2017 Fall

"Phase Equilibria *in* Materials"

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- Binary System mixture/ solution / compound

- Gibbs Free Energy in Binary System

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Ideal solution ($\Delta H_{mix}=0$) $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Regular solution $\Delta H_{mix} = P_{AB}\varepsilon$ where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

- Chemical potential and Activity

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T, P, n_B}$$

- $\mu_A = G_A + RT\ln a_A$

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

μ는 조성에 의해 결정되기 때문에 dn_A가 매우 작아서 조성변화 없어야

- Chemical equilibrium → Gibbs phase rule

Regular Solutions

$G_2 = G_1 + \Delta G_{mix}$

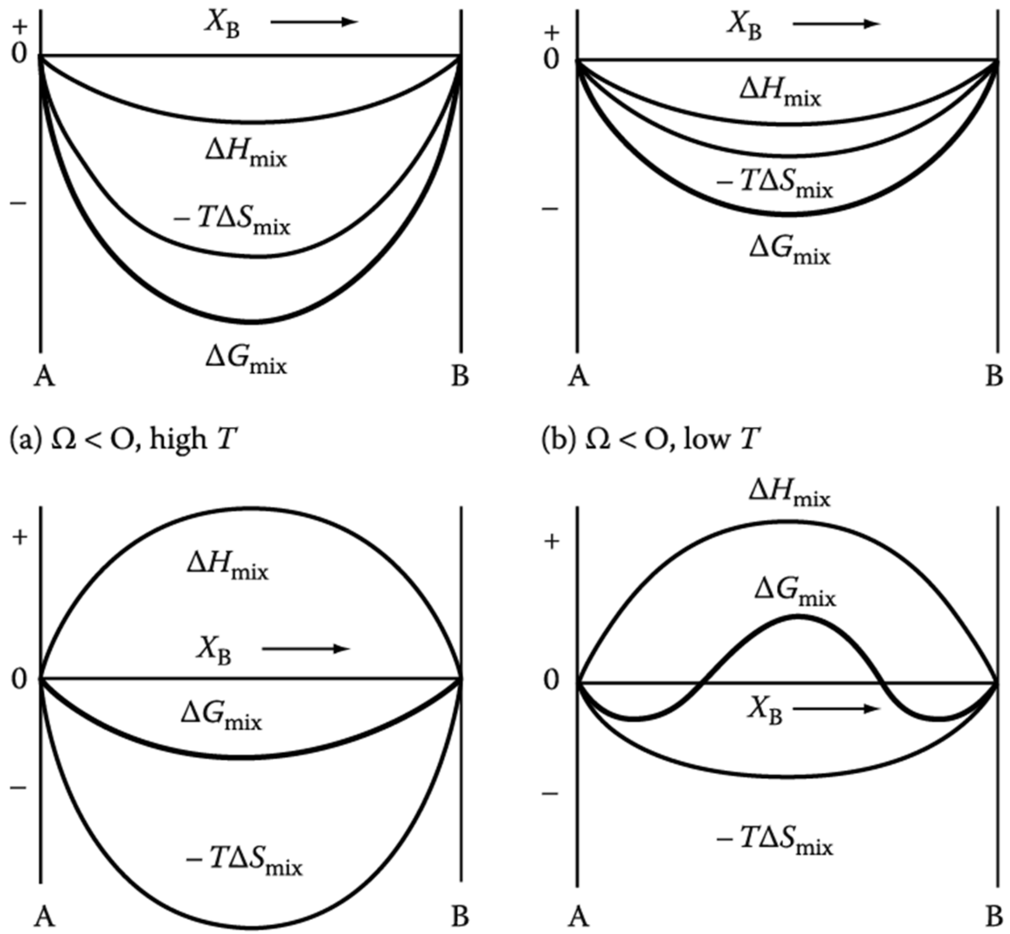
ΔH_{mix} $\quad$ $-T\Delta S_{mix}$

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Reference state

Pure metal $G_A^0 = G_B^0 = 0$

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$



(a) Ω < O, high T $\quad$ (b) Ω < O, low T

(c) Ω > O, high T $\quad$ (d) Ω > O, low T

At T_c the term $d^2(\Delta G_m)/d(X_A)^2$ will be zero.

Since

$$\frac{d^2(\Delta G_m)}{d(X_A)^2} = -2NC + NkT_c\left(\frac{1}{X_A} + \frac{1}{1-X_A}\right) = 0$$

then

$$2C = \frac{kT_c}{X_A(1-X_A)} \quad \text{or} \quad T_c = \frac{2CX_A(1-X_A)}{k}$$

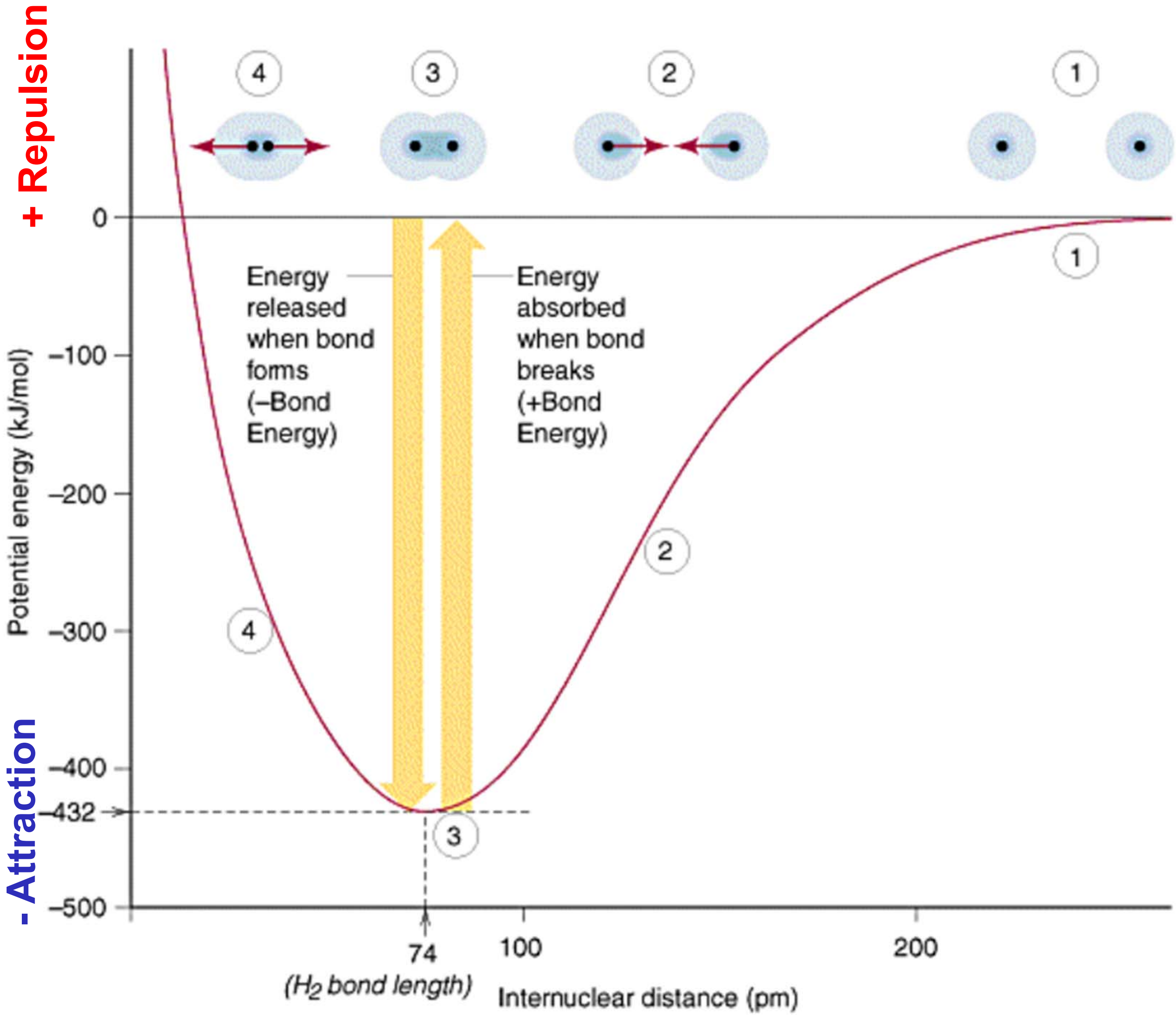
The term T_c will be a maximum when $X_A = (1-X_A) = 0.5$. It follows that

$$T_c = \frac{C}{2k}. \tag{101}$$

A high value of the critical temperature is associated with a high positive value for C $(= z[H_{AB} - \frac{1}{2}(H_{AA} + H_{BB})])$.

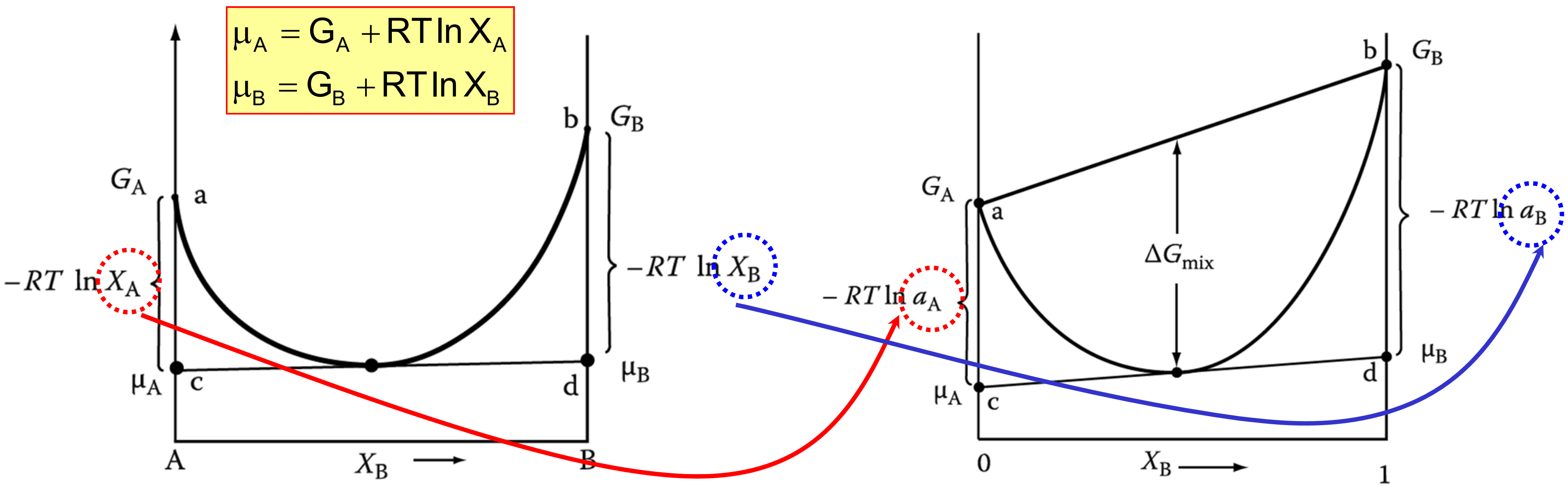
The stronger the attraction between similar atoms, the higher T_c. In those binary phase diagrams with a miscibility gap in the solid state the gap has not the symmetrical form shown in Fig. 21. This is primarily because the initial simplifying assumption that the energy is the sum of interaction between pairs of atoms is never absolutely valid. The systems Pd–Ir*, Pt–Ir** and Pt–Au*** all have miscibility gaps in the solid state with varying degrees of asymmetry. Most binary phase diagrams with a positive value of ΔH_m do not show a miscibility gap with a closure at temperature T_c since melting occurs before T_c is reached (for example the Ag–Cu system).

$$\Delta H_{mix} = P_{AB}\varepsilon \quad \text{where } \varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$



Activity, a : effective concentration for mass action

ideal solution **regular solution**



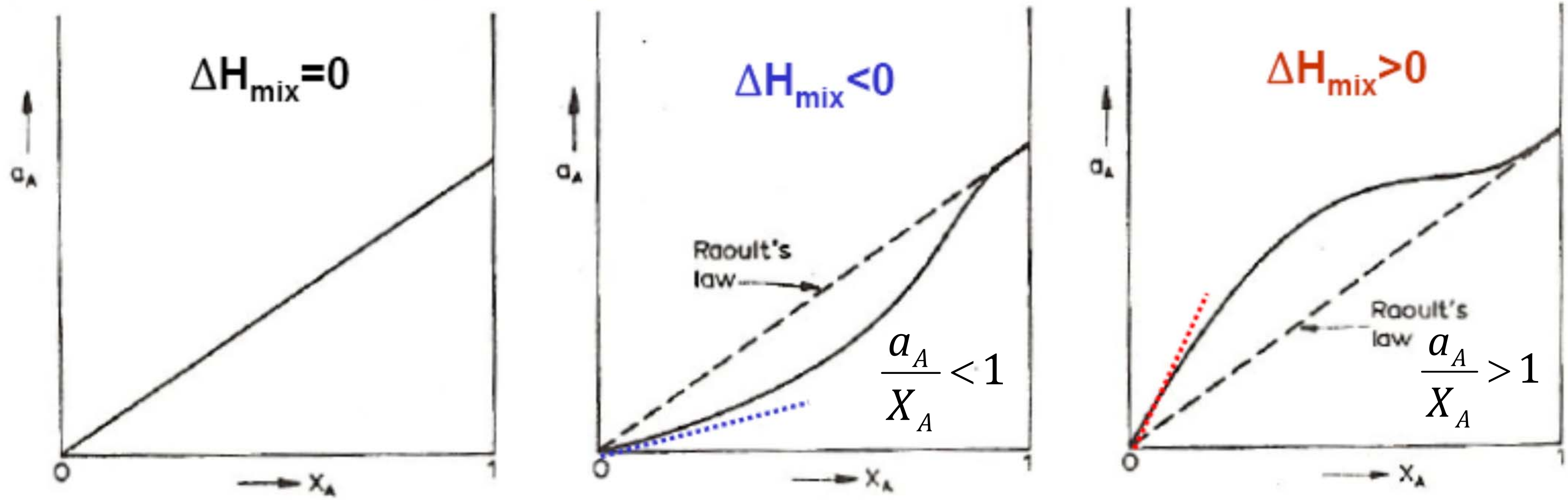
$$\mu_A = G_A + RT\ln a_A \qquad \mu_B = G_B + RT\ln a_B$$

$$\mu_A = G_A + \Omega(1-X_A)^2 + RT\ln X_A \qquad \mu_B = G_B + \Omega(1-X_B)^2 + RT\ln X_B$$

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1-X_A)^2 \qquad \ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1-X_B)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient} \qquad \gamma_B = \frac{a_B}{X_B}$$

Activity-composition curves for solutions



(a)
Ideal solution
A↔B = ½(A↔A + B↔B)
e.g. Bi–Sn at 335°C
$a_A = a_{Sn}$

(b)
Actual solution
A↔B > ½(A↔A + B↔B)
e.g. Au–Sn at 600°C
$a_A = a_{Sn}$

(c)
Actual solution
A↔B < ½(A↔A + B↔B)
e.g. Cd–Pb at 500°C
$a_A = a_{Cd}$

Degree of non-ideality

- **For a dilute solution of B in A ($X_B \to 0$)**

$$\gamma_B = \frac{a_B}{X_B} \cong \text{constant} \quad \text{(Henry's Law)}$$

$$\gamma_A = \frac{a_A}{X_A} \cong 1 \quad \text{(Rault's Law)}$$

The Gibbs Phase Rule

Degree of freedom (number of variables that can be varied independently)

= the number of variables – the number of constraints

- Number of phases : p, number of components : c,
- # of controllable variable : composition (c-1)p, temperature : p, pressure : p
- # of restrictions :

(p-1)c from chemical equilibrium $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots = \mu_i^p$

p-1 from thermal equilibrium $T^\alpha = T^\beta = T^\gamma = \cdots = T^p$

p-1 from mechanical equilibrium $P^\alpha = P^\beta = P^\gamma = \cdots = P^p$

- Number of variable can be controlled with maintaining equilibrium

$$f = (c-1)p + p + p - (p-1)c - (p-1) - (p-1) = c - p + 2$$

$$\boxed{f = c - p + 2}$$

- If pressure is constant : $f = (c-1)p + p - (p-1)c - (p-1) = \boxed{c - p + 1}$

Q1: What is “Real Solution”?

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

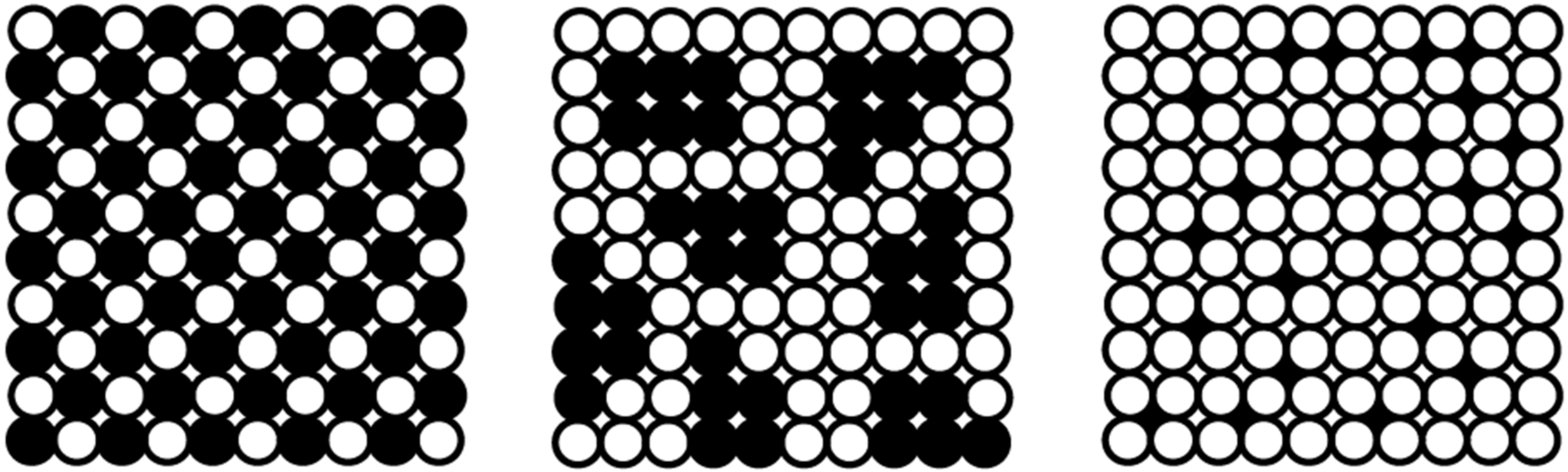
Real solution: sufficient disorder + lowest internal E

Ideal or Regular solution : over simplification of reality

Config. Entropy $S = k \ln w$ + mixing enthalpy $\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$

$S_{thermal} = 0$

$\varepsilon \approx 0$



(a) $\varepsilon < 0, \ \Delta H_{mix} < 0$

(b) $\varepsilon > 0, \ \Delta H_{mix} > 0$

(c) when the size difference is large
strain effect

Ordered alloys — P_{AB} ↑ ⟶ **Internal** E ↓

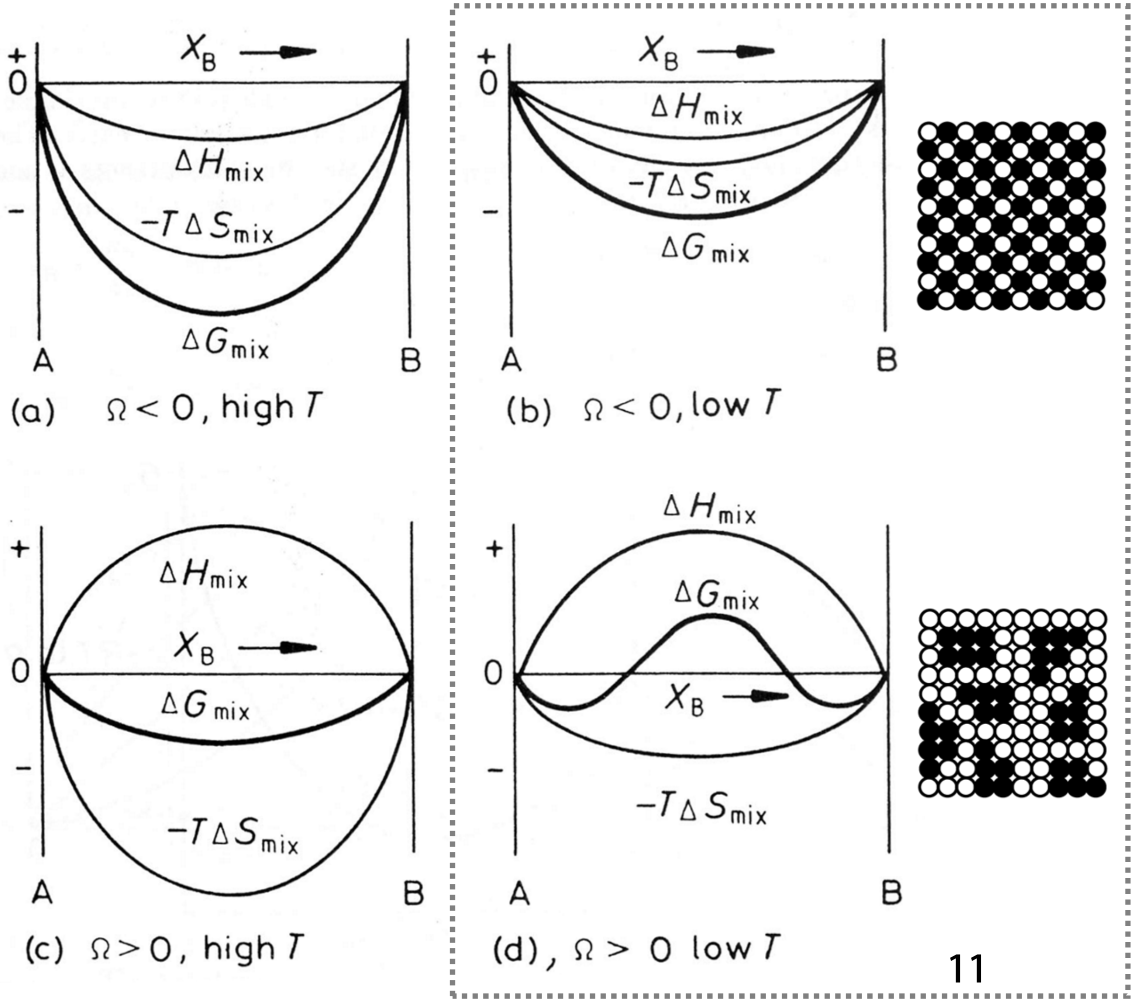
Clustering — P_{AA}, P_{BB} ↑

Interstitial solution

* The degree of ordering or clustering will decrease as temp. increases due to the increasing importance of entropy.

High temp. → Entropy effect ↑ → Solution stability ↑

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

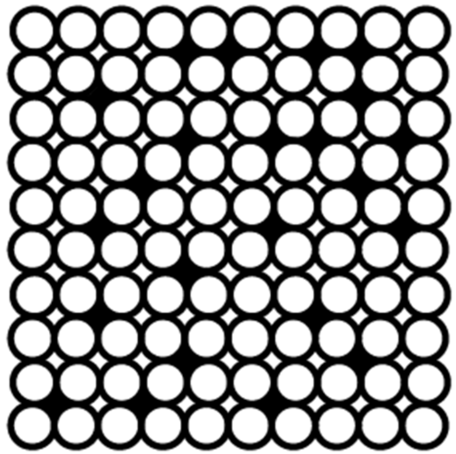


Real solution: sufficient disorder + lowest internal E

2) In systems where there is a size difference between the atom e.g. interstitial solid solutions,

➡ $\Delta E = \Delta H_{mix} + \text{elastic strain}$

➡ quasi- chemical model ~ underestimate ΔE due to no consideration of elastic strain field



➡ **New mathematical models are needed to describe these solutions.**

Q2: Short range order in solid solution?

1.3 Binary Solutions

Ordered phase $\varepsilon < 0, \; \Delta H_{mix} < 0$

SRO (Short Range Ordering) or LRO (Long Range Ordering)

- $\Omega < 0 \Rightarrow$ contain short-range order (SRO)

$\Delta\Omega = N_a z \varepsilon$

SRO parameter = *s* _ degree of ordering

$$s = \frac{P_{AB} - P_{AB}(random)}{P_{AB}(max) - P_{AB}(random)}$$

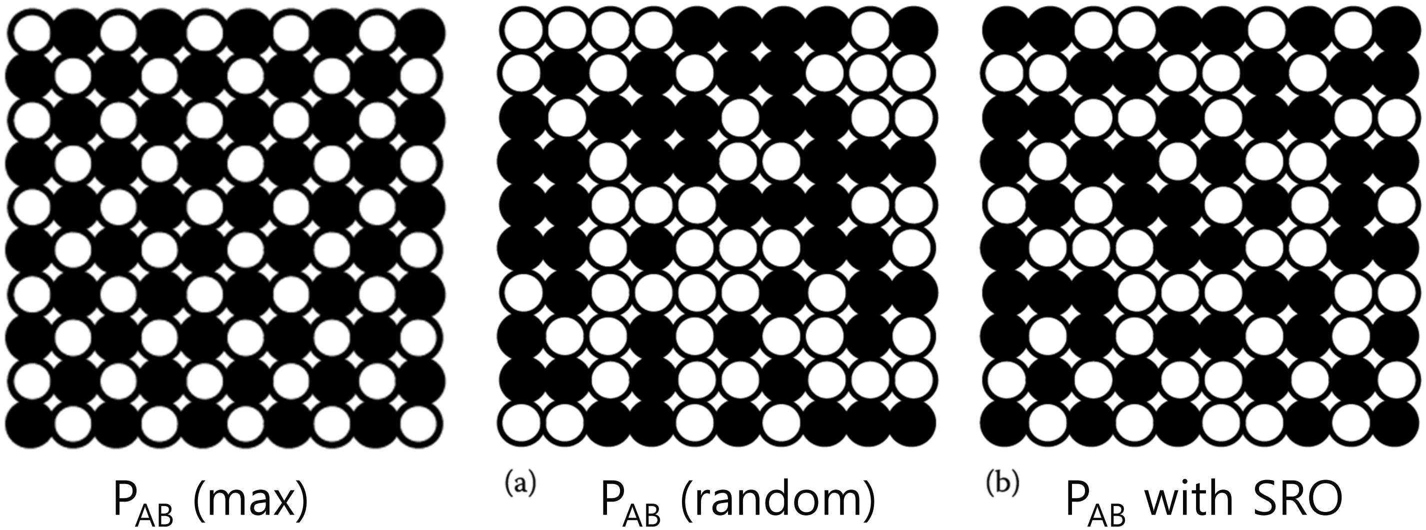
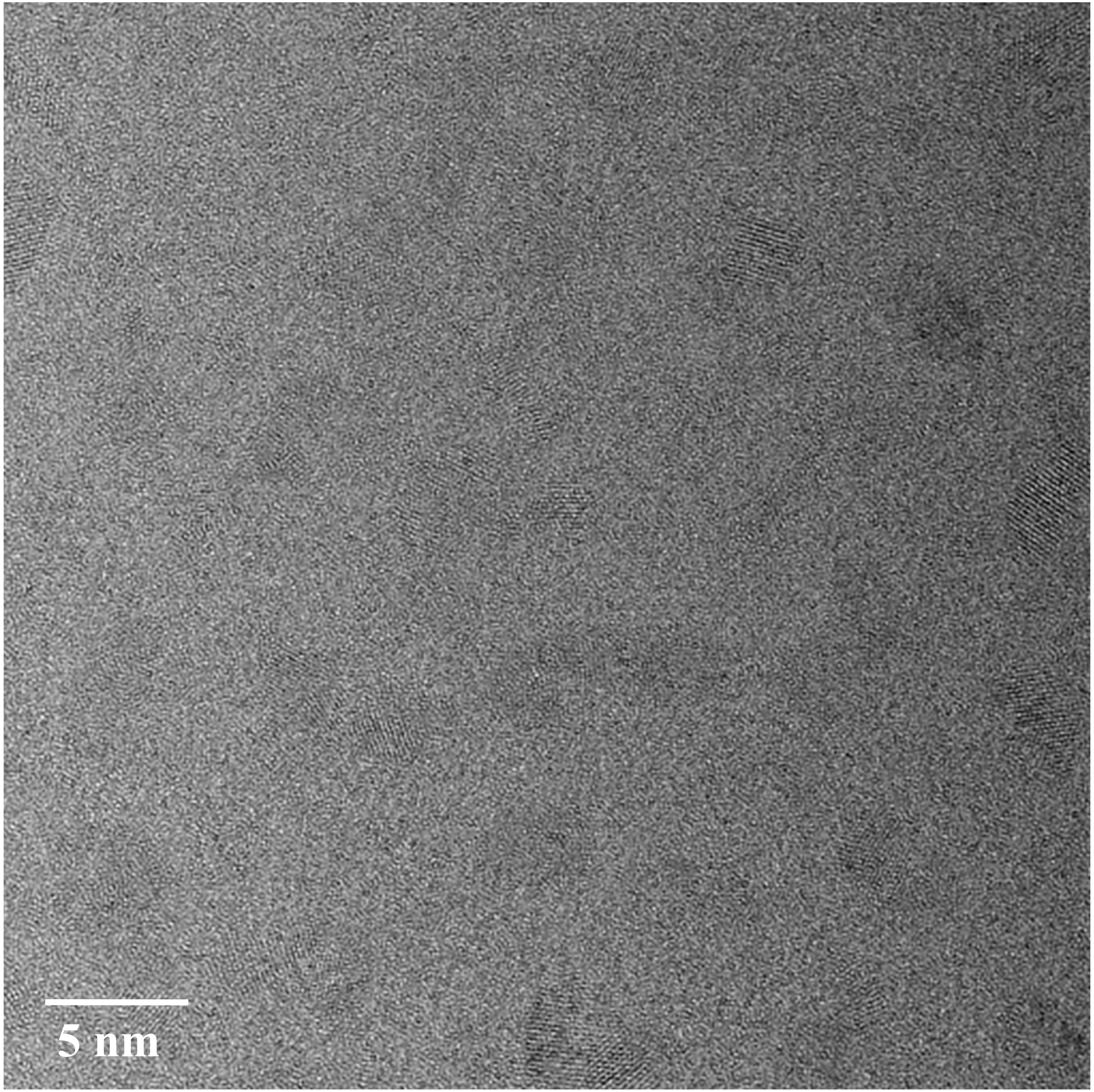
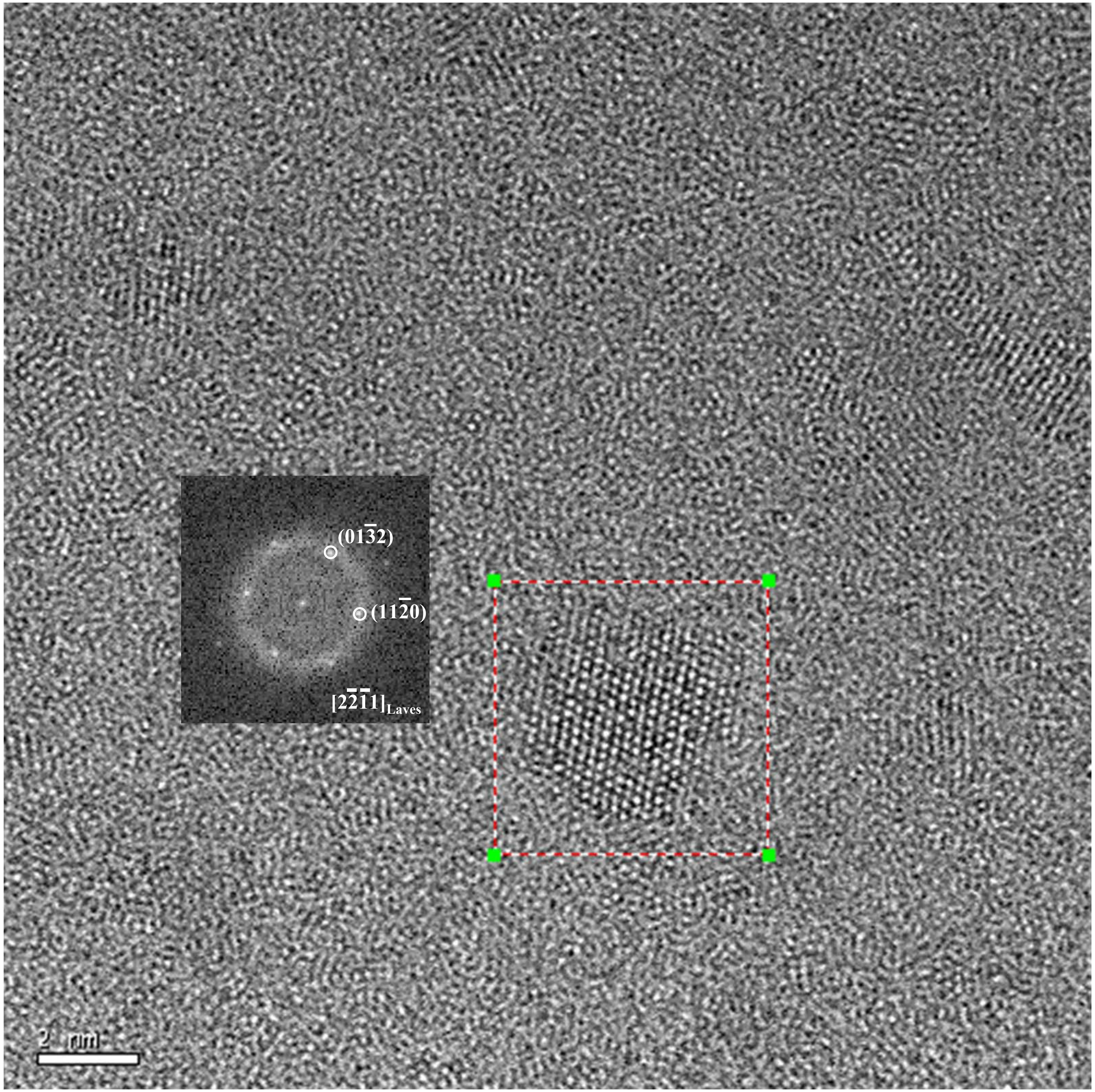


Fig. 1.19 (a) Random A-B solution with a total of 100 atoms and $X_A=X_B=0.5$, P_{AB}~100, S=0.
(b) Same alloy with short-range order $P_{AB}=132$, $P_{AB}(max)$~200, S=(132-100)/(200-100)=0.32.


5 nm



(01$\bar{3}$2)
(11$\bar{2}$0)
[2$\bar{2}\bar{1}$1]$_{Laves}$
2 nm

Ordered phase: "Long range order (LRO)"

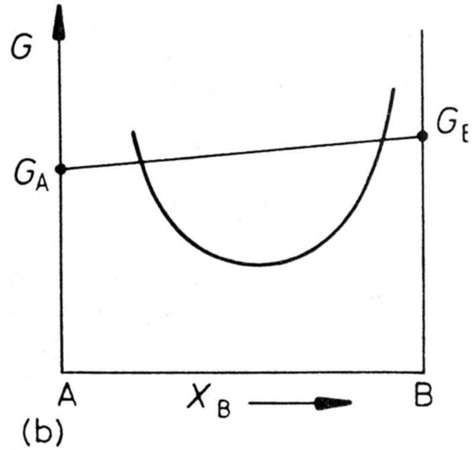
(①superlattice, ②intermediate phase, ③intermetallic compound)

$\Delta H^S_{mix} < 0$: Solid solution → ordered phase $\Delta H^S_{mix} << 0$: Compound : AB, A_2B…

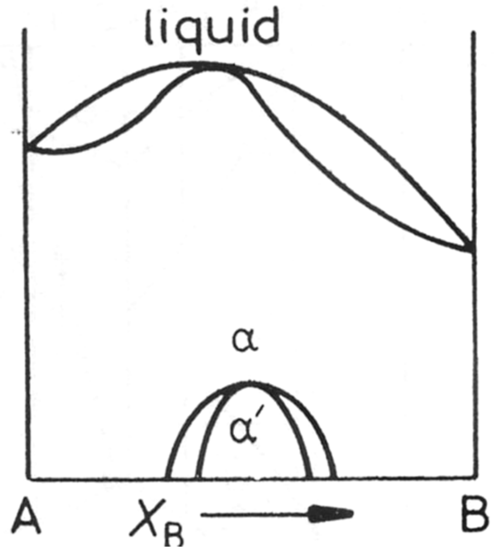
* Solid solution → ordered phase
  - → random mixing
  - → entropy ↑
    negative enthalpy ↓

$$\Delta H^S_{mix} < 0$$

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 contribution.
  - → enthalpy more negative ↓

$$\Delta H^S_{mix} << 0$$

Small composition range
➔ G ↓

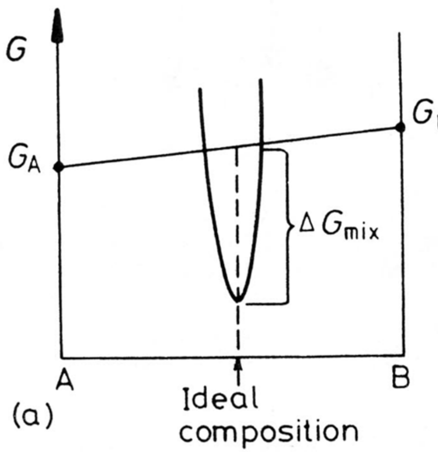
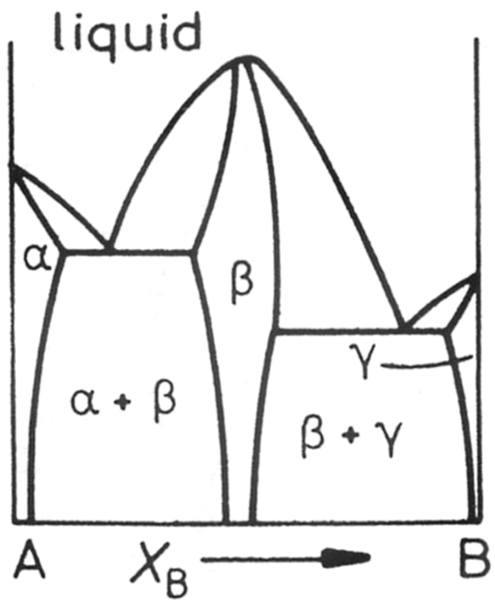


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.

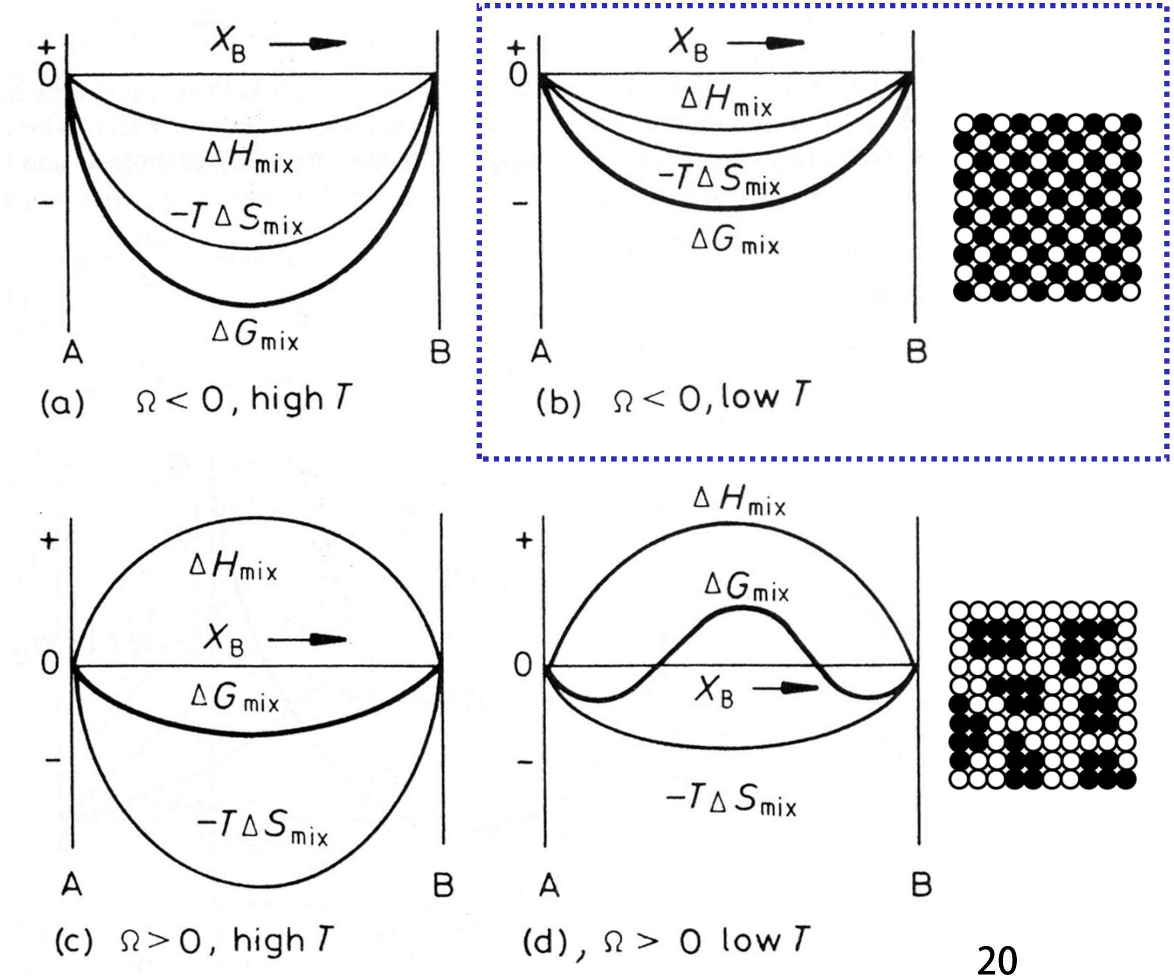


Q3: Superlattice

* The degree of **ordering or clustering** will **decrease as temp. increases** due to the increasing importance of **entropy**.

High temp. → Entropy effect ↑ → Solution stability ↑

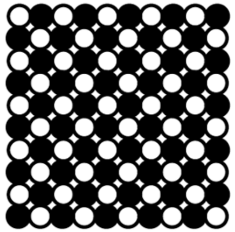
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



Ordered phase $\varepsilon < 0, \ \Delta H_{mix} < 0$

* In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found.

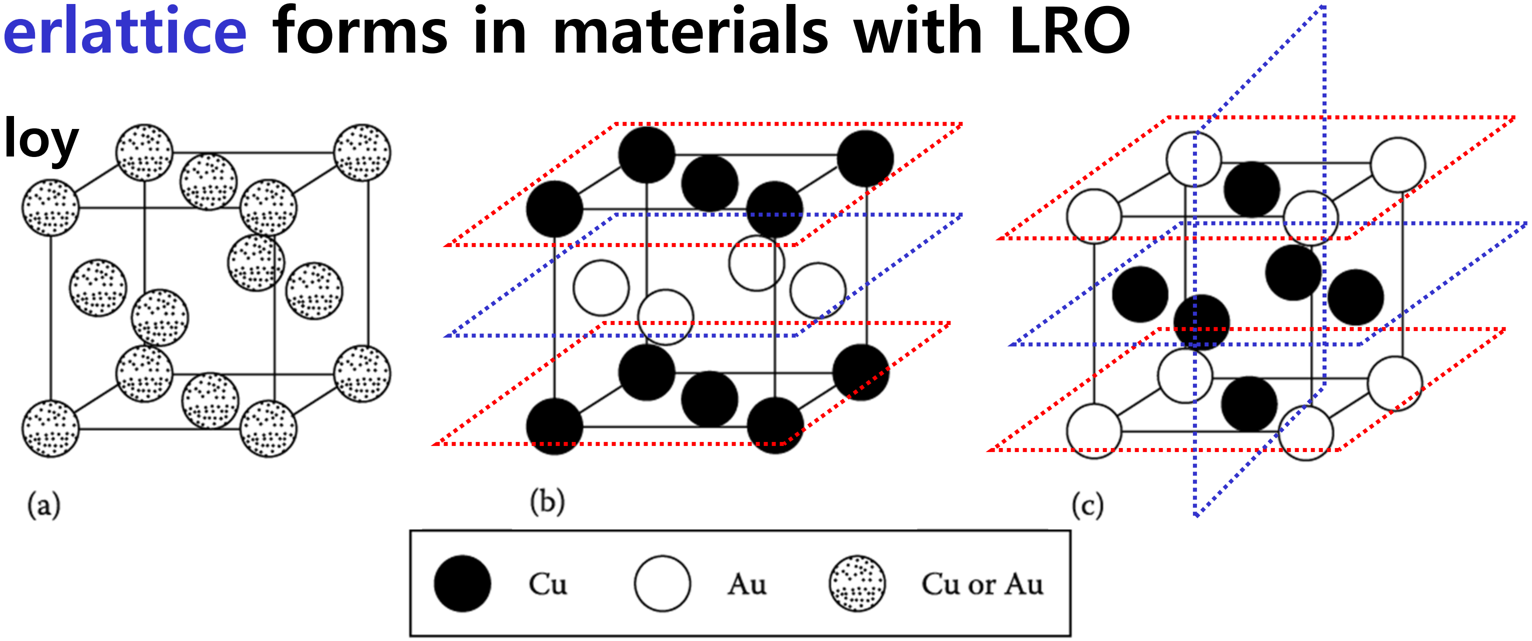
* This is known as long-range order (LRO) CuAu, Cu_3Au and many other intermetallics show LRO.



(The atom sites are no longer equivalent but can be labelled as A-sites and B-sites.)

* A superlattice forms in materials with LRO

Cu–Au alloy



High temp.
Disordered Structure

Low temp.
CuAu superlattice

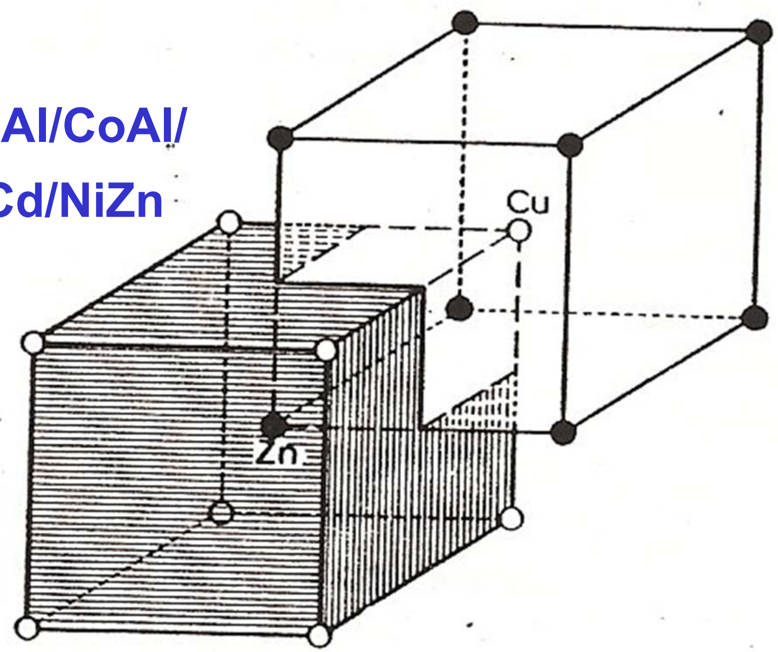
Cu_3Au superlattice

Superlattice formation: order-disorder transformation

- $\varepsilon < 0$, $\Delta H_{mix} < 0$
- between dissimilar atoms than between similar atoms
- Large electrochemical factor: tendency for the solute atoms to avoid each other and to associate with the solvent atoms
- Size factor just within the favorable limit: lead to atomic rearrangement so as to relieve the lattice distortion imposed by the solute atoms

(a)$L2_0$:

CuZn/FeCo/NiAl/CoAl/FeAl/AgMg/AuCd/NiZn



β brass superlattice viewed as two inter-penetrating cubic lattices

Five common ordered lattices

(a) $L2_0$:

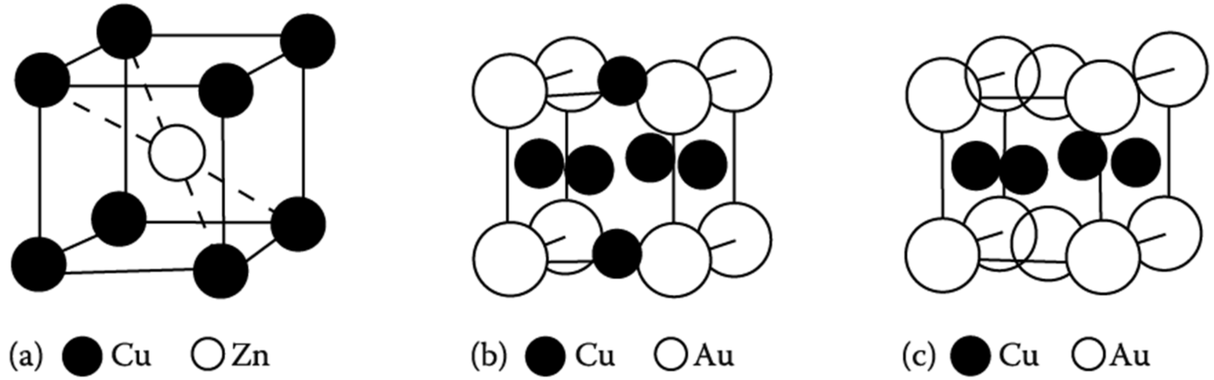
CuZn/FeCo/NiAl/CoAl/FeAl/AgMg/AuCd/NiZn

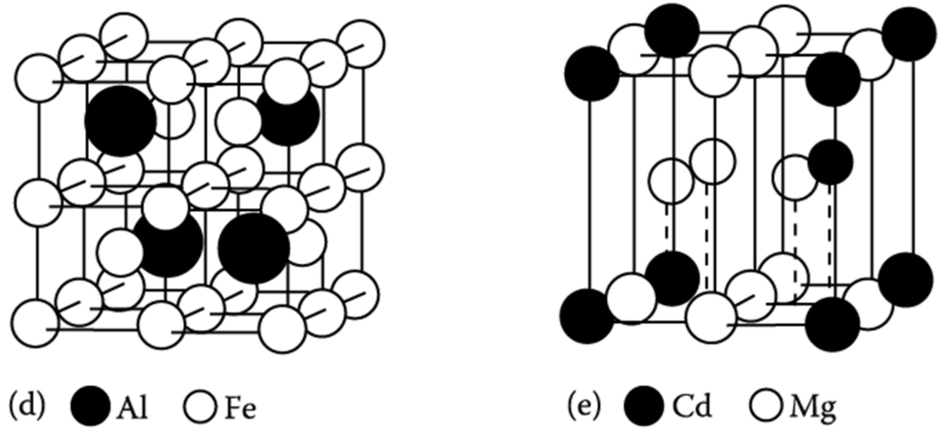
(b) $L1_2$:

$Cu_3Au/Ni_3Mn/Ni_3Fe/Ni_3Al/Pt_3Fe/Au_3Cd/Co_3V/TiZn_3$

(c) $L1_0$:

CuAu/CoPt/FePt





(d) $D0_3$:

$Fe_3Al/Cu_3Sb/Mg_3Li/Fe_3Al/Fe_3Si/Fe_3Be/Cu_3Al$

(e) $D0_{19}$:

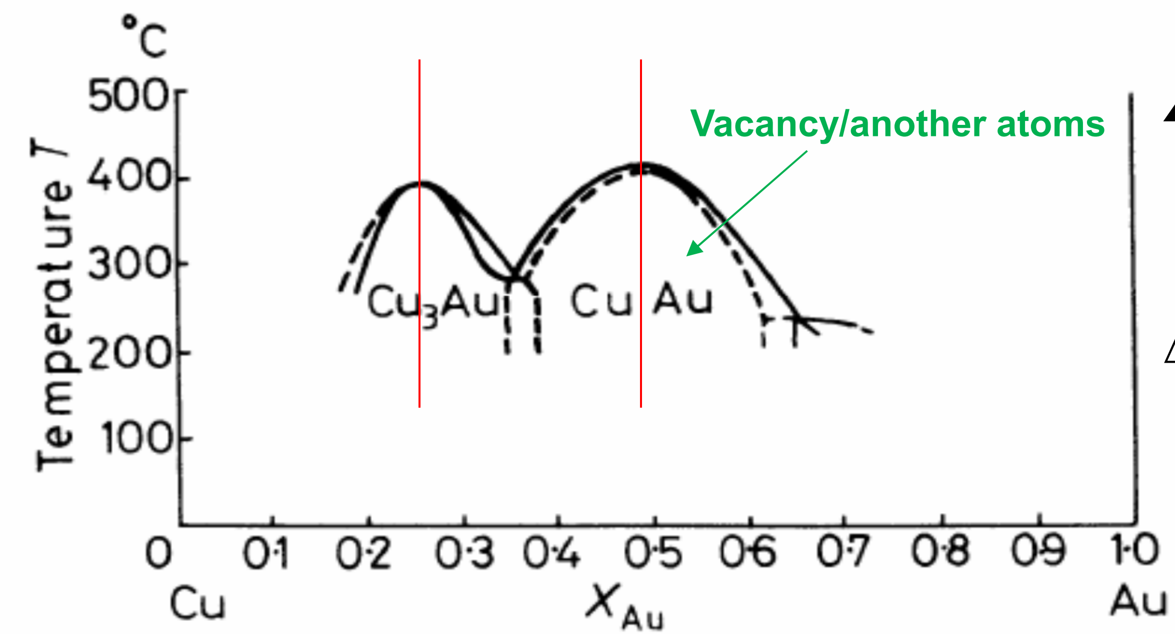
$Mg_3Cd/Cd_3Mg/Ti_3Al/Ni_3Sn/Ag_3In/Co_3Mo/Co_3W/Fe_3Sn/Ni_3In/Ti_3Sn$

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

Ordered phase

$\varepsilon < 0, \Delta H_{mix} < 0$

Fig. 1.21. Part of the Cu-Au phase diagram showing the regions where the Cu_3Au and CuAu superlattices are stable.



ΔS_{mix}~*small*

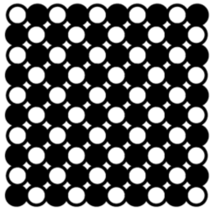
At high Temp.,

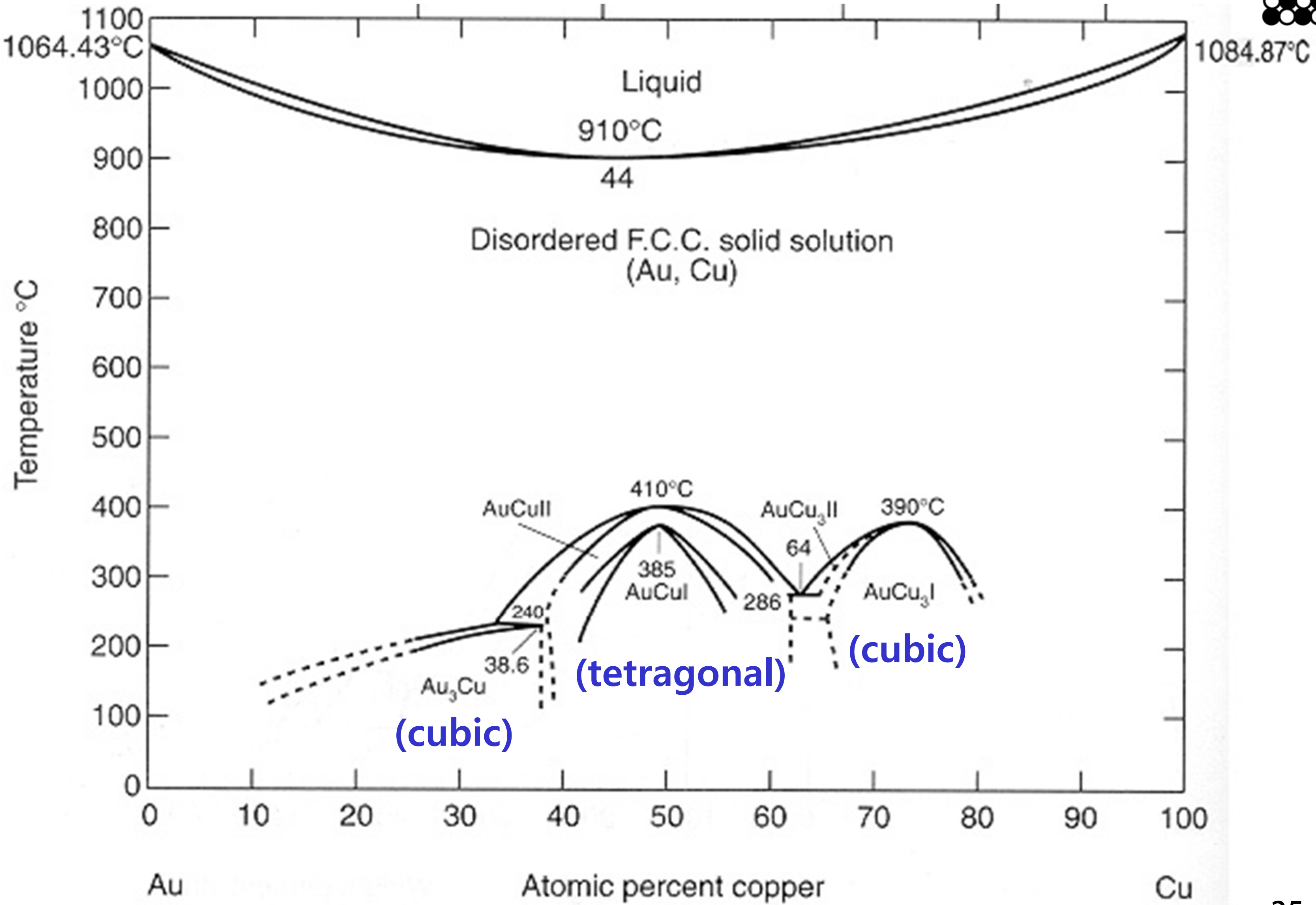
ΔG_{mix}~ *large (-)*

- **The entropy of mixing of structure with LRO is extremely small and the degree of order decrease with increasing temperature until above some critical temperature there is no LRO at all.**
- **This temperature is a maximum when the composition is the ideal required for the superlattice.**
- **The critical temperature for loss of LRO increases with increasing Ω or ΔH_{mix}, and in many systems the ordered phase is stable up to the melting point.**

Ordered Phase

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim -20$ kJ/mol





(tetragonal)

(cubic)

(cubic)

(fcc)

(complete solid solution)

(fcc)

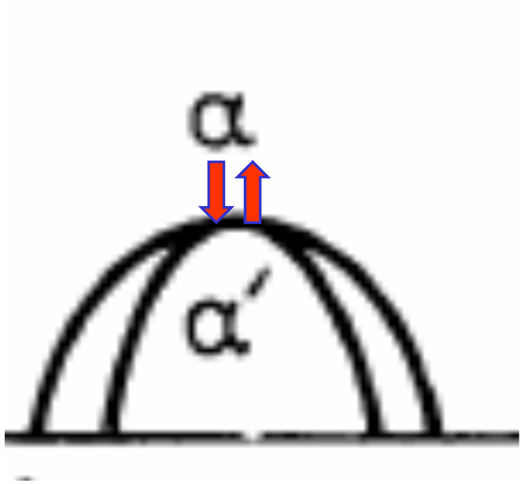
Q4: Order-disorder transition

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 = “2nd order transition”
- boundary: ordered lattice & disordered lattice/phase rule could not applied

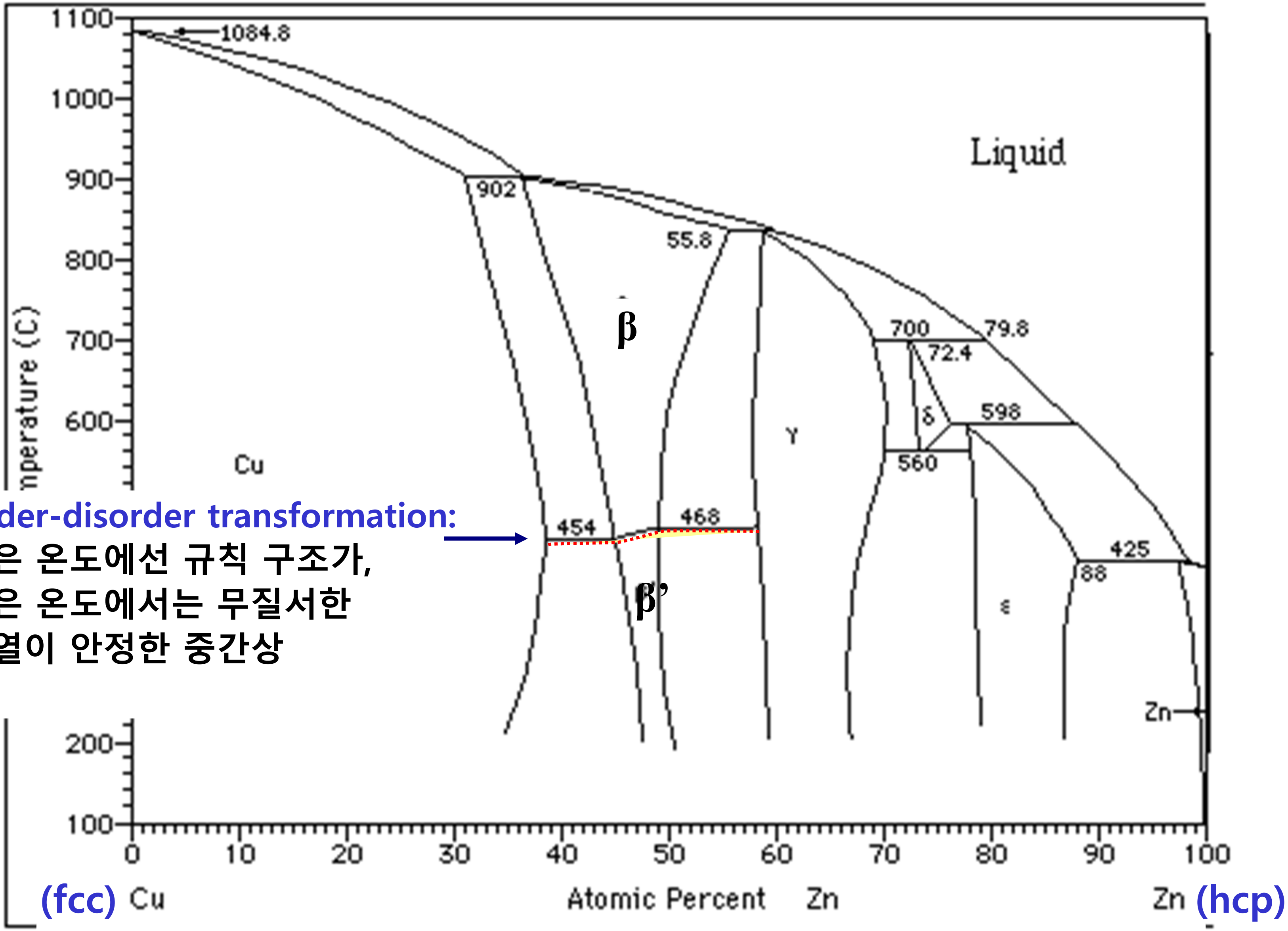
  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.

- Simple composition of the type AB or AB_3 can the transformation (i.e. at the temperature maximum) be considered diffusionless.



Intermediate Phase

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

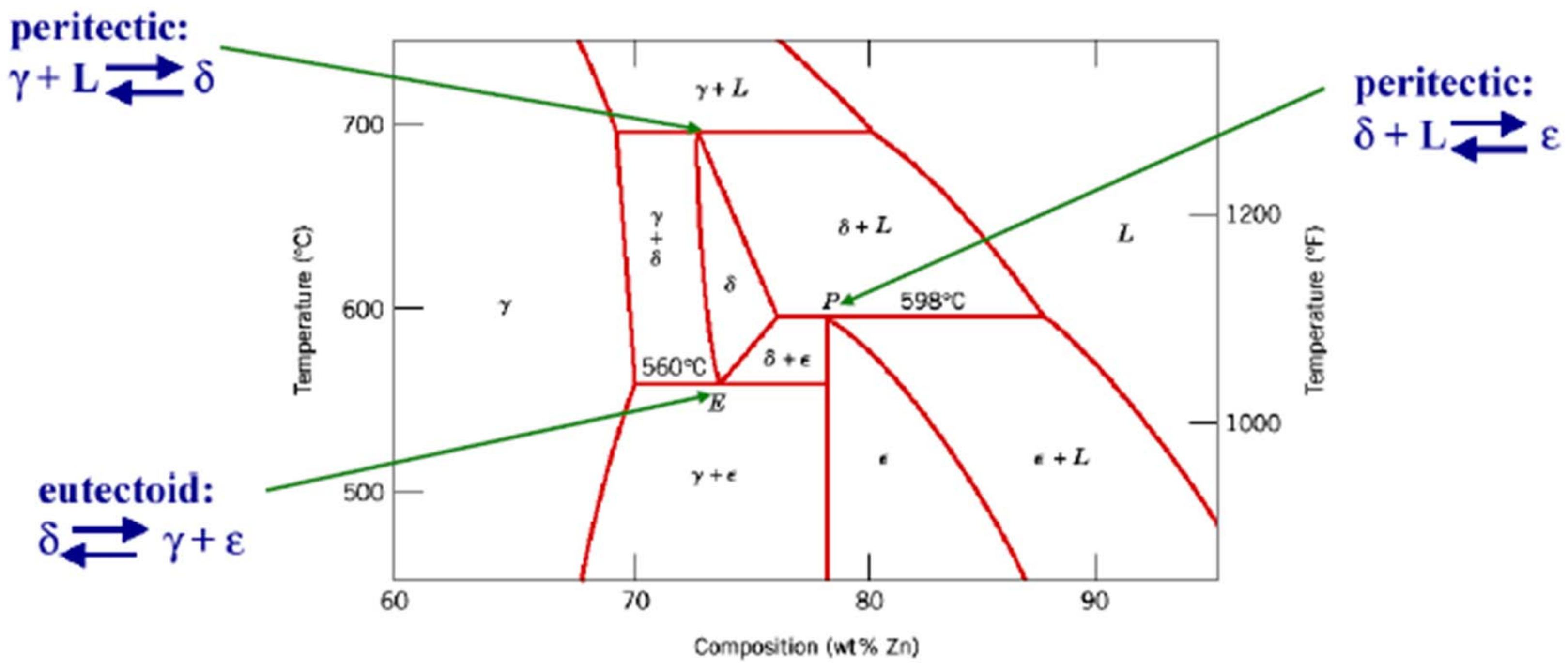


Order-disorder transformation:
낮은 온도에선 규칙 구조가, 높은 온도에서는 무질서한 배열이 안정한 중간상

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

Cu-Zn Phase Diagram

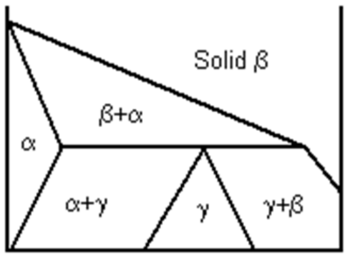
Eutectoid and Peritectic Reactions



Eutectoid: one solid phase transforms into two other solid phases upon cooling

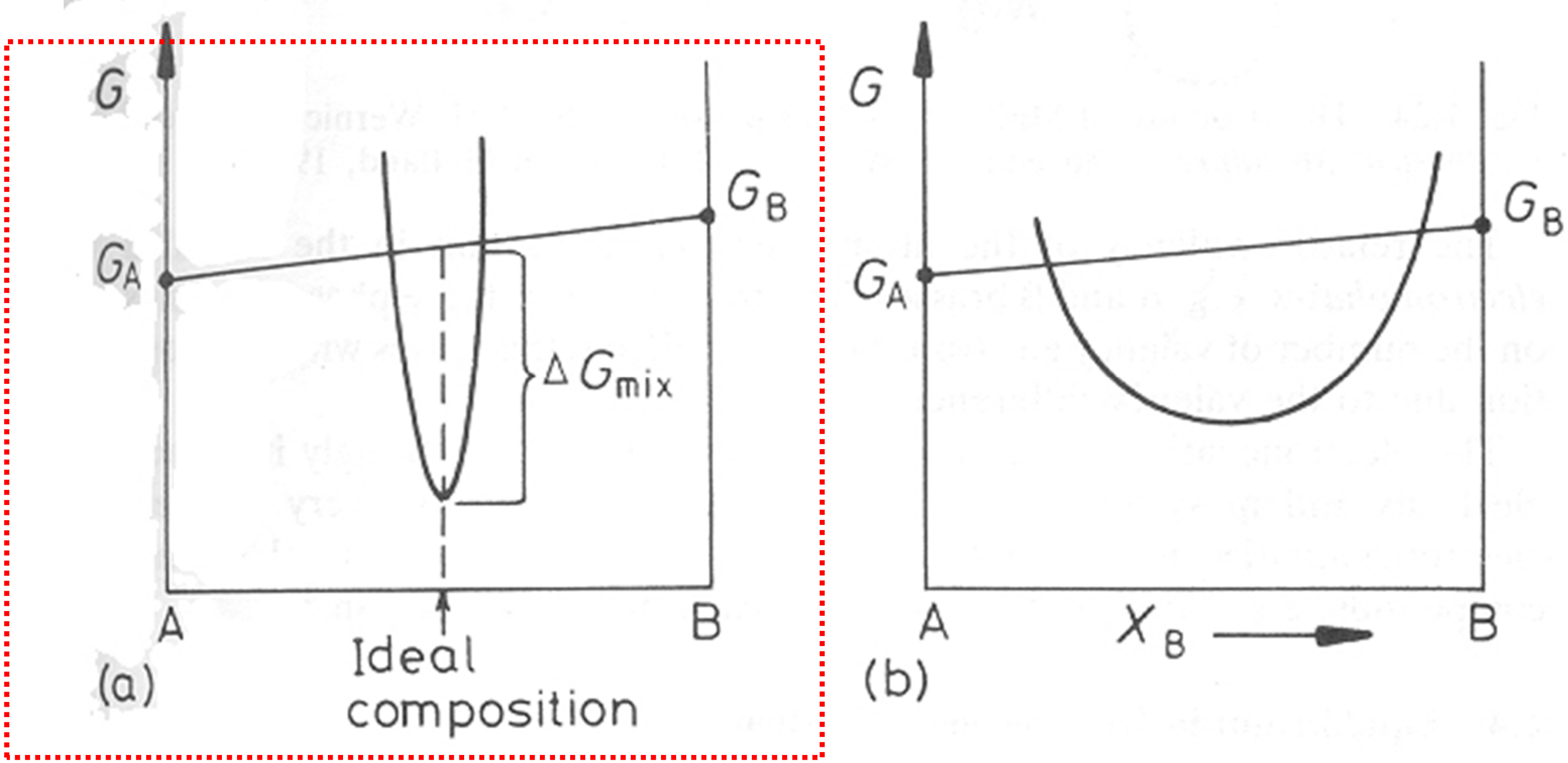
Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

Peritectoid: two other solid phases transform into another solid phase upon cooling



Q5: Intermediate phase vs Intermetallic compound

Intermediate Phase



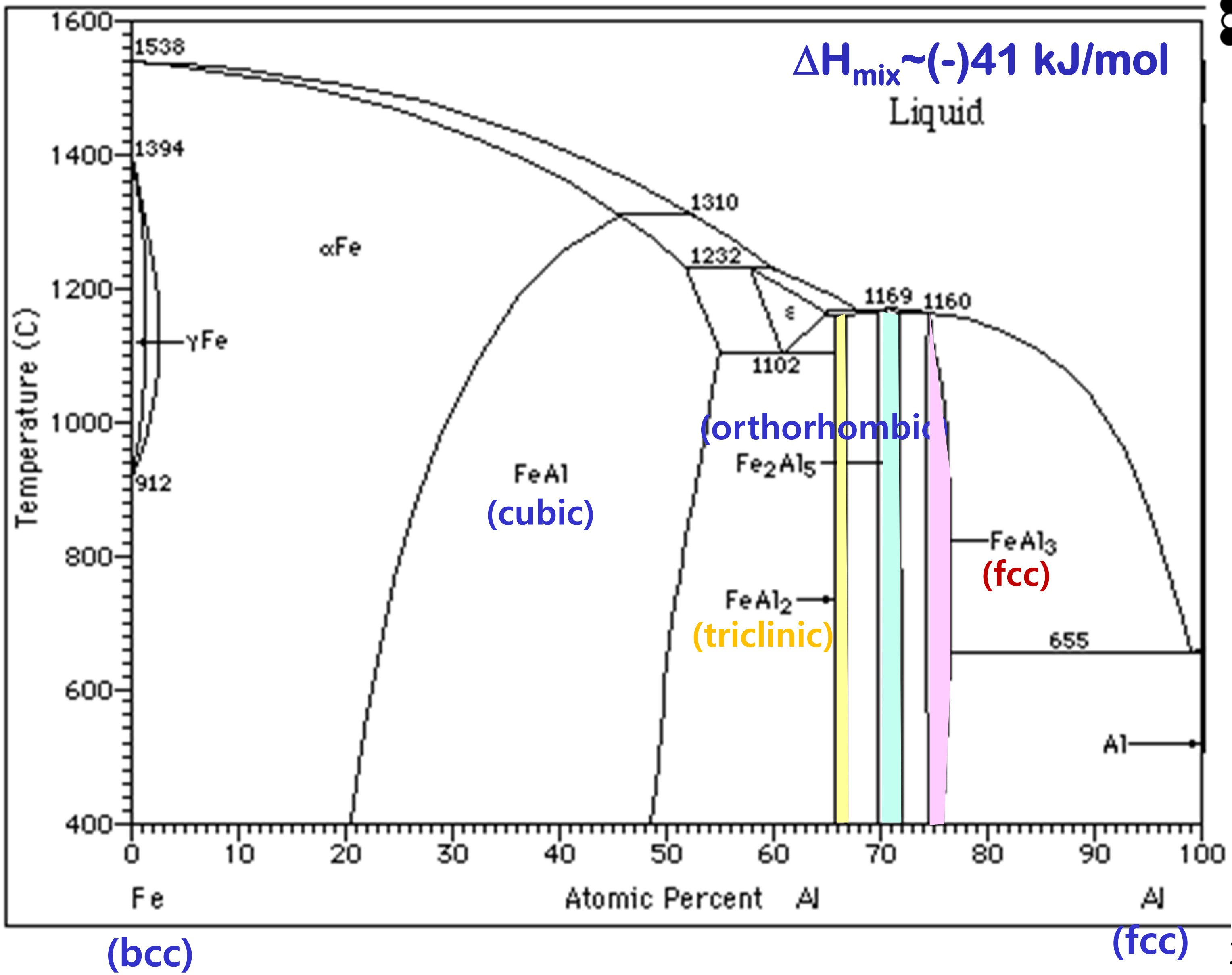
* **Many intermetallic compounds** have **stoichiometric composition** A_mB_n **and a characteristic free energy curve as shown in Fig (a).**

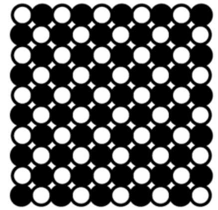
* **In other structure, <u>fluctuations in composition can be tolerated</u> by some atoms occupying 'wrong' position or by atom sites being left vacant, and in these cases the curvature of the G curve is much less, Fig (b).**

Intermediate Phase

$\varepsilon < 0$, $\Delta H_{mix} < 0$

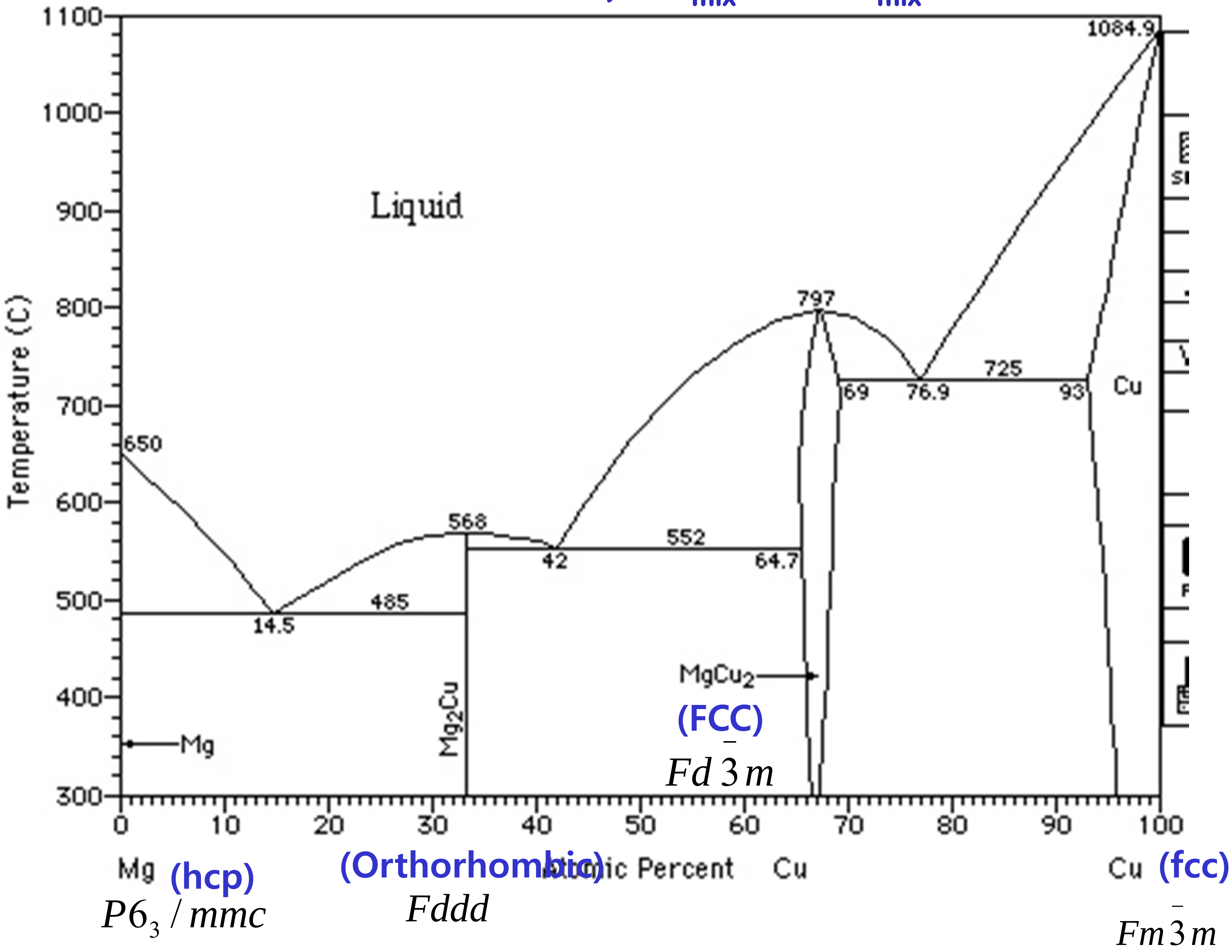
$\Delta H_{mix} \sim (-)41$ kJ/mol





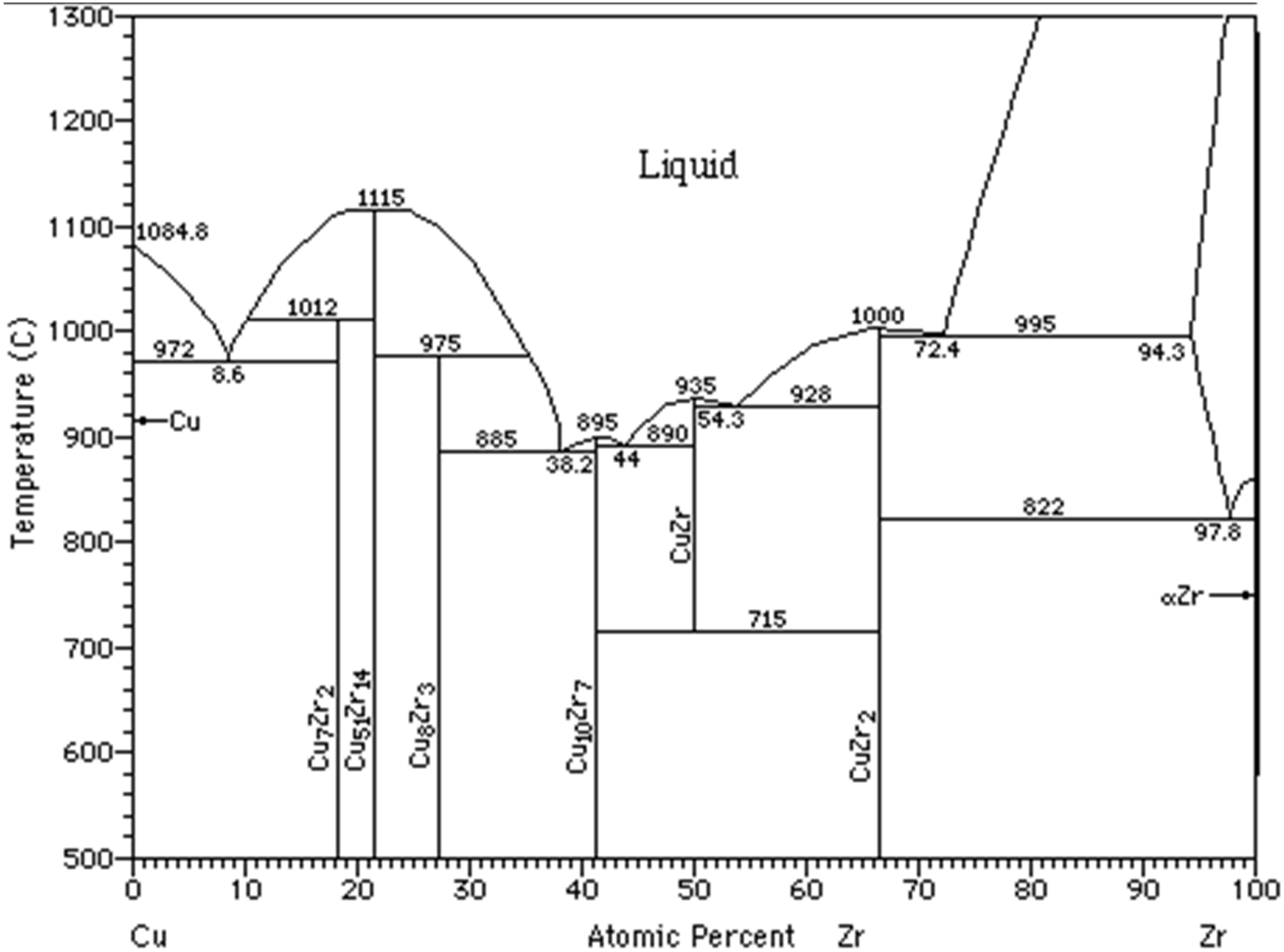
Intermediate Phase

$\varepsilon < 0,\ \Delta H_{mix} < 0 \ / \ \Delta H_{mix} \sim -38$ kJ/mol



Intermediate Phase

ε << 0, ΔH_{mix} << 0 / ΔH_{mix} ~ -142 kJ/mol



Q6: Main factors determining the structure of intermediate phase

Intermediate Phase

_"different crystal structure as either of the pure component"

3 main factors

determining the structure of Intermediate phase ?

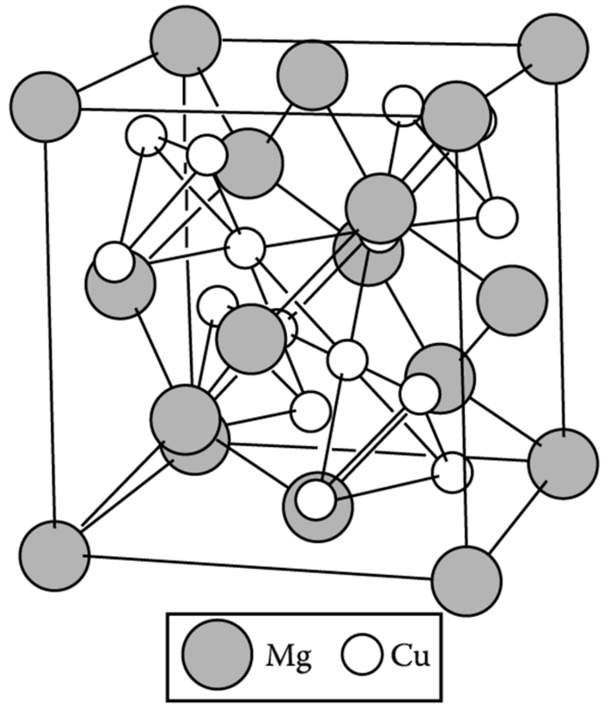
1) Relative atomic size

- Laves phase (size difference: 1.1~1.6 ex: $MgCu_2$)

  fill space most efficiently ~ stable

- Interstitial compound: MX, M_2X, MX_2, M_6X

  M= Cubic or HCP ex: Zr, Ti, V, Cr, etc, X= H, B, C, and N



$MgCu_2$ (A Laves phase)

2) Relative valency electron

- electron phases ex_α & β brass

  # of valency electrons per unit cell

  → depending on compositional change

3) Electronegativity

- very different electronegativites → ionic bond_normal valency compounds

  ex Mg_2Sn

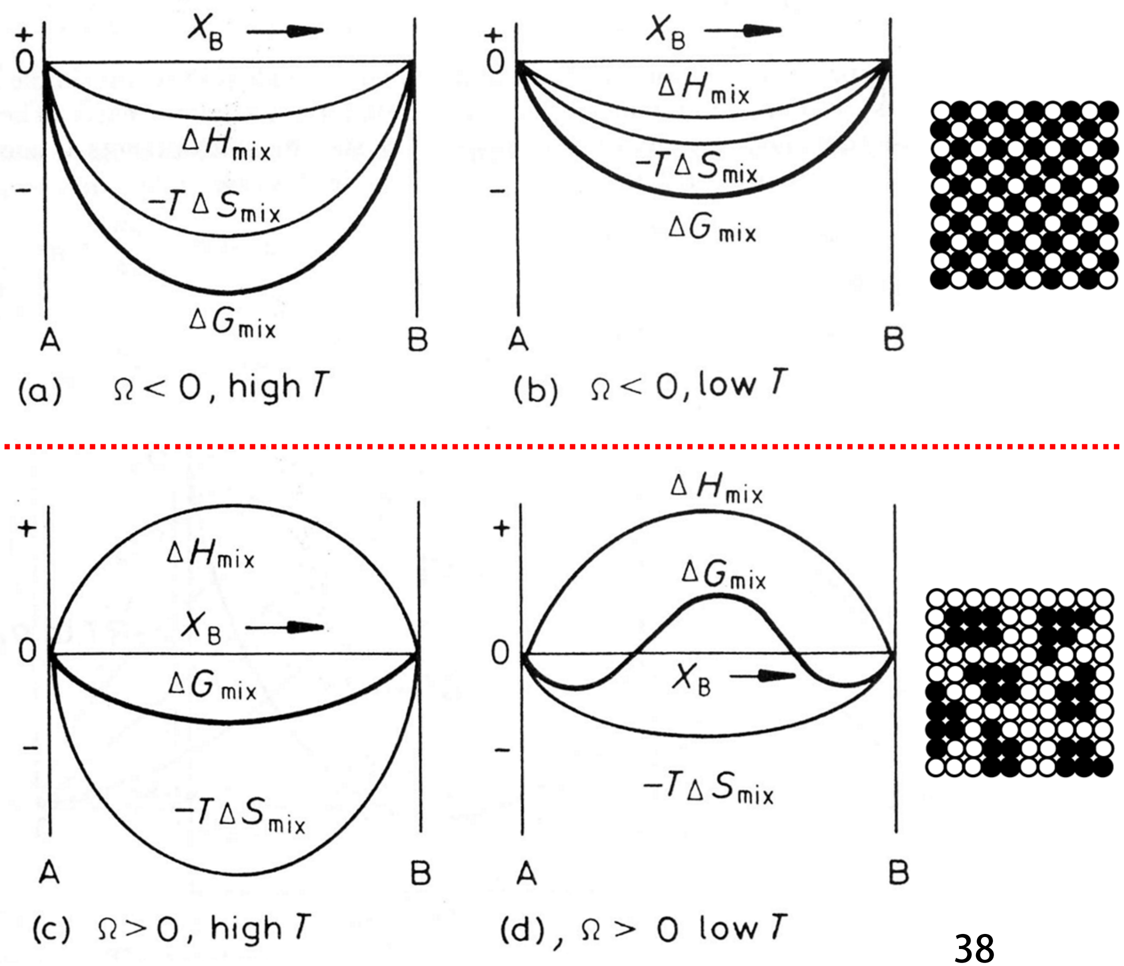
"Clustering"? → Phase separation

Q7: Metastable vs Stable miscibility gap

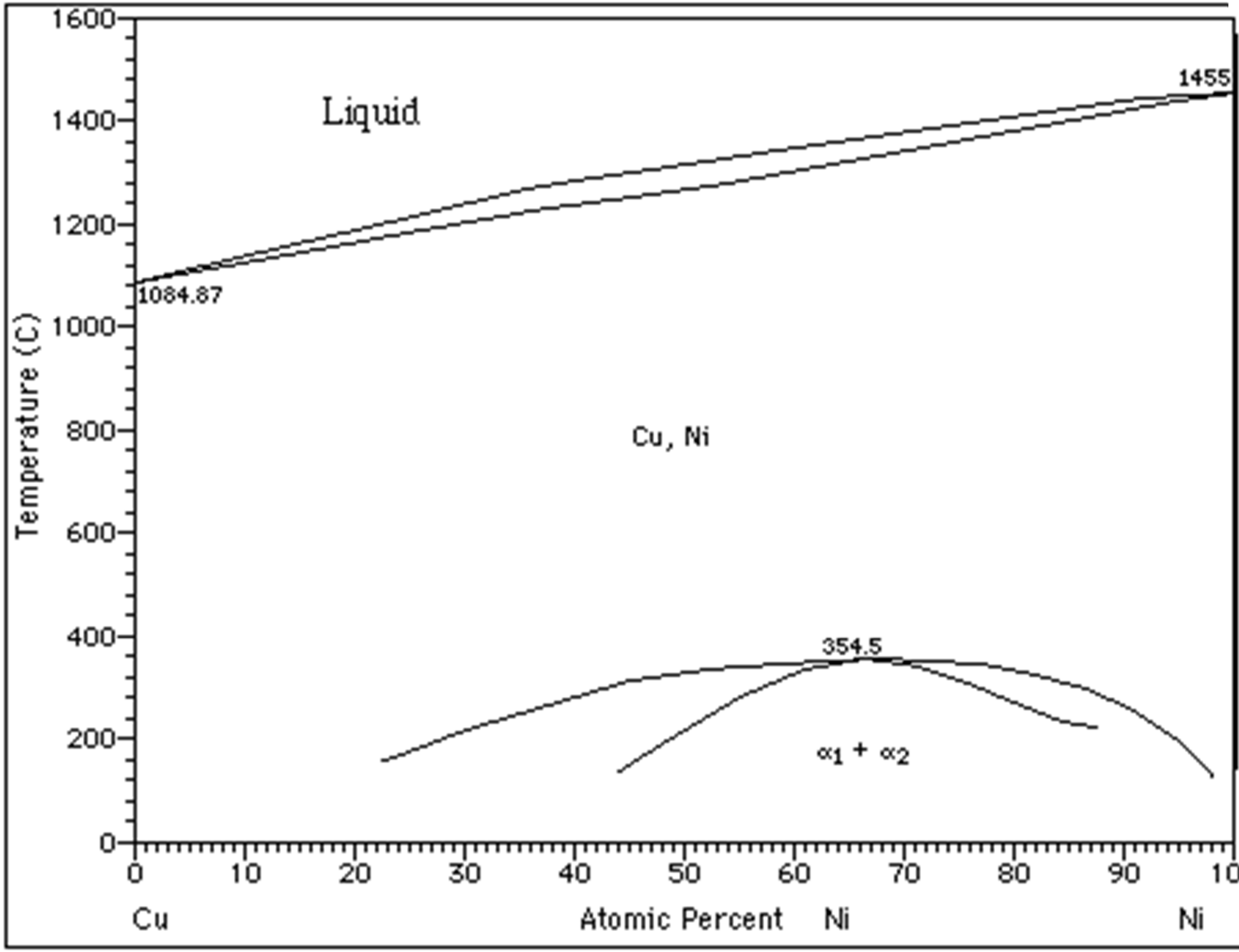
* The degree of **ordering or clustering** will **decrease as temp. increases** due to the increasing importance of **entropy**.

High temp. → **Entropy effect** ↑ → **Solution stability** ↑

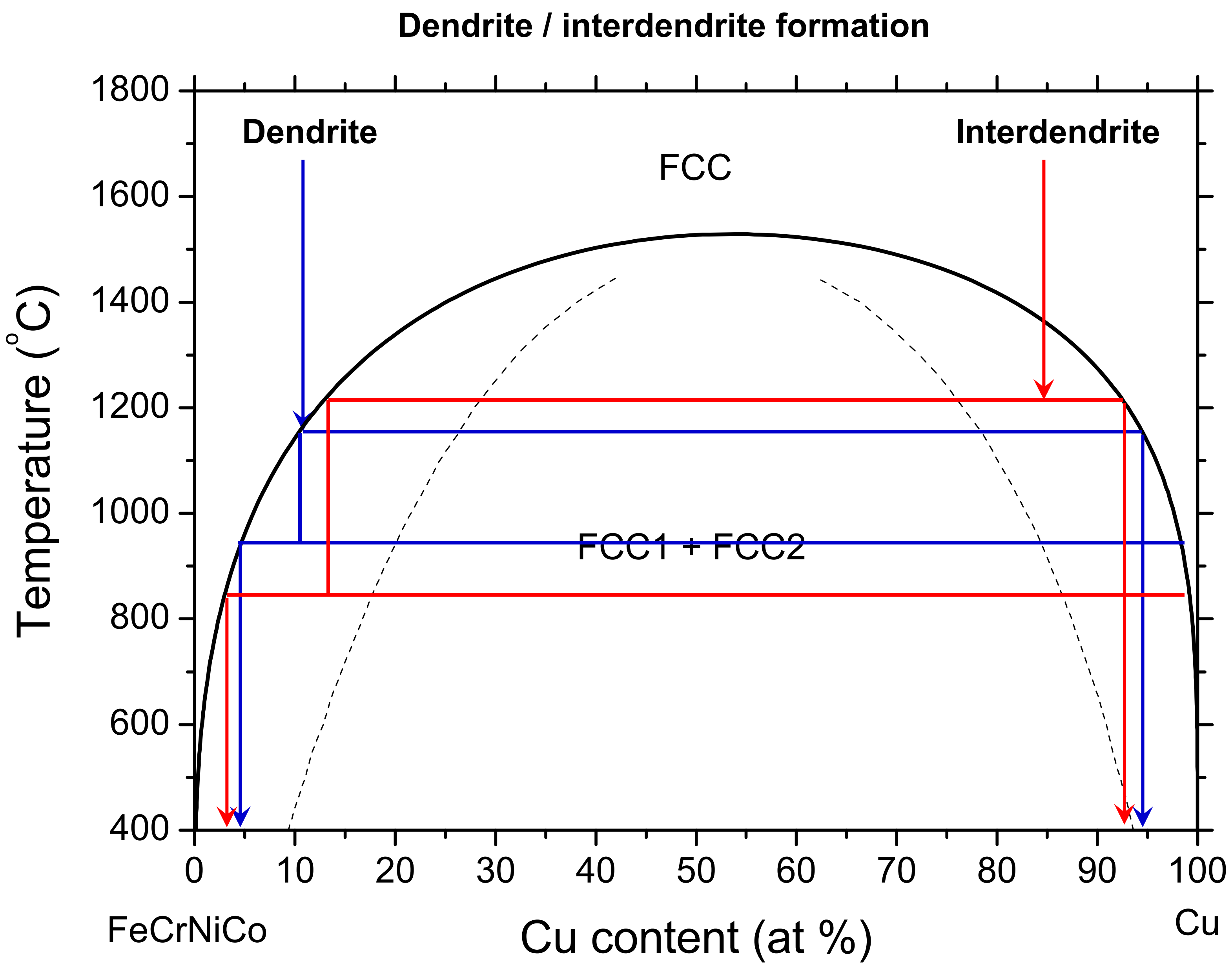
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



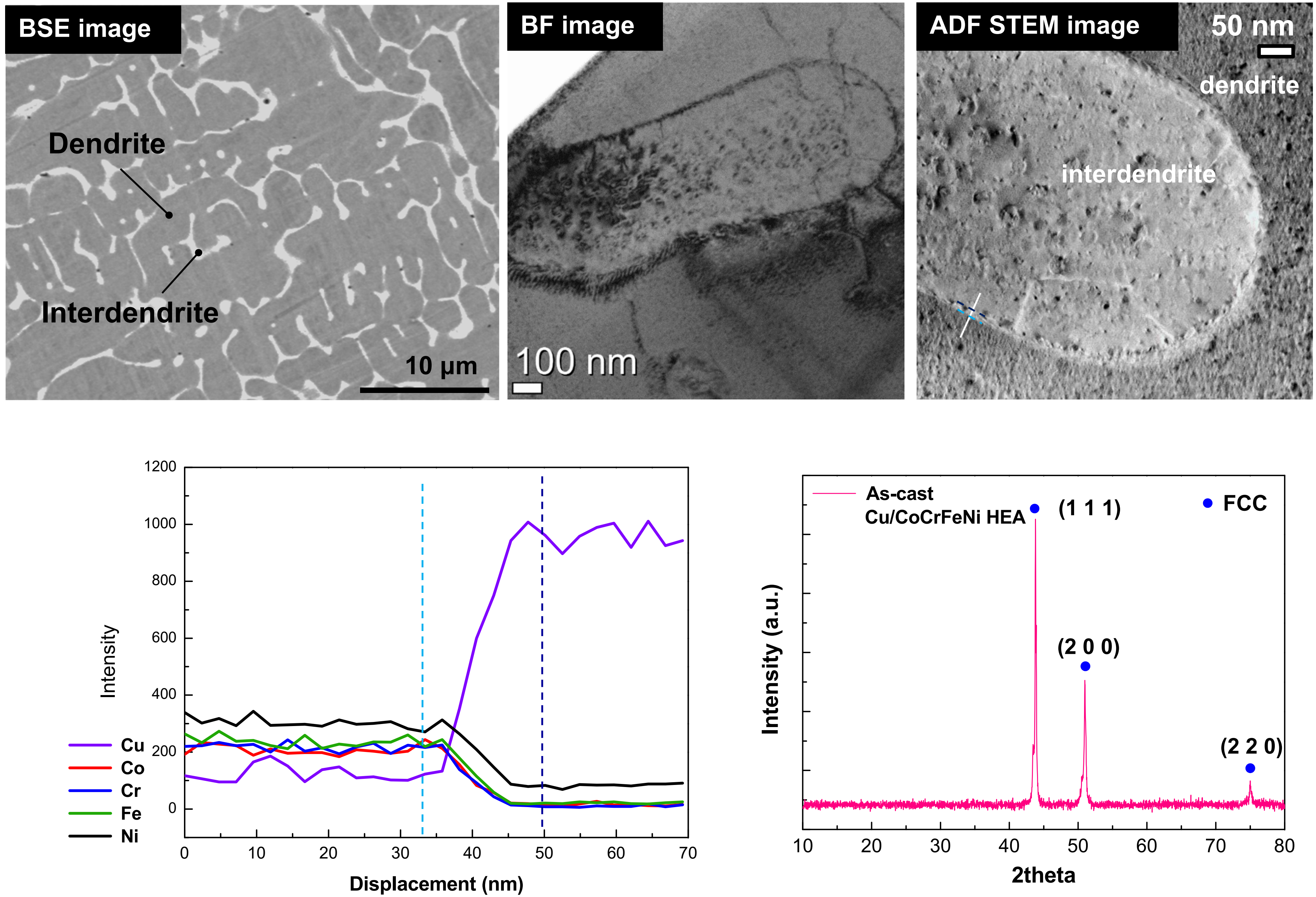
$\varepsilon > 0, \ \Delta H_{mix} > 0 \ / \Delta H_{mix} \sim +26$ kJ/mol



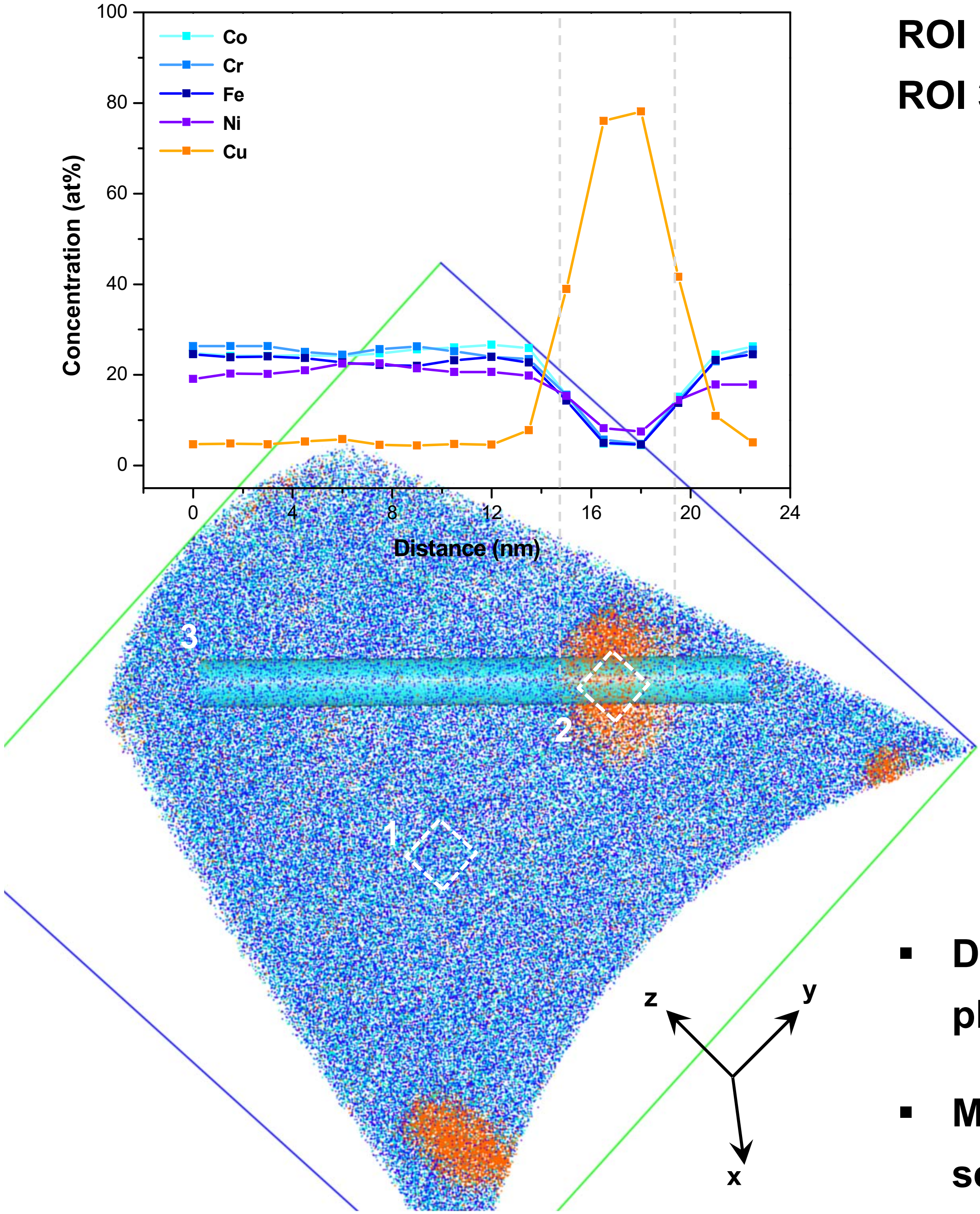
Cooling process in the miscibility gap



Microstructure of as-cast CoCrFeNiCu HEA



Compositional analysis of as-cast CoCrFeNi/Cu HEA (dendrite)



ROI 1, 2 : 1.4 nm x 2 nm x 2 nm

ROI 3 : 1.2 nm x 2 nm x 23 nm

(1D concentration profile)

1	at%
Co	26.19
Cr	24.15
Fe	24.59
Ni	19.59
Cu	4.74

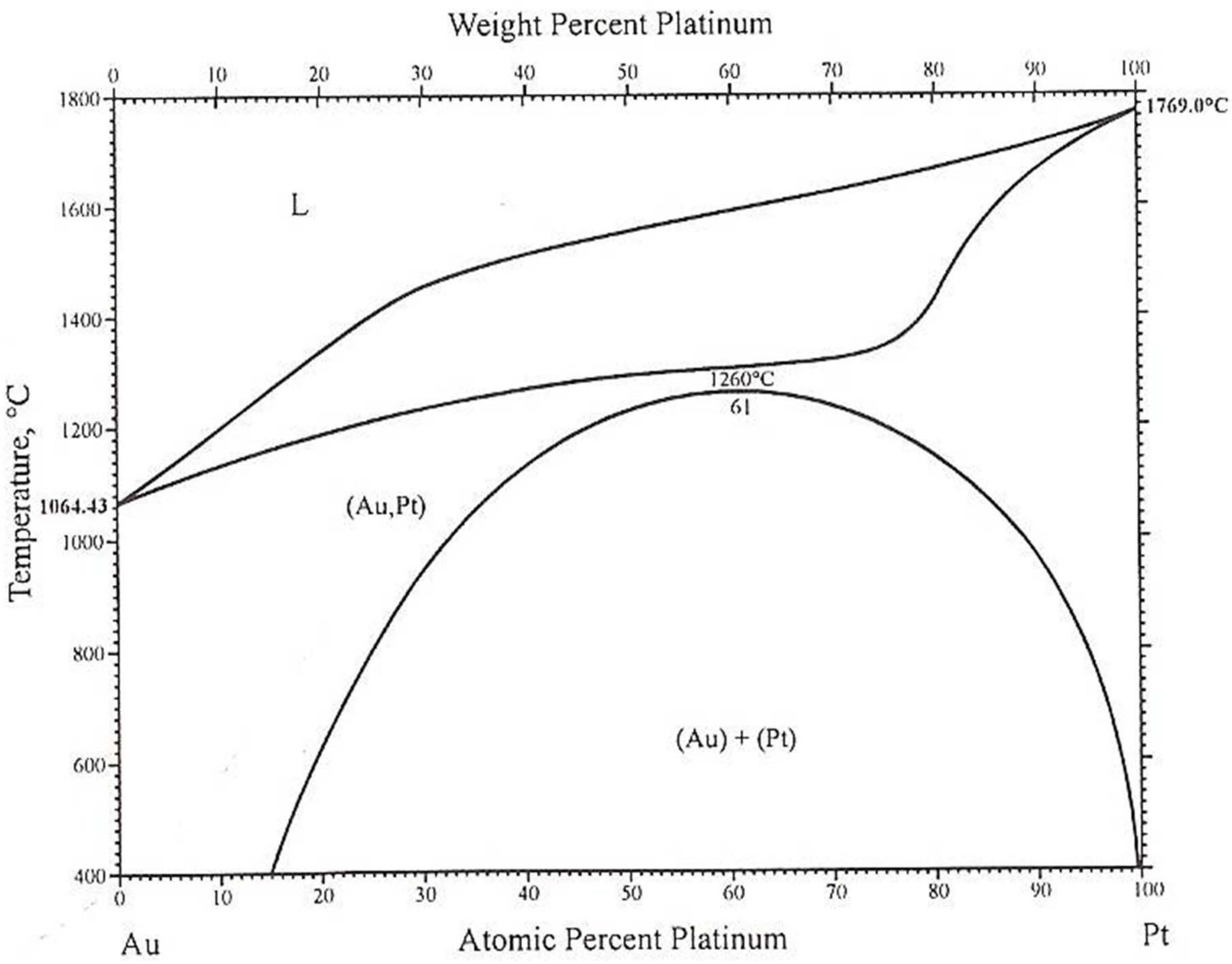
2	at%
Co	0.33
Cr	0.46
Fe	0.39
Ni	5.00
Cu	93.56

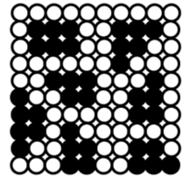
3-1’	at%
Co	25.29
Cr	25.63
Fe	23.63
Ni	20.66
Cu	4.42

3-2’	at%
Co	2.01
Cr	3.35
Fe	2.56
Ni	6.90
Cu	84.92

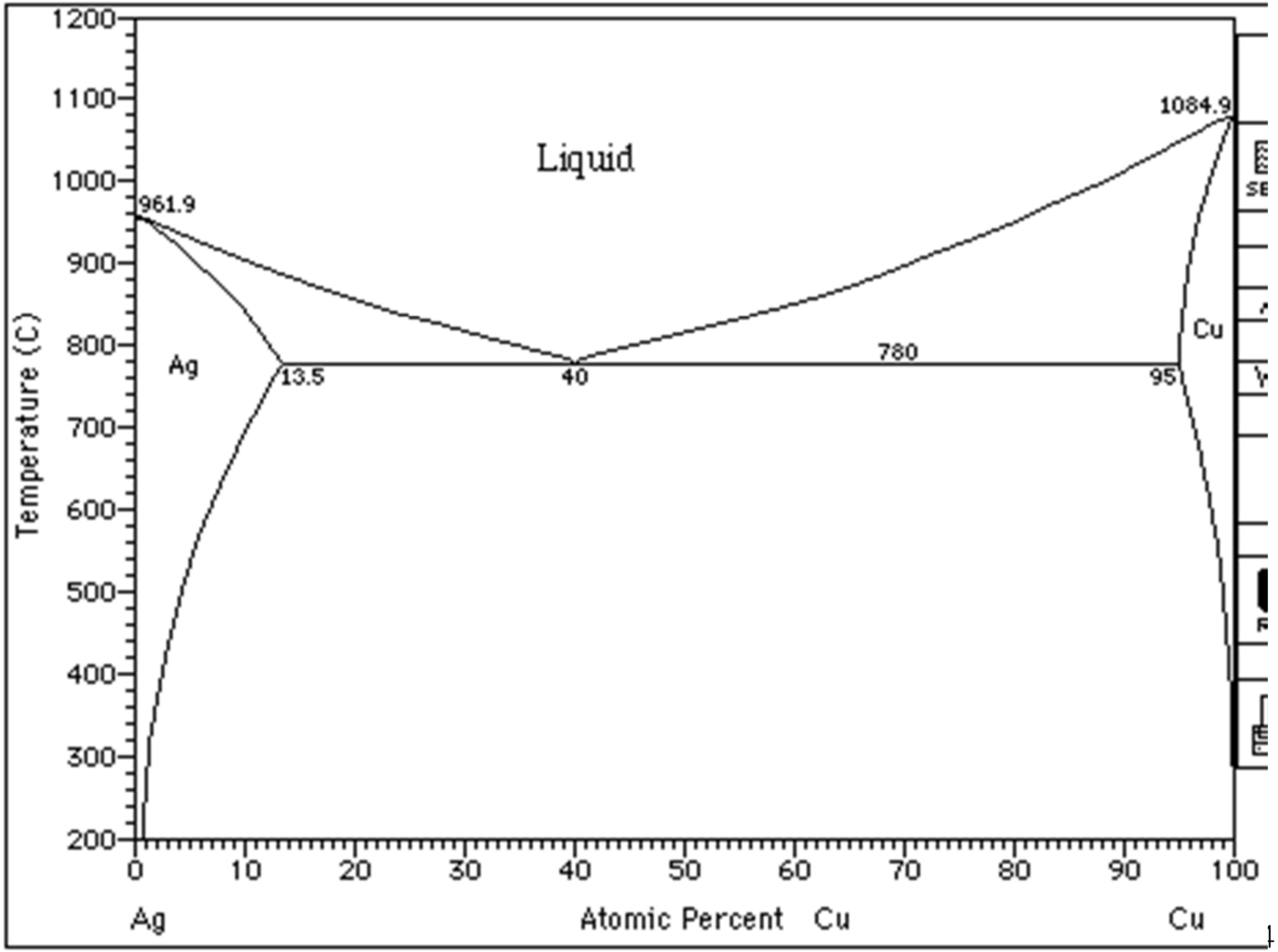
- Dendrite 는 matrix (4.74 at%Cu) 와 2nd phase (93.56 at%Cu)로 구성됨
- Matrix 와 2nd phase 계면에서의 segregation 없음

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim$ **+17** kJ/mol

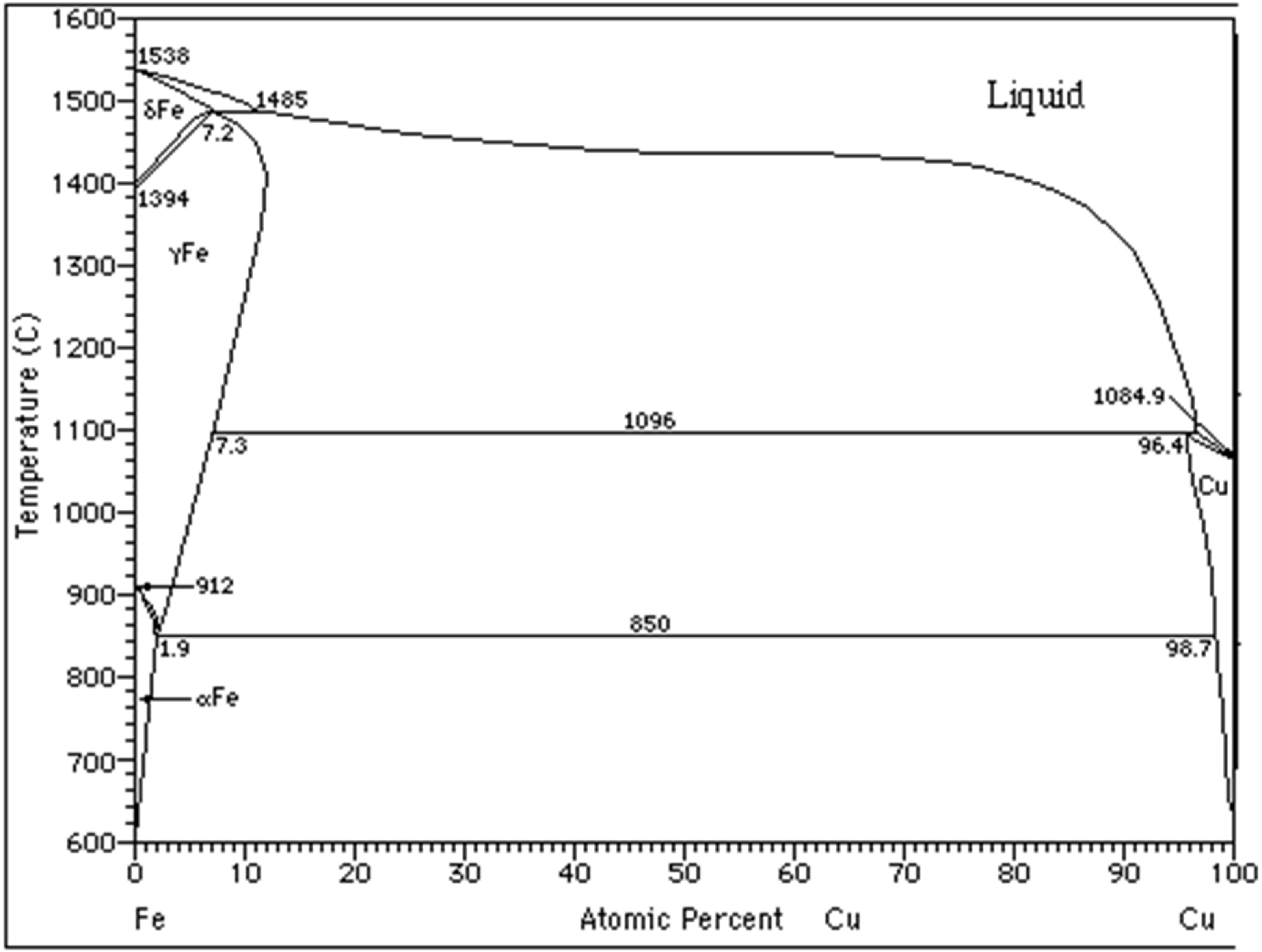




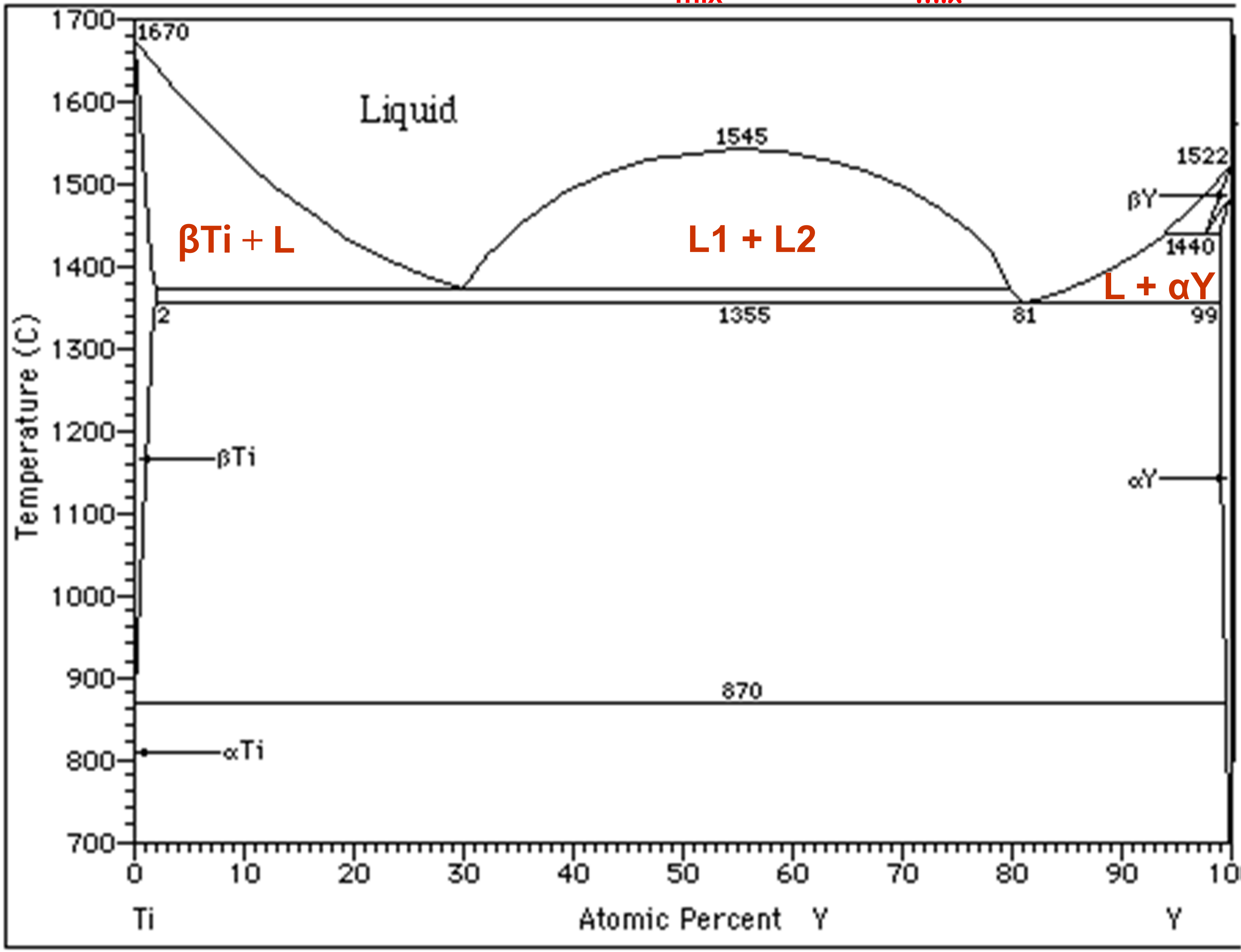
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol



$\varepsilon >> 0$, $\Delta H_{mix} >> 0$ / $\Delta H_{mix} \sim +60$ kJ/mol



$\varepsilon >> 0, \ \Delta H_{mix} >> 0 \ / \Delta H_{mix} \sim +58$ kJ/mol



“Clustering”? → Phase separation

Q8: Spinodal decomposition

5.5.5 Spinodal Decomposition

Spinodal mode of transformation has no barrier to nucleation

: describing the transformation of a system of two or more components in a metastable phase into two stable phases

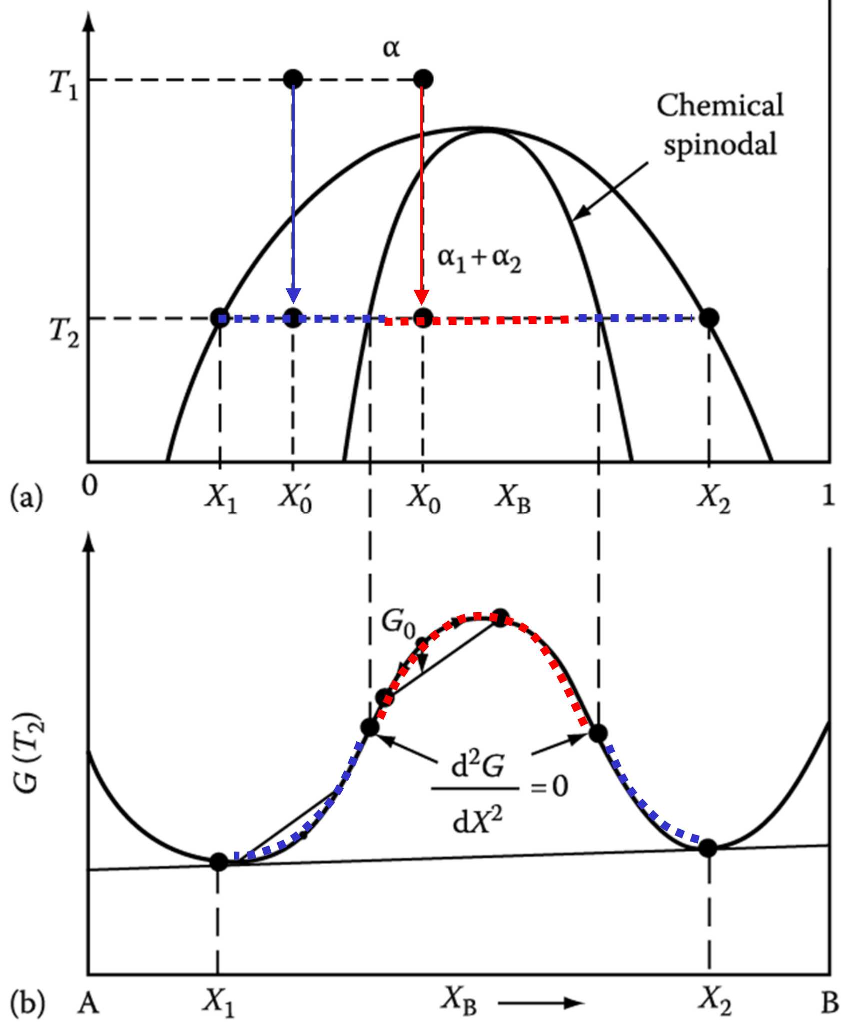


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

How does it differ between inside and outside the inflection point of Gibbs free energy curve?

1) Within the spinodal $\frac{d^2G}{dX^2} < 0$

: phase separation by small fluctuations in composition/ "up-hill diffusion"

2) If the alloy lies outside the spinodal, small variation in composition leads to an increase in free energy and the alloy is therefore metastable.

The free energy can only be decreased if nuclei are formed with a composition very different from the matrix.

→ nucleation and growth

: "down-hill diffusion"

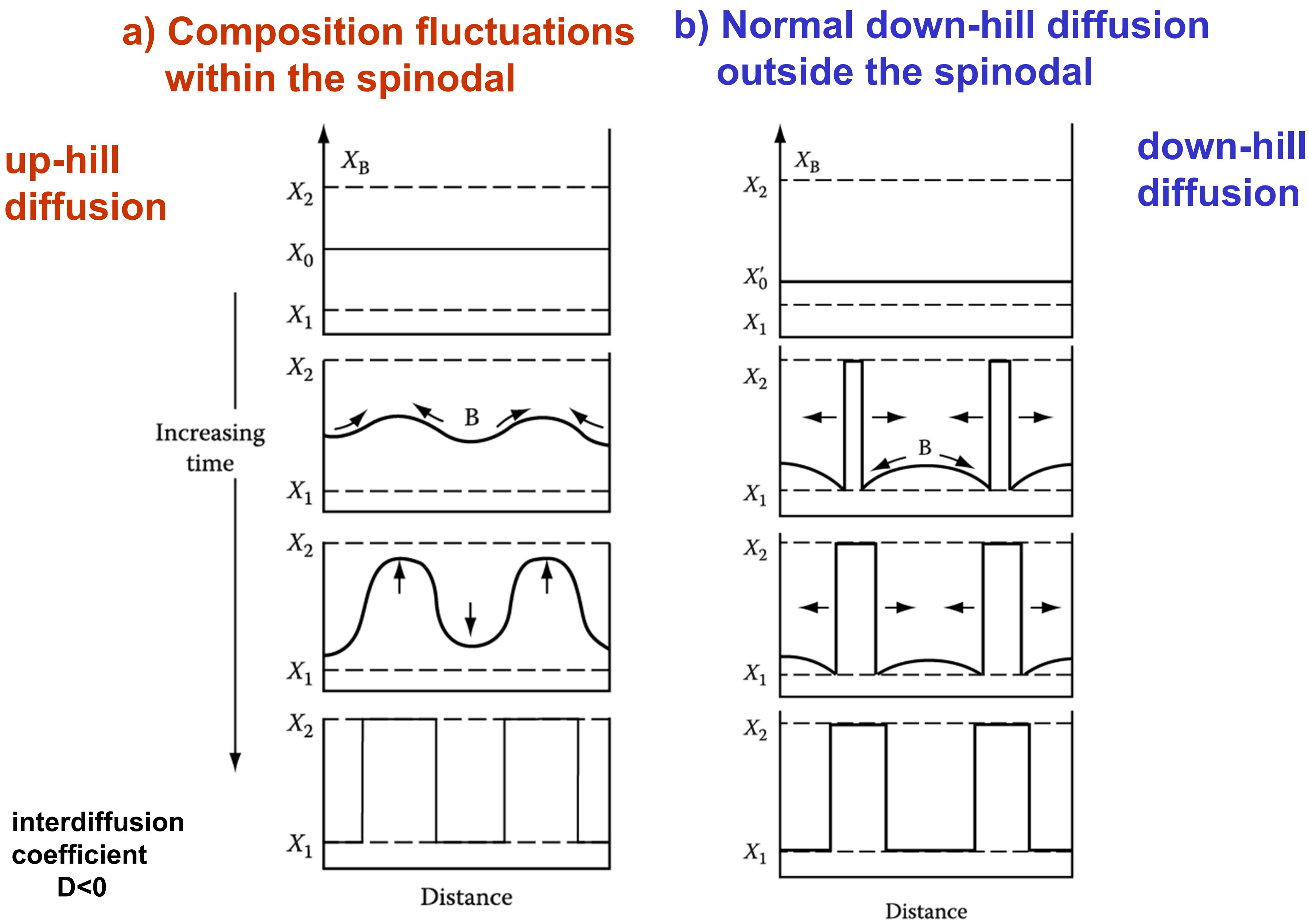


Fig. 5.39 & 5.40 schematic composition profiles at increasing times in (a) an alloy quenched into the spinodal region (X_0 in Figure 5.38) and (b) an alloy outside the spinodal points (X_0' in Figure 5.38)

Q9: Phase separation

Positive heat of mixing relation among constituent elements

- **Alloy design considering heat of mixing relation among constituent elements**

$\Delta H_{mix} \gg 0$ between A & B

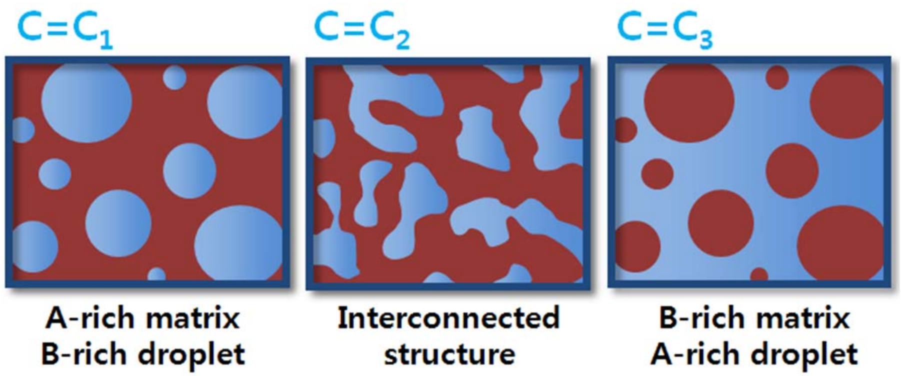
⬇

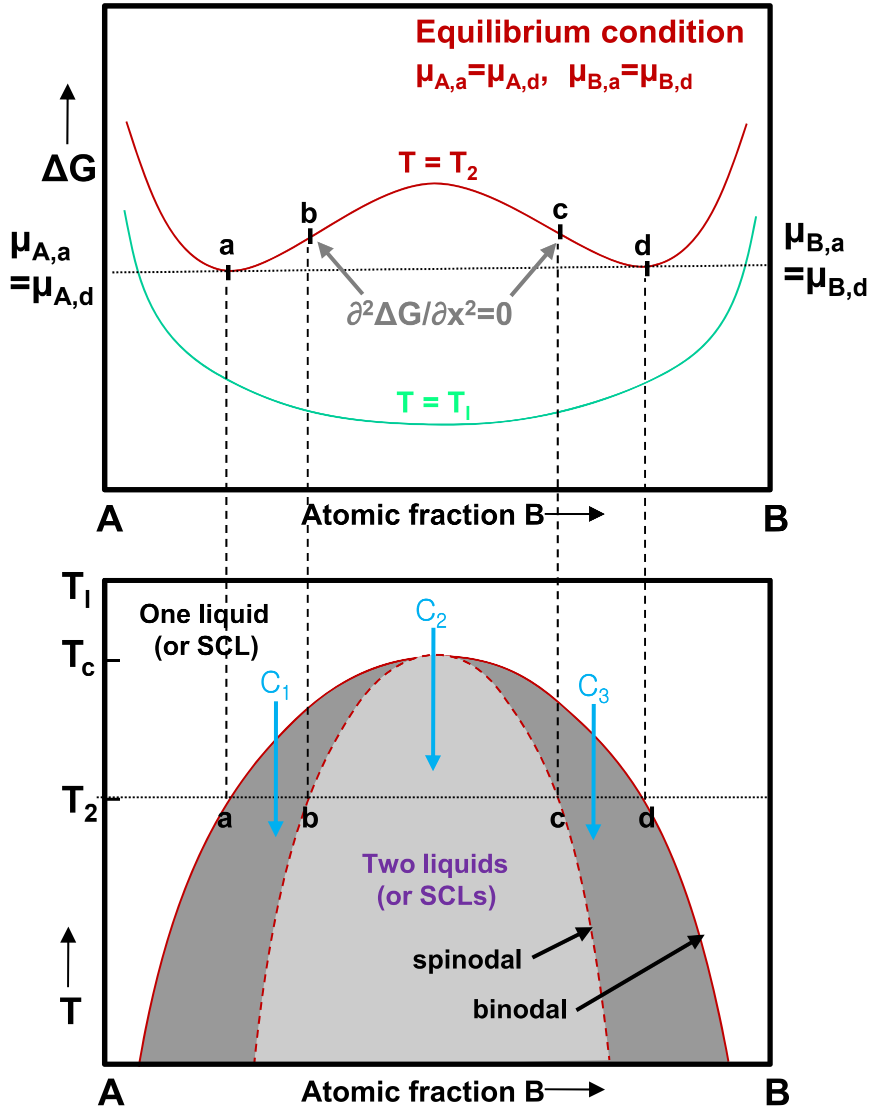
creates (meta)stable miscibility gap in limited composition range

⬇

Phase separation to A-rich & B-rich phase

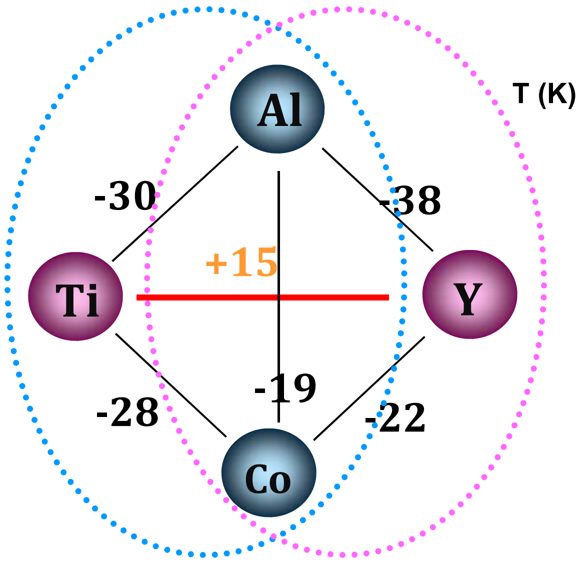
- **Different two-phase structure by initial composition before phase separation**

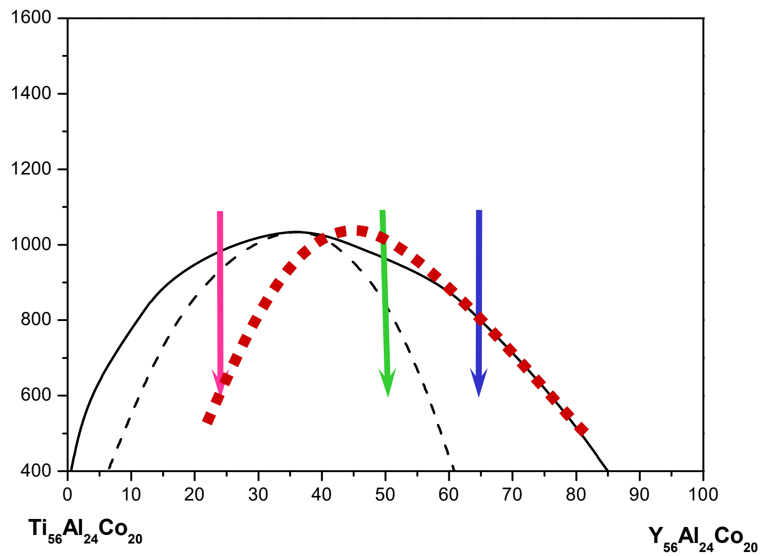


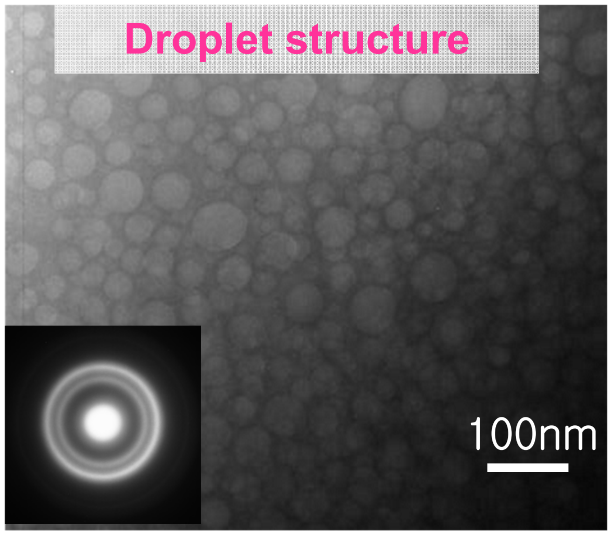


Nucleation and growth ↔ Spinodal decomposition without any barrier to the nucleation process

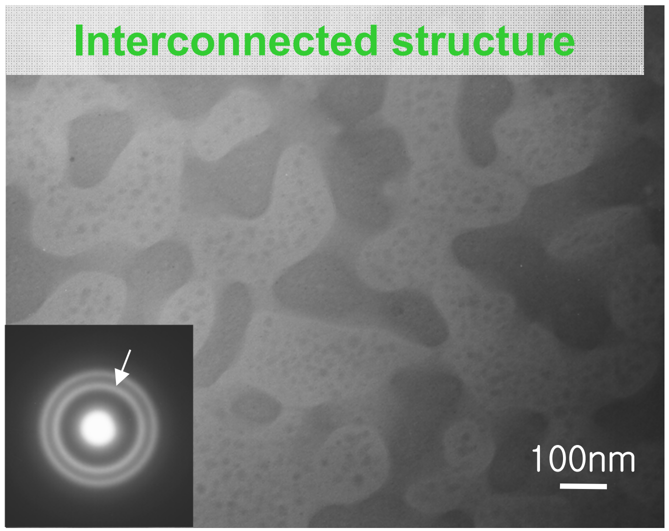
* Ti-Y-Al-Co system



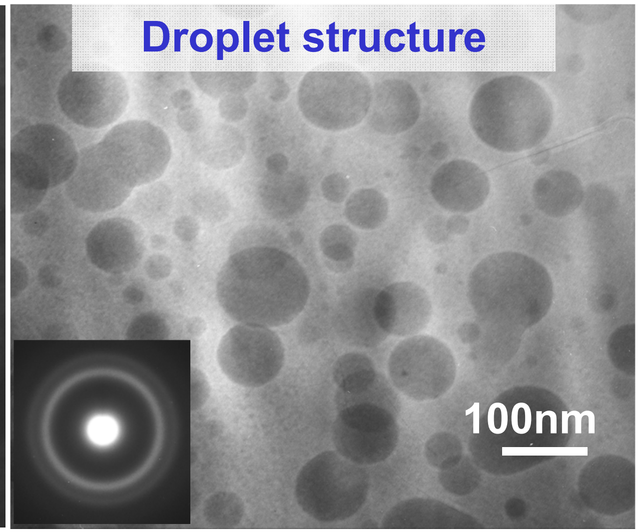




$(Y_{56}Al_{24}Co_{20})_{25}(Ti_{56}Al_{24}Co_{20})_{75}$



$(Y_{56}Al_{24}Co_{20})_{50}(Ti_{56}Al_{24}Co_{20})_{50}$



$(Y_{56}Al_{24}Co_{20})_{65}(Ti_{56}Al_{24}Co_{20})_{35}$

* La-Zr-Al-Cu-Ni system

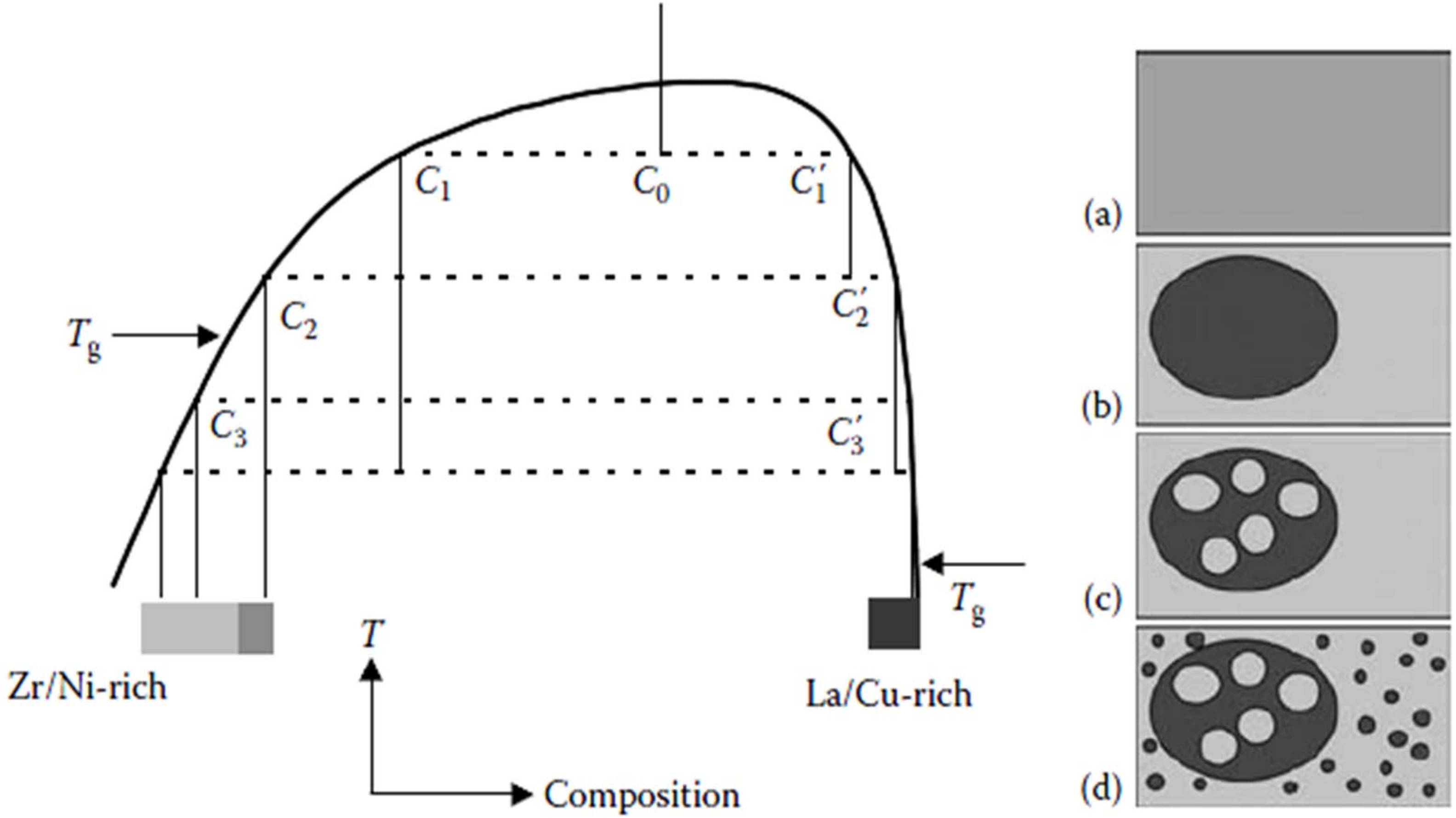
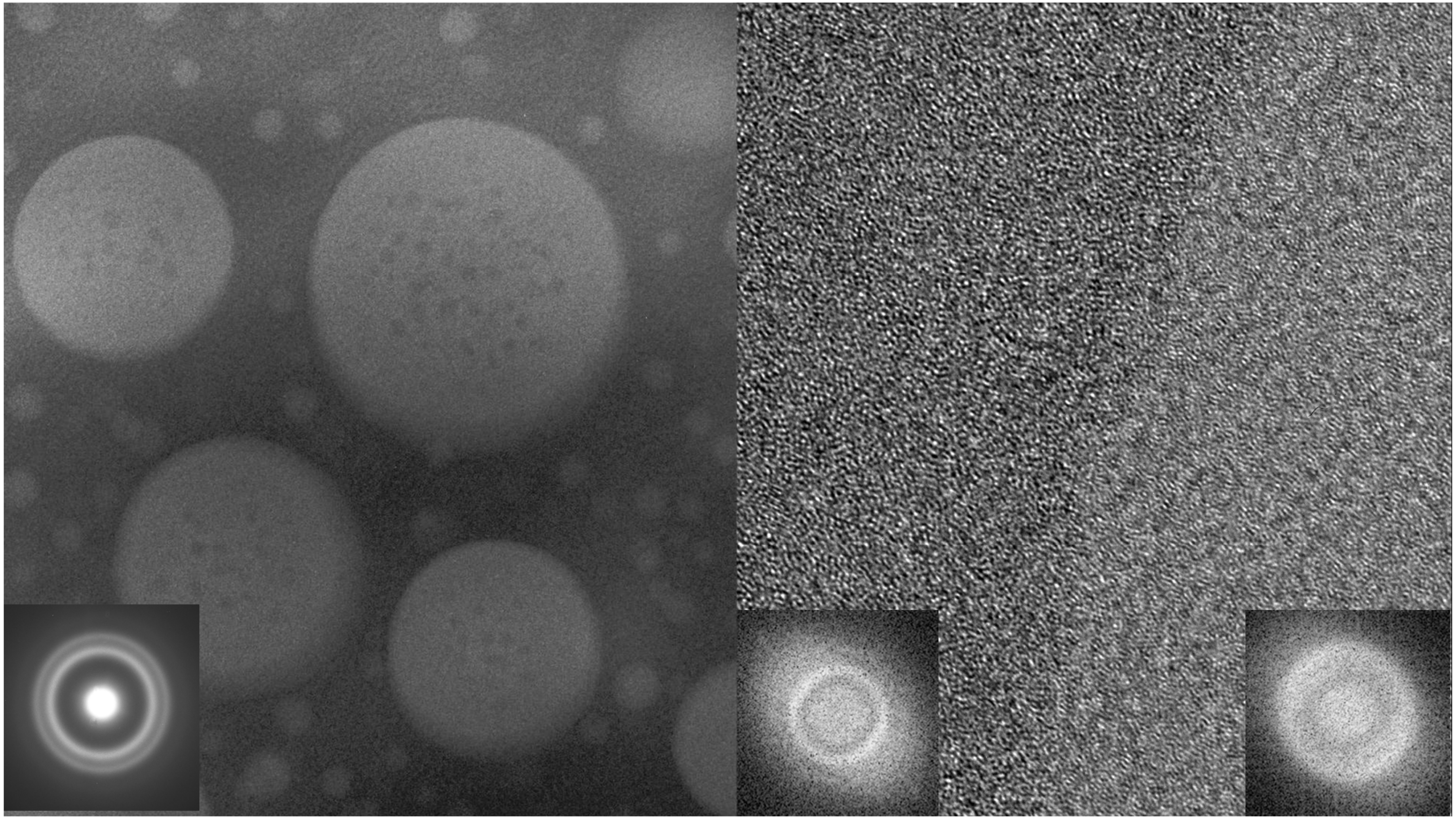


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta Mater.*, 52, 2441, 2004. With permission.)

Phase separation in metallic glasses



Q10: Microstructure determining parameters of phase separation in metallic glasses

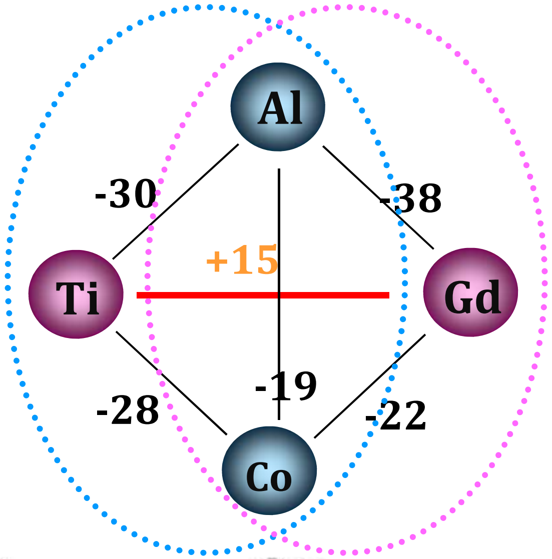
(a) Composition

(b) Critical temperature, T_c

(c) Asymmetry of the spinodal curve/decomposition range

(d) Glass-forming ability of the separated liquid

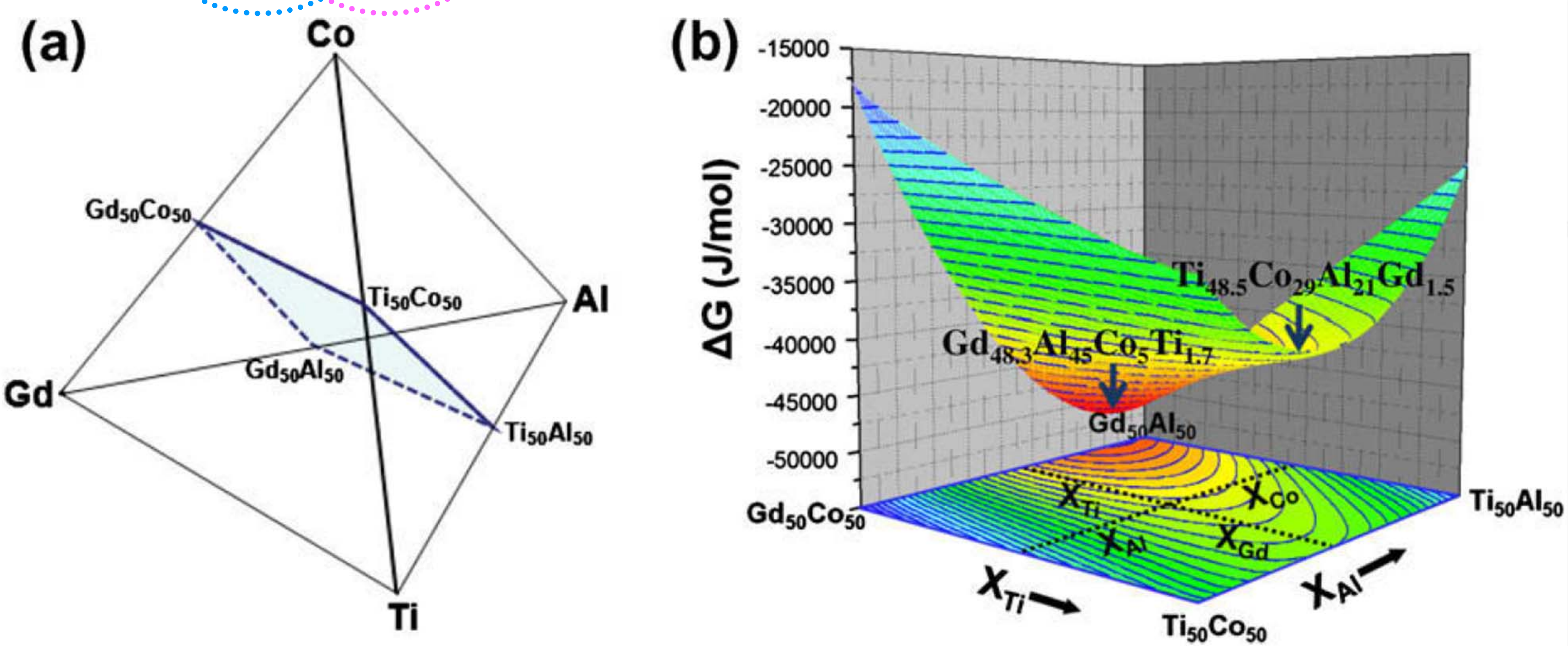
Synthesis of metallic glass composites using phase separation phenomenon



Possibility of two phase !!!

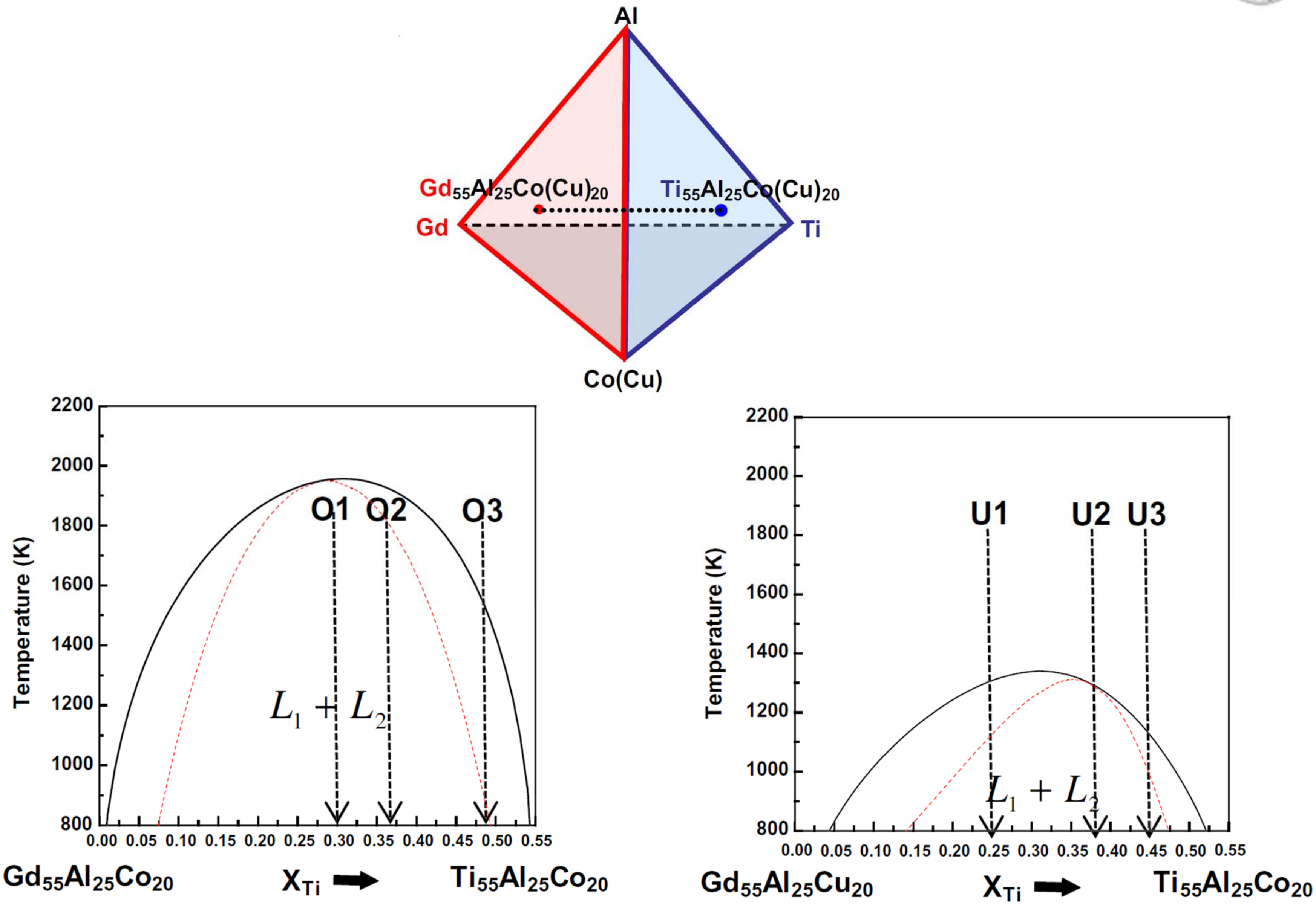
→ **Ti-Al-Co, Gd-Al-Co**

(a) Composition section selected by rectangular plane intersection in quaternary Gd–Ti–Al–Co composition tetrahedron. (b) Gibbs free energy surface of liquid phase at 1000 K for the composition section given in (a). This Gibbs free energy surface shows two minima (arrows), implying that the phase separation can occur in that region.



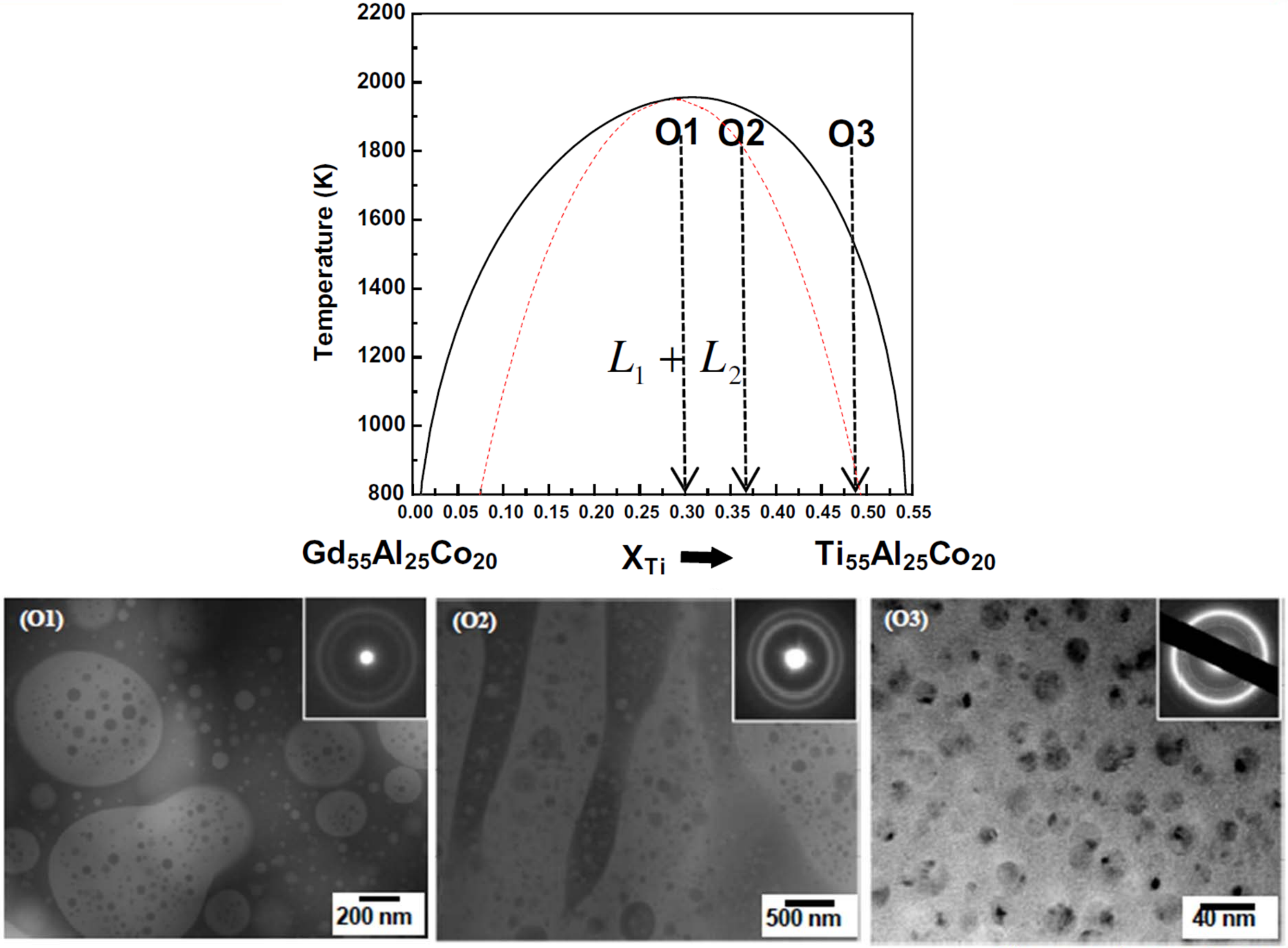
(a) Composition

Thermodynamic calculation using CALPHAD



(a) Composition

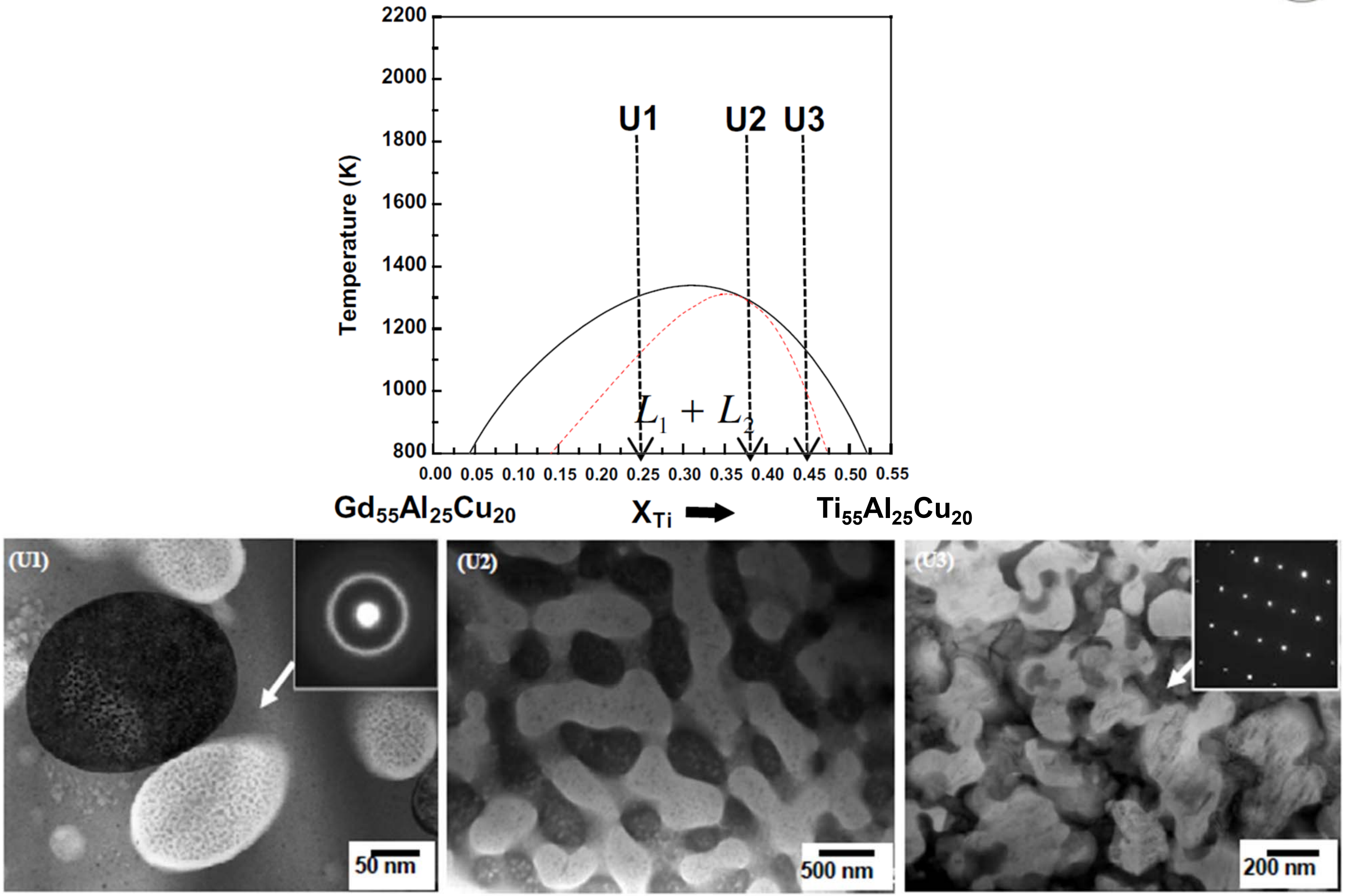
Microstructure evolution (GdTiAlCo)



Chang et al., Acta Mater (2010)

(a) Composition

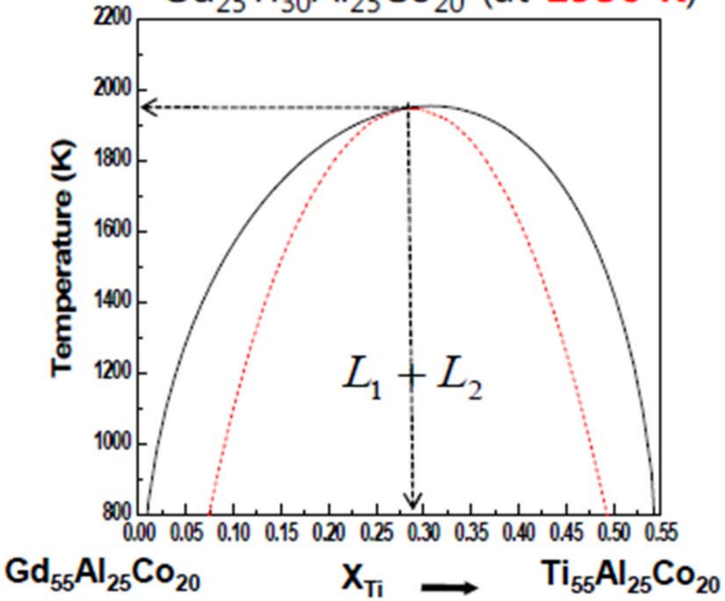
Microstructure evolution (GdTiAlCu)



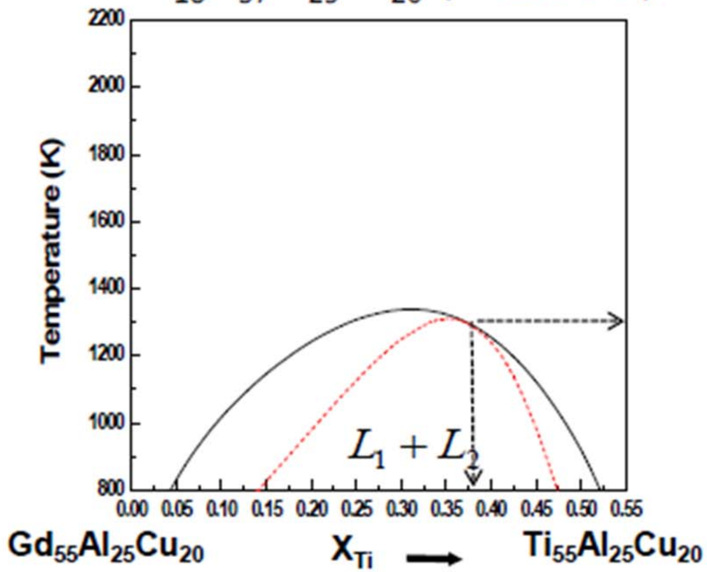
Chang et al., Acta Mater (2010)

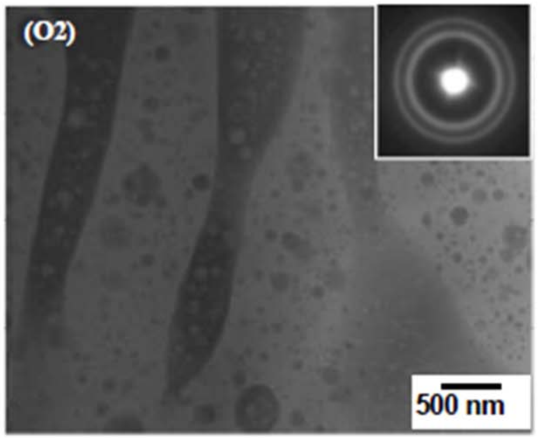
(b) Critical temperature

Spinodal critical point
$Gd_{25}Ti_{30}Al_{25}Co_{20}$ (at **1950 K**)



Spinodal critical point
$Gd_{18}Ti_{37}Al_{25}Cu_{20}$ (at **1300 K**)

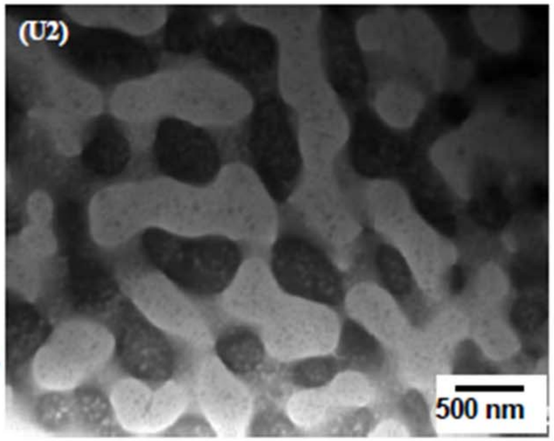




Scale of interconnected structure

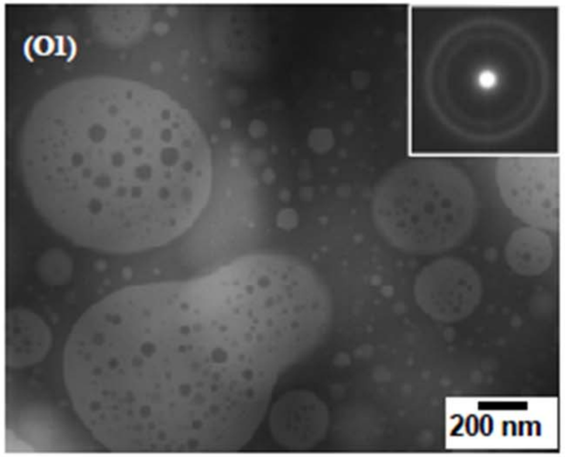
←Several um

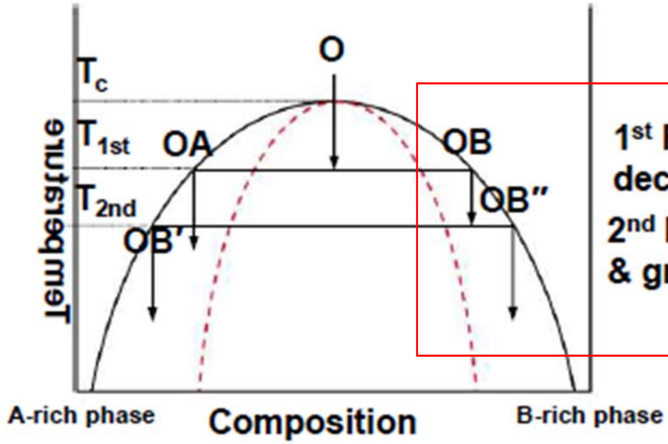
200~300 nm→



(c) Asymmetry of spinodal curve / Decomposition range

❖ Symmetric spinodal curve / smaller decomposition range

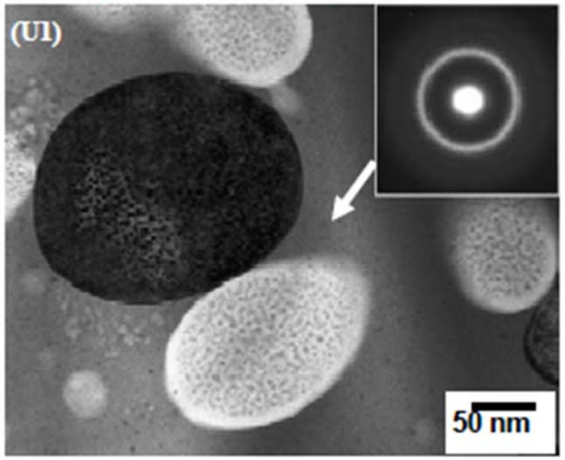


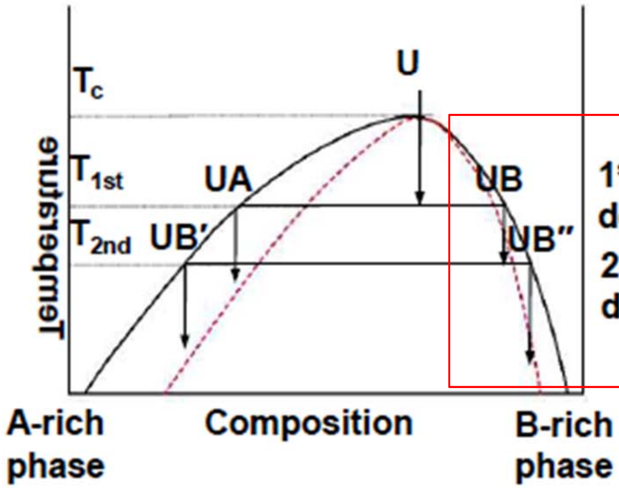


1^{st} P.S.; spinodal decomposition

2^{nd} P.S.; nucleation & growth

❖ Asymmetric spinodal curve / larger decomposition range

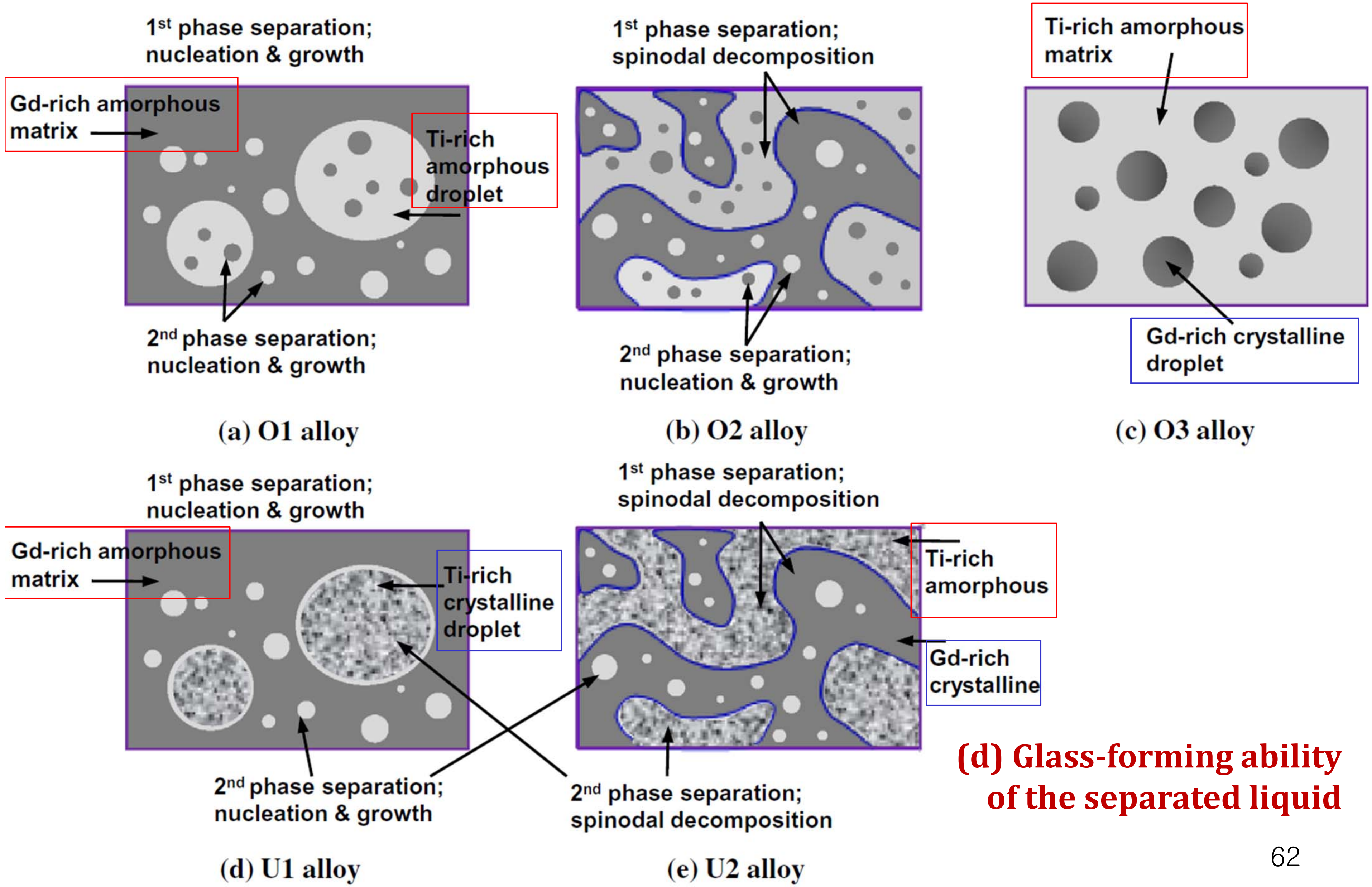




1^{st} P.S.; spinodal decomposition

2^{nd} P.S.; spinodal decomposition

*** Schematic drawings of the microstructures showing variation of microstructure depending on alloy composition and second phase separation mechanism.**



(d) Glass-forming ability of the separated liquid

Contents for today's class

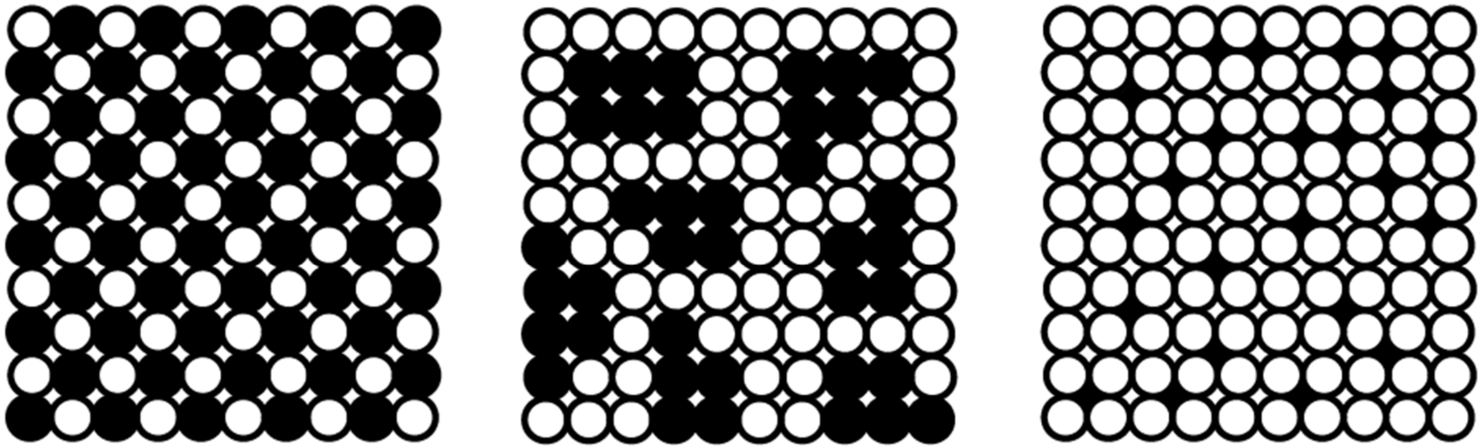
- Binary System   mixture/ solution / compound

Ideal solution $(\Delta H_{mix}=0)$ **Random distribution**

Regular solution $\Delta H_{mix} = P_{AB}\varepsilon$ where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$ $\varepsilon \approx 0$

$\Delta H_{mix} > 0$ or $\Delta H_{mix} < 0$

Real solution   **Ordered structure**

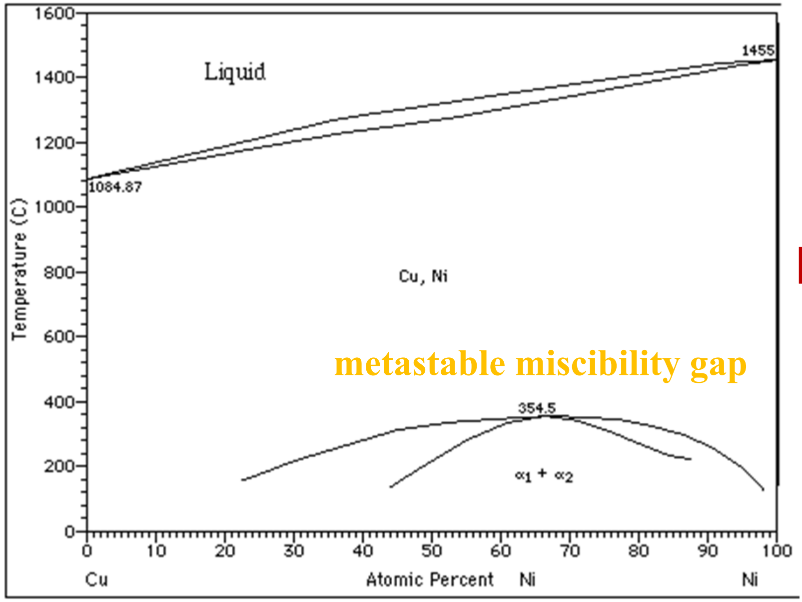


(a) $\varepsilon < 0$, $\Delta H_{mix} < 0$
Ordered alloys
$P_{AB}\uparrow \longrightarrow$ Internal E $\downarrow$

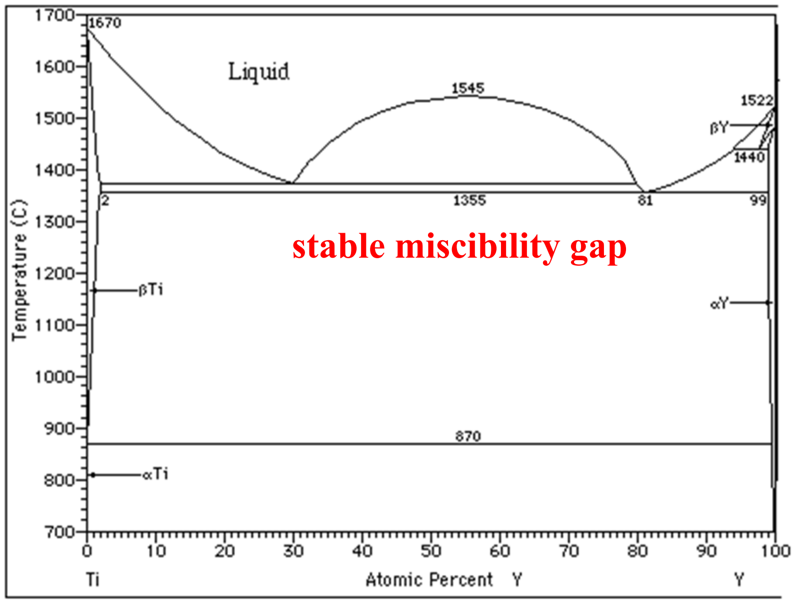
(b) $\varepsilon > 0$, $\Delta H_{mix} > 0$
Clustering
$P_{AA}, P_{BB}\uparrow$

(c) when the size difference is large
strain effect
Interstitial solution

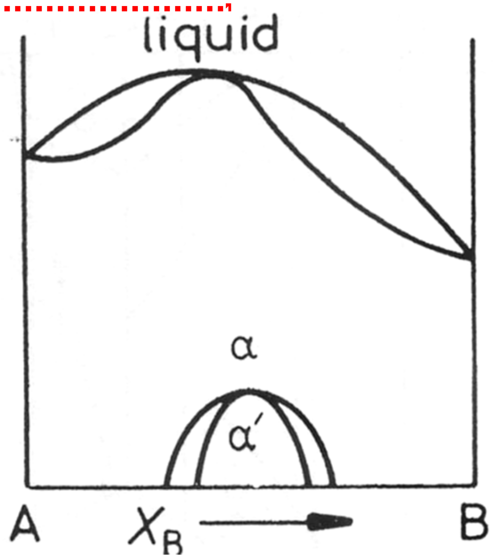
$\Delta H^{S}_{mix} > 0$: Solid solution → solid state phase separation (two solid solutions)

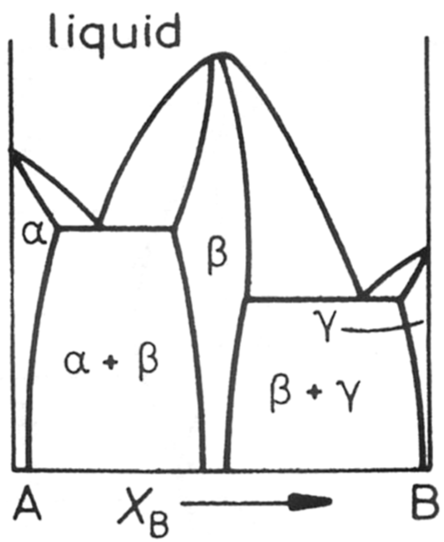


$\Delta H^{S}_{mix} >> 0$: liquid state phase separation (up to two liquid solutions)



$\Delta H^{S}_{mix} < 0$: Solid solution → ordered phase





$\Delta H^{S}_{mix} << 0$: Compound : AB, A_2B…