2010 Spring

"Amorphous Materials"

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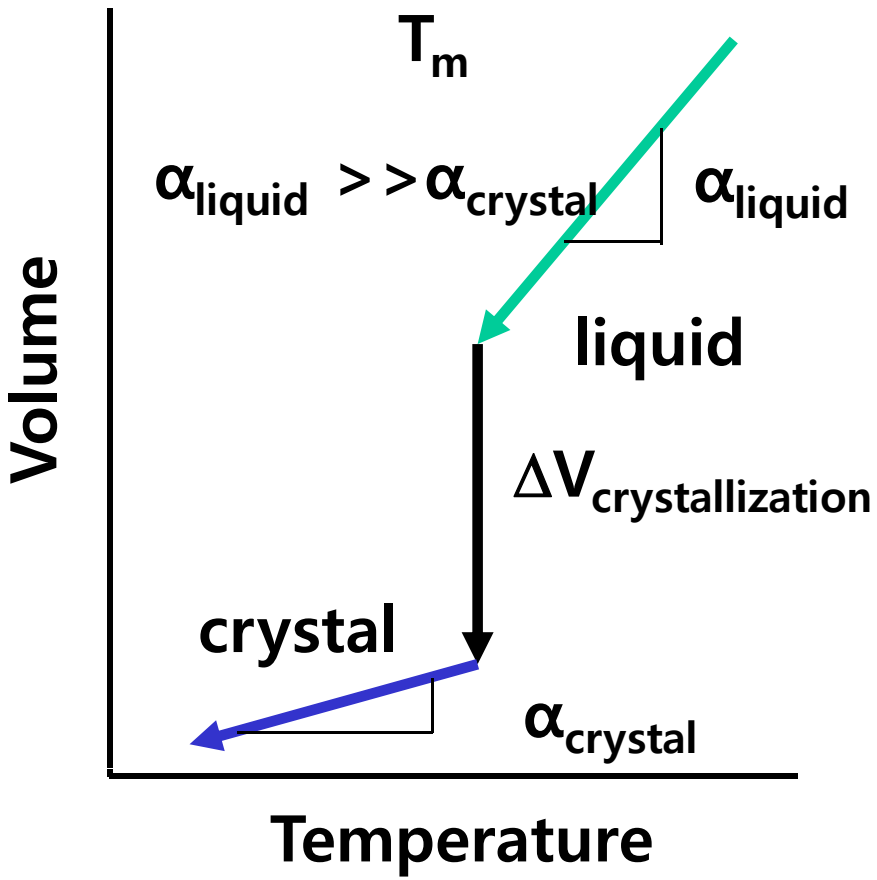
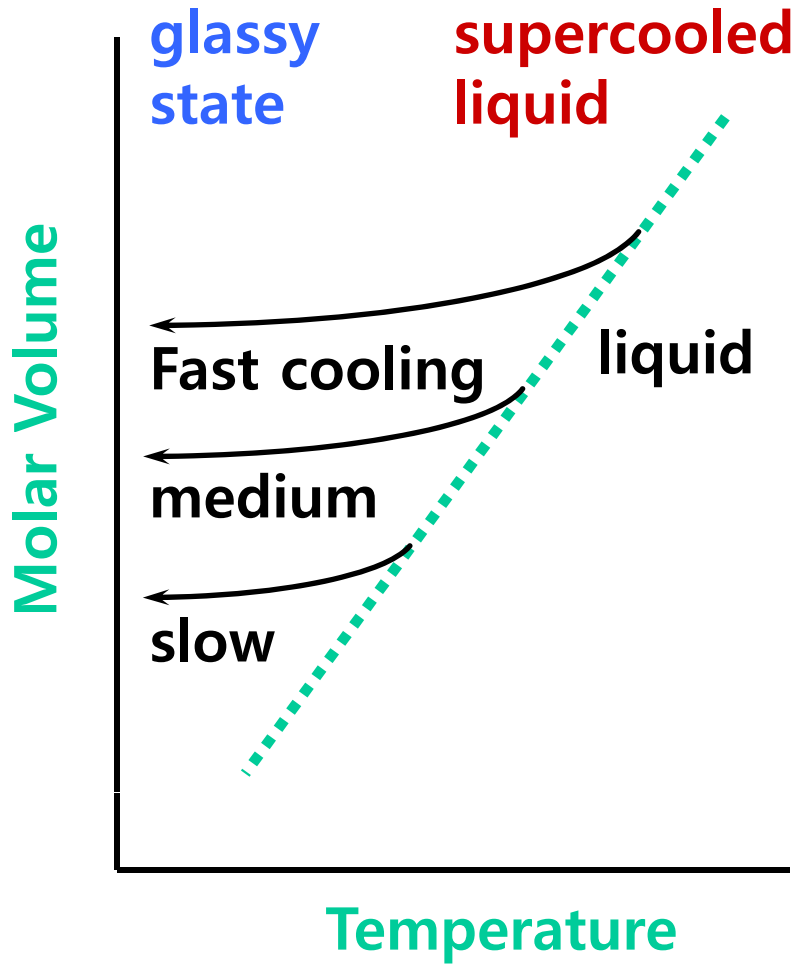
Contents for previous class

- **Melting and Crystallization:**
  Thermodynamic Transitions

- **Glass Transition:**
  Kinetic Transition

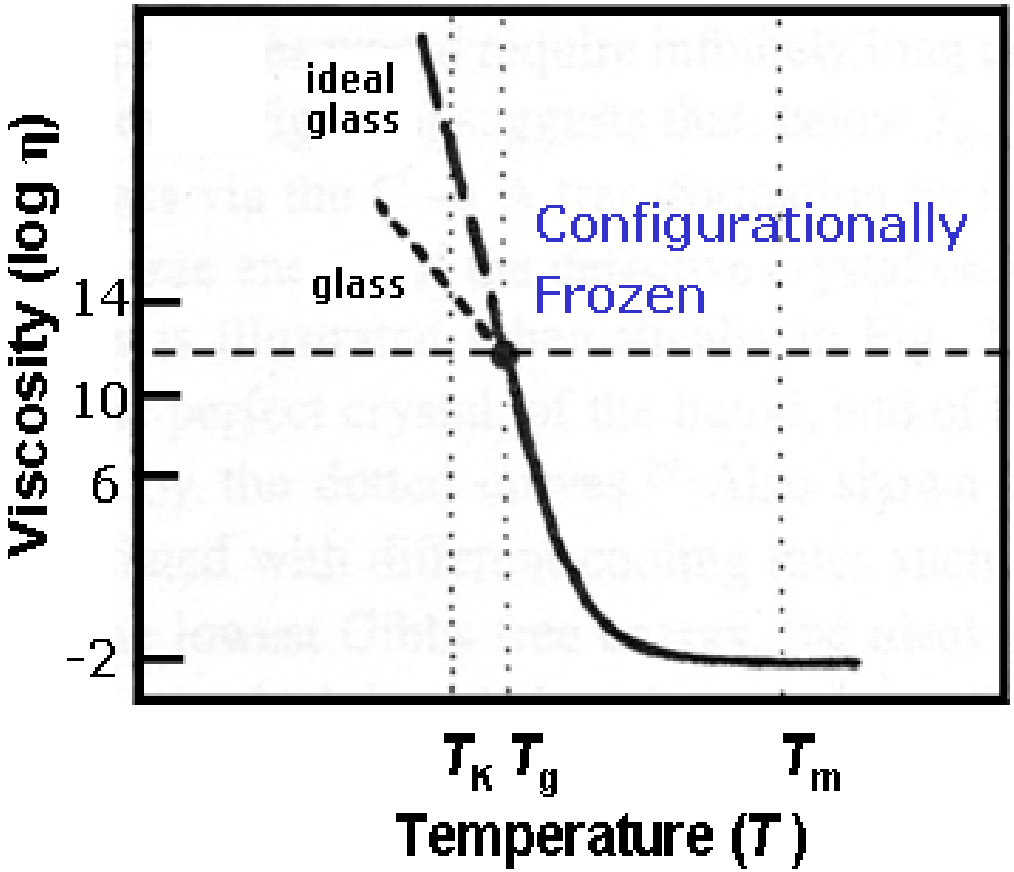




Glass : undercooled liquid with high viscosity

(~10$^{14.6}$ poise)

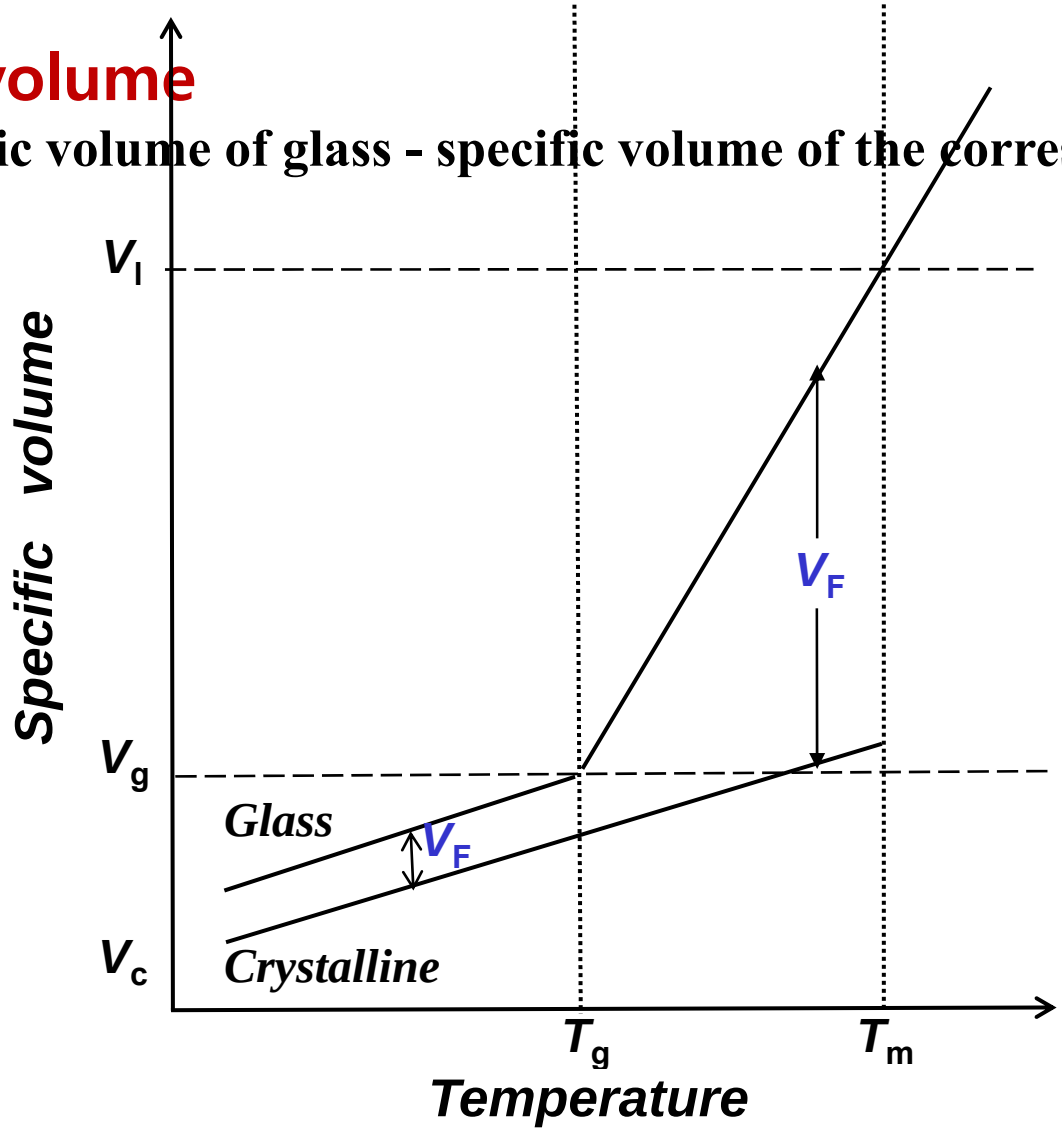
cf) liquid *~10^{-2} poise*



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

Free volume

= specific volume of glass - specific volume of the corresponding crystal



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

Contents for today's class

- **Glass transition**

  - Classification of phase transition

- $T_f \geq T_g$ (***T_f = fictive temperature***)

- **Amorphous vs Nanocrystalline**

  1) Microstructural observation

  2) Thermal analysis

  - DSC (Differential Scanning Calorimetry)

→ **local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.**

: Characterization of structure by pair distribution function

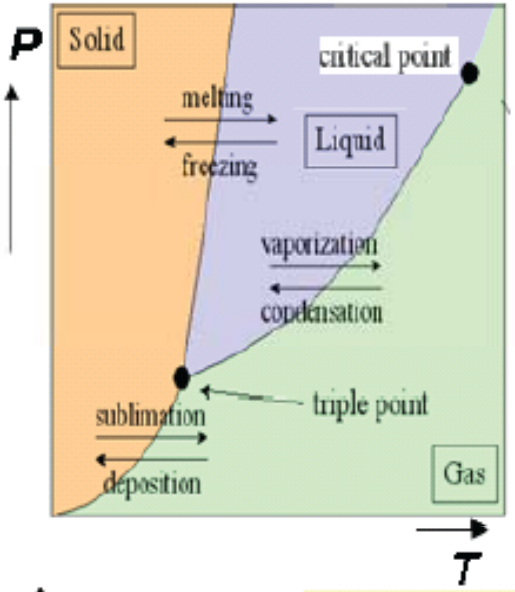
Glass transition

❖ The glass transition is not first order transition (such as melting), meaning there is no discontinuity in the thermodynamic functions (energy, entropy, density).

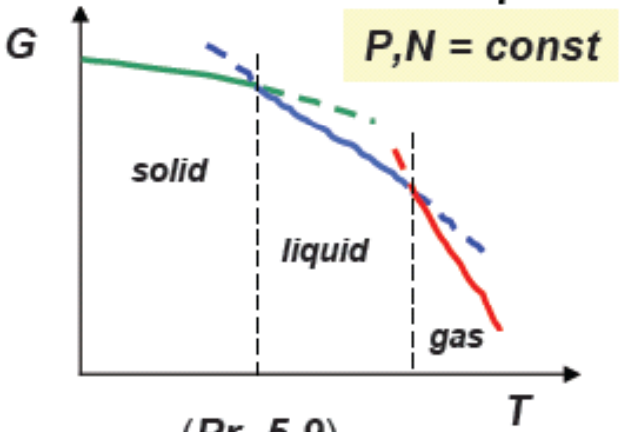
❖ The glass transition is 'pseudo' second-order phase transition. And the transition depends on kinetic factors (cooling rate).

❖ Sometimes the glass transition is a first order transition, most prominently in Si where the structure changes from 4 coordinated amorphous solid to 6 coordinated liquid. And the same applies to water (amorphous ice).

The First-Order Transitions



Latent heat
Energy barrier
Discontinuous entropy, heat capacity



(*Pr. 5.9*).

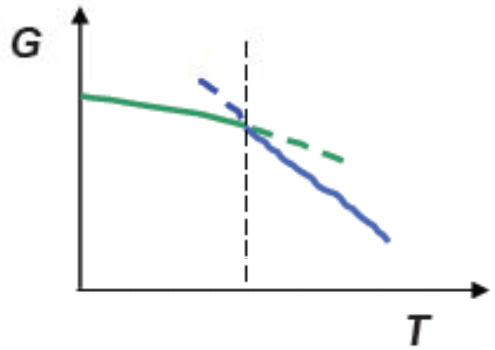
On the graph ***G*(*T*)** at ***P,N*** = const, the slope **d*G*/d*T*** is always negative:

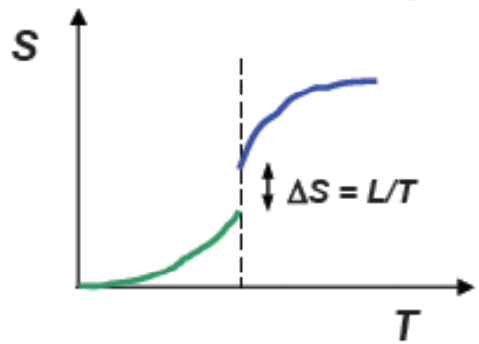
$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

In the first-order transitions, the ***G(T)*** curves have a real meaning even beyond the intersection point, this results in ***metastability*** and ***hysteresis***.

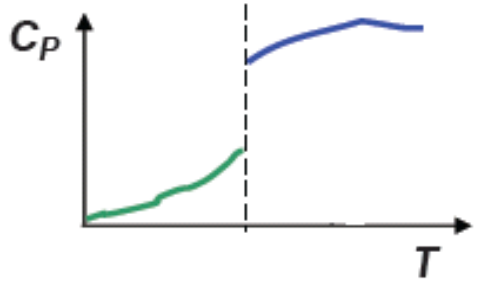
An energy barrier that prevents a transition from the higher μ to the lower μ phase. (e.g., gas, being cooled below T_{tr} does not immediately condense, since surface energy makes the formation of very small droplets energetically unfavorable).

Water in organic cells can avoid freezing down to –20^{0}C in insects and down to –47^{0}C in plants.





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



Ehrenfest Classification of Phase Transitions

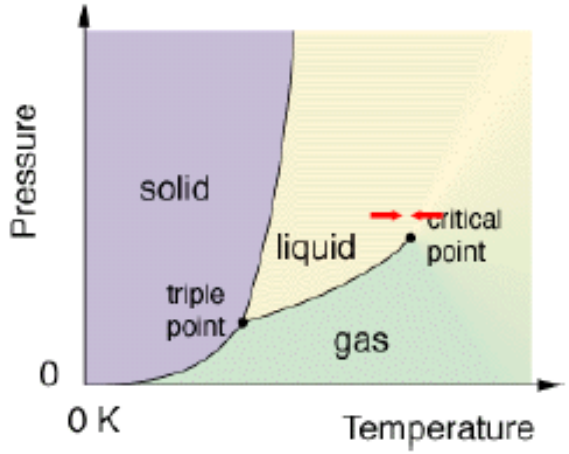
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

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

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

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

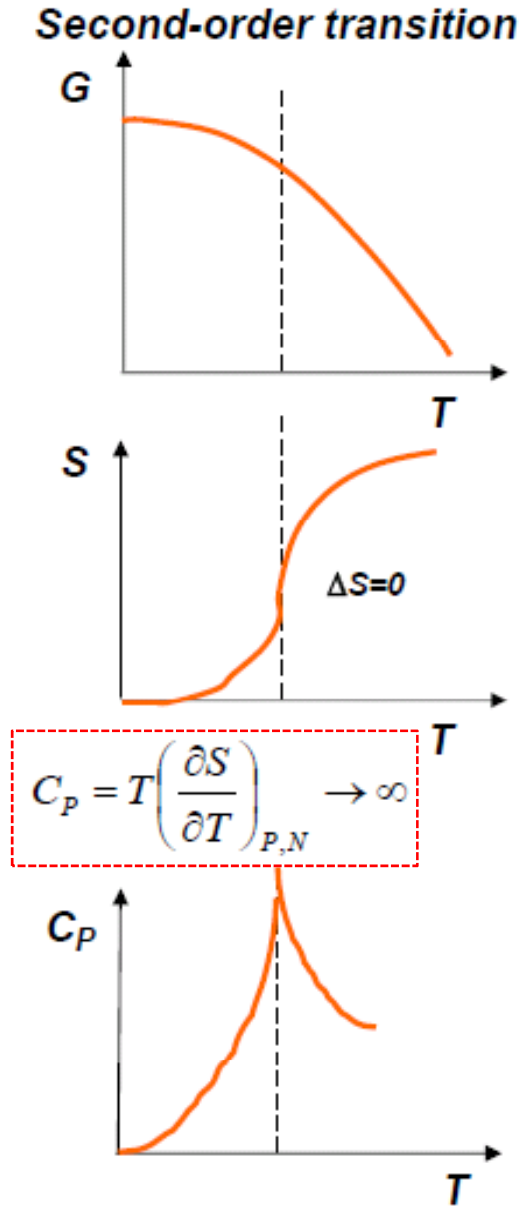
  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.



The Second Order Transition

No Latent heat
Continuous entropy

Discontinuous heat capacity



As one moves along the coexistence curve toward the critical point, the distinction between the liquid phase on one side and the gas phase on the other gradually decreases and finally disappears at (T_C, P_C). The T-driven phase transition that occurs *exactly* at the critical point is called a second-order phase transition. Unlike the 1st-order transitions, the 2nd-order transition does not require any latent heat (L=0). In the *second-order transitions* (*order-disorder transitions* or *critical phenomena*) the entropy is continuous across the transition. The specific heat $C_P = T(\delta S/\delta T)_P$ diverges at the transition.

Whereas in the 1st-order transitions the $G(T)$ curves have a real meaning even beyond the intersection point, nothing of the sort can occur for a 2nd-order transition – the Gibbs free energy is a continuous function around the critical temperature.

- 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

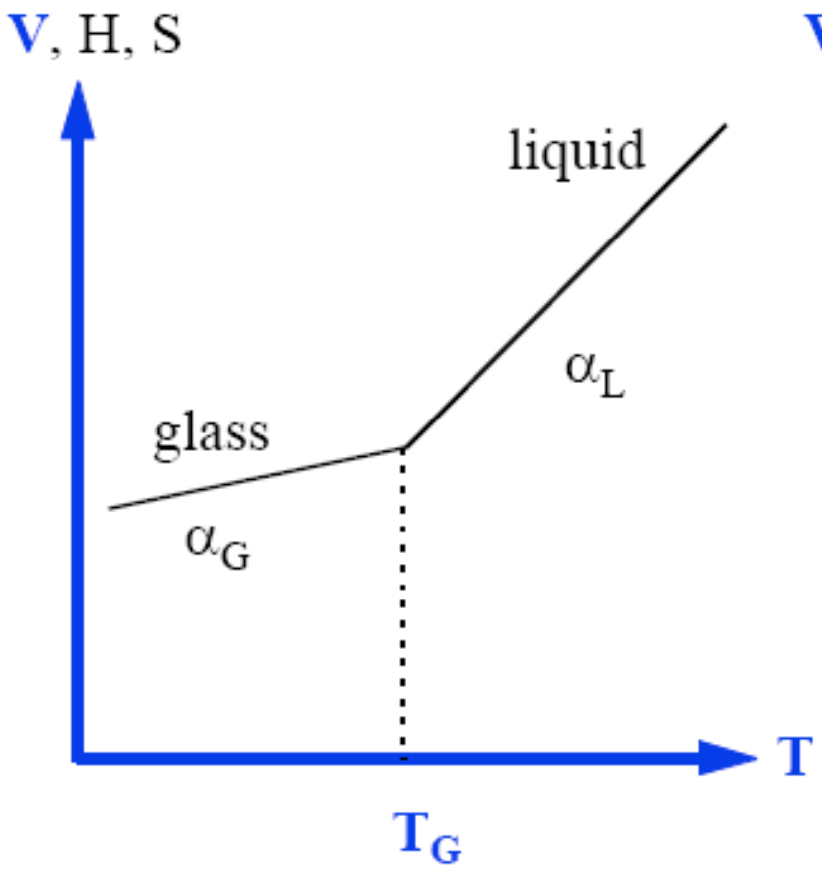
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

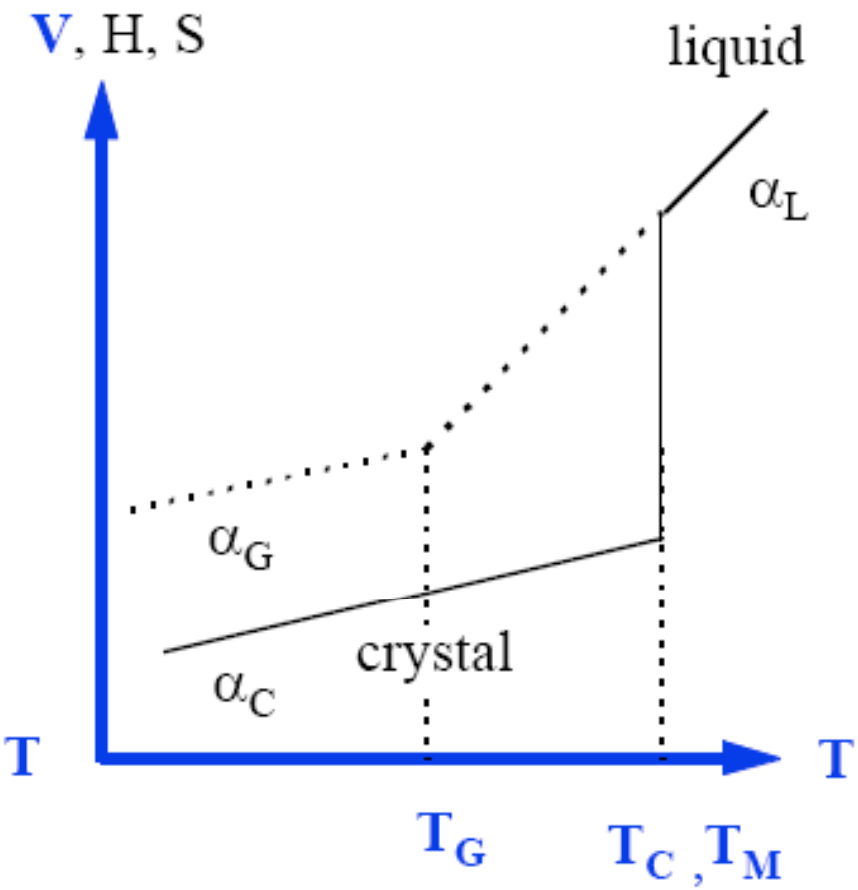
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

Experimental Evidence: Dilatometry **V**= f(**T**,P)



Liquid to Glass Transition
"Second Order" Transition



Liquid to Crystal Transition
First Oder Transition

- 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

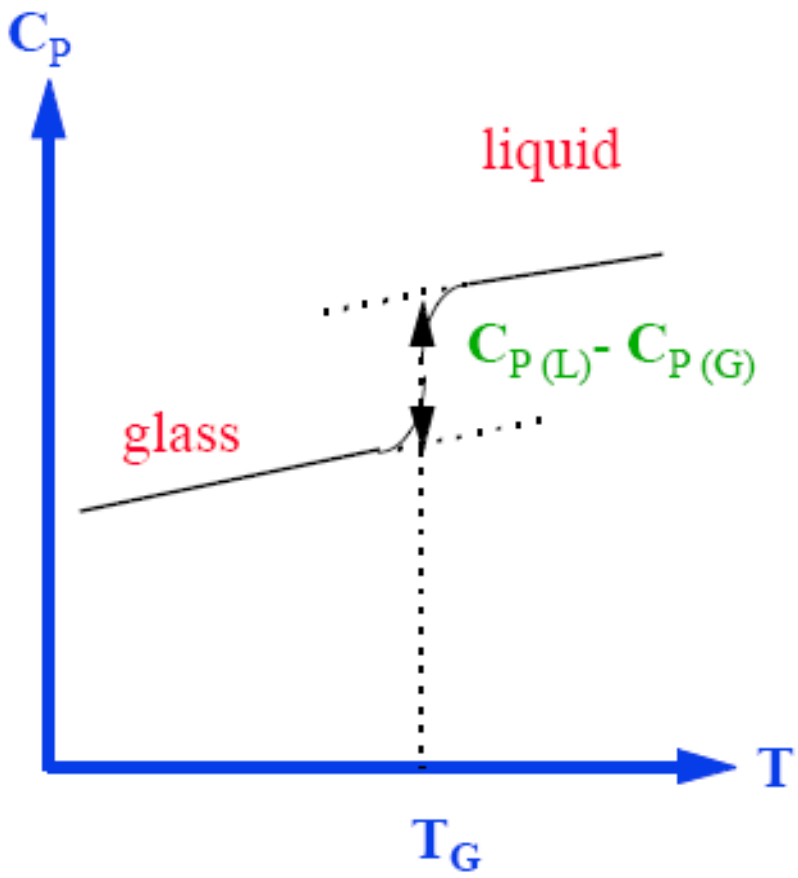
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

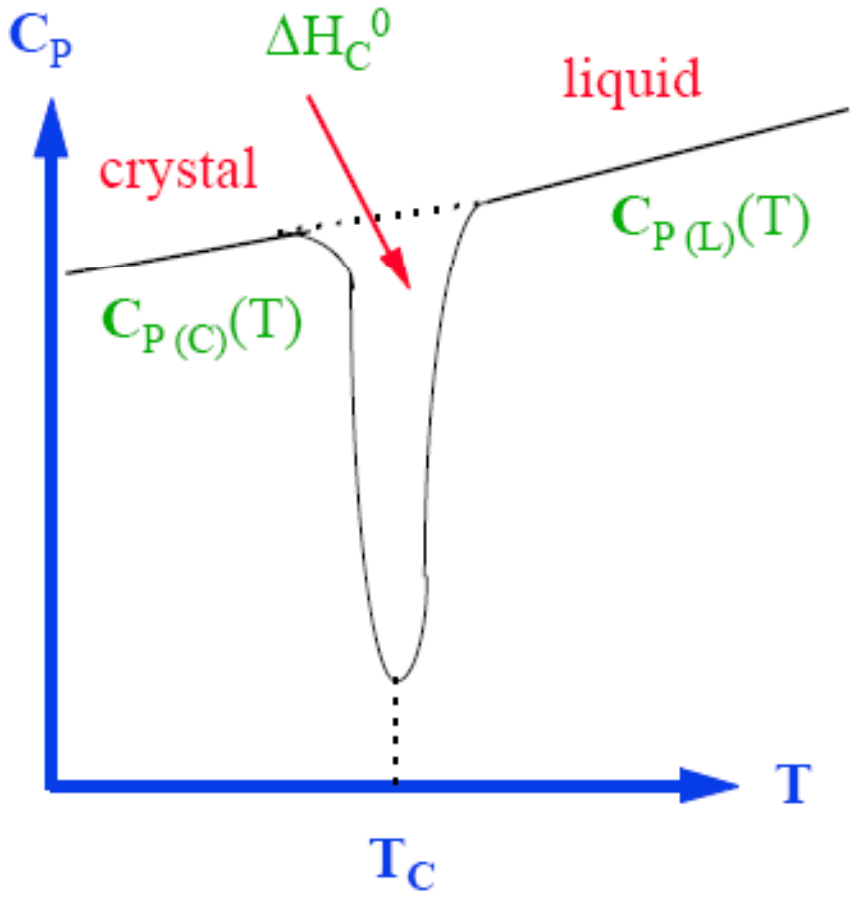
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

Experimental Evidence: Calorimetry $C_p = f(T)$

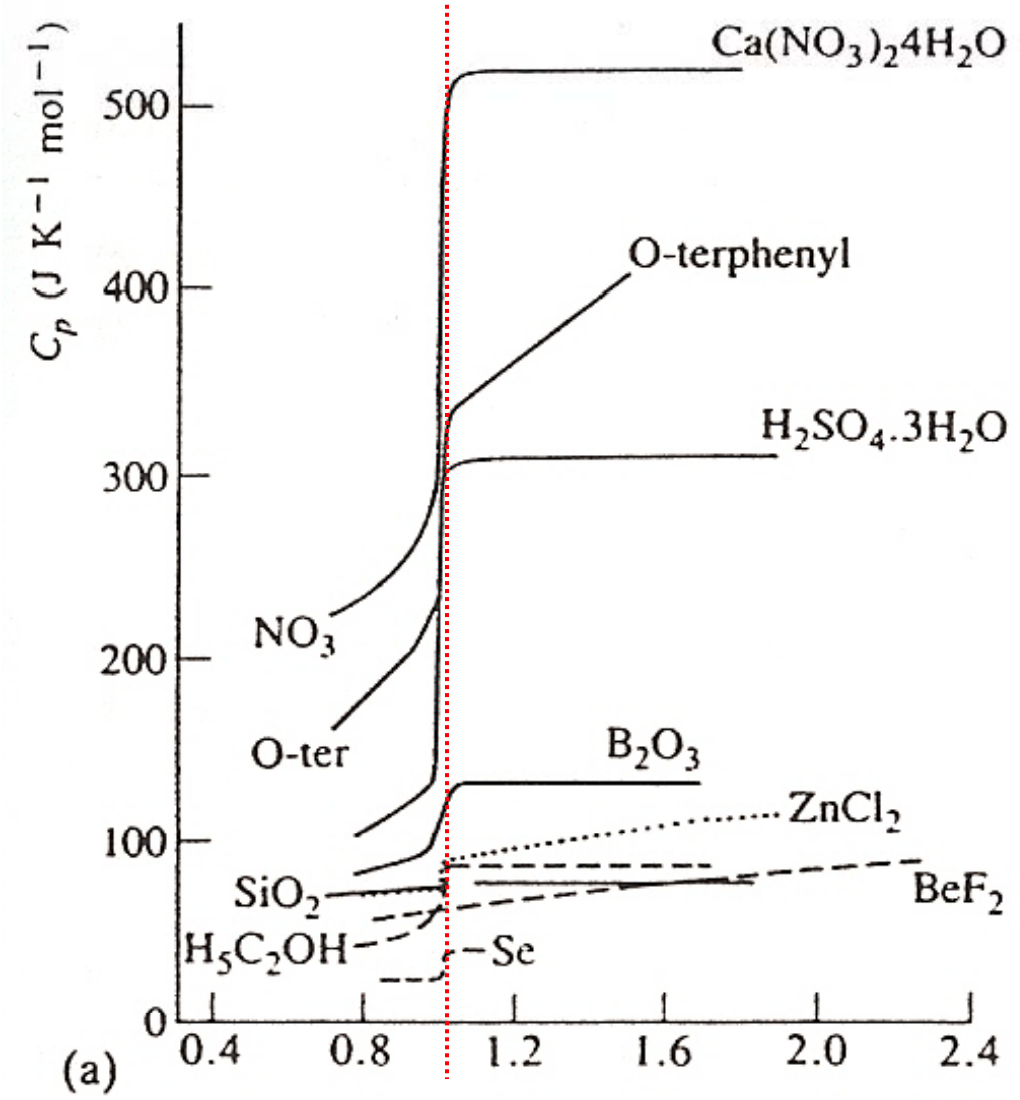




Liquid to Glass Transition
"Second Order" Transition

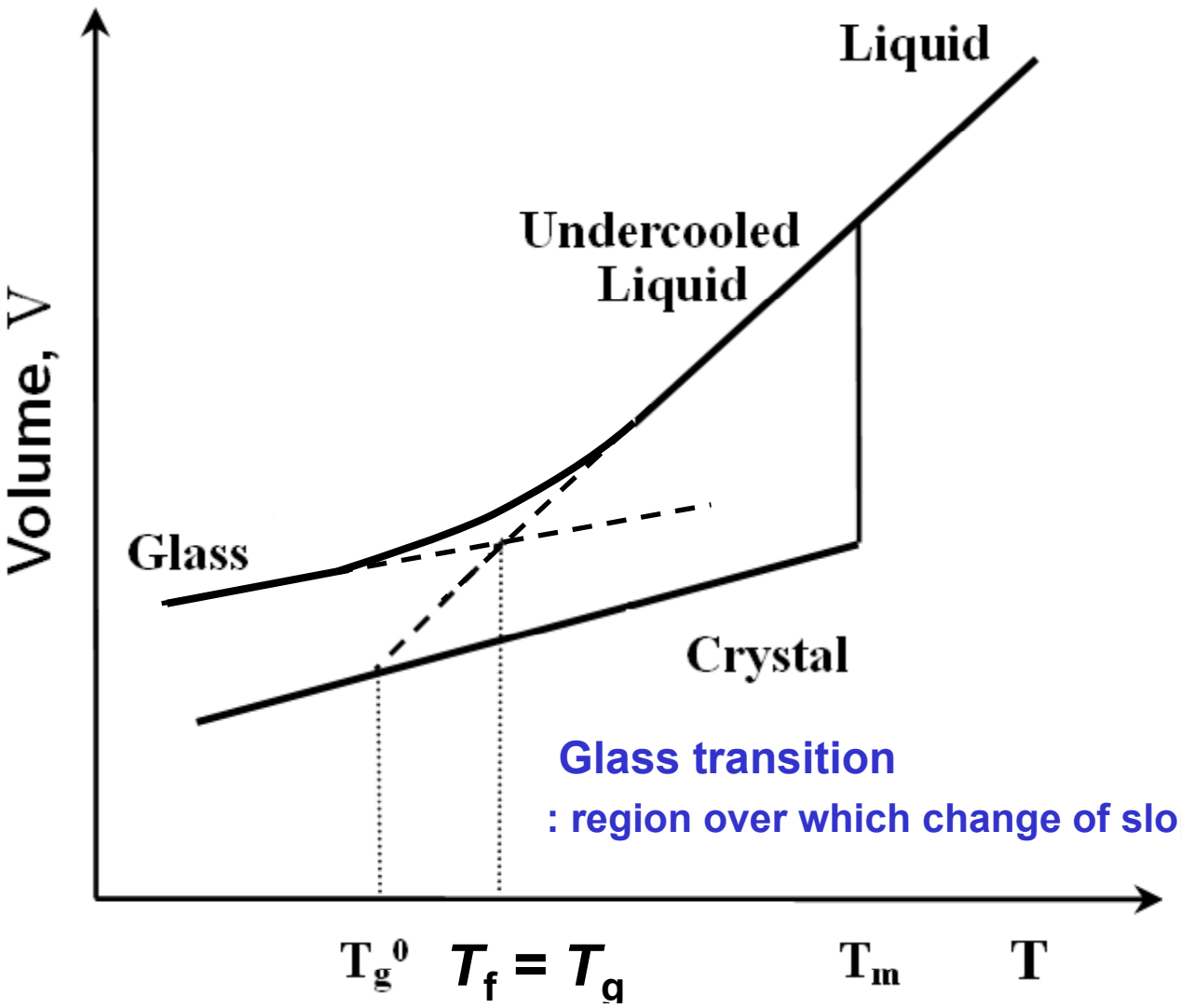
Liquid to CrystalTransition
First Order Transition

Difference of C_p at T_g depending on materials



T/T_g ←—Normalizing as T_g

T_g = *fictive temperature*, T_f



Glass transition

: region over which change of slope occurs

thermodynamic property ?

thermodynamic property

T_f = *fictive temperature*

This is the temperature at which the actual atomic scale structure of a quenched glass would be the *metastable equilibrium* structure (relative to the crystalline state) of the corresponding supercooled liquid (SCL). One always has:

$$T_f \geq T_g$$

T_f can also be defined as the temperature at which the strucuture of the SCL was *instantaneously frozen* into the glassy state, which has therefore kept the original structure of the SCL and it can be estimated by the intersection between the SCL line and the extrapolated glass line, in a specific volume vs temperature diagram of the type previously shown. For slow enough cooling rates, $T_f \rightarrow T_g$. For fast cooling, T_f may become considerably larger than the value of T_g measured at typical heating rate of ~10-20 K/s.

• Amorphous vs Nanocrystalline

1) ***Microstructural observation***
XRD, (HR)TEM, EXAFS ...

2) *Thermal analysis*
DSC (Differential Scanning Calorimetry)

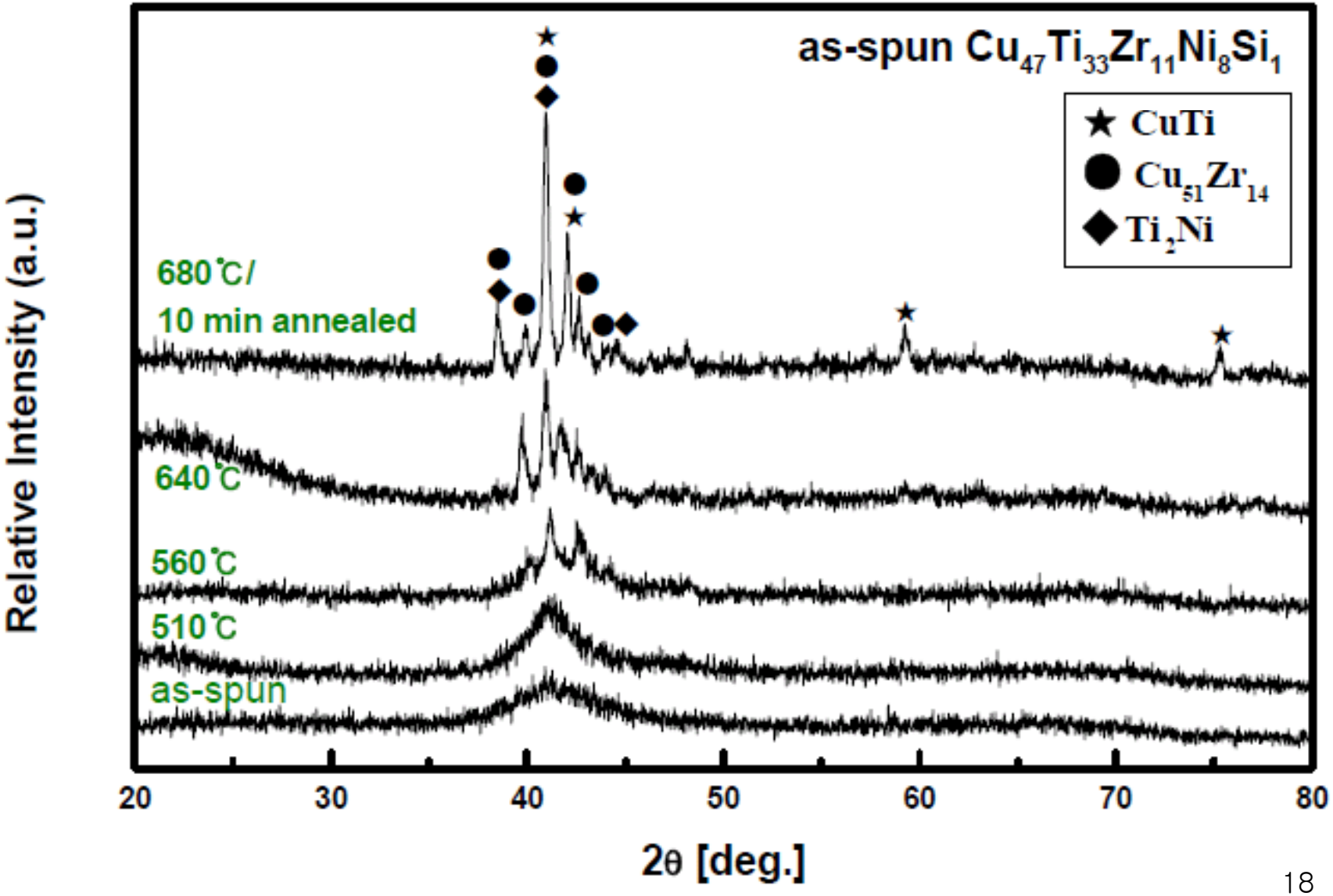
: Measure heat absorbed or liberated during heating or cooling

cf) - *glass* → *nucleation & growth*
(perfect random)
- *local clustering*: quenched-in nuclei → *only growth*
- *Nanocrystalline* → *growth*

→ local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.

: *Characterization of structure by pair distribution function*

Crystallization after annealing

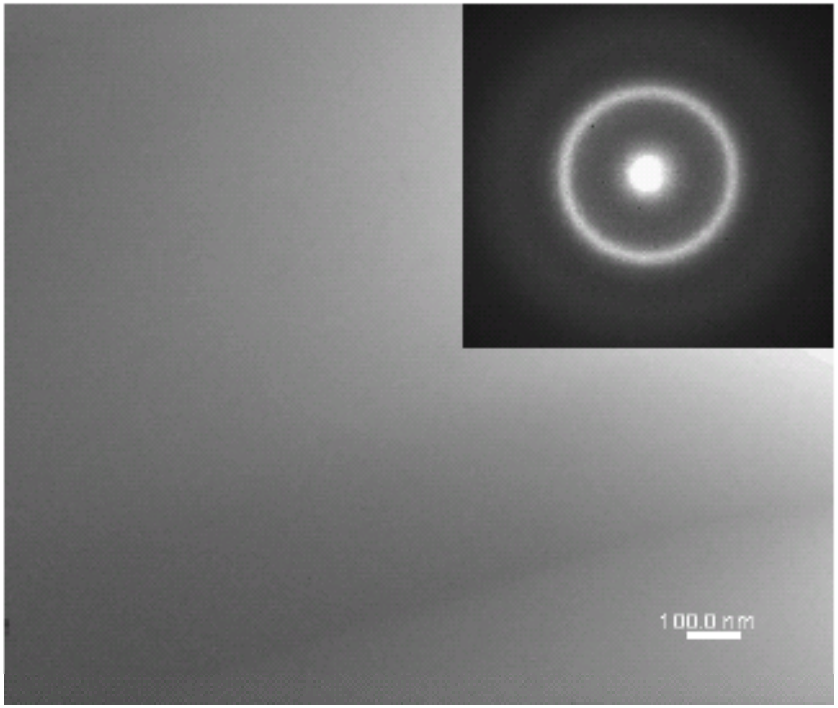


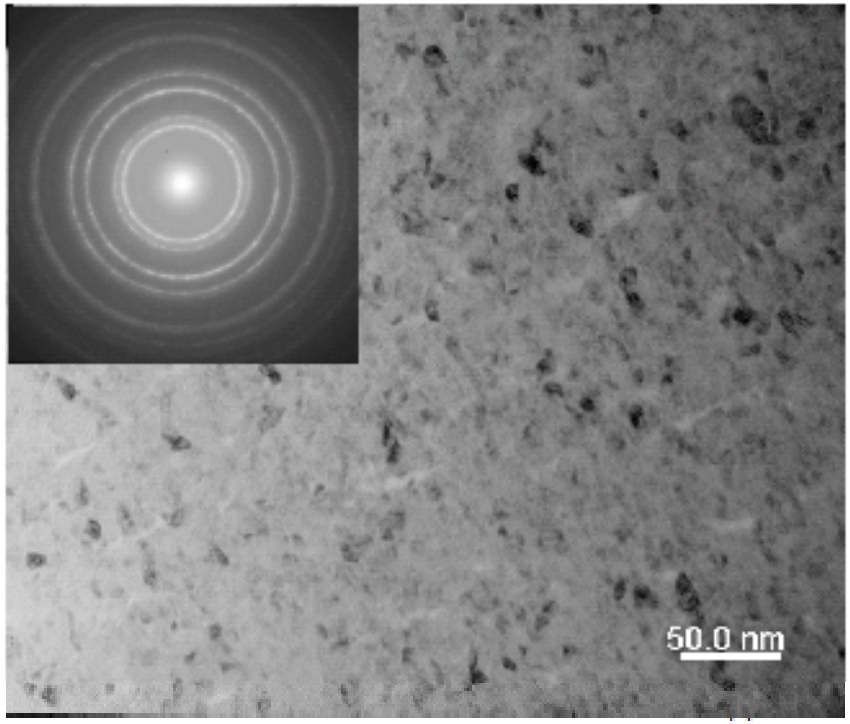
- ***Glass*: diffraction**
  - diffuse halo
  - X-ray: electron diffraction

- ***Crystalline*: sharp diffraction peaks**
  - grain size → nanoscle

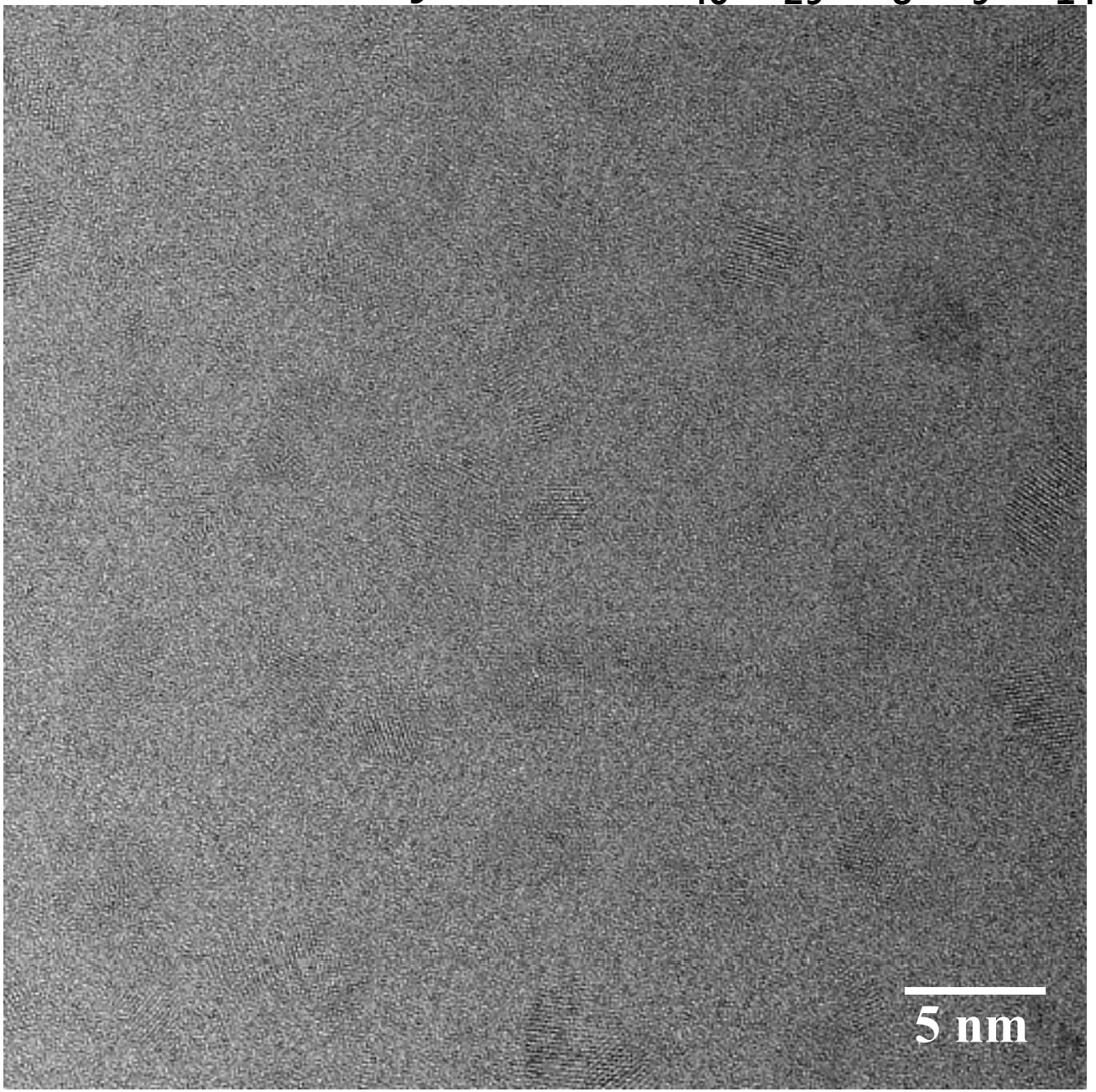
    ~ continuous ring pattern

    ~ sharp diffuse halo



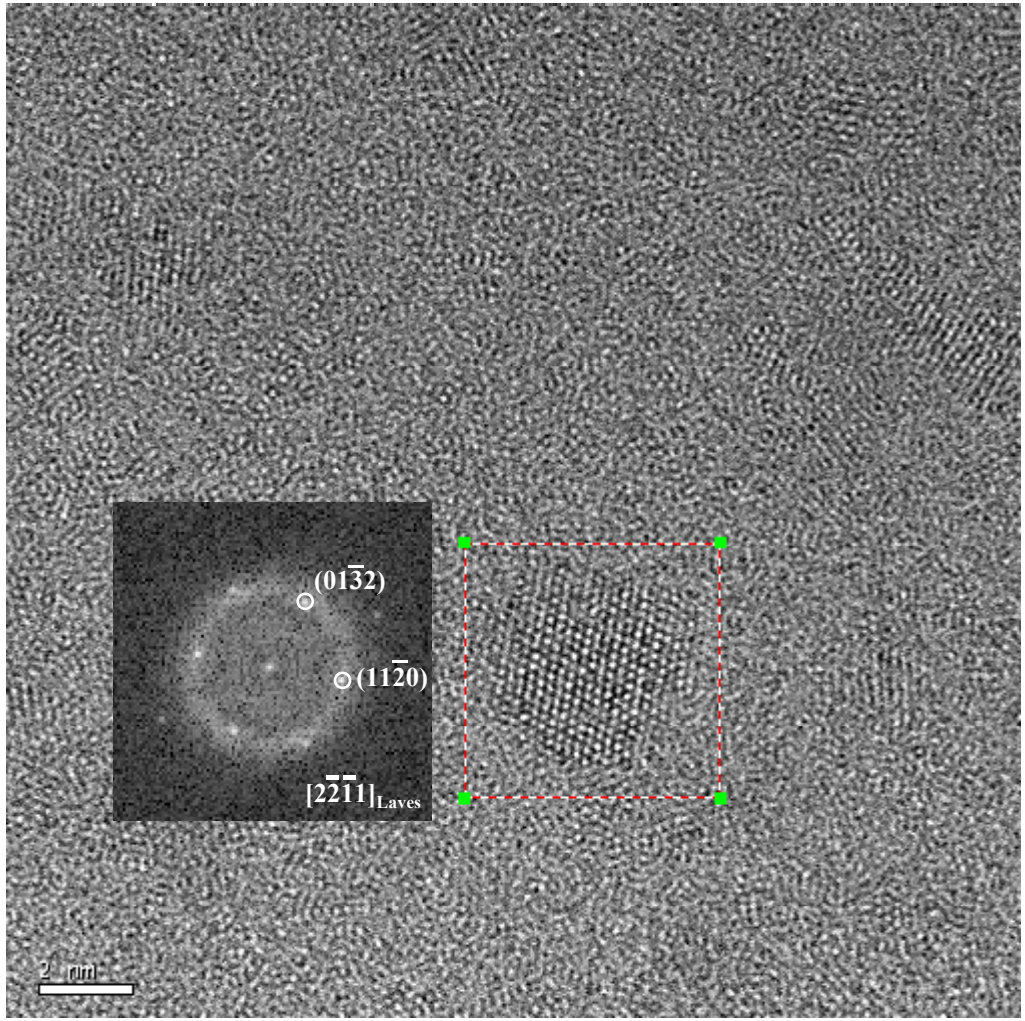


Formation of Nanocrystalline-$Ti_{40}Zr_{29}Cu_8Ni_9Be_{14}$ BMG



Indexing – crystalline : Laves phase

- MgZn2 type hexagoanl
- space group : p63/mmc
- a = 5.3Å, c = 8.6Å



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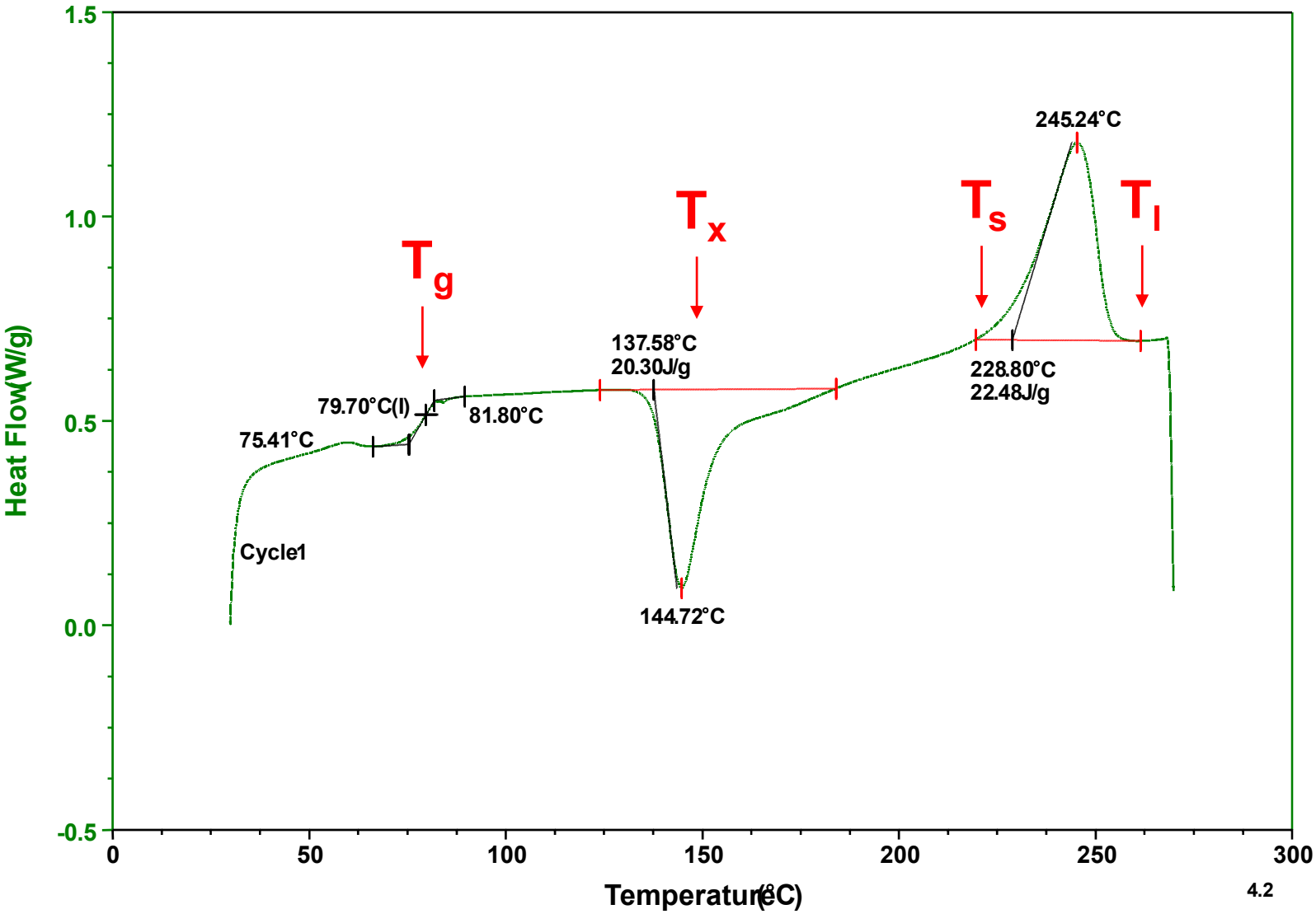
: *Characterization of structure by pair distribution function*

3) Intensive Structural Analysis: radial distribution function

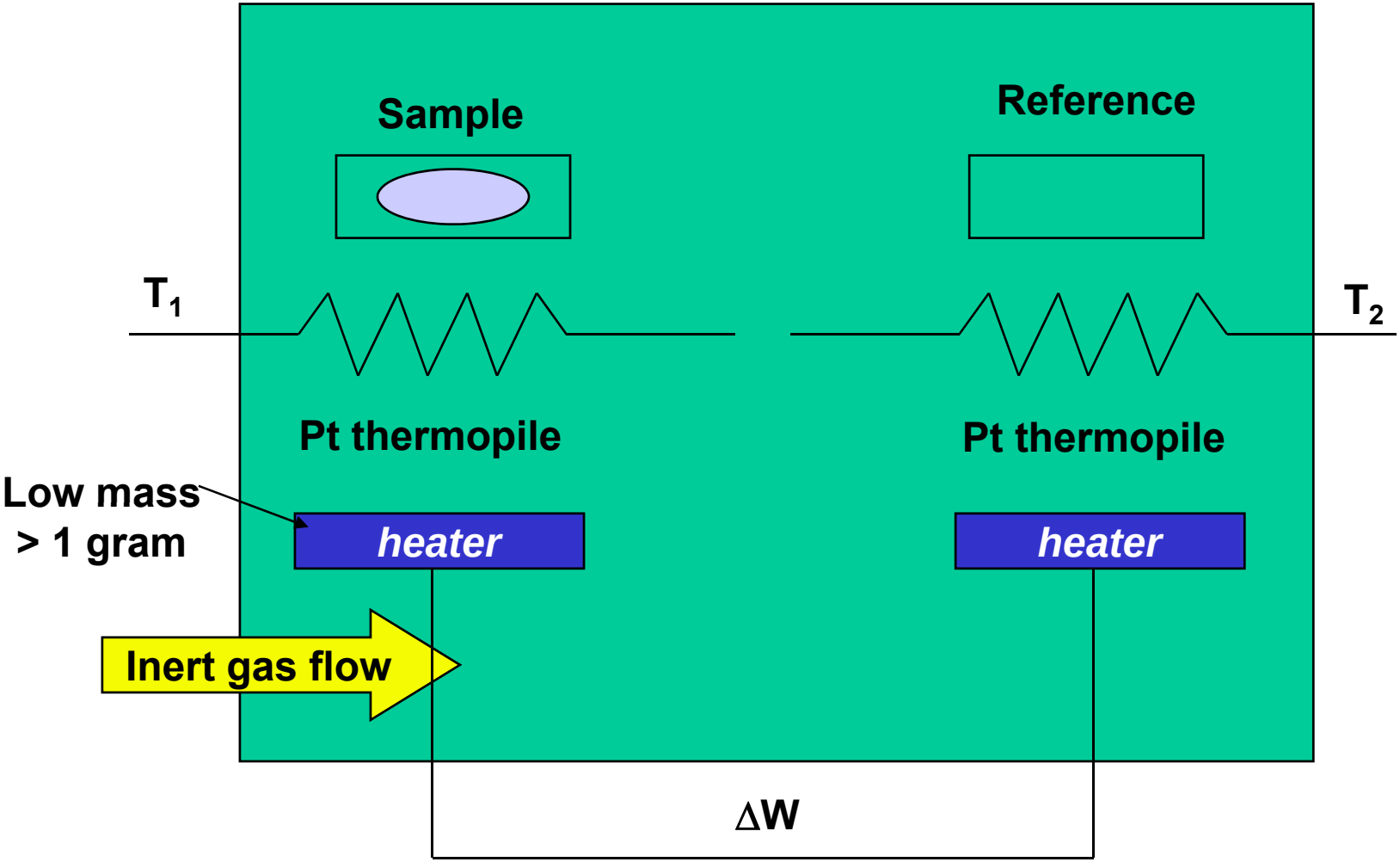
Example DSC – PET (polyethylene terephthalate)



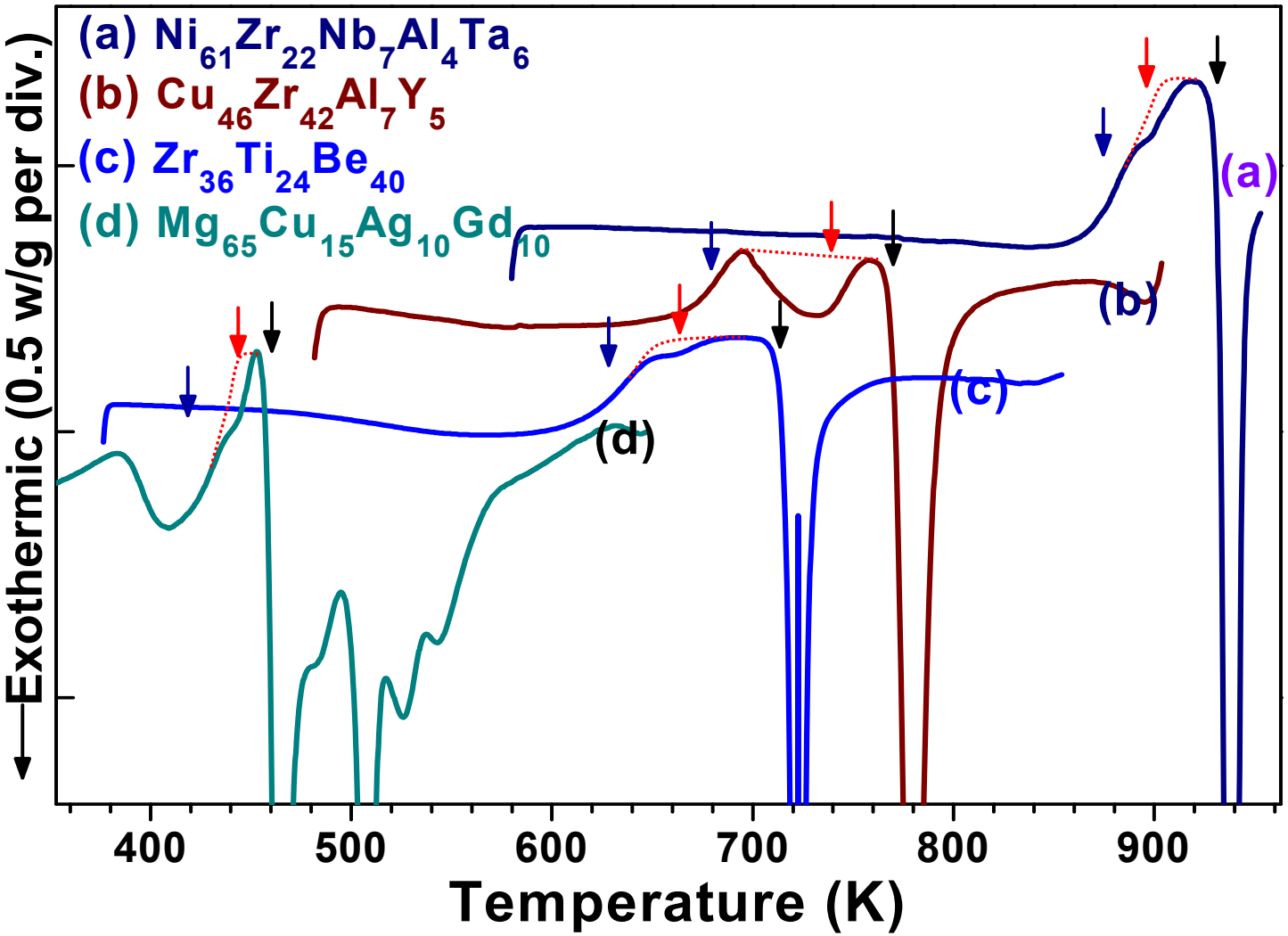
Thermal analysis: DSC

- 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.

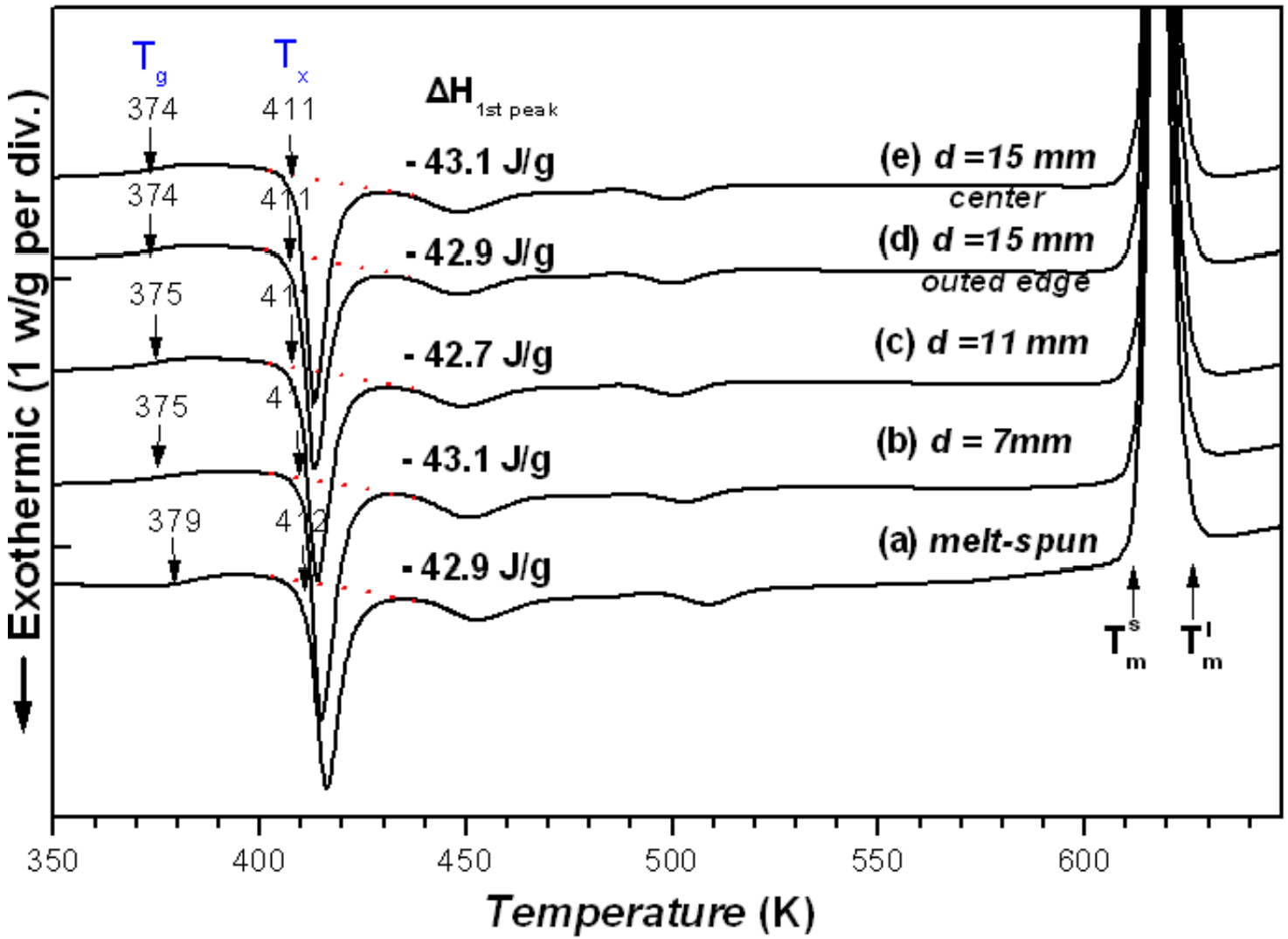
Schematic of DSC Instrument



Variation of T_g depending on alloy compositions

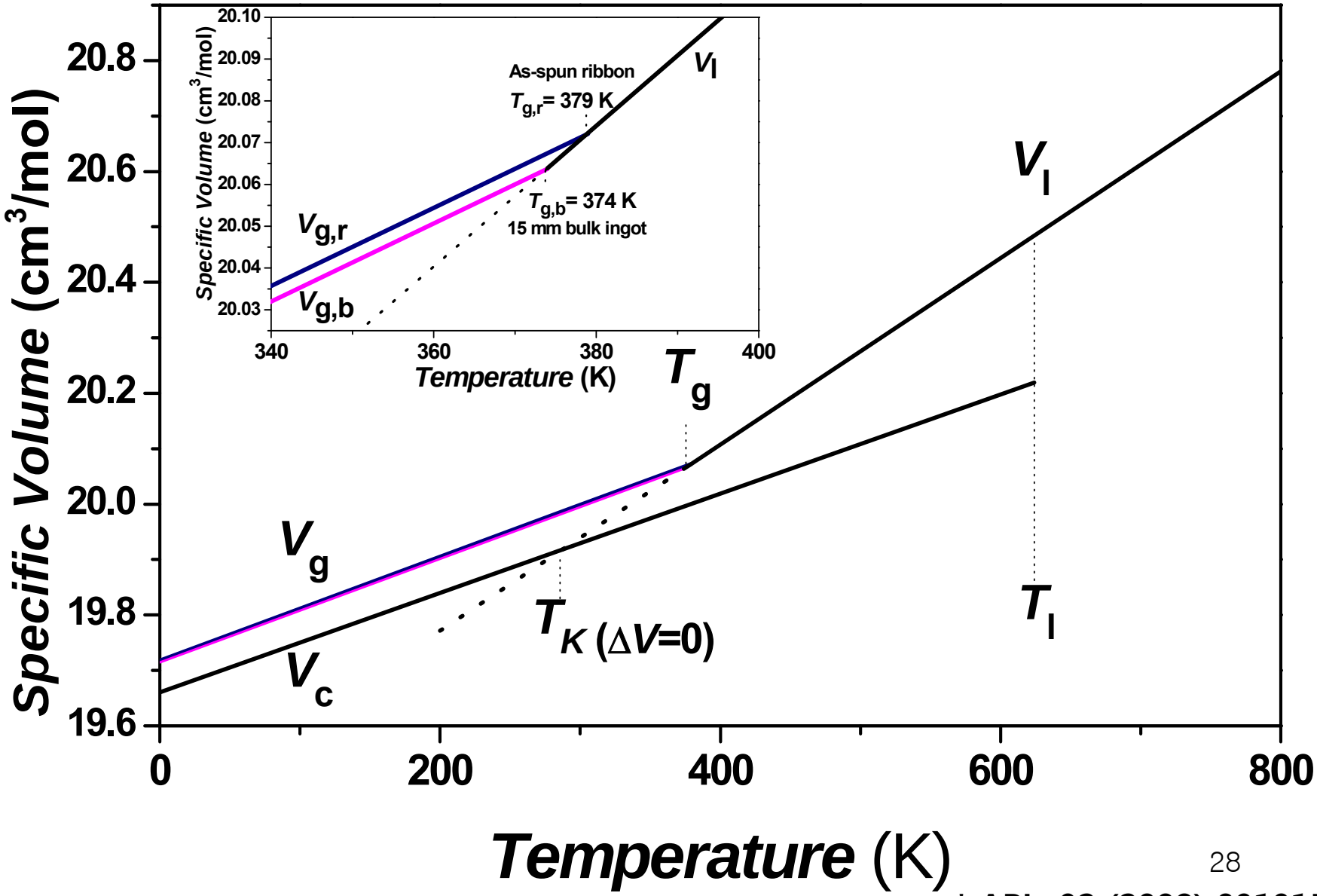


❖ **Typically T_g is ~ 50-60% of the melting point.**



* J Mater Res, 19 (2004) 685.

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



* APL, 92 (2008) 091915.