2014 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

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Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

Chapter 1. Introduction Development of New Materials

* Search for new and advanced materials

: addition of alloying elements, microstructural modification and by subjecting the materials to thermal, mechanical, or thermo-mechanical processing methods

→ Completely new materials

"Stronger, Stiffer, Lighter and Hotter…"

: Nanocrystalline Materials, High Temperature Superconductors,

Metallic Glass (1960), Quasi-crystal (1984), Gum Metal (2003), High Entropy Alloy (2004)

* 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

What is an Amorphous Materials?

- ***Amorphous*** **– from the Greek for "without form"**
  not to materials that have no shape,
  but rather to materials with no particular structure

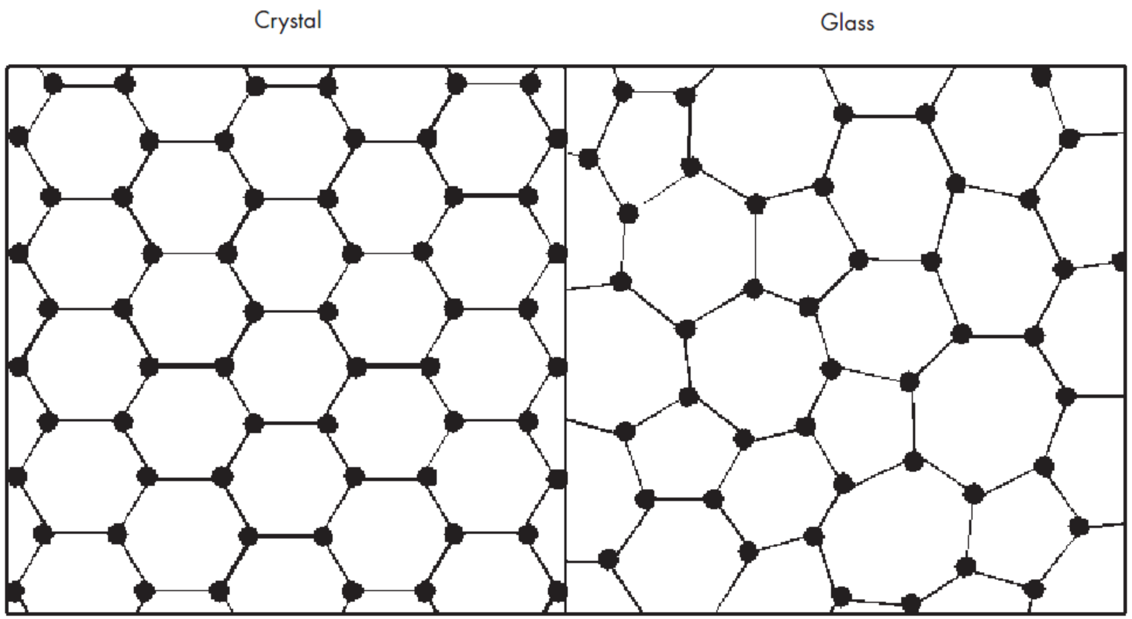


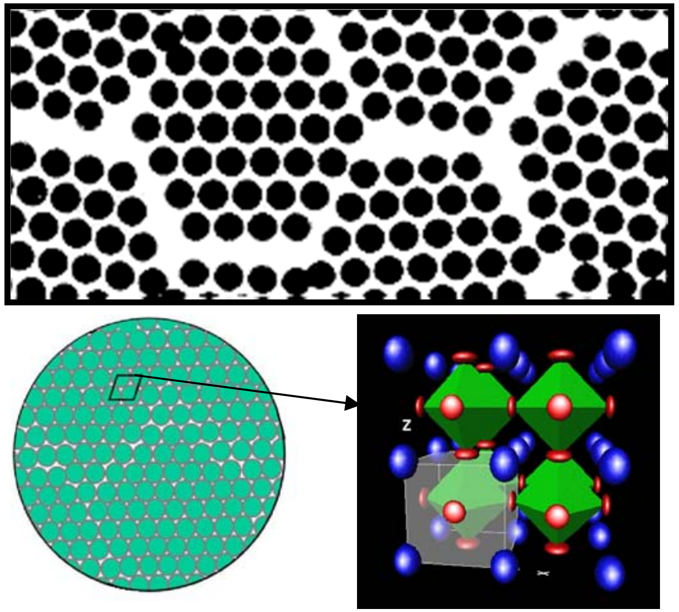
Figure 1. Schematic Illustration of the Structures of Crystals and Glasses.

closely packed and chemically bonded solid
~ elastic response to shear stress

2.2 Distinction between crystals and glasses

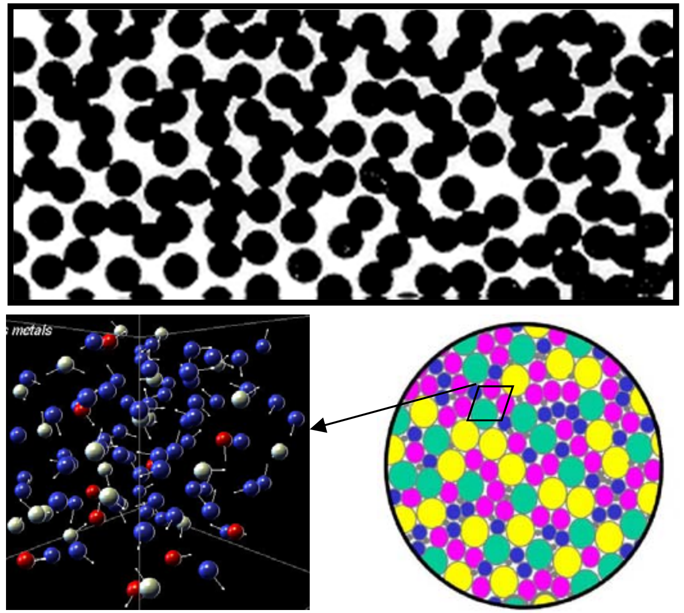
Structure of crystals, liquids and glasses

Crystals



- **periodic**
- **grain boundaries**

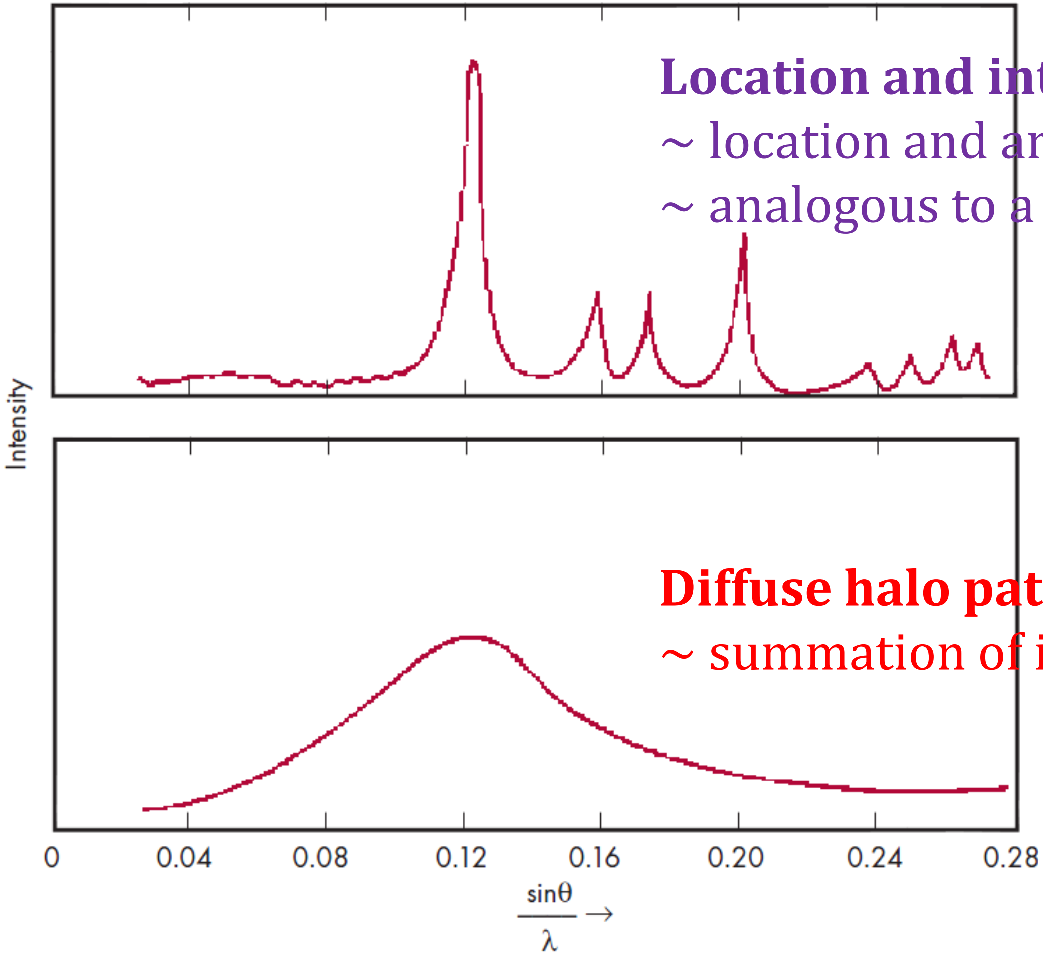
Liquids, glasses



- **amorphous = non-periodic**
- **no grain boundaries**

* Each atom in the noncrystalline solid will have different nearest neighbors and CNs. But, it can be safely sated that the nearest neighbor distances are longer and the CNs smaller in a noncrsytalline solid in comparison to its crystal counterpart.

X-ray or Neutron results

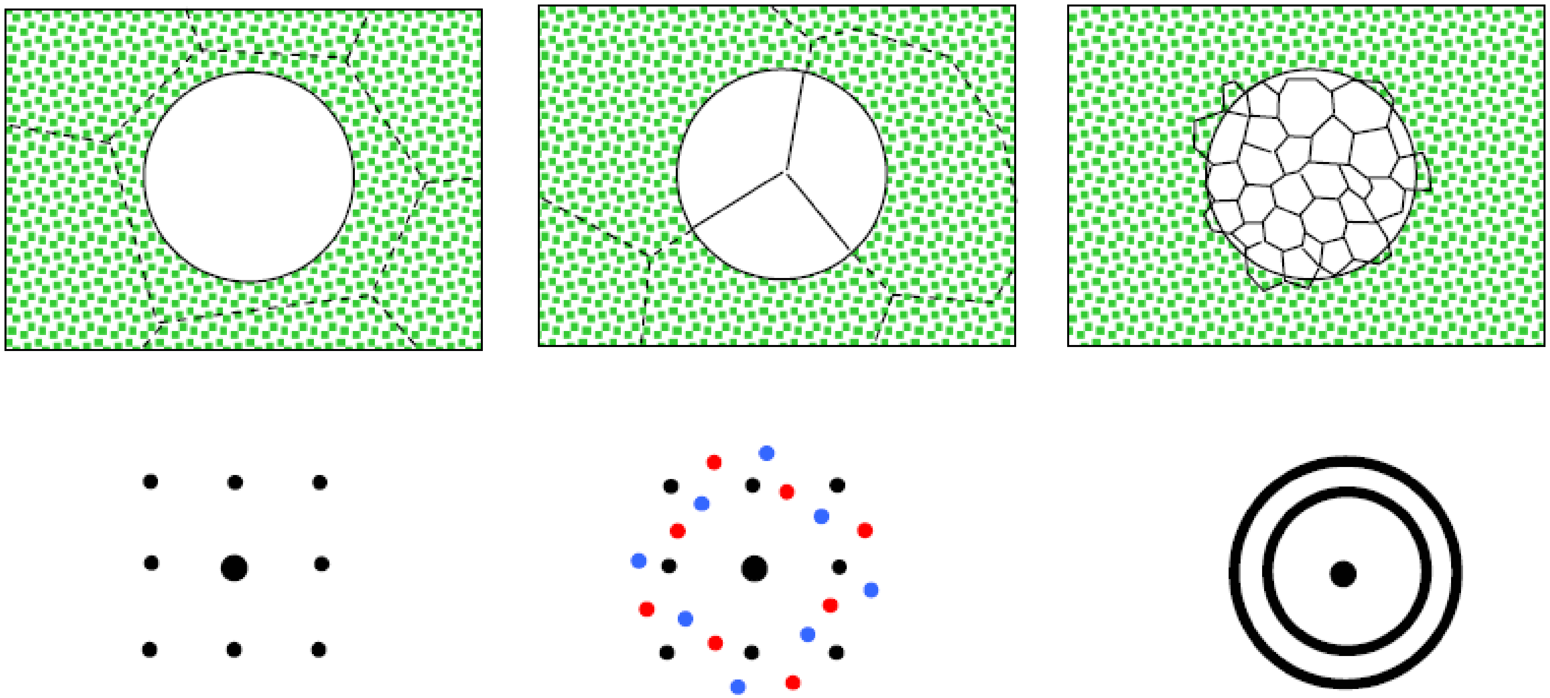


Location and intensity of peaks
~ location and arrangement of atoms
~ analogous to a fingerprint

Diffuse halo pattern
~ summation of interference

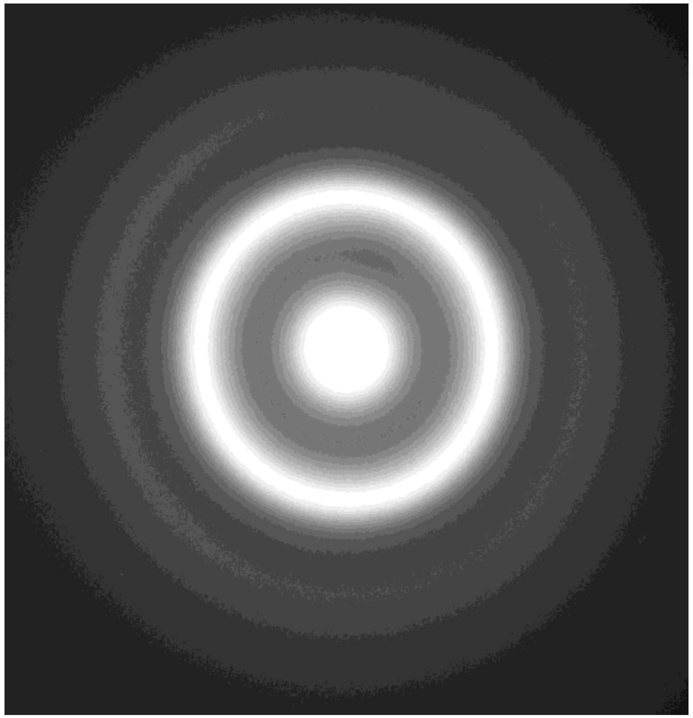
Figure 3. **Characteristic Diffraction Patterns from Crystalline Material (Top) and Amorphous Material (Bottom).**

Electron Diffraction Pattern--Spot to Ring

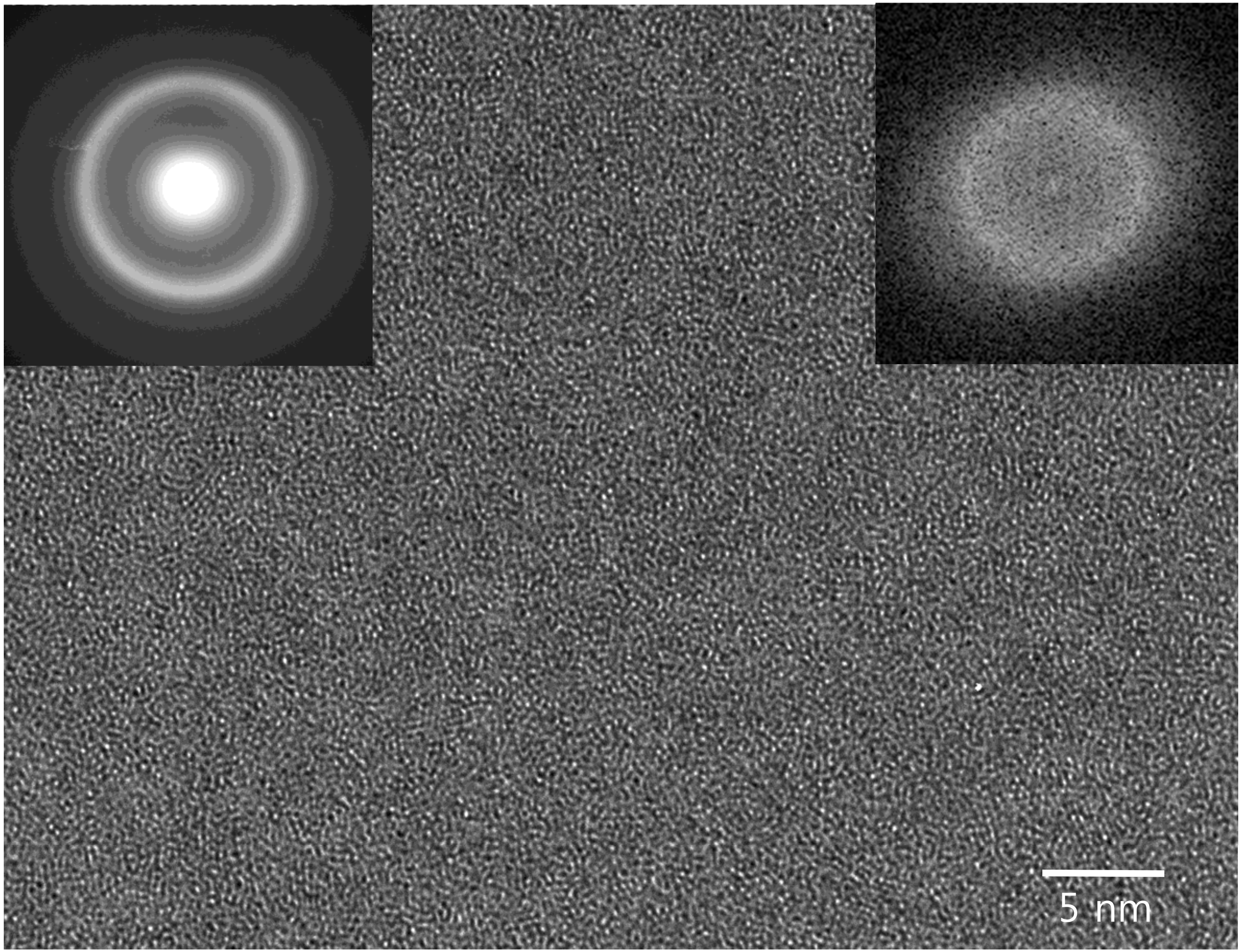

(a)
(b)
(c)

Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film



TEM results_Zr-based BMGs

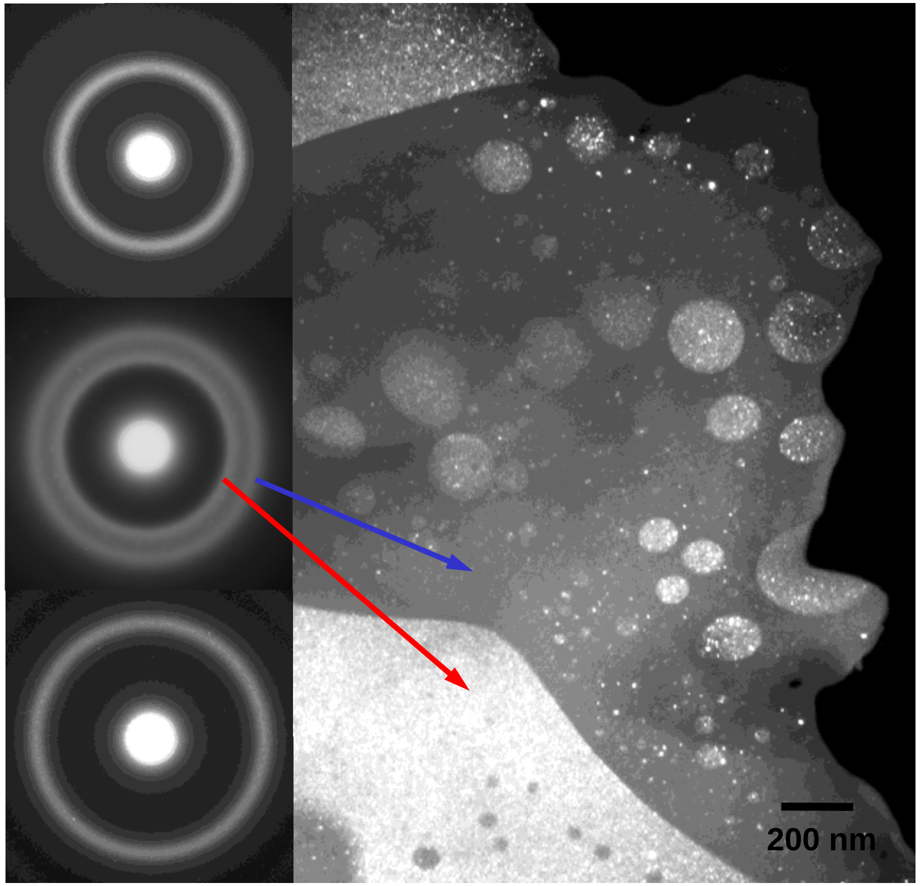


TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy

$Nd_{60}Al_{10}Co_{30}$
2.91 Å

$Nd_{30}Zr_{30}Al_{10}Co_{30}$
2.37 Å, 2.99 Å

$Zr_{60}Al_{10}Co_{30}$
2.40 Å



SADP and Dark-field TEM image

Classification of materials with structure

Perfect crystal → *disorder* → *quasicrystal* → *amorphous*

: *unit cell*

: *underlying perfect crystalline lattice*

(a), (b), (c), (d)

Spin disorder   Vibrational disorder

ex) *icosahedral phase*

: *no topological ordering*

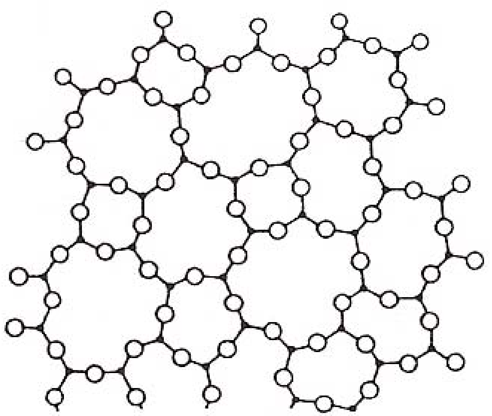
ex) *icosahedral glass*

(a) Topological disorder : various defects

(c) Substitutional disorder: Solid solution vs intermetallic compounds

➡ Hume-Rothery Empirical Rules for Alloys

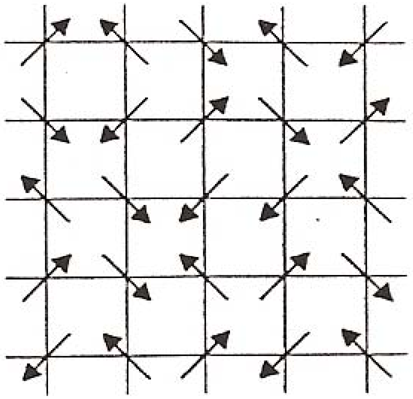
* Four types of disorder



a) Topological (or geometric) disorder

: no translational order at all

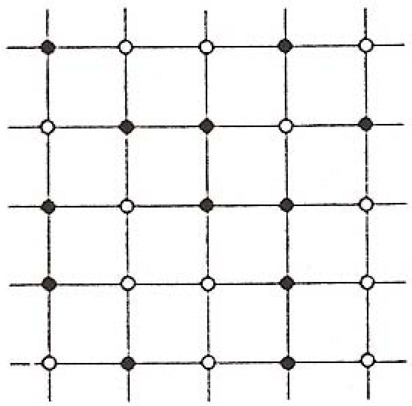
: but some degree of short range ordering



b) Spin disorder

: spin (or magnetic moment) exhibits random orientation.

: underlying perfect crystalline lattice

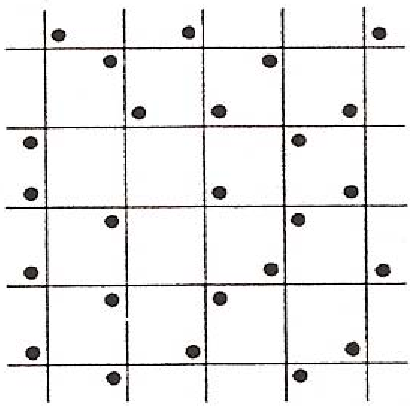


c) Substitutional disorder

: metallic alloy

: solid solution

: underling perfect crystalline lattice



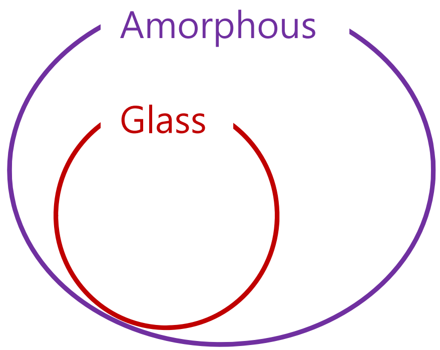
d) Vibrational disorder

at any finite temperature the random motion of atoms about their equilibrium position destroys the perfect periodicity

2.3 differences between Amorphous Alloys and Metallic Glasses

Non-crystalline solid : Amorphous solid vs 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.



* presence of a glass transition temperature, T_g

Exception: In the case of bulk metallic glasses (BMGs), there is usually a large supercooled liquid region, $\Delta T_x = T_x - T_g$, and in such cases it is relatively easy to locate the T_g. But, there are instances even in the case of BMGs, which exhibit a very large ΔT_x value, but the presence of T_g could not be clearly identified. For example, an $Nd_{70}Fe_{20}Al_{10}$ ternary alloy melt could be cast into a 7 mm diameter glassy rod, but the DSC curves did not indicate the presence of a T_g [14].

Angell [15] mentions that the presence of T_g is not essential for a material to be called a glass!

Fundamentals of the Glass Transition

If liquid is cooled, two events can occur.

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

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

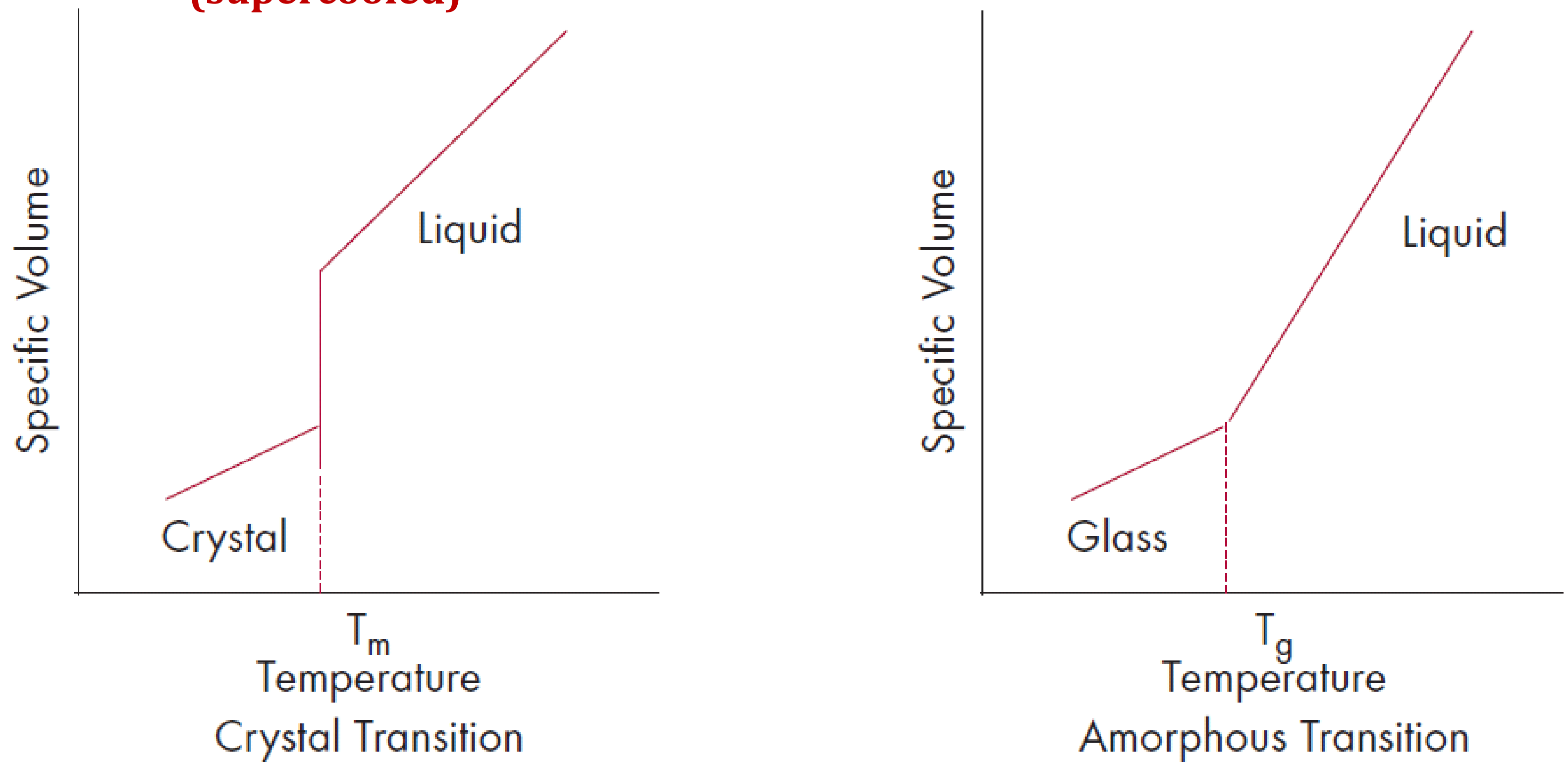


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

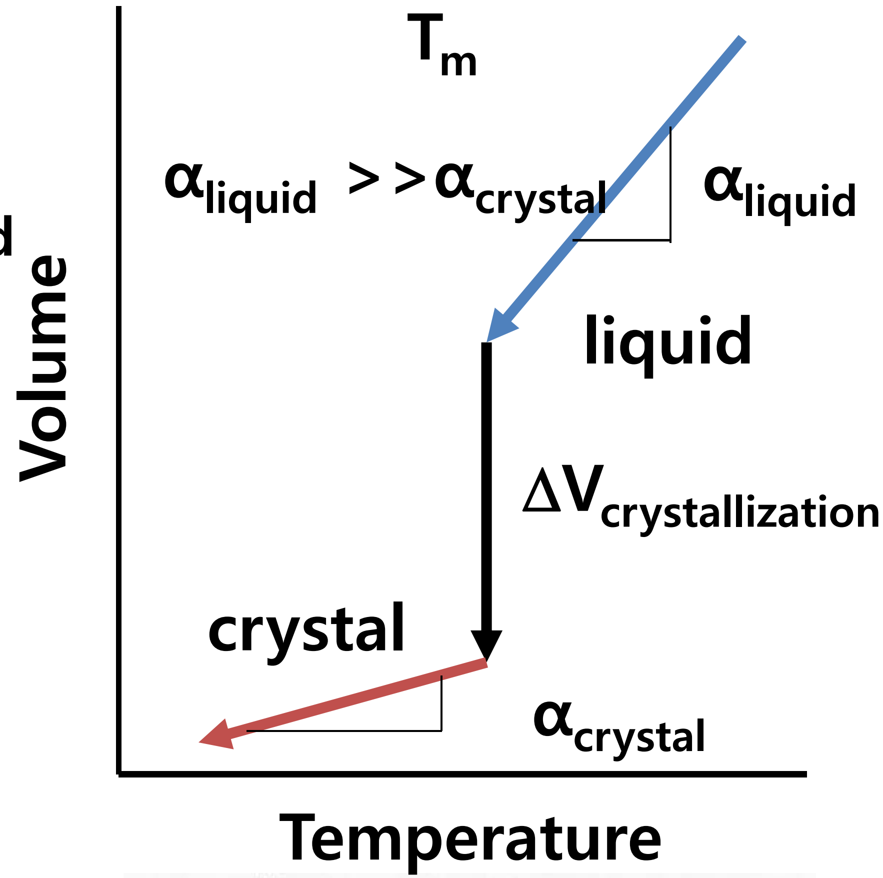
Fundamentals of the Glass Transition

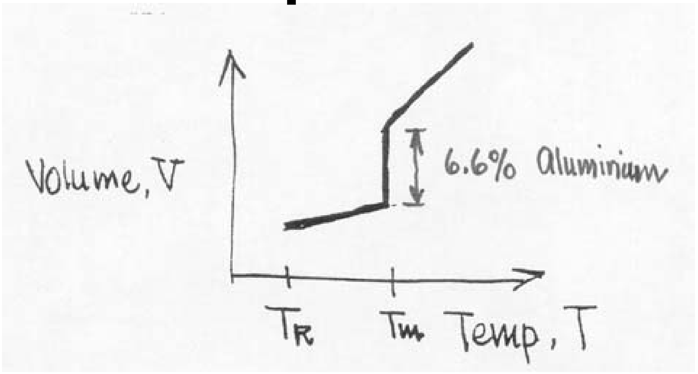
- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at T_m
  - Structures are thermodynamically controlled and described by the
  - Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2,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

Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α





Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

*** Volumetric solidification expansion: H_2O (10%), Si (20%), Ge**

ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

→ precipitation of graphite during solidification reduces shrinkage.

Shrinkage effect

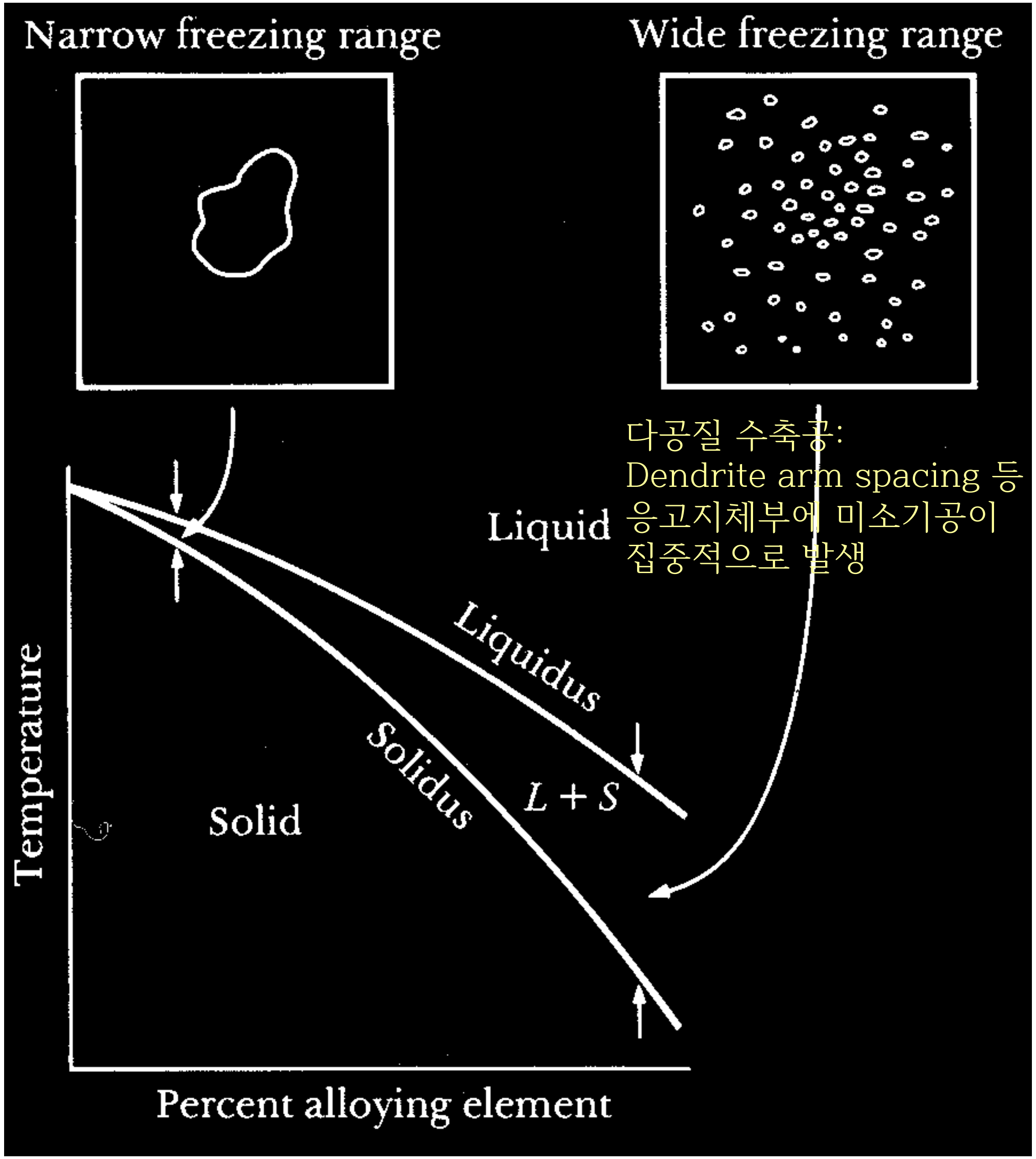
* Formation of Voids during solidification

중심수축공: 조성 변화가 크지 않은 주물의 응고시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

분산형 미소기공:
상당히 넓은 범위에 분산된 미소기공

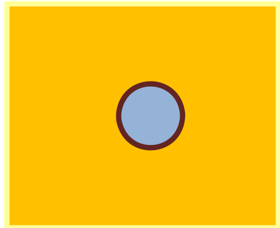
외부수축 (몰드 주위) 및 1차수축공 (표면)을 제외하면, 이러한 수축공 결함은 주로 기포 결함임

기포 내에는 철합금에서는 CO, 질소, 산소, 수소 등이, 동합금에서는 수소, 산소, 알루미늄 합금에서는 수소 등의 가스가 존재



Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

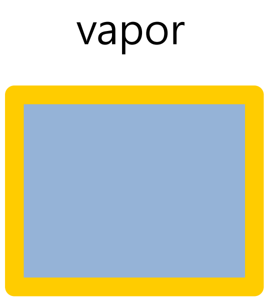
- Interfacial energy ⇨ ΔT_N

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!

Homogeneous Nucleation

Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

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

L : $\Delta H = H^L - H^S$

(Latent heat)

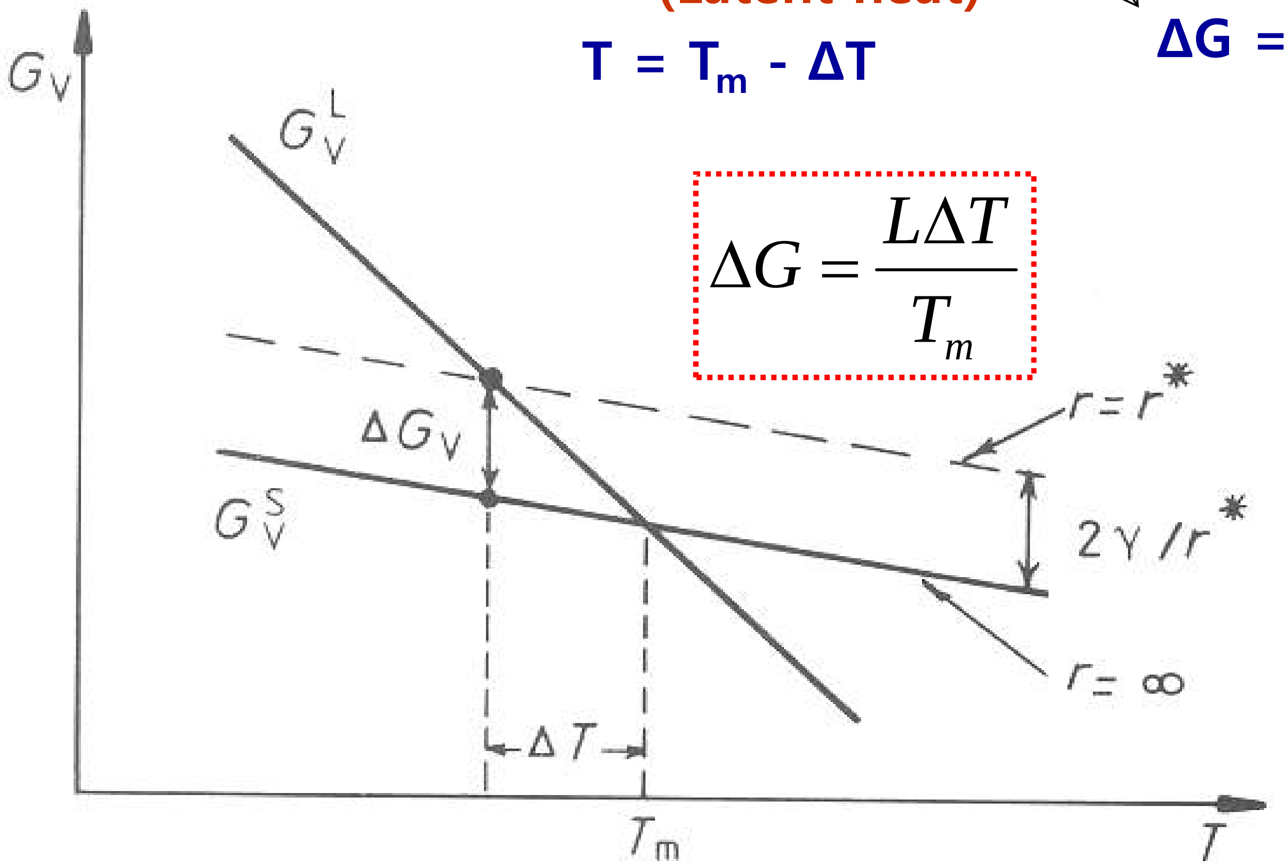
$T = T_m - \Delta T$

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

$\Delta S = \Delta H / T_m = L / T_m$

$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

$$\Delta G = \frac{L\Delta T}{T_m}$$



* Quasi-chemical approach

* 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

4.1.4. Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

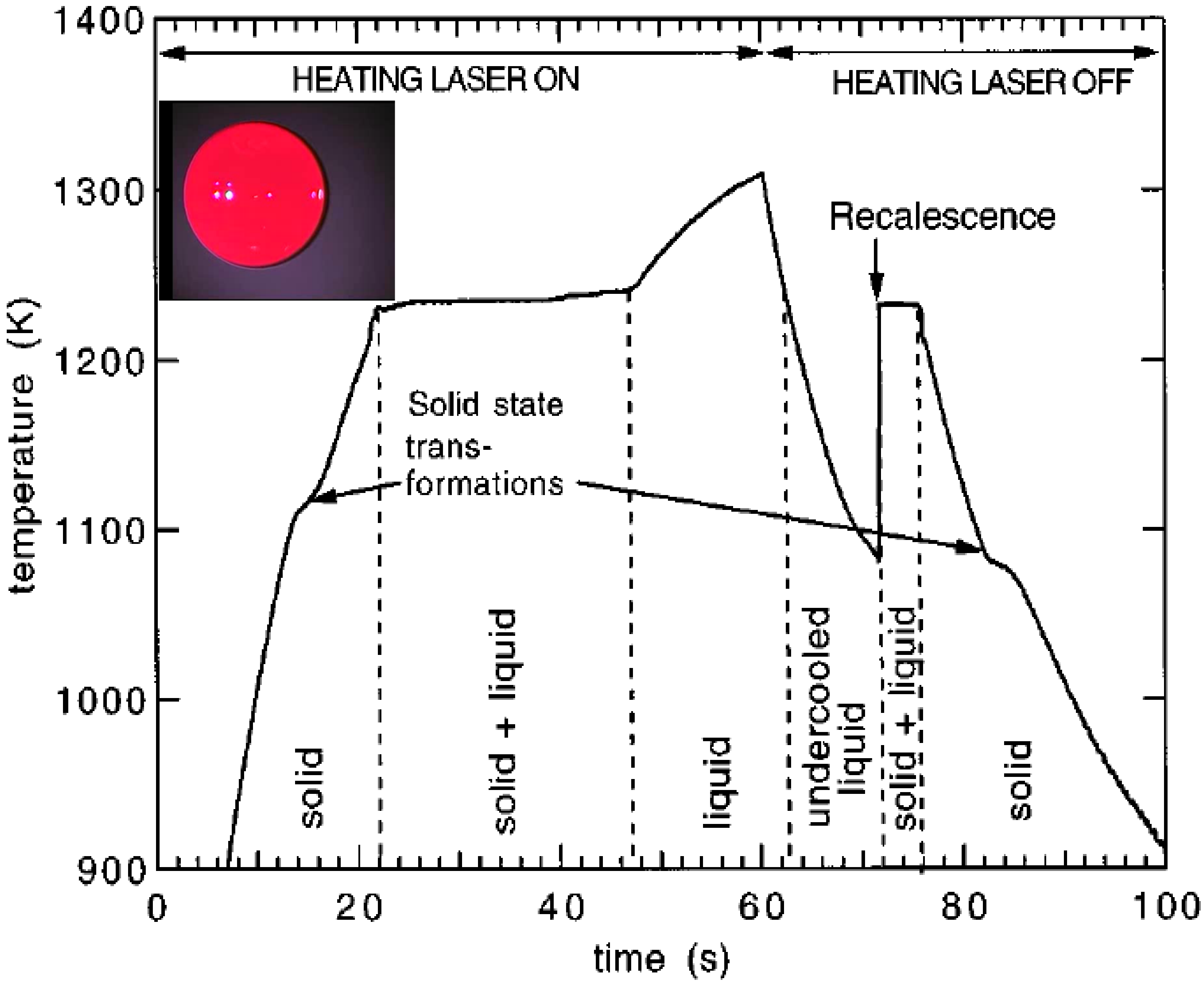
Why?

개념적으로 생각해보면

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ (commonly)

Solid -> liquid 로 원자 떼어내는데 드는 힘	+	Liquid-> Vapor 로 원자 떼어내는데 드는 힘	<	Solid-> Vapor 로 원자 떼어내는데 드는 힘

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


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

Cyclic cooling curves in ESL