2018 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

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* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

Equilibrium conditions → Non-equilibrium conditions

: non-equilibrium processing = “energize and quench” a material

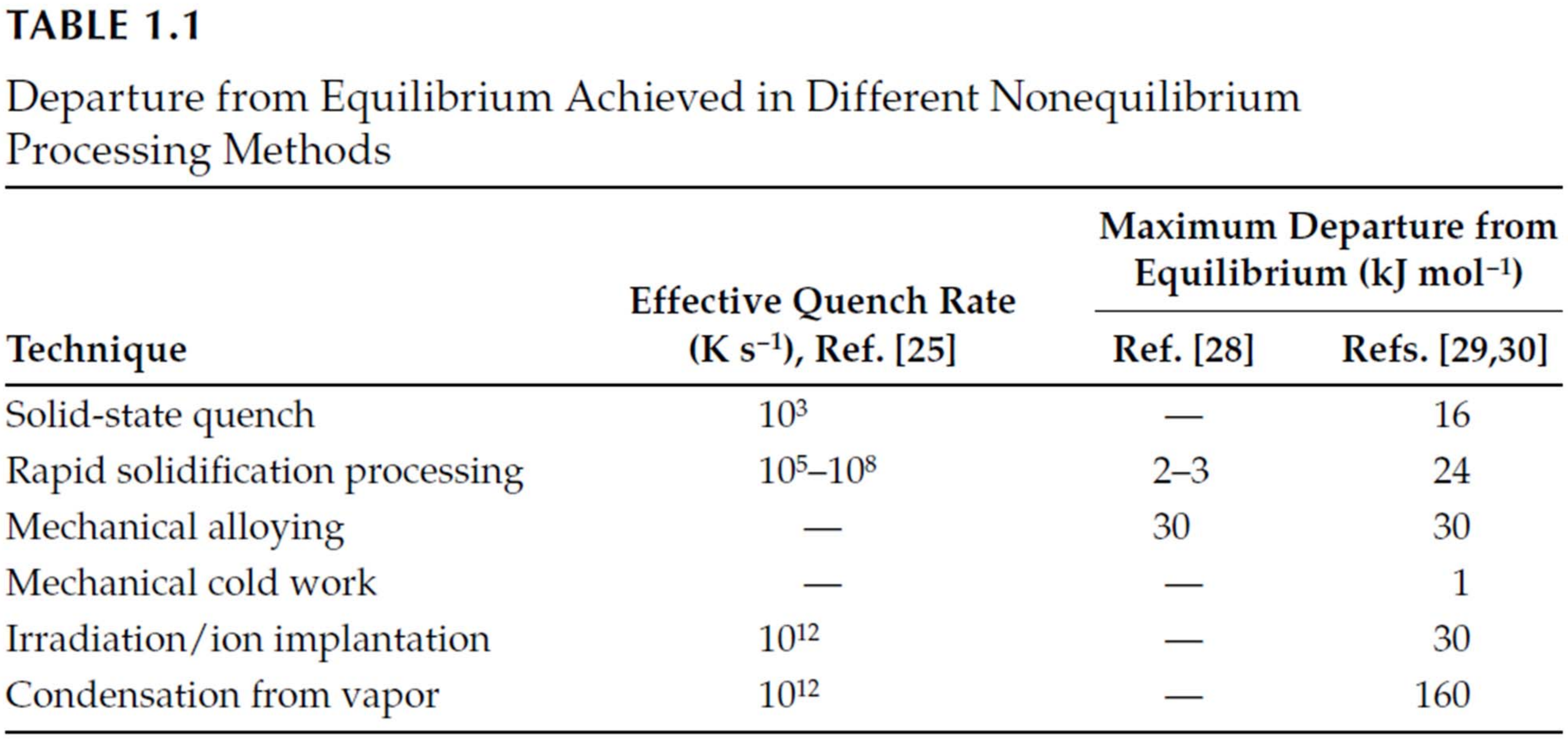


TABLE 1.1

Departure from Equilibrium Achieved in Different Nonequilibrium Processing Methods

Technique	Effective Quench Rate (K s^{-1}), Ref. [25]	Maximum Departure from Equilibrium (kJ mol^{-1}) Ref. [28]	Refs. [29,30]
Solid-state quench	10^3	—	16
Rapid solidification processing	10^5–10^8	2–3	24
Mechanical alloying	—	30	30
Mechanical cold work	—	—	1
Irradiation/ion implantation	10^{12}	—	30
Condensation from vapor	10^{12}	—	160

Chapter 2. Metallic Glass

Glass is any noncrystalline solid obtained by continuous cooling from the liquid state, and *amorphous solid* is any noncrystalline material obtained by any other method, except by continuous cooling from the liquid state.

If liquid is cooled, two events can occur.

1) Crystallization (solidification at $T_{m.p.}$)

2) Undercooled below $T_{m.p.}$ → More viscous → Glass
(supercooled)

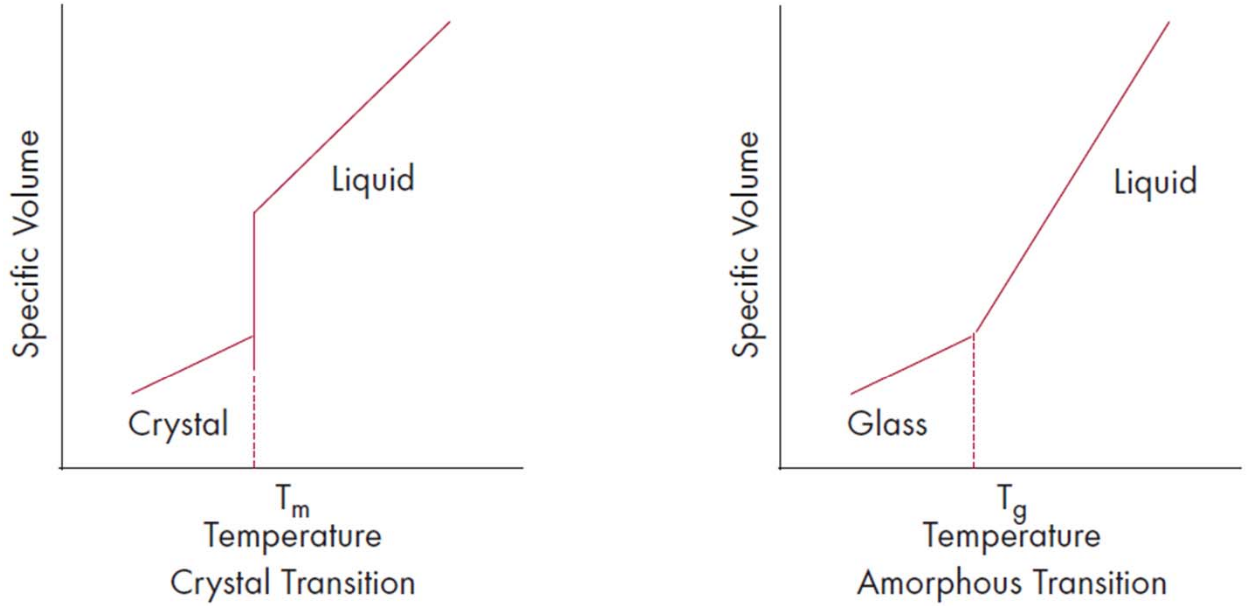


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

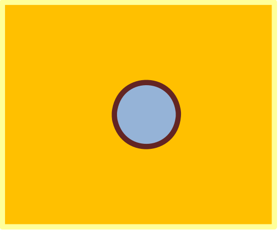
If liquid is cooled, two events can occur.

- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at T_m
  - Structures are thermodynamically controlled and described by the Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2, for example

- **The Glass Transition is a Kinetic Transition**
  - Continuous changes in structure and properties near T_g
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid

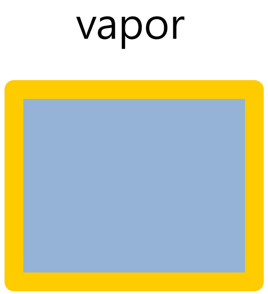
T_m Undercooled Liquid

Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL}+\gamma_{LV}<\gamma_{SV}$$



Melting: Liquid ← Solid

In general, wetting angle = 0 ⇨ No superheating required!

*** Quasi-chemical approach**

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$

- Solid: force between pairs of atoms

→ vaporize: break all "pairwise" bonds

For, example: Copper (Cu)

Vaporization **Melting**

Heat of vaporization 80 Kcal/mole vs Heat of fusion 3.1 Kcal/mole

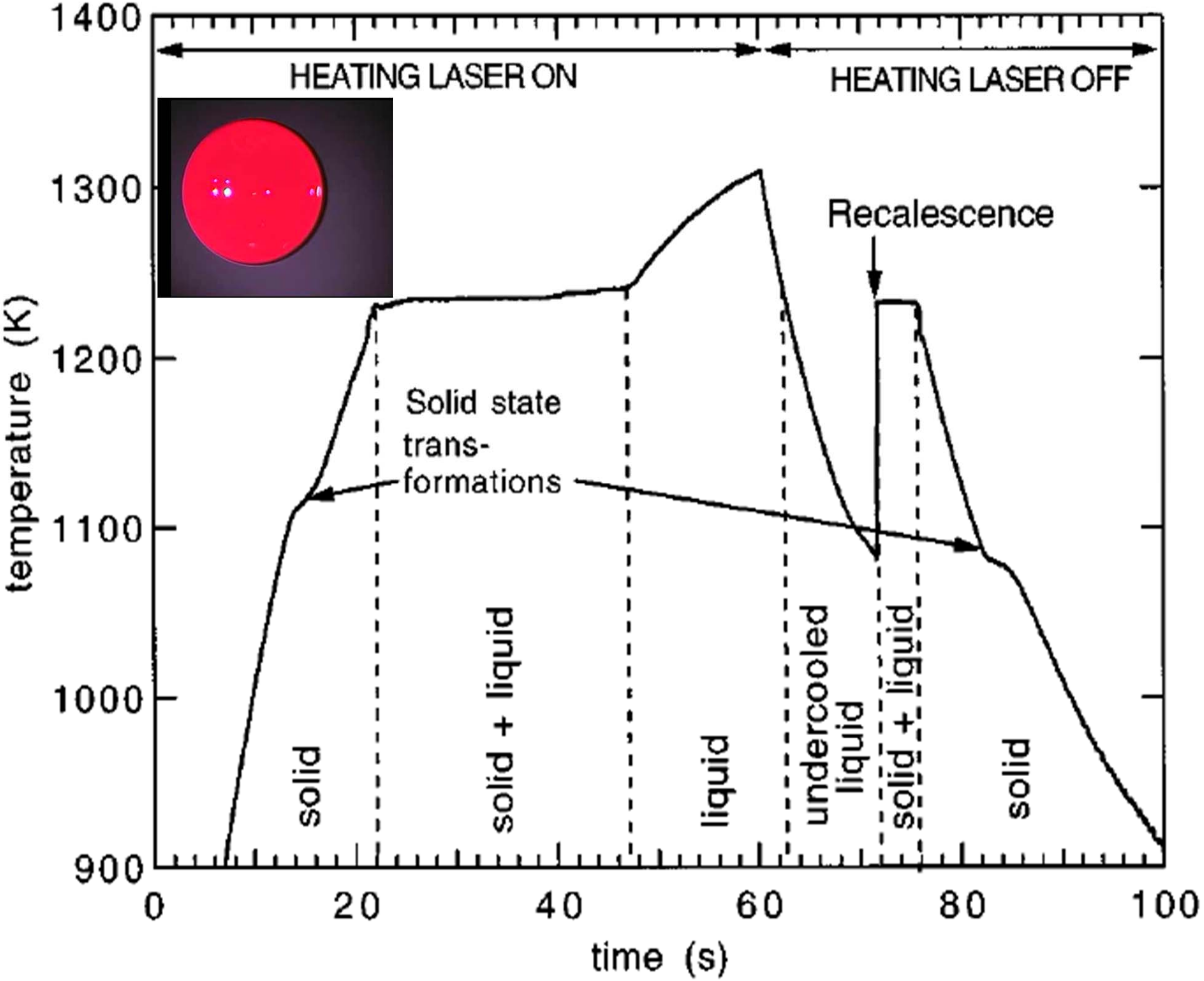
↔

25 times → 1/25 broken

Melting: each bond is replaced by one with 4 percent less E,

although bond energy of liquid is changed by the positions.

→ Heat of fusion during melting: need to generate weaker liquid bonds


HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans-formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

* Comparison between experiment and theory

Most metal ΔT_N < several K

but Turnbull and his coworker ΔT_N → larger (~several hundreds K)

by formation of large number of very small drops

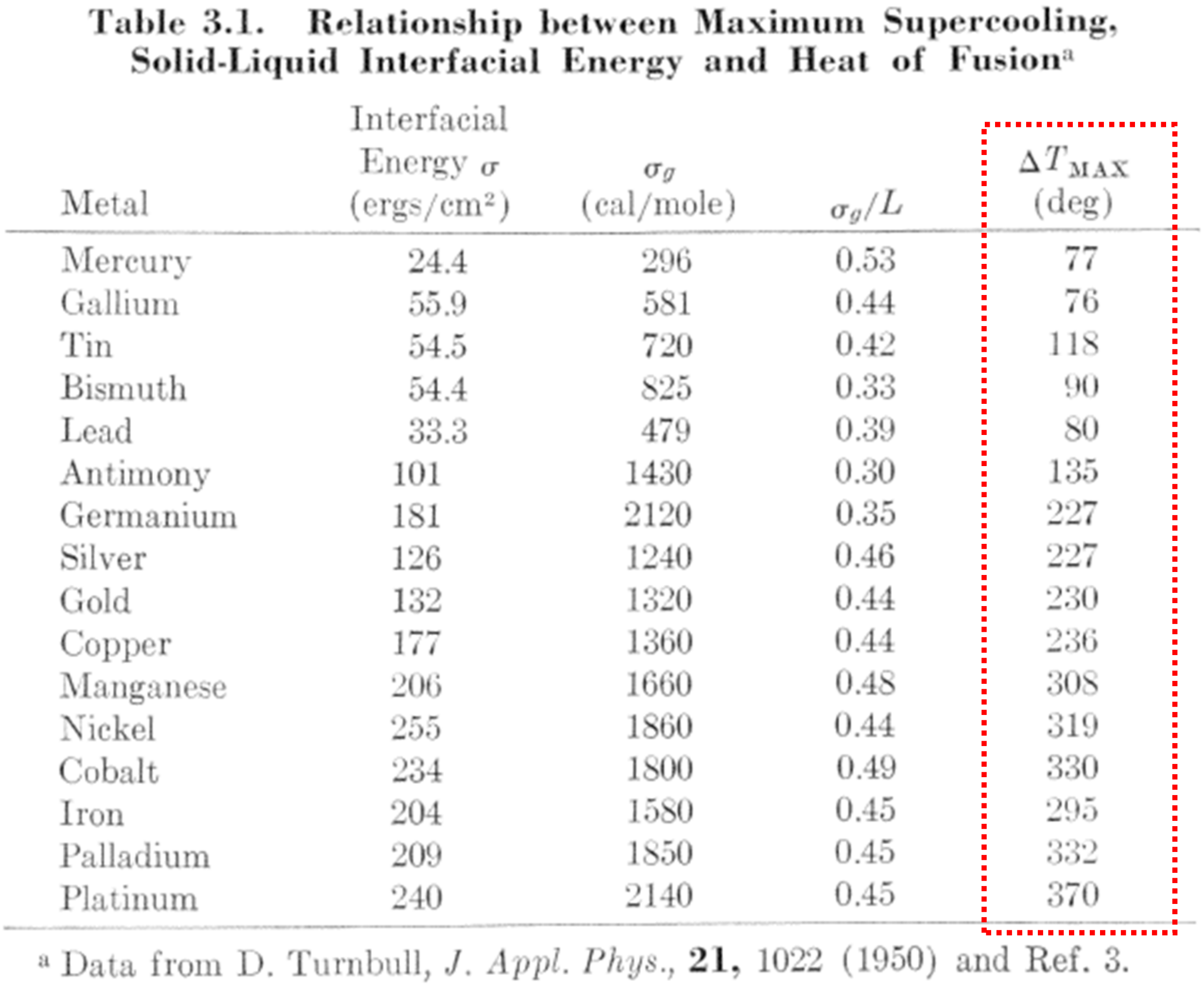


Table 3.1. Relationship between Maximum Supercooling, Solid-Liquid Interfacial Energy and Heat of Fusion[a]

Metal	Interfacial Energy σ (ergs/cm²)	σ_g (cal/mole)	σ_g/L	ΔT_{MAX} (deg)
Mercury	24.4	296	0.53	77
Gallium	55.9	581	0.44	76
Tin	54.5	720	0.42	118
Bismuth	54.4	825	0.33	90
Lead	33.3	479	0.39	80
Antimony	101	1430	0.30	135
Germanium	181	2120	0.35	227
Silver	126	1240	0.46	227
Gold	132	1320	0.44	230
Copper	177	1360	0.44	236
Manganese	206	1660	0.48	308
Nickel	255	1860	0.44	319
Cobalt	234	1800	0.49	330
Iron	204	1580	0.45	295
Palladium	209	1850	0.45	332
Platinum	240	2140	0.45	370

[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

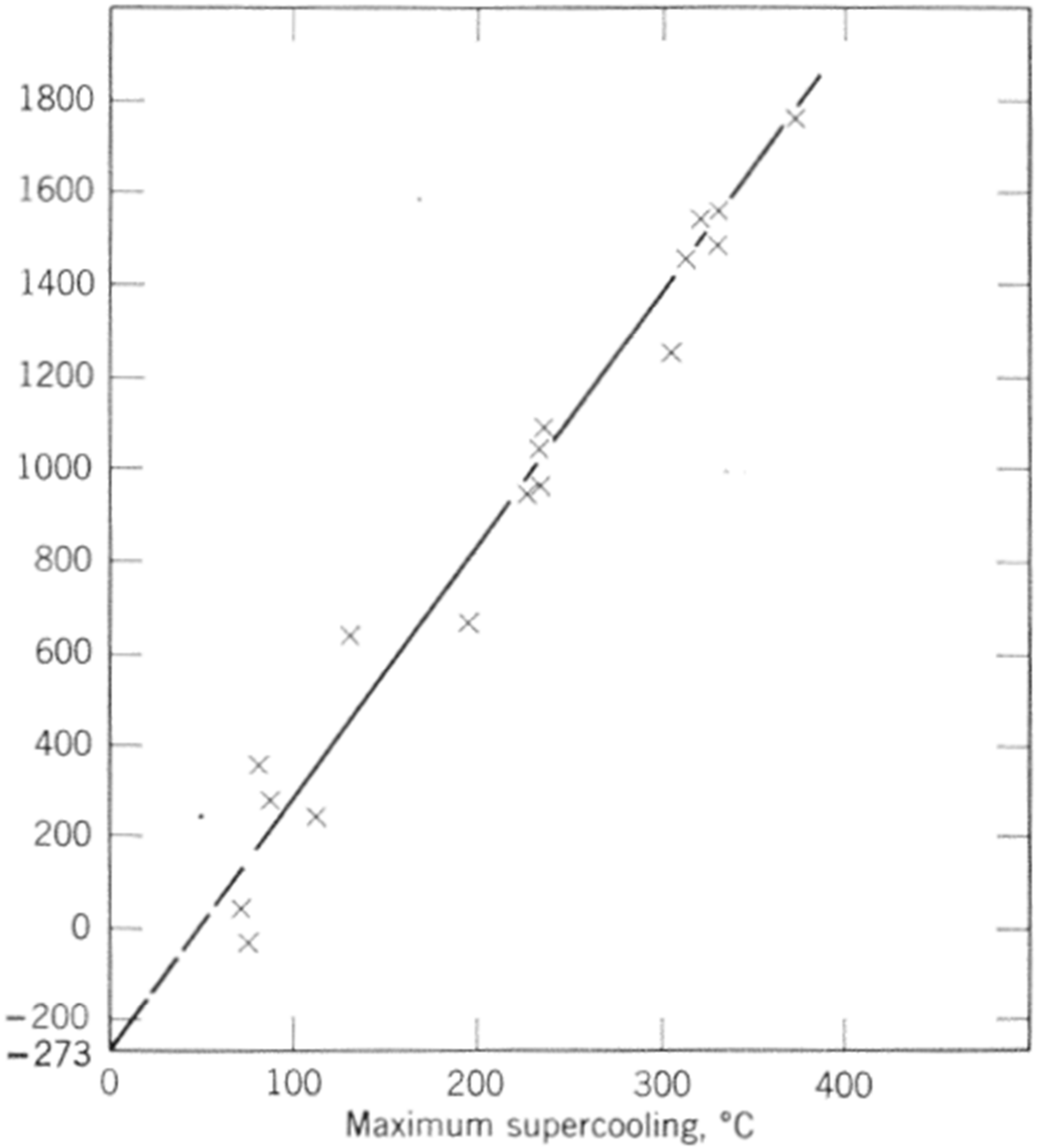
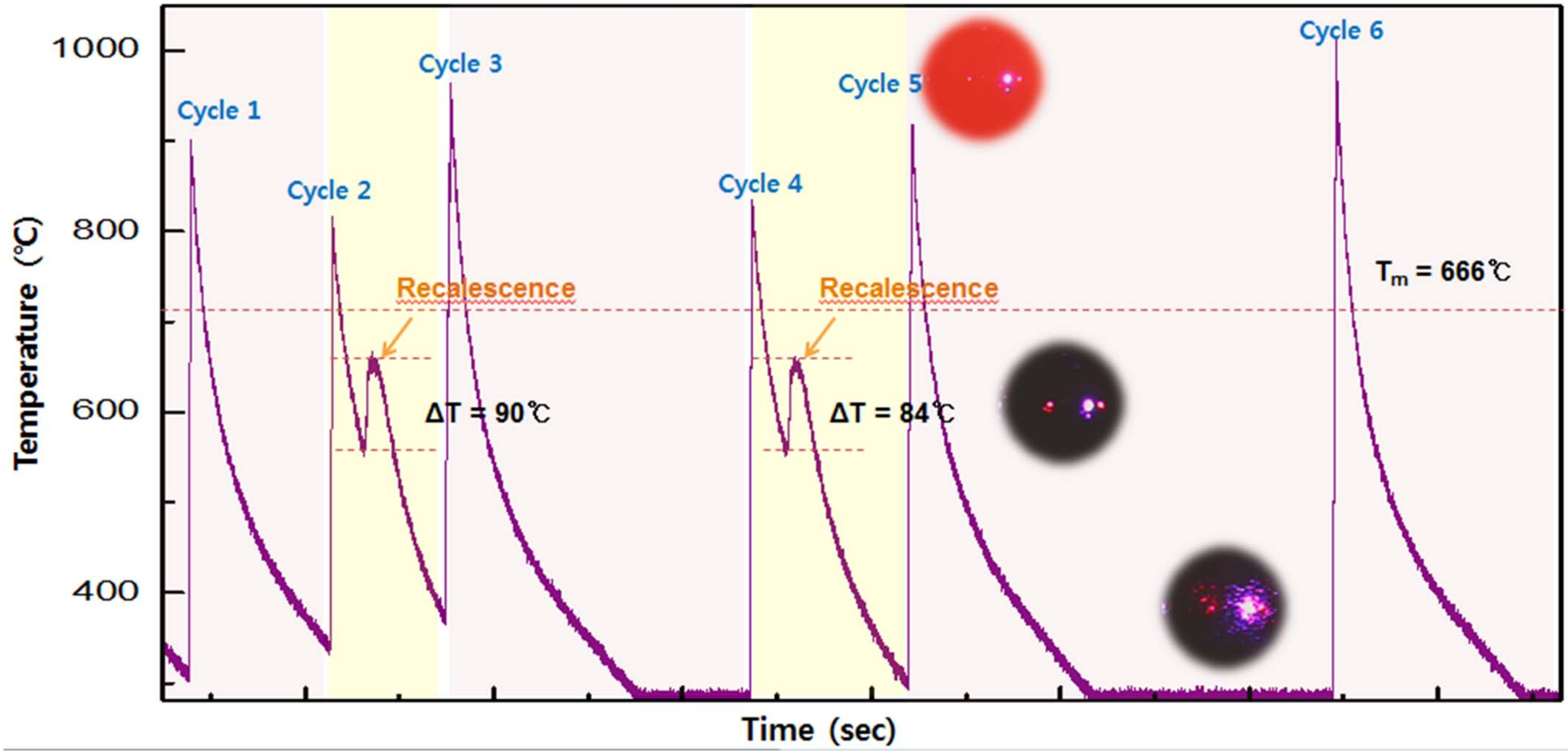


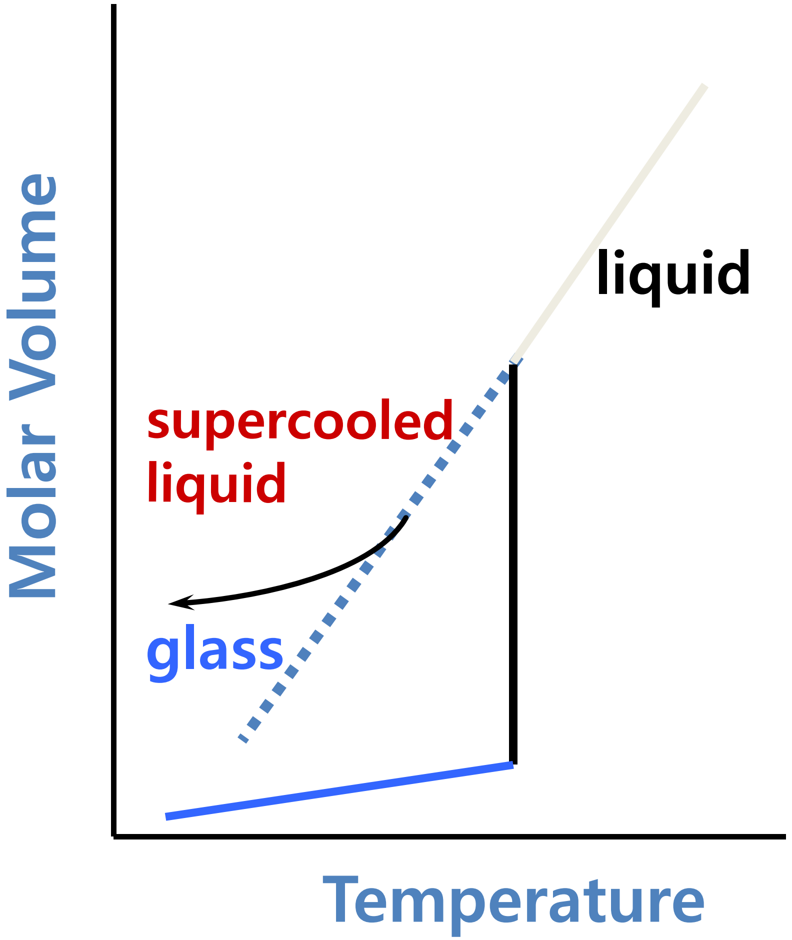
Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy,* American Society for Metals, Cleveland, 1911, p. 11.)

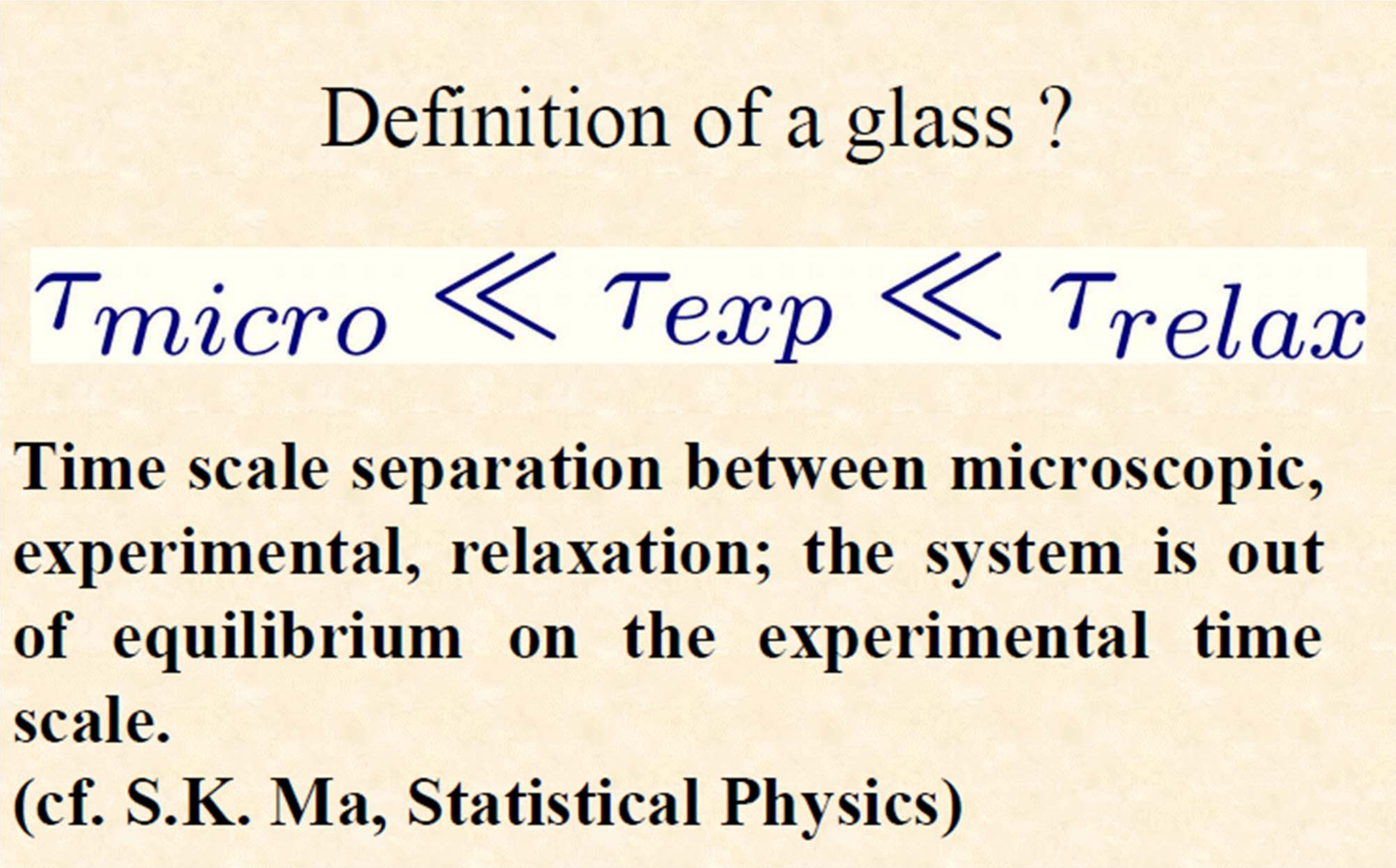
Cyclic cooling curves in ESL



Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - "Internal" time scale controlled by the viscosity (bonding) of the liquid
  - "External" timescale controlled by the cooling rate of the liquid





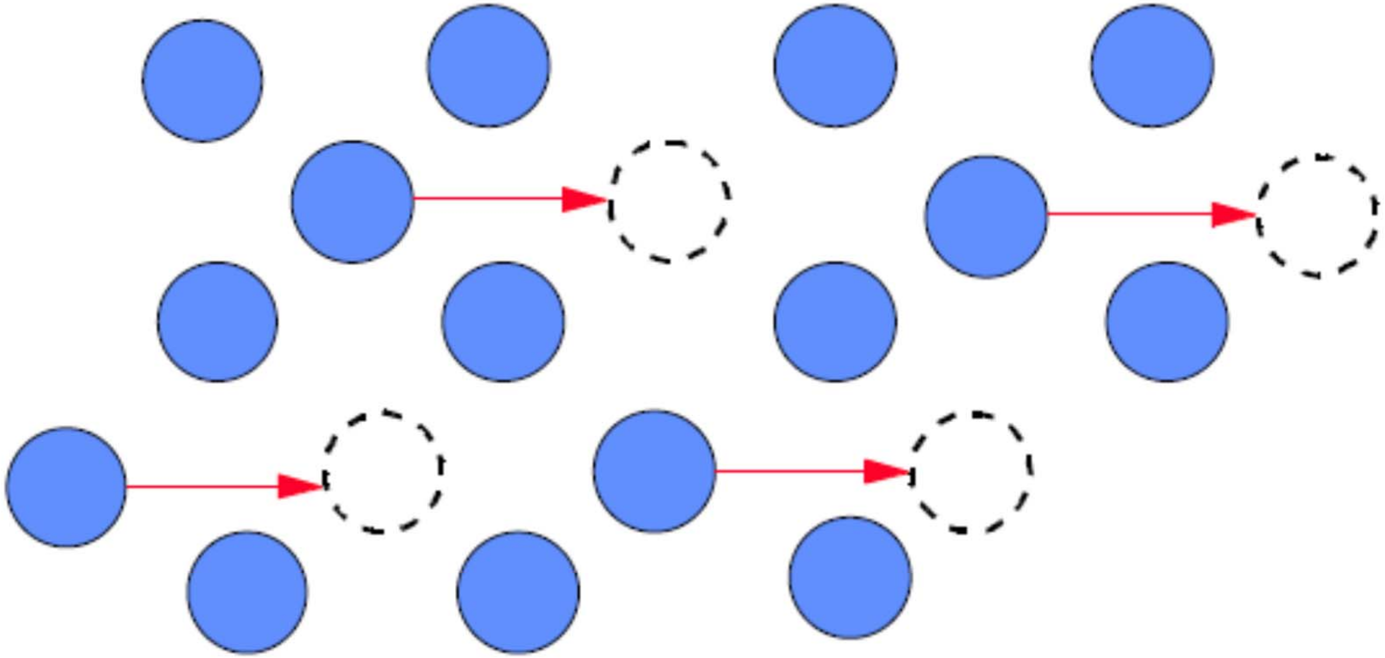
Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

Microscopic time: time for events at sub-atomic distance and duration

Temperature Dependence of Liquid Viscosity



Viscosity is a measure of the resistance to flow. The higher T, the larger the average size of the holes and the larger the energy of the molecules, the easier the molecule move past oneanother, the lower the resistance to flow.

Viscosity indicates the resistance to flow of a system and is a measure of its internal friction. The International System unit of viscosity is Pa s = kg m^{-1} s^{-1}. An older unit is Poise, P with the relationship:

$$1 \text{ P} = 0.1 \text{ Pa s} \tag{2.1}$$

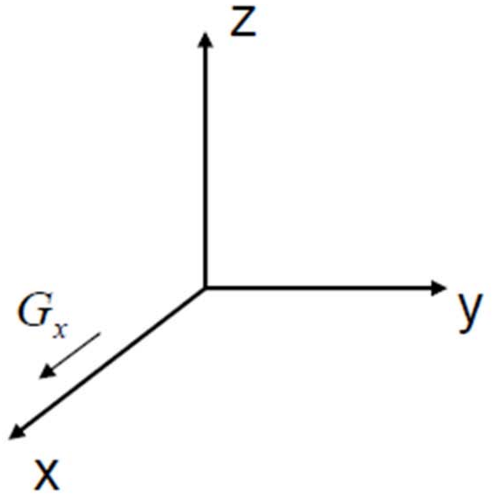
As a reference point, water at 20°C has a viscosity of 1 centiPoise, cP (10^{-2} Poise). The viscosities of some substances of common use are:

Water at 20°C	1.002 cP (1.002×10^{-3} Pa s)
Mercury at 20°C	1.554 cP (1.554×10^{-3} Pa s)
Pancake syrup at 20°C	2,500 cP (2.5 Pa s)
Peanut butter at 20°C	250,000 cP (250 Pa s)
Soda glass at 575°C	1×10^{15} cP (1×10^{12} Pa s)

As defined above, the glass transition temperature, T_g, is the temperature at which the supercooled liquid becomes solid glass. To be more accurate, this should be called the thermal or calorimetric glass transition. It is also important to realize that this "transition" is not a true thermodynamic phase transition, but its origin is strictly kinetic, since the value of T_g depends on the cooling rate and, more generally, on the way the glass is prepared.

* Glass: Solid? or liquid?

$$\eta = G_x / (\frac{dv_x}{dz})$$



G_x : *Shear stress in x direction*

→ causing velocity gradient: $\frac{dv_x}{dz}$

dz: thickness of element perpendicular to the applied stress

small stress

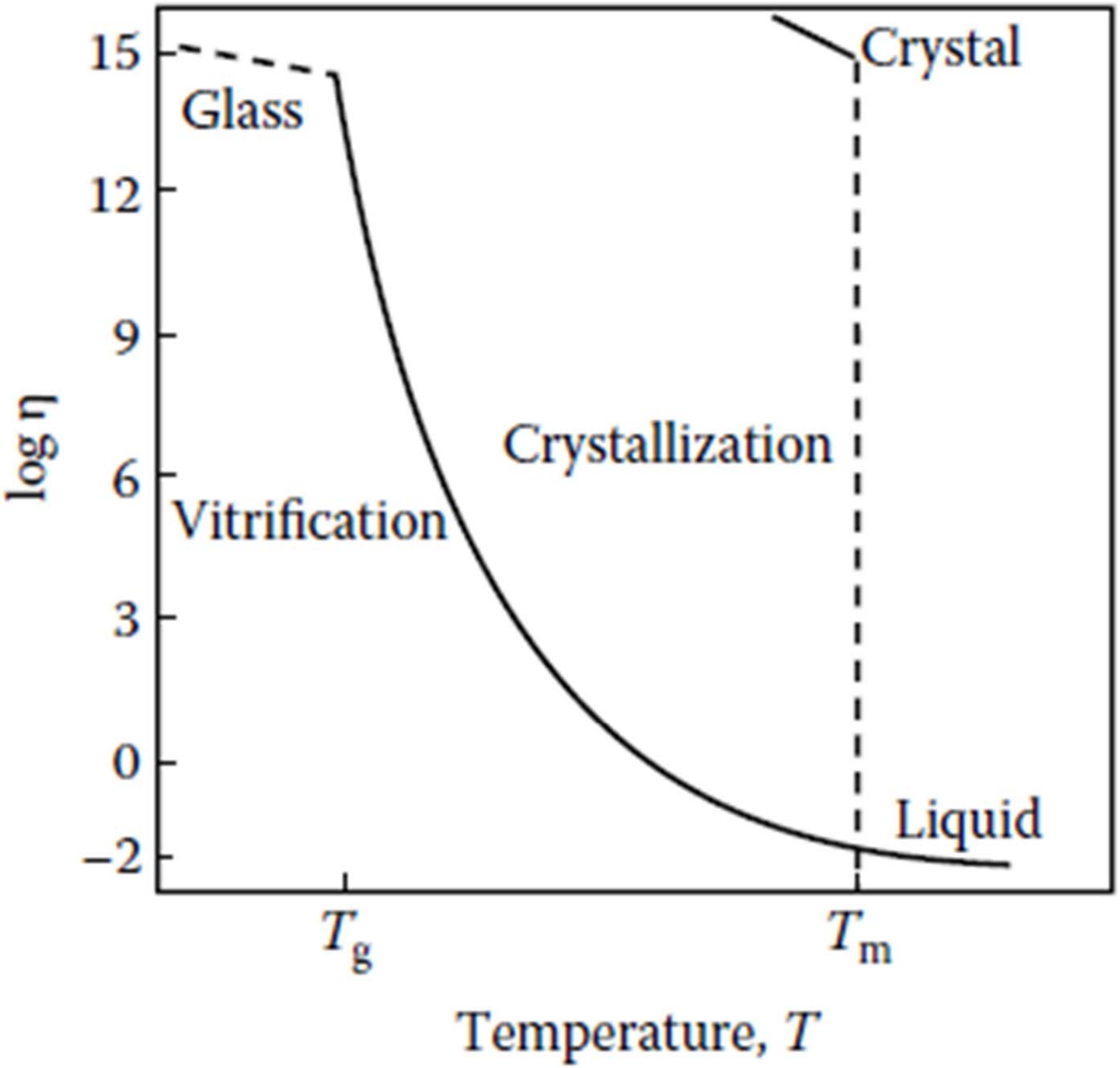
ex) *100 N applies for one day to 1 cm^3 of material having viscosity of $10^{14.6}$ poise*

→ *yield deformation of* <u>*0.02 mm*</u>

just measurable

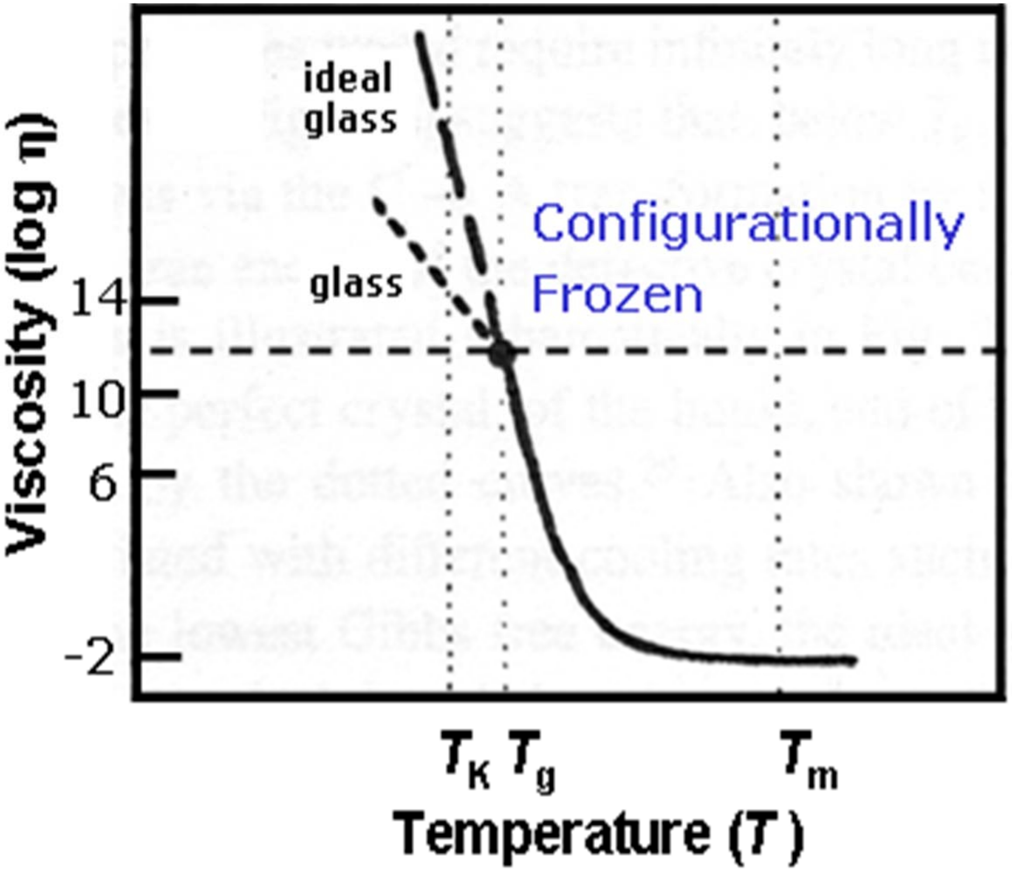
→ ***Solid*** **: application of small force for one day produces no permanent change.**

Variation of viscosity with temperature for crystal and glass formation



Glass : undercooled liquid with high viscosity

The higher the structural relaxation, the closer it moves toward a "true" glass.

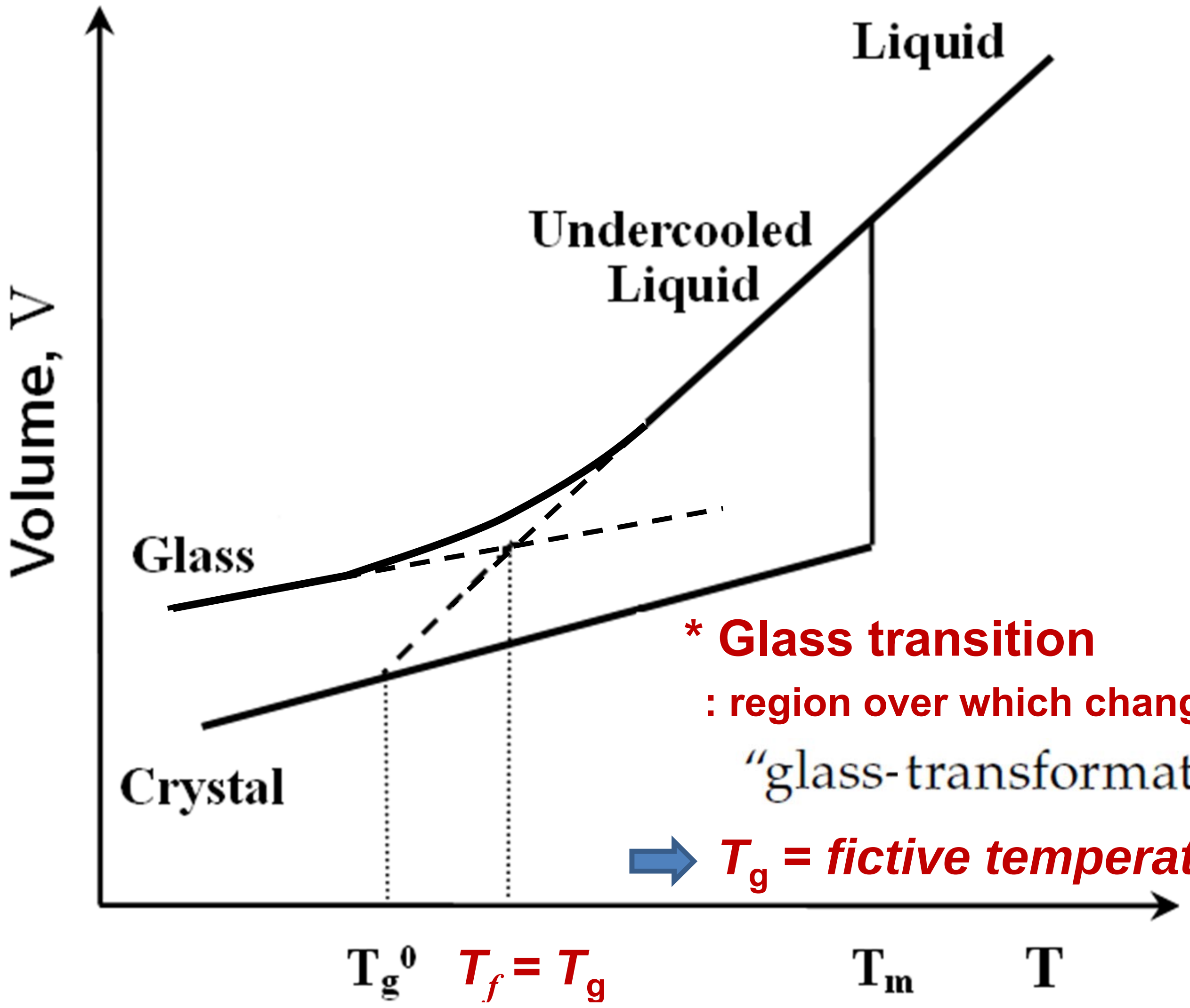


A solid is a materials whose viscosity exceeds $10^{14.6}$ centiPoise (10^{12} Pa s)

cf) liquid ~*10^{-2} poise*

* Glass transition

On cooling, although the driving force for nucleation is continually increasing, this is opposed by the rapidly decreasing atomic mobility which, at very high undercoolings, dominates. Eventually, homogeneously frozen at T_g.



* Glass transition

: region over which change of slope occurs

"glass-transformation interval."

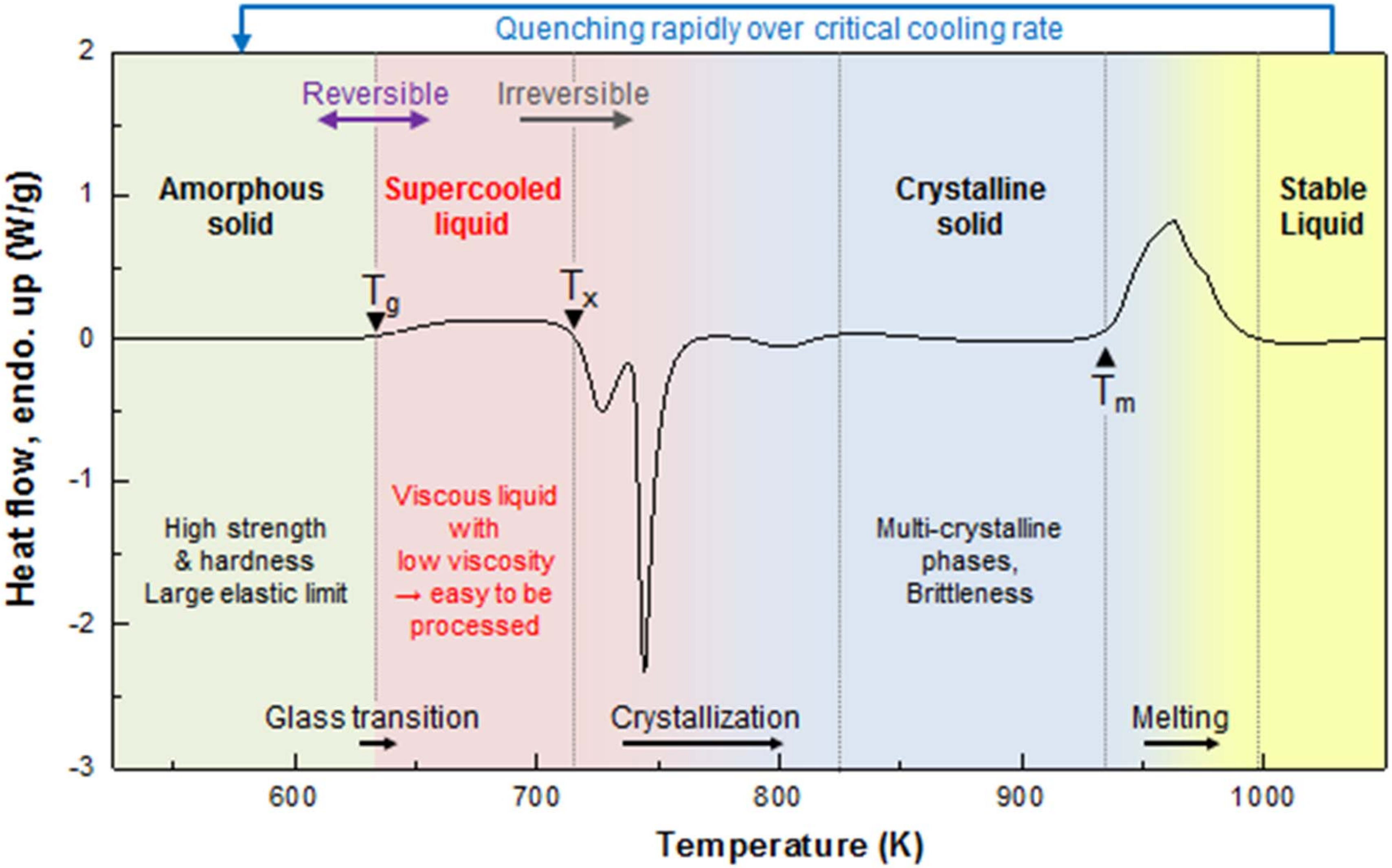
⇨ ***T_g = fictive temperature, T_f***

thermodynamic property ?

thermodynamic property

DSC trace of Vitreloy 1

: the temperature regions sectioned according to phase transformations

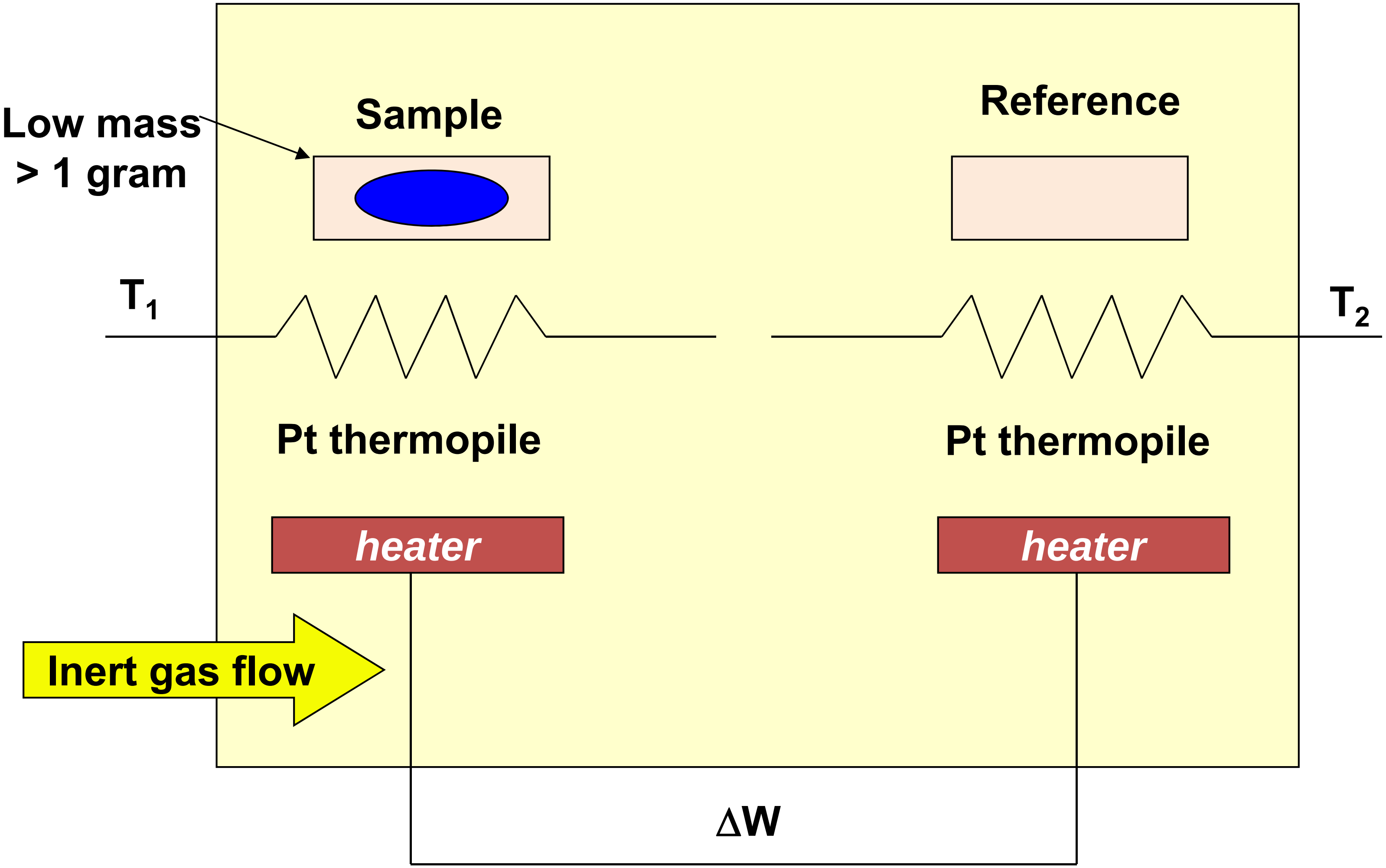


ΔT_x : indication of thermal stability of the glass produced

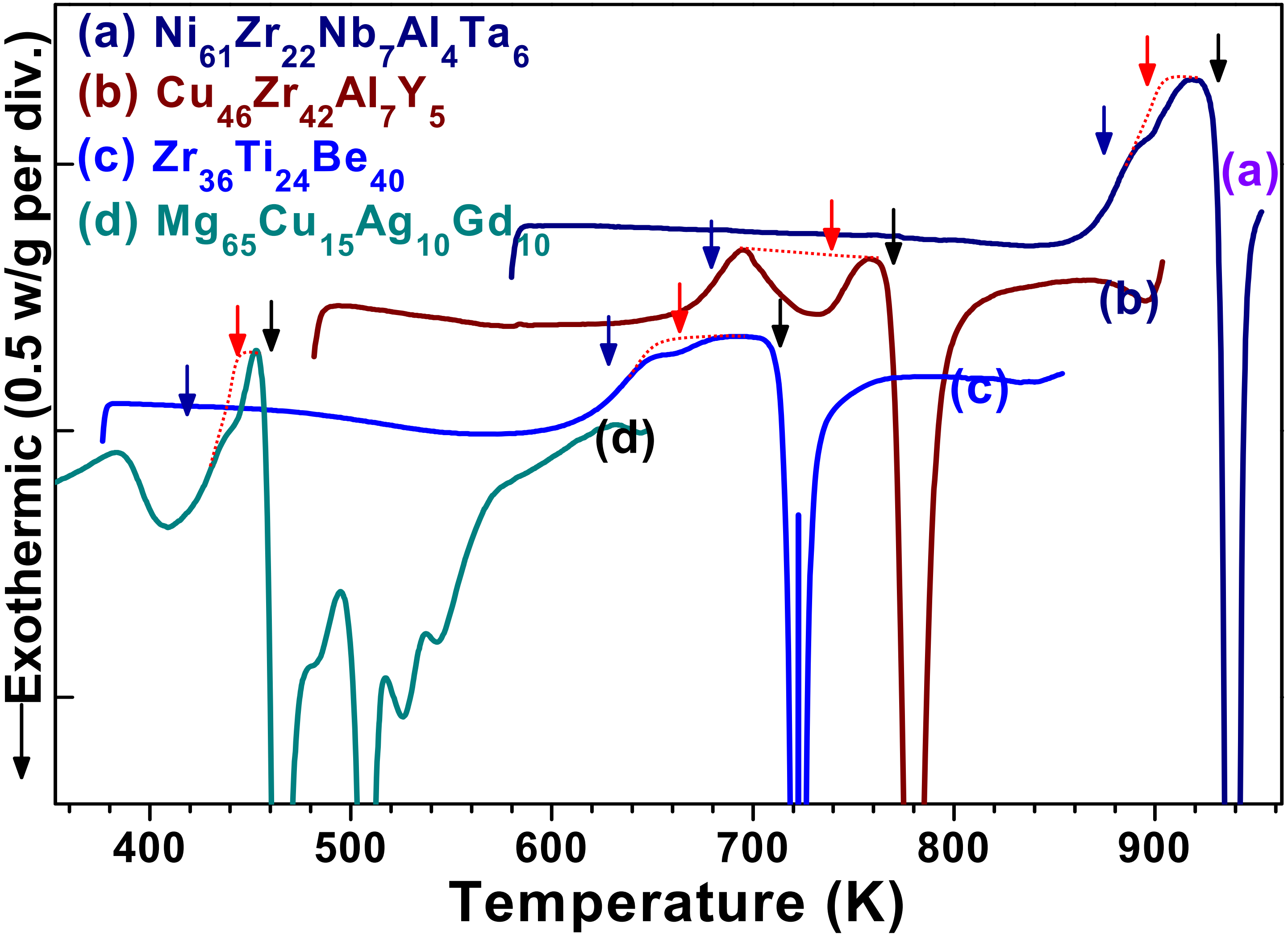
Thermal analysis: DSC

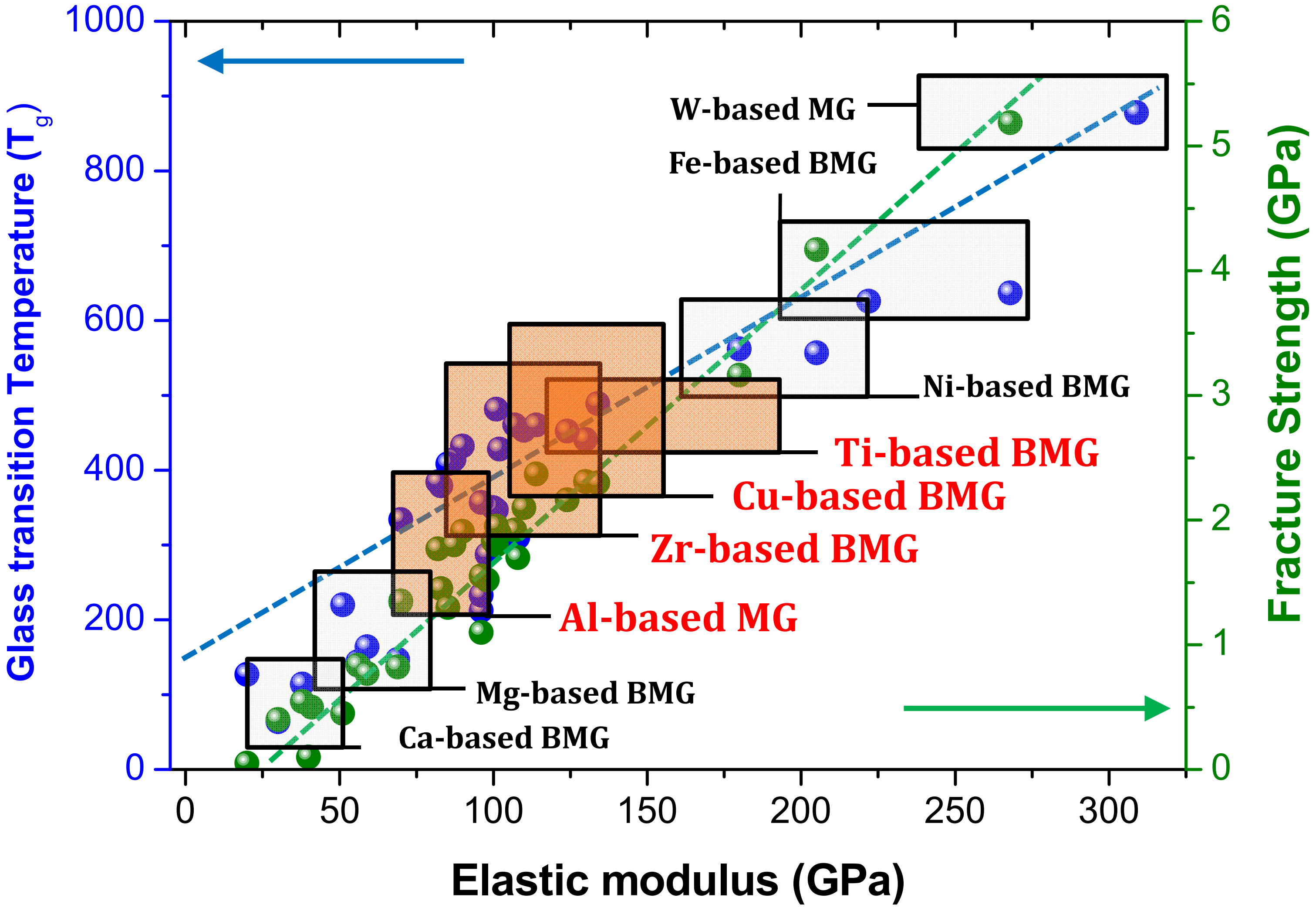
- A *calorimeter* measures the heat into or out of a sample.
- A *differential calorimeter* measures the heat of a sample relative to a reference.
- A *differential scanning calorimeter* does all of the above and heats the sample with a linear temperature ramp.
- Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere.

Schematic of DSC Instrument



Variation of T_g depending on alloy compositions → Broken Bonds




Glass transition Temperature (T_g)
1000
800
600
400
200
0
Fracture Strength (GPa)
6
5
4
3
2
1
0
0
50
100
150
200
250
300
Elastic modulus (GPa)
W-based MG
Fe-based BMG
Ni-based BMG
Ti-based BMG
Cu-based BMG
Zr-based BMG
Al-based MG
Mg-based BMG
Ca-based BMG

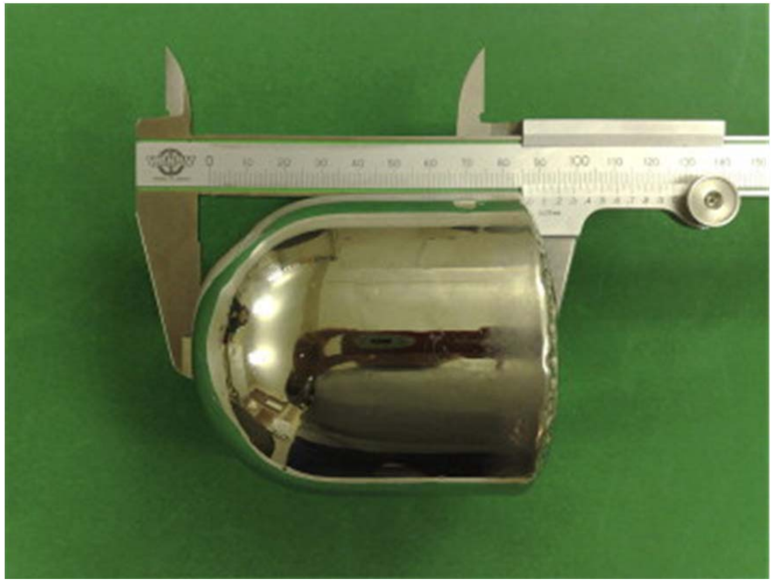
At a temperature T_x, which is higher than T_g, the supercooled liquid transforms into the crystalline phase(s). As mentioned earlier, the temperature interval between T_x and T_g is referred to as the width of the supercooled liquid region (SLR), that is, $\Delta T_x = T_x - T_g$. The value of ΔT_x is different for different glasses, and is usually taken as an indication of the thermal stability of the glass produced. In the case of BMGs, this temperature interval is usually quite large and values of over 120 K have been reported; the highest reported to date is 131 K in a $Pd_{43}Cu_{27}Ni_{10}P_{20}$ BMG alloy [17]. In the case of rapidly solidified thin ribbon glasses, and marginal glass-formers, the value of ΔT_x is very small, if observed at all.

$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

2012

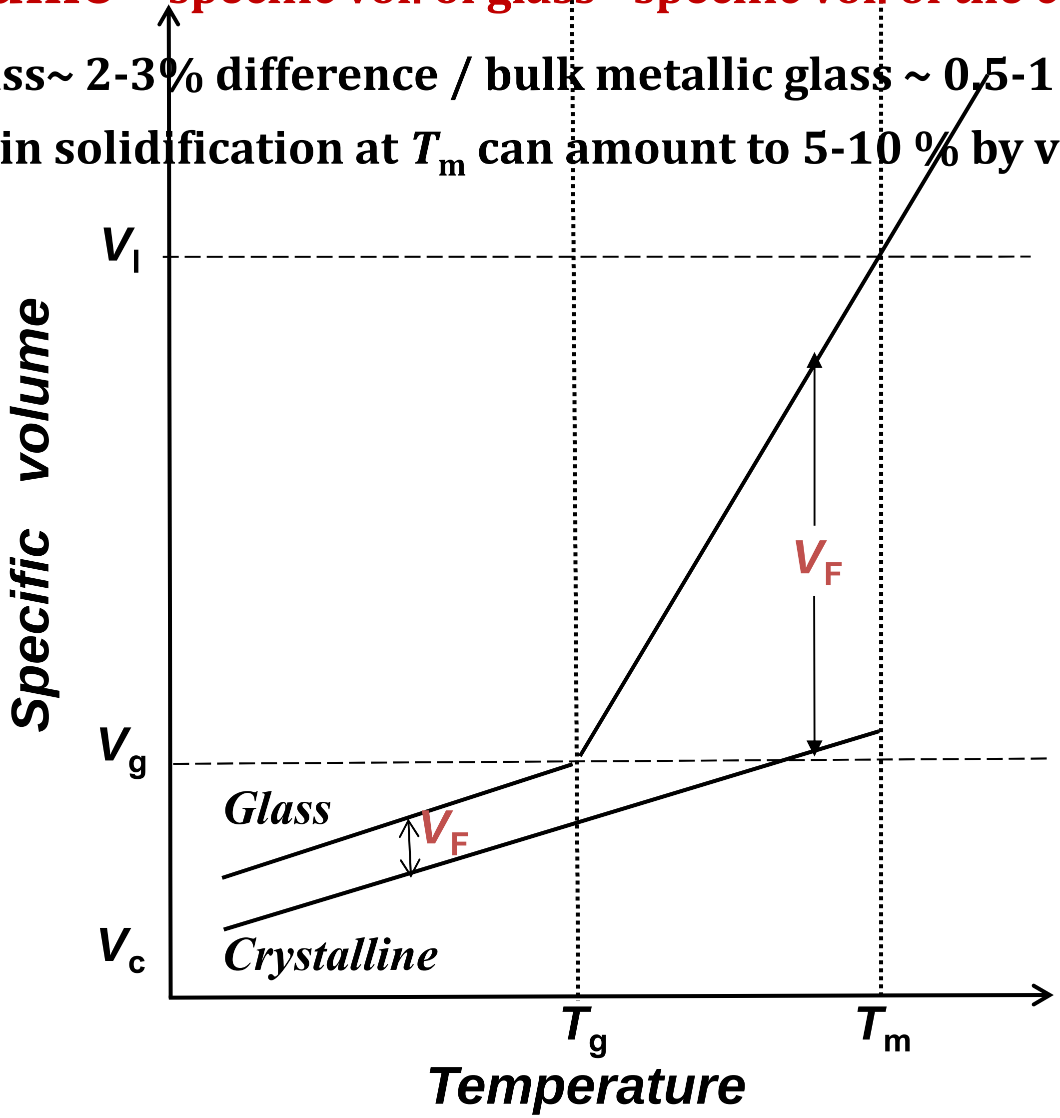
D_{max} 80mm

Intermetallics, Vol30, Nov2012, P 19–24



* **Free volume** = specific vol. of glass - specific vol. of the corresponding crystal

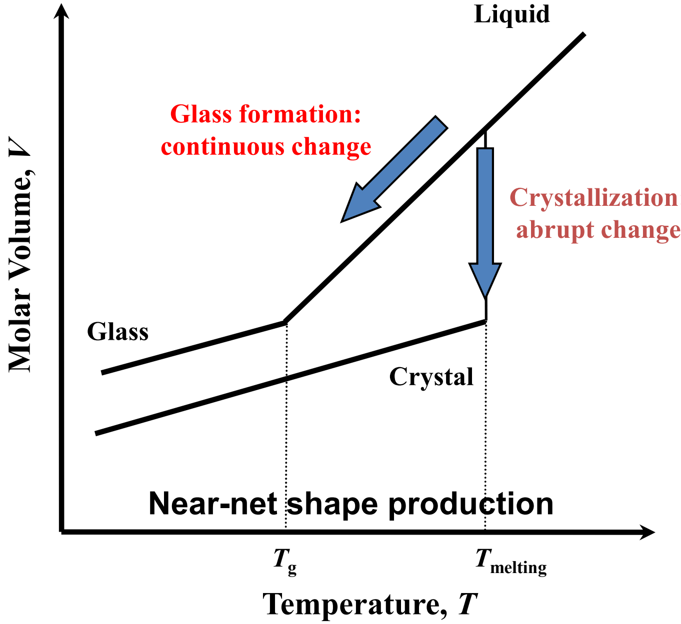
- normal glass~ 2-3% difference / bulk metallic glass ~ 0.5-1 % difference
- Shrinkage in solidification at T_m can amount to 5-10 % by volume.



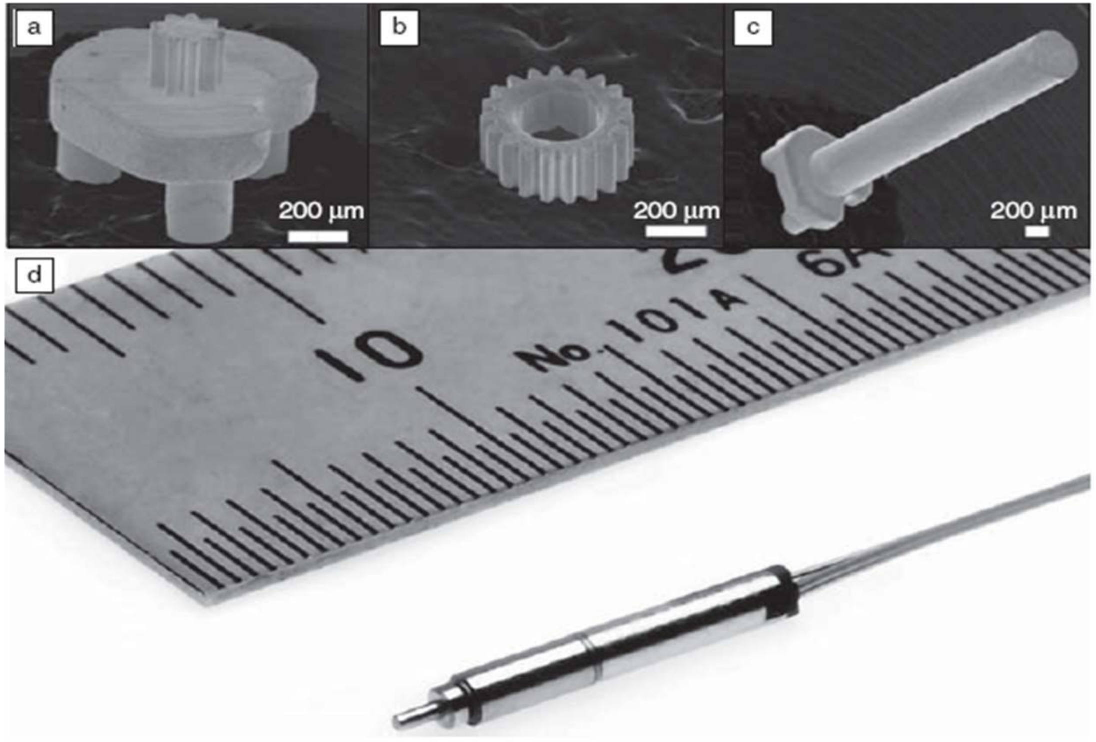
At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior.

Below the glass transition temperature, atoms (ions) are not mobile and the material behaves like solid

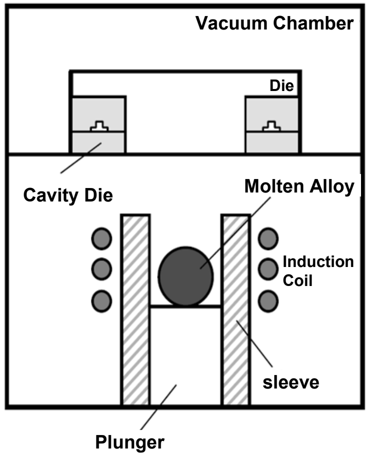
* Micro/Nano casting



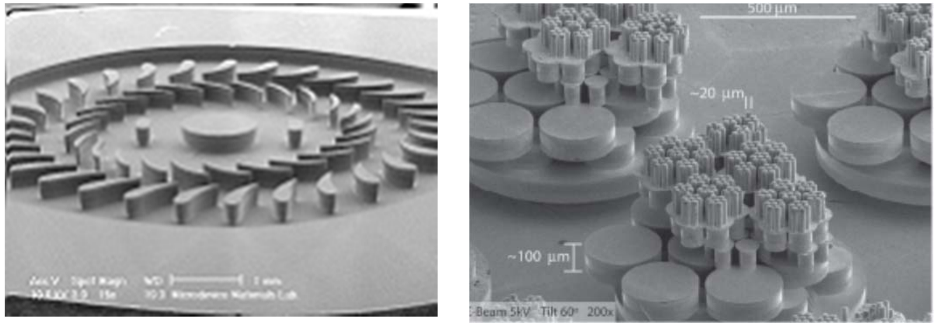
Near-net shape production



Precision Gears for Micro-motors



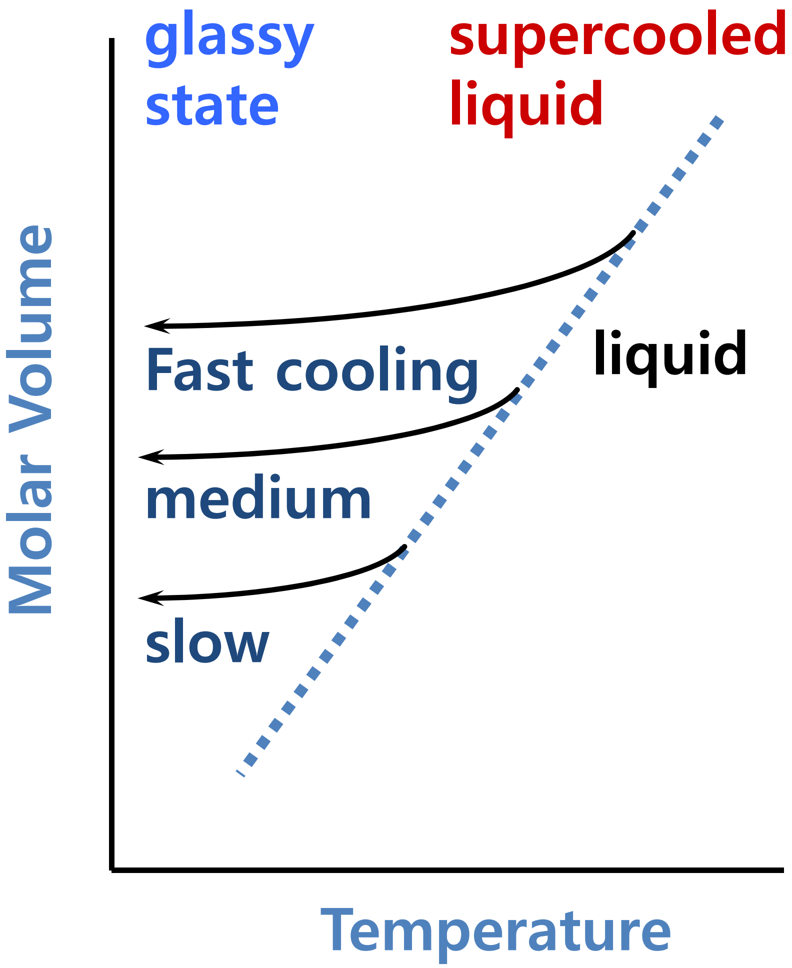
Precision die casting



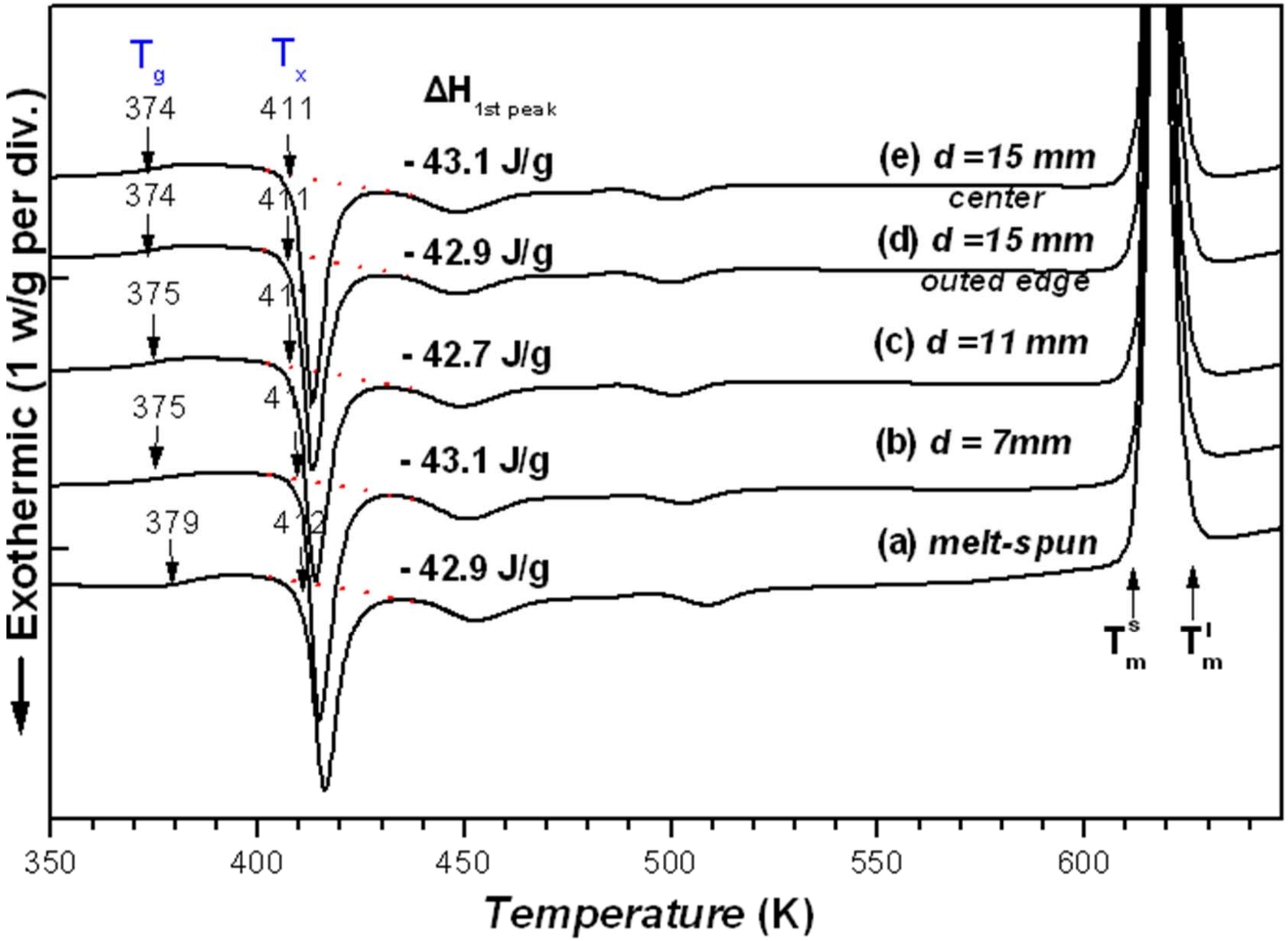
MRS BULLETIN ***32*** *(2007)654.*

The Cooling Rate Affects the Properties of Glass

- Faster cooling freezes in the glass at a higher temperature
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature

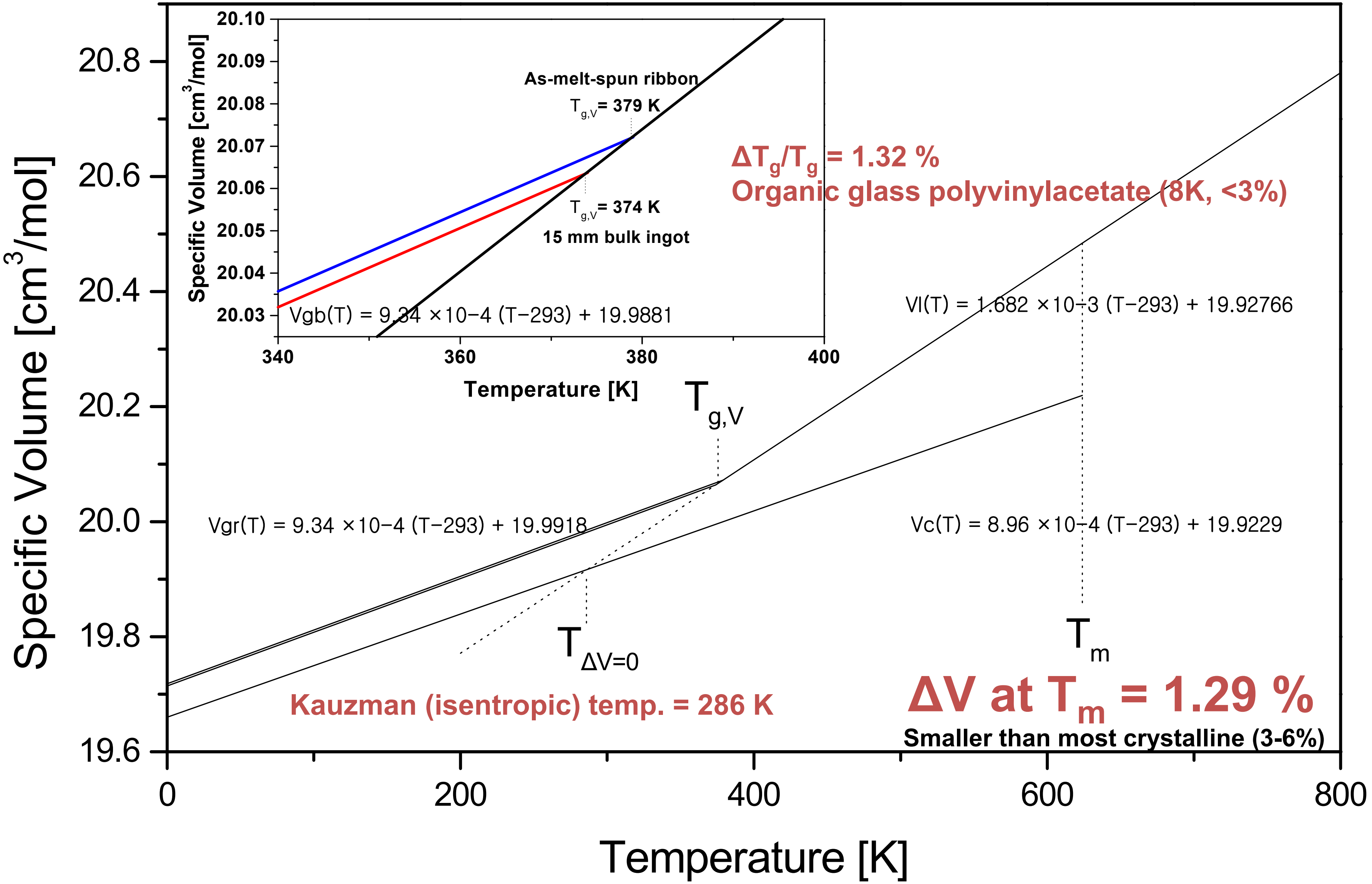


❖ Typically T_g is ~ 50-60% of the melting point. (0.6T_m)



*** J Mater Res, 19 (2004) 685.**

* T_g depends on thermal history even in same alloy composition.



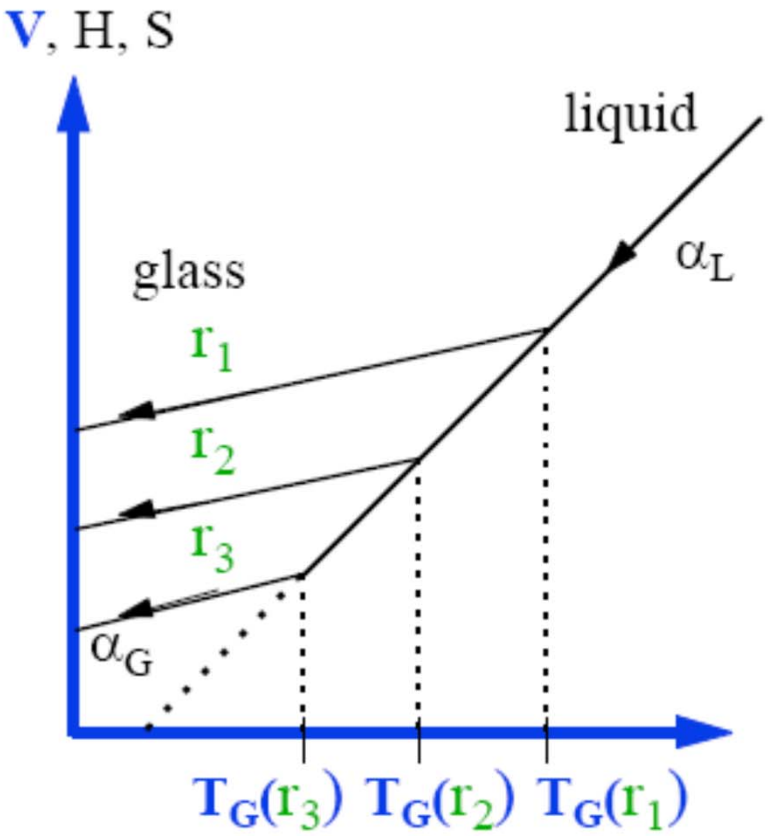
$\Delta T_g/T_g$ = 1.32 %
Organic glass polyvinylacetate (8K, <3%)

Kauzman (isentropic) temp. = 286 K

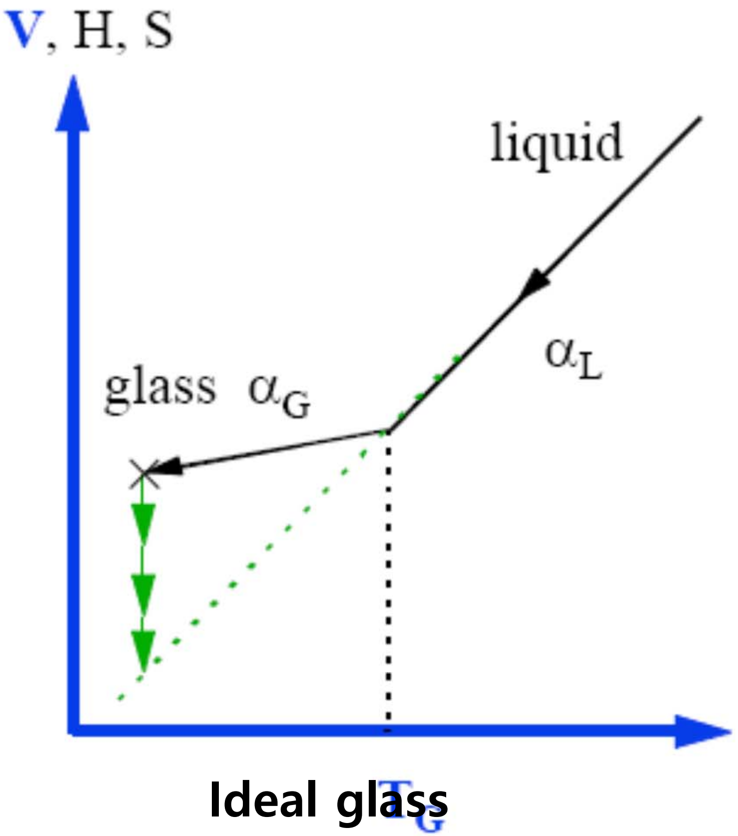
ΔV at T_m = 1.29 %
Smaller than most crystalline (3-6%)

*** APL, 92 (2008) 091915.**

* Kinetic Nature of the Glass Transition



Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



Specific Volume (density) of the glass depends on the time at a given $T < T_g$

* Glass → exited state –(sufficient time)→ relax and eventually transform to crystalline ground state

2.5 Thermodynamics and Kinetics of Glass Formation

"Phase Transition"

Thermodynamically: what is possible!
Kinetics: speed/rate of the transition

Thermodynamical classification: first order & second order

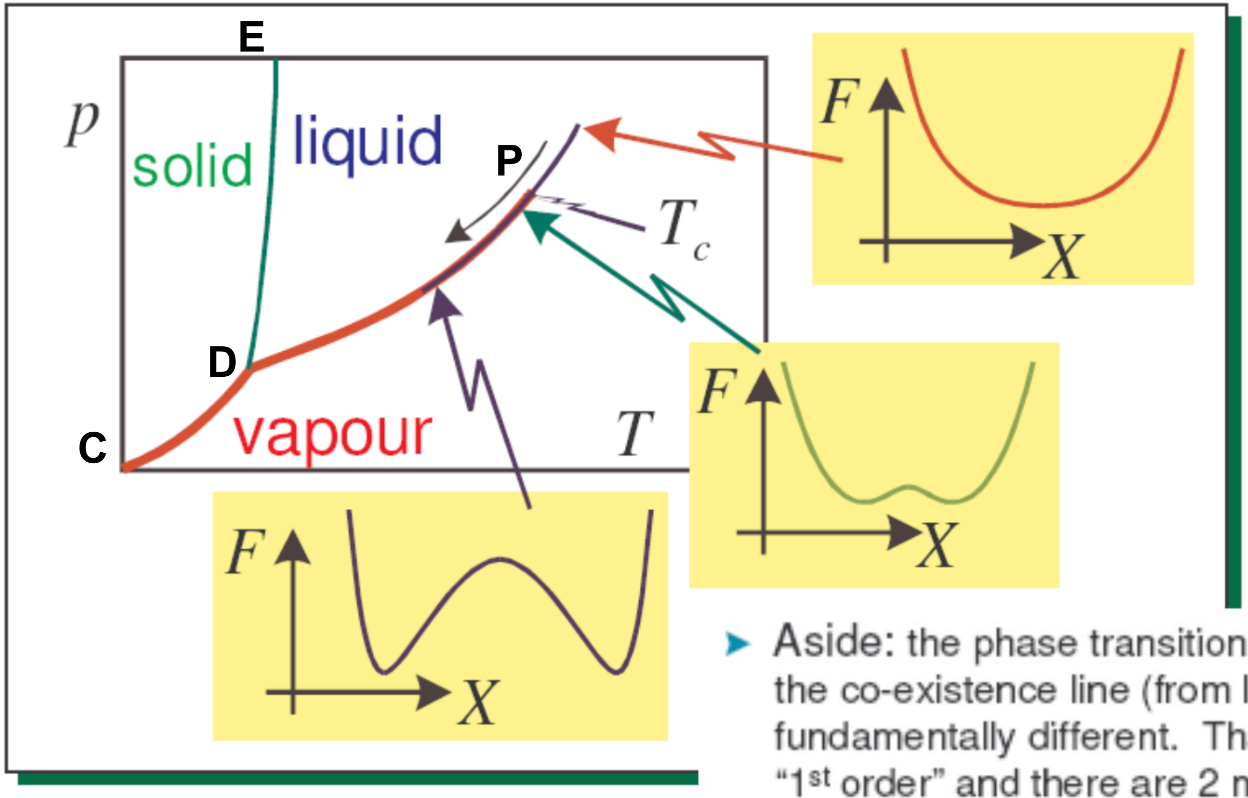
$$\Delta G = \Delta H - T\Delta S = 0$$

- ## Order (degree) of transition

Continuous phase transitions:

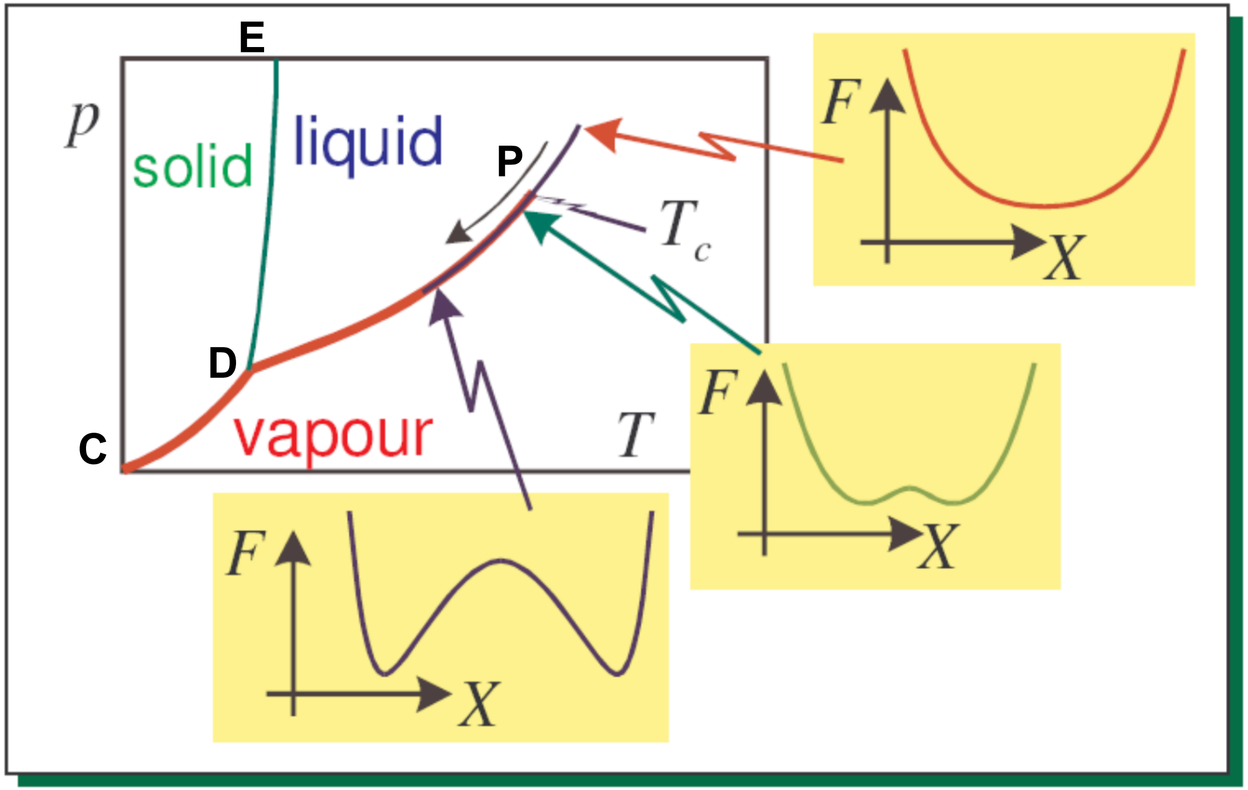
occur when the minimum in the thermodynamic potential evolves smoothly into two equal minima.

An example is seen in the model of phase separation, along the co-existence line.



- Aside: the phase transition as one moves across the co-existence line (from liquid to vapour) is fundamentally different. That transition is known as "1st order" and there are 2 minima in the potential throughout. In the transition the lowest minimum changes from liquid to vapour (and vice-versa).

- **Order (degree) of transition**



- CD, DE, DP: Equilibrium of 2 phases

  → latent heat

  → Volume change

  → 1st order transition

- T and P beyond point p

  : vapor and liquid are indistinguishable.

  → Single phase: only property changes.

  → No boiling pt. / no latent heat

  → Higher order transition

First-order transition:
a discontinuity occurs in the first derivative of the free energy with respect to T and P.

Discontinuous enthalpy, entropy and volume

$$\frac{dG}{dT} = -S$$

$$\frac{dG}{dP} = V$$

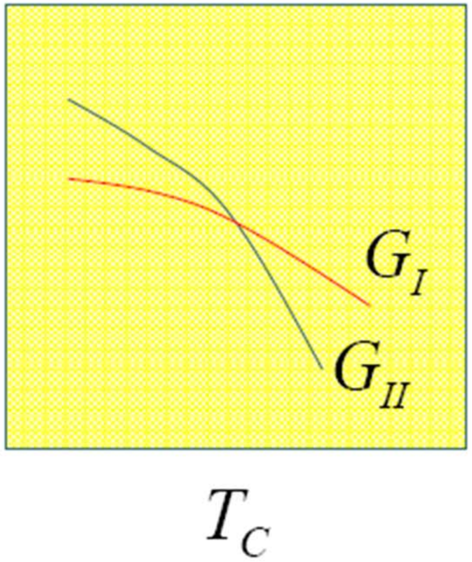
Examples: CsCl structure to NaCl structure; T =479 C.

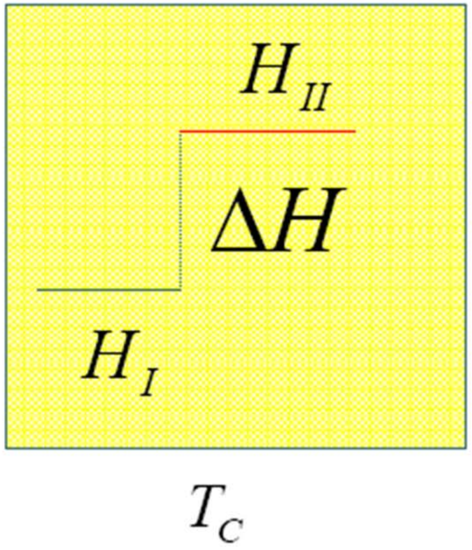
$$\Delta V = 10.3 cm^3$$

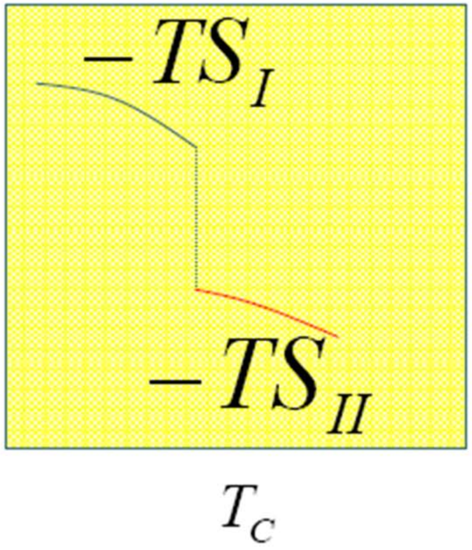
$$\Delta H = 2.424 kJ/mol$$

Melting, freezing, vaporization, condensation…

First-order transition:







Second order transition: Discontinuities in the second derivatives of the free energy, i.e. heat capacity, thermal expansion, compressibility.

Enthalpy, entropy and volume, continuous functions of T

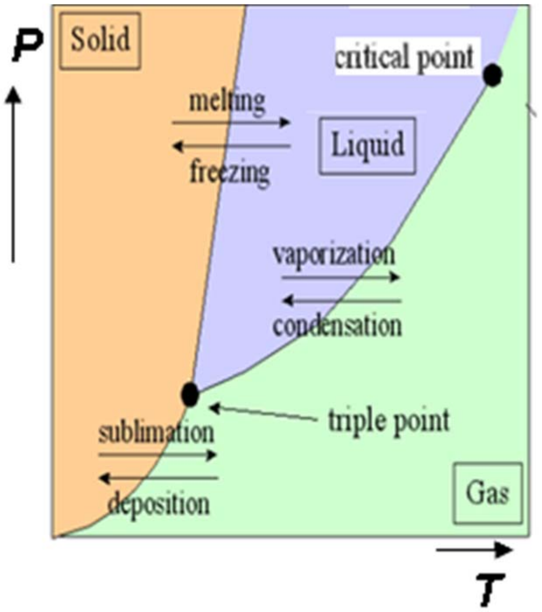
$$\frac{\partial^2 G}{\partial P_T^2} = \frac{\partial V}{\partial P_T} = -V\beta(compressibility)$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T_P} = V\alpha(thermal \exp ansion)$$

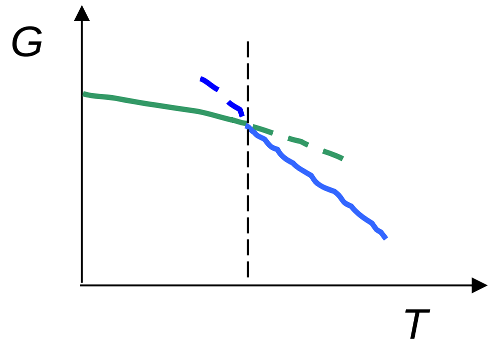
$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T_P} = -\frac{C_p}{T}$$

Measurement of heat capacities (calorimetry)

The First-Order Transitions



Latent heat
Energy barrier
Discontinuous entropy, heat capacity



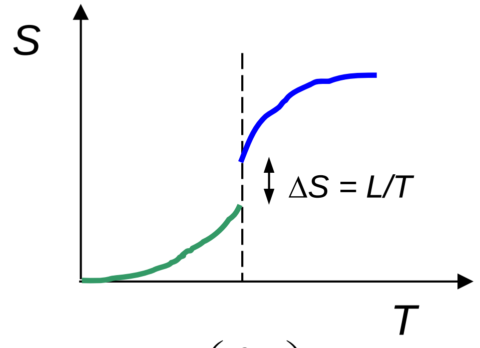
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

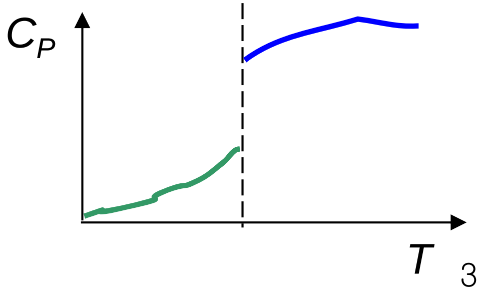
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

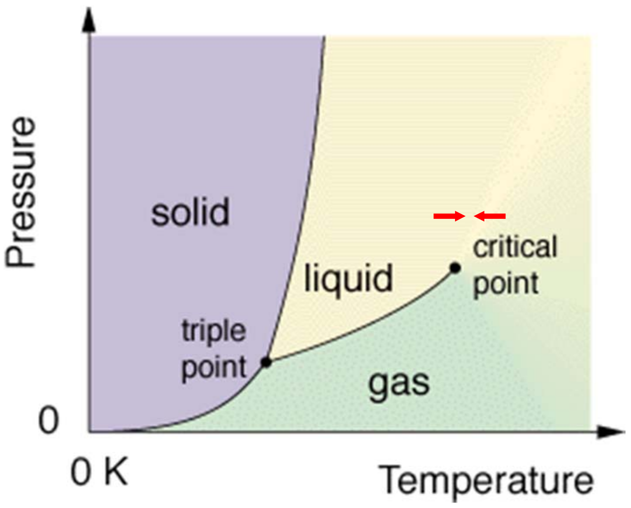
  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.



$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$



The Second Order Transition



No Latent heat
Continuous entropy

- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

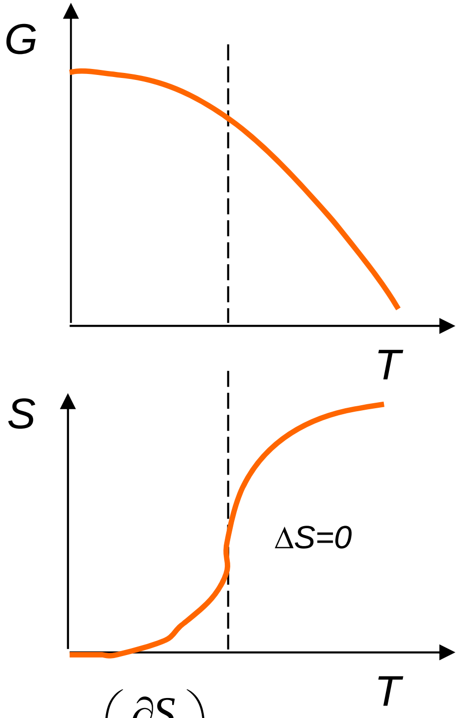
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

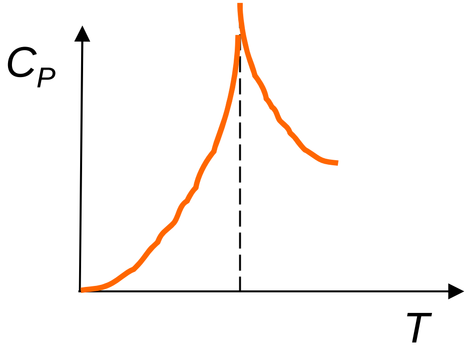
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Second-order transition



$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \to \infty$$

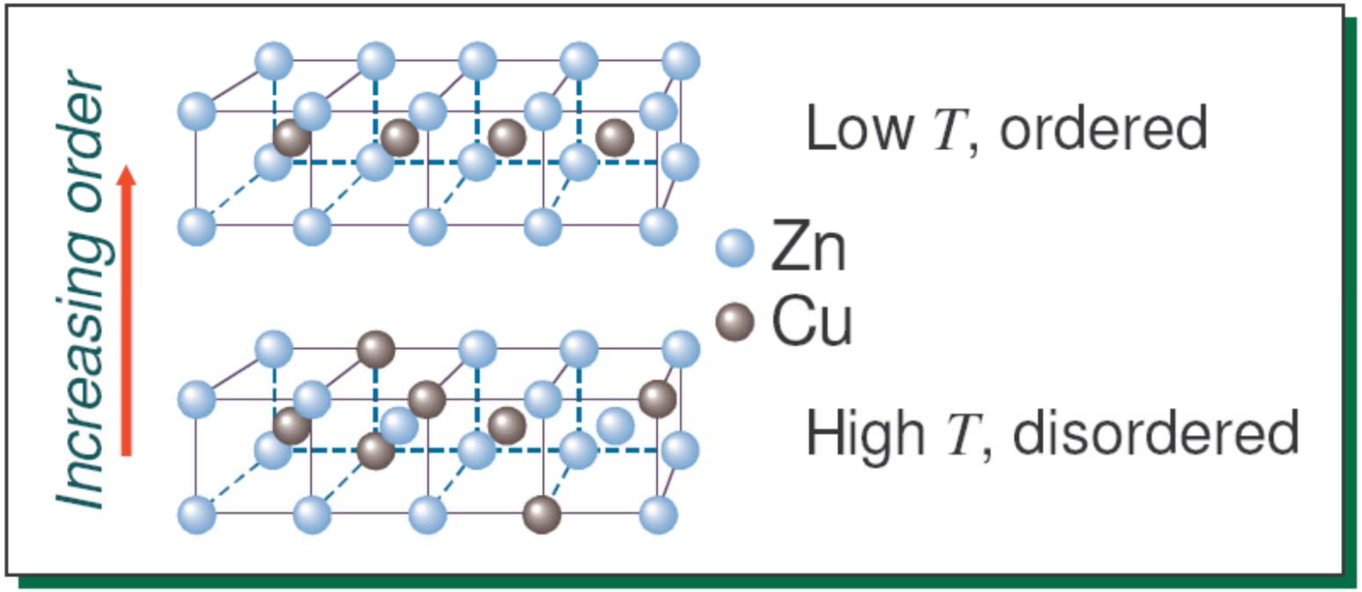


Order-disorder transition: 2nd order transition

- *β*-brass.

~ **Brass is a 50:50, Cu:Zn alloy with a b.c.c structure.**

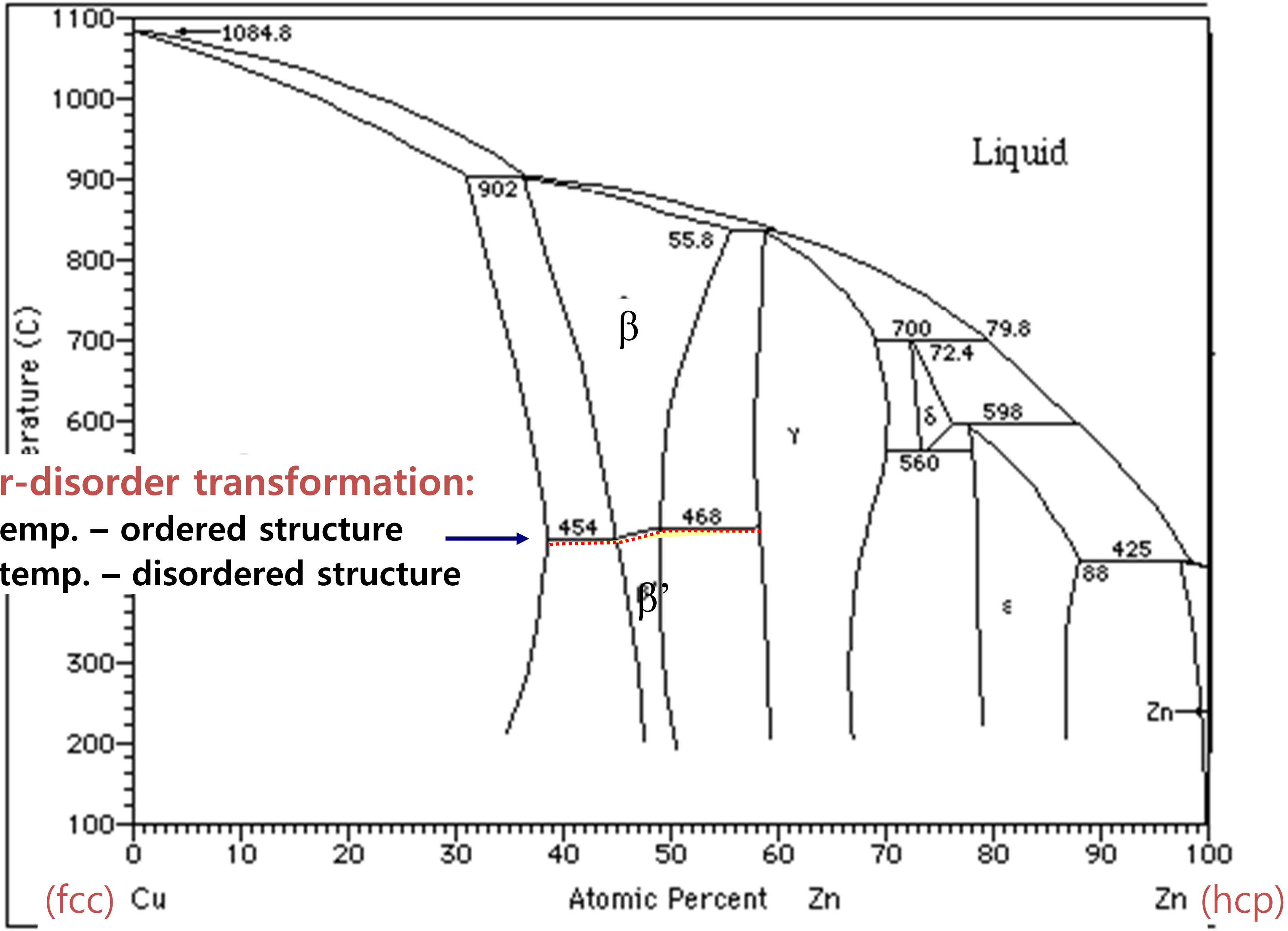
~ **At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diagram)**



- Two types of site call them: A-sites and B-sites.
- At high *T*, equal probability for any site to be occupied by Cu or Zn.

Intermediate Phase

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim -21$ kJ/mol



Order-disorder transformation:

Low temp. – ordered structure

High temp. – disordered structure

- α and η are terminal solid solutions
- β, β', γ, δ and ε are intermediate solid solutions.

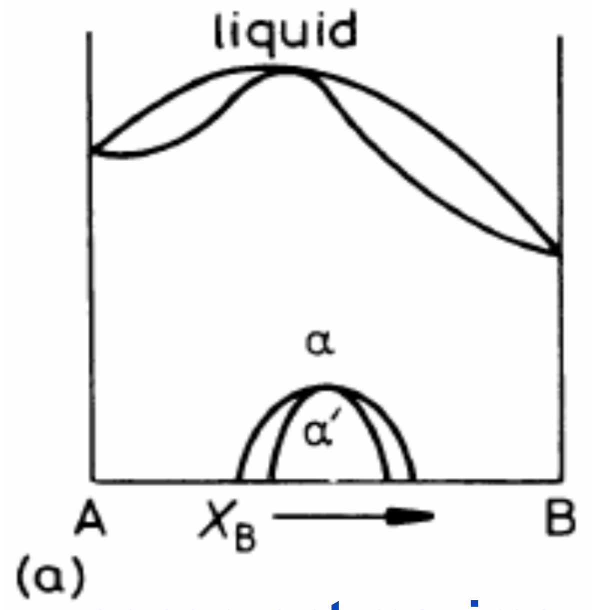
Ordered Alloys $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} < 0$

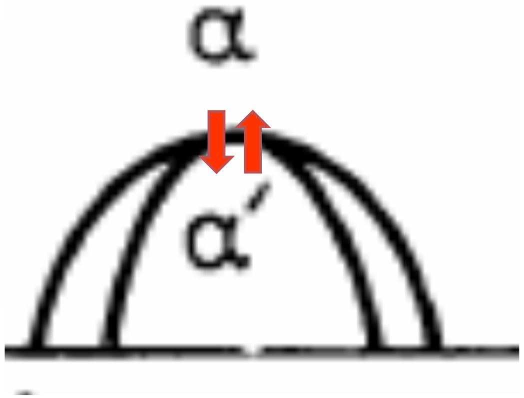
a. **$\Delta H_{mix} < 0$ → A atoms and B atoms like each other.**

How does the phase diagram differ from the previous case?

b. **What would happen when $\Delta H_{mix} \ll 0$?**

→ The ordered state can extend to the melting temperature.



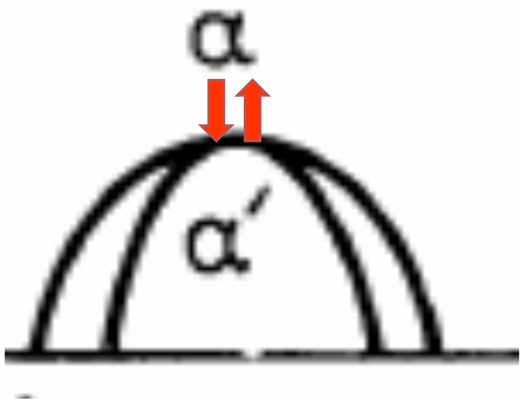


congruent maxima

Order-disorder phase transformation

- Not classical phase change=~not depend on diffusion process
- change of temperature allowed a continuous re-arrangement of atoms without changing the phase
- boundary: ordered lattice & disordered lattice/phase rule could not applied

  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB_3 can the transformation (i.e. at the temperature maximum) be considered diffusionless.

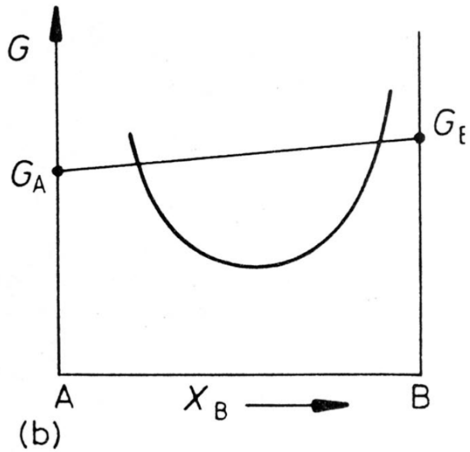


* Solid solution

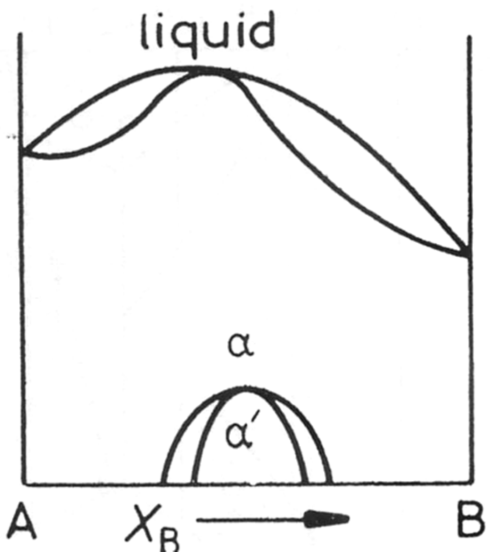
→ random mixing
→ entropy ↑
negative enthalpy ↓

$$\boxed{\Delta H_{mix}^{S} < 0}$$

Large composition range
➔ G ↓



diate phases: (a) for an intermetallic com-
(b) for an intermediate phase with a wide



* Compound : AB, A_2B…

→ entropy↓
→ covalent, ionic contributio
→ enthalpy more negative ↓

$$\boxed{\Delta H_{mix}^{S} << 0}$$

Small composition range
➔ G ↓

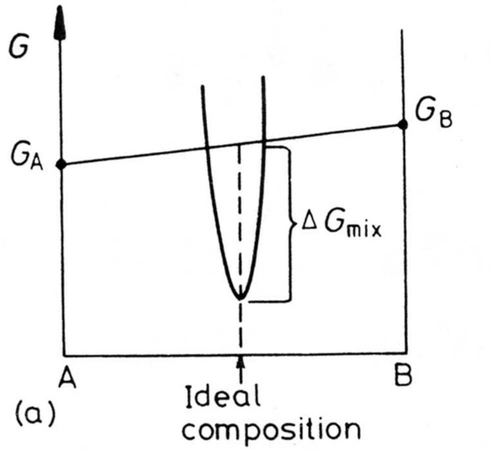
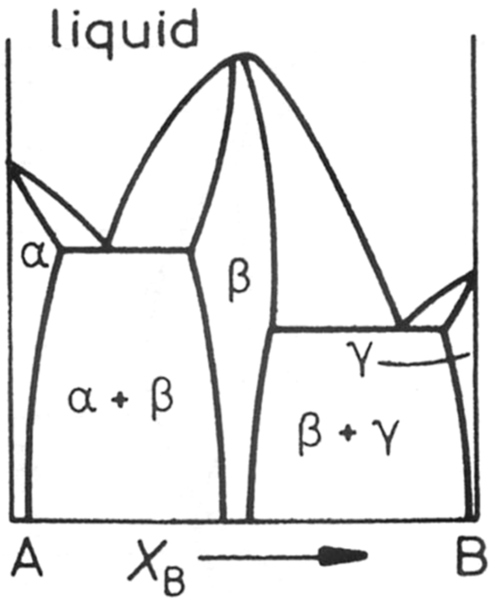


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.

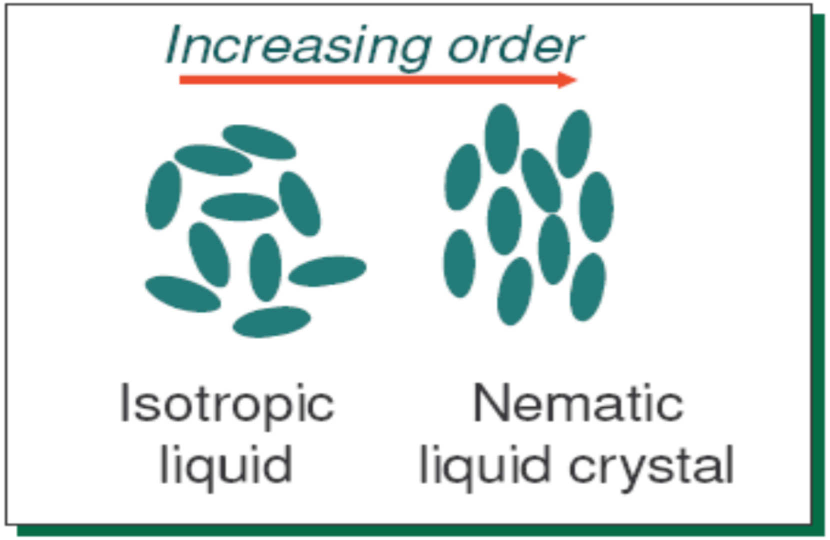


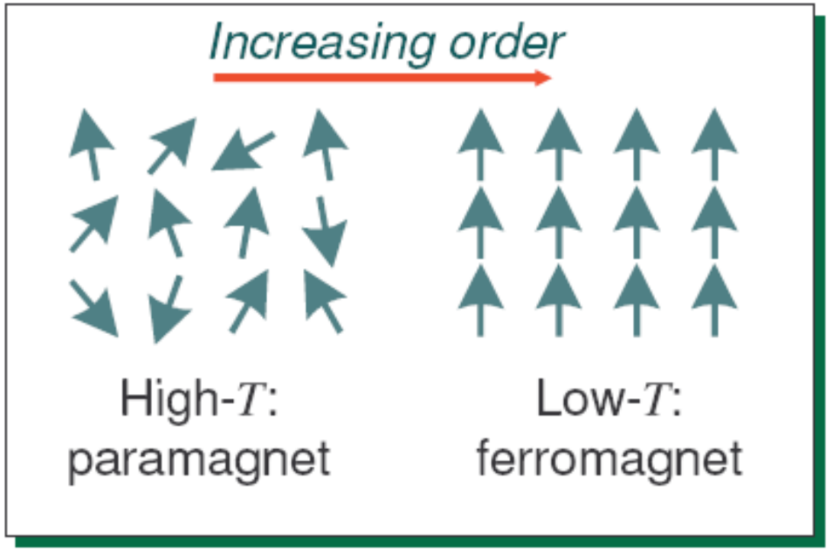
Order-disorder transition: 2nd order transition

- Other examples (there are many):

- Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).

- Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.





액정의 가는 분자가 서로의 위치는 불규칙하지만
모두 일정방향으로 향하고 있는 상태

• Thermodynamics for glass transition

~ not thermodynamic nature
~ close to second order phase transition

➡ *at T_g* → *G changes continuously.*

→ *V, H. S changes continuously.*

– First derivatives of G (V, S, H) are continuous at T_T

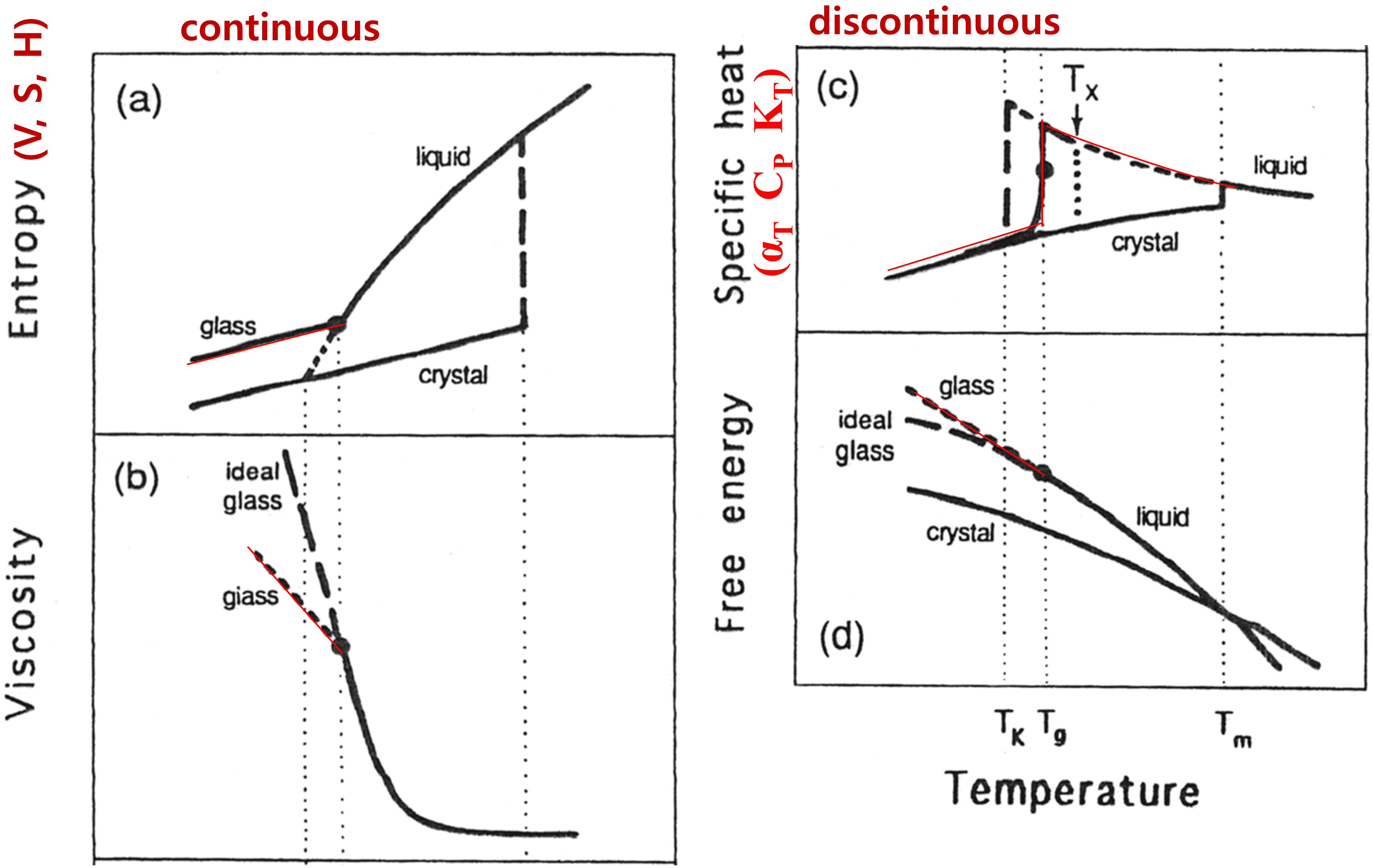
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

→ α_T C_P K_T *changes discontinuously.*

– Second derivatives of G (α, β, C_p) are discontinuous at T_T

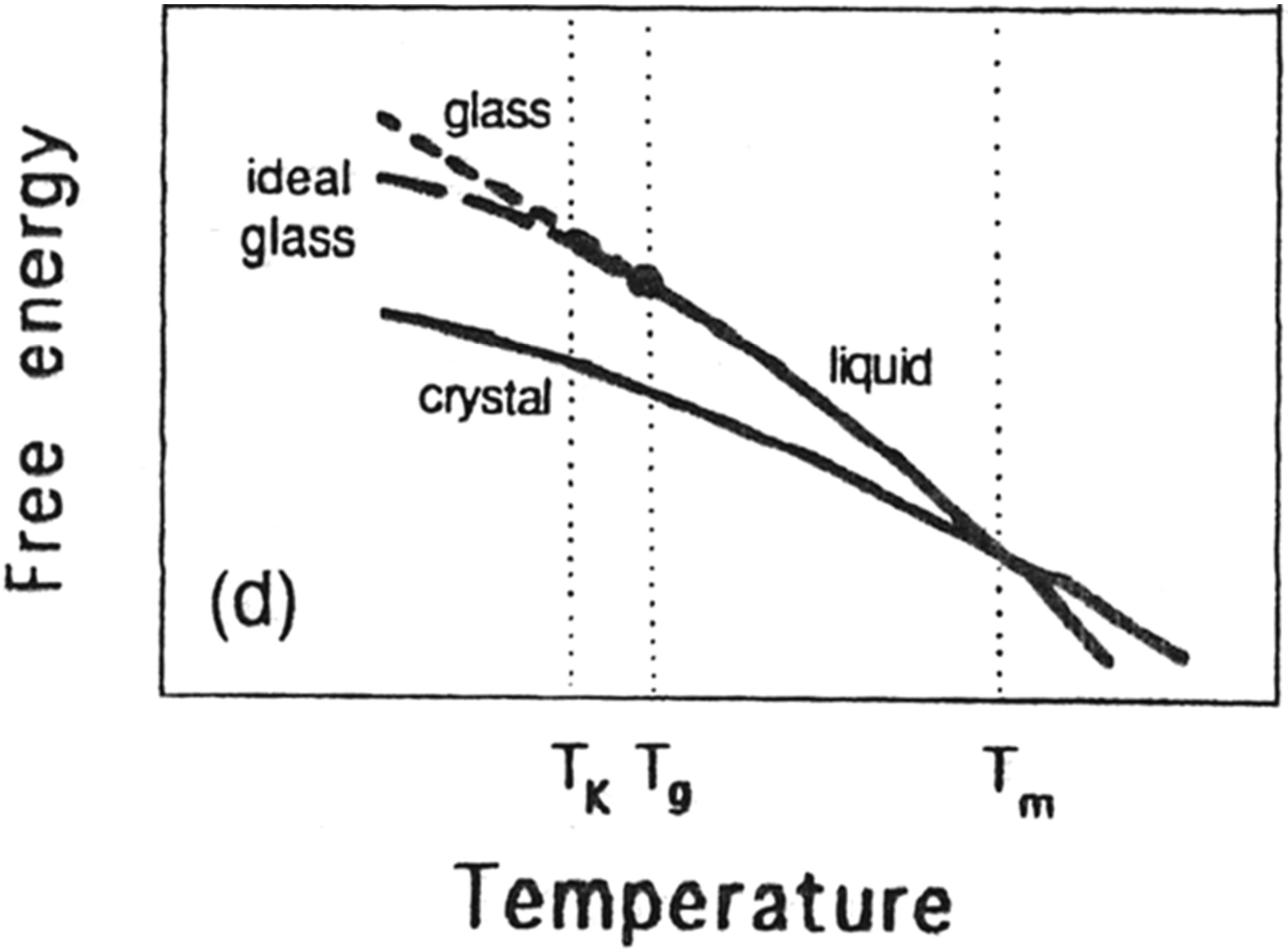
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

❖ **The glass transition is 'pseudo' second-order phase transition.**
And the transition depends on kinetic factors.



Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Schematic of the glass transition showing the effects of temperature on free energy



2.5.1 Thermodynamic Stability

The thermodynamic stability of a system at constant temperature and pressure is determined by its Gibbs free energy, G, defined as

$$G = H - TS$$

H is the enthalpy
T is the absolute temperature
S is the entropy

Using the above concepts, it may be stated that a glass becomes more "stable" when the free energy of the glassy phase is lower than that of the competing crystalline phase(s). In other words, the change in free energy, ΔG ($= G_{\text{glass}} - G_{\text{crystal}}$) becomes negative. Mathematically expressed:

$$\Delta G = \Delta H_f - T\Delta S_f$$

where

- the Δ symbol represents the change in these quantities between the final and initial states
- H_f and S_f represent the enthalpy of fusion and entropy of fusion, respectively

1) multi component system: ΔS↑_high order alloy → easy

2) low chemical potential due to ① low enthalpy ② large interfacial E between liquid and solid phase :
ΔH_f↓ _constituents with large negative heat of mixing →
solid/liquid interface E ↑

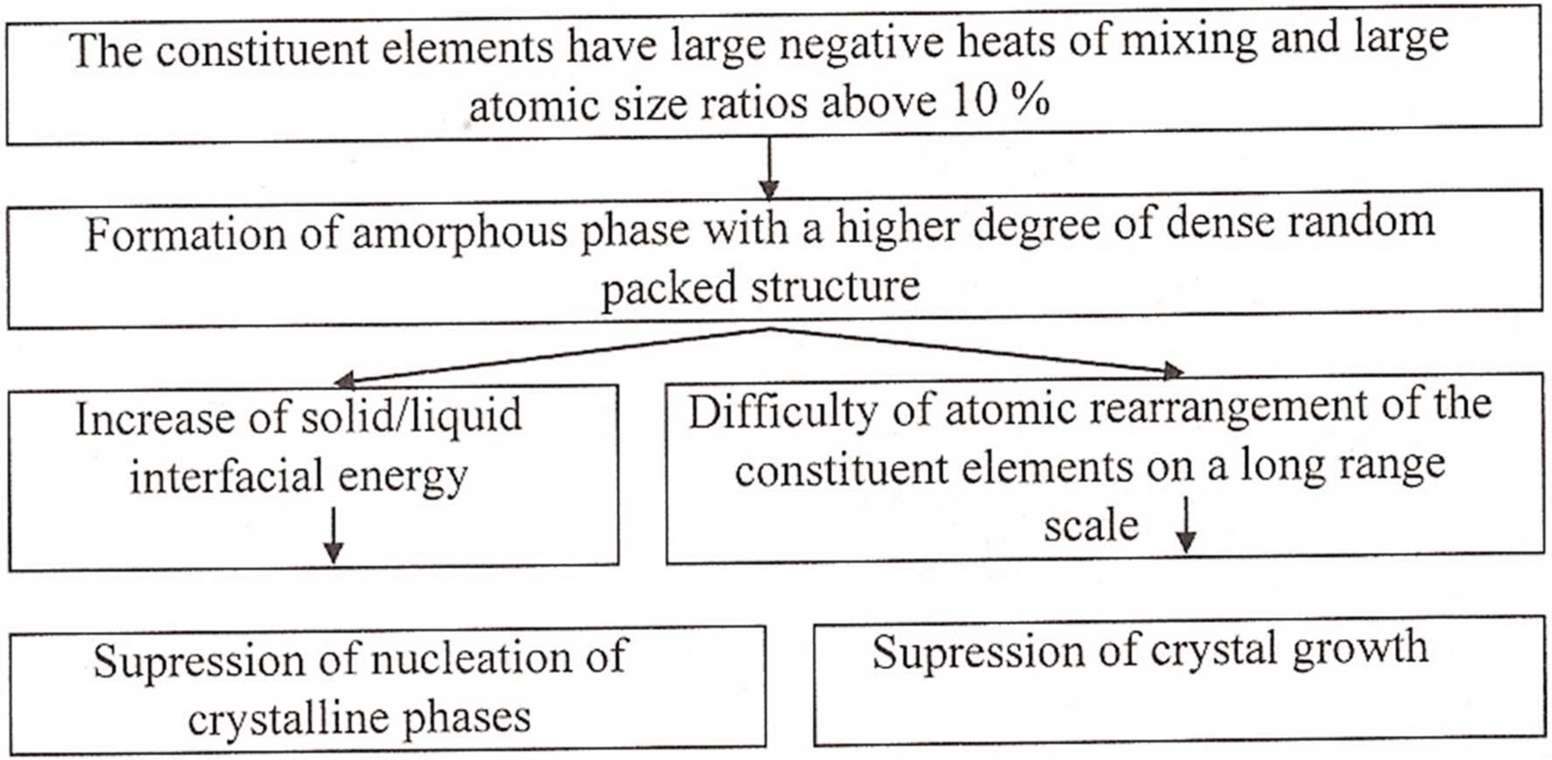
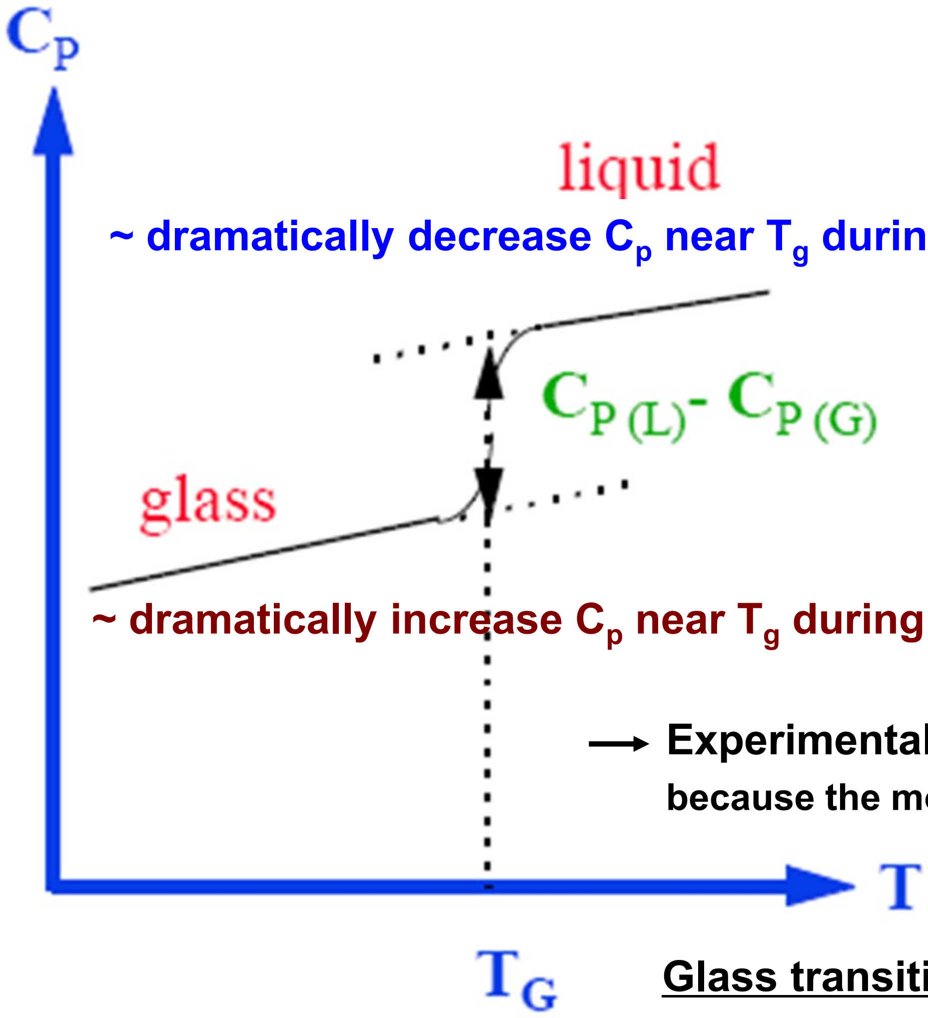


Fig. 5. *Summary of the reasons for the achievement of the high glass-forming ability for some ternary alloy systems such as Ln-Al-TM, Mg-Ln-TM and Zr-Al-TM, etc. (Ln=lanthanide metal, TM=transition metal).*

- **derivative of thermodynamic properties**

→ ***discontinuous*** **(C_p, α_T, K_T)**



~ dramatically decrease C_p near T_g during cooling

~ dramatically increase C_p near T_g during heating

→ **Experimental observation during heating**

because the monitoring is very difficult during cooling

<u>Glass transition</u>: heat → endothermic

Intermetallics 30 (2012) 19–24

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Intermetallics

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The world's biggest glassy alloy ever made

Nobuyuki Nishiyama [a,*], Kana Takenaka [a], Haruko Miura [a], Noriko Saidoh [a], Yuqiao Zeng [b], Akihisa Inoue [b]

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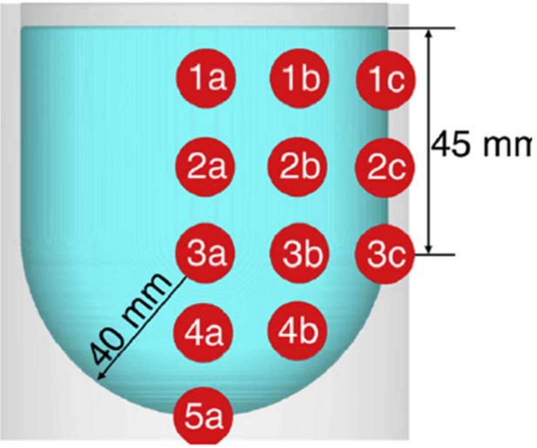
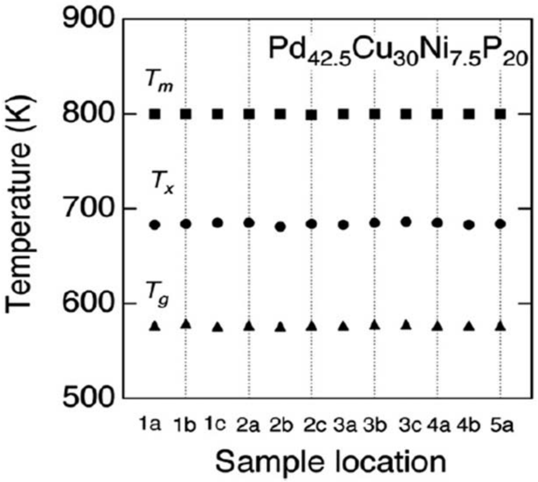




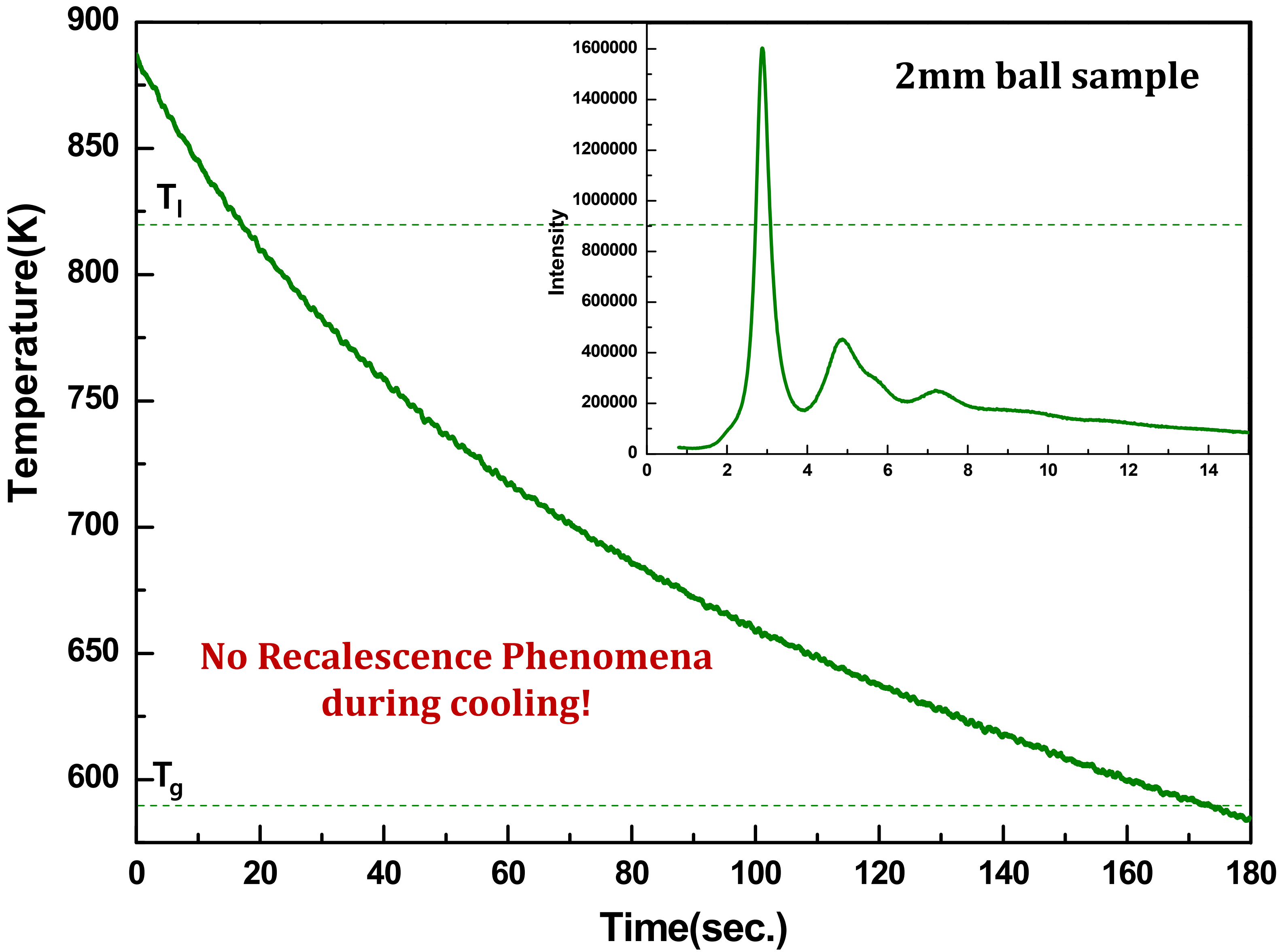
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

2012

D_{max} 80mm

Intermetallics, Vol30, Nov2012, P 19–24

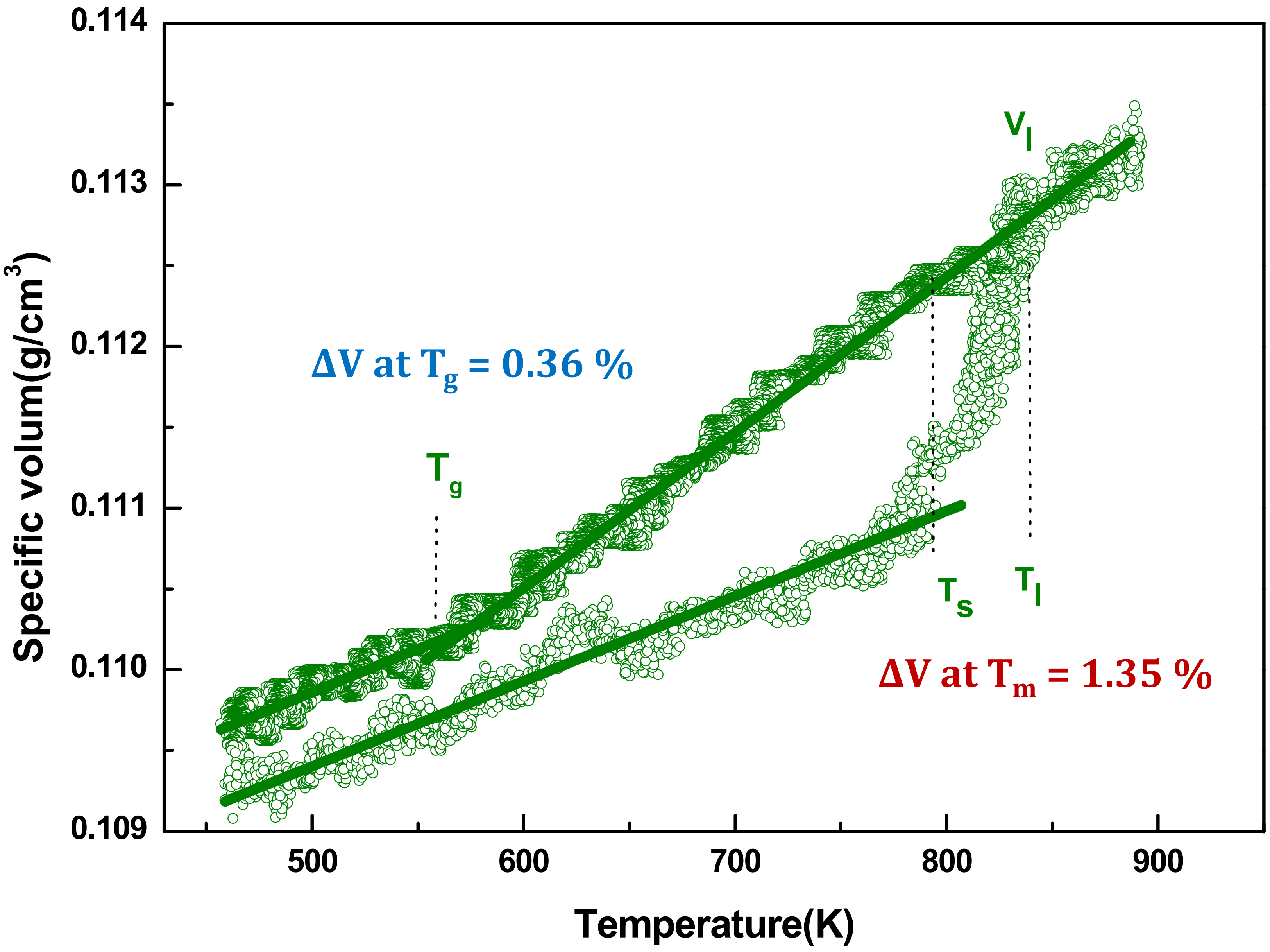
BMG-formation of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ Alloy under Radiative Cooling



2mm ball sample

No Recalescence Phenomena during cooling!

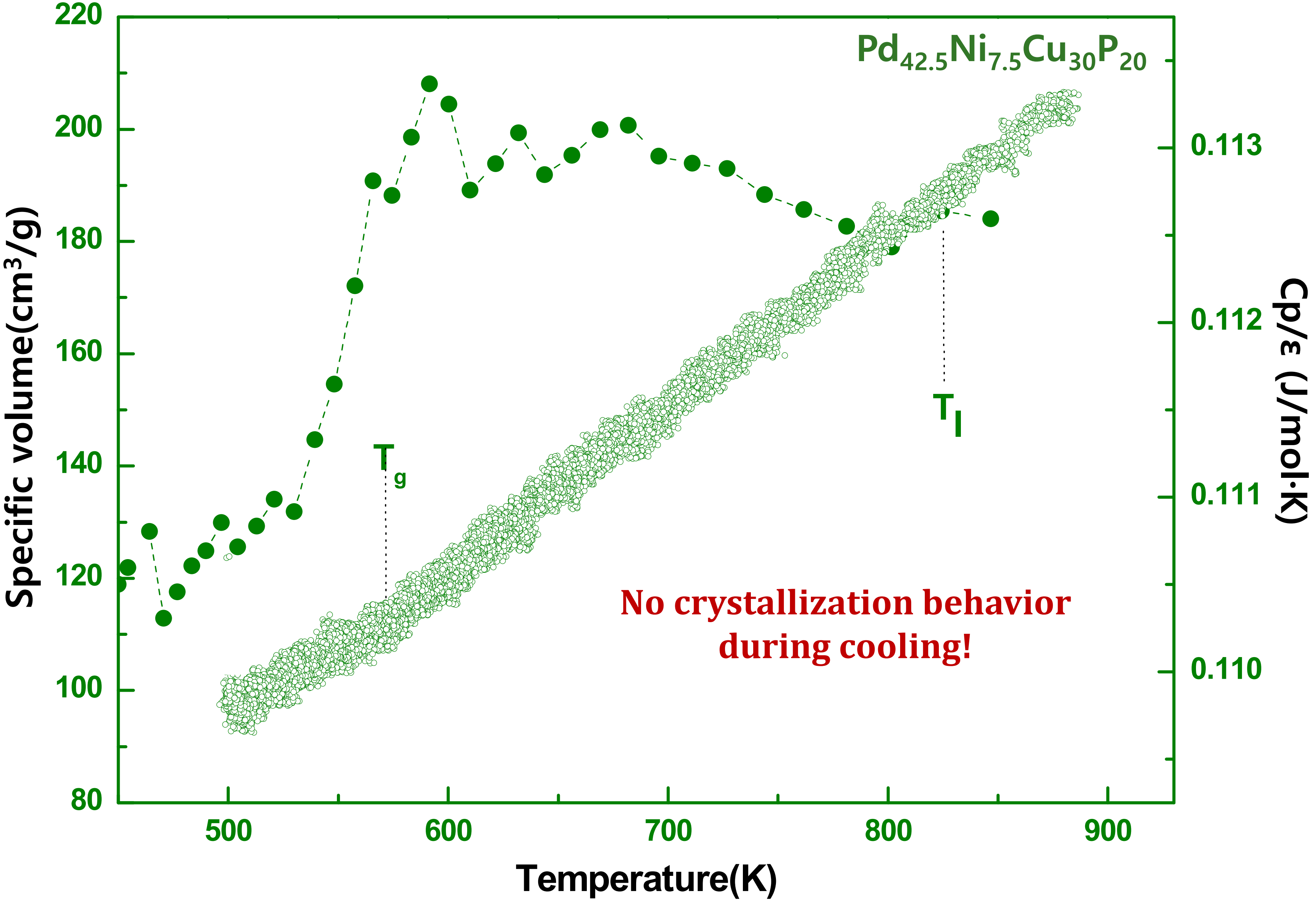
V-T Diagram of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



ΔV at T_g = 0.36 %

ΔV at T_m = 1.35 %

V-T Diagram & C_p/ε-T Diagram of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



No crystallization behavior during cooling!