealing time



Microalloying – Atom Probe Tomography Results



- Phase separation in base glass ($Al_{88}Y_7Fe_5$)
  - Al concentration varies by ~ 7 %
  - Regions separated by ~ 65 nm



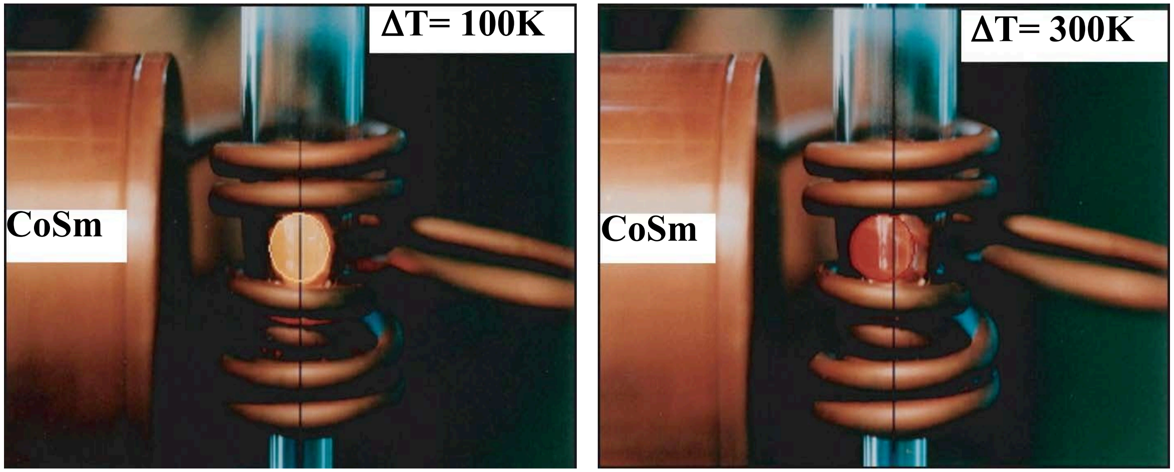
- No evidence for phase separation in microalloy

⇒ Improved glass formation and stability due to suppression of phase separation

Coupling with Higher Order Phase Transitions

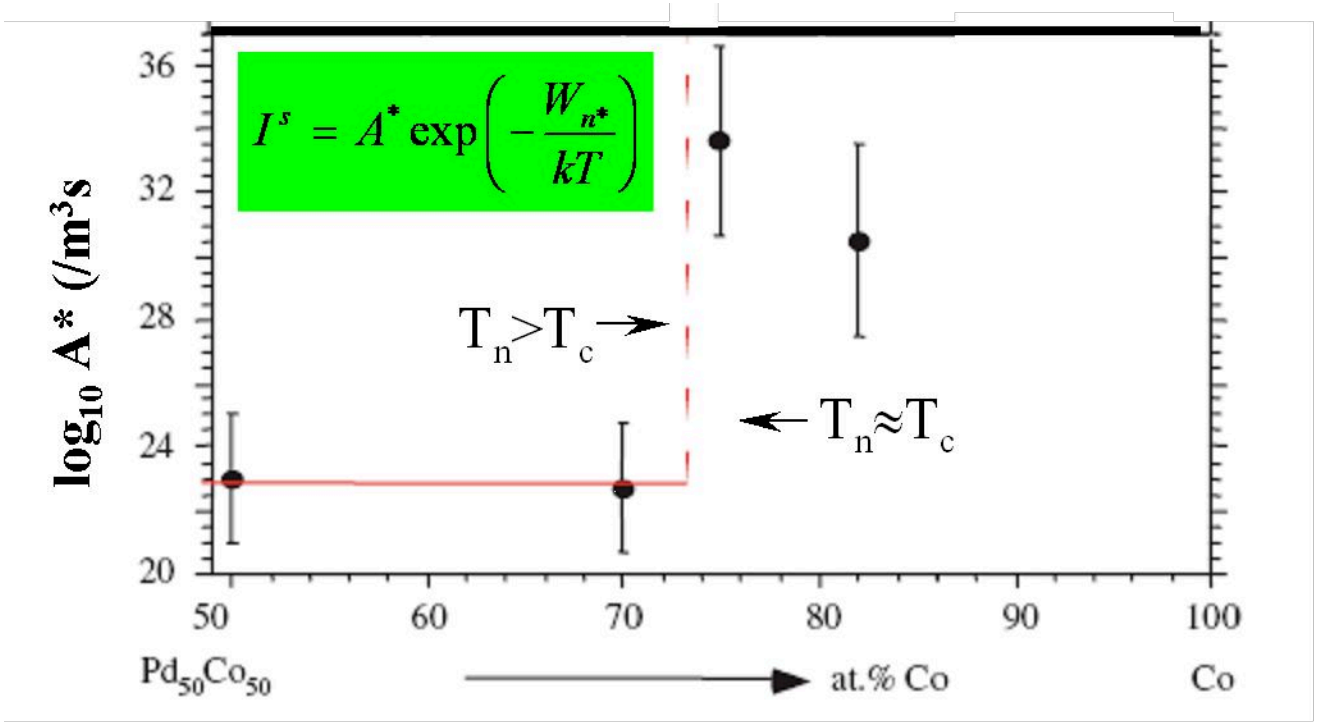
Coupling with Magnetic Ordering

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

Magnetic contribution to driving free energy (Holland-Moritz, Spaepen, Phil. Mag. **84**, 957 (2004))



Summary and Conclusions

- Classical Theory of Nucleation
  - Fits temperature dependent data in terms of effective Interfacial - provides some measure of the structural and chemical differences in initial and new phases
    - capillarity assumption questionable for small clusters
    - Incorrect pre-term predicted (sometimes by orders of magnitude)
  - Quantitatively explains time-dependent nucleation behavior
- Correction to Thermodynamics
  - Phenomenological diffuse interface theory
  - Density Functional Theories
- Coupling is important
  - With amorphous structure
  - With other phase transitions
- Correction for kinetics when interfacial and diffusion processes are similar
  - K. Russell, Acta Met., **16**, 761 (1968).
  - K. F. Kelton, Acta Mater. **48**, 1967 (2000)
  - H. Diao, R. Salazar, K. F. Kelton, L. Gelb, Acta. Mater., **56**, 2585 (2008).