Microstructural
Kinetics
Group

UNIVERSITY OF CAMBRIDGE
Department of Materials Science and Metallurgy

Les Verres Métalliques:

— parvenus du monde vitreux
— et du monde métallique!

A. Lindsay Greer
Dept. of Materials Science & Metallurgy
University of Cambridge

Structural role of elements in glasses:
from classical concepts to a reflexion over broad composition range?

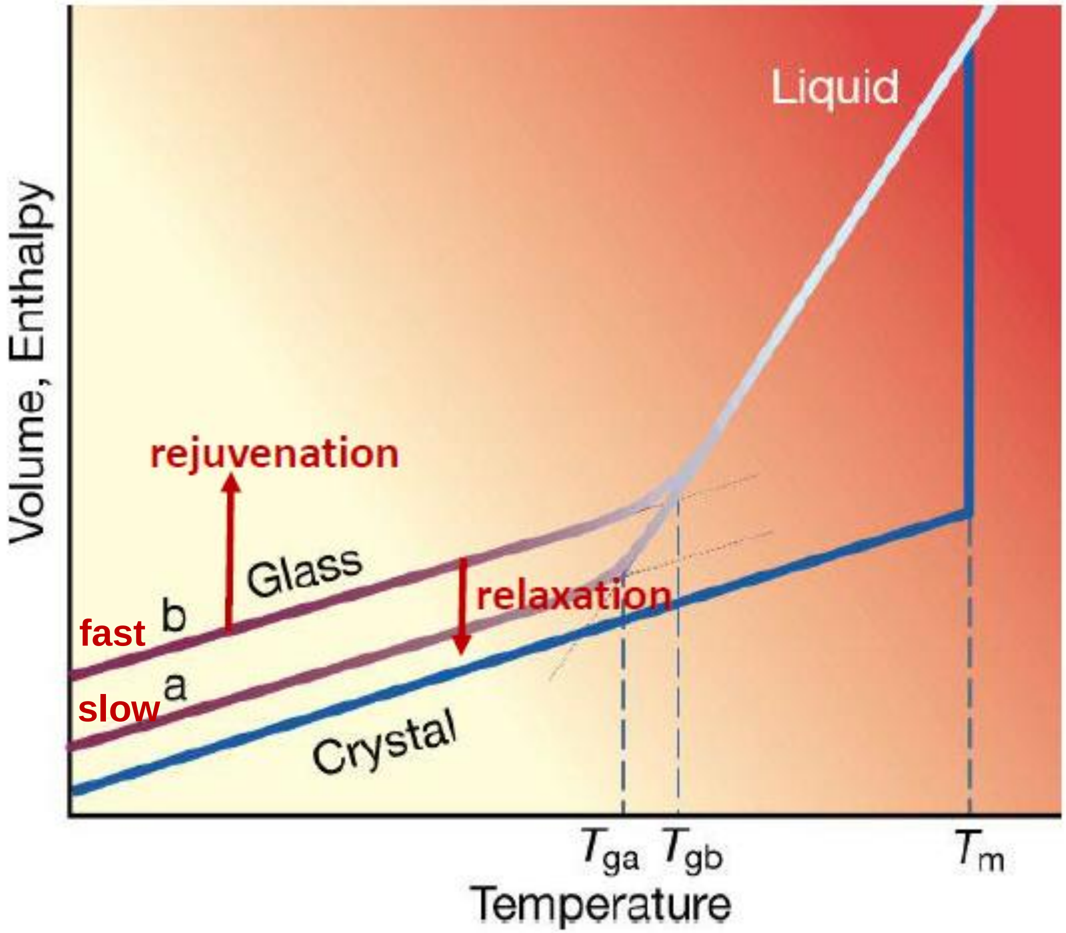
GDR Verres, Cargèse
27–31 March 2017

erc

SEVENTH FRAMEWORK PROGRAMME

Vitri Met Tech

- The liquid → glass transition is kinetic
- Therefore there is a range of glassy states depending on cooling rate



Conventionally:

- relaxation (to states of lower energy) – achieved by annealing
- rejuvenation (to states of higher energy – achieved by reheating to liquid

Metallic Glasses

• metals and alloys are naturally crystalline

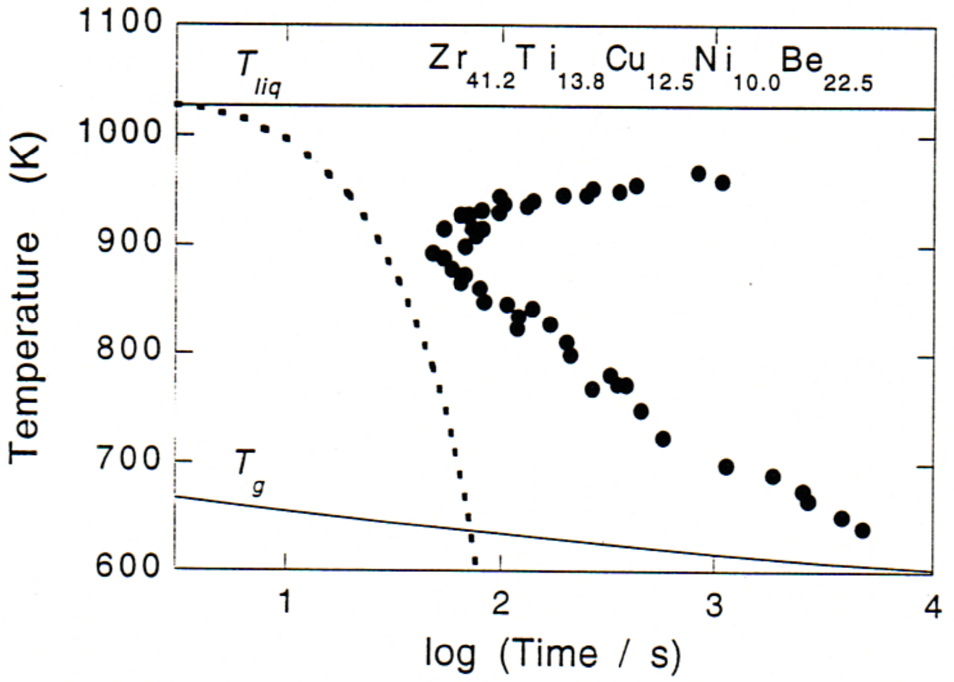
• pure metals cannot easily form glasses — their simple crystal structures facilitate nucleation and growth

• liquid metals have a low viscosity, very similar to that of water

• alloying can stabilize the liquid, and aids glass formation (“confusion principle”)

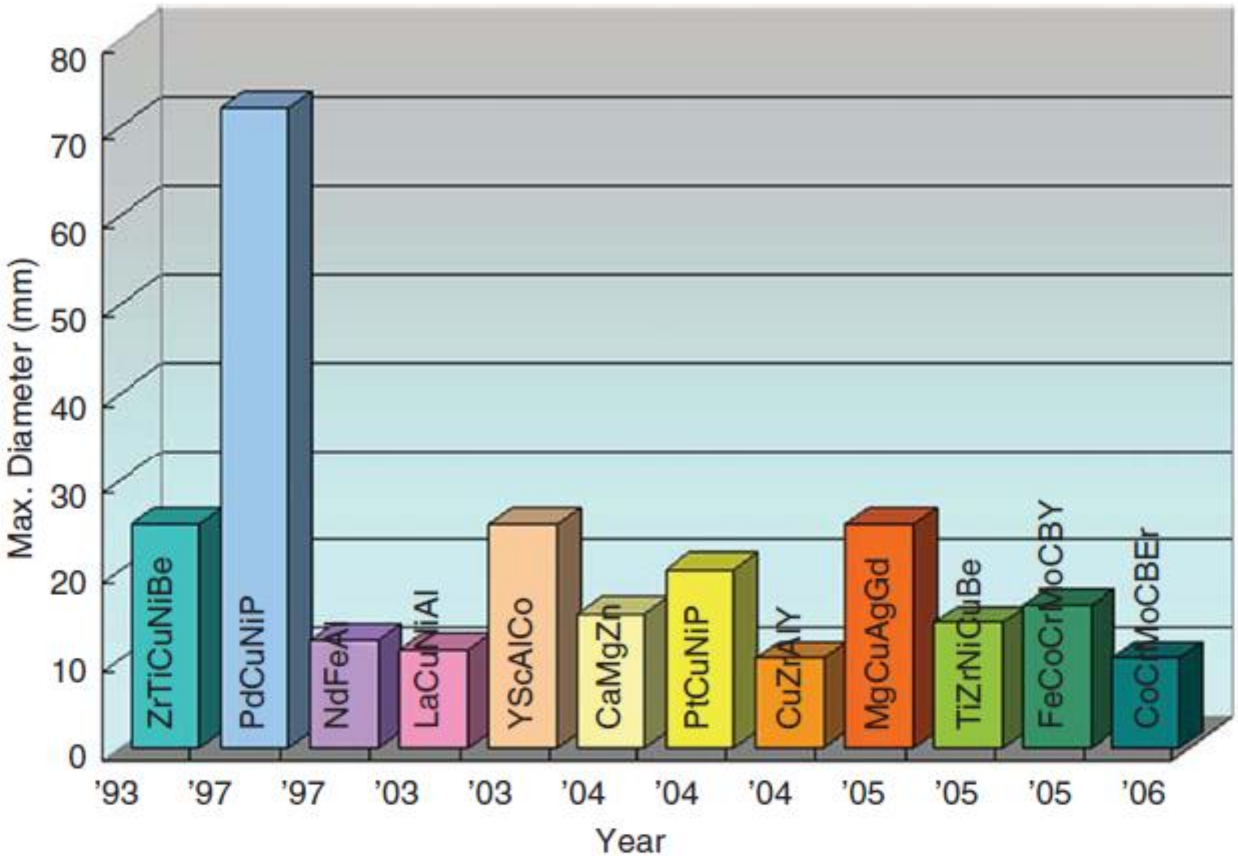
• for a binary alloy such as $Fe_{80}B_{20}$ (atomic %), the critical cooling rate for glass formation is
10^5 to 10^6 K s^{-1}

Bulk Metallic Glasses



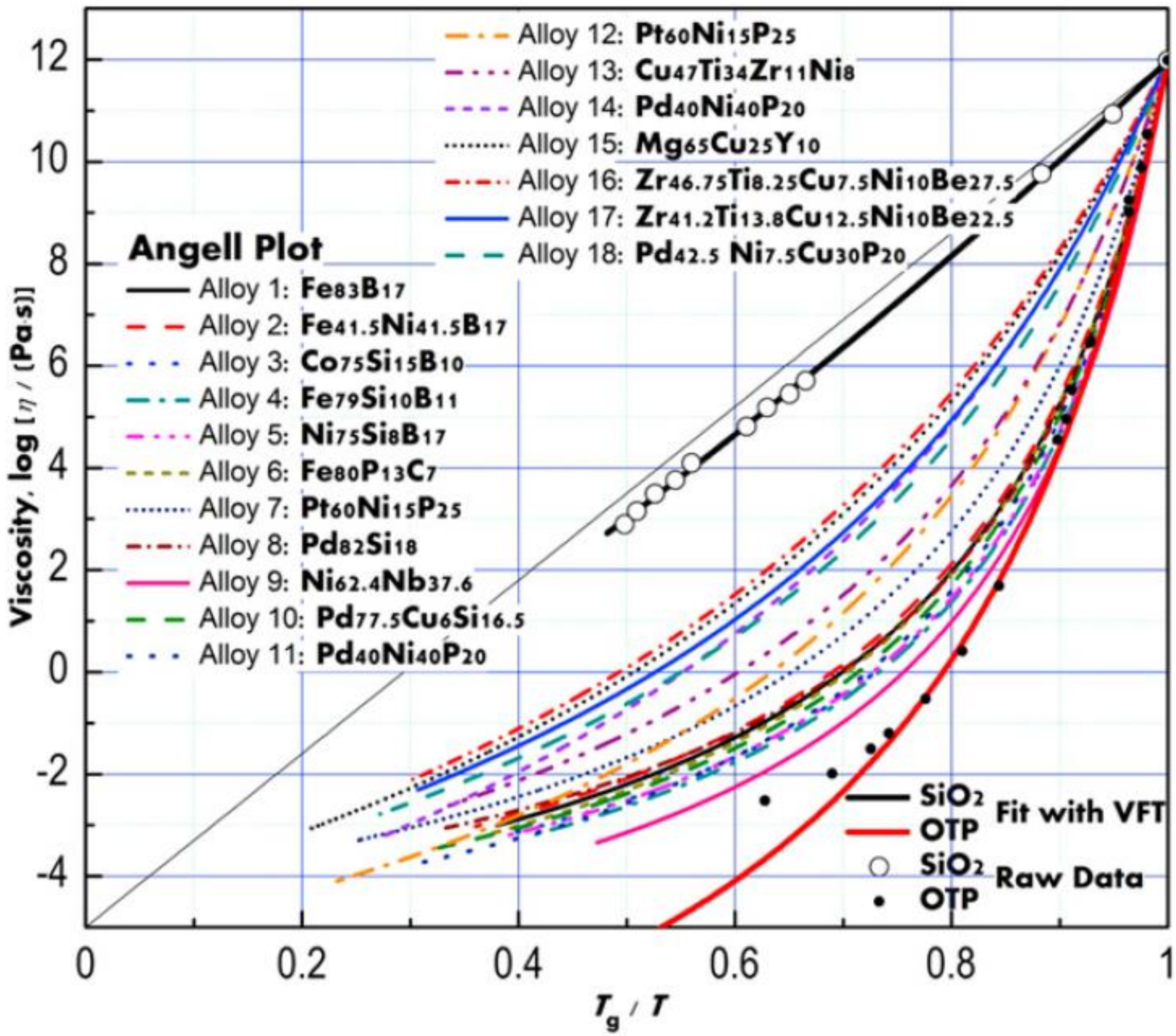
- multicomponent compositions aid glass formation
- the critical cooling rate is low (~1 K s^{-1})
- glasses can be formed in bulk

  (maximum diameters mm up to a few cm)

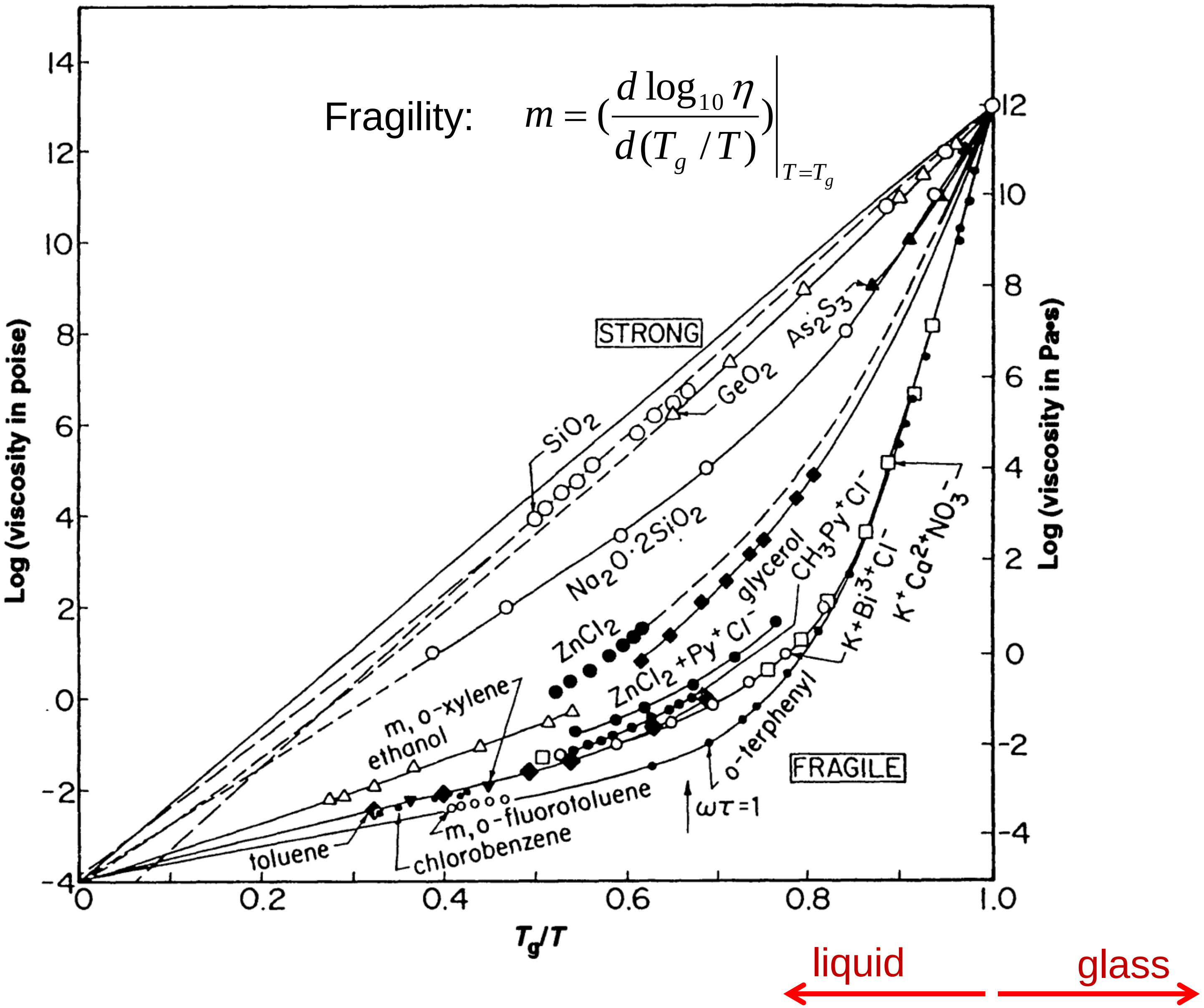


Bulk metallic glasses — at the cutting edge of metals research
AL Greer and E Ma,
MRS Bulletin **32** (2007) 611-615.

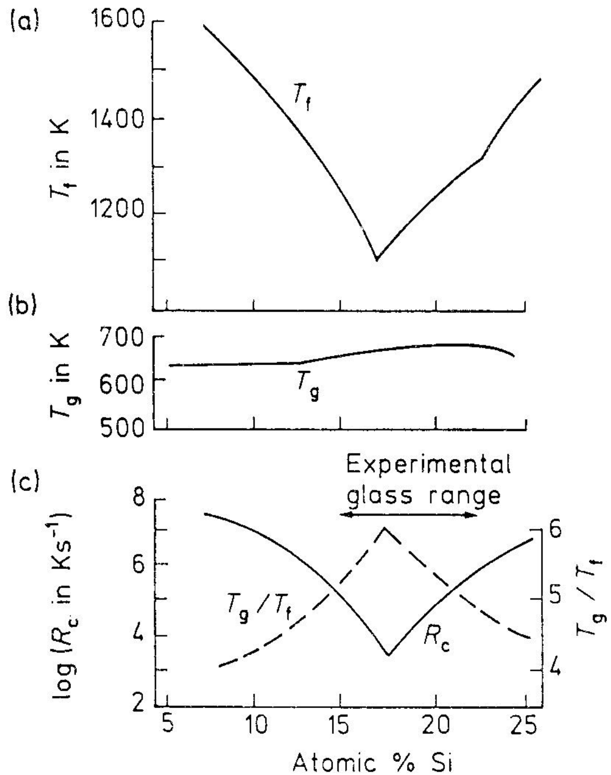
Angell plot for metallic glass-forming systems

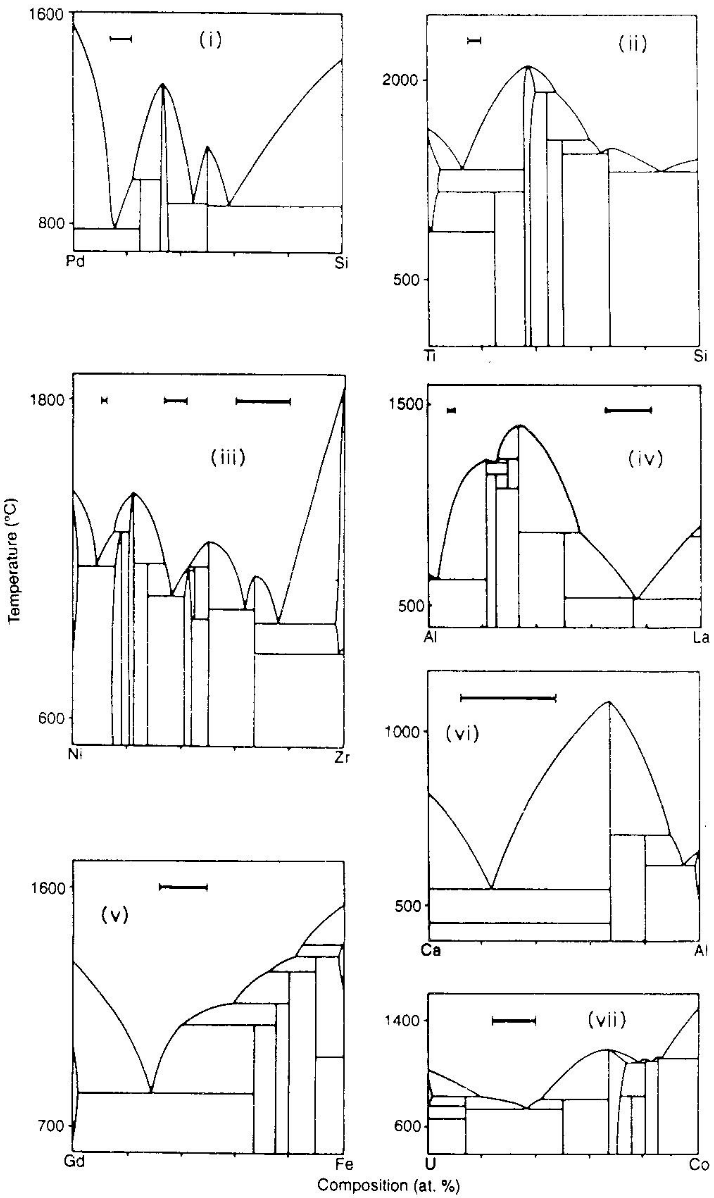


A Takeuchi, H Kato & A Inoue
Vogel–Fulcher–Tammann plot for viscosity scaled with temperature interval between actual and ideal glass transitions for metallic glasses in liquid and supercooled liquid states
Intermetallics **18** (2010) 406–411.

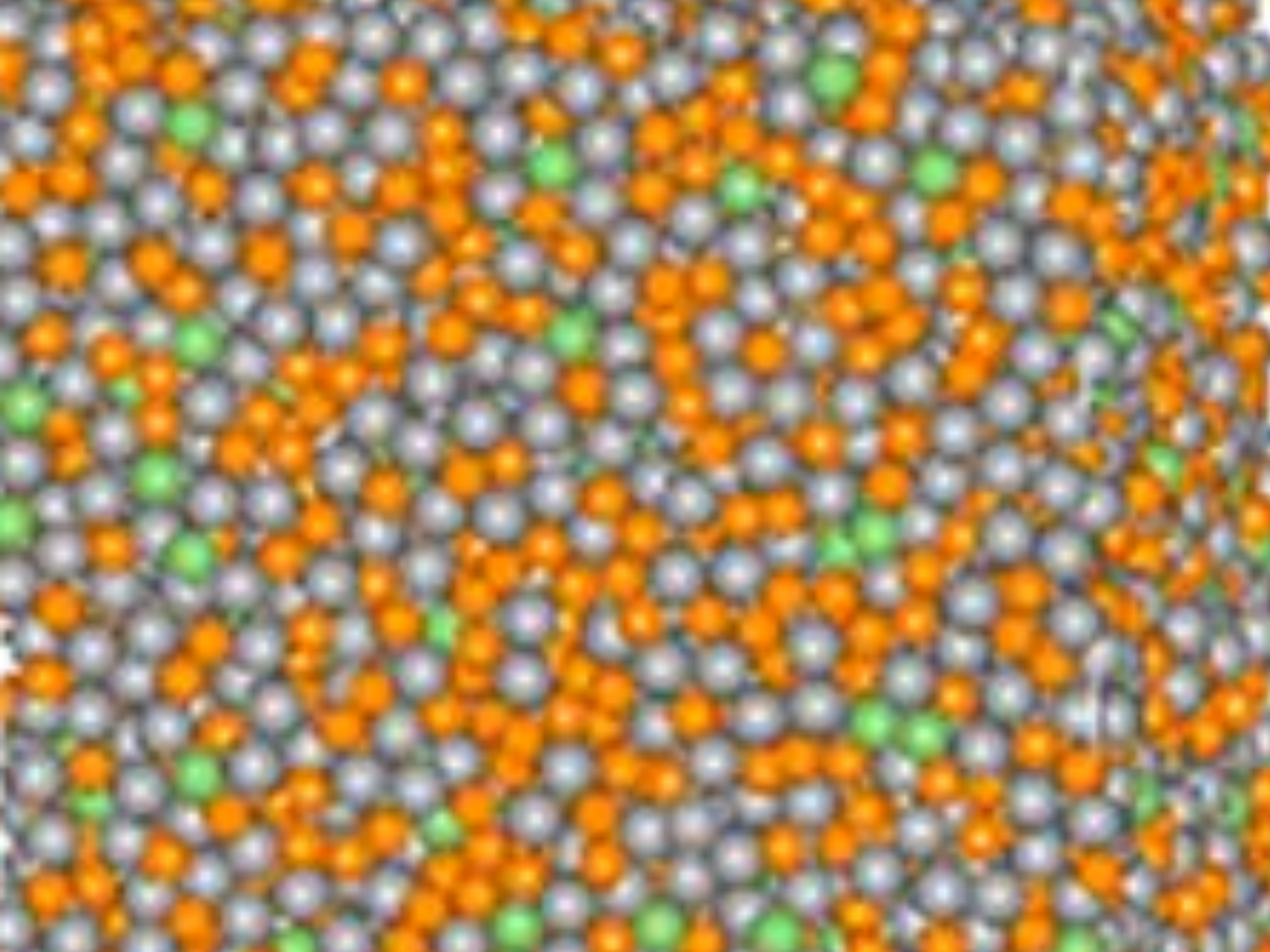


CA Angell: *Science* **267** (1995) 1924.





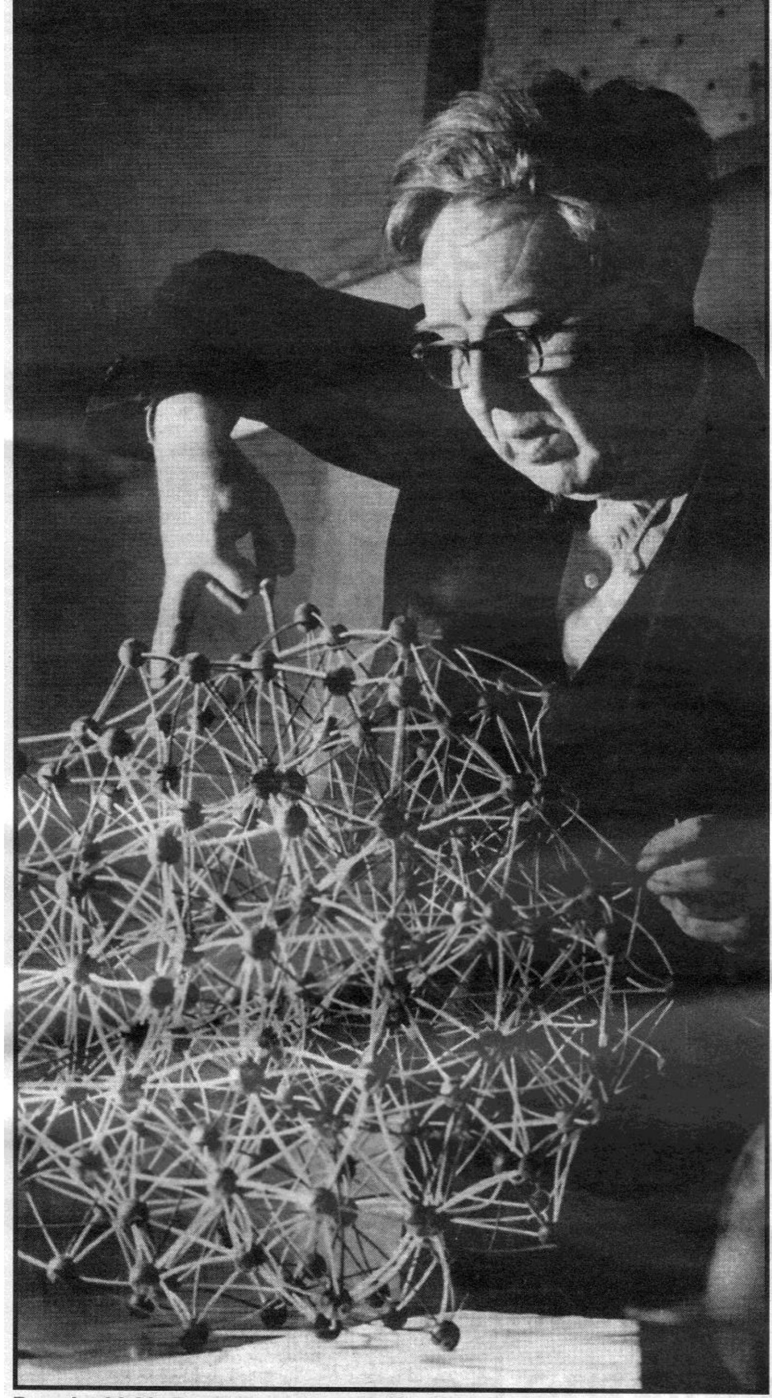
AL Greer: *Metallic glasses*
Chapter 4 in *Physical Metallurgy*, 5th edition (eds DE Laughlin & K Hono), Elsevier, Oxford (2014), Vol. 1, pp. 305–385.



John Desmond Bernal
1901-1971

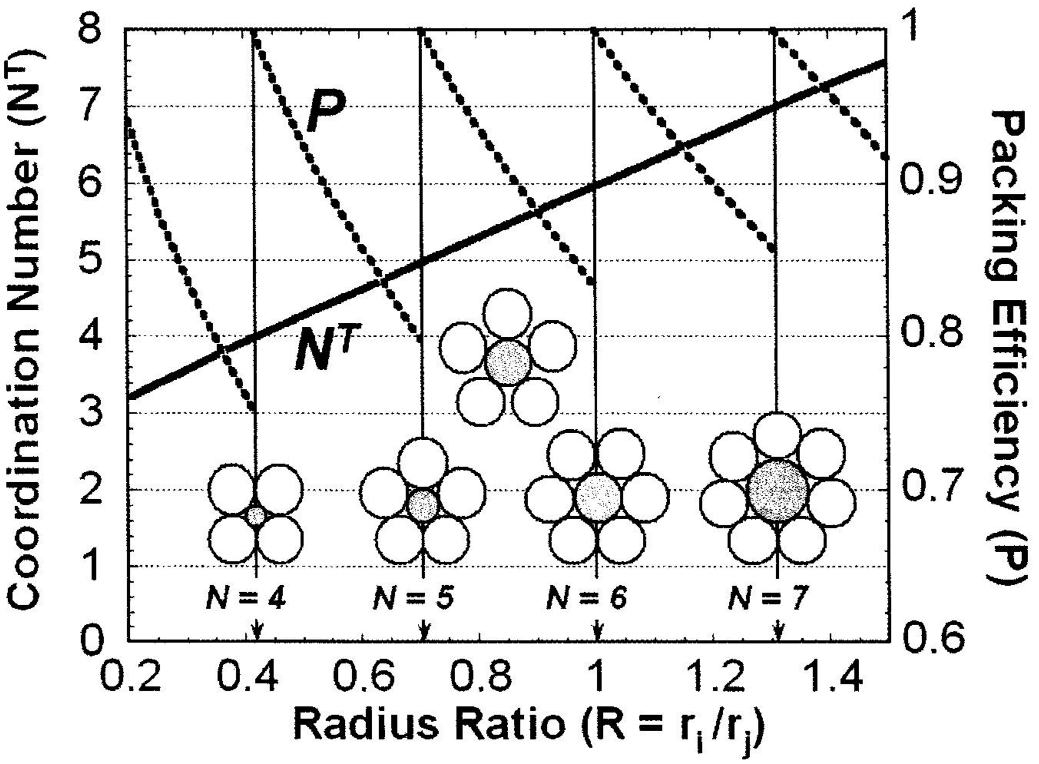
The **dense random packing** model for the structure of liquids.

from *The Times Higher Education Suppl*. 3 Feb. 2006

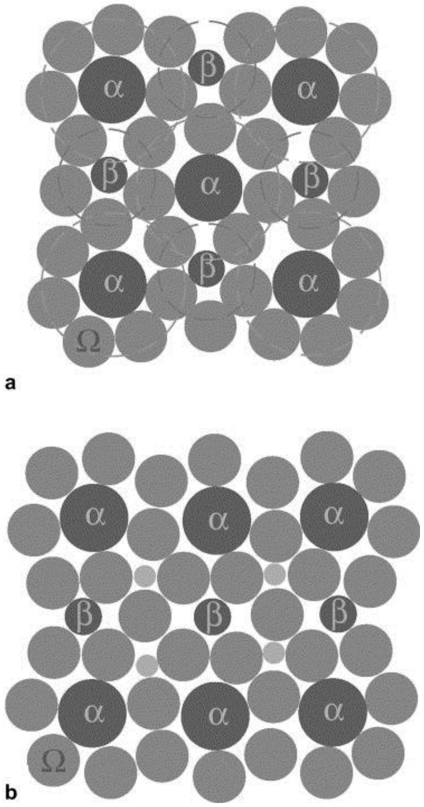


Bernal: with his first ball-and-spoke model of liquid structure

Close packing of discs in 2D —



DB Miracle, WS Sanders & ON Senkov, *Philos. Mag.* **83** (2003) 2409.

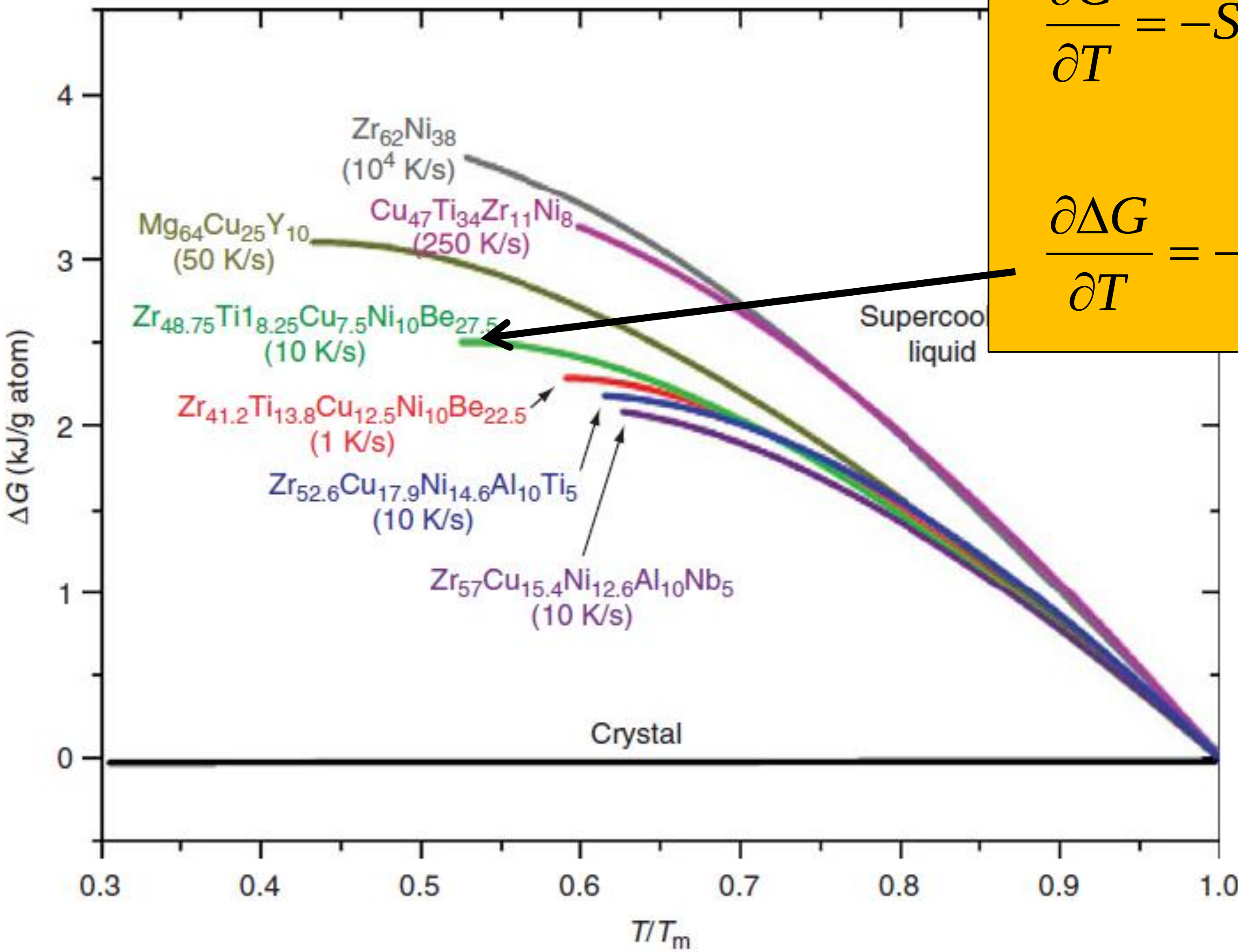


Interpenetrating clusters in the efficient cluster packing model of Miracle et al.

DB Miracle, *Acta Mater*. **54** (2006) 4317.

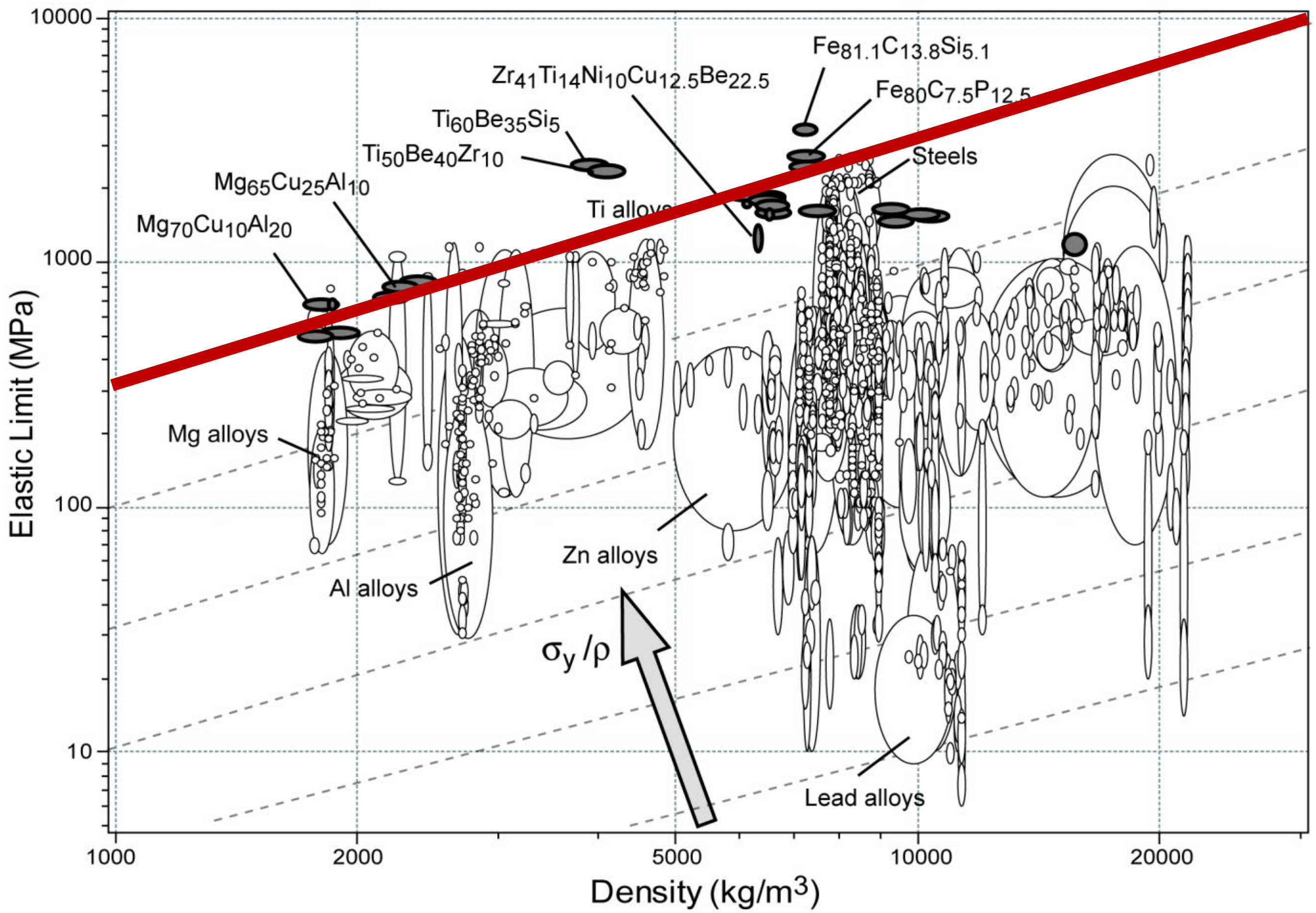
$$\frac{\partial G}{\partial T} = -S$$

$$\frac{\partial \Delta G}{\partial T} = -\Delta S \approx 0$$



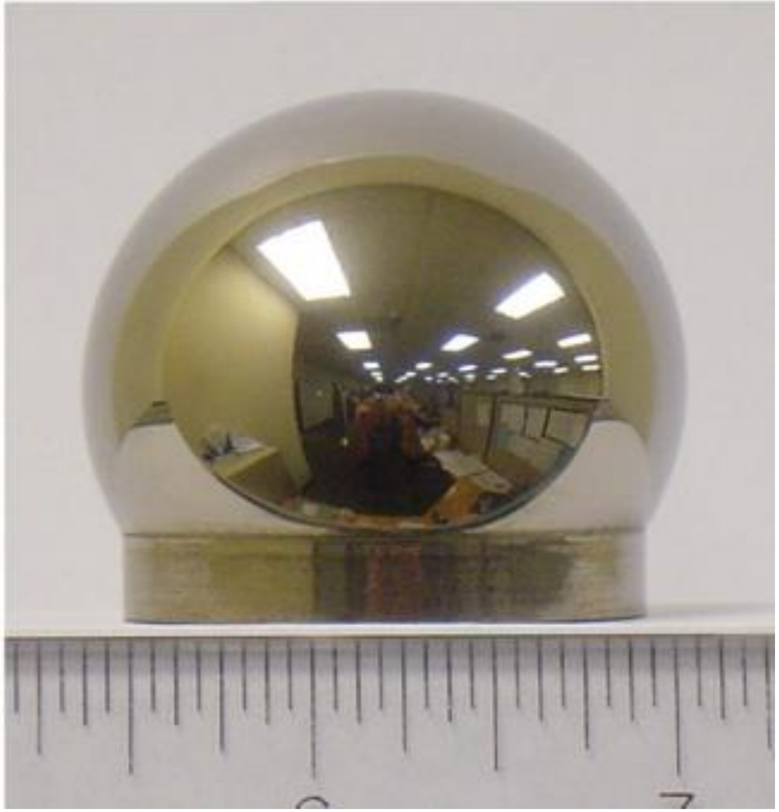
R Busch, J Schroers & WH Wang
Thermodynamics and kinetics of bulk metallic glass
MRS Bulletin **32** (2007) 620–623.

Metallic glasses for structural applications



Elastic limit σ_y plotted against **density** ρ for 1507 metals, alloys, metal-matrix composites and metallic glasses. The contours show the **specific strength** σ_y/ρ.

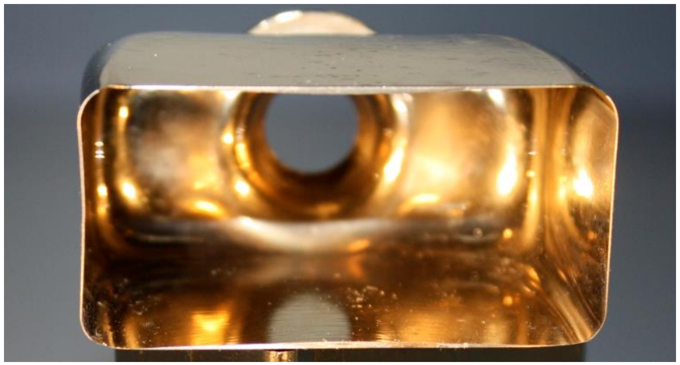
MF Ashby & AL Greer: *Scripta Materialia* **54** (2006) 321.
(in Viewpoint Set on *Mechanical Behavior of Metallic Glasses*, edited by TC Hufnagel)

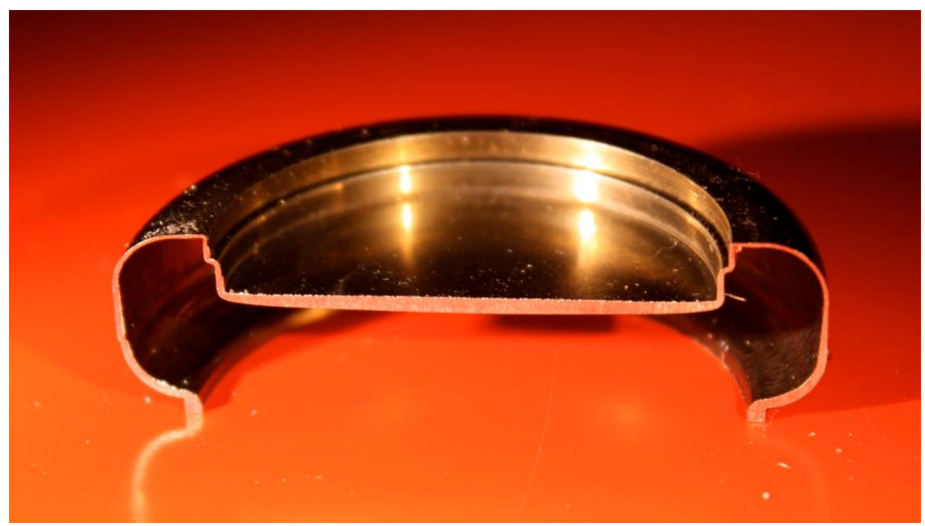


J Schroers *et al*., *Scripta Mater*. 57 (2007) 341.

Unachievable shapes for metals?

Hollow, thin, seamless, complex parts —





[courtesy: Jan Schroers, Yale]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CHANEL
PARIS
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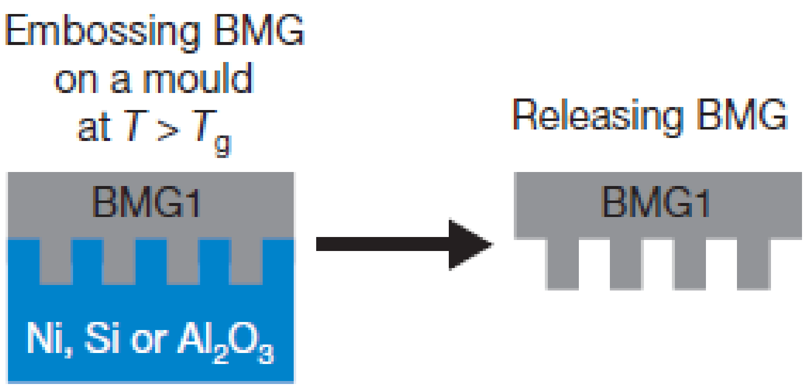
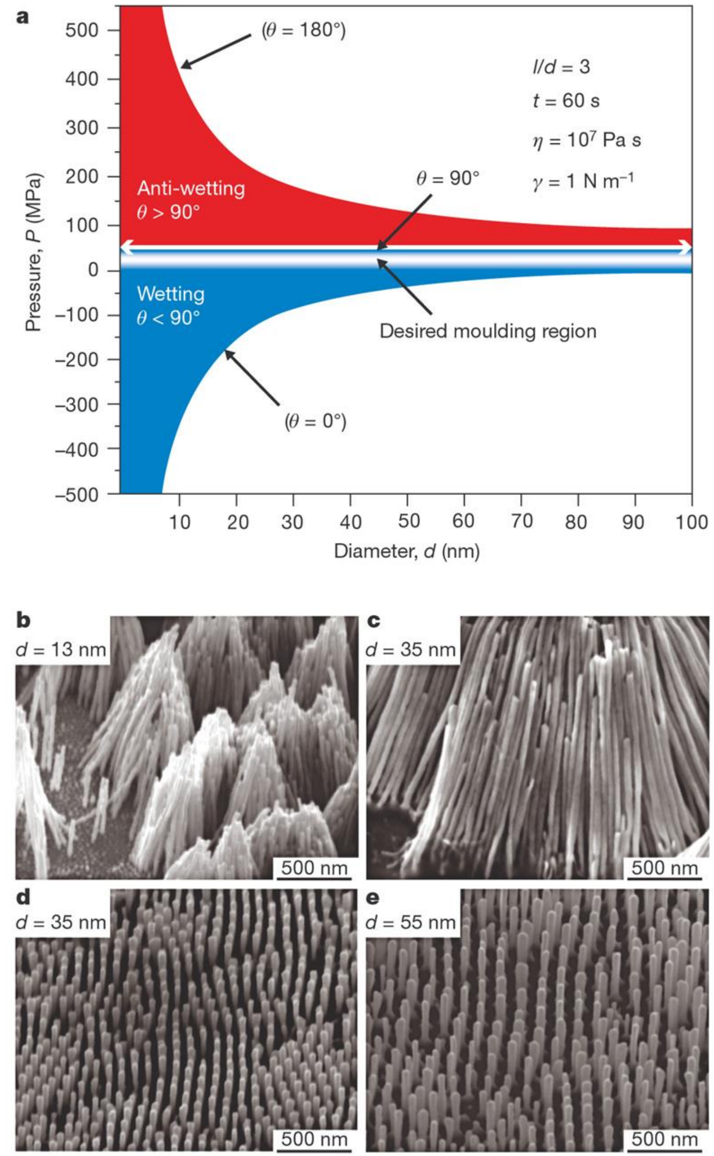
Nanomoulding with amorphous metals

Controlling metallic glass moulding on scales smaller than 100 nm

Pt-based BMG

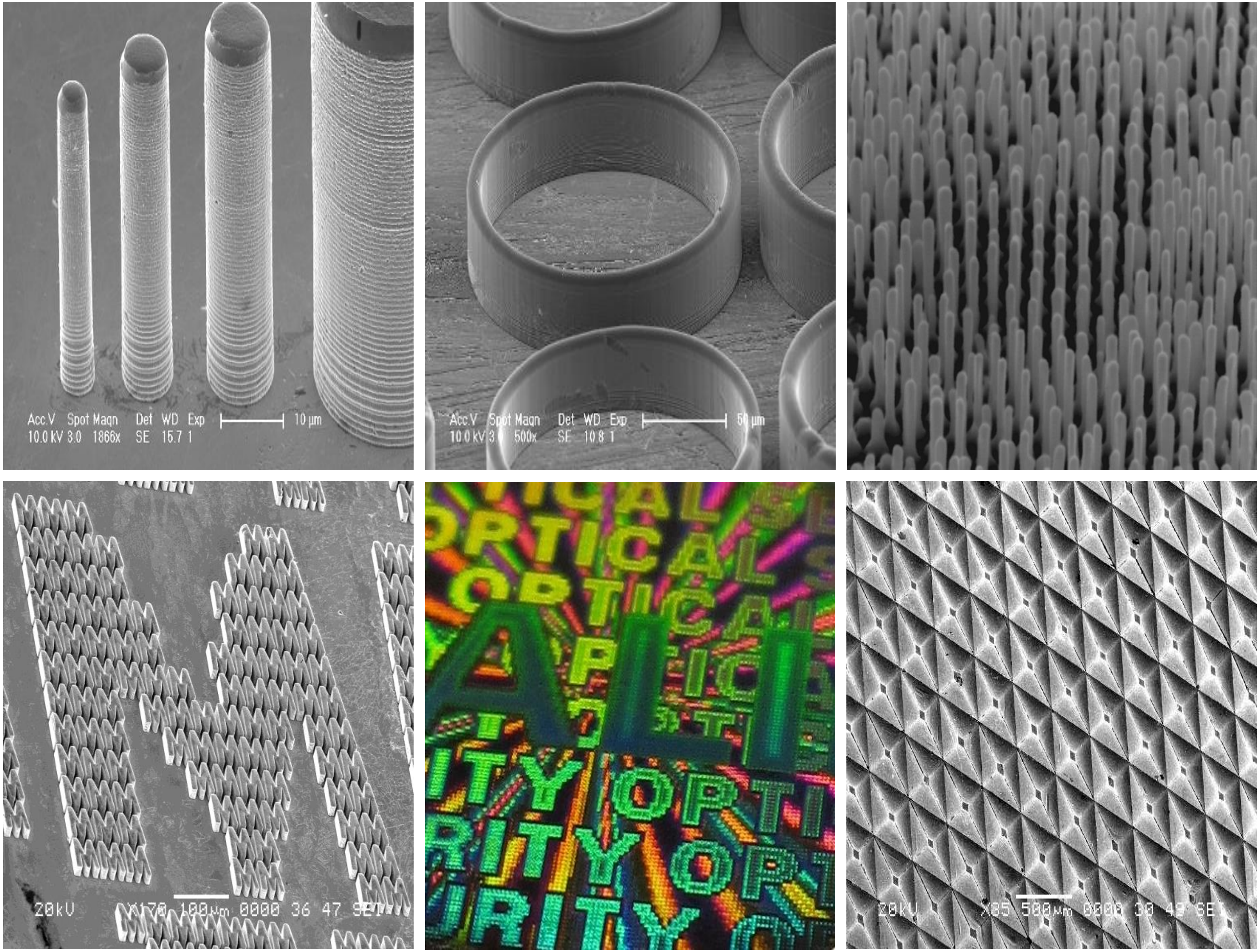




G Kumar, HX Tang & J. Schroers, *Nature* **457**, 868-872 (2009)

nature

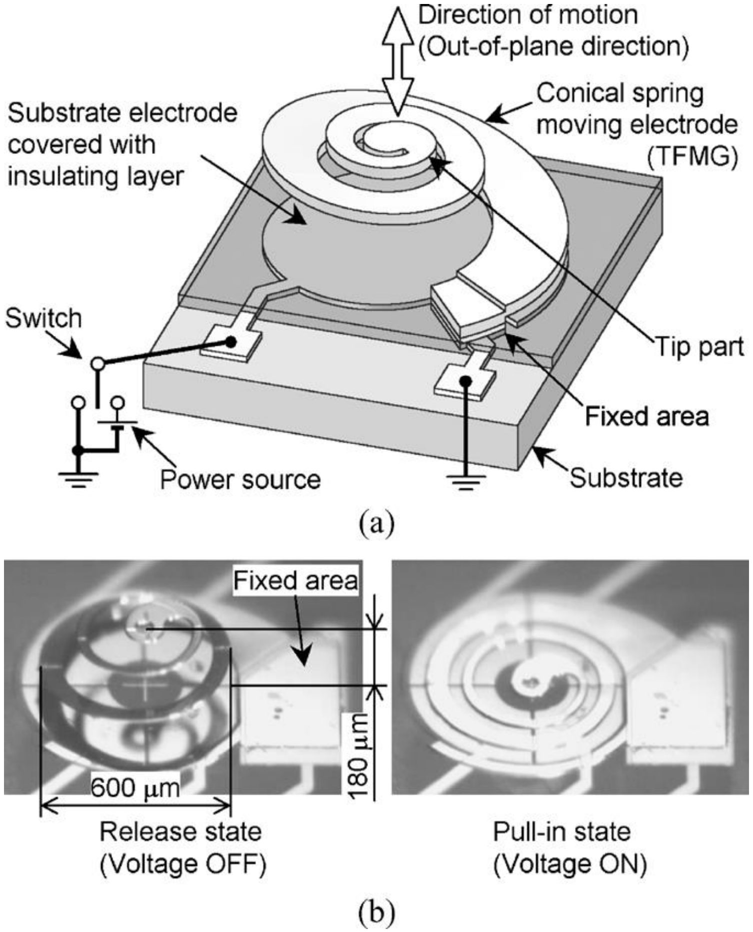
Surface Replication with BMGs



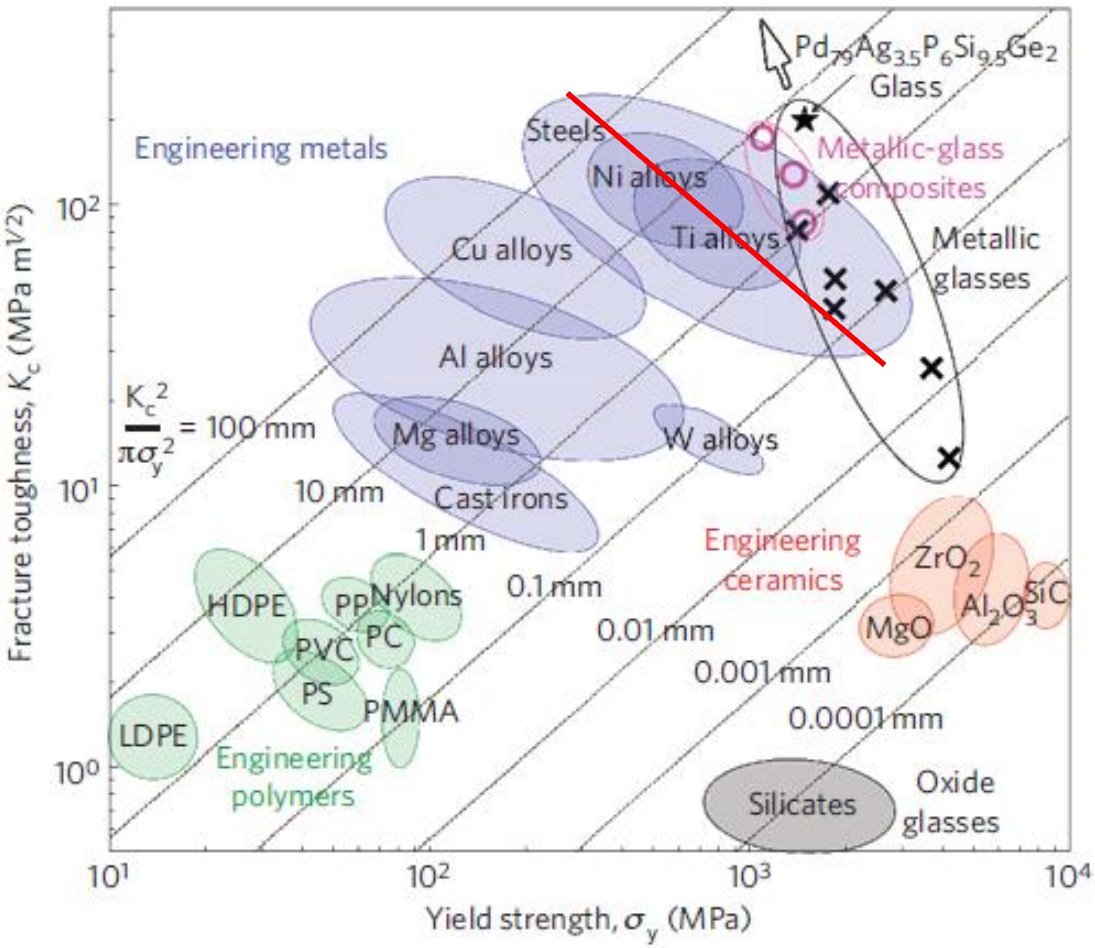
J. Schroers, *Advanced Materials*, **21** (2010)

MEMS Applications

A conical spring microactuator with a long stroke of 200 μm normal to the substrate. The spring is a 7.6 μm thick film of $Pd_{76}Cu_7Si_{17}$ metallic glass.

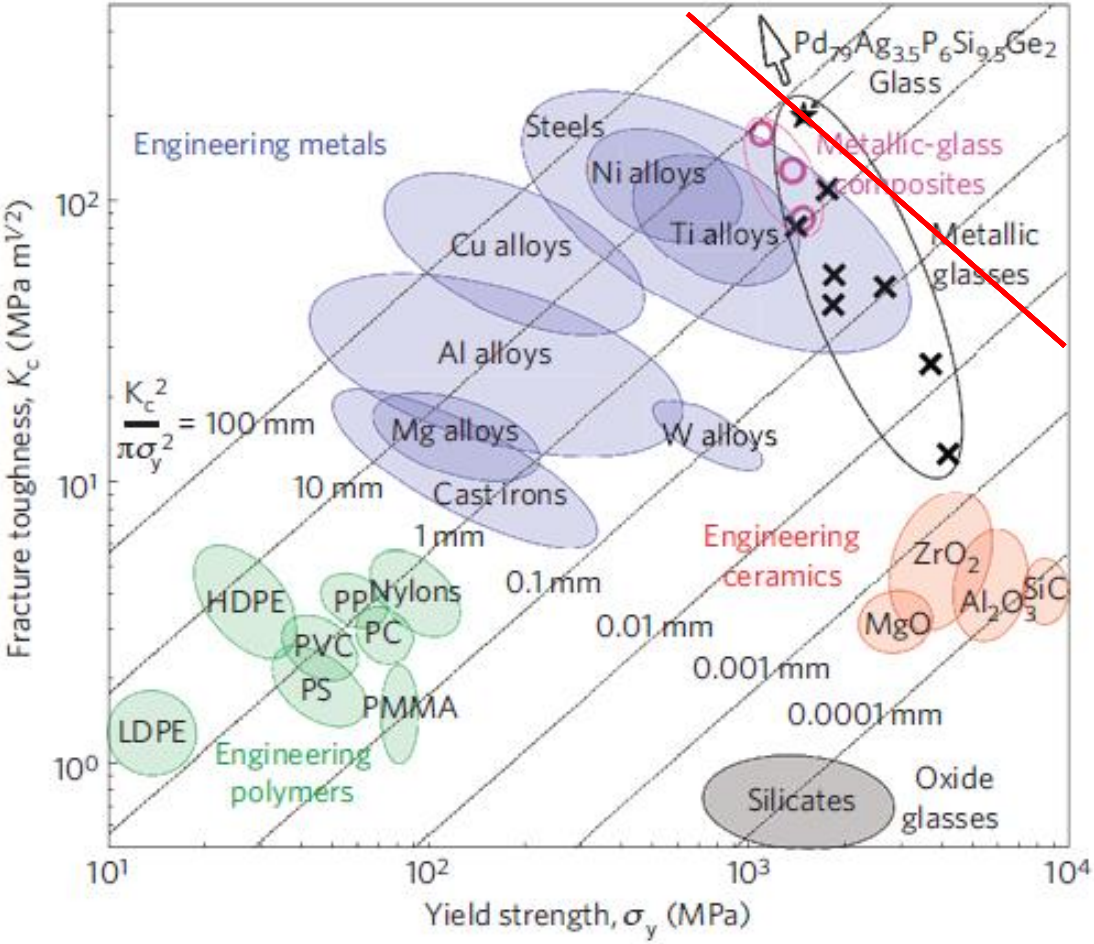


T Fukushige, S Hata & A Shimokohbe, *J. Microelectro. Syst*. **14** (2005) 243.



typical trade-off between σ_y and K_c

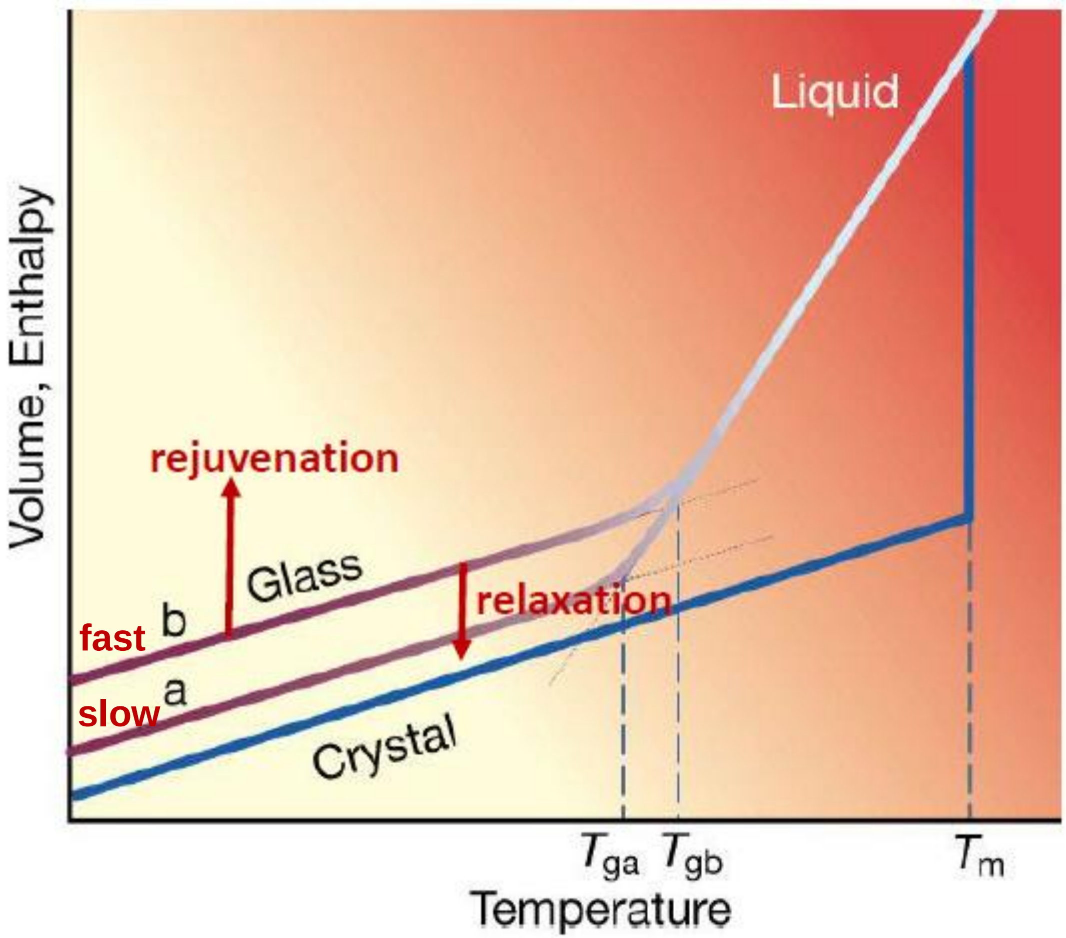
MD Demetriou et al., A damage-tolerant glass, *Nature Mater*. **10** (2011) 123–128.
AL Greer, Damage tolerance at a price, *Nature Mater*. **10** (2011) 88–89.



highest known product of σ_y and K_c

‘damage tolerance’

- The liquid → glass transition is kinetic
- Therefore there is a range of glassy states depending on cooling rate



Conventionally:

- relaxation (to states of lower energy) – achieved by annealing
- rejuvenation (to states of higher energy – achieved by reheating to liquid

- can a wider range of states be accessed by thermomechanical processing?
- will focus on metallic glasses

nature materials

ARTICLES

PUBLISHED ONLINE: 6 JANUARY 2013 | DOI: 10.1038/NMAT3521

Ultrastable glasses from *in silico* vapour deposition

Sadanand Singh[1], M. D. Ediger[2] and Juan J. de Pablo[1,3,4]*

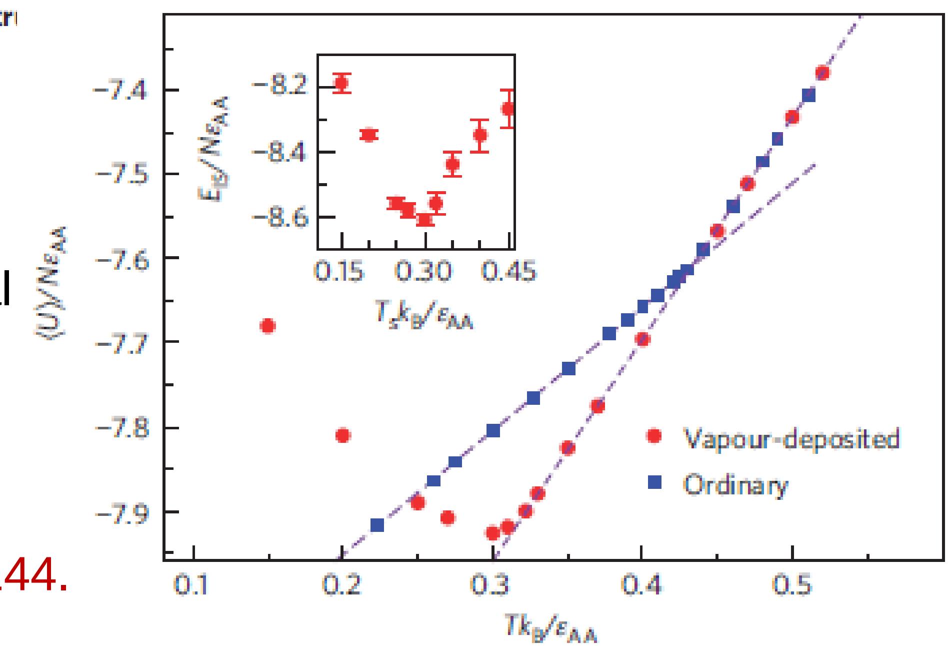
Glasses are generally prepared by cooling from the liquid phase, and their properties depend on their thermal history. Recent experiments indicate that glasses prepared by vapour deposition onto a substrate can exhibit remarkable stability, and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. Here we create ultrastable glasses by means of a computer-simulation process that mimics physical vapour deposition. These stable glasses have, far below the conventional glass-transition temperature, the properties expected for the equilibrium supercooled liquid state, and optimal stability is attained when deposition occurs at the Kauzmann temperature. We also show that the glasses' extraordinary stability is associated with distinct str

and the relative lack of irregular polyhedra.

binary mixture of LJ particles

potential energy

minimum energy at ~0.85 T_g



Nature Mater. **12** (2013) 139–144.

Why expand the range of the glassy state? (in metals)

Relaxation, ultimately to ultrastable states, offers the prospect of:

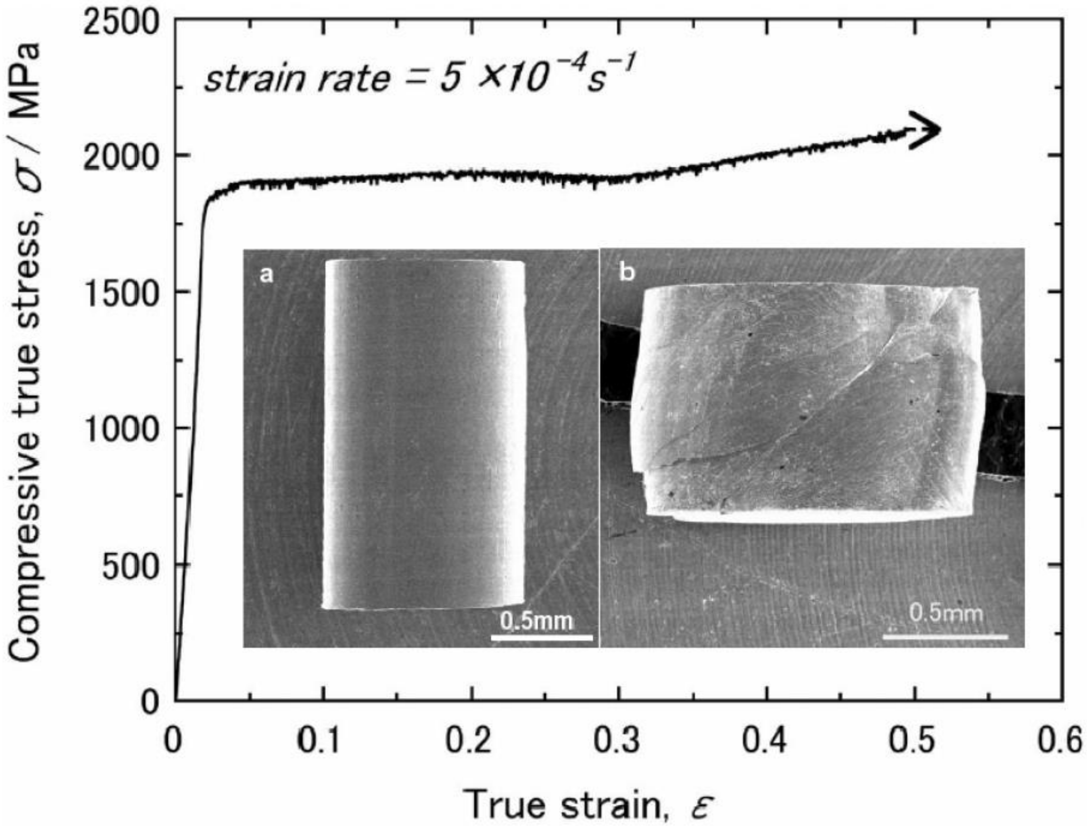
- great resistance to crystallization
- ultra-high hardness, scratch resistance
- creep resistance
- altered glass-transition behaviour (analogous to melting)

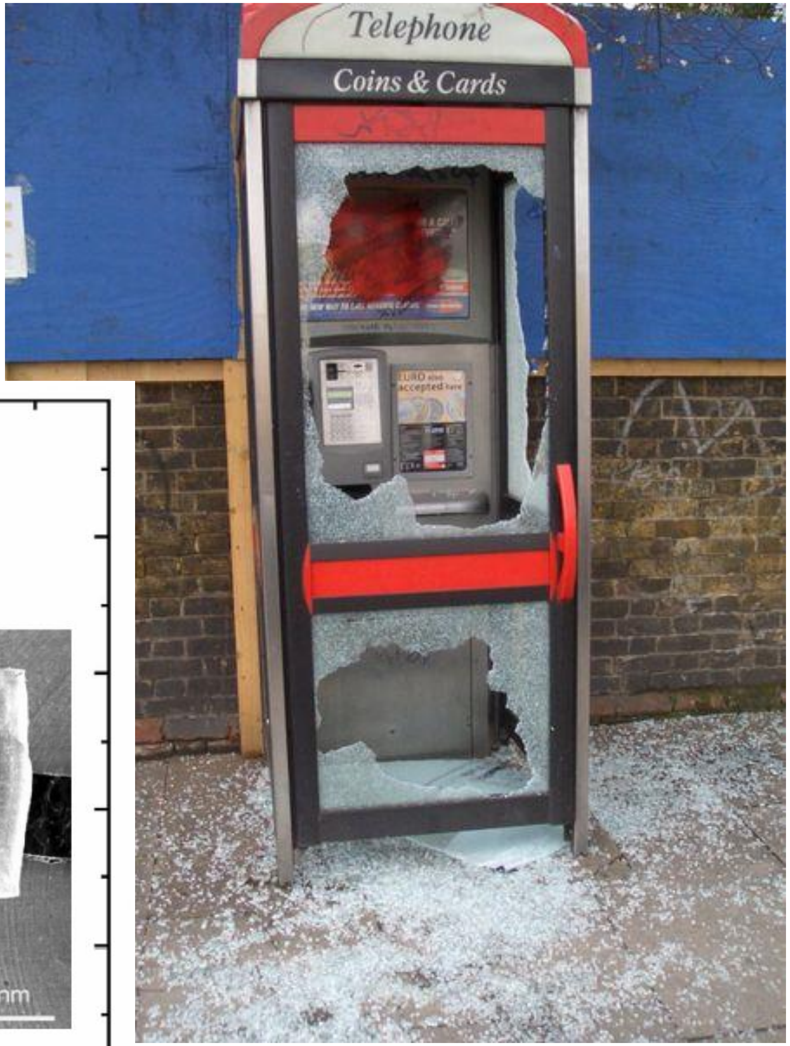
Rejuvenation, to highly unstable states, offers the prospect of:

- fast crystallization
- greater plasticity
- perhaps even tensile ductility

Conventional glasses are **brittle** —

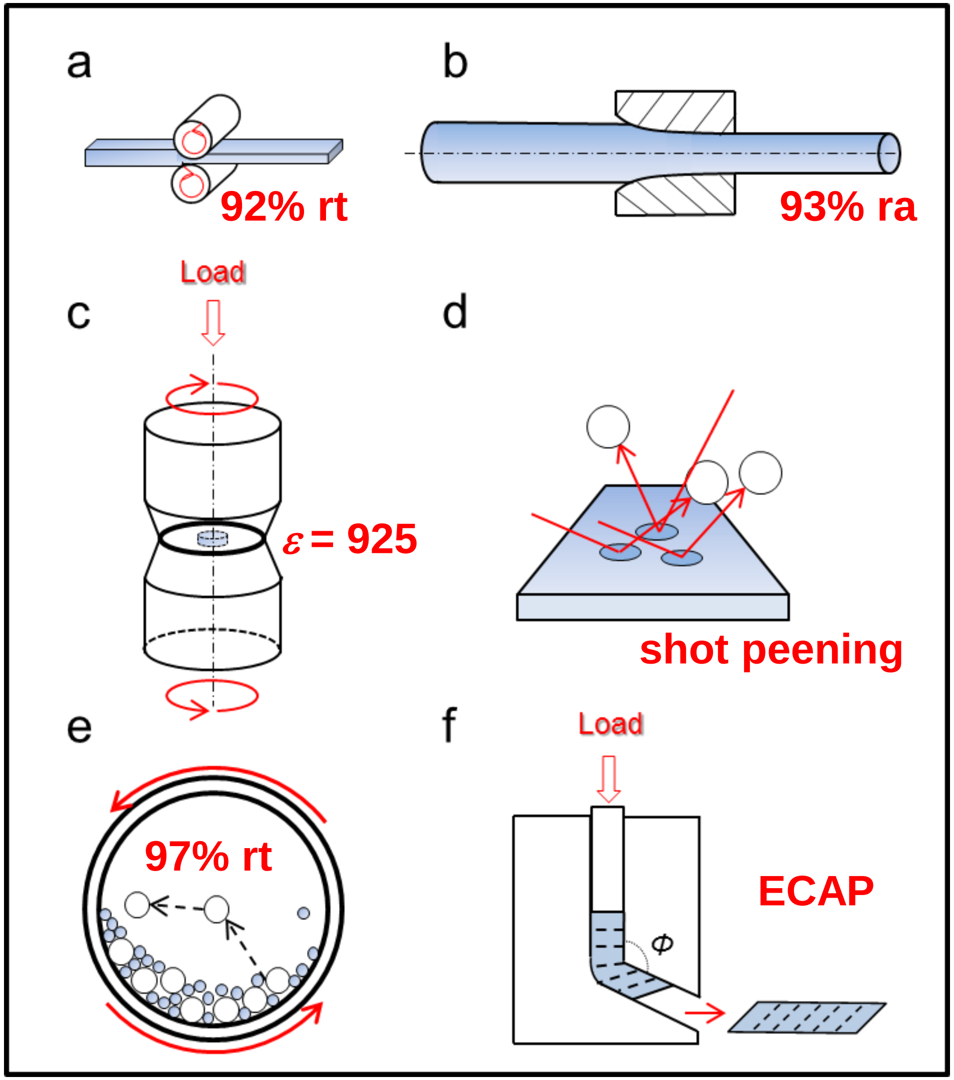
— but metallic glasses can show **considerable plasticity**:





Methods of cold work applied to metallic glasses:

Very high plastic strains have been achieved —



YH Sun, A Concustell & AL Greer: Thermomechanical processing of metallic glasses: extending the range of the glassy state, *Nature Reviews Mater.* **1** (2016) 16039.

Cold-rolling

Stored energy of cold work

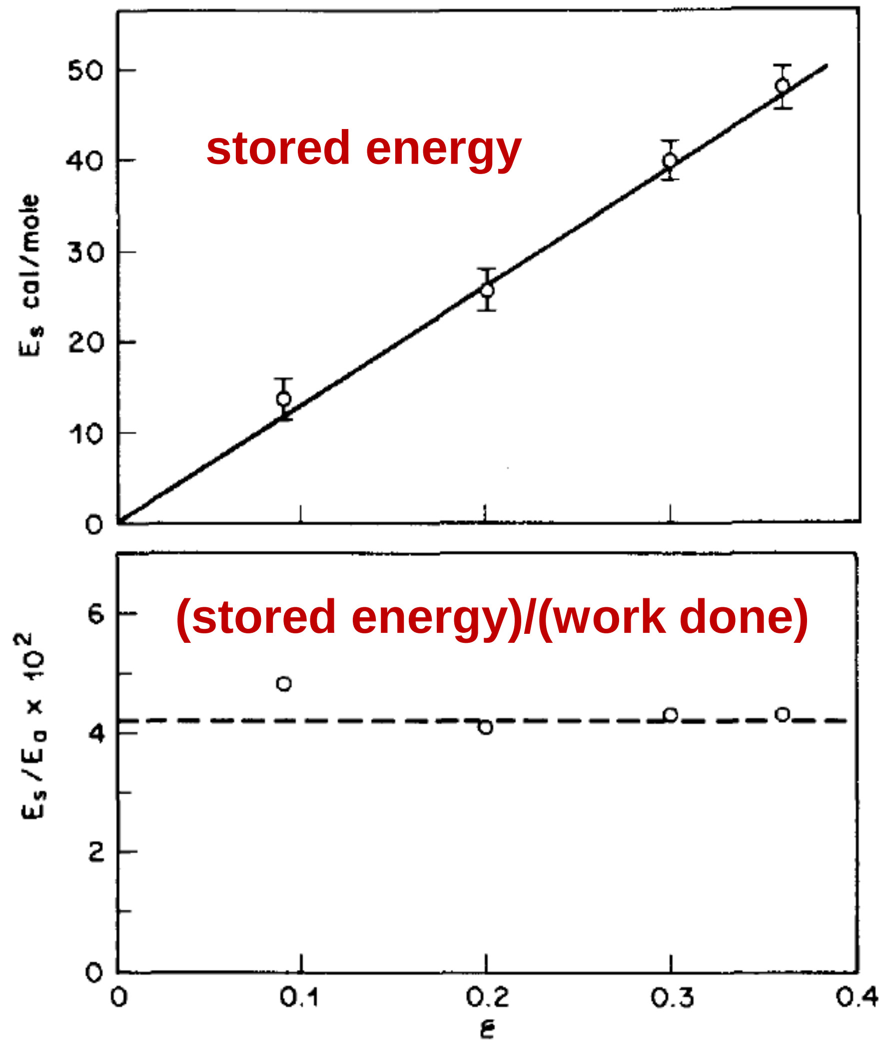
Melt-spun ribbons of glassy $Pd_{77.5}Cu_6Si_{16.5}$

annealed by heating to T_g and then cooling at 20 K min^{-1}

then cold-rolled

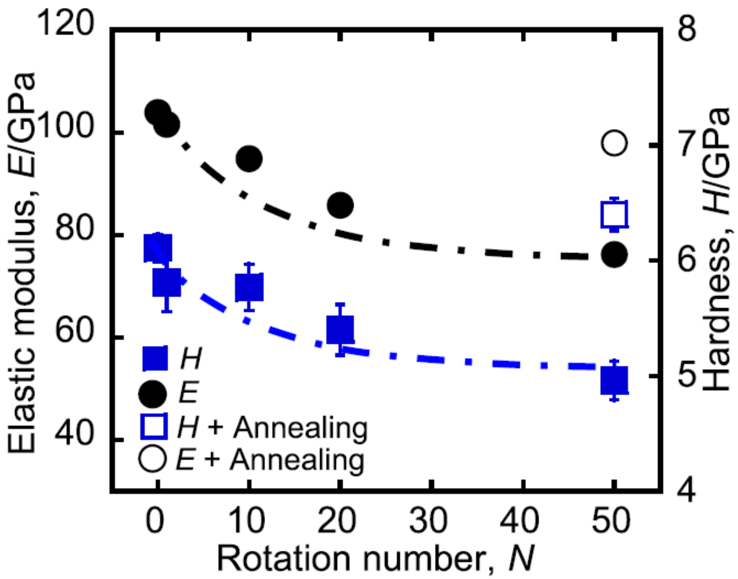
the stored energy is ~4% of the work done

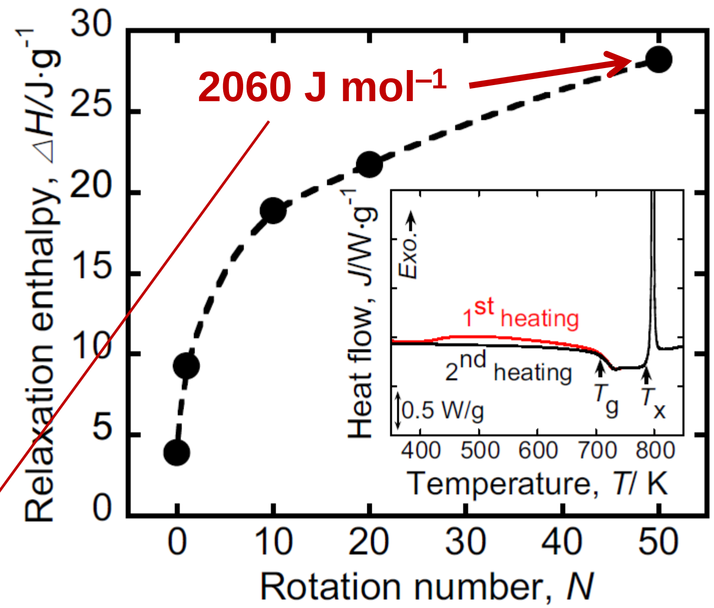
-- has a maximum value of 1000 J mol^{-1}



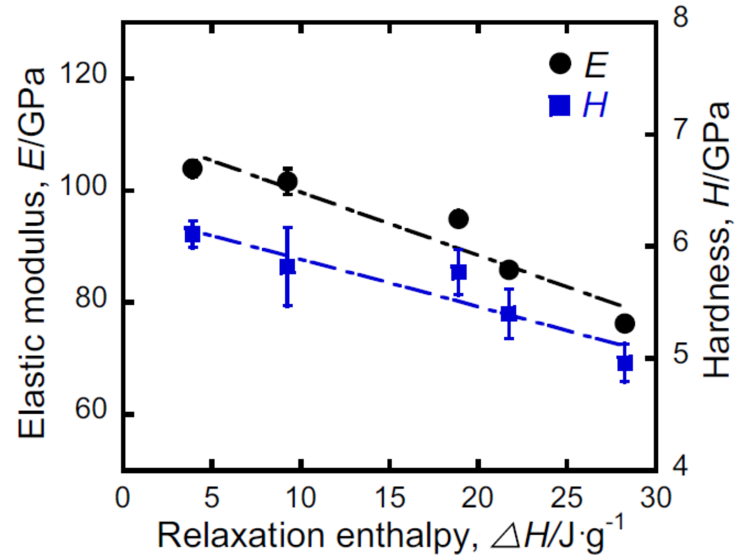
HS Chen: Stored energy in a cold-rolled metallic glass, *Appl. Phys. Lett*. **29** (1976) 328–330.

High-pressure torsion of $Zr_{50}Cu_{40}Al_{10}$ MG





this is ~24% of ΔH_{melt}

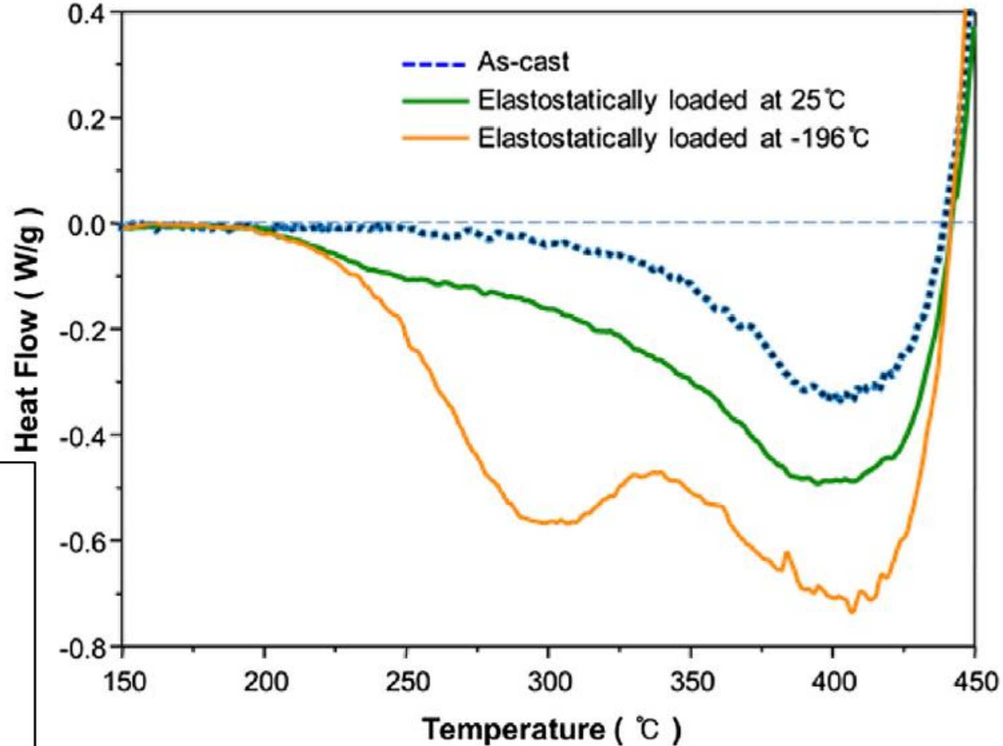


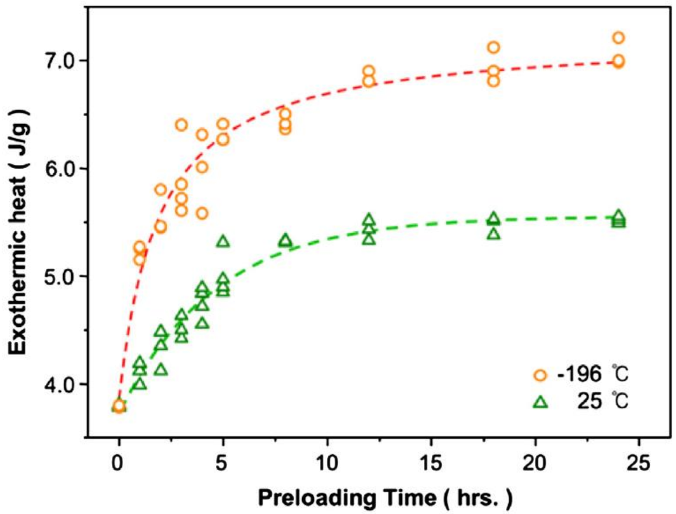
F Meng, K Tsuchiya, S Il & Y Yokoyama: Reversible transition of deformation mode by structural rejuvenation and relaxation in bulk metallic glass, *Appl. Phys. Lett.* **101** (2012) 121914.

Elastostatic loading of $Cu_{57}Zr_{43}$ at 85% of T_g for 24 h

Stored energy:

415 J mol^{-1} at RT
530 J mol^{-1} at 77 K





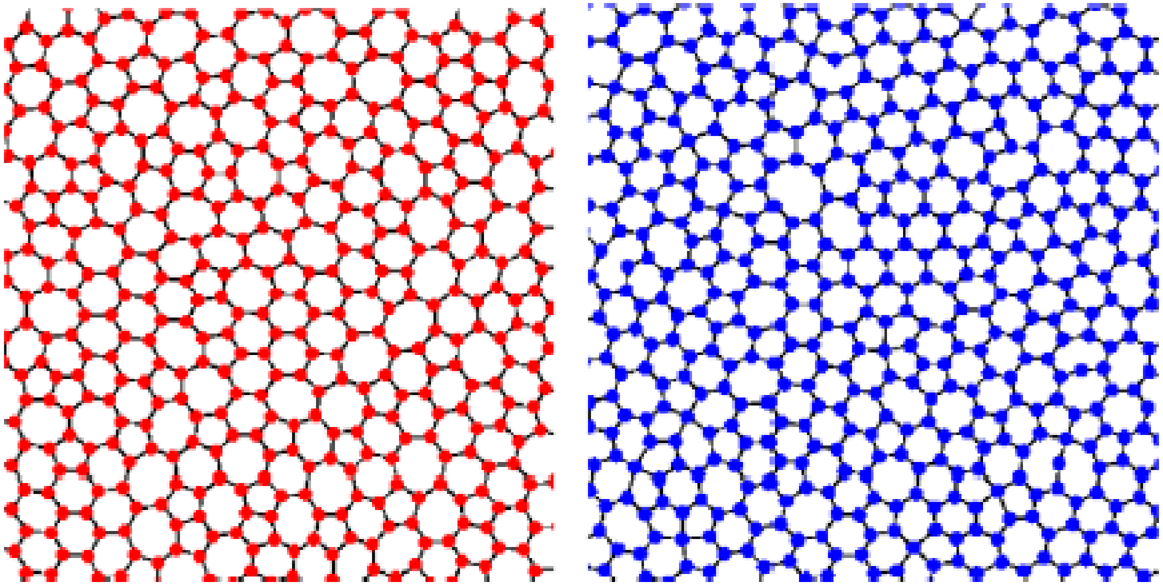
J-C Lee: Calorimetric study of β-relaxation in an amorphous alloy: An experimental technique for measuring the activation energy for shear transformation, *Intermetallics* **44** (2014) 116–120.

	Glass composition (at.%)	Stress (GPa)	$\frac{\text{Stress}}{\sigma_y}$	Time (h)	Temp.	ΔH_{rel} (J g-atom^{-1})	WD (J g-atom^{-1})	$\frac{\Delta H_{rel}}{\text{WD}}$
1	$Cu_{65}Zr_{35}$	2.07	0.90	12	RT	133	52.1	2.55
2	$Cu_{65}Zr_{35}$	2.07	0.90	24	RT	194	34.25	5.66
3	$Ni_{62}Nb_{38}$	3.0	0.95	30	RT	179	95.9	1.87
4	$Cu_{50}Zr_{50}$	1.44	0.90	24	RT	49.5	6.68	7.41
5	$Cu_{65}Zr_{35}$	1.44	0.63	24	RT	116	6.24	18.6
6	$Cu_{50}Zr_{50}$	1.44	0.90	12	RT	43.3	5.77	7.50
7	$Cu_{57}Zr_{43}$	1.80	0.90	12	RT	127	20.19	6.28
8	$Cu_{65}Zr_{35}$	2.07	0.90	12	RT	174	35.41	4.92
9	$Cu_{57}Zr_{43}$	1.7	0.85	24	RT	132	—	—
10	$Cu_{57}Zr_{43}$	1.7	0.85	24	77 K	247	—	—

The extra energy stored in BMG samples as a result of elastostatic loading exceeds the mechanical work done on them!

— the loading must induce an **endothermic disordering** process that draws heat from the surroundings.

AL Greer & YH Sun: Stored energy in metallic glasses due to strains within the elastic limit, *Philos. Mag*. **96** (2016) 1643–1663.



In a glass:

- if **elastic** strains in a glass are non-affine, then
- then **thermal** strains should be non-affine also

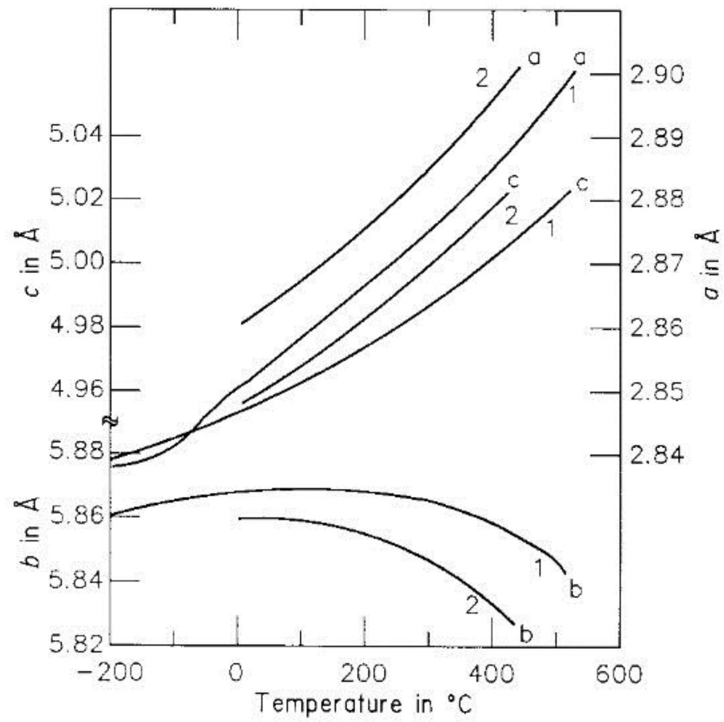
Thermal-cycling growth of uranium metal

Uranium has three crystalline polymorphs:

$$\alpha \xrightarrow{669^\circ C} \beta \xrightarrow{772^\circ C} \gamma \xrightarrow{1132^\circ C} \text{liquid}$$

Single-crystal α-U is strongly *anisotropic*.

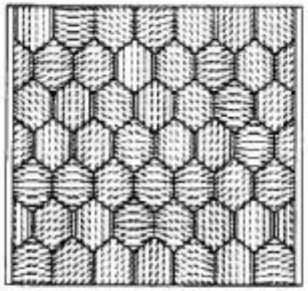
Temperature dependence of the lattice parameters of: (1) α-U; (2) α-U-15 at.% Pu.

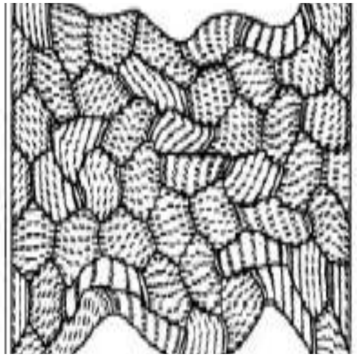


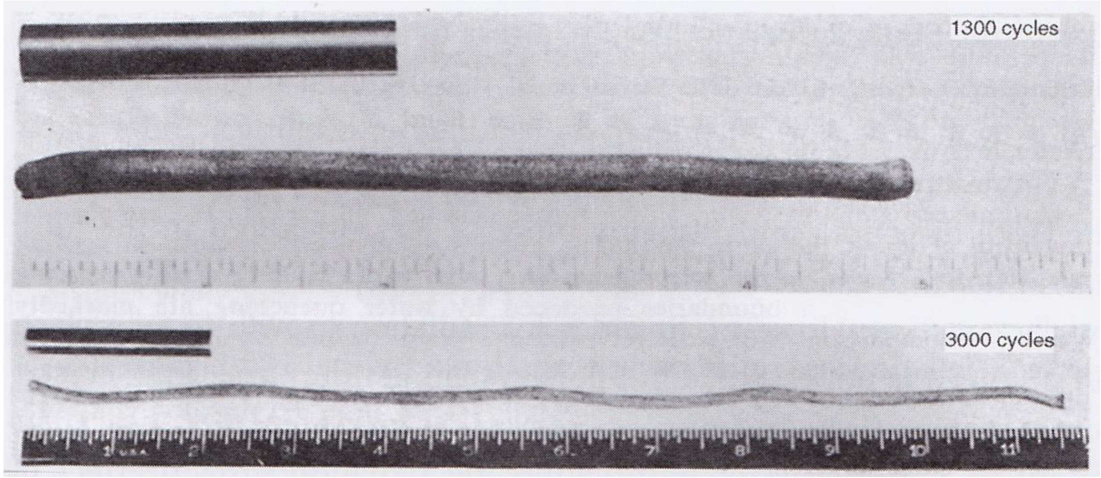
- α is orthorhombic:
  (at RT: a = 2.852 Å, b = 5.865 Å, c = 4.945 Å)
- β is tetragonal:
  (at 720°C: a = 10.790 Å, c = 5.656 Å)
- γ is cubic (bcc):
  (at 850°C: a = 3.538 Å)

BRT Frost (ed.), *Nuclear Materials* (Vols 10A & 10B, *Materials Science & Technology*), VCH (1994)
BM Ma, *Nuclear Reactor Materials and Applications*, Van Nostrand (1983)

Thermal-cycling growth of uranium fuel rods:



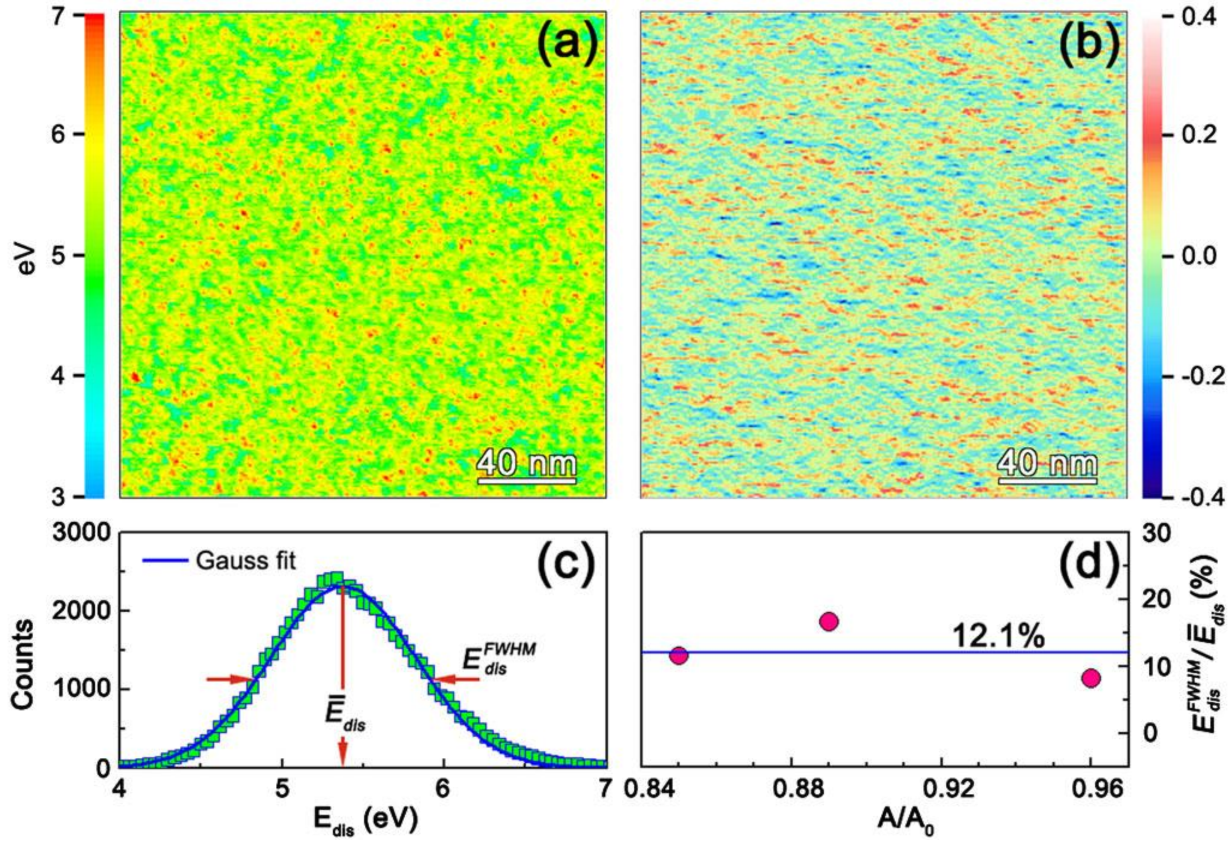




Effect of thermal cycling highly oriented fine-grained α-uranium between 50°C and 500°C.

KL Murty, I Charit: *An Introduction to Nuclear Materials*, Wiley (2013)

Mapping of heterogeneity in a MG



Energy-dissipation and height-difference maps for a sputter-deposited $Zr_{55}Cu_{30}Ni_5Al_{10}$ metallic glass

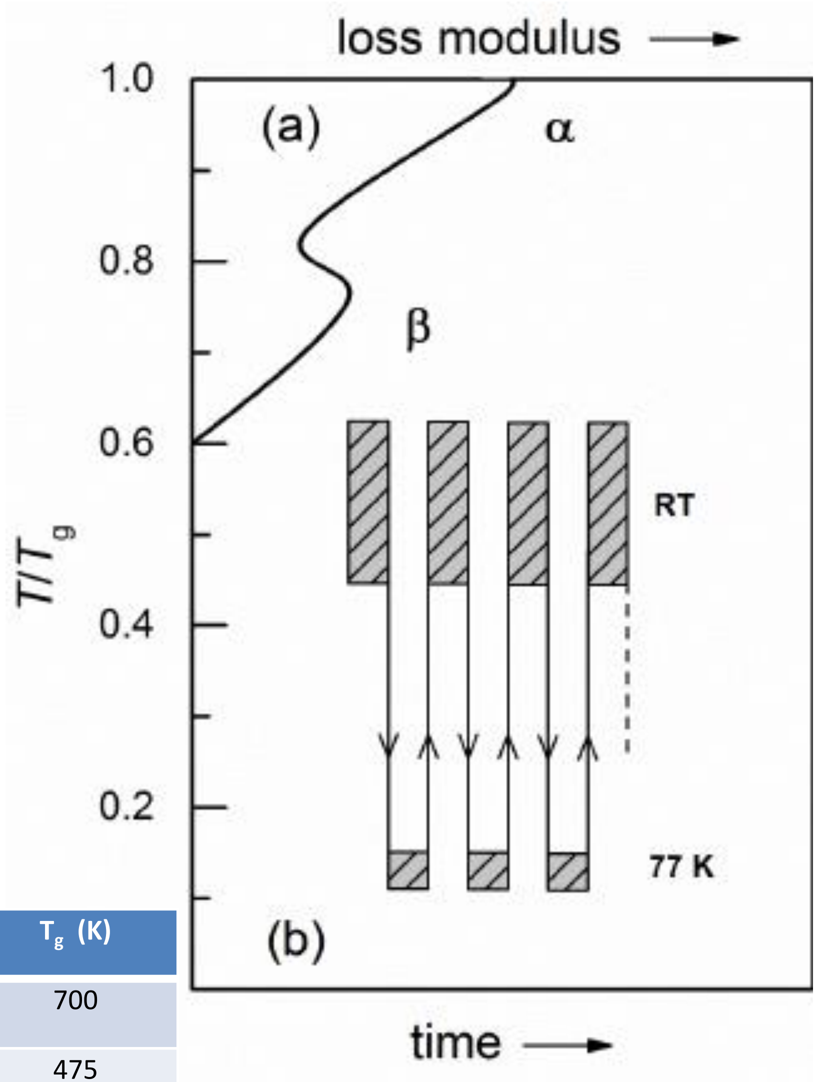
YH Liu, D Wang, K Nakajima, W Zhang, A Hirata, T Nishi, A Inoue & MW Chen: Characterization of nanoscale mechanical heterogeneity in a metallic glass by dynamic force microscopy, *Phys. Rev. Lett.* **106** (2011) 125504.

Thermal cycling of MGs

Metallic glass samples are cycled between room temperature (RT) (or ethanol at 60–70°C) and liquid nitrogen (77 K).

For different glasses, RT and 77 K are different fractions of T_g.

The cycling is below the temperature for thermal relaxation.



Composition (at.%)	Form	T_g (K)
$Cu_{46}Zr_{46}Al_7Gd_1$	rod, 3 μm diam.	700
$La_{55}Ni_{20}Al_{25}$	melt-spun ribbon, 40 μm thick	475
$La_{55}Ni_{10}Al_{35}$	rod, 3 mm diam.	474
$Zr_{62}Cu_{24}Fe_5Al_9$	rod, 1.5, 2.0, 2.5 mm diam.	658

SV Ketov et al., *Nature* **524** (2015) 200–203.

Enthalpies of Relaxation in Metallic Glasses

Increases observed as a result of mechanical treatments

	$J\ mol^{-1}$
heavily cold-rolled (50–60% red. thickn.)	200–250 (1.5–3% of ΔH_{melt})
Thermal cycling (10 cycles RT – 77 K)	340

Initial yield pressure, P_y

cumulative distributions for 40 to 50 indents

median value decreases:

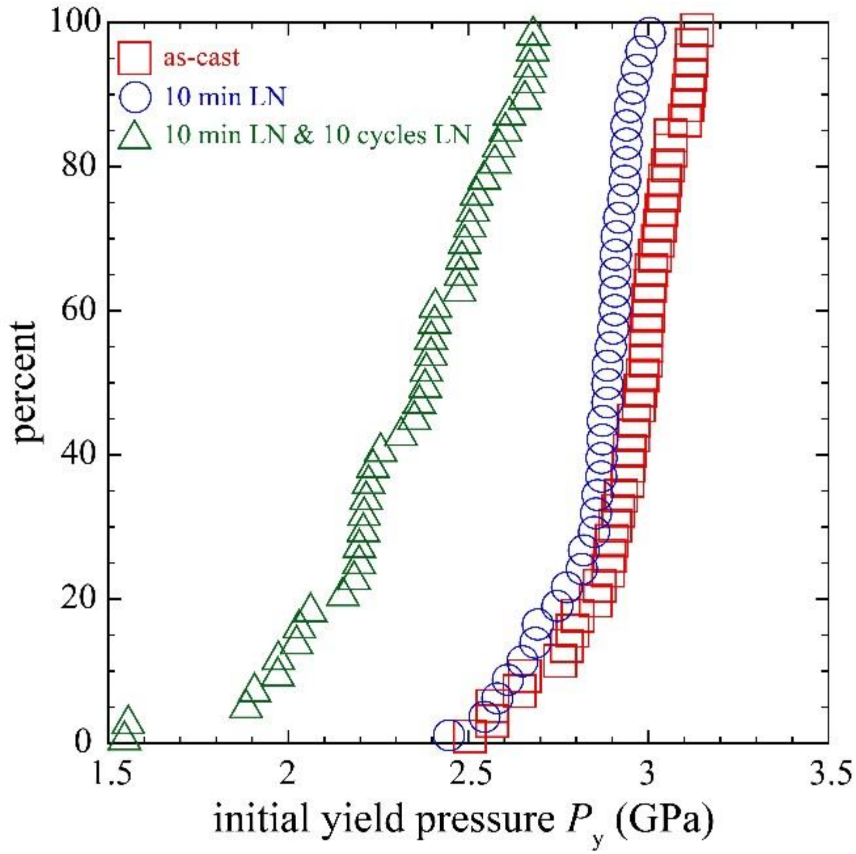
by **3%** after 10-min hold at 77 K

by further **17%** after ten 1-min holds

The width (1[st] to 9[th] decile) of the distribution is:

± 7% in the as-cast ribbon

± 15% after all cycles



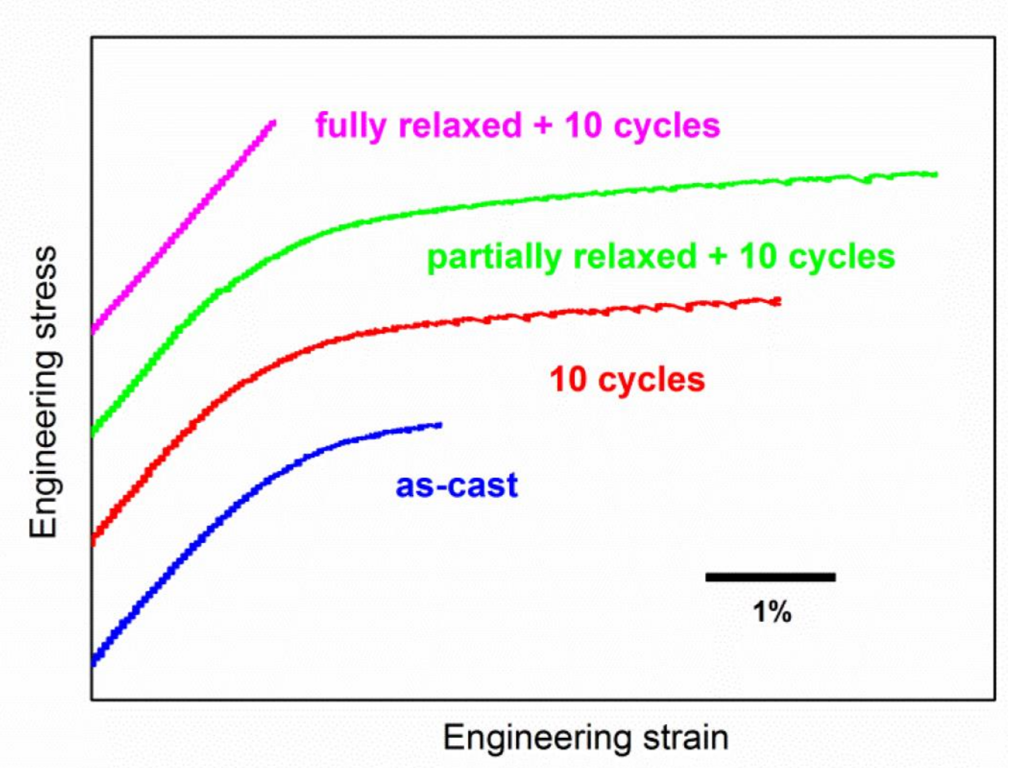
Nanoindentation of $La_{55}Ni_{20}Al_{25}$ glass ribbon

Thermal cycling softens and introduces greater heterogeneity

SV Ketov et al., *Nature* **524** (2015) 200–203.

Compression of bulk $Cu_{46}Zr_{46}Al_7Gd_1$

Cuboids, 3 mm high, 1.5×1.5 mm² cross-section, strain rate ≈ 10^{-4} s^{-1}

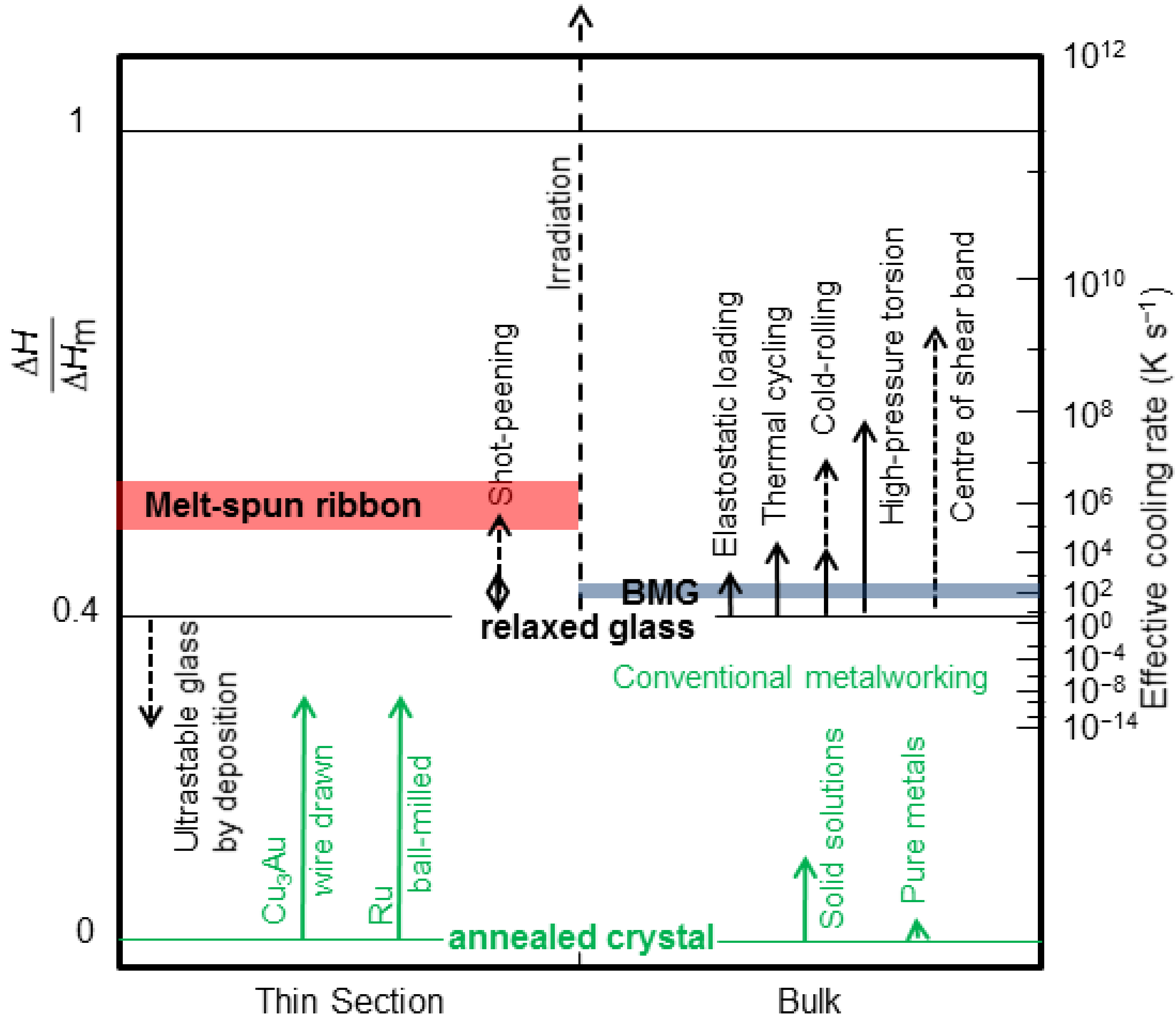


Comparison of as-cast, partially relaxed (1.0 hr at 400°C) and fully relaxed (1.5 hr at 400°C):

Plastic strain increases from 1.4% (as-cast) to 5.1% after 10 RT-77K cycles

Similar rejuvenation is possible after partial, but not full relaxation

SV Ketov et al., *Nature* **524** (2015) 200–203.



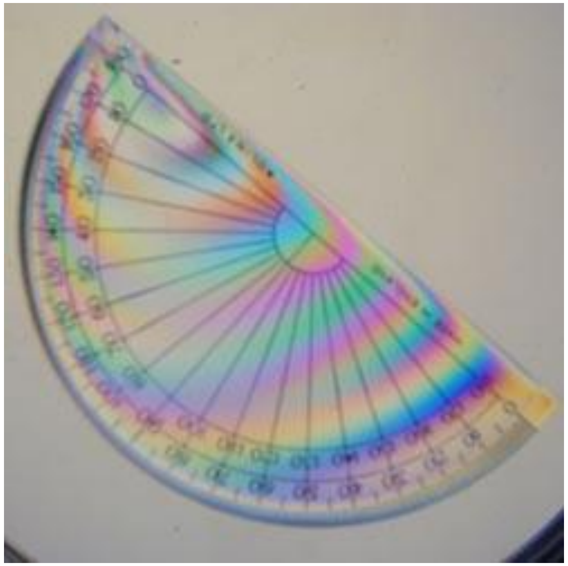
YH Sun, A Concustell & AL Greer: Thermomechanical processing of metallic glasses: extending the range of the glassy state, *Nature Reviews Mater.* **1** (2016) 16039.

Anisotropy

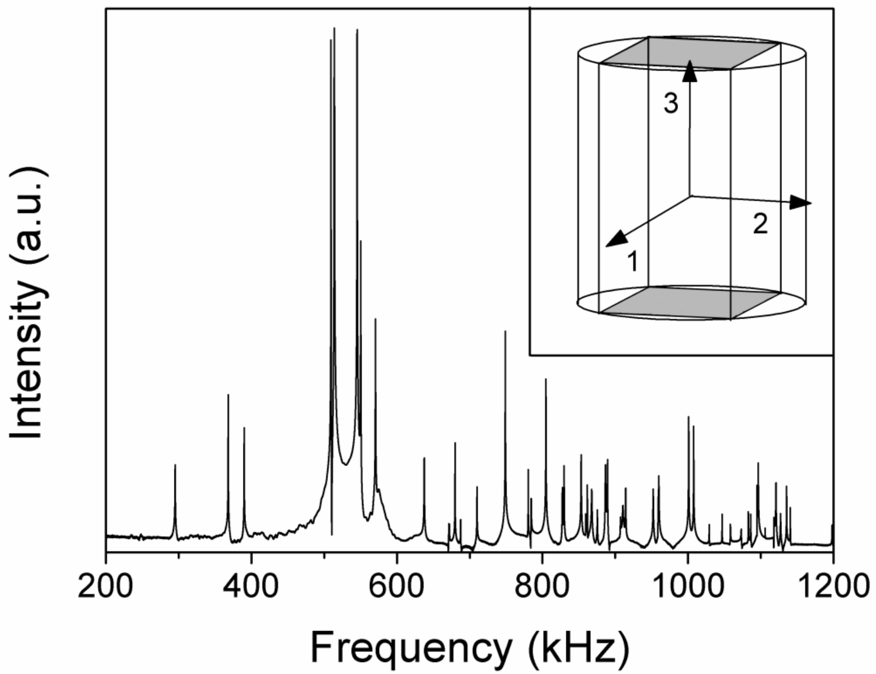
The ideal state of a glass or amorphous solid is isotropic.

But a glass can be anisotropic:

In this case frozen-in anisotropy comes from the alignment of the polymer chains as they flow into the mould cavity.



RUS studies of a BMG: $Pd_{40}Cu_{30}Ni_{10}P_{20}$



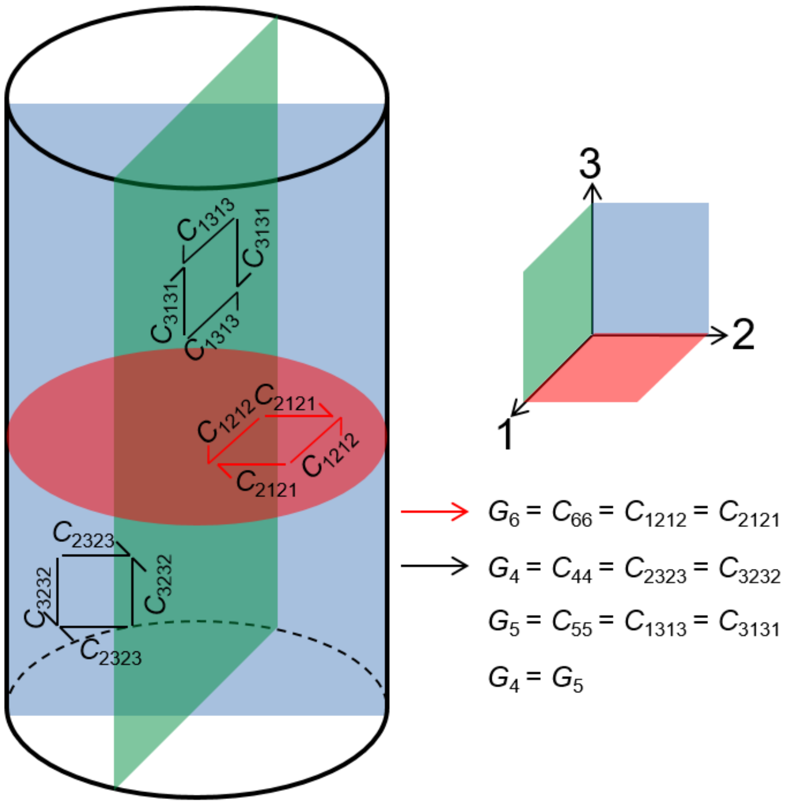
as-cast sample

Approximate sample size: 1.5×2×5 mm^3
Fitting of 40 resonant frequencies.

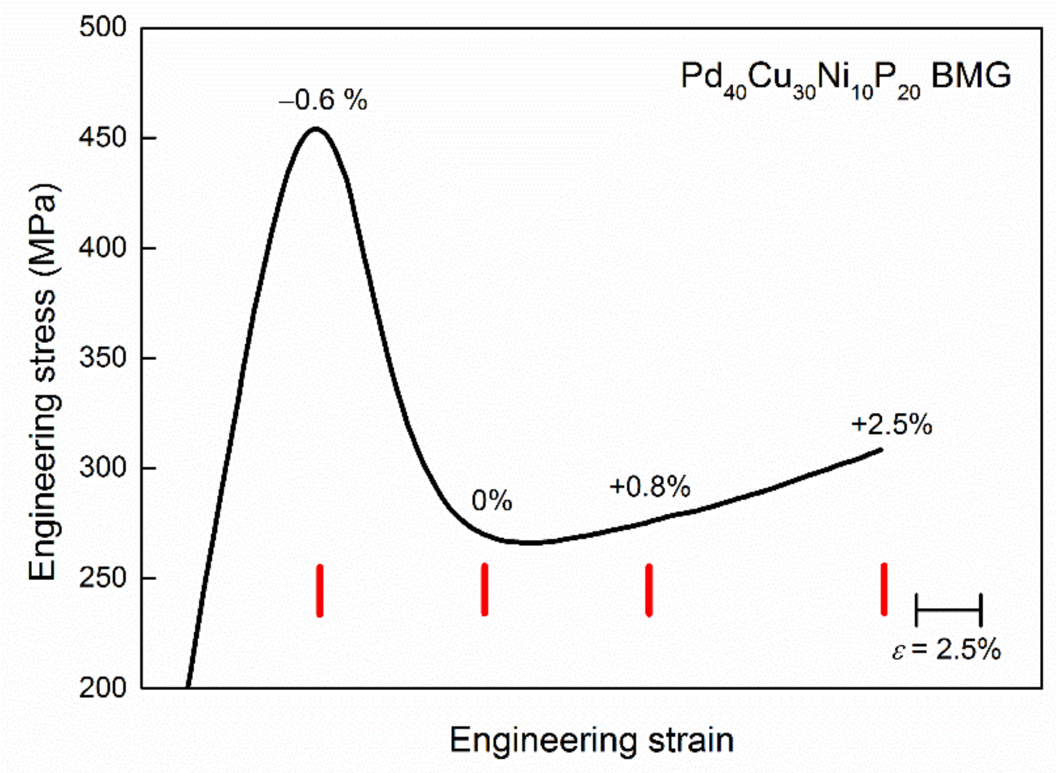
A Concustell, S Godard-Desmarest, MA Carpenter, N Nishiyama & AL Greer: Induced elastic anisotropy in a bulk metallic glass *Scripta Mater.* **64** (2011) 1091–1094.

New tests, focusing on the shear moduli: G_4 & G_6

— characterize the anisotropy as: $A = (G_4 - G_6)/G_4$



YH Sun, A Concustell, MA Carpenter, JC Qiao, AW Rayment & AL Greer: Flow-induced elastic anisotropy of metallic glasses, *Acta Mater*. **112** (2016) 132–140.



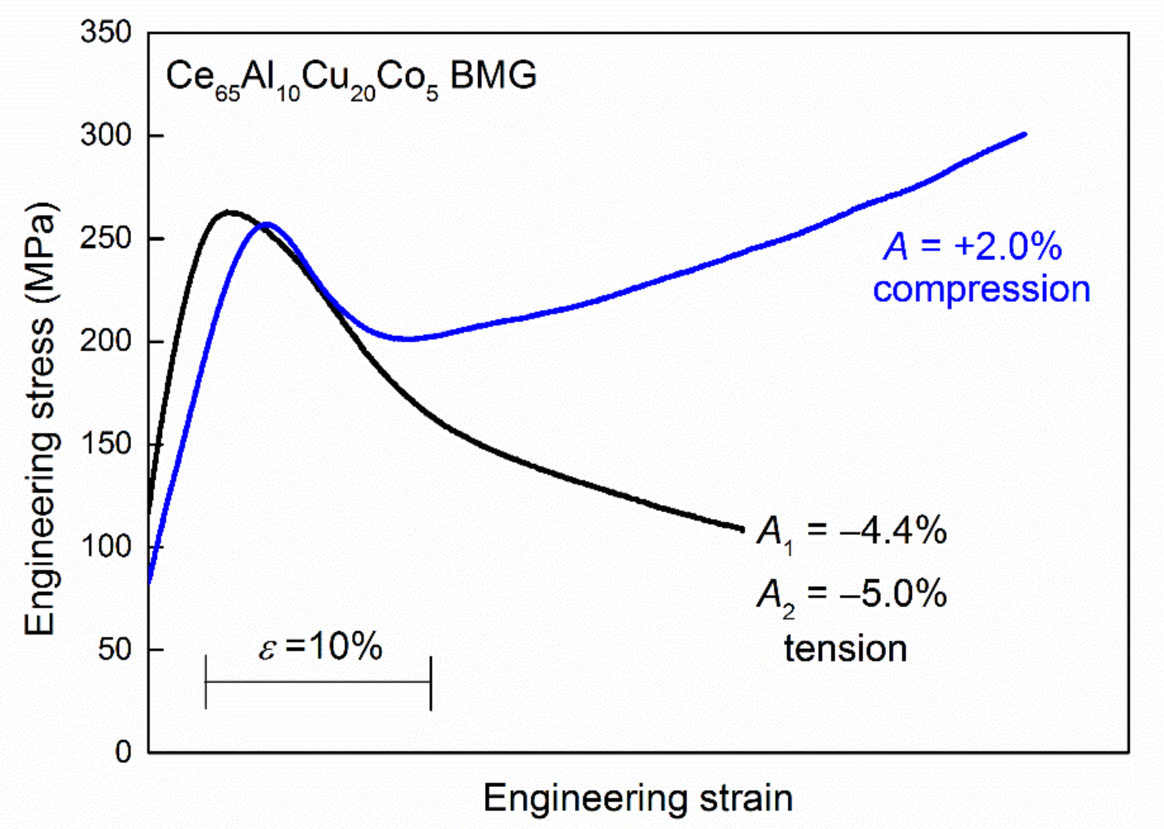
Constant engineering-strain rate tests:

— uniaxial compression at 548 K (0.96 T_g) and 10^{-3} s^{-1}

— the as-cast glass is isotropic

— cuboid samples cut at various stages show evolving anisotropy

YH Sun, A Concustell, MA Carpenter, JC Qiao, AW Rayment & AL Greer: Flow-induced elastic anisotropy of metallic glasses, *Acta Mater*. **112** (2016) 132–140.



Constant engineering-strain rate (at 10^{-2} s^{-1}) tests:

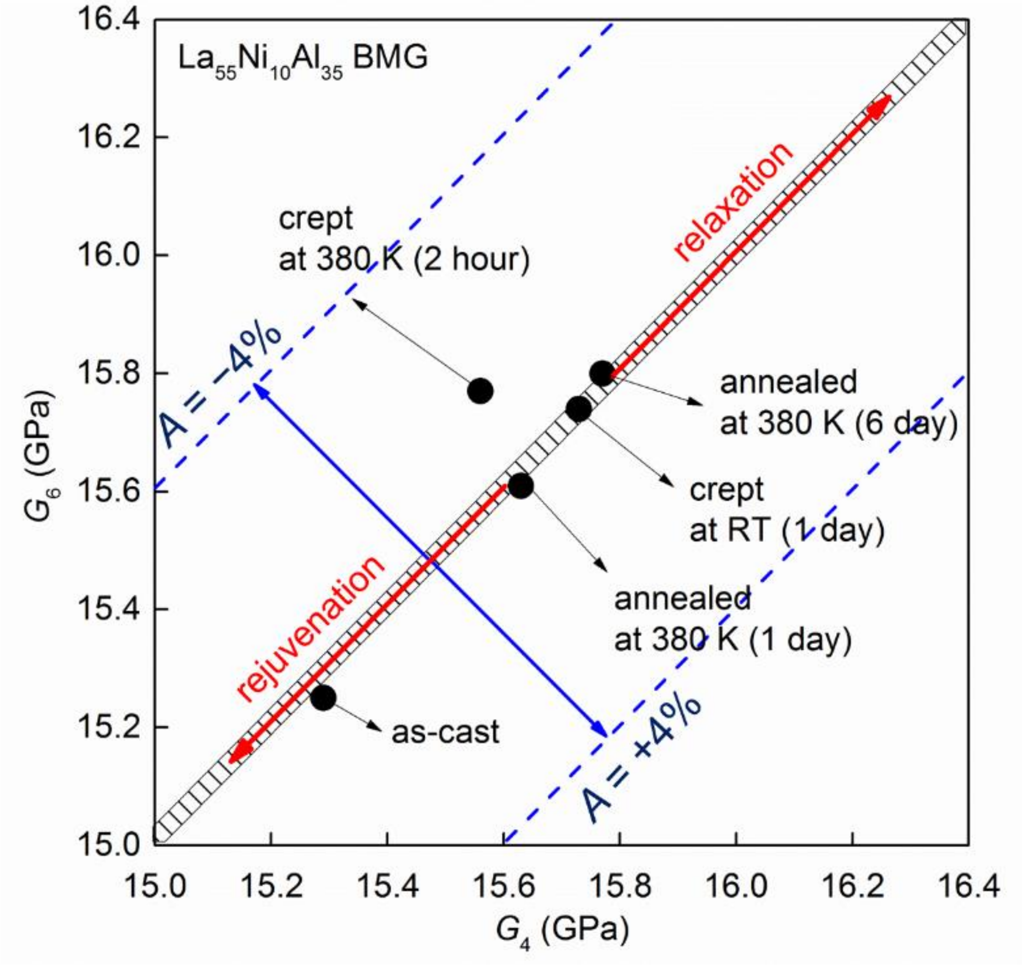
— uniaxial compression (at 363 K, 0.97 T_g)

— uniaxial tension (at 368 K, 0.99 T_g)

— final values of anisotropy *A* are shown.

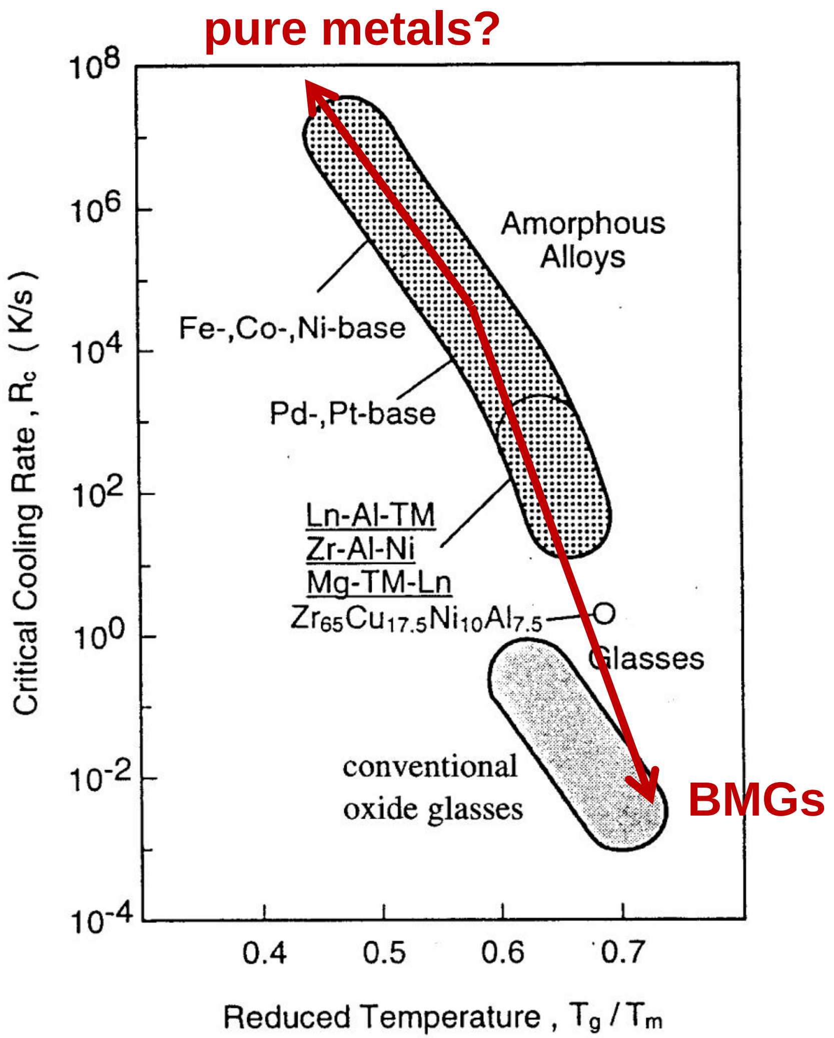
YH Sun, A Concustell, MA Carpenter, JC Qiao, AW Rayment & AL Greer: Flow-induced elastic anisotropy of metallic glasses, *Acta Mater*. **112** (2016) 132–140.

Effects of **annealing** and **creep in compression:**

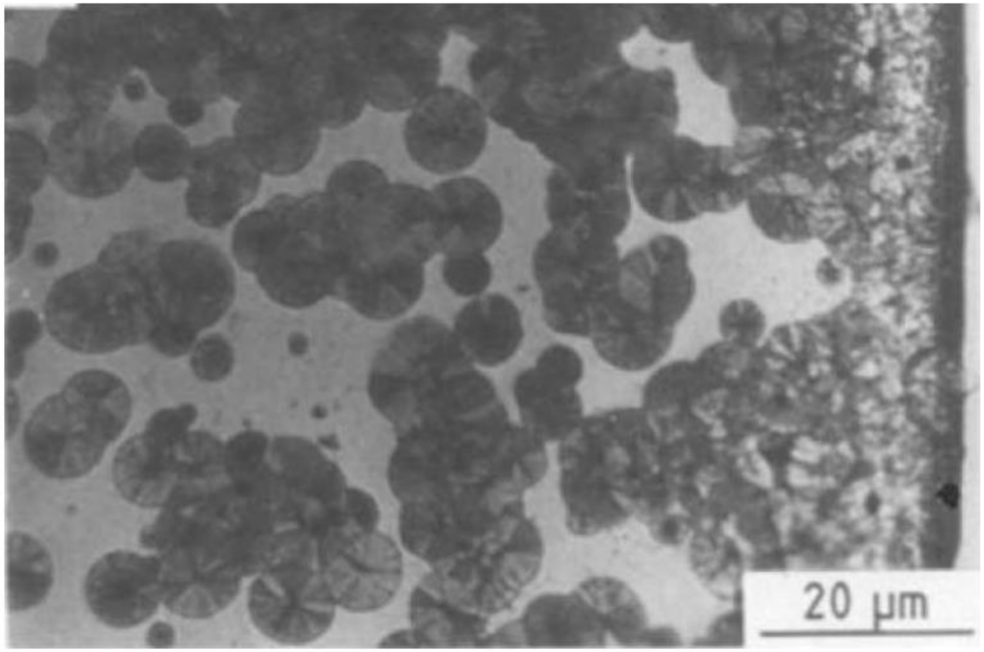


Anisotropy from frozen-in anelastic strain

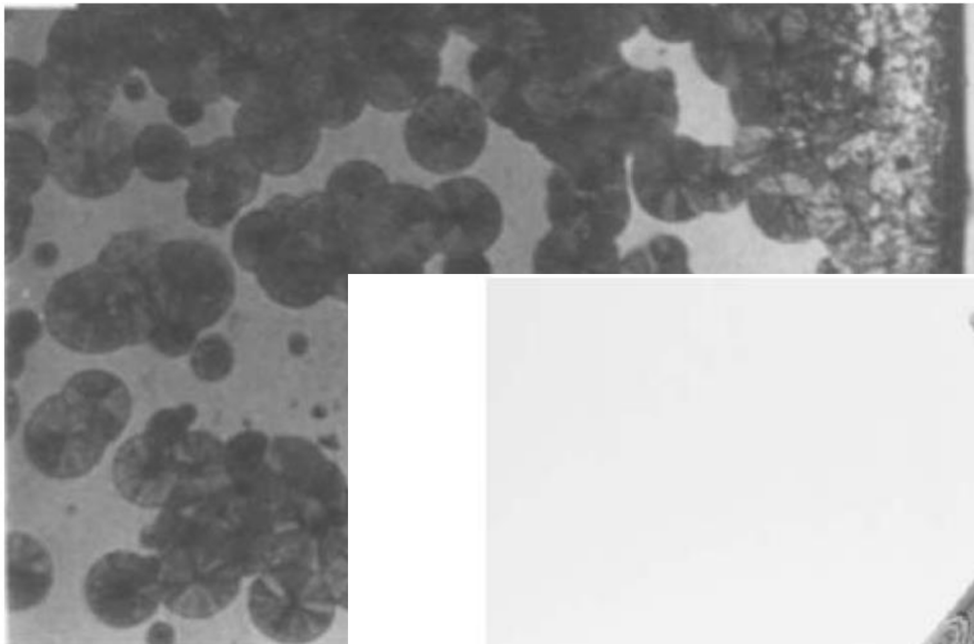
YH Sun, A Concustell, MA Carpenter, JC Qiao, AW Rayment & AL Greer: Flow-induced elastic anisotropy of metallic glasses, *Acta Mater*. **112** (2016) 132–140.



T Masumoto: *Mater. Sci. Eng. A* **179–180** (1994) 8–16.

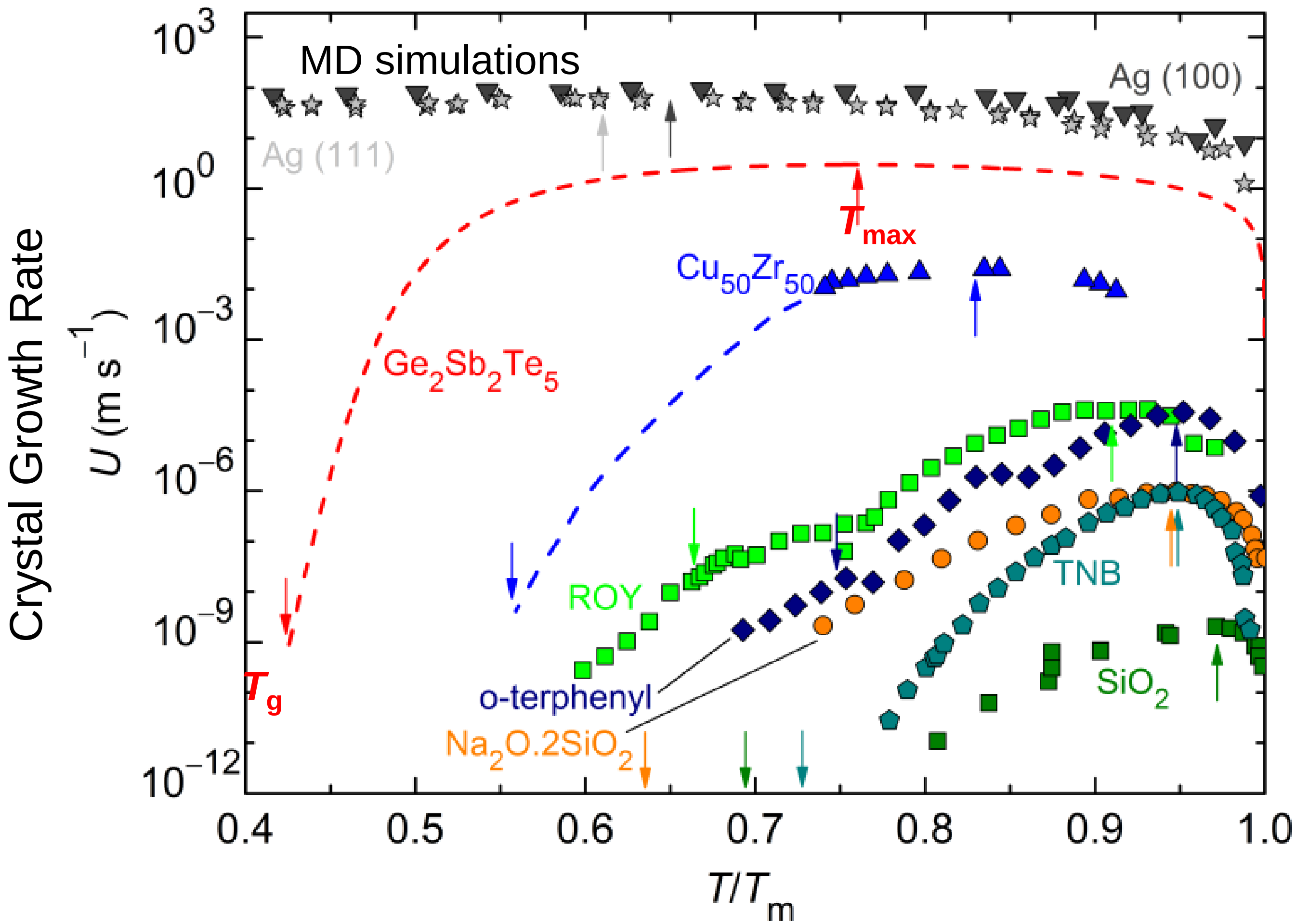


Crystals in $Pd_{40}Ni_{40}P_{20}$ metallic glass



Crystals in Pd_4

Fig. 1 A vase coated with a glaze that has been partially crystallized during firing.



J Orava & AL Greer: Fast and slow crystal growth kinetics in glass-forming melts
J. Chem. Phys. **140** (2014) 214504.

Wang et al. *Phys. Rev. B* **83** (2011) 014202.

Nascimento et al. *J. Chem. Phys*. **133** (2010) 174701.

Ashkenazy et al. *Acta Mater*. **58** (2010) 524. Sun et al. *J. Chem. Phys*. **31** (2009) 074509.

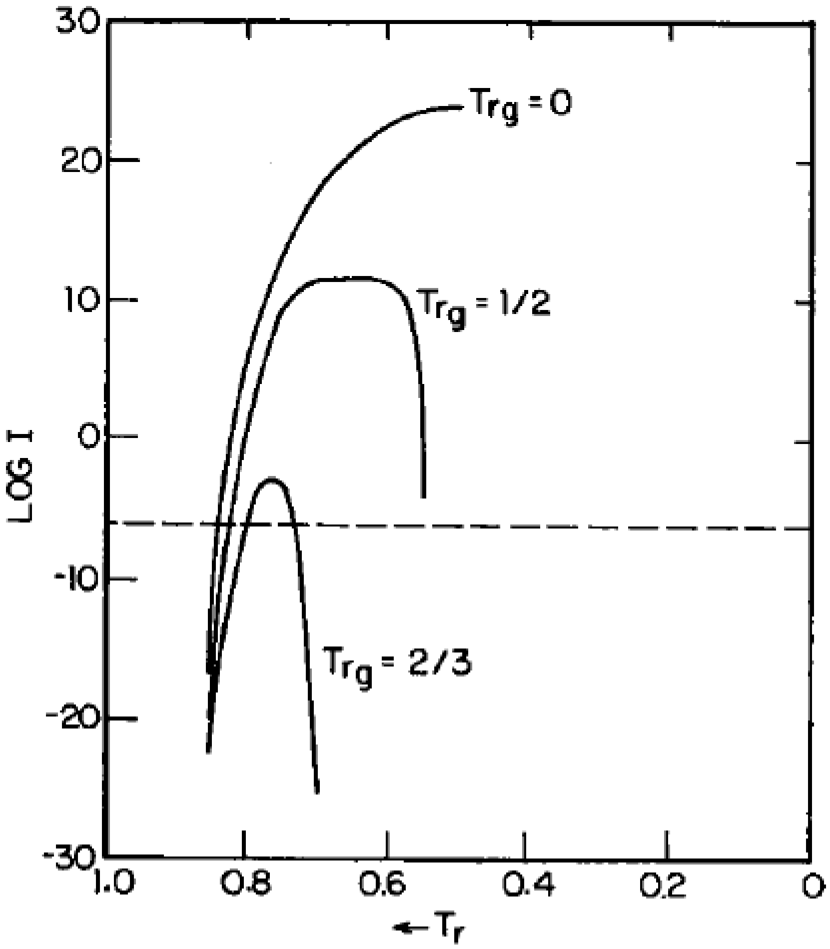
Turnbull (1969):

Rate of homogeneous crystal nucleation

Simple scaling analysis

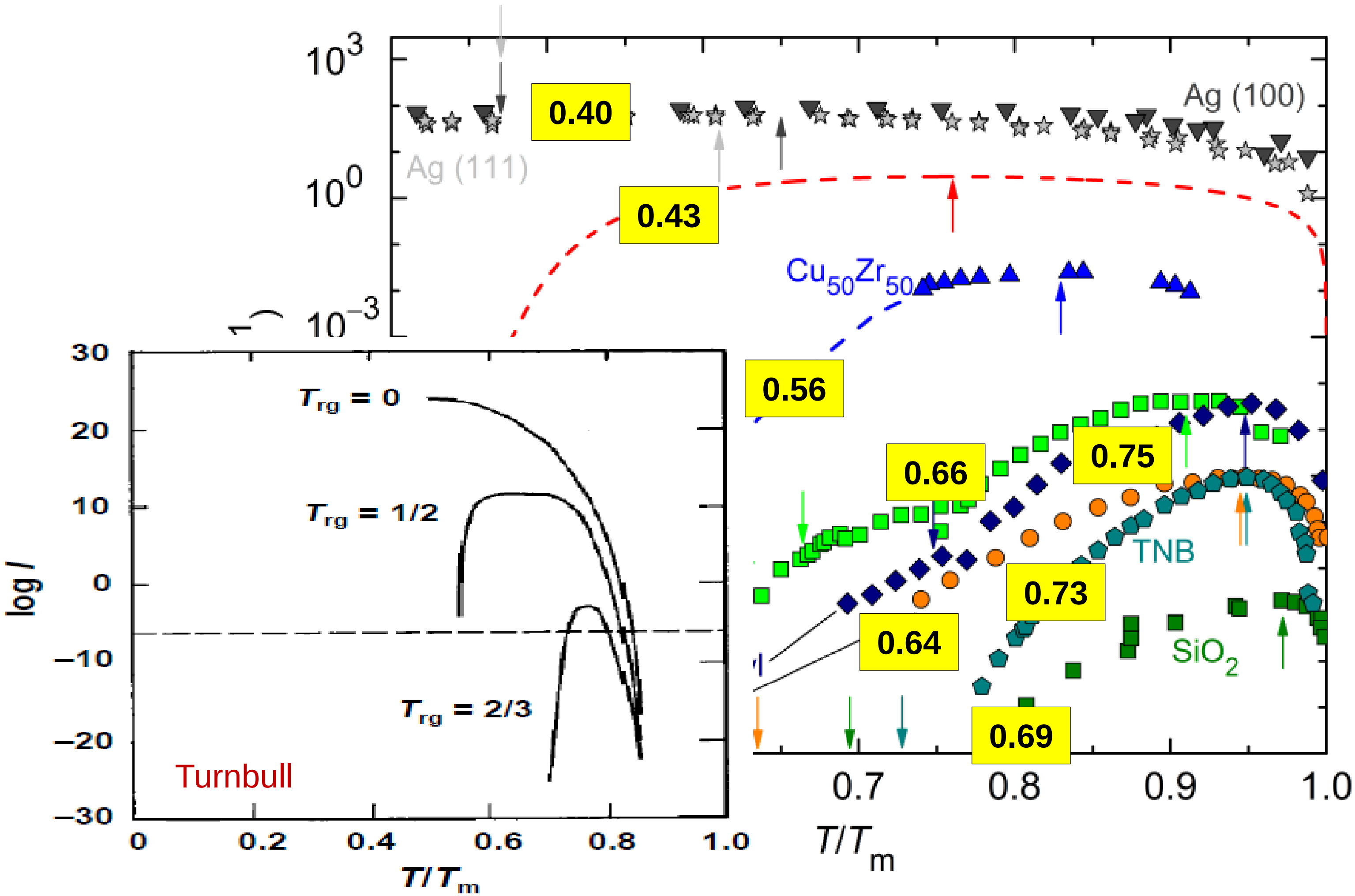
Shows importance of the width of the labile range between T_g and T_m

Characterize in terms of the reduced glass-transition temperature $T_{rg} = T_g/T_m$

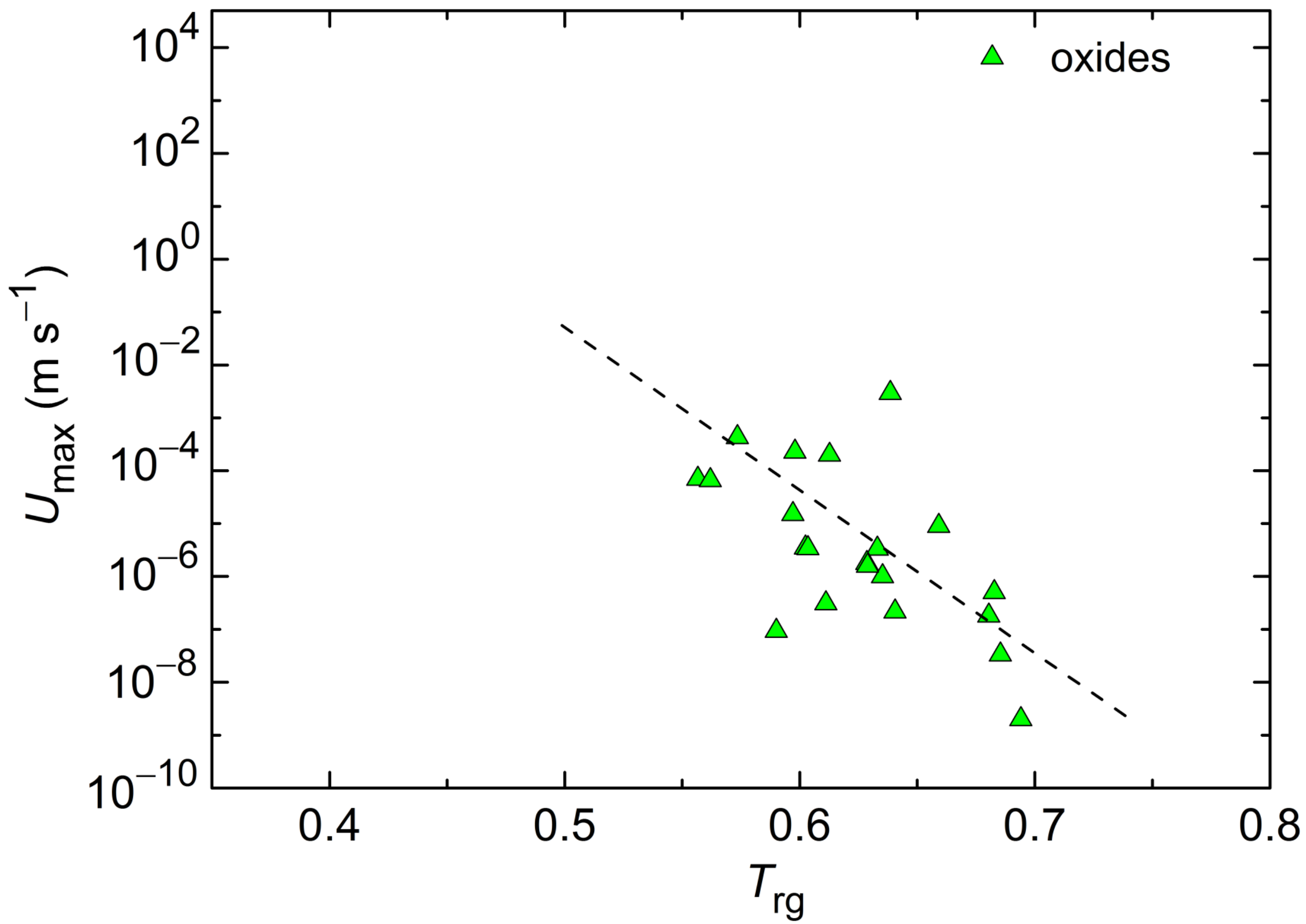


D Turnbull: Under what conditions can a glass be formed? *Contemp. Phys.* **10** (1969) 473–488.

T_{rg} values

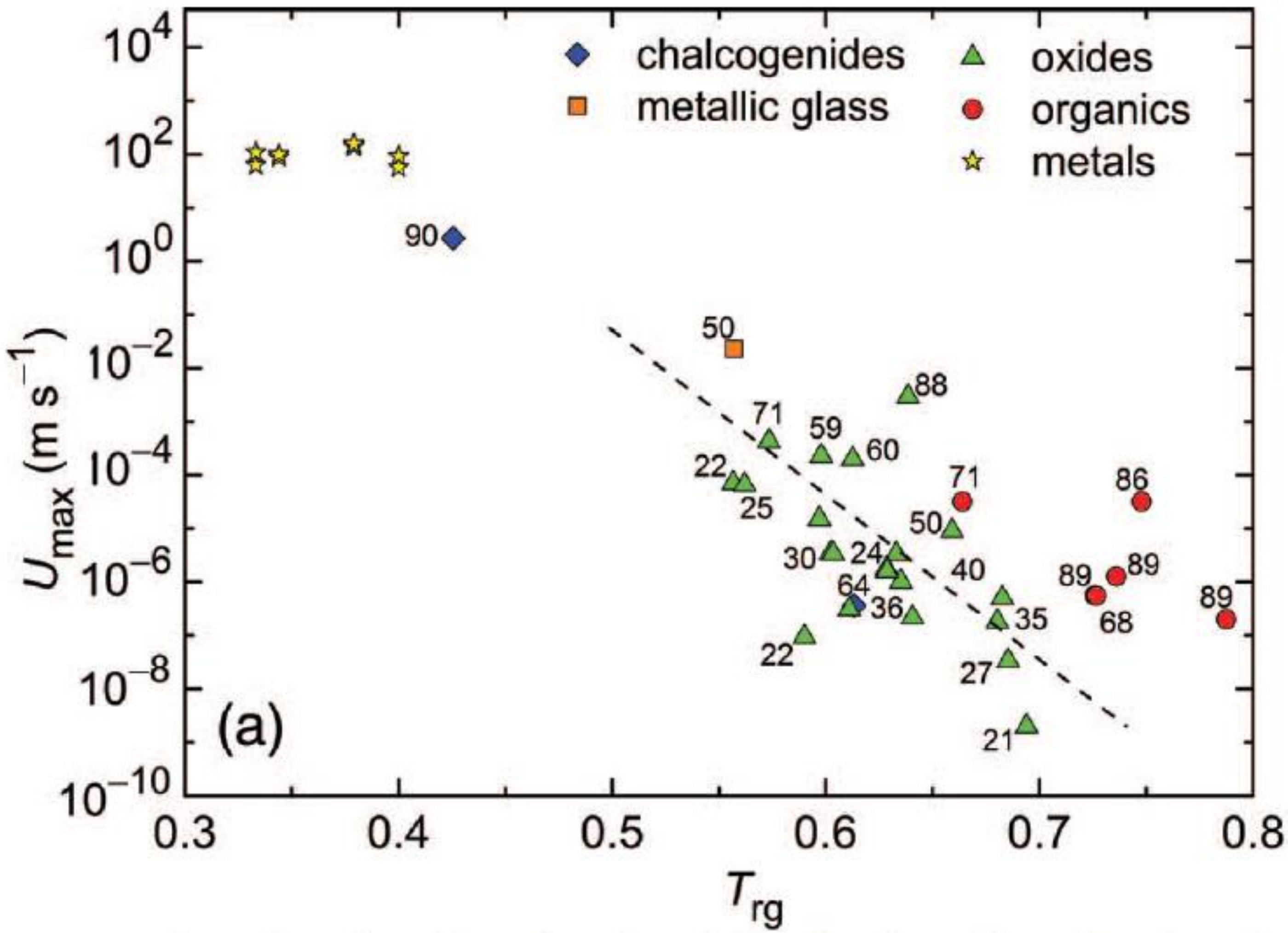


J Orava & AL Greer: Fast and slow crystal growth kinetics in glass-forming melts
J. Chem. Phys. **140** (2014) 214504.



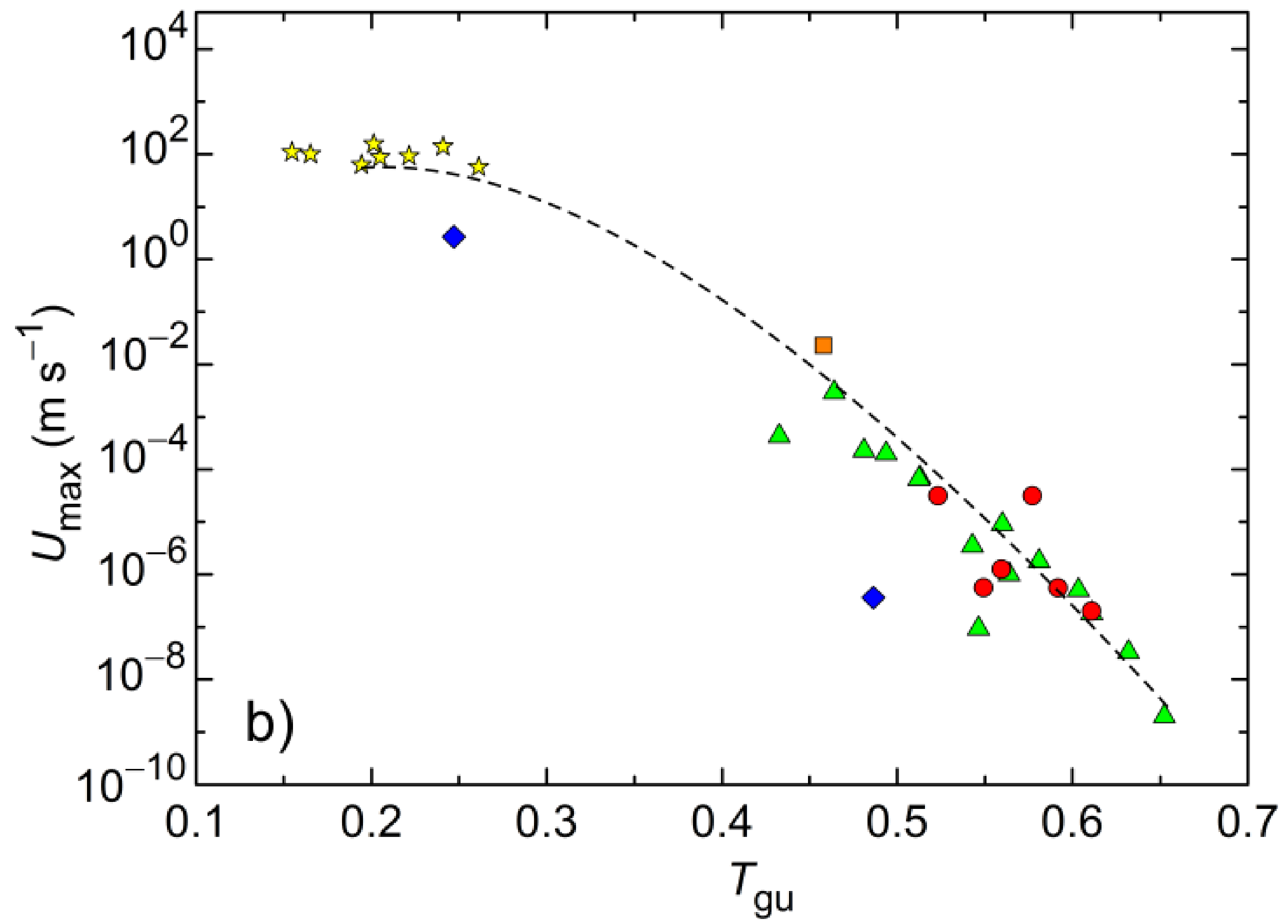
The correlation of U_{max} and T_{rg} suggested by Fokin et al. for oxide glass-formers

Fokin et al.: Correlation between maximum crystal growth rate and glass transition temperature of silicate glasses, *J. Non-Cryst. Solids* **351** (2005) 789–794.



Higher fragility gives points above the correlation line and vice versa

J Orava & AL Greer: "Fast and slow crystal growth kinetics in glass-forming melts"
J. Chem. Phys. **140** (2014) 214504.



$T_{gu} = T_{rg} - (m/505)$

— effectively T_{rg} ‘corrected’ for fragility *m* meanwhile — a group at **Glassimetal Technology Inc.** and the **California Institute of Technology** was working on:

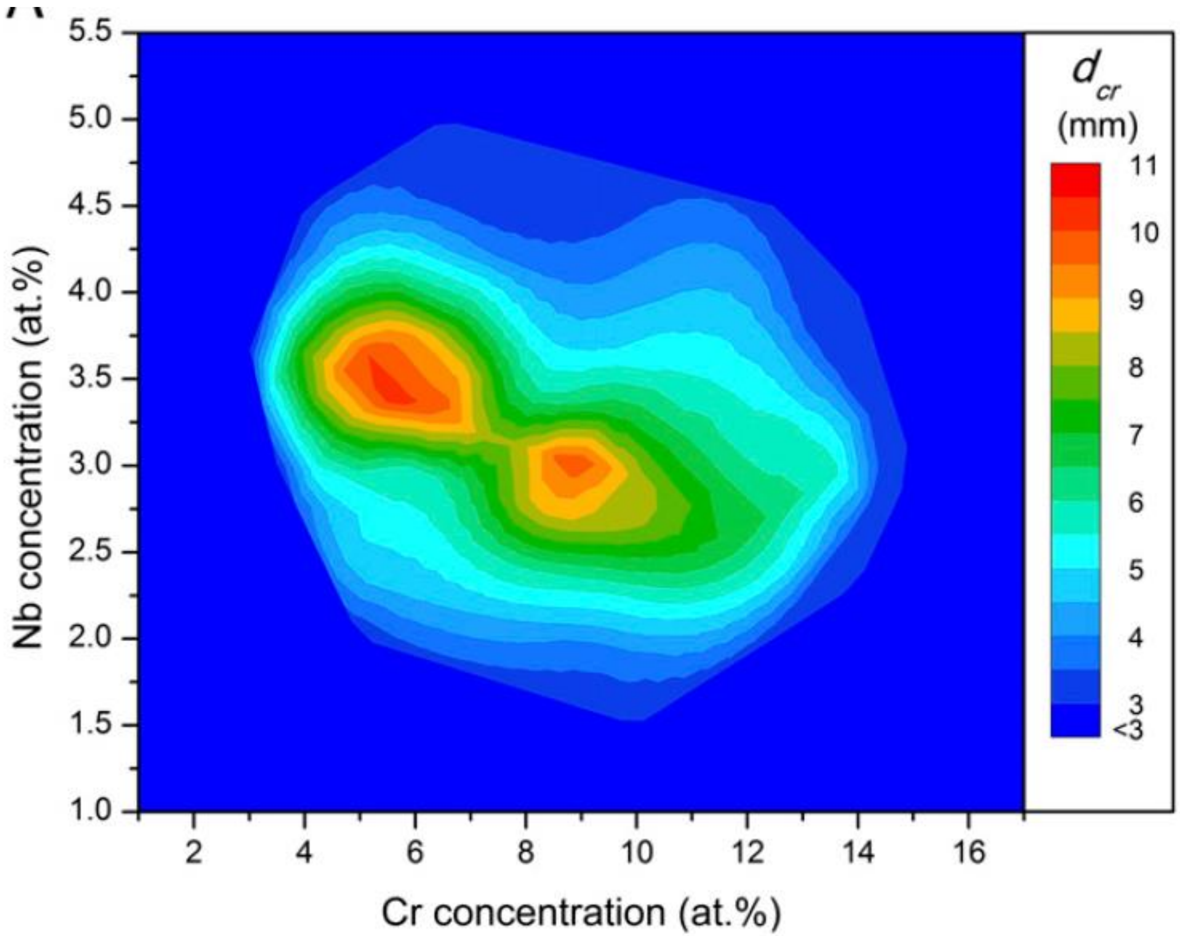
Composition dependence of glass-forming ability in the Ni-Cr-Nb-P-B system

The glass-forming ability (GFA) is characterized by the maximum rod diameter d_{cr} that can be cast fully glassy.

d_{cr} shows a strong (exponential) dependence on composition

d_{cr} is maximum at eutectic compositions

JH Na, MD Demetriou, M Floyd, A Hoff, GR Garrett & WL Johnson: Compositional landscape for glass formation in metal alloys, *PNAS* **111** (2014) 9031–9036.



JH Na, MD Demetriou, M Floyd, A Hoff, GR Garrett & WL Johnson: Compositional landscape for glass formation in metal alloys, *PNAS* **111** (2014) 9031–9036.

GFA is correlated with both T_{rg} and m

T_{rg} and m are independent parameters

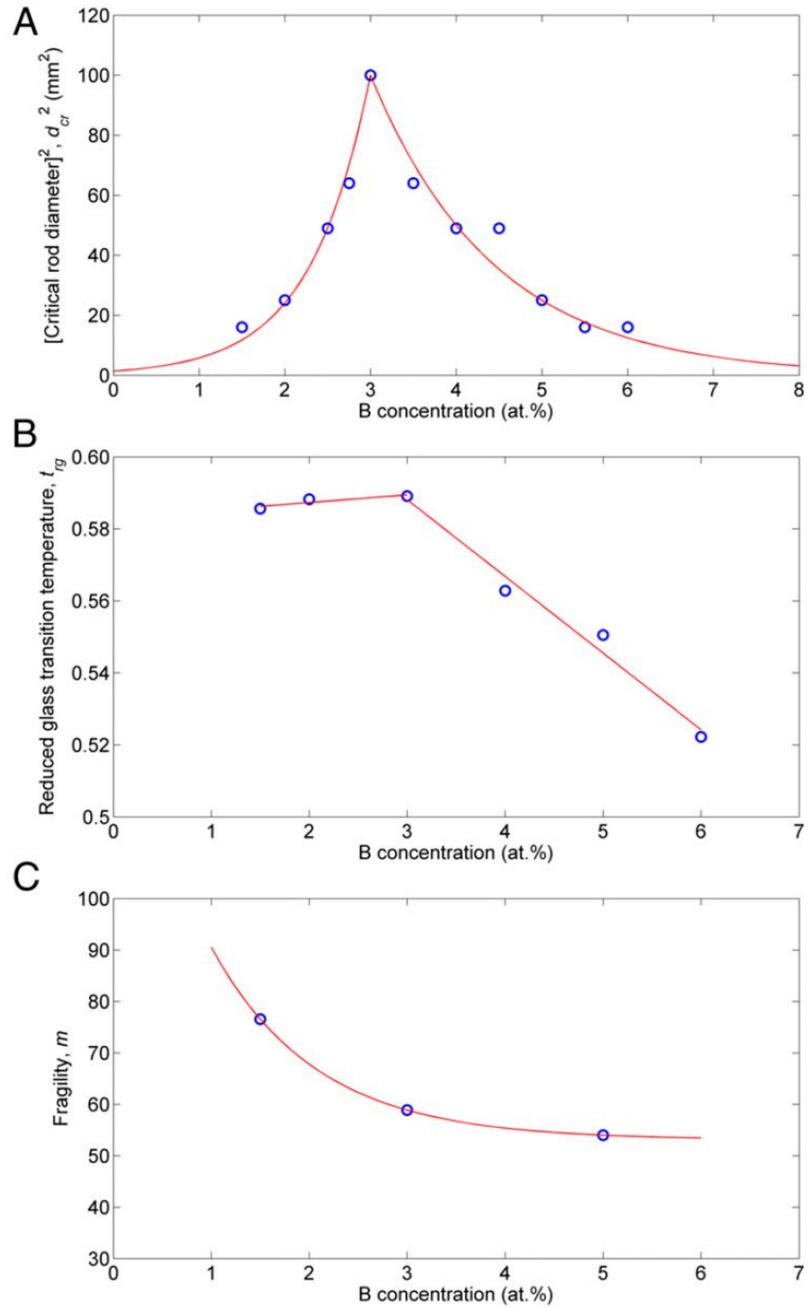
GFA is exceptionally well correlated with a single parameter:

$T_{rg} – (m/390)$ (in PNAS)

— and with more data revised to:

$\mathbf{T_{rg} – (m/520)}$

JH Na, MD Demetriou, M Floyd, A Hoff, GR Garrett, WL Johnson: Compositional landscape for glass formation in metal alloys, *PNAS* **111** (2014) 9031–9036.



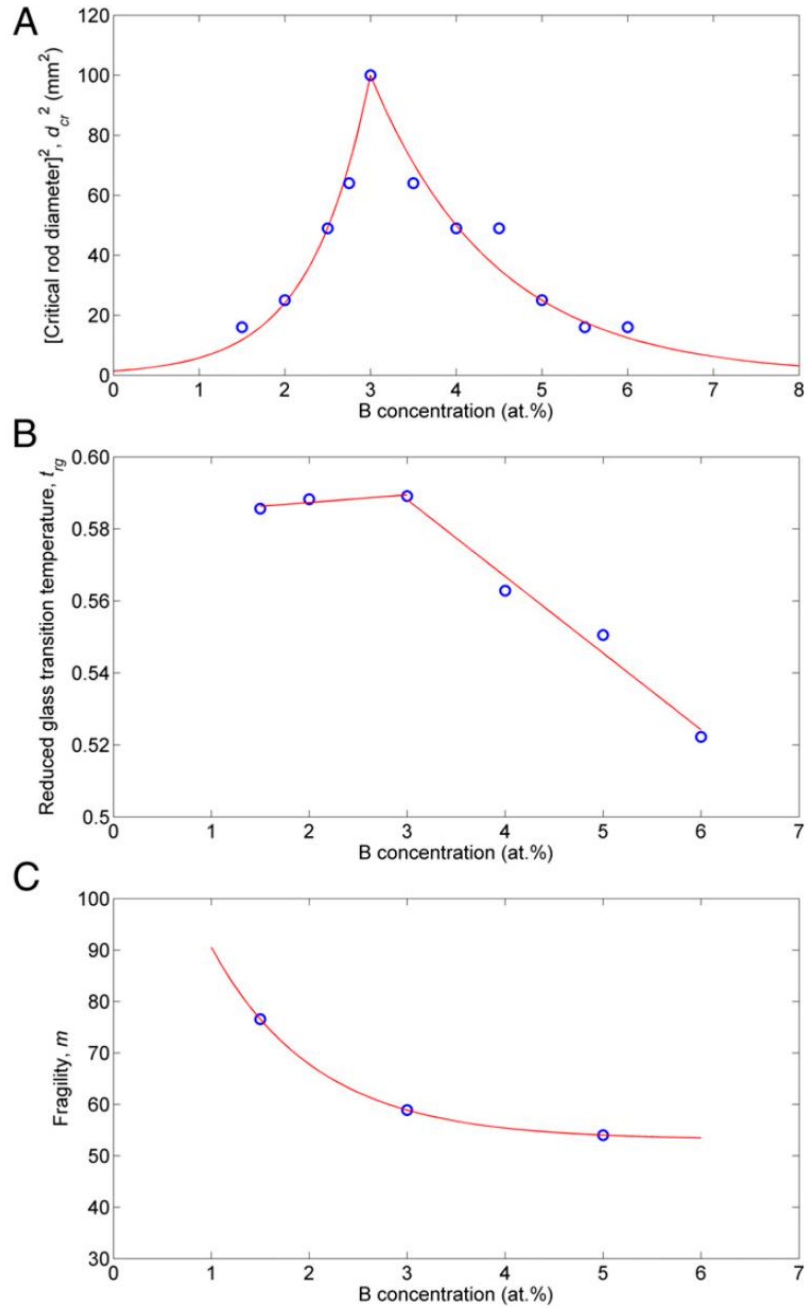
parameter:

$T_{rg} - (m/390)$ (in PNAS)

— and with more data revised to:

$\boldsymbol{T_{rg} - (m/520)}$

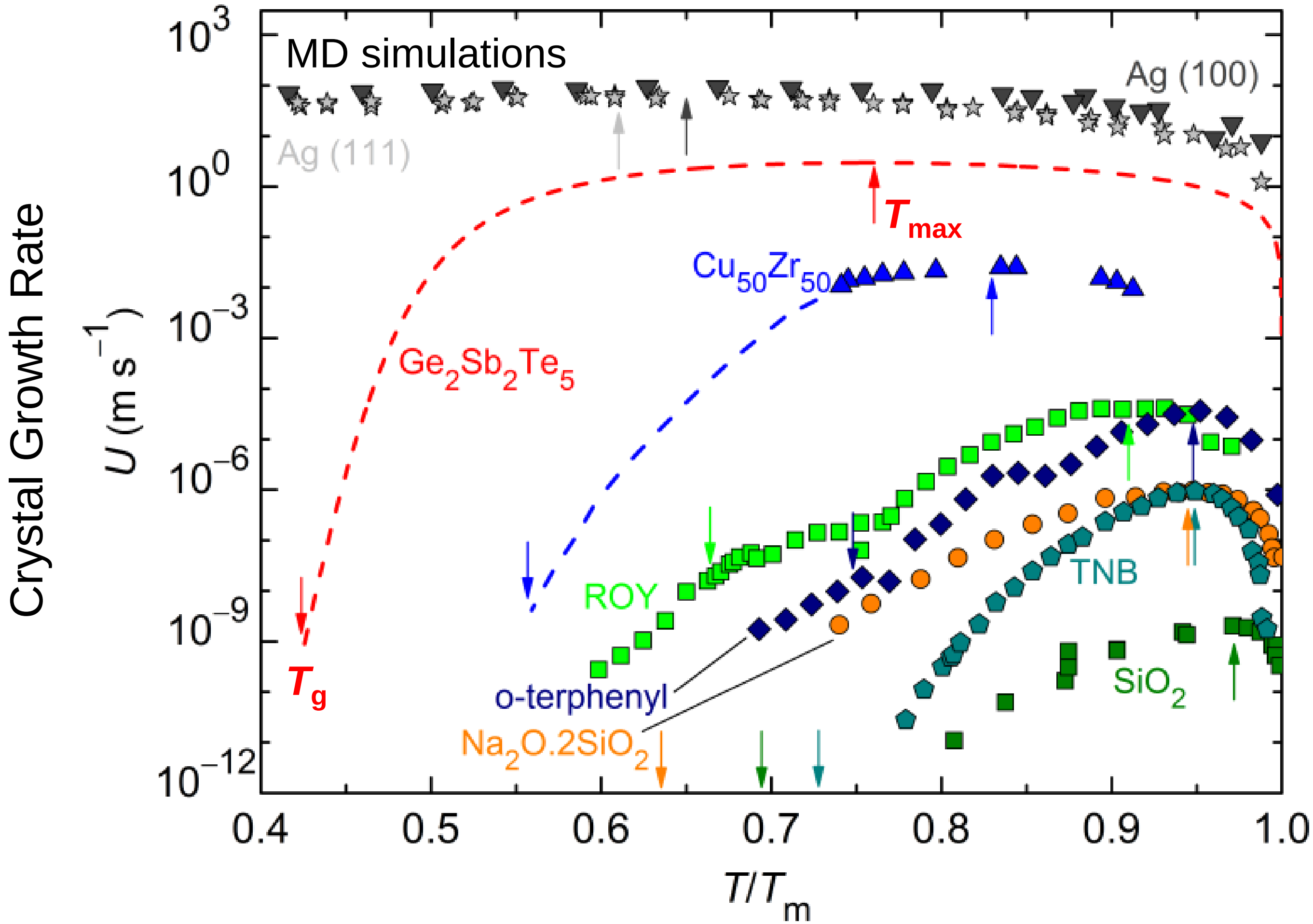
JH Na, MD Demetriou, M Floyd, A Hoff, GR Garrett, WL Johnson: Compositional landscape for glass formation in metal alloys, *PNAS* **111** (2014) 9031–9036.



It seems that GFA can be accurately predicted from **just two** parameters:

- reduced glass-transition temperature T_{rg}
- liquid fragility m

— but is this effect through **nucleation** or **growth**, or both?



GST lies:

between pure metals and glass-forming alloys

The growth rate for chalcogenide GST lies between pure metals and the glass-forming $Cu_{50}Zr_{50}$.

J Orava & AL Greer: "Fast and slow crystal growth kinetics in glass-forming melts" *J. Chem. Phys.* **140** (2014) 214504.

Rewritable optical discs are a successful technology

but the key goal for the future of chalcogenide phase-change media is —

random-access memory (RAM)

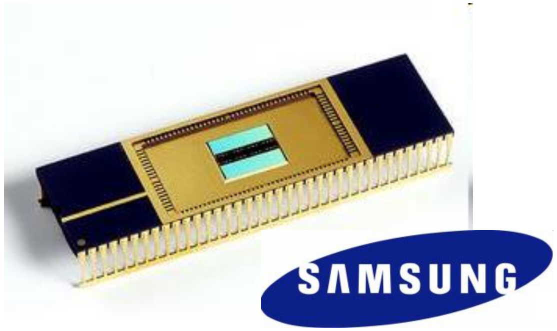
- the leading manufactures and developers are:
  Ovonyx → Ovonic Unified Memory (OUM) ("*ECD Ovonics has invented a basic phase-change solid-state storage technology, which is now being developed by joint venture Ovonyx, Inc.*") – founded by S. R. Ovshinsky

  Numonyx (2007 - STMicroelectronics + Intel "*to better face increasingly stiff competition in the Flash memory market"* – working on RAM cells as well)

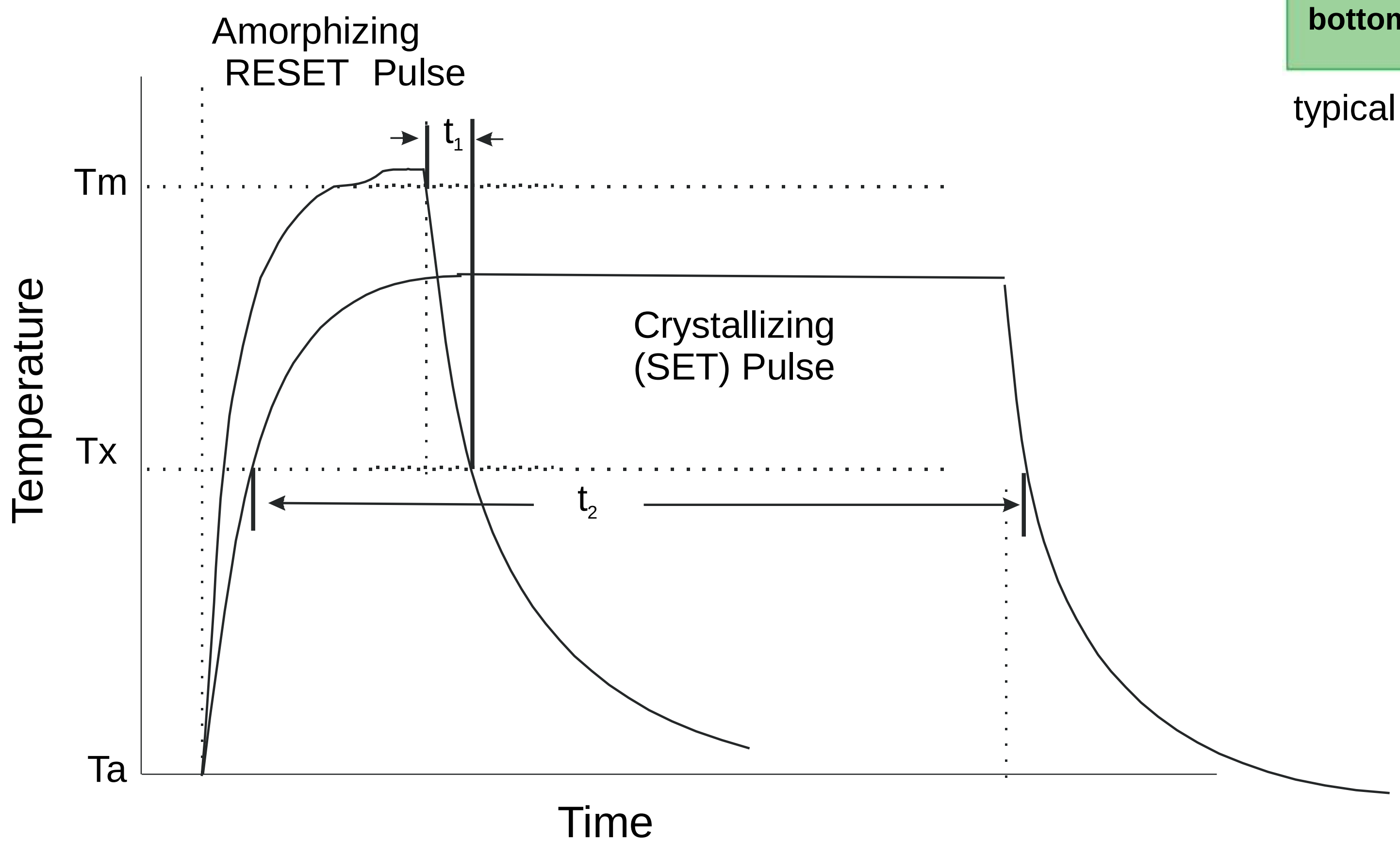
  Samsung *"09/22/2009, LONDON - South Korean electronics giant Samsung Electronics Co. Ltd. has announced that it has begun production of a* 512-Mbit *phase-change random access memory and is aiming it at mobile phone handsets and other battery-operated applications."*

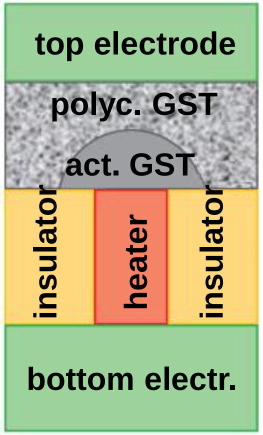
  - others on the market: Panasonic, IBM, LETI...

- heating by electric current through the chalcogenide



Programming of memory devices (schematic)

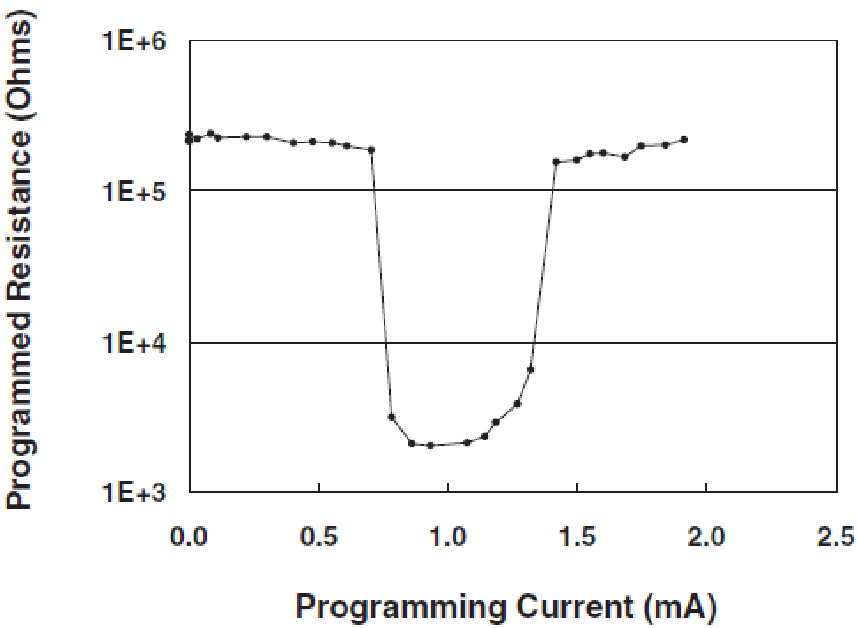




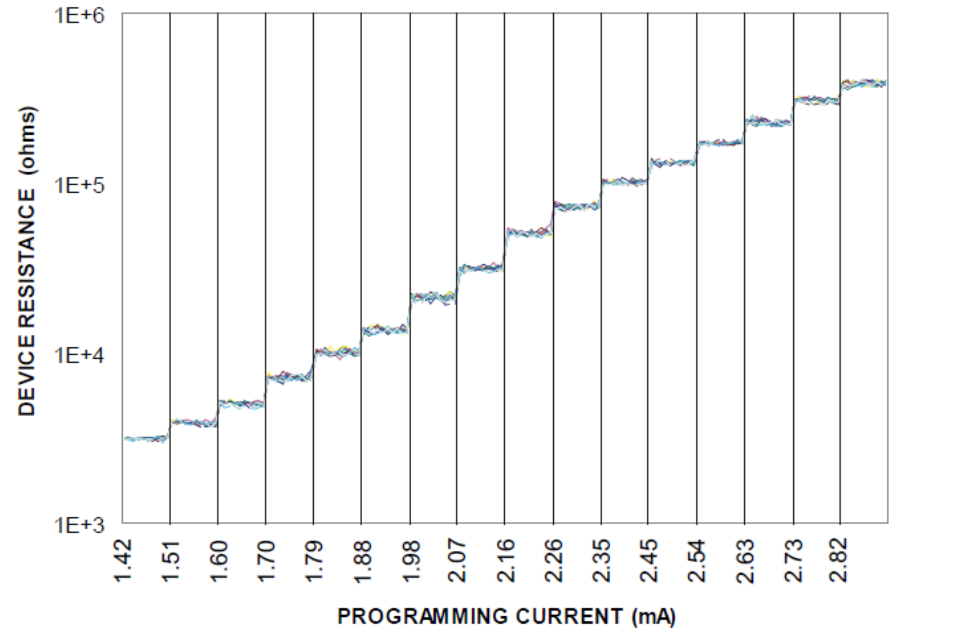
typical heater

Resistance vs current for a phase-change memory device

"Threshold switching"



Multi-state electrical phase-change memory



(12) **United States Patent**
Lee

(10) **Patent No.:** **US 7,488,968 B2**
(45) **Date of Patent:** **Feb. 10, 2009**

(54) **MULTILEVEL PHASE CHANGE MEMORY**

(75) Inventor: **Jong-Won S. Lee**, San Francisco, CA (US)

(73) Assignee: **Ovonyx, Inc.**, Rochester Hills, MI (US)

2003/0052351	A1*	3/2003	Xu et al.	257/296
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* cited by examiner

SR Ovshinsky: "Optical cognitive information processing — a new field" *Jpn. J. Appl. Phys.* **43** (7B) (2004) 4695.

LETTER

14 August 2014:
Nature **512** (2014) 177–182

doi:10.1038/nature13617

Formation of monatomic metallic glasses through ultrafast liquid quenching

Li Zhong[1], Jiangwei Wang[1], Hongwei Sheng[2,3], Ze Zhang[4] & Scott X. Mao[1]

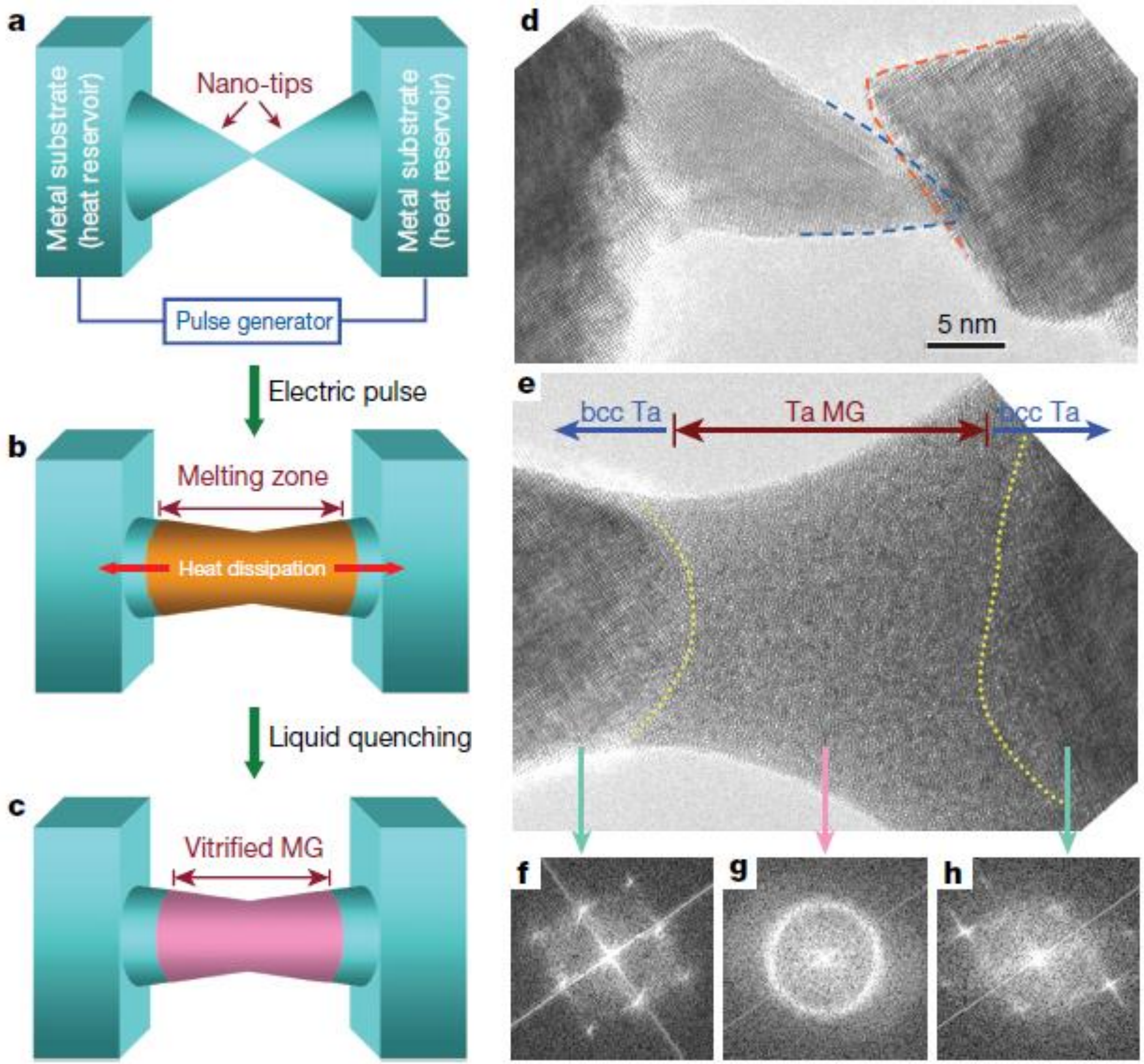
- formation of pure glassy Mo, Ta, V, W (all bcc) by liquid quenching
- e.g. for Ta, the cooling rate is as high as **10^{14} K s^{-1}** at 4200 K
- failed to make fcc metals glassy (Ag, Al, Au, Cu, Ir, Pd, Rh)
- the glass formation is by suppression of growth
- the glasses show clear structural relaxation at RT (XRD)
- W glass is unstable at RT.

L Zhong, J Wang, H Sheng, Z Zhang & SX Mao: Formation of monatomic metallic glasses through ultrafast liquid quenching, *Nature* **512** (2014) 177–182.

Ta

Heating by 4 ns electric pulse at 0.5–3 V.

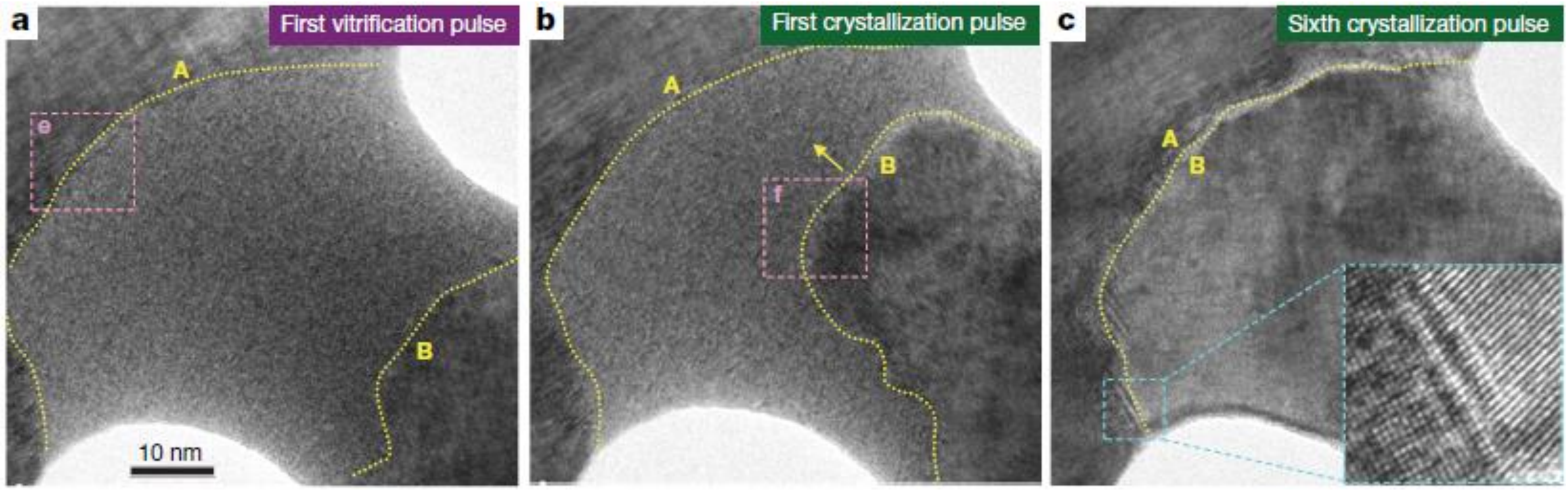
The fully glassy region is 20 nm long and 15 nm thick.



L Zhong, J Wang, H Sheng, Z Zhang & SX Mao: Formation of monatomic metallic glasses through ultrafast liquid quenching, *Nature* **512** (2014) 177–182.

Controlled gradual crystallization of glassy Ta

Reversible vitrification–crystallization



L Zhong, J Wang, H Sheng, Z Zhang & SX Mao
Formation of monatomic metallic glasses through ultrafast liquid quenching
Nature **512** (2014) 177–182.

nature materials

ARTICLES

PUBLISHED ONLINE: 6 JANUARY 2013 | DOI: 10.1038/NMAT3521

Ultrastable glasses from *in silico* vapour deposition

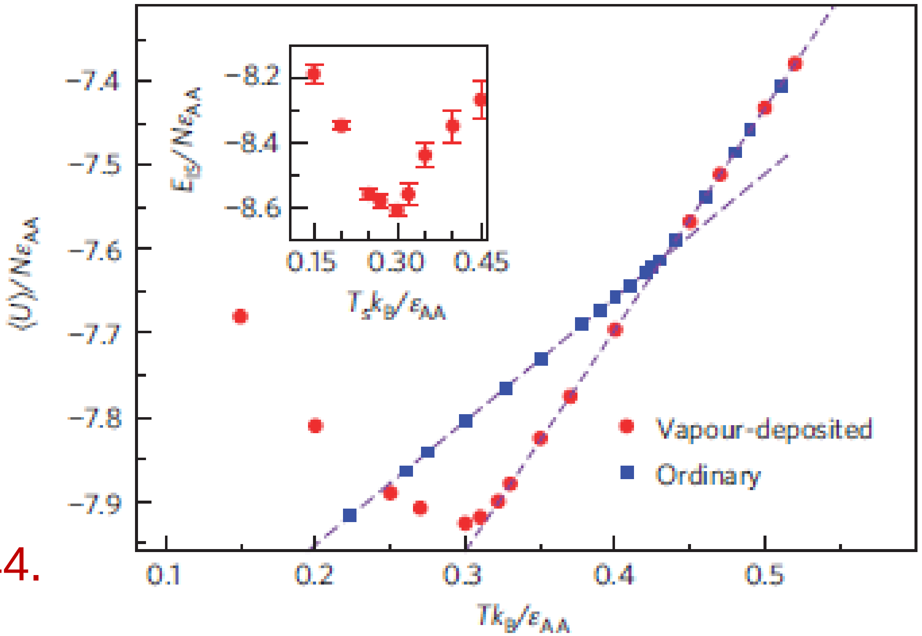
Sadanand Singh[1], M. D. Ediger[2] and Juan J. de Pablo[1,3,4]*

Glasses are generally prepared by cooling from the liquid phase, and their properties depend on their thermal history. Recent experiments indicate that glasses prepared by vapour deposition onto a substrate can exhibit remarkable stability, and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. Here we create ultrastable glasses by means of a computer-simulation process that mimics physical vapour deposition. These stable glasses have, far below the conventional glass-transition temperature, the properties expected for the equilibrium supercooled liquid state, and optimal stability is attained when deposition occurs at the Kauzmann temperature. We also show that the glasses' extraordinary stability is associated with distinct str[...] and the relative lack of irregular polyhedra.

binary mixture of LJ particles

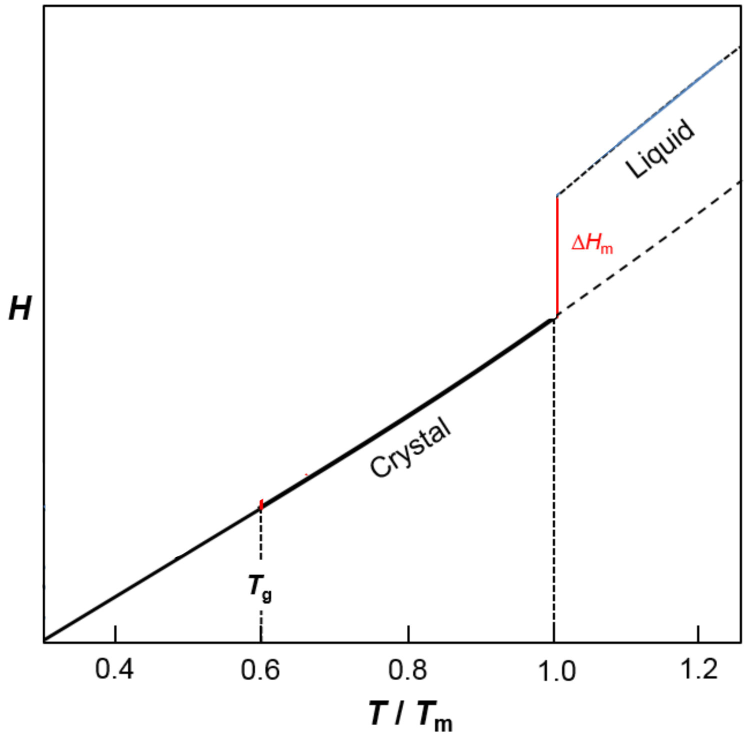
potential energy

minimum energy at ~0.85 T_g

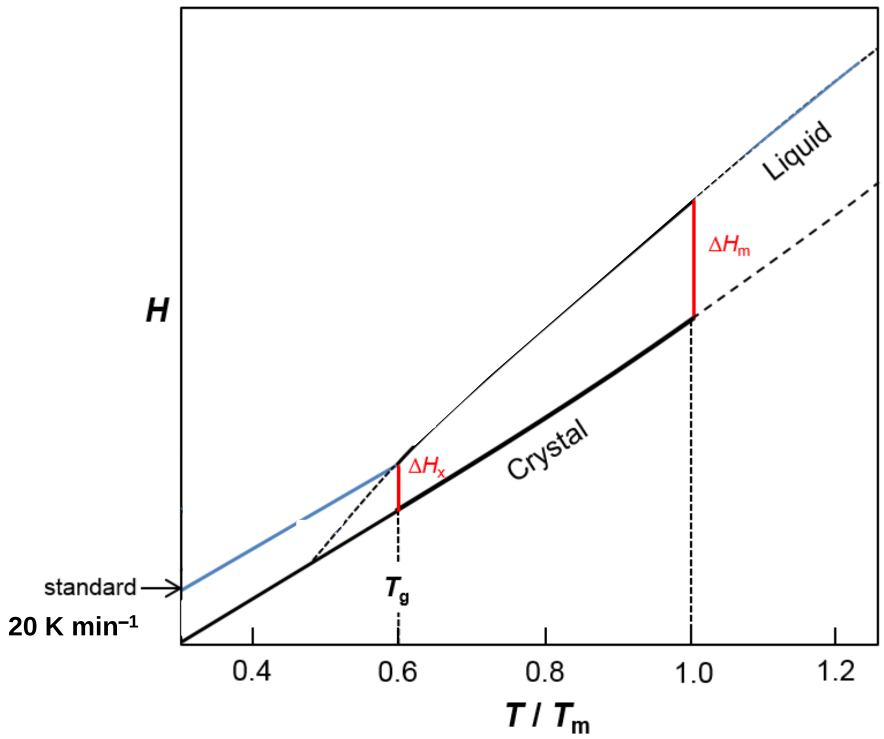


Nature Mater. **12** (2013) 139–144.

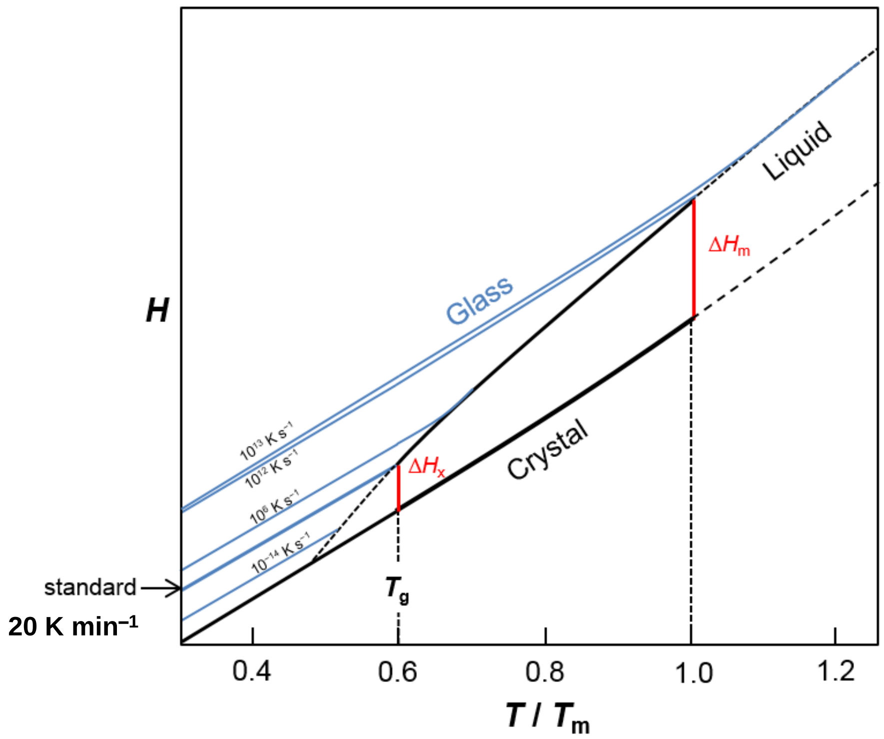
Relative enthalpies based on measured data for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG:



S.C. Glade, R. Busch, D.S. Lee, W.L. Johnson, R.K. Wunderlich and H.J. Fecht: Thermodynamics of $Cu_{47}Ti_{34}Zr_{11}Ni_8$, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ and $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ bulk metallic glass forming alloys, *J. Appl. Phys.* **87** (2000) 7242–7248.



Relative enthalpies based on measured data for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG



Relative enthalpies based on measured data for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG

Conclusions

- metallic glasses form mainly at deep eutectic compositions
- structure is based on dense packing
- glass-forming ability is correlated with T_{rg} and liquid fragility m
- can plastically deform at room temperature
- can induce anisotropy

Energy:

- elastostatic loading induces endothermic disordering
- **rejuvenation** is possible (by irradiation, 'elastic'/plastic deformation)
- show a wide range of states ($\Delta energy \approx \Delta H_m$)

Thermal cycling:

- stored energy, softening and improved plasticity

Crystallization:

- much to understand; possible interest in fast crystallization

Record-breaking mechanical properties:

- 'damage tolerance' ($\sigma_y \times K_c$)