2021 Spring

"Phase Equilibria *in* Materials"

03.16.2021

Eun Soo Park

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

- 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

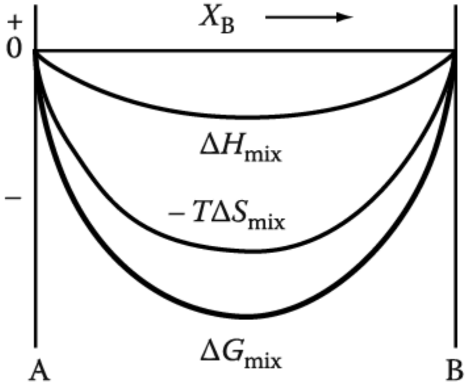
$$G_2 = G_1 + \Delta G_{mix}$$

$$G = X_A G_A + X_B G_B + \overbrace{\Omega X_A X_B}^{\Delta H_{mix}} + \overbrace{RT(X_A \ln X_A + X_B \ln X_B)}^{-T\Delta S_{mix}}$$

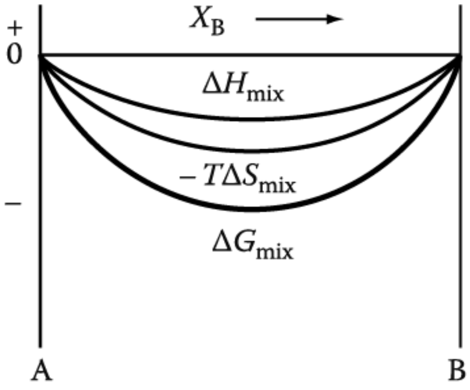
Reference state

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

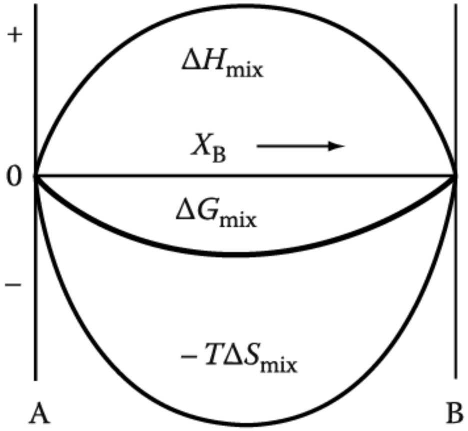
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



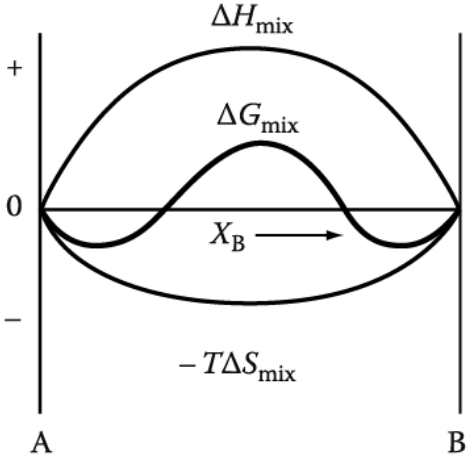
(a) $\Omega < 0$, high T



(b) $\Omega < 0$, low T



(c) $\Omega > 0$, high T



(d) $\Omega > 0$, 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

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

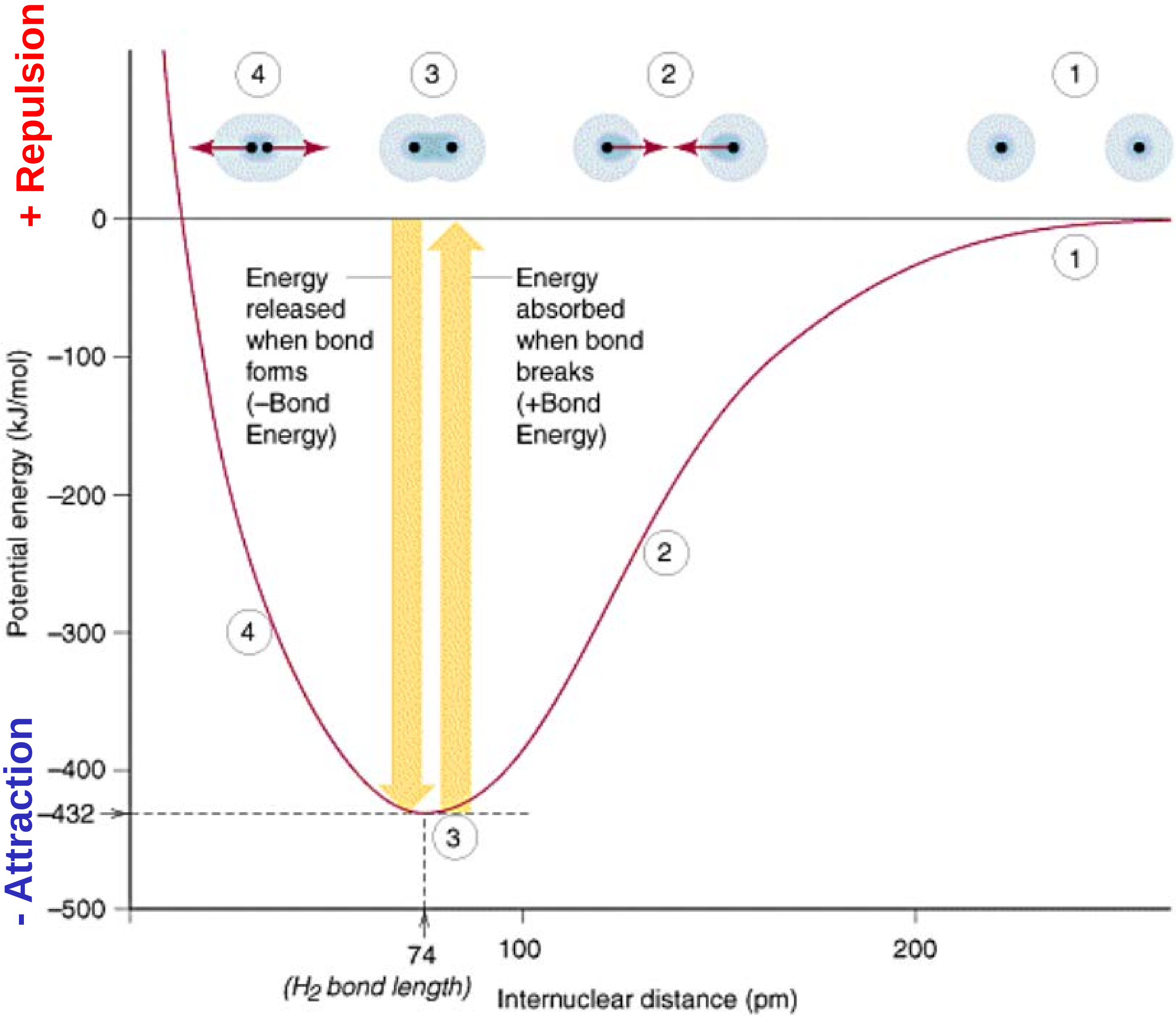
The term T_c will be a maximum when $X_A = (1-X_A) = 0.5$. It follows that

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

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).

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



+ Repulsion

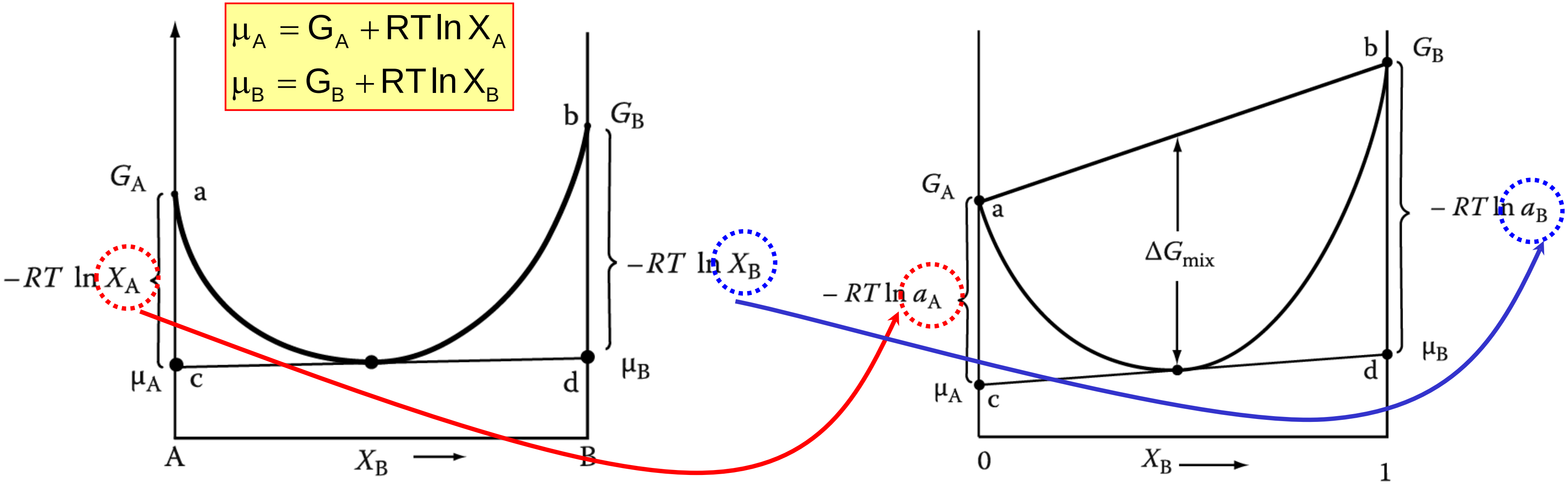
- Attraction

Activity, a : effective concentration for mass action

ideal solution

regular solution

$$\mu_A = G_A + RT\ln X_A$$
$$\mu_B = G_B + RT\ln X_B$$



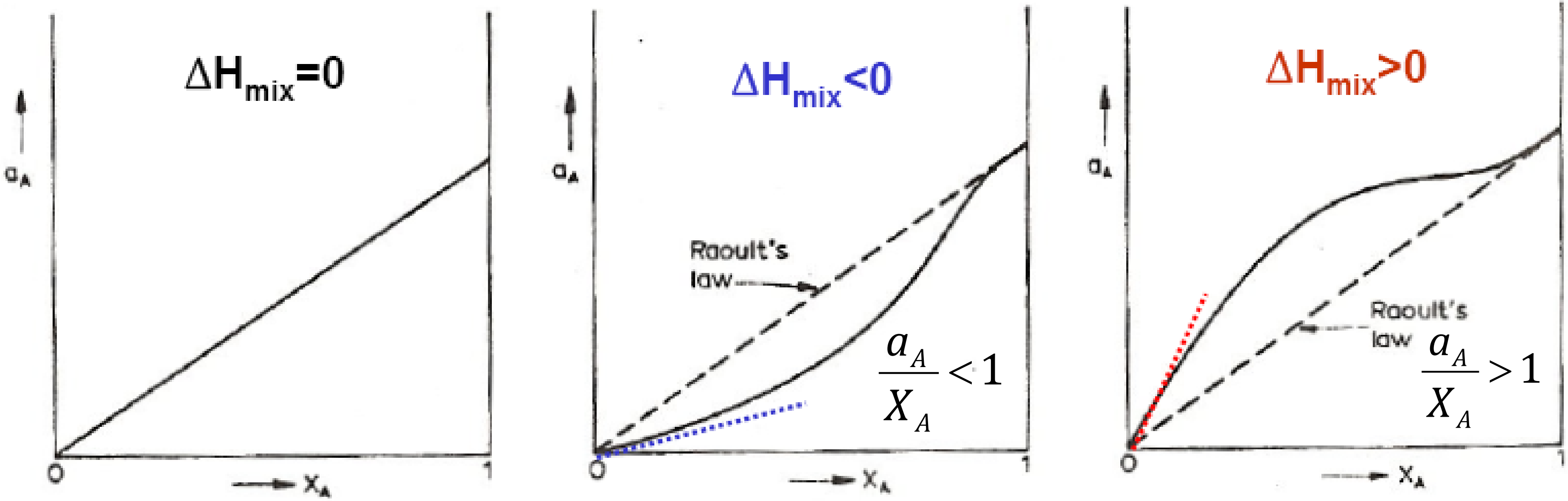
$$\mu_A = G_A + RT\ln a_A \qquad \mu_B = G_B + RT\ln a_B$$

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

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

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

Activity-composition curves for solutions



$\Delta H_{mix}=0$

$\Delta H_{mix}<0$

$\frac{a_A}{X_A} < 1$

$\Delta H_{mix}>0$

$\frac{a_A}{X_A} > 1$

(a)
Ideal solution
$A \leftrightarrow B = \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Bi-Sn at 335°C
$a_A = a_{Sn}$

(b)
Actual solution
$A \leftrightarrow B > \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Au-Sn at 600°C
$a_A = a_{Sn}$

(c)
Actual solution
$A \leftrightarrow B < \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Cd-Pb at 500°C
$a_A = a_{Cd}$

Degree of non-ideality

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

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

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

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”?

1.3 Binary Solutions

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

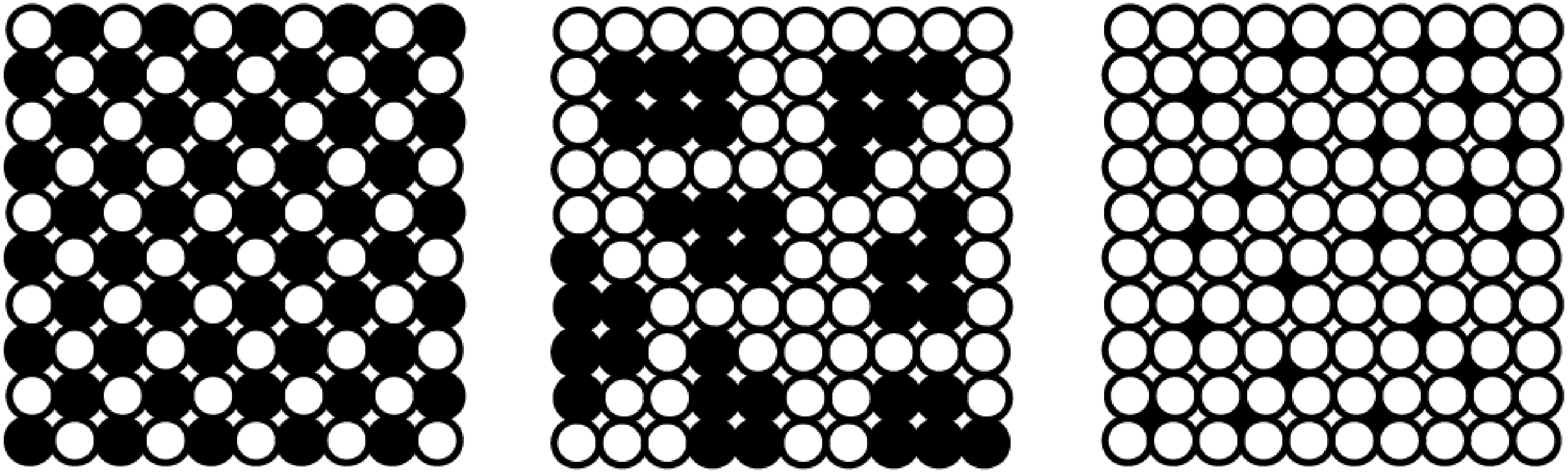
Real solution: sufficient disorder + lowest internal E

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

Clustering

Interstitial solution

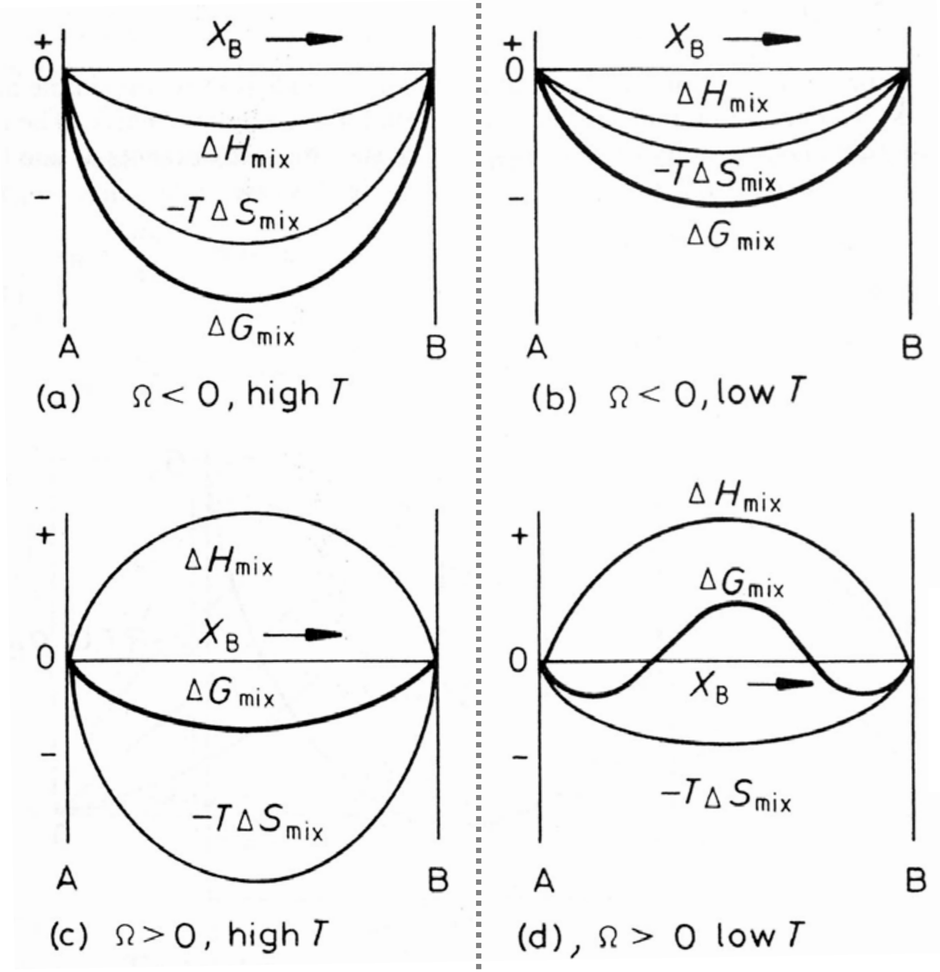
$P_{AB} \uparrow \longrightarrow$ **Internal** E $\downarrow$

$P_{AA}, P_{BB} \uparrow$

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

High temp. ⟶ Entropy effect ↑ ⟶ Solution stability ↑

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

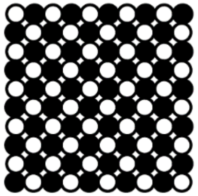


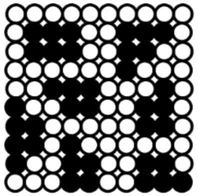
(a) $\Omega < 0$, high T

(b) $\Omega < 0$, low T

(c) $\Omega > 0$, high T

(d), $\Omega > 0$ low T

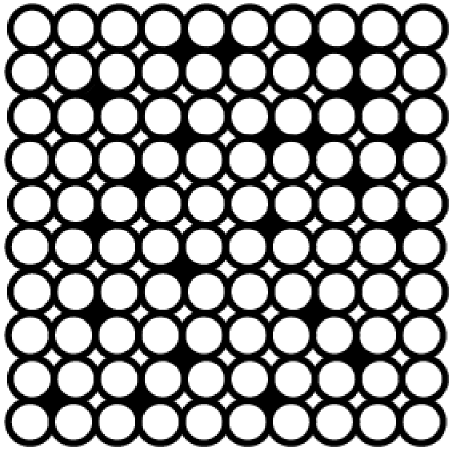




1.3 Binary Solutions

Real solution: sufficient disorder + lowest internal E

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



➡ $\Delta E = \boxed{\Delta H_{mix}}$ + 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?

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

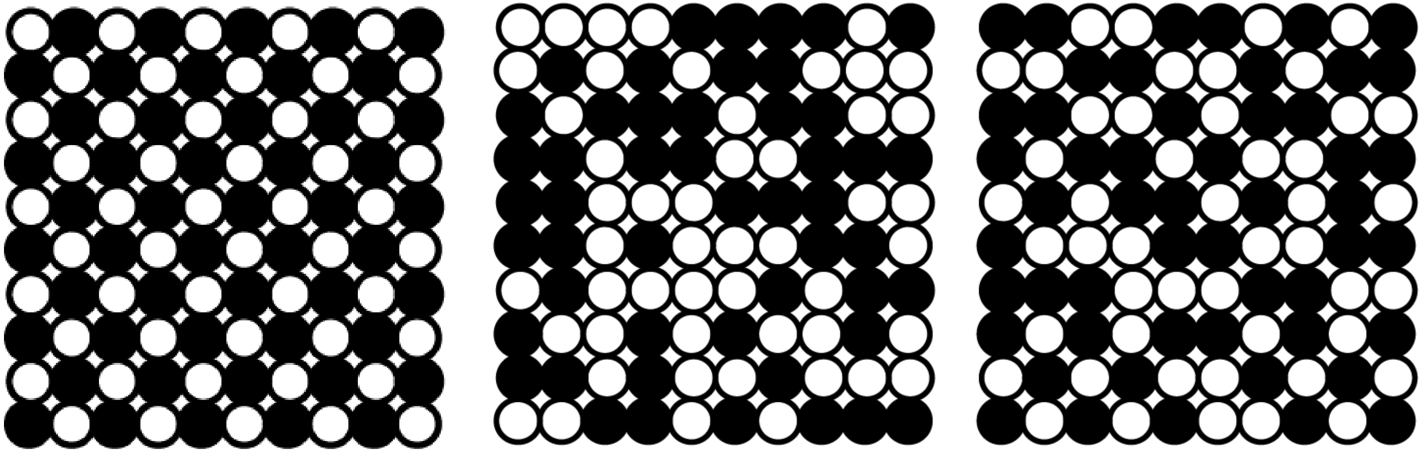
SRO (Short Range Ordering) or LRO (Long Range Ordering)

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

$\Delta\Omega = N_a z\varepsilon$

SRO parameter = s _ degree of ordering

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

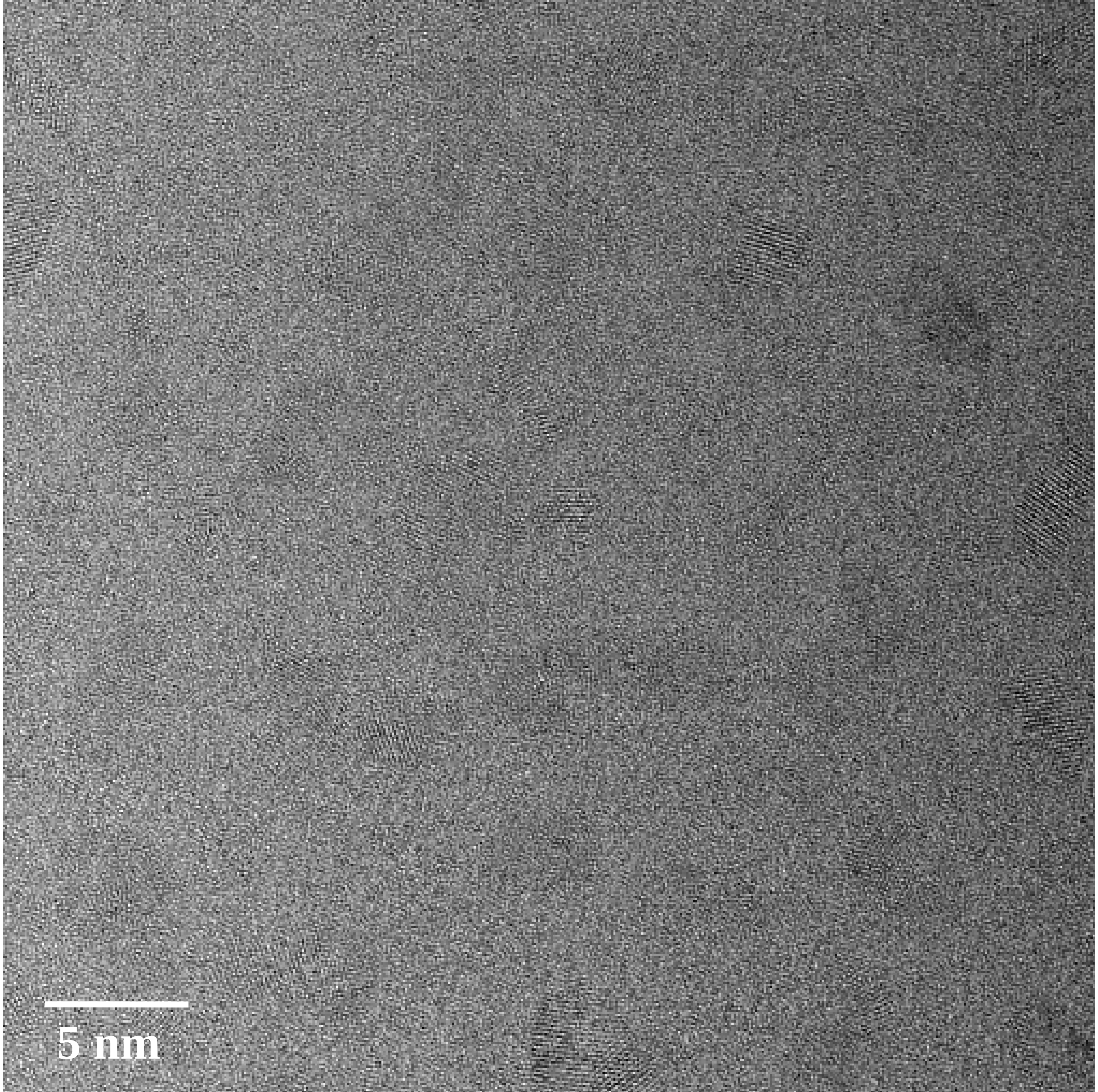


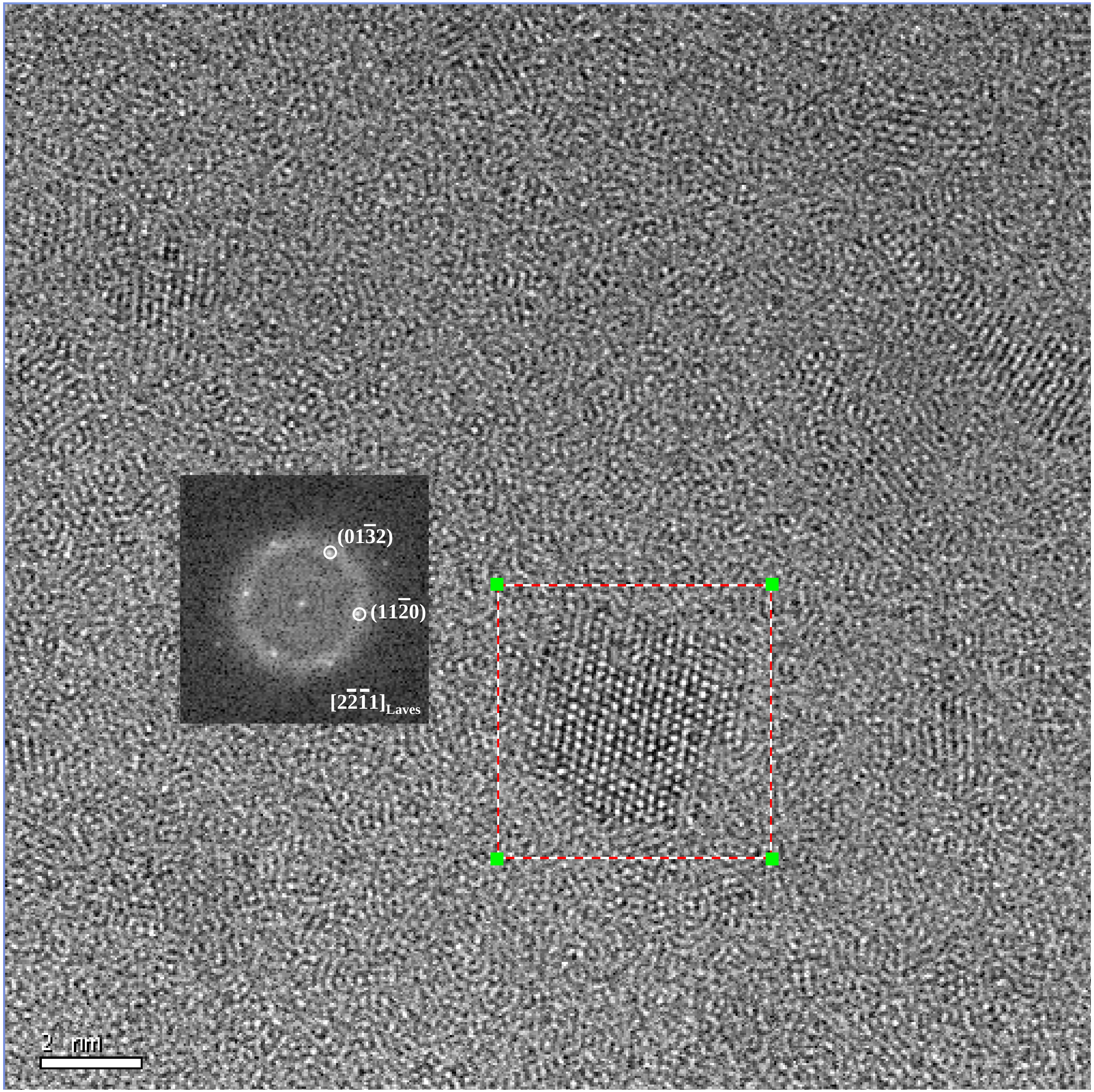
P_{AB} (max)

(a) P_{AB} (random)

(b) P_{AB} with SRO

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


5 nm


(013̄2)
(112̄0)
[22̄1̄1]Laves
2 nm

Ordered phase: “Long range order (LRO)”

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

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

*** Solid solution → ordered phase**

→ random mixing

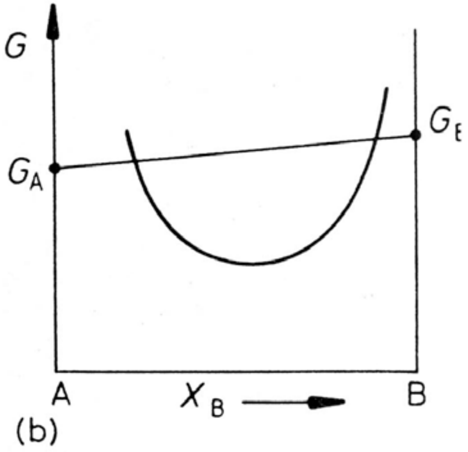
→ entropy ↑

negative enthalpy ↓

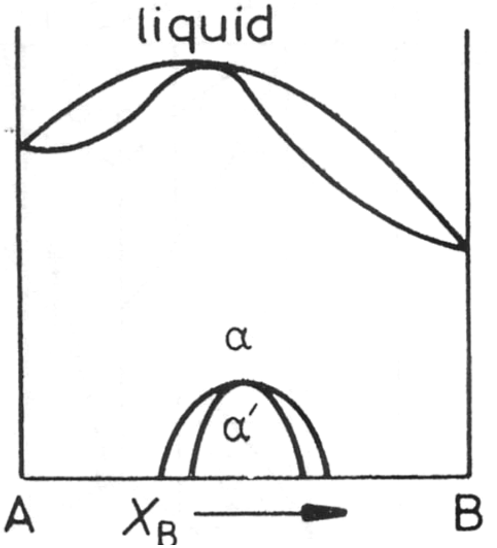
$$\boxed{\Delta H^{S}_{mix} < 0}$$

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 ↓

$$\boxed{\Delta H^{S}_{mix} << 0}$$

Small composition range

➔ G ↓

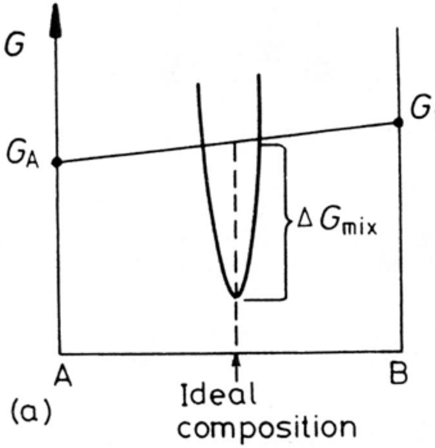
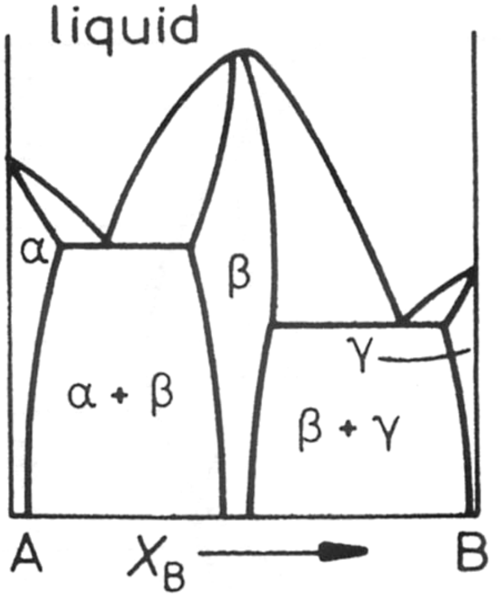


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.

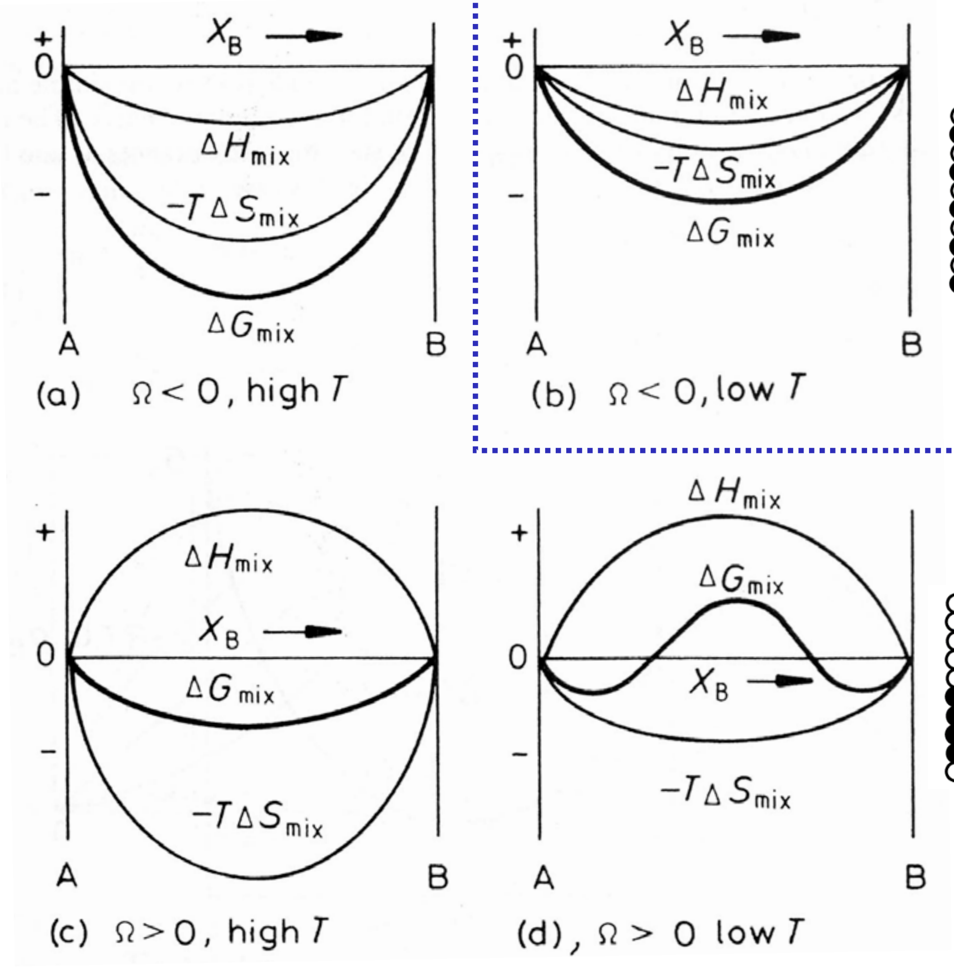


Q3: Superlattice

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

High temp. → Entropy effect ↑ → Solution stability ↑

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

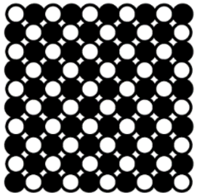


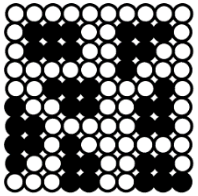
(a) $\Omega < 0$, high T

(b) $\Omega < 0$, low T

(c) $\Omega > 0$, high T

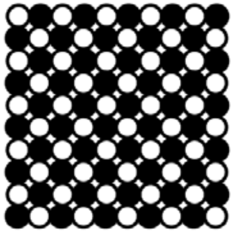
(d), $\Omega > 0$ low T





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.

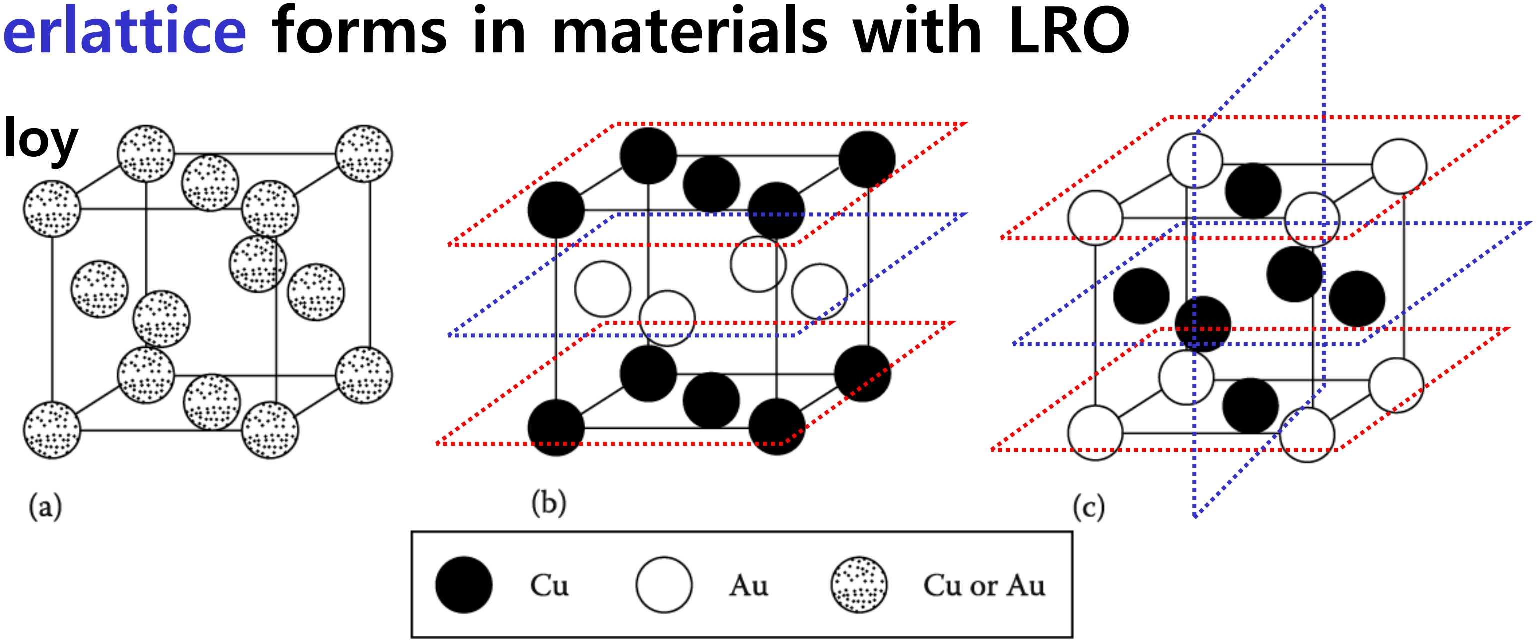


* This is known as long-range order (LRO) CuAu, Cu_3Au and many other intermetallics show LRO.

(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

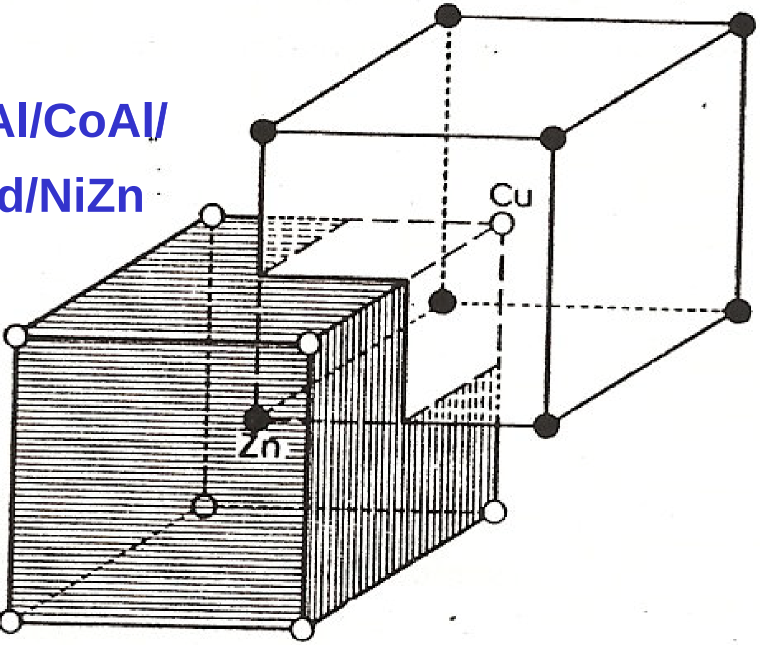
Superlattice formation: order-disorder transformation

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

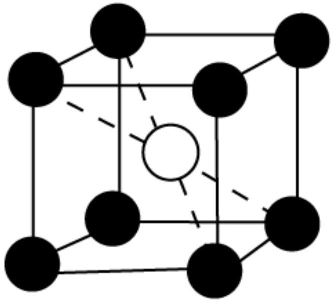


β brass superlattice viewed as two inter-penetrating cubic lattices

Five common ordered lattices

(a) $L2_0$:

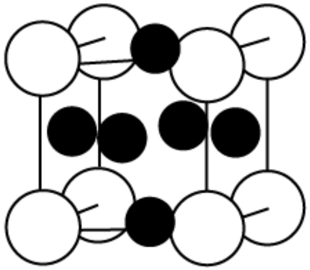
CuZn/FeCo/NiAl/CoAl/
FeAl/AgMg/AuCd/NiZn



(a) ● Cu ○ Zn

(b) $L1_2$:

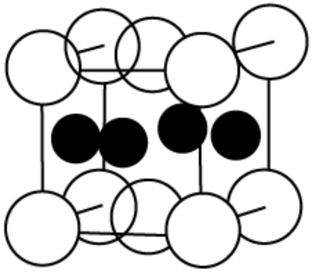
Cu_3Au/Ni_3Mn/Ni_3Fe/Ni_3Al/
Pt_3Fe/Au_3Cd/Co_3V/$TiZn_3$



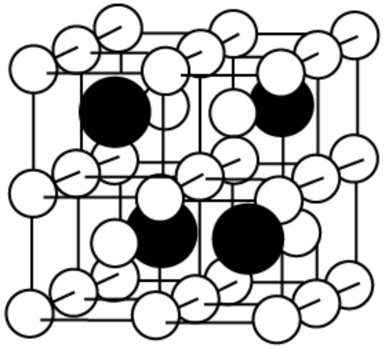
(b) ● Cu ○ Au

(c) $L1_0$:

CuAu/CoPt/FePt



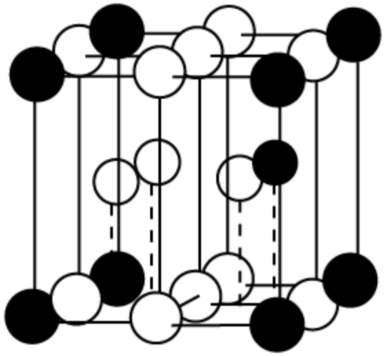
(c) ● Cu ○ Au



(d) ● Al ○ Fe

(d) $D0_3$:

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



(e) ● Cd ○ Mg

(e) $D0_{19}$:

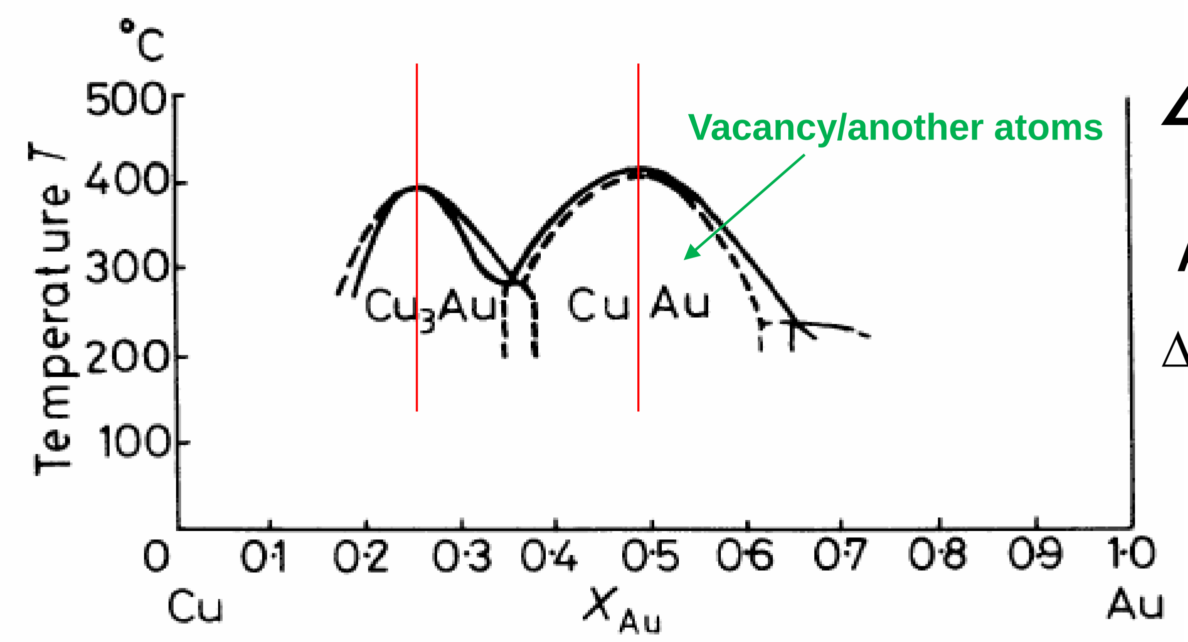
Mg_3Cd/Cd_3Mg/Ti_3Al/Ni_3Sn/Ag_3In/
Co_3Mo/Co_3W/Fe_3Sn/Ni_3In/Ti_3Sn

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

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.



Vacancy/another atoms

ΔS_{mix}~small

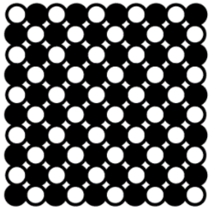
At high Temp.,

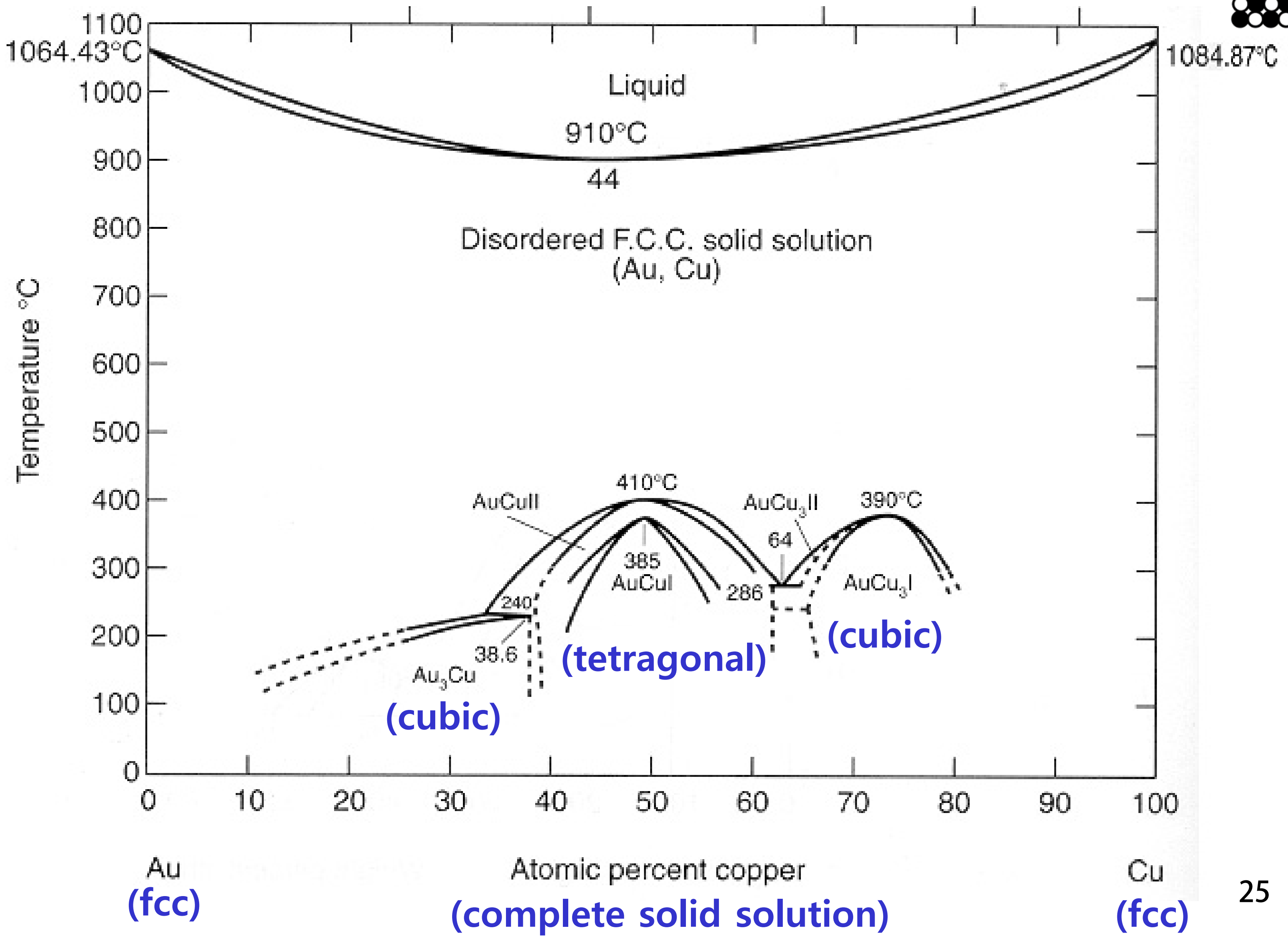
ΔG_{mix}~ large (-)

- 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



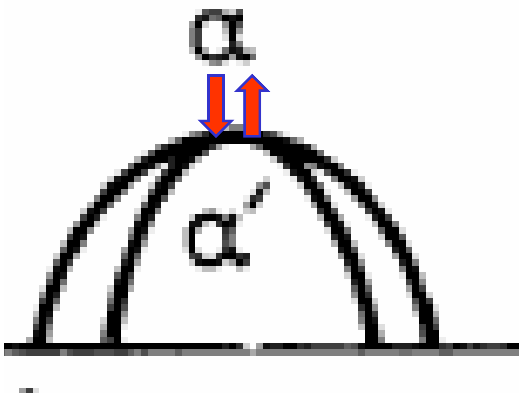


Q4: Order-disorder transition

Order-disorder phase transformation

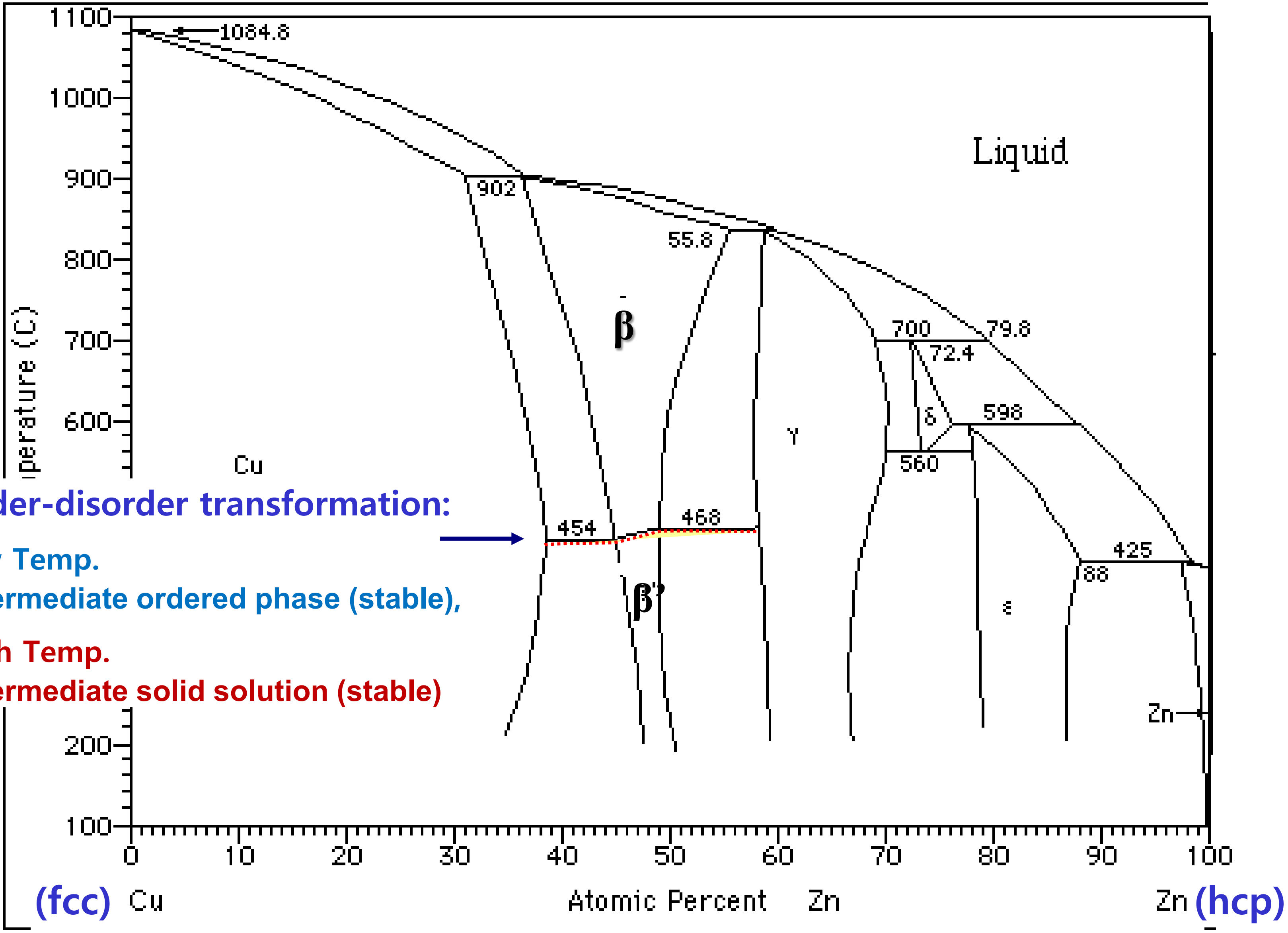
- **Not classical phase change=~not depend on diffusion process**
- **change of temperature allowed a continuous re-arrangement of atoms without changing the phase = "2nd order transition"**
- **boundary: ordered lattice & disordered lattice/phase rule could not applied**

  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:

Low Temp.

→ intermediate ordered phase (stable),

High Temp.

→ intermediate solid solution (stable)

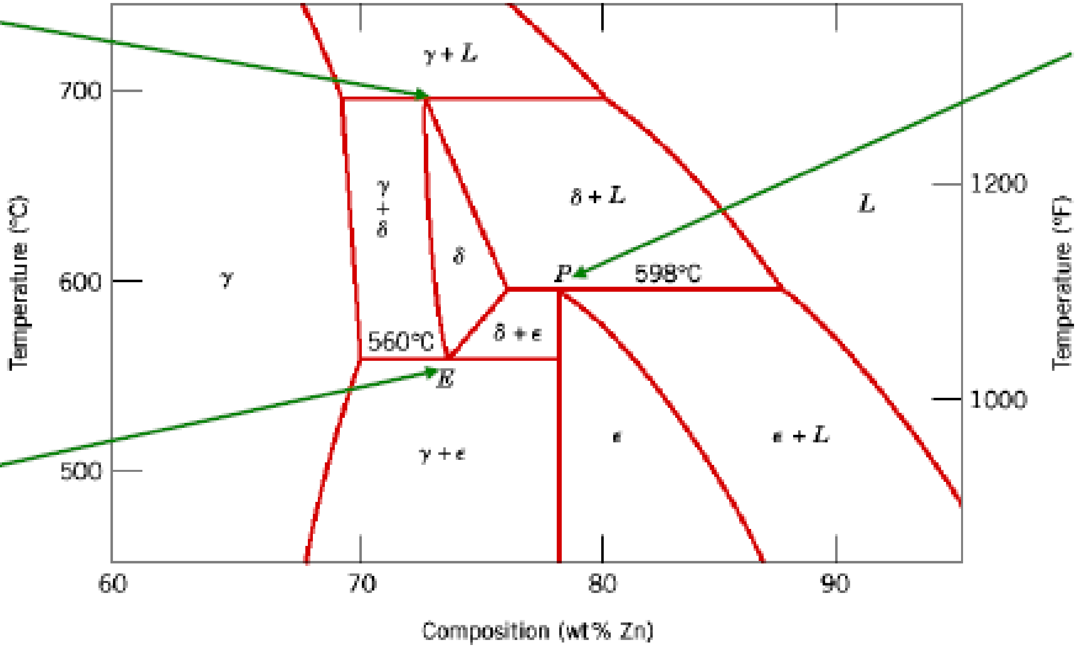
- α and η are terminal solid solutions
- β, β', γ, δ and ε are intermediate solid solutions.

Cu-Zn Phase Diagram

Eutectoid and Peritectic Reactions

peritectic:
$\gamma + L \rightleftarrows \delta$

peritectic:
$\delta + L \rightleftarrows \varepsilon$

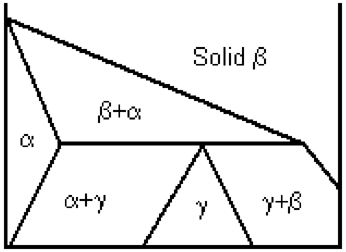


eutectoid:
$\delta \rightleftarrows \gamma + \varepsilon$

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

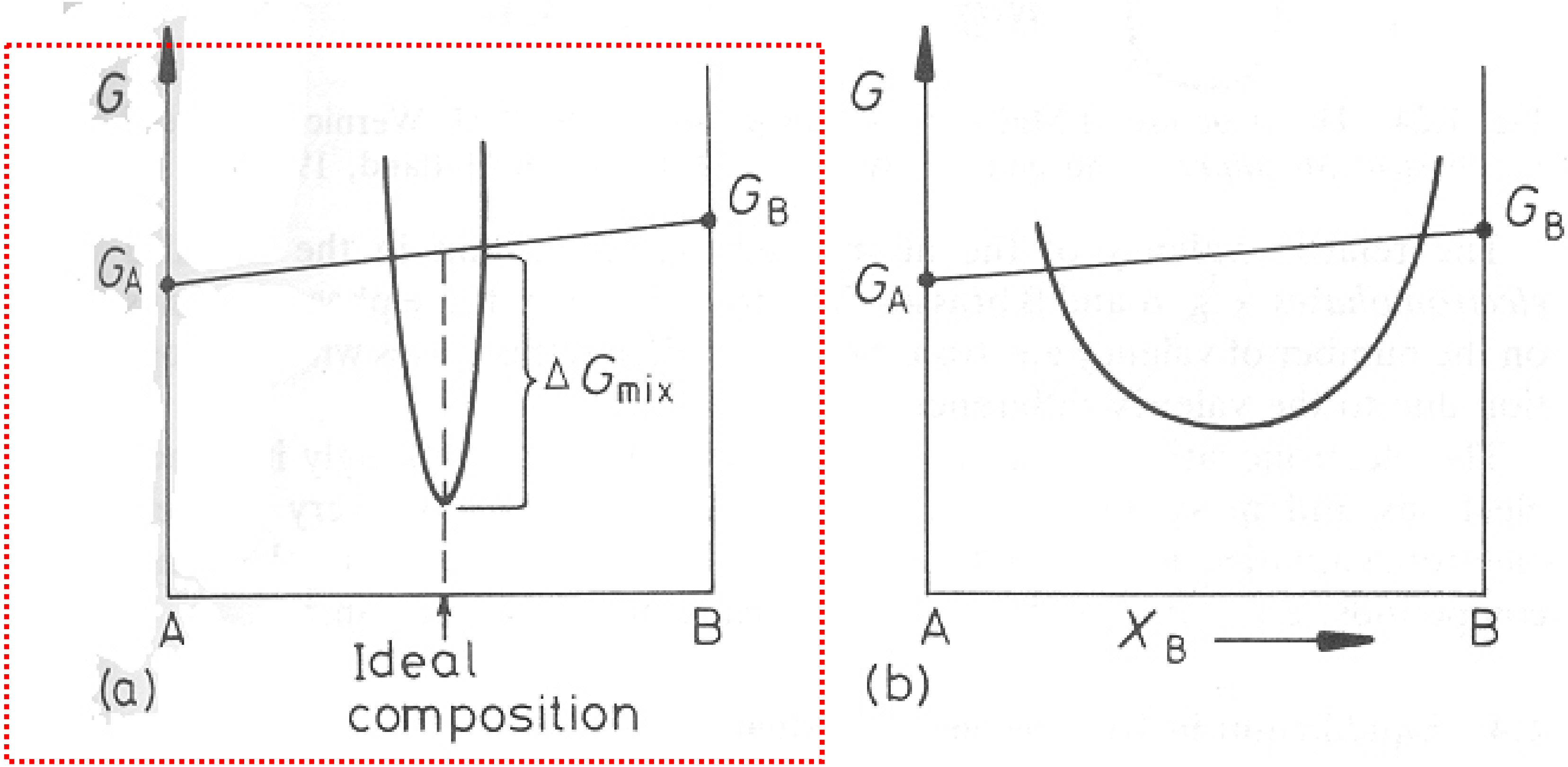
Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

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



Q5: Intermediate phase vs Intermetallic compound

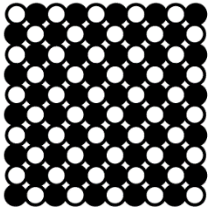
Intermediate Phase



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

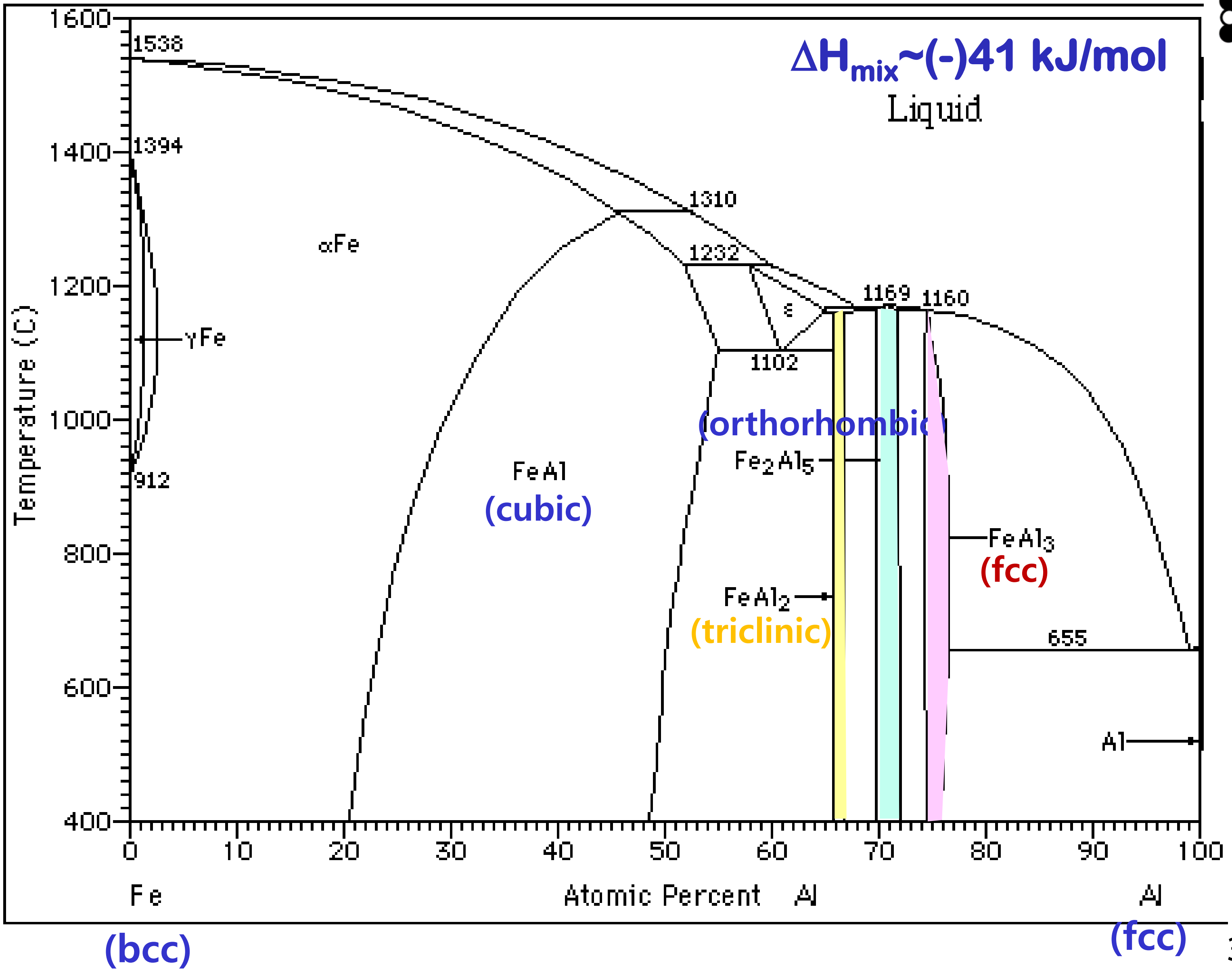
- **In other structure, fluctuations in composition can be tolerated by some atoms occupying 'wrong' position or by atom sites being left vacant, and in these cases the curvature of the G curve is much less, Fig (b).**

Intermediate Phase



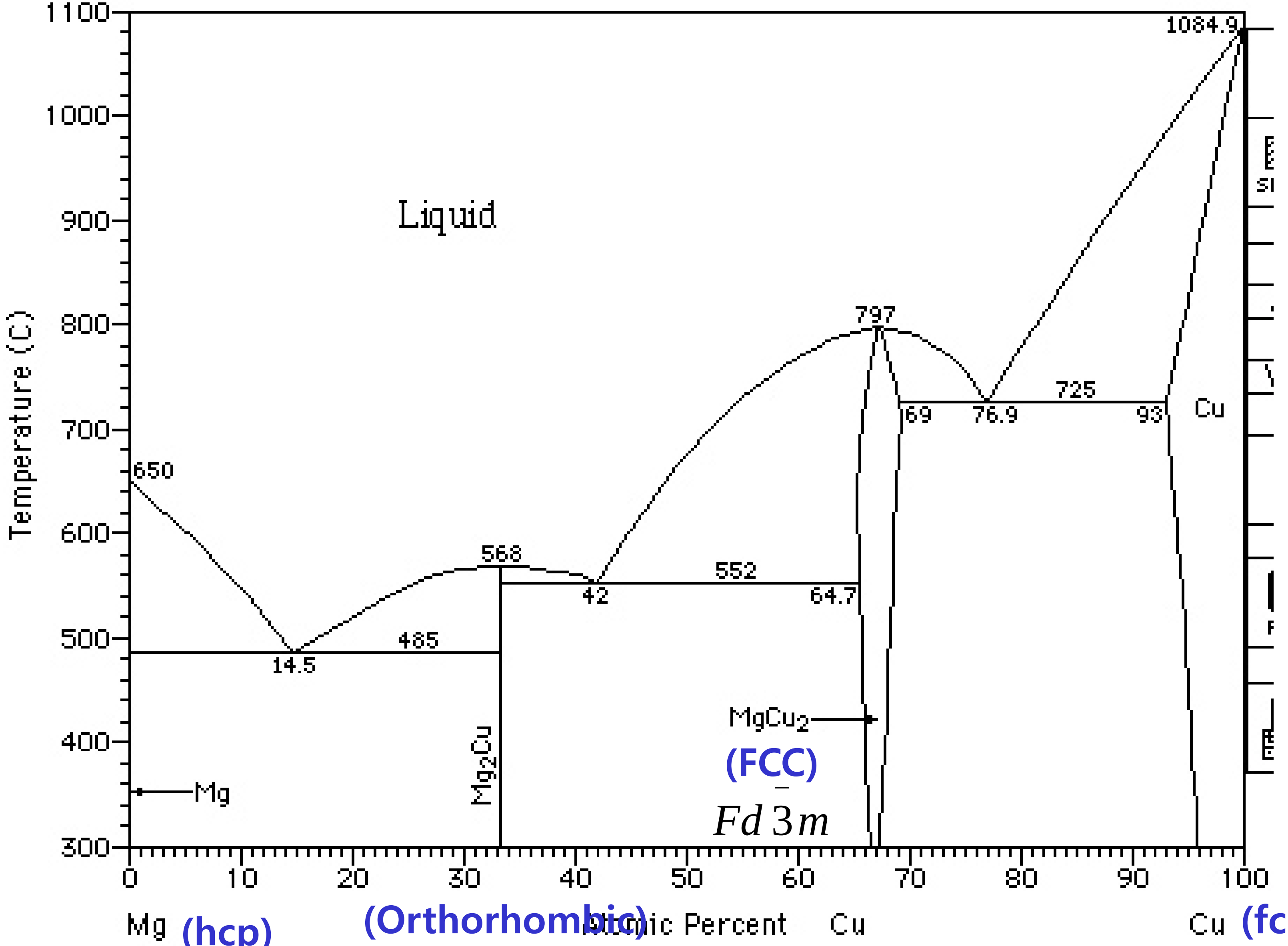
$\varepsilon < 0,\ \Delta H_{mix} < 0$

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



Intermediate Phase

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



(hcp) $P6_3/mmc$

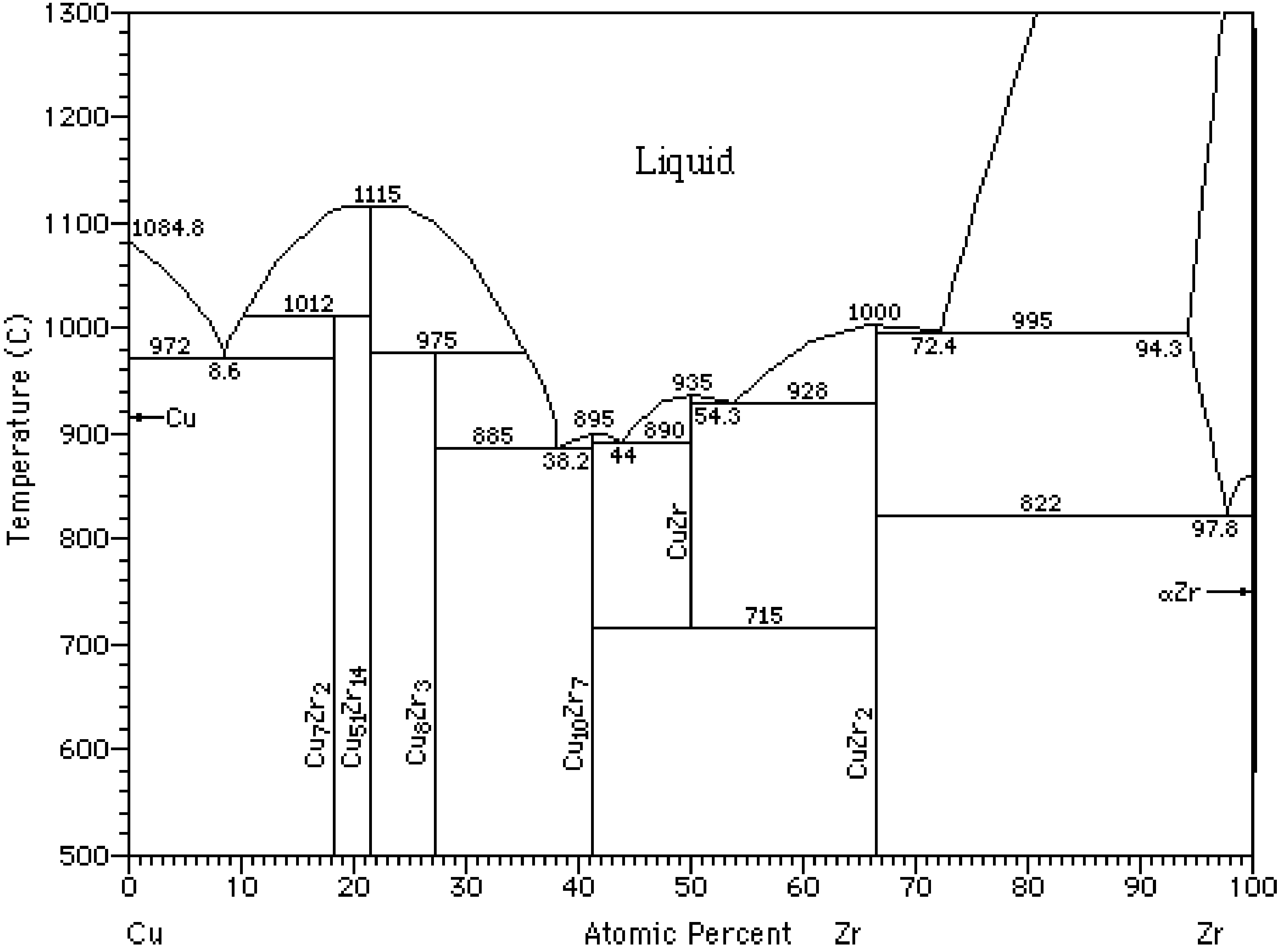
(Orthorhombic) $Fddd$

(FCC) $Fd\bar{3}m$

(fcc) $Fm\bar{3}m$

Intermediate Phase

$\varepsilon \ll 0,\ \Delta H_{mix} \ll 0\ /\ \Delta H_{mix} \sim -142\ \text{kJ/mol}$



Q6: Main factors determining the structure of intermediate phase

Intermediate Phase

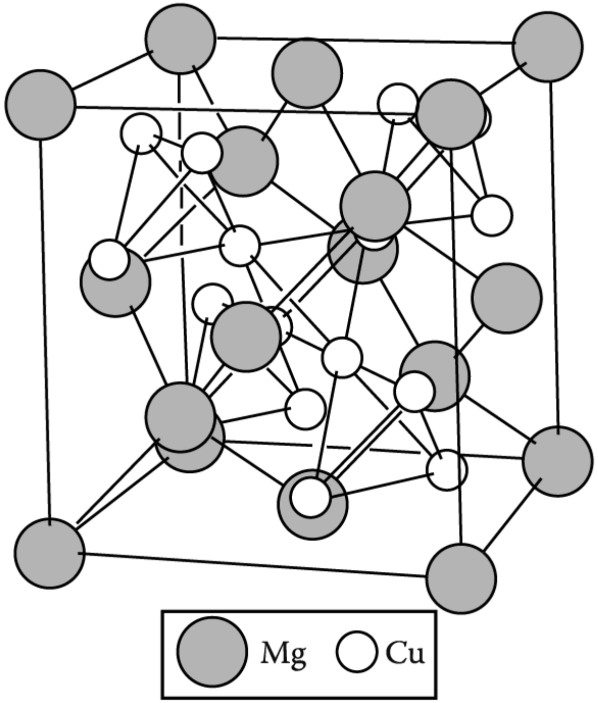
_"different crystal structure as either of the pure component"

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

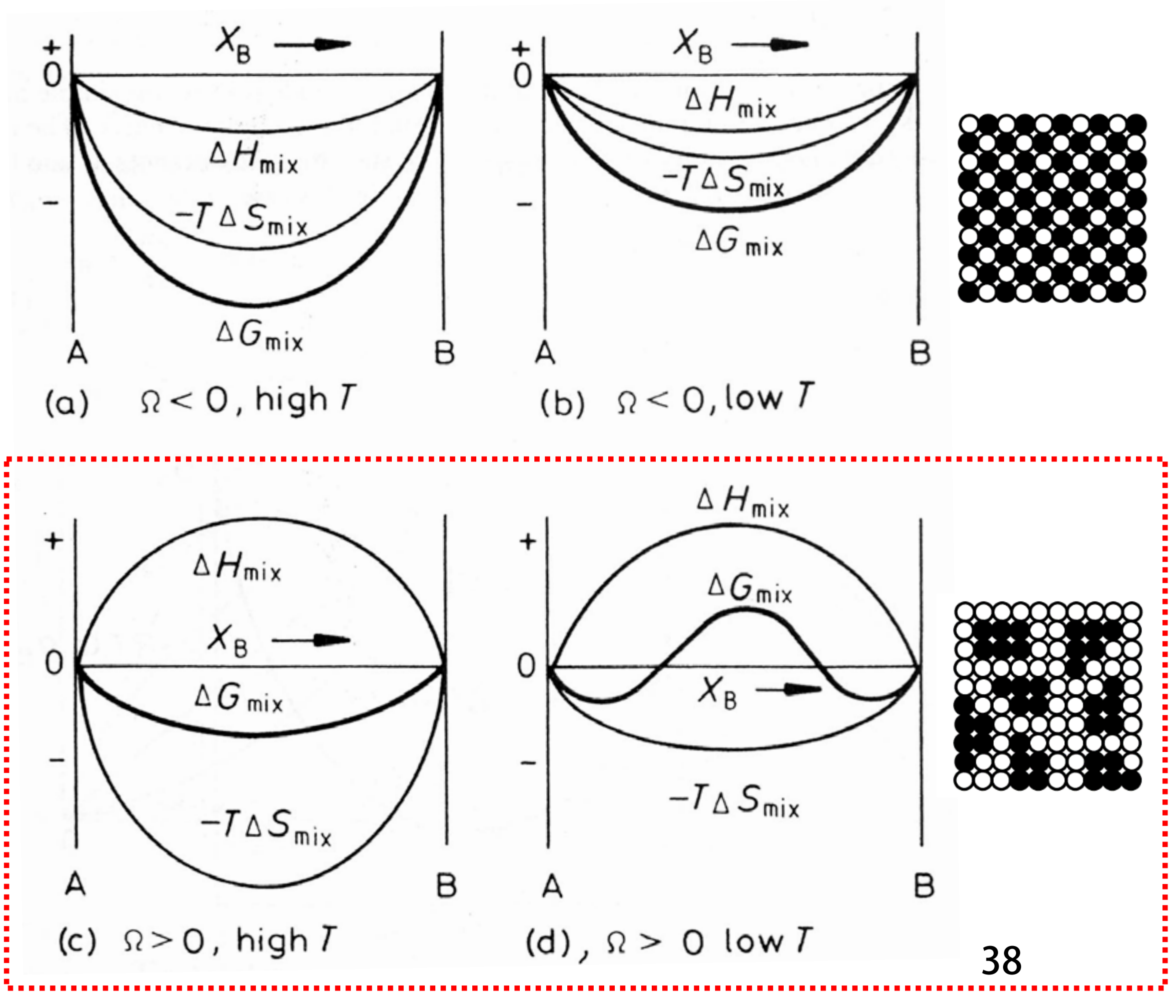
“Clustering”? → Phase separation

Q7: Metastable vs Stable miscibility gap

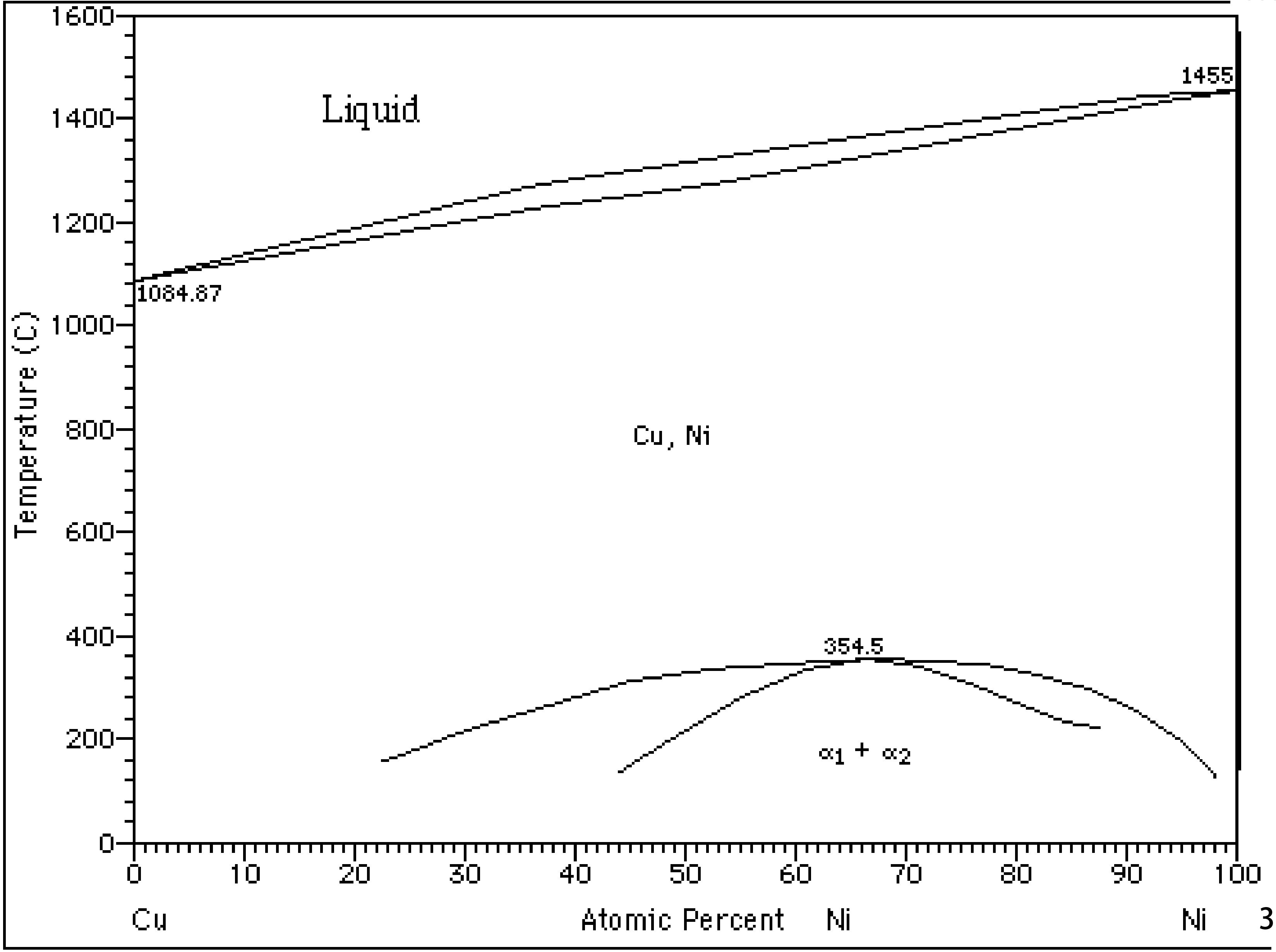
*** The degree of ordering or clustering will decrease as temp. increases due to the increasing importance of entropy.**

High temp. → Entropy effect ↑ → Solution stability ↑

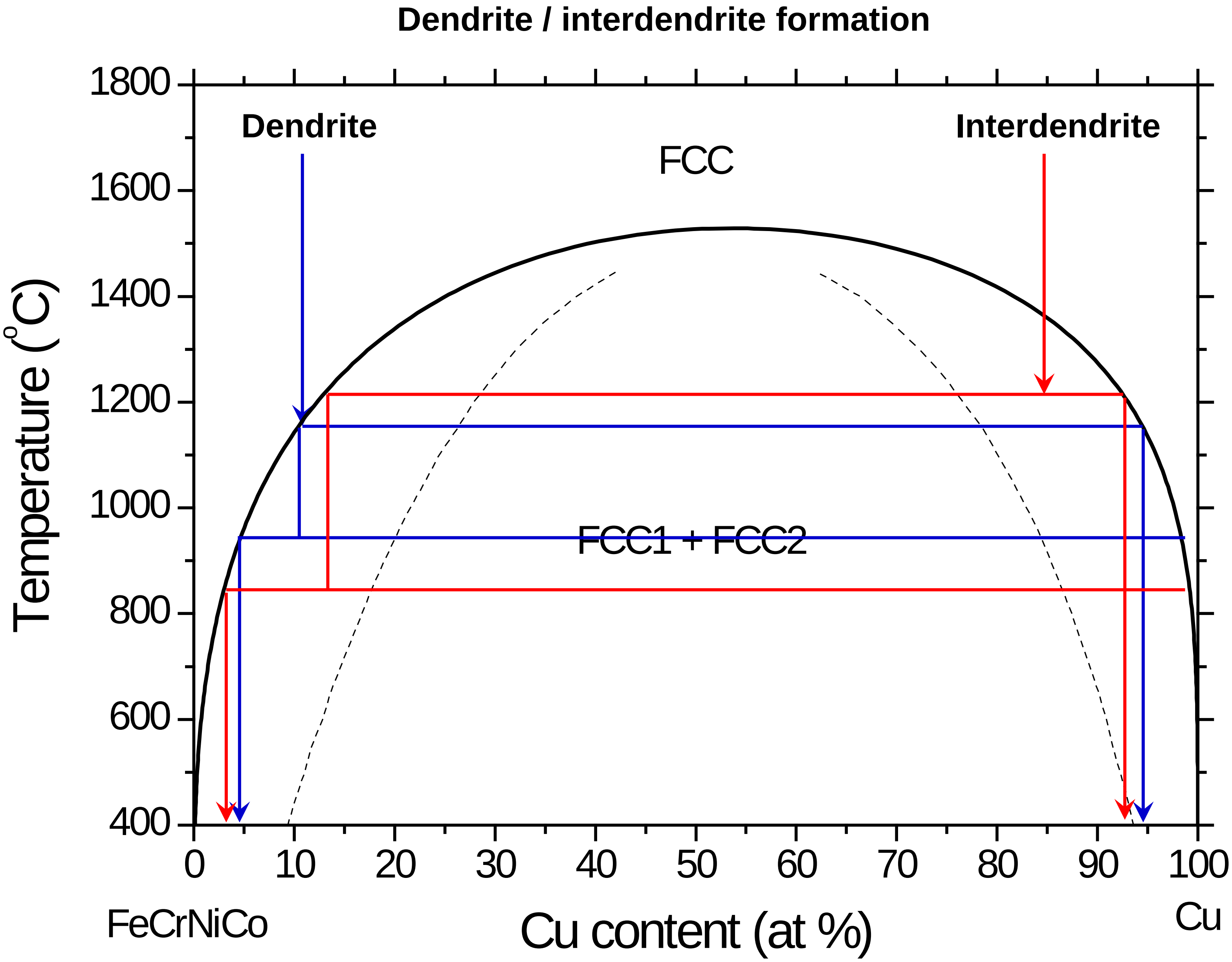
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



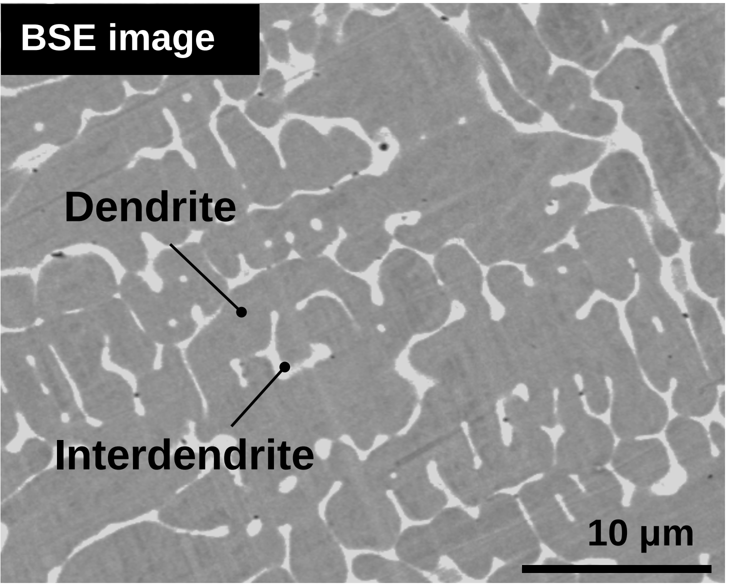
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +26$ kJ/mol

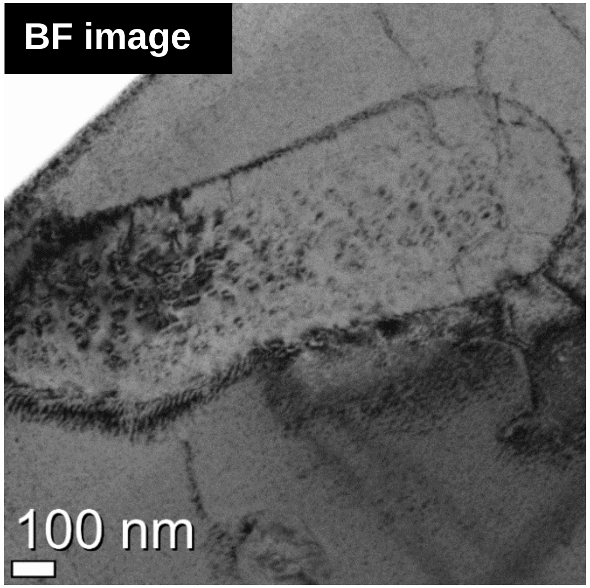


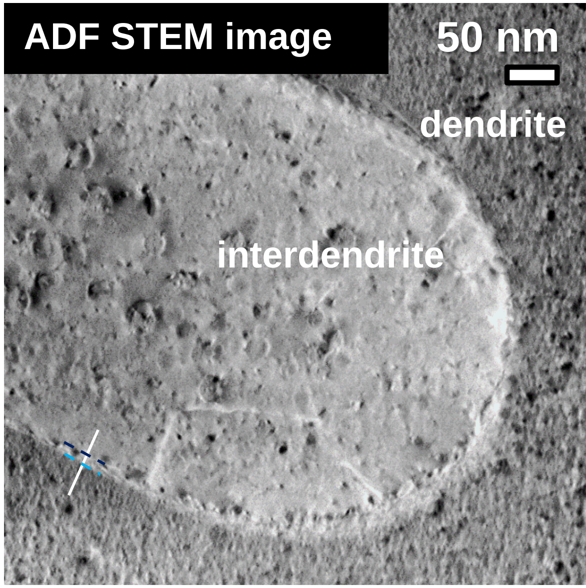
Cooling process in the miscibility gap

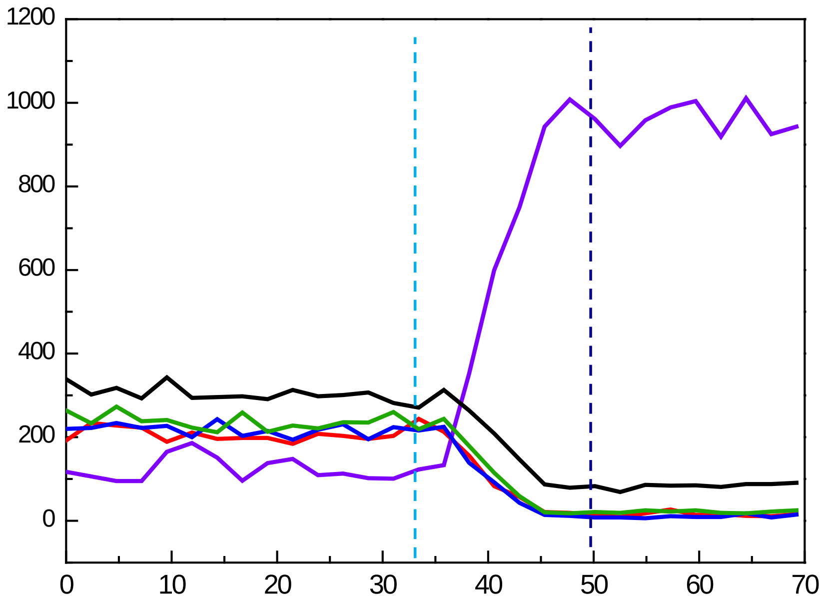


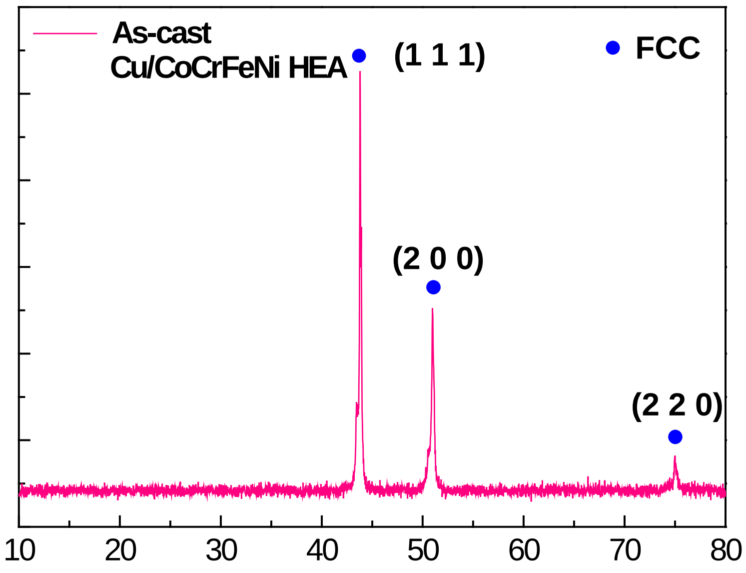
Microstructure of as-cast CoCrFeNiCu HEA



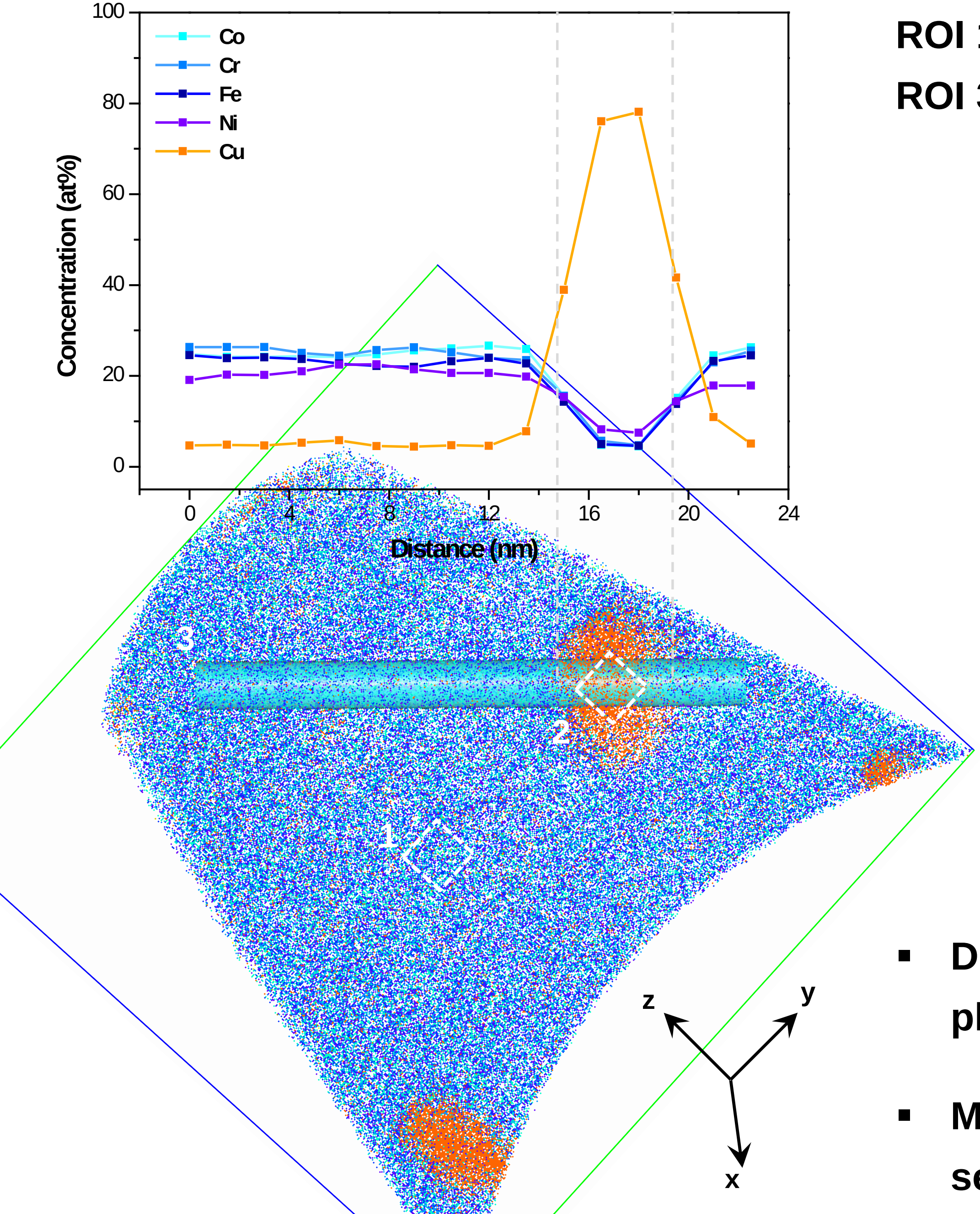








Compositional analysis of as-cast CoCrFeNi/Cu HEA (dendrite)



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

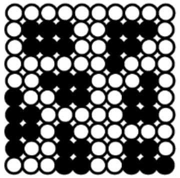
2	at%
Co	0.33
Cr	0.46
Fe	0.39
Ni	5.00
Cu	93.56

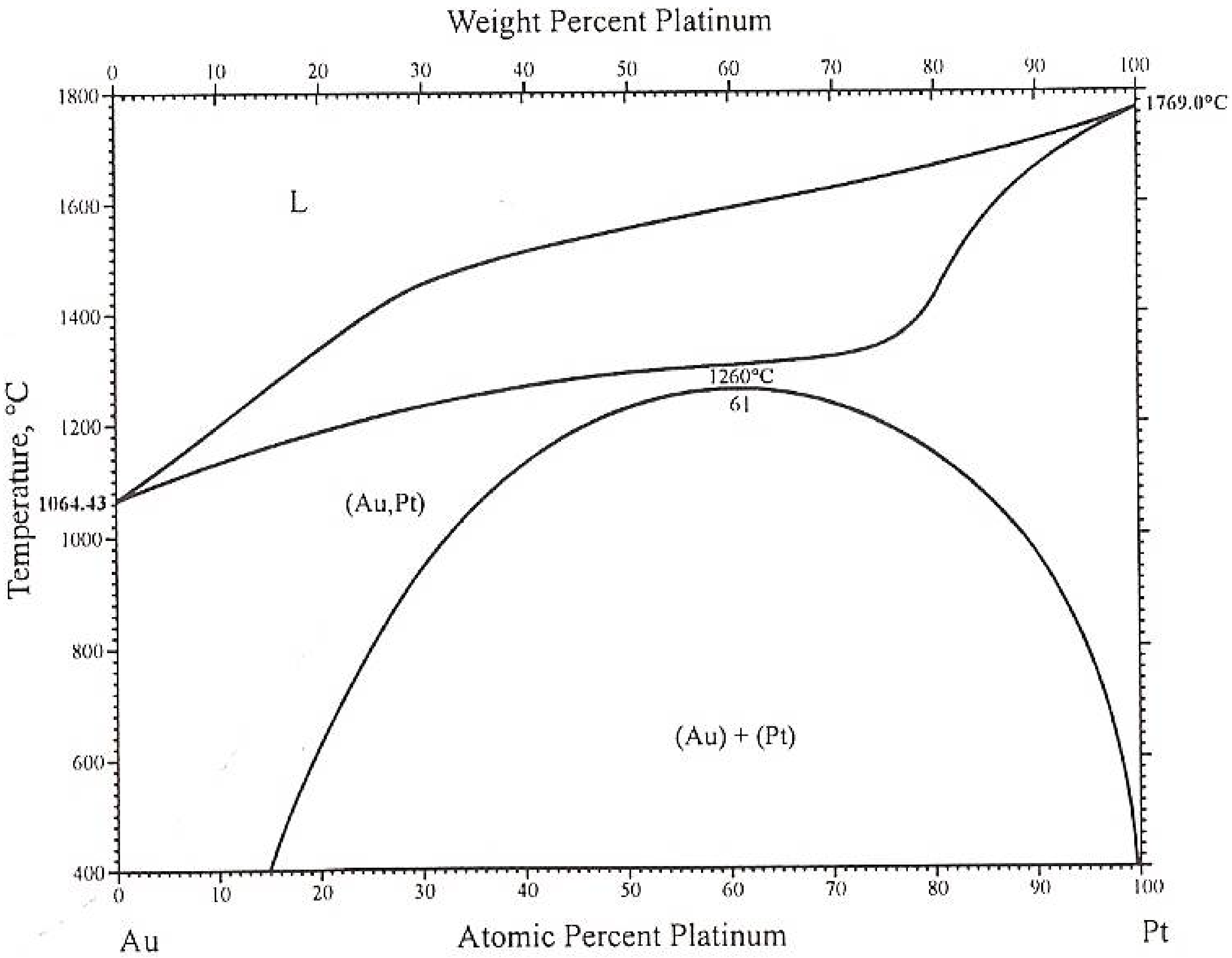
3-1’	at%
Co	25.29
Cr	25.63
Fe	23.63
Ni	20.66
Cu	4.42

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

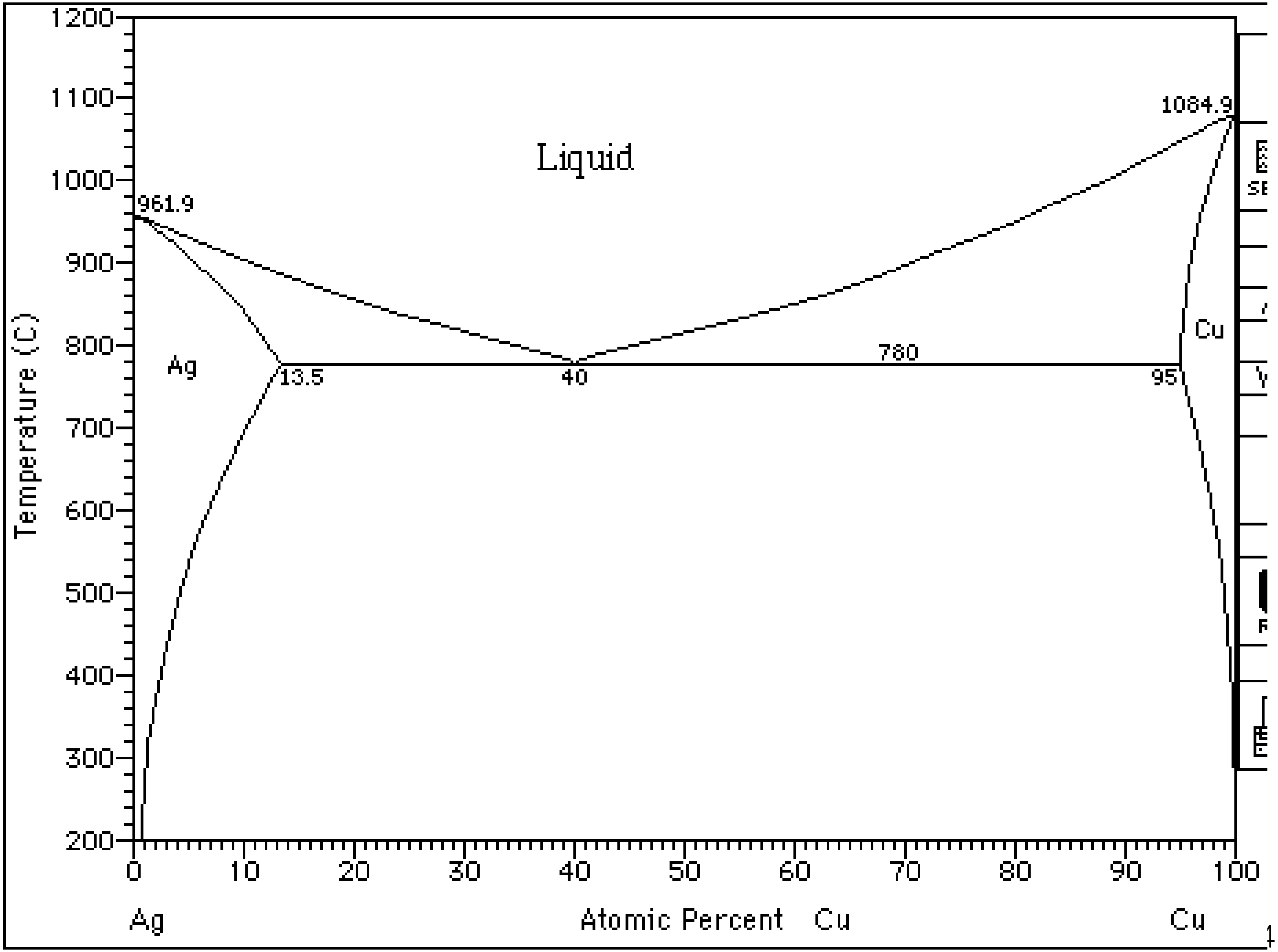
- Dendrite 는 matrix (4.74 at%Cu) 와 2nd phase (93.56 at%Cu)로 구성됨
- Matrix 와 2nd phase 계면에서의 segregation 없음

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

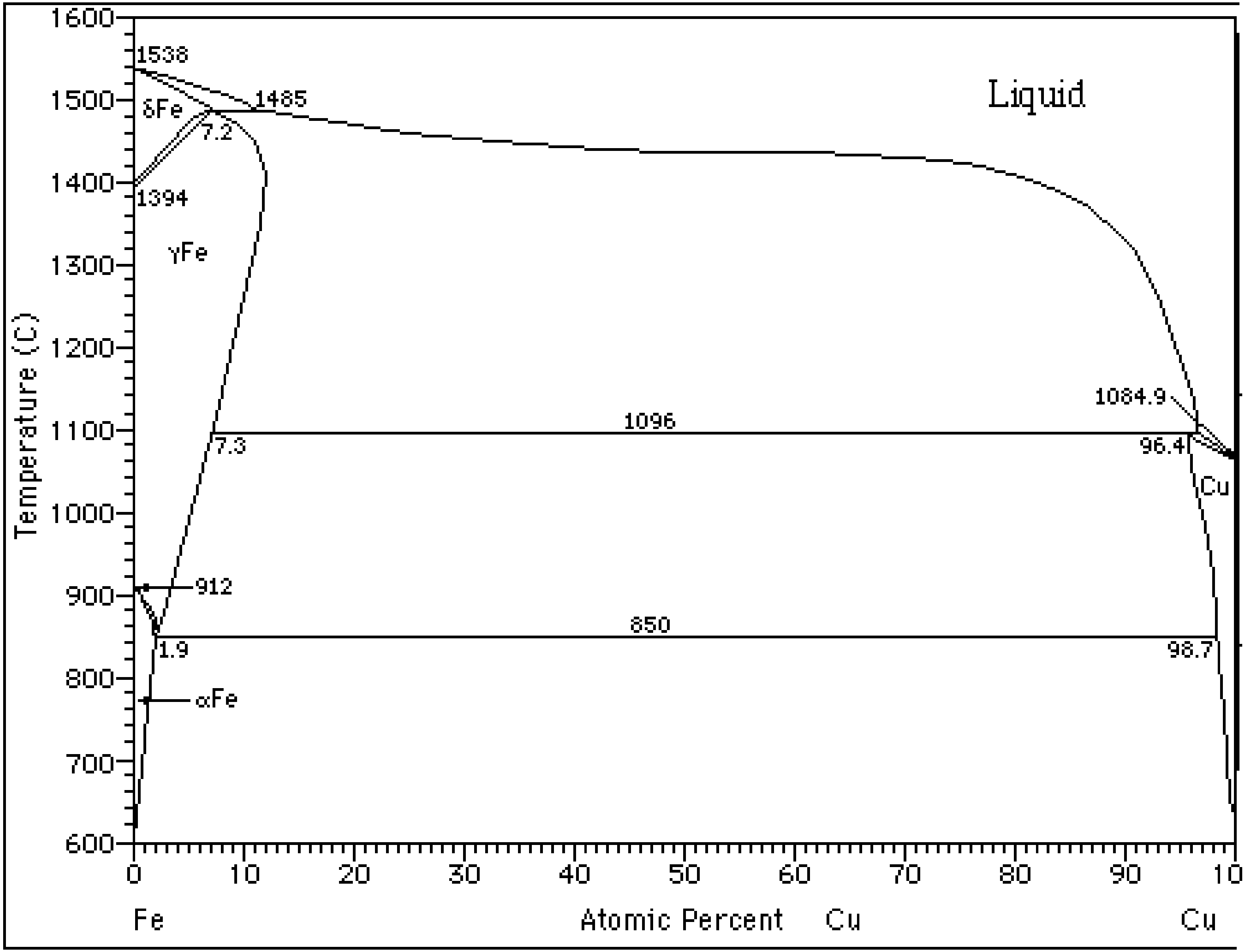


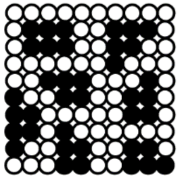


$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol

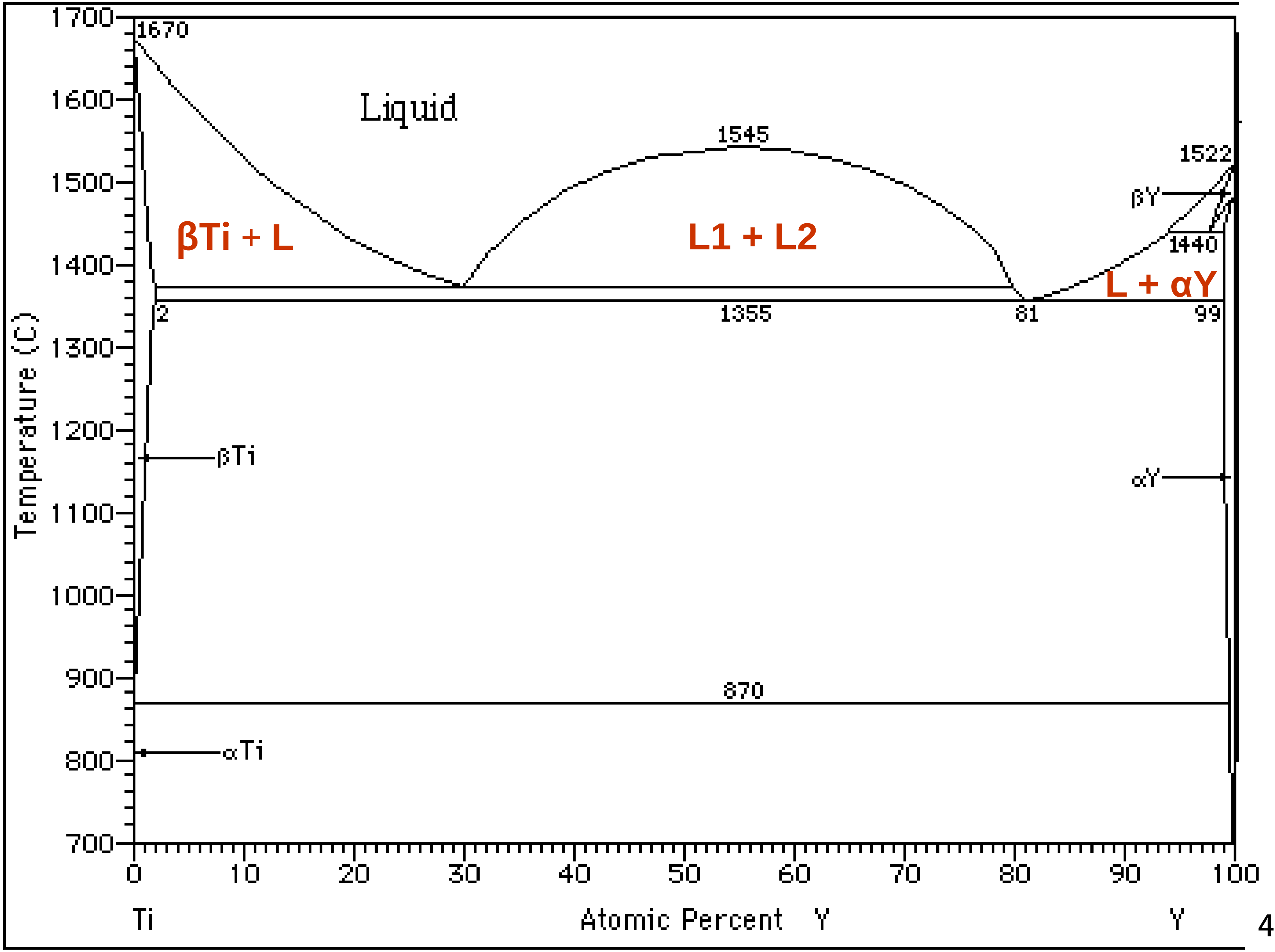


$\varepsilon >> 0, \ \Delta H_{mix} >> 0 \ / \Delta H_{mix} \sim +60$ kJ/mol





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

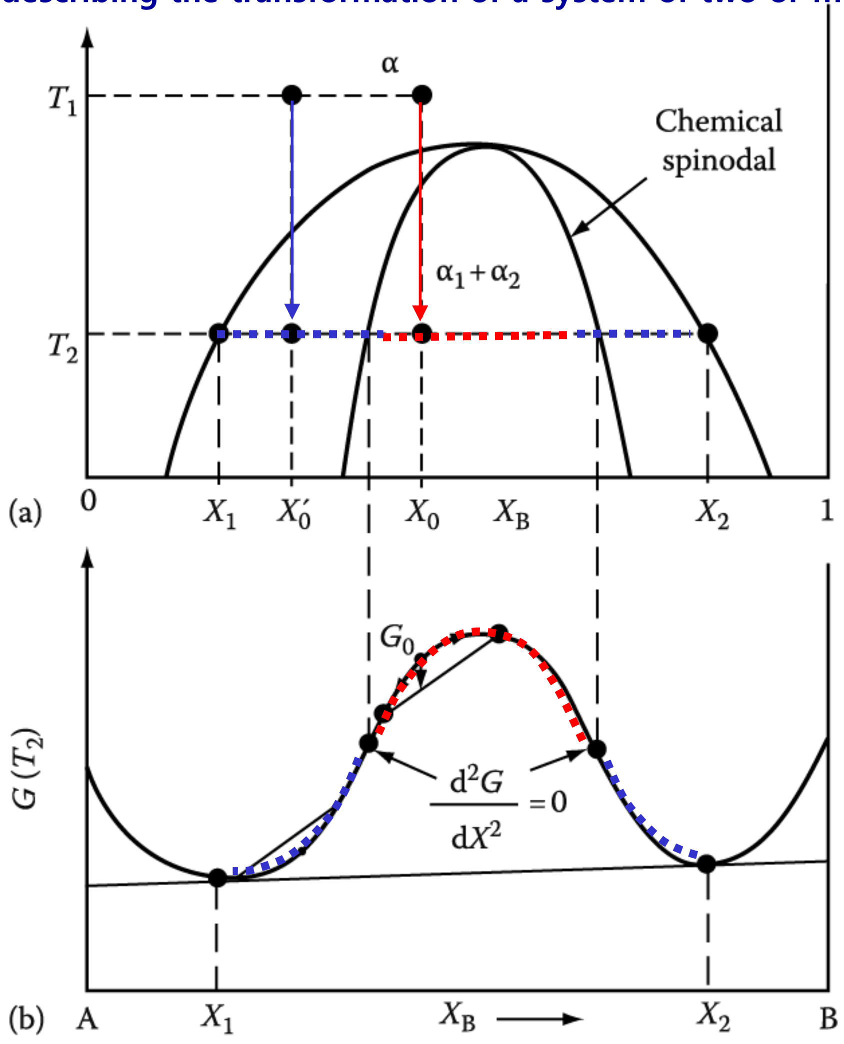


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

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

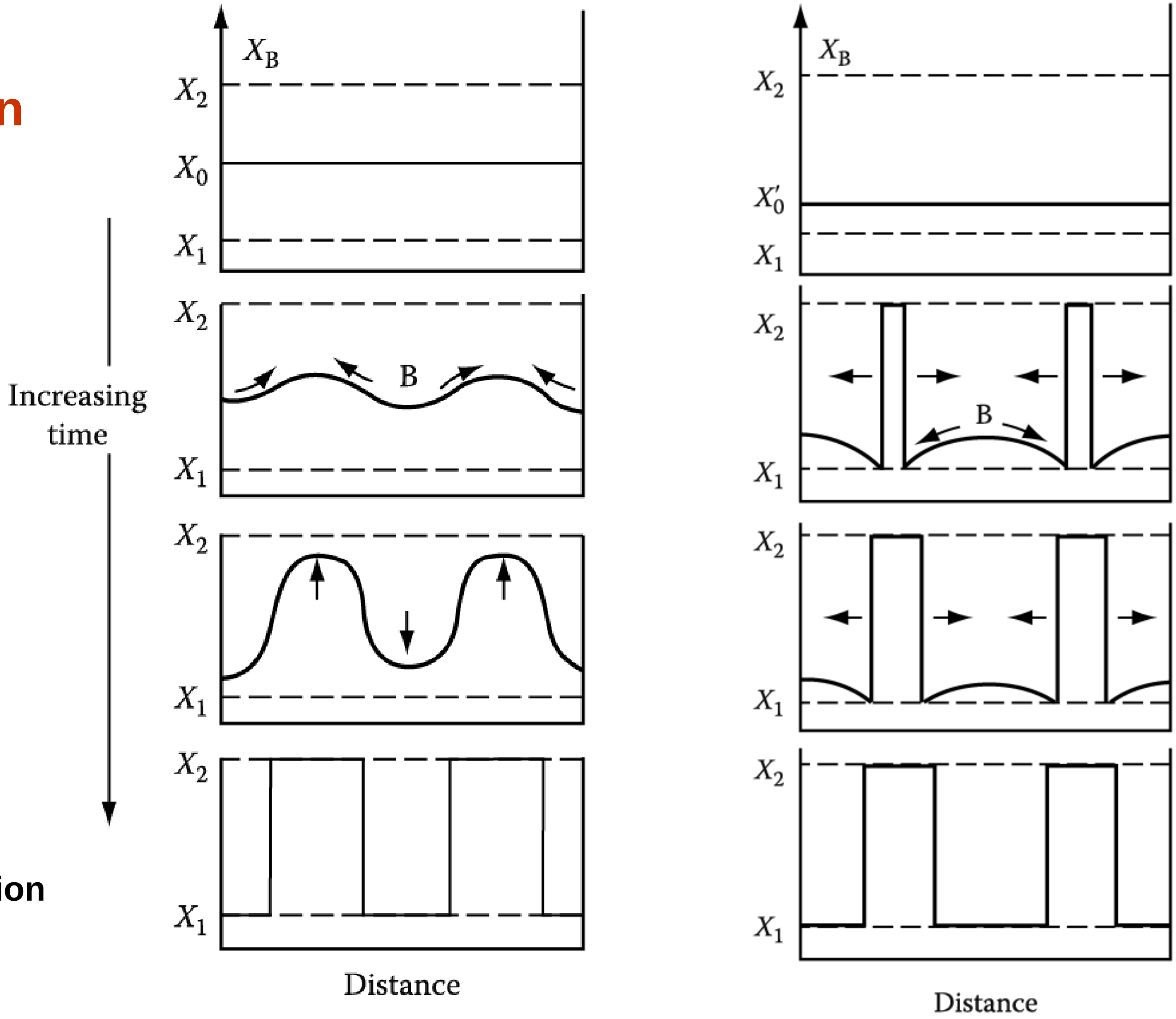
: "down-hill diffusion"

a) Composition fluctuations within the spinodal

b) Normal down-hill diffusion outside the spinodal

up-hill diffusion

down-hill diffusion



interdiffusion coefficient
D<0

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**

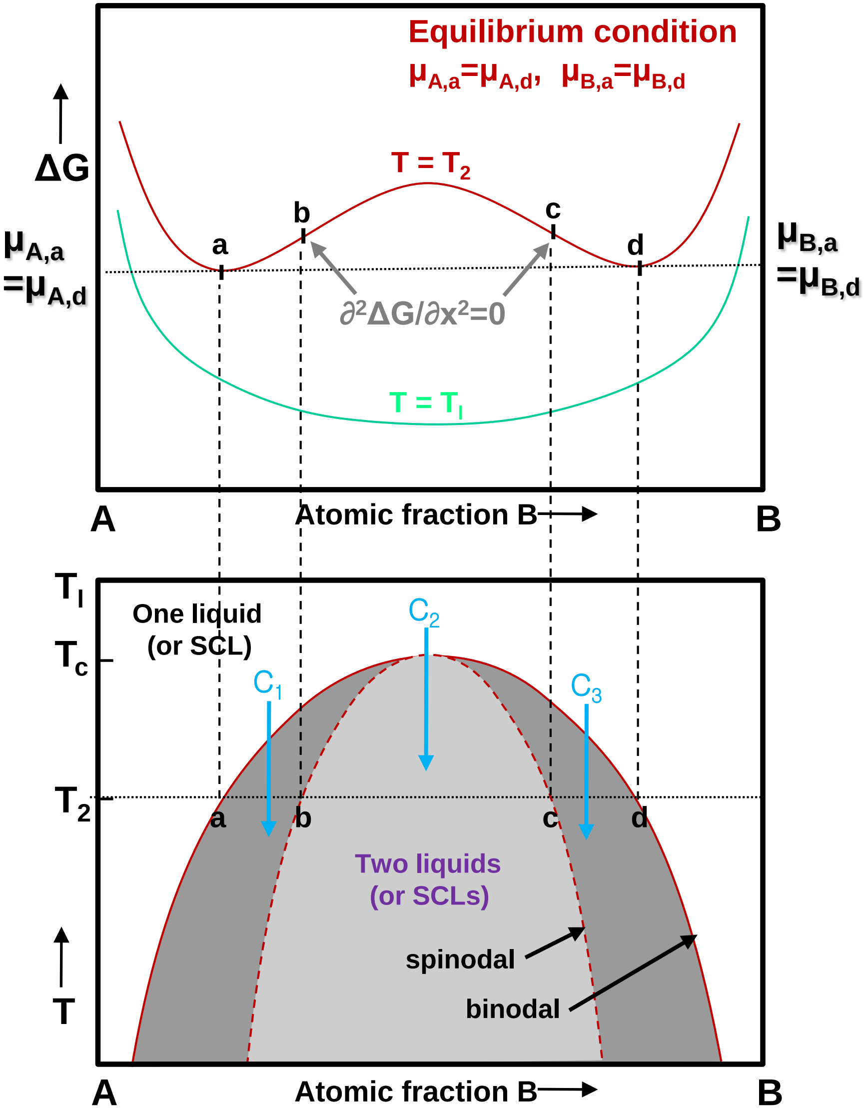
$\Delta H_{mix} \gg 0$ between A & B

⬇

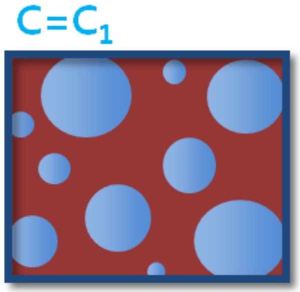
creates (meta)stable miscibility gap in limited composition range

⬇

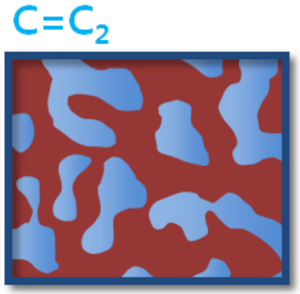
Phase separation to A-rich & B-rich phase



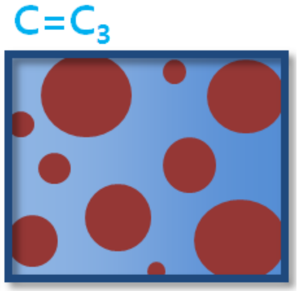
- **Different two-phase structure by initial composition before phase separation**



A-rich matrix B-rich droplet



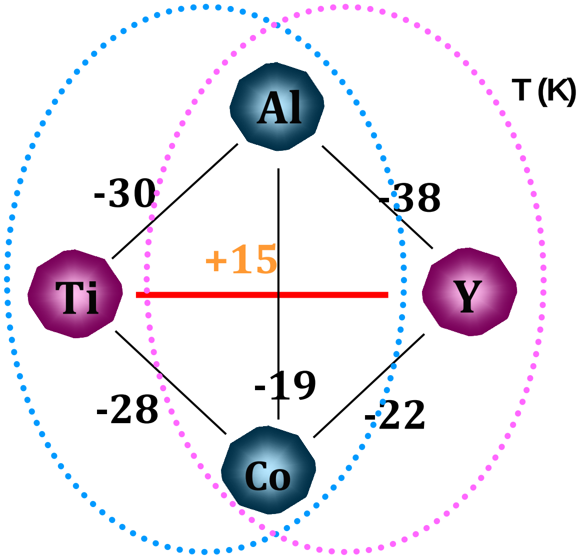
Interconnected structure

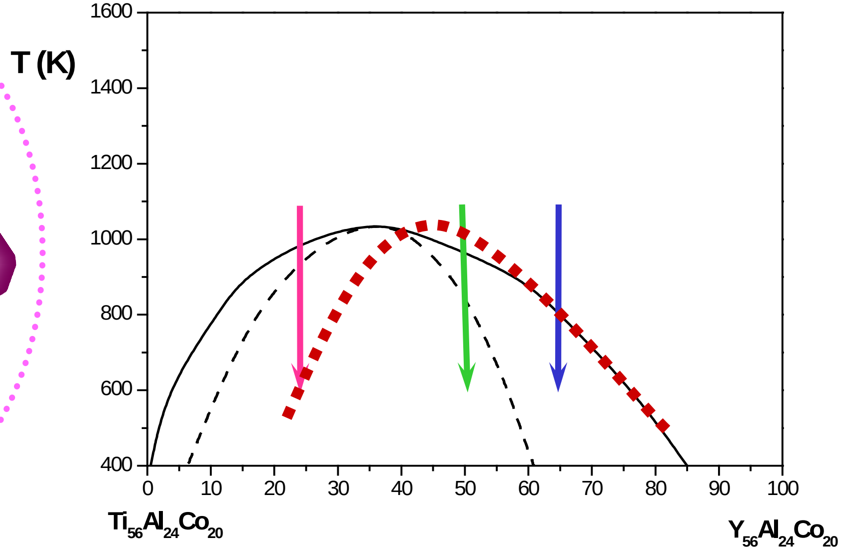


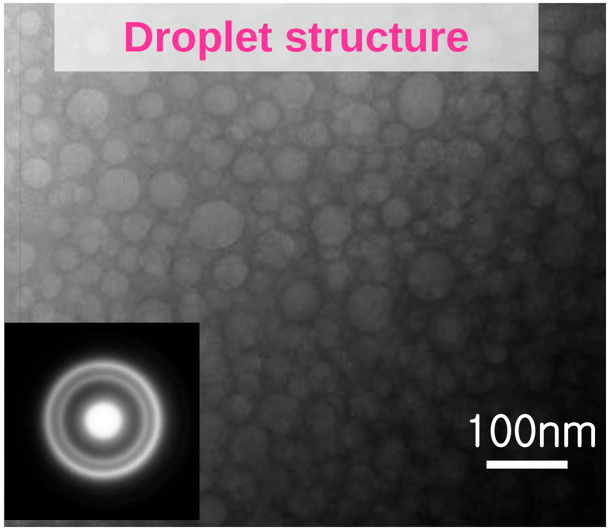
B-rich matrix A-rich droplet

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

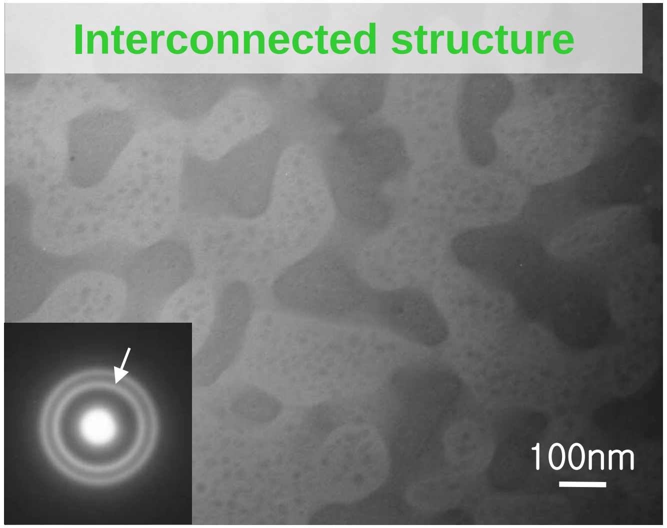
* Ti-Y-Al-Co system



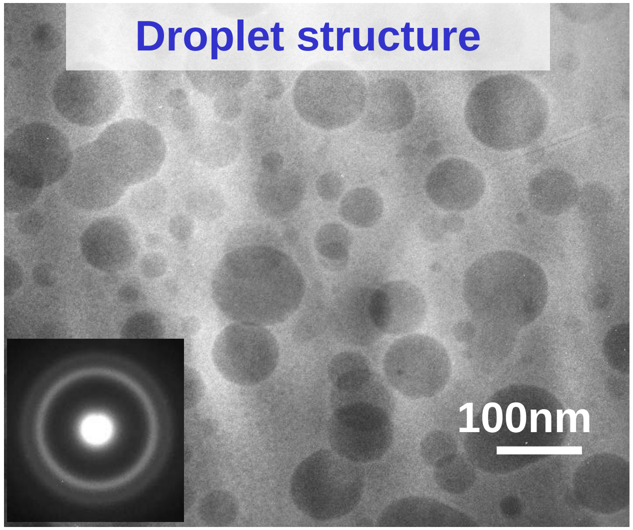




$(Y_{56}Al_{24}Co_{20})_{25}(Ti_{56}Al_{24}Co_{20})_{75}$



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



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

* La-Zr-Al-Cu-Ni system

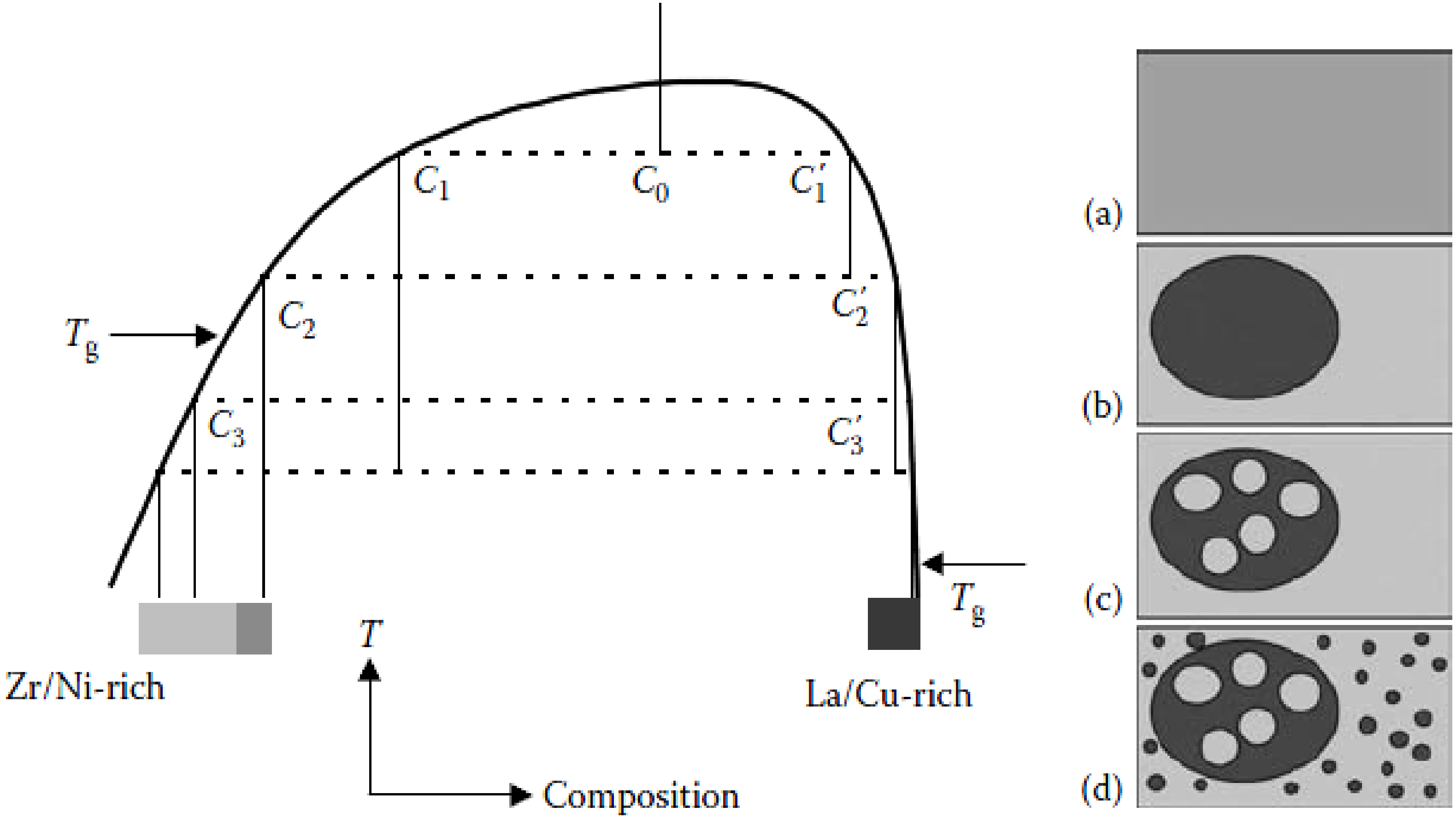
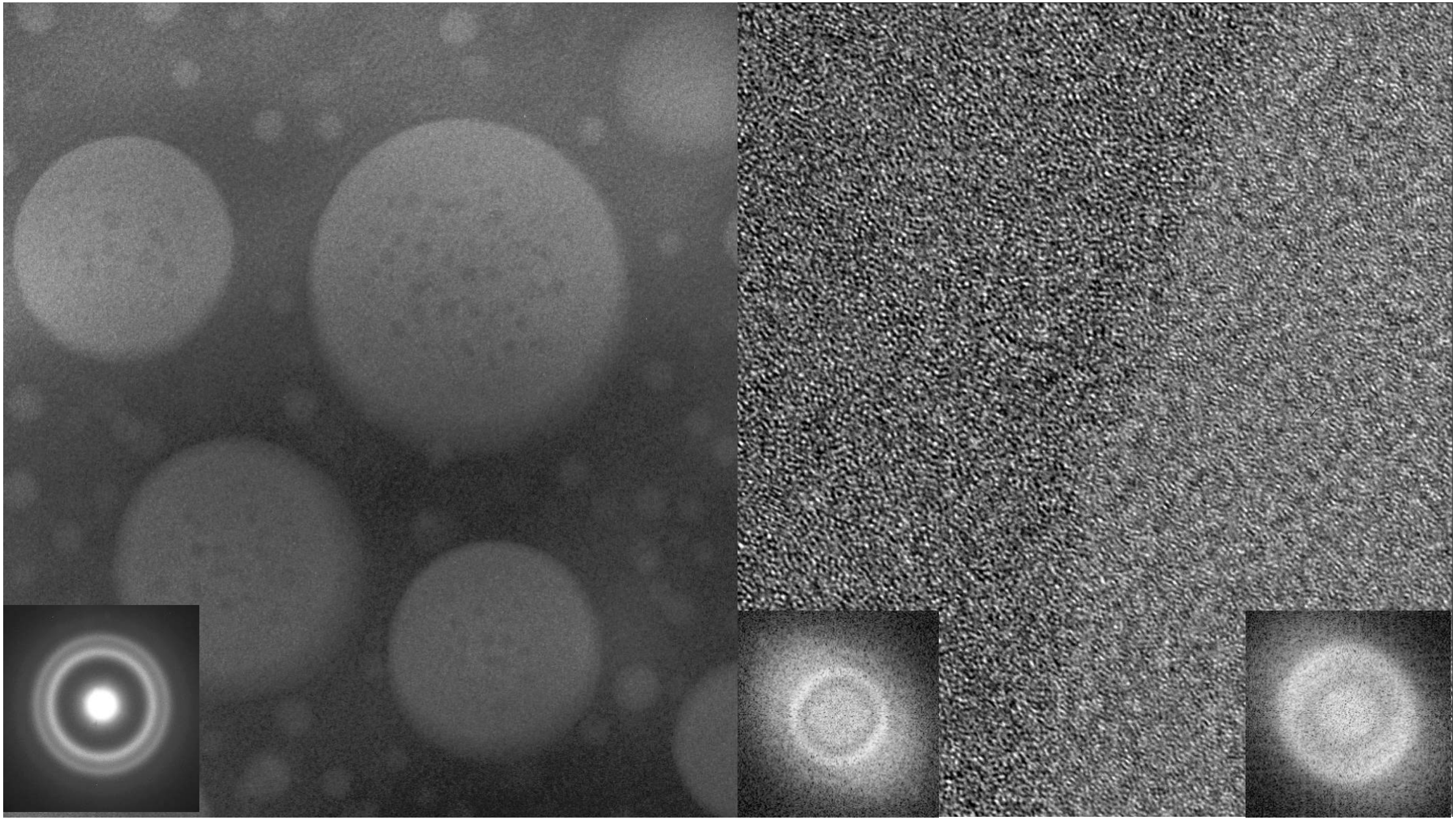


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta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

Phase separation in metallic glasses



Q10: Microstructure determining parameters of phase separation in metallic glasses

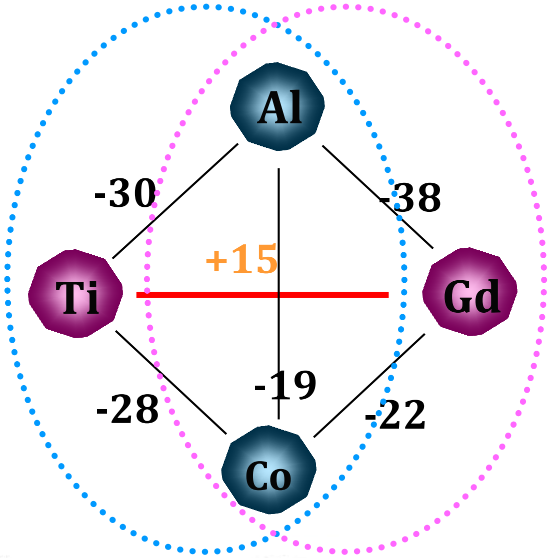
(a) Composition

(b) Critical temperature, T_c

(c) Asymmetry of the spinodal curve/decomposition range

(d) Glass-forming ability of the separated liquid

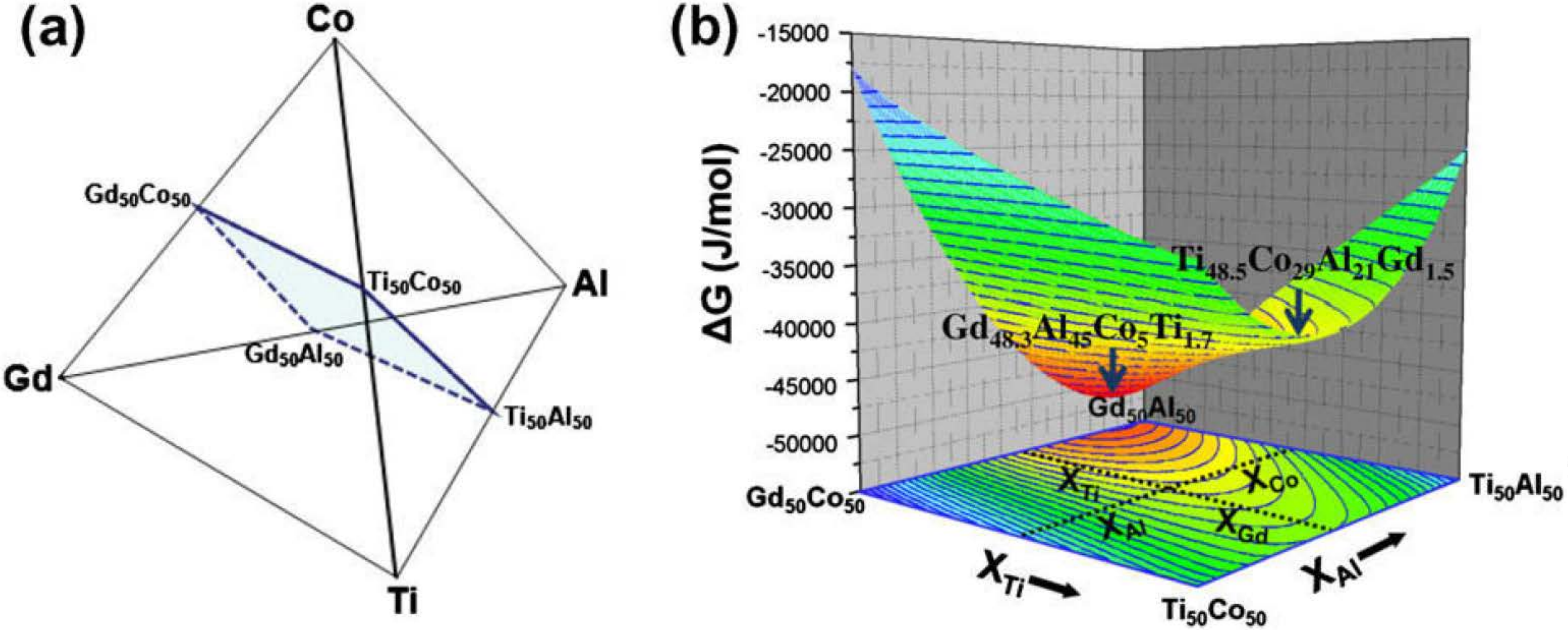
Synthesis of metallic glass composites using phase separation phenomenon



Possibility of two phase !!!

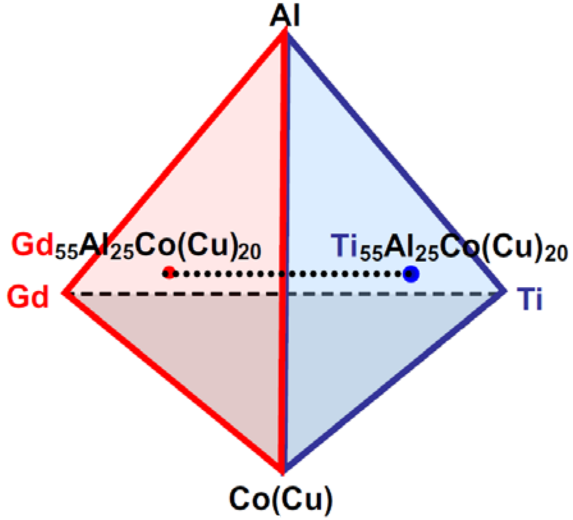
→ **Ti-Al-Co, Gd-Al-Co**

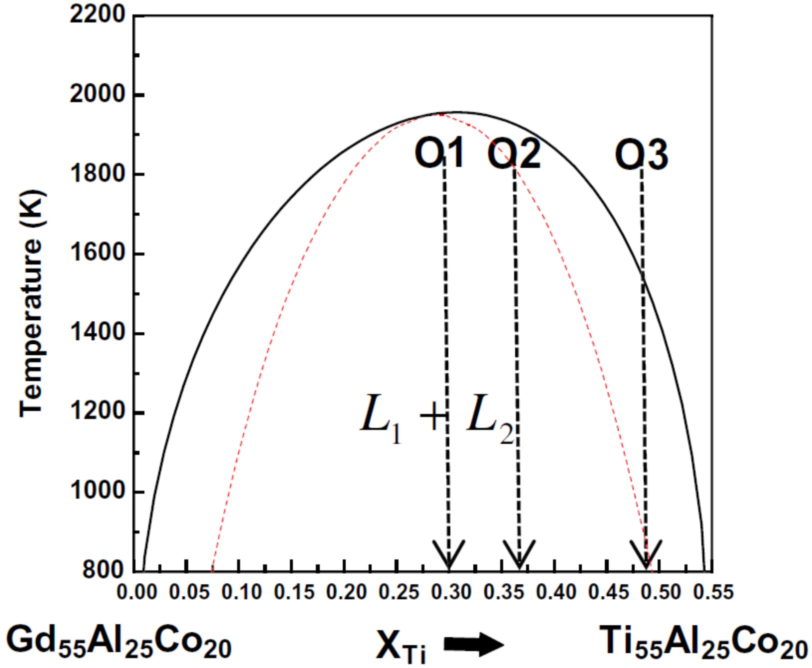
(a) Composition section selected by rectangular plane intersection in quaternary Gd–Ti–Al–Co composition tetrahedron. (b) Gibbs free energy surface of liquid phase at 1000 K for the composition section given in (a). This Gibbs free energy surface shows two minima (arrows), implying that the phase separation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

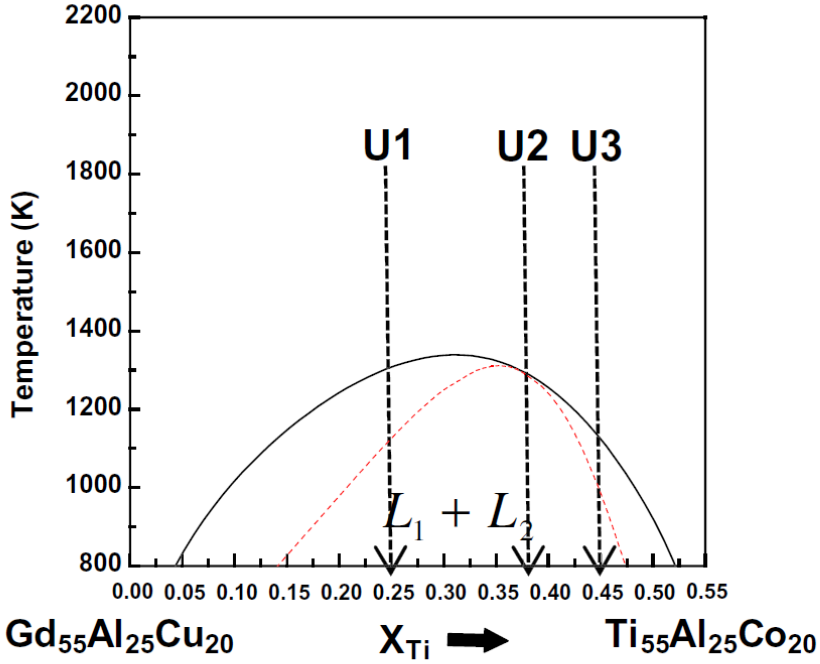


(a) Composition

Thermodynamic calculation using CALPHAD

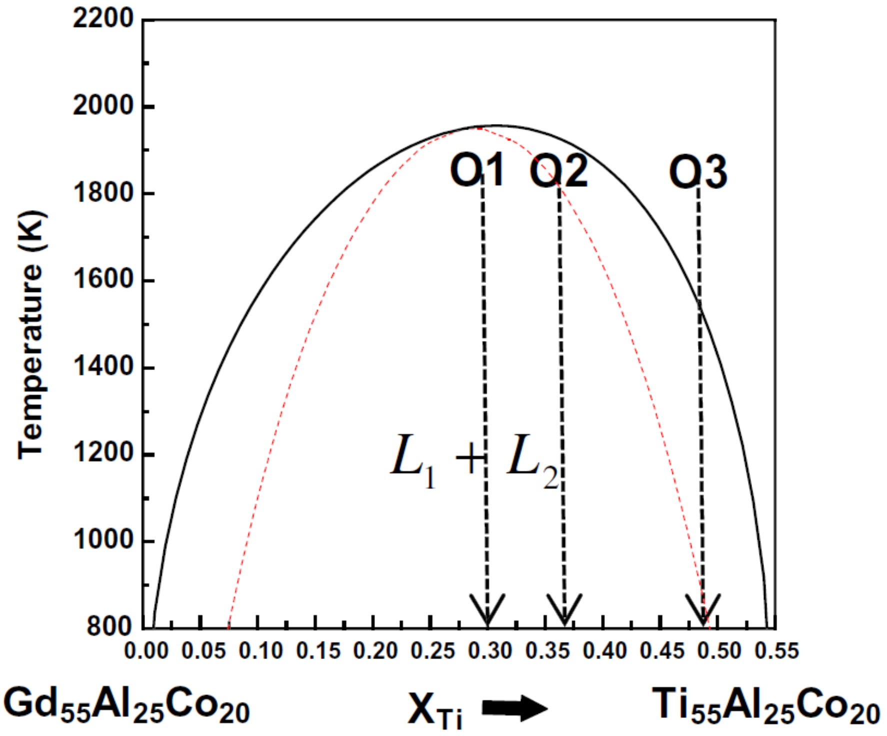


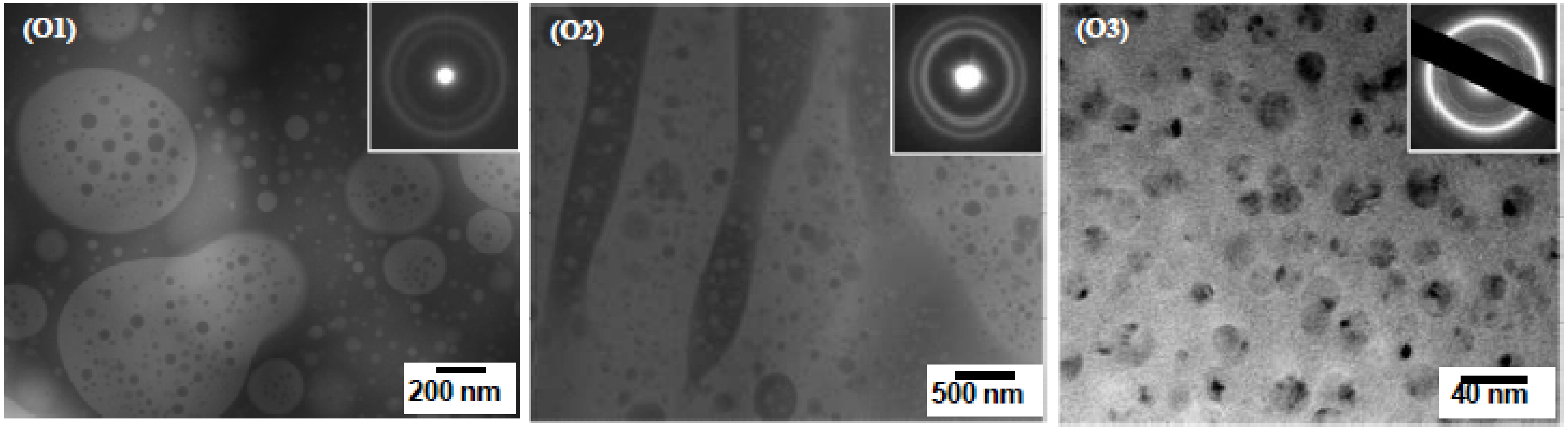




(a) Composition

Microstructure evolution (GdTiAlCo)

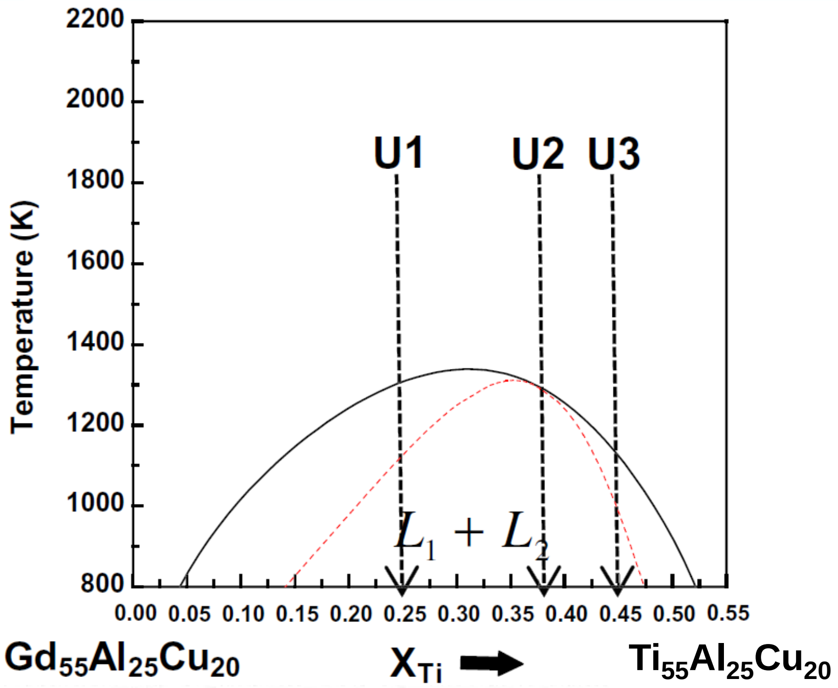


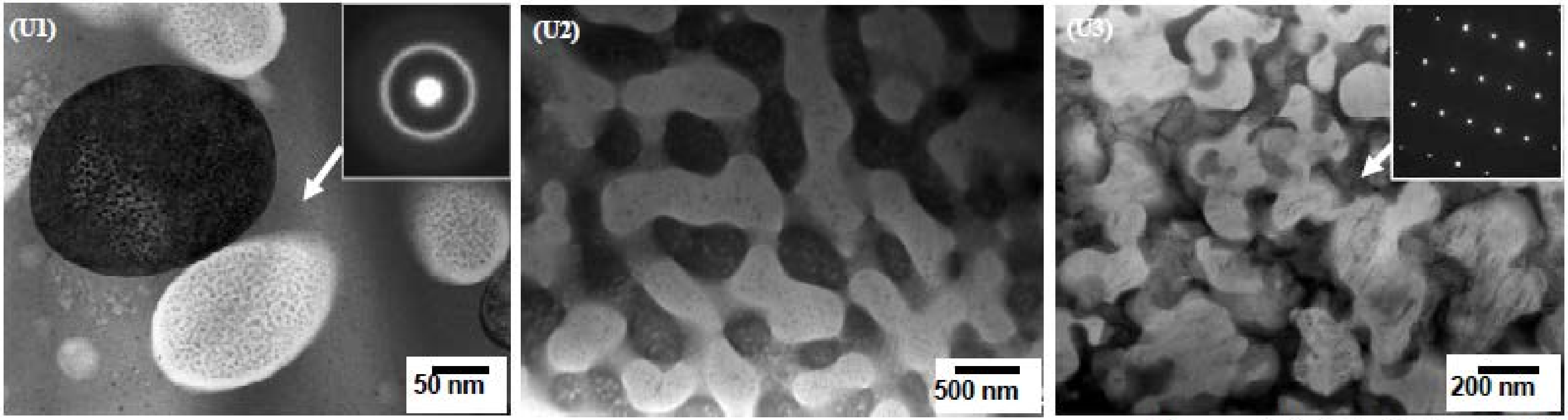


Chang et al., Acta Mater (2010)

(a) Composition

Microstructure evolution (GdTiAlCu)

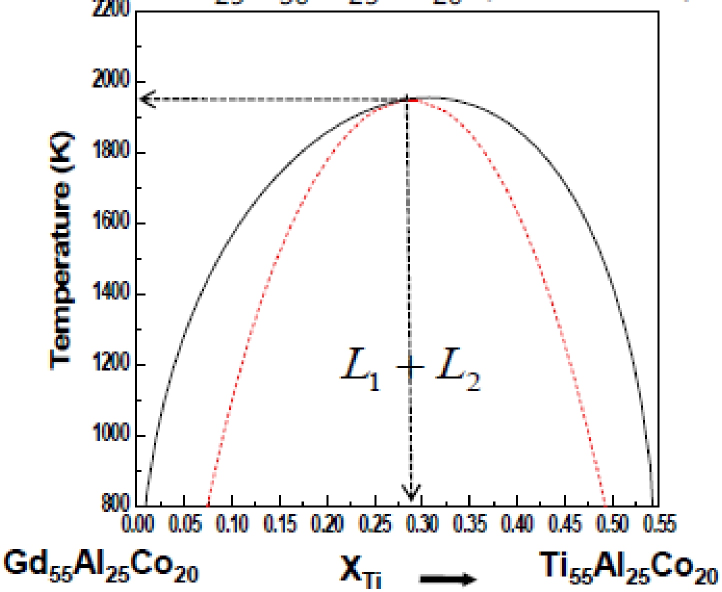




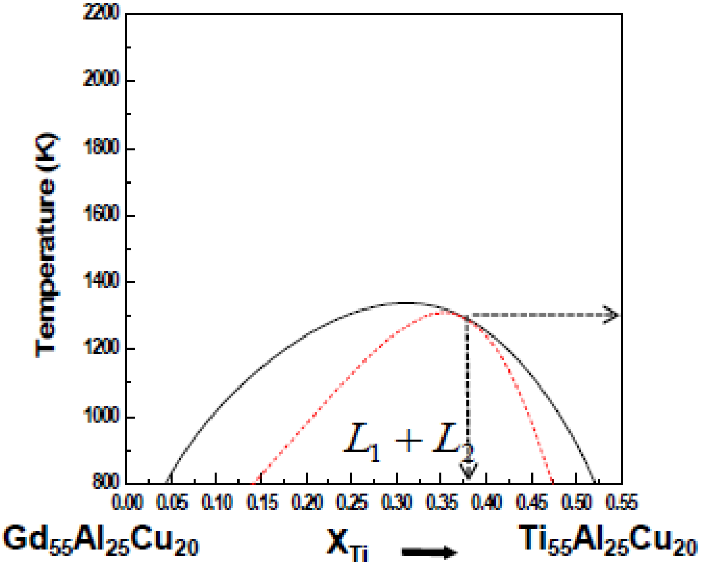
Chang et al., Acta Mater (2010)

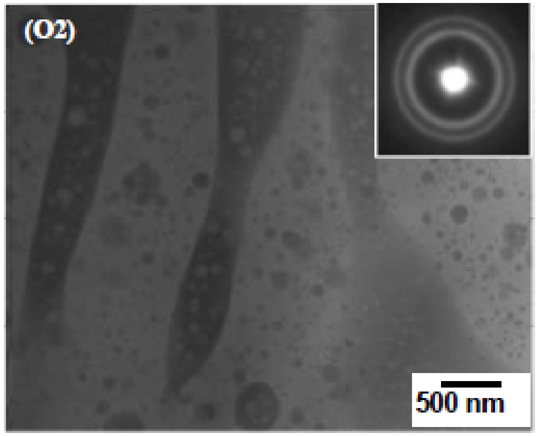
(b) Critical temperature

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**)

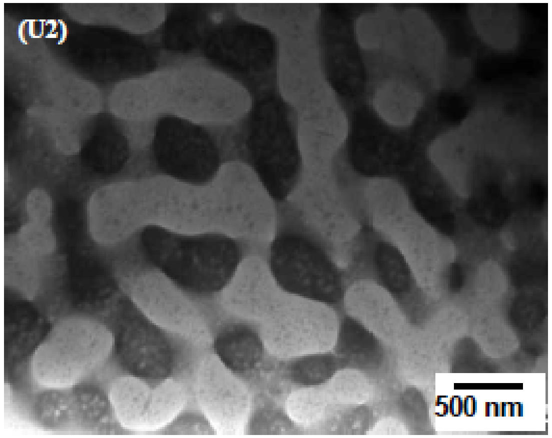




Scale of interconnected structure

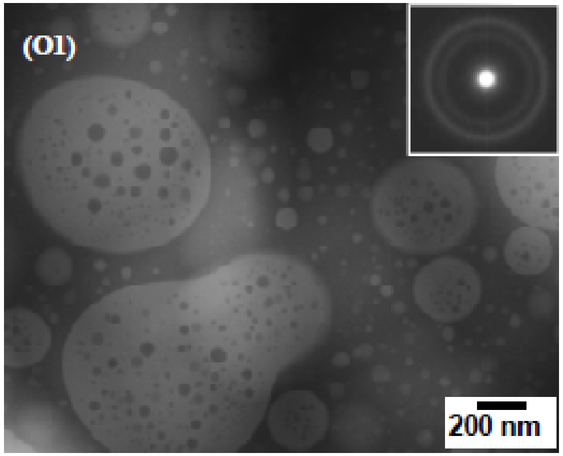
←Several um

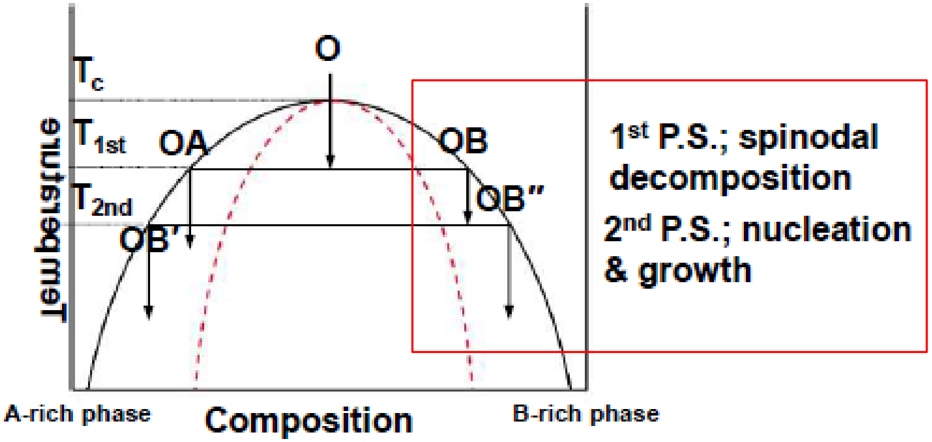
200~300 nm→



(c) Asymmetry of spinodal curve / Decomposition range

❖ Symmetric spinodal curve / smaller decomposition range

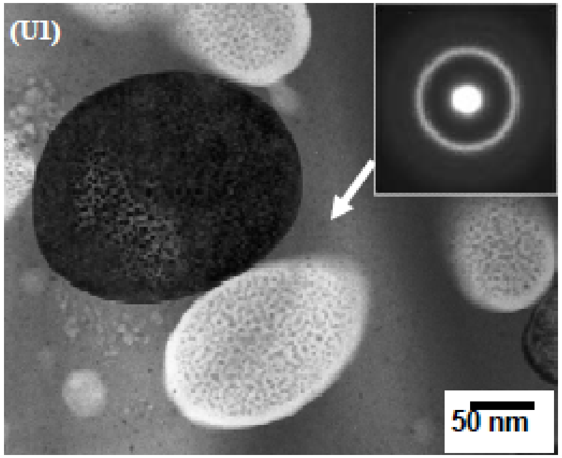


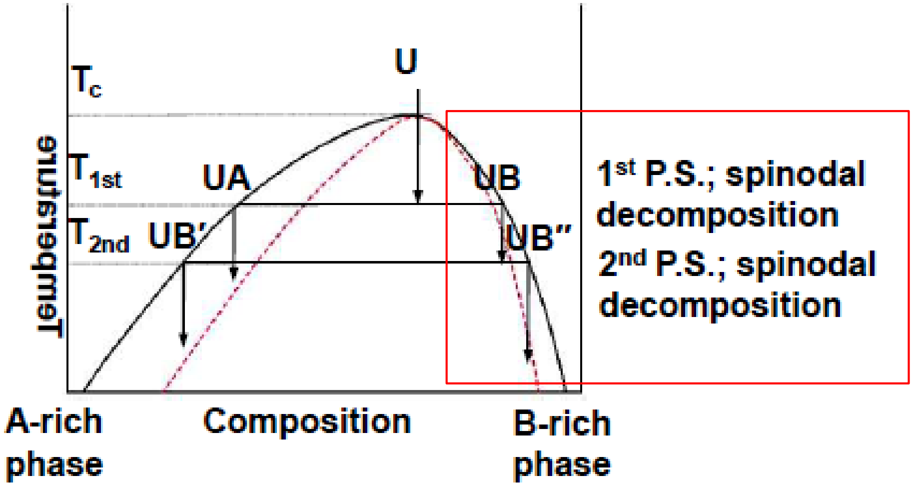


1st P.S.; spinodal decomposition

2nd P.S.; nucleation & growth

❖ Asymmetric spinodal curve / larger decomposition range

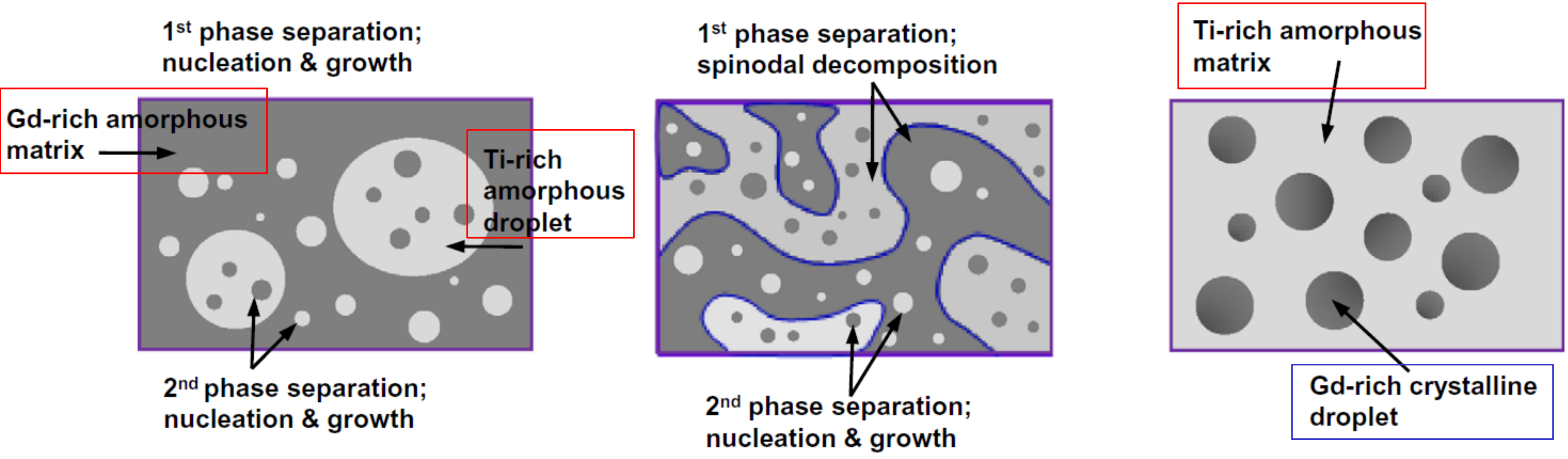




1st P.S.; spinodal decomposition

2nd P.S.; spinodal decomposition

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



1st phase separation; nucleation & growth

Gd-rich amorphous matrix

Ti-rich amorphous droplet

2nd phase separation; nucleation & growth

1st phase separation; spinodal decomposition

2nd phase separation; nucleation & growth

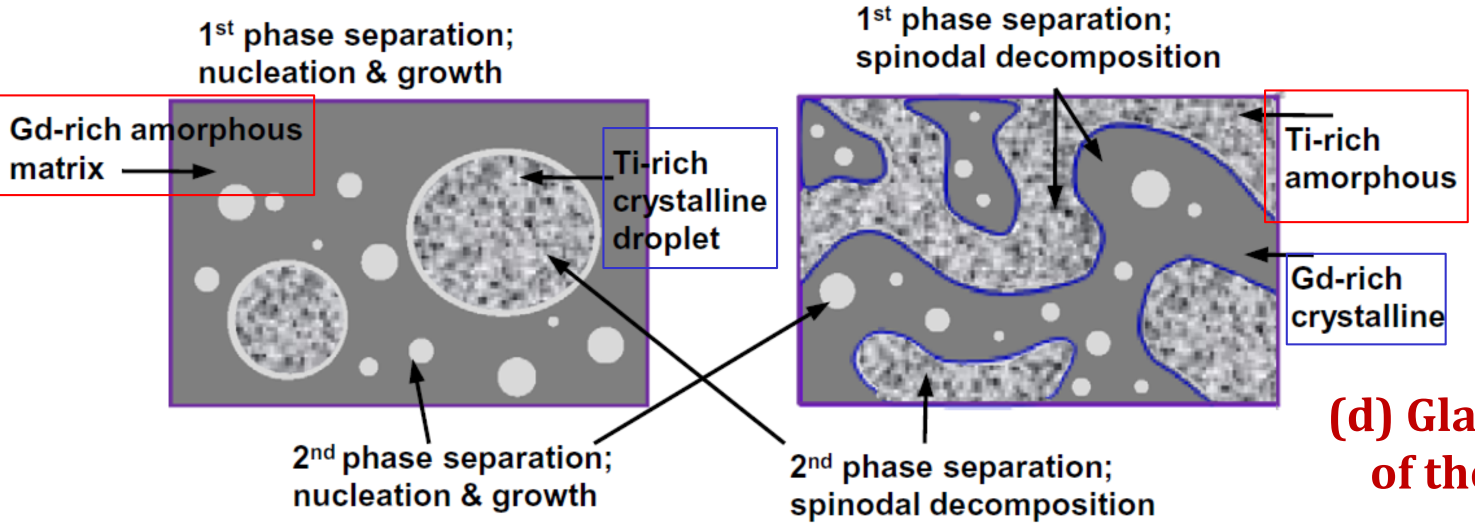
Ti-rich amorphous matrix

Gd-rich crystalline droplet

(a) O1 alloy

(b) O2 alloy

(c) O3 alloy



1st phase separation; nucleation & growth

Gd-rich amorphous matrix

Ti-rich crystalline droplet

2nd phase separation; nucleation & growth

1st phase separation; spinodal decomposition

Ti-rich amorphous

Gd-rich crystalline

2nd phase separation; spinodal decomposition

(d) U1 alloy

(e) U2 alloy

(d) Glass-forming ability of the separated liquid

Contents for today's class

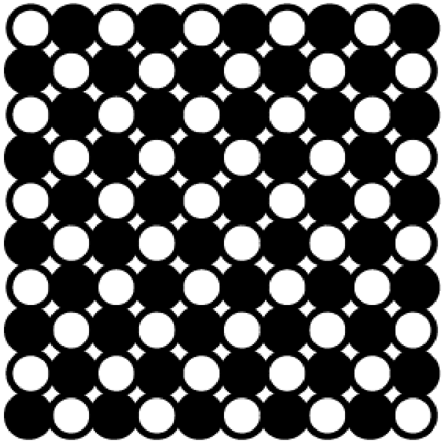
- Binary System mixture/ solution / compound

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

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

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

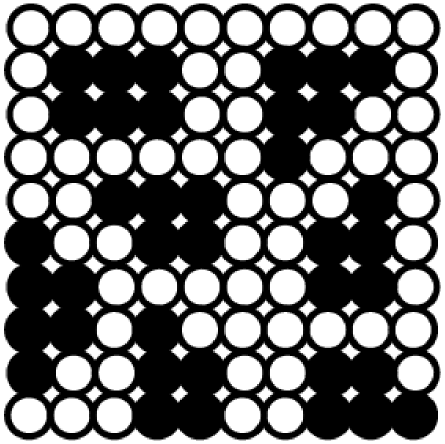
Real solution **Ordered structure**



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

Ordered alloys

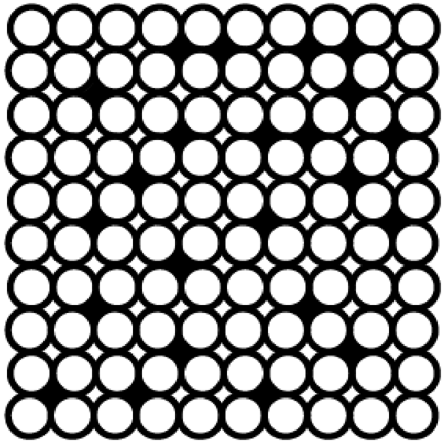
P_{AB} ↑ → Internal E ↓



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

Clustering

P_{AA}, P_{BB} ↑

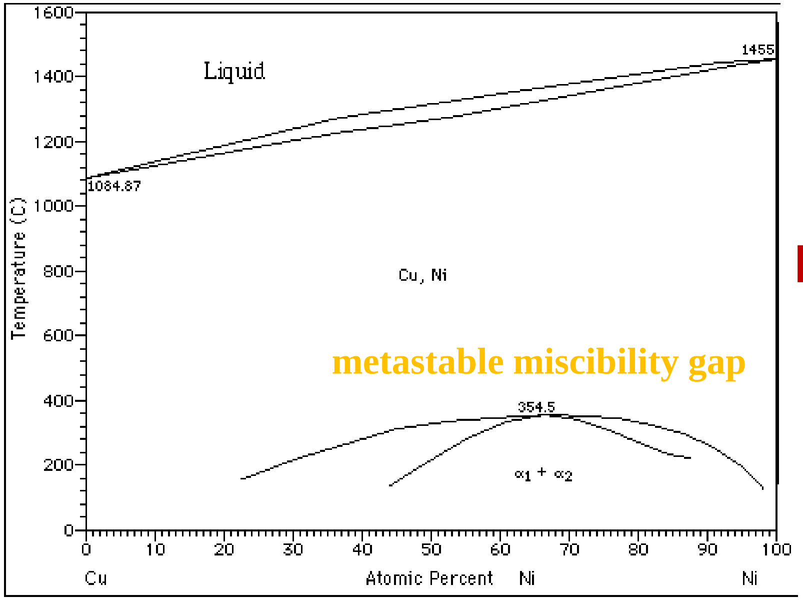


(c) when the size difference is large

strain effect

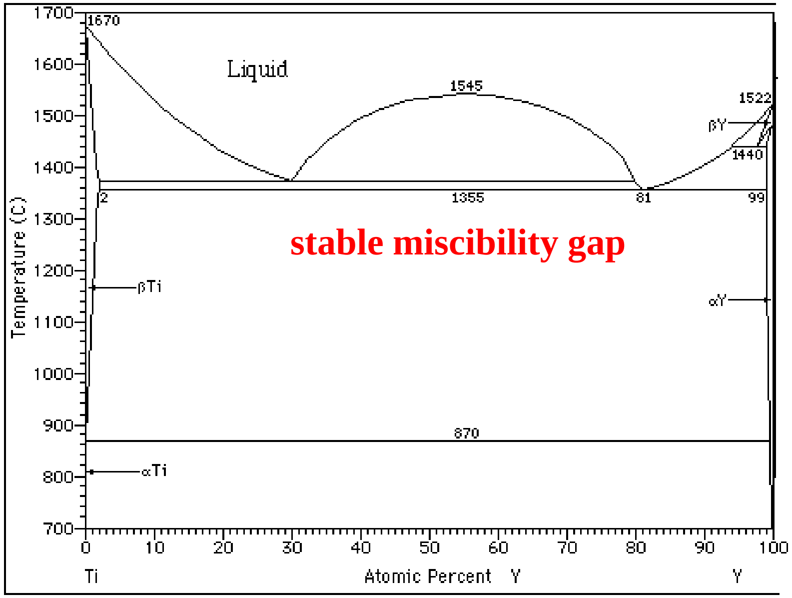
Interstitial solution

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



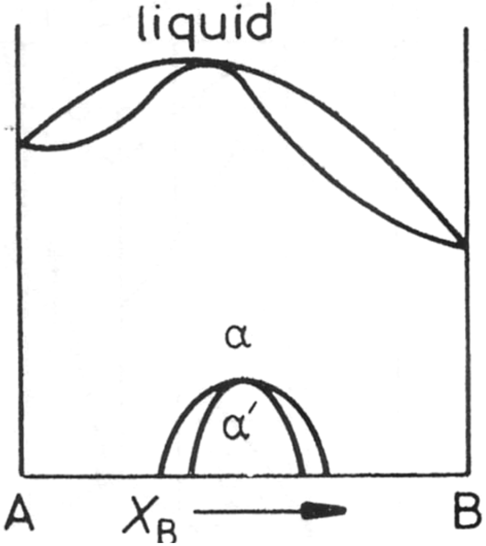
metastable miscibility gap

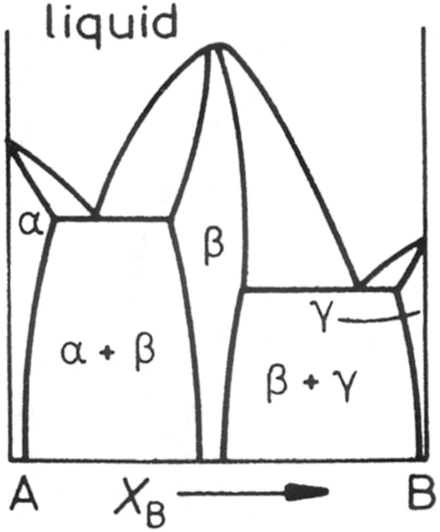
$\Delta H^{S}_{mix} \gg 0$: liquid state phase separation (up to two liquid solutions)



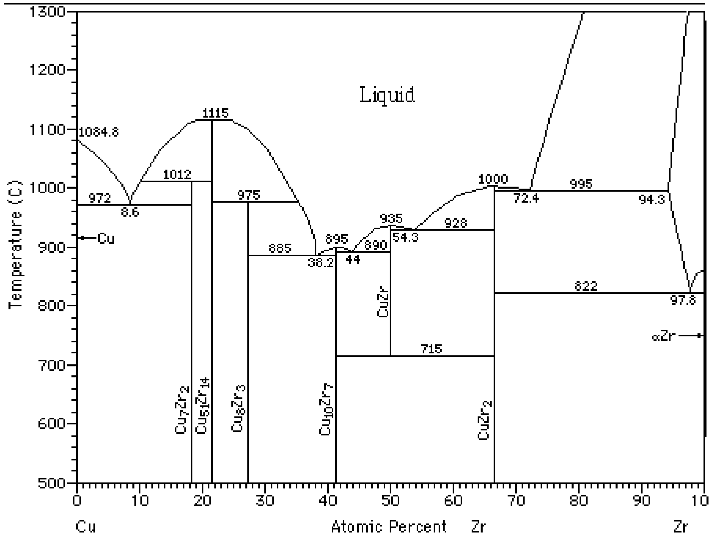
stable miscibility gap

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





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



2021 Spring

“Phase Equilibria *in* Materials”

03.18.2021

Eun Soo Park

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

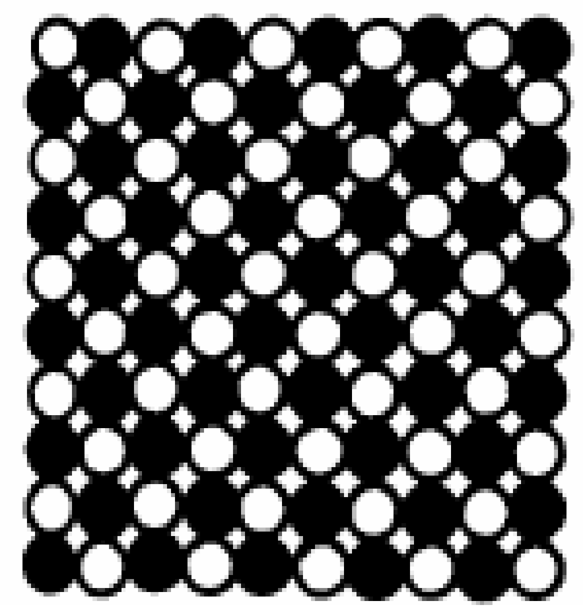
Contents for previous class

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

Ideal or Regular solution : over simplification of reality

Entropy $S = k \ln w$ + $\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$ $\varepsilon \approx 0$

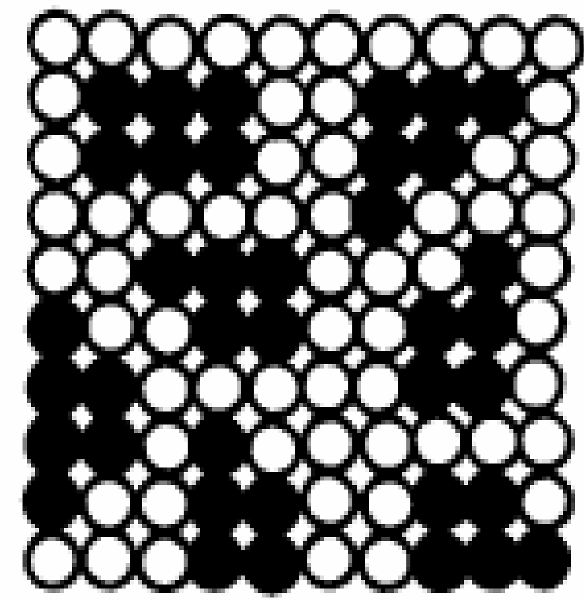
elastic strain



Ordered alloys

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

$P_{AB} \uparrow \longrightarrow$ Internal E $\downarrow$

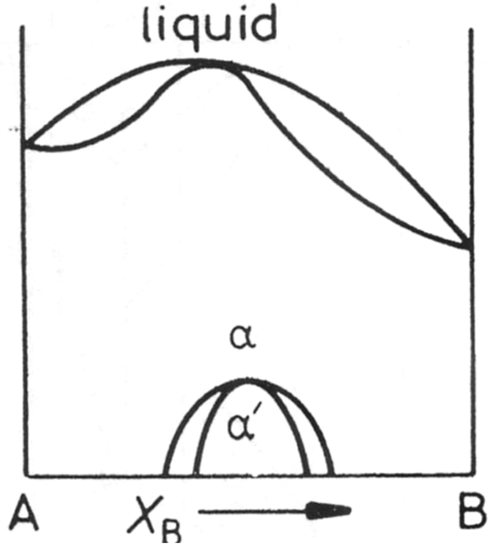


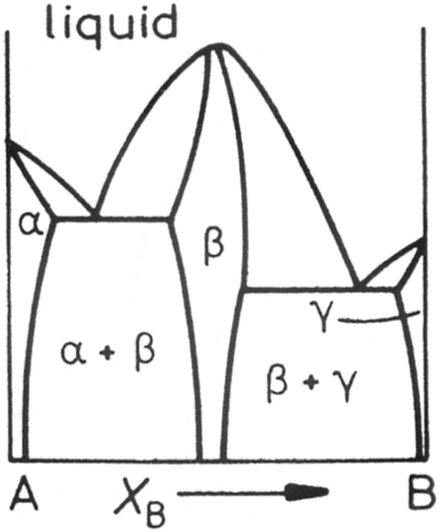
Clustering

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

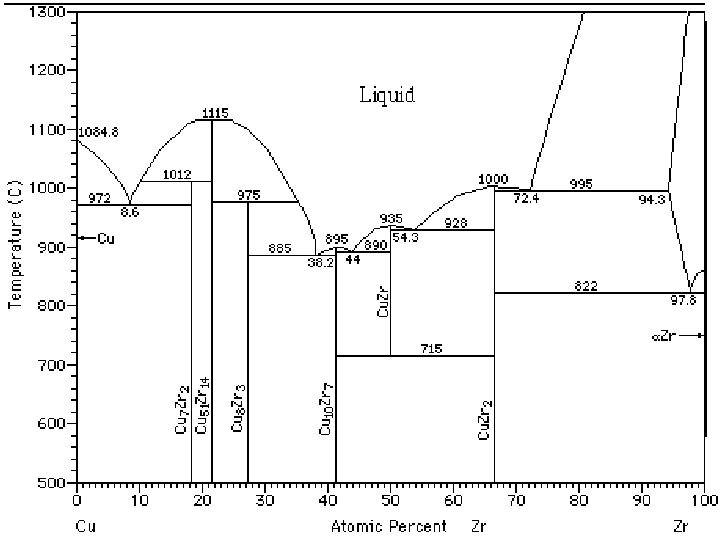
$P_{AA}, P_{BB} \uparrow$

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

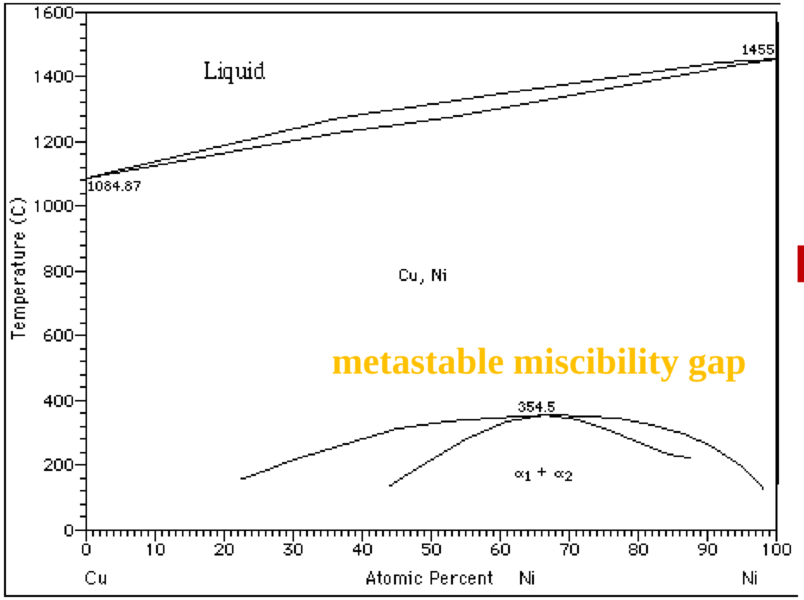




$\Delta H^{S}_{mix} << 0$: Compound : AB, A_2B…

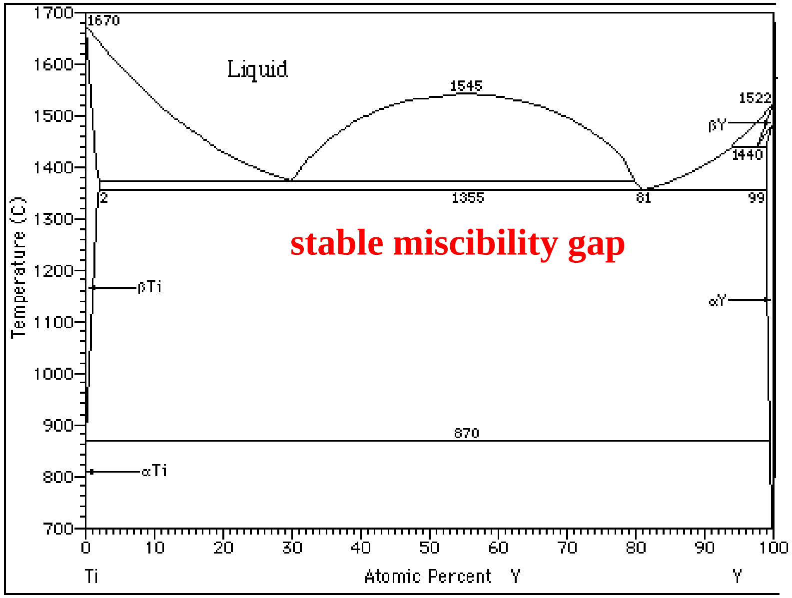


ΔH^{S}_{mix} > 0 : Solid solution → solid state phase separation (two solid solutions)



metastable miscibility gap

ΔH^{S}_{mix} >> 0 : liquid state phase separation (up to two liquid solutions)



stable miscibility gap

Ordered phase: “Long range order (LRO)”

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

*** Solid solution → ordered phase**

→ random mixing

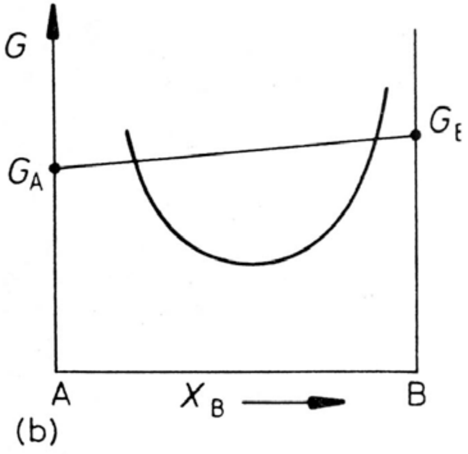
→ entropy ↑

negative enthalpy ↓

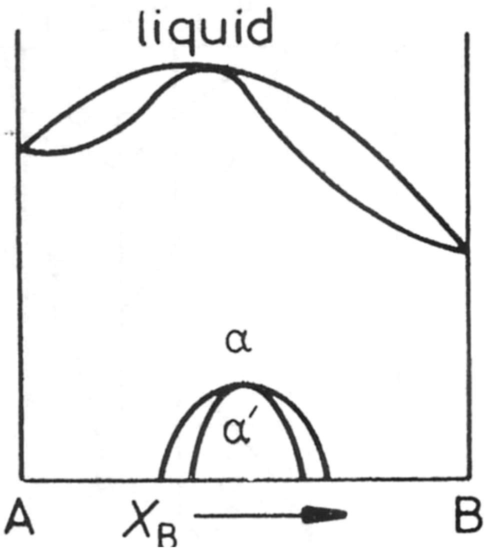
$$\Delta H^{S}_{mix} < 0$$

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 ↓

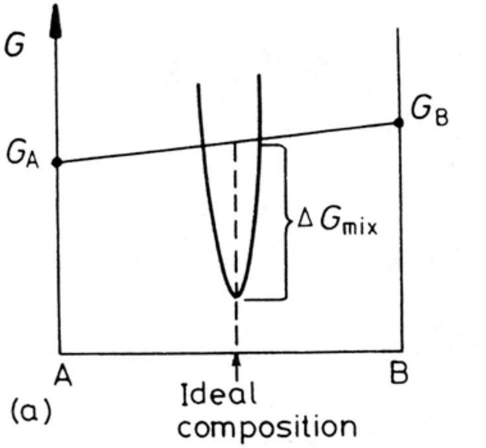
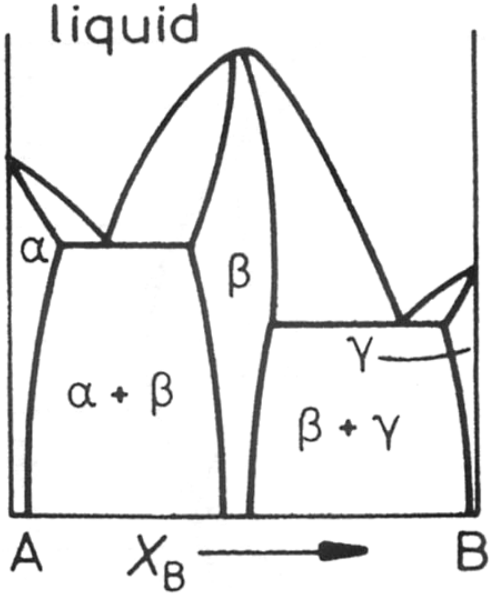
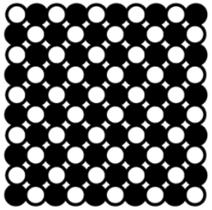


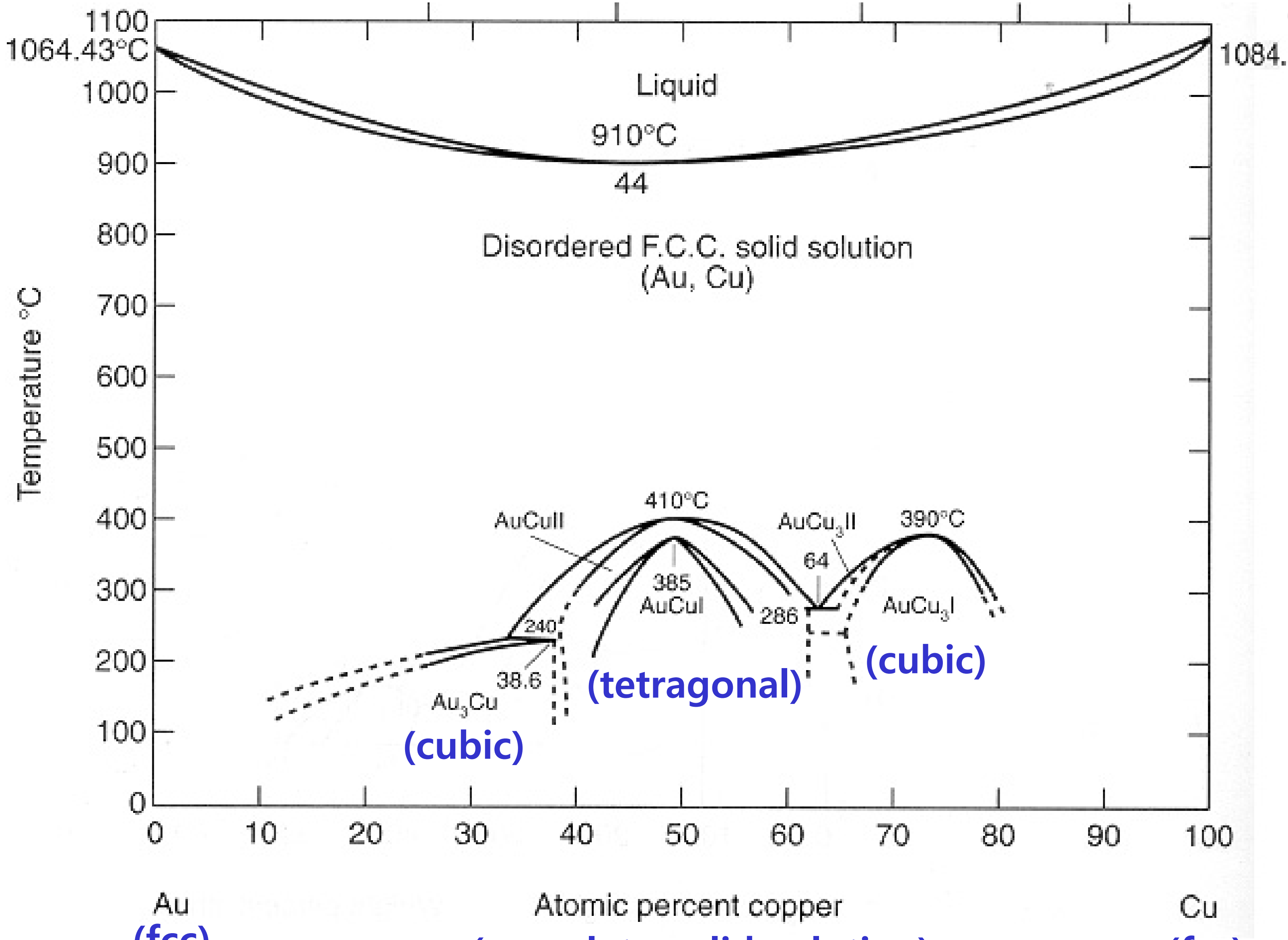
Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



Ordered Phase

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





(cubic)

(tetragonal)

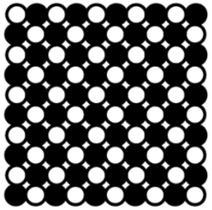
(cubic)

(fcc)

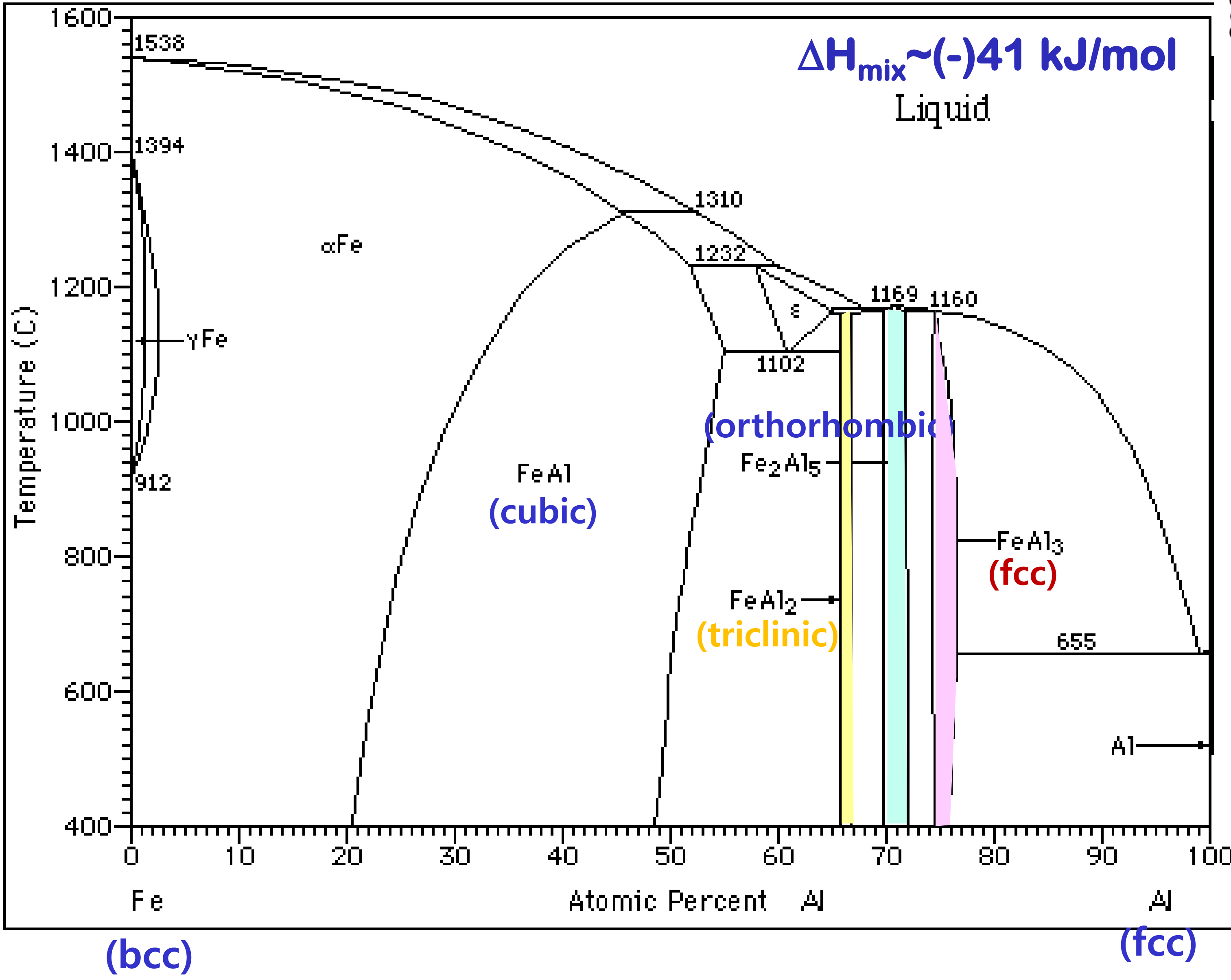
(complete solid solution)

(fcc)

Intermediate Phase



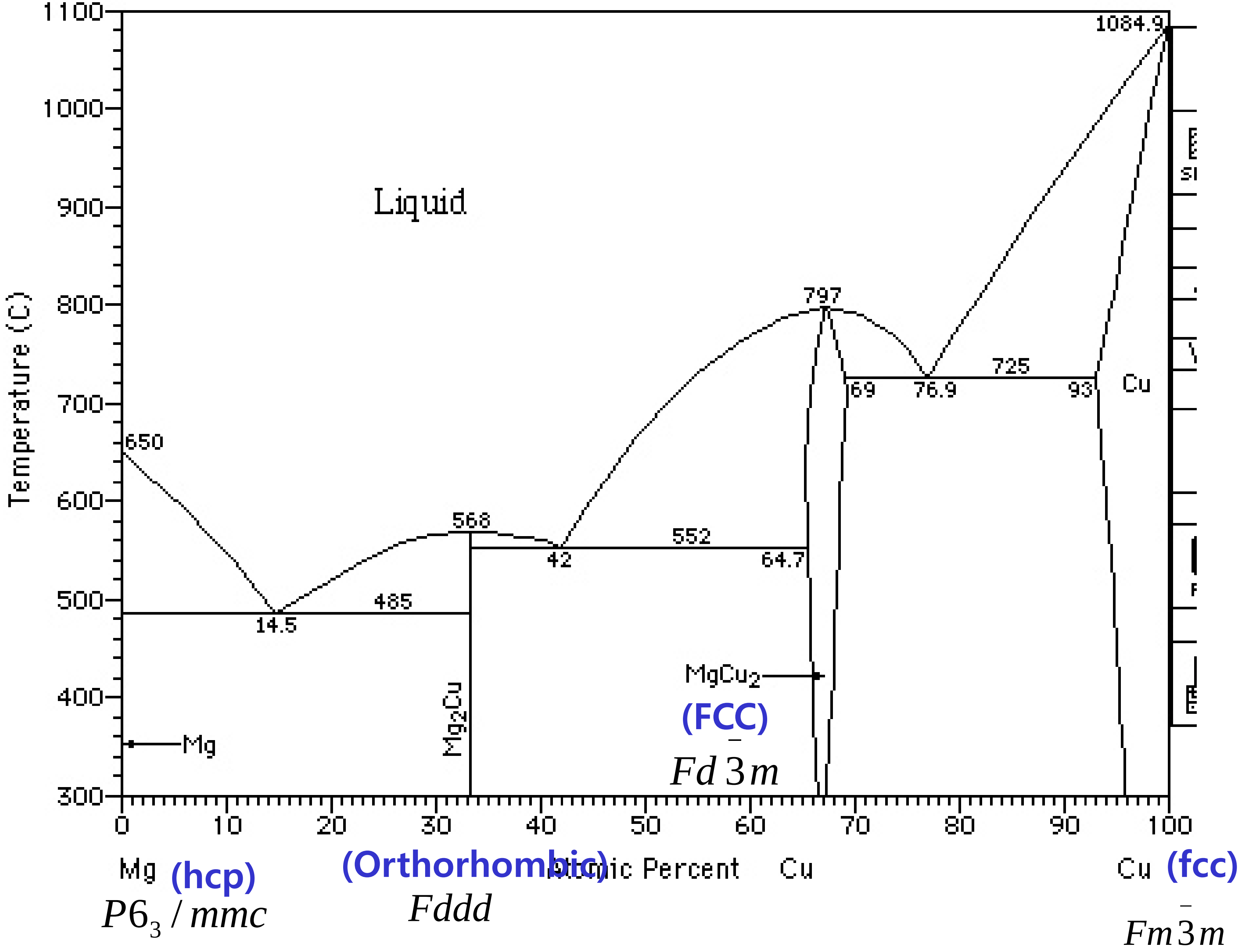
$\varepsilon < 0,\ \Delta H_{mix} < 0$



ΔH_{mix}~(-)41 kJ/mol

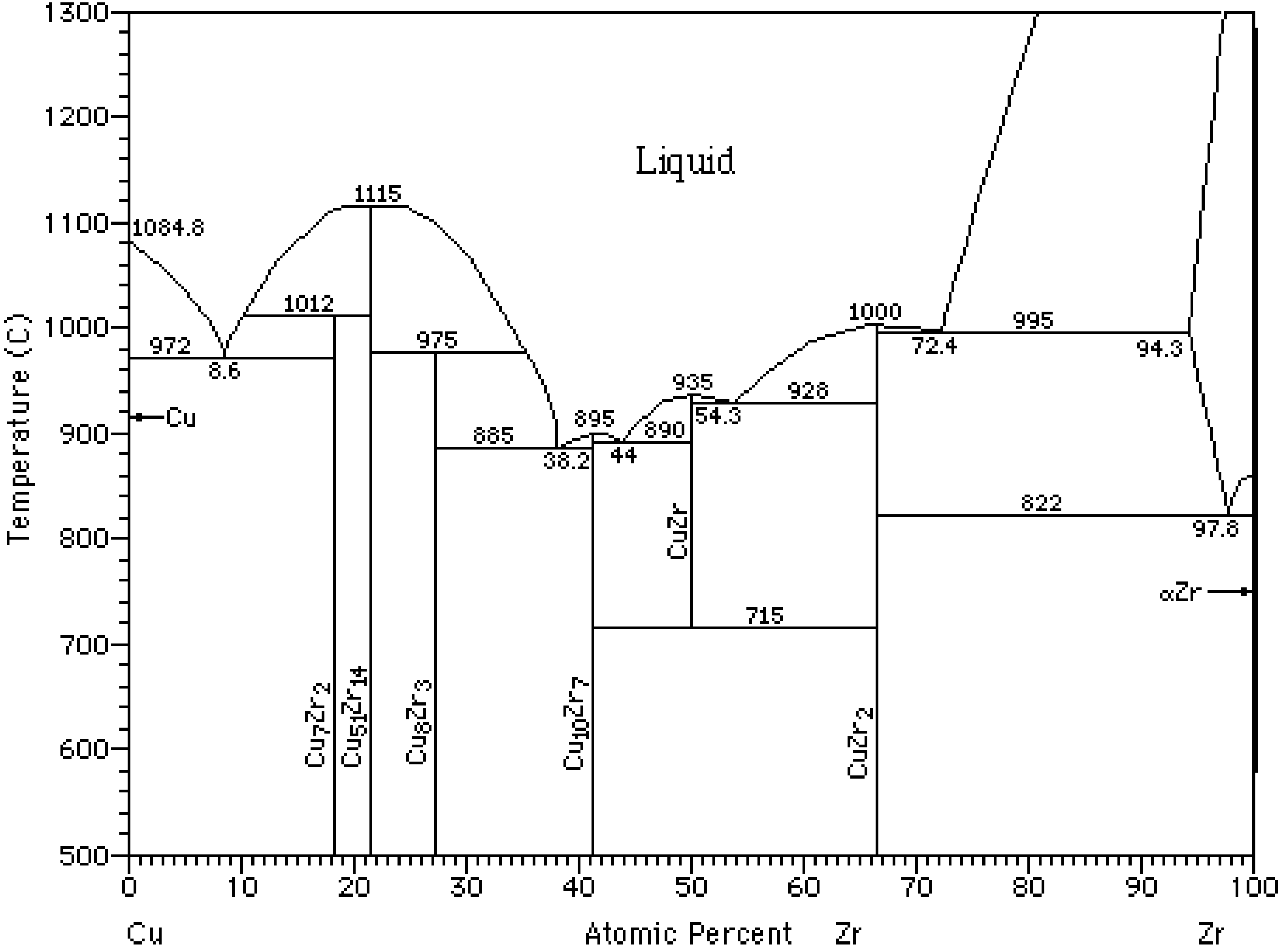
Intermediate Phase

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



Intermetallic compound

$\varepsilon \ll 0$, $\Delta H_{mix} \ll 0$ / $\Delta H_{mix} \sim -142$ kJ/mol

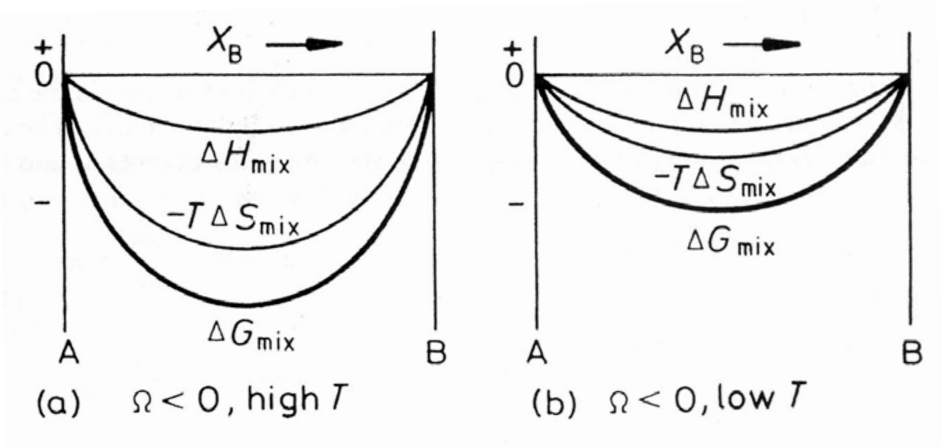


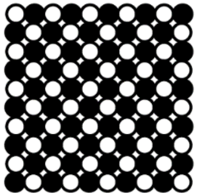
Clustering → "Phase separation"

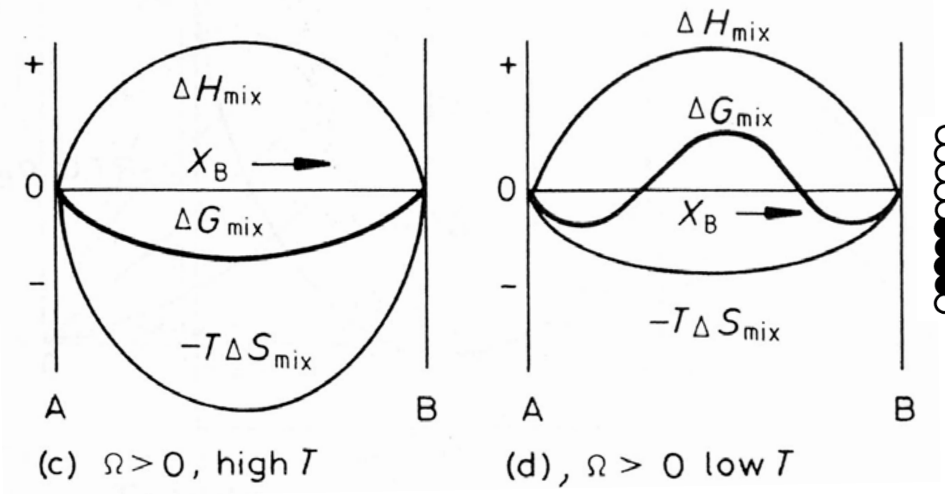
* The degree of ordering or clustering will decrease as temp. increases due to the increasing importance of entropy.

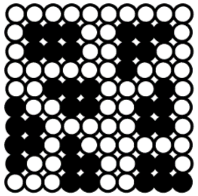
High temp. ⟶ Entropy effect ↑ ⟶ Solution stability ↑

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

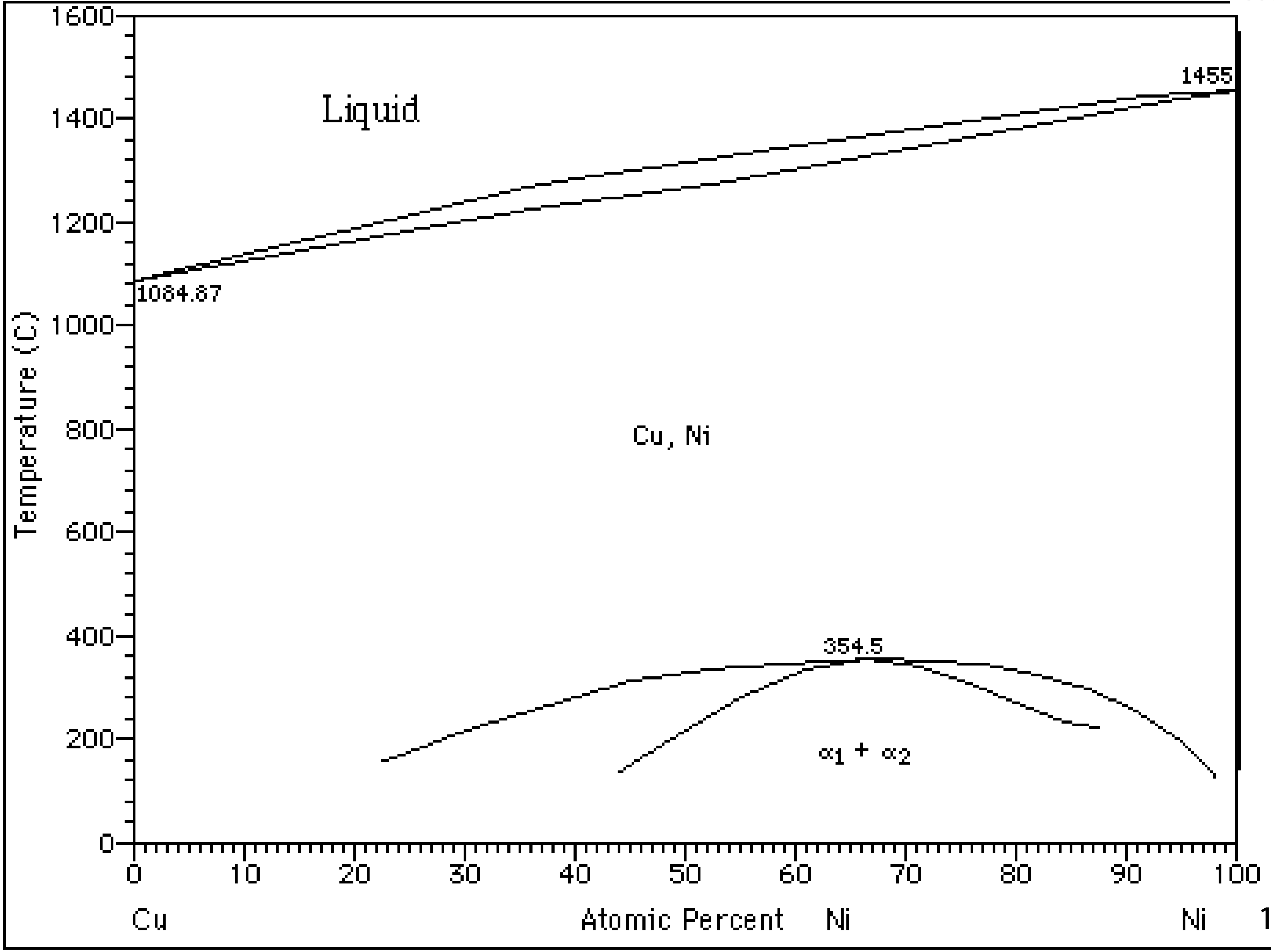




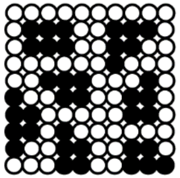


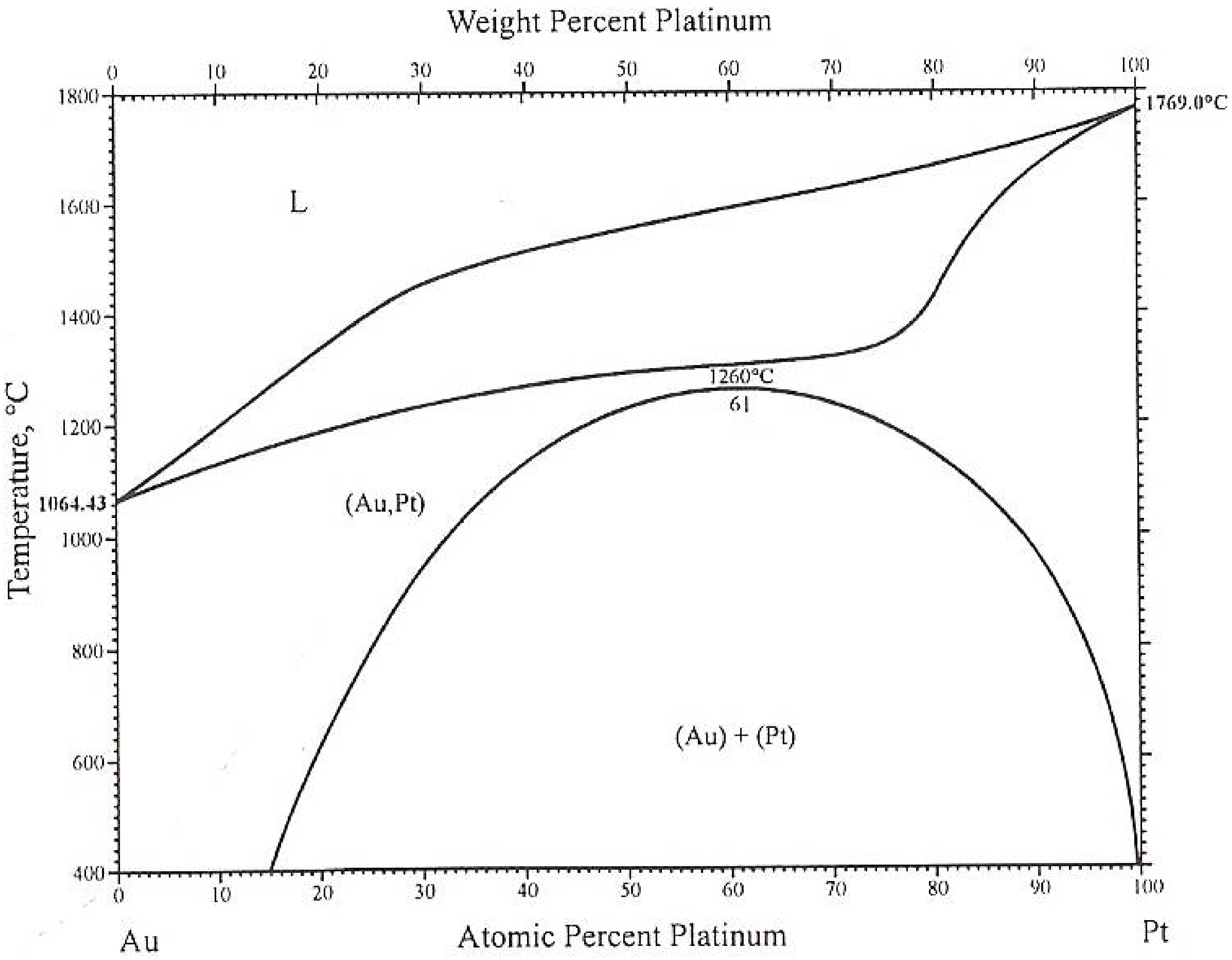


$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +26$ kJ/mol

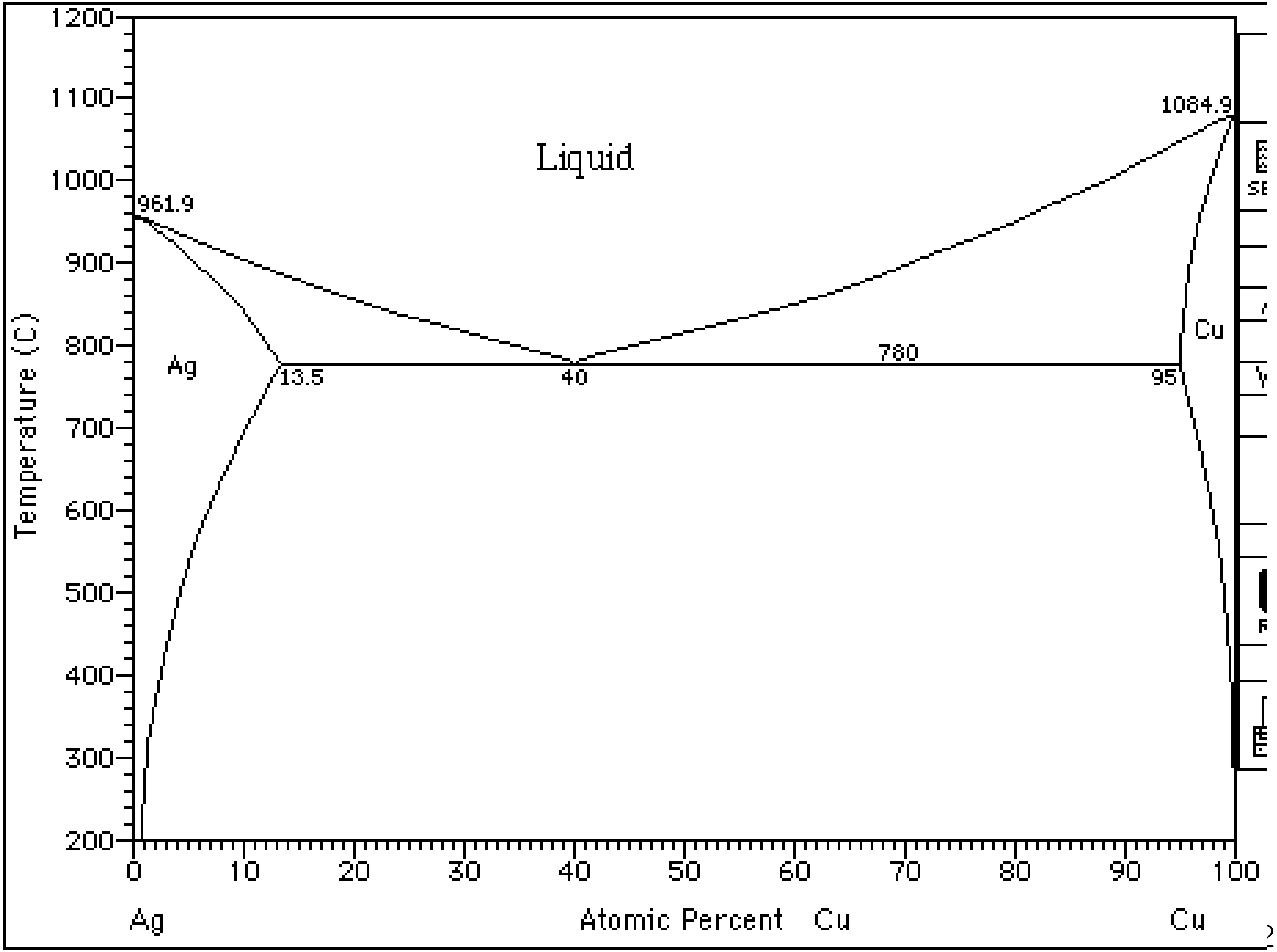


$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +17$ kJ/mol

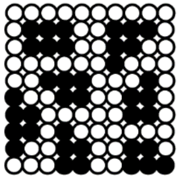


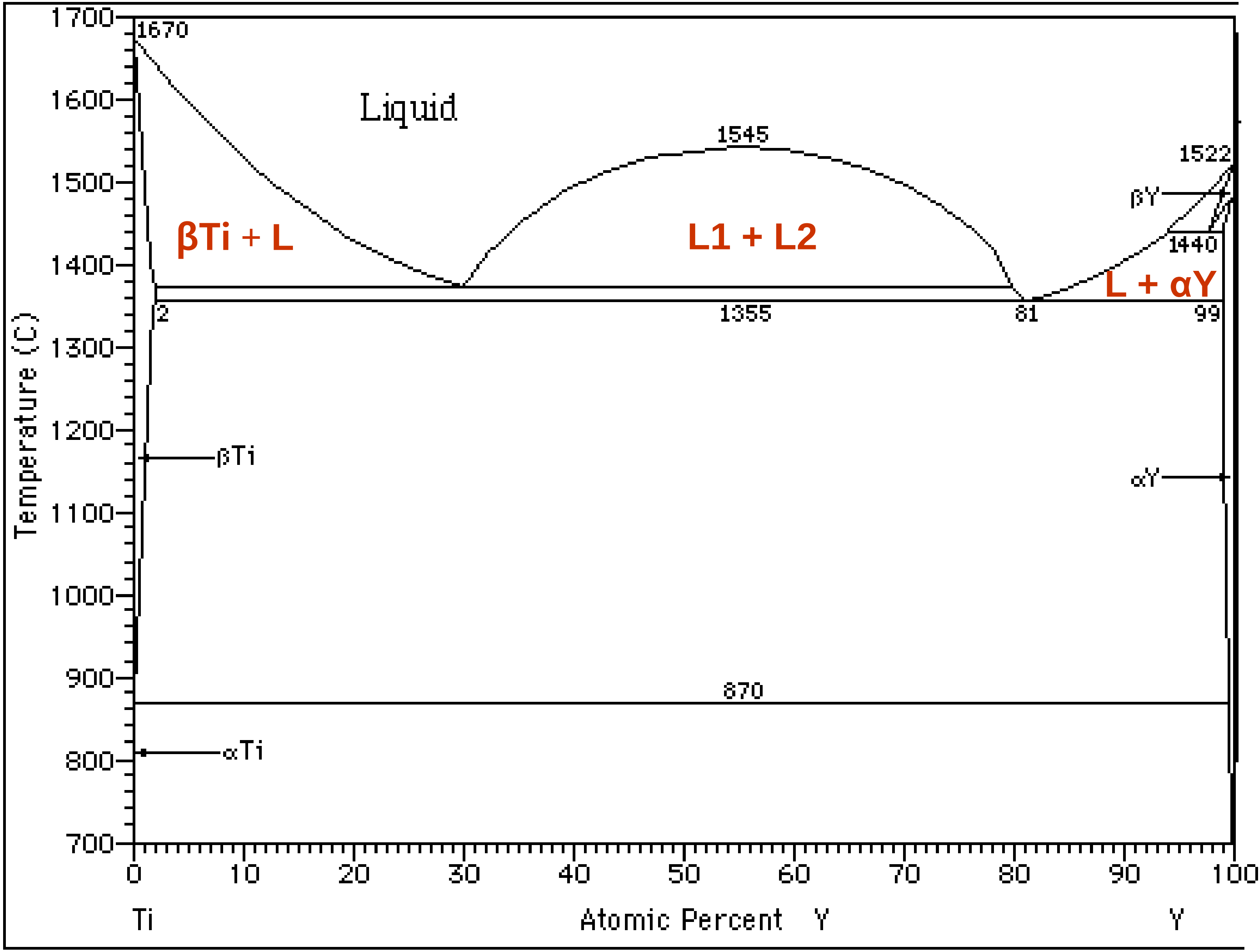


$\varepsilon > 0, \ \Delta H_{mix} > 0 \ / \ \Delta H_{mix} \sim +5 \text{ kJ/mol}$



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





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

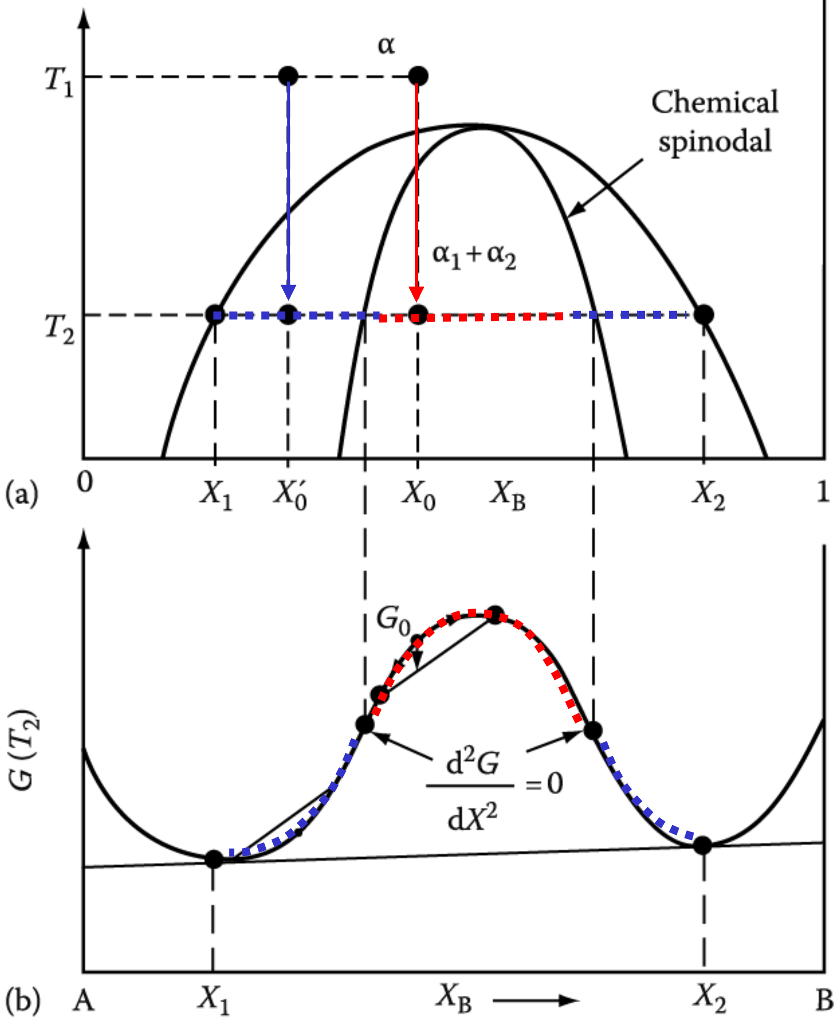


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

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"

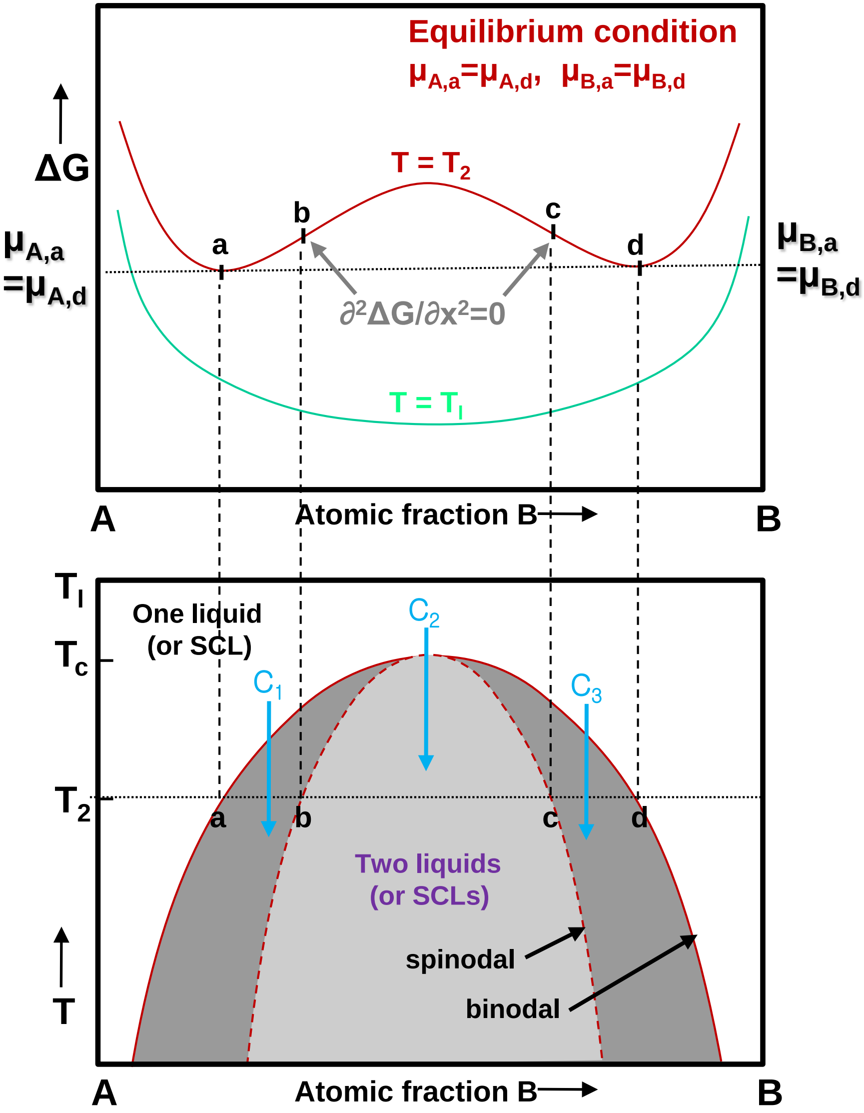
Positive heat of mixing relation among constituent elements

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

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

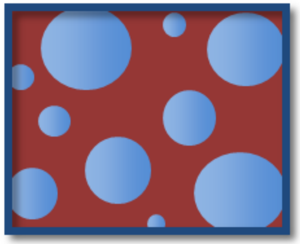
creates (meta)stable miscibility gap in limited composition range

Phase separation to A-rich & B-rich phase



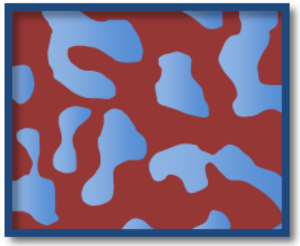
- **Different two-phase structure by initial composition before phase separation**

$C=C_1$



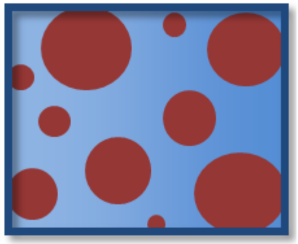
A-rich matrix
B-rich droplet

$C=C_2$



Interconnected
structure

$C=C_3$



B-rich matrix
A-rich droplet

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

* La-Zr-Al-Cu-Ni system

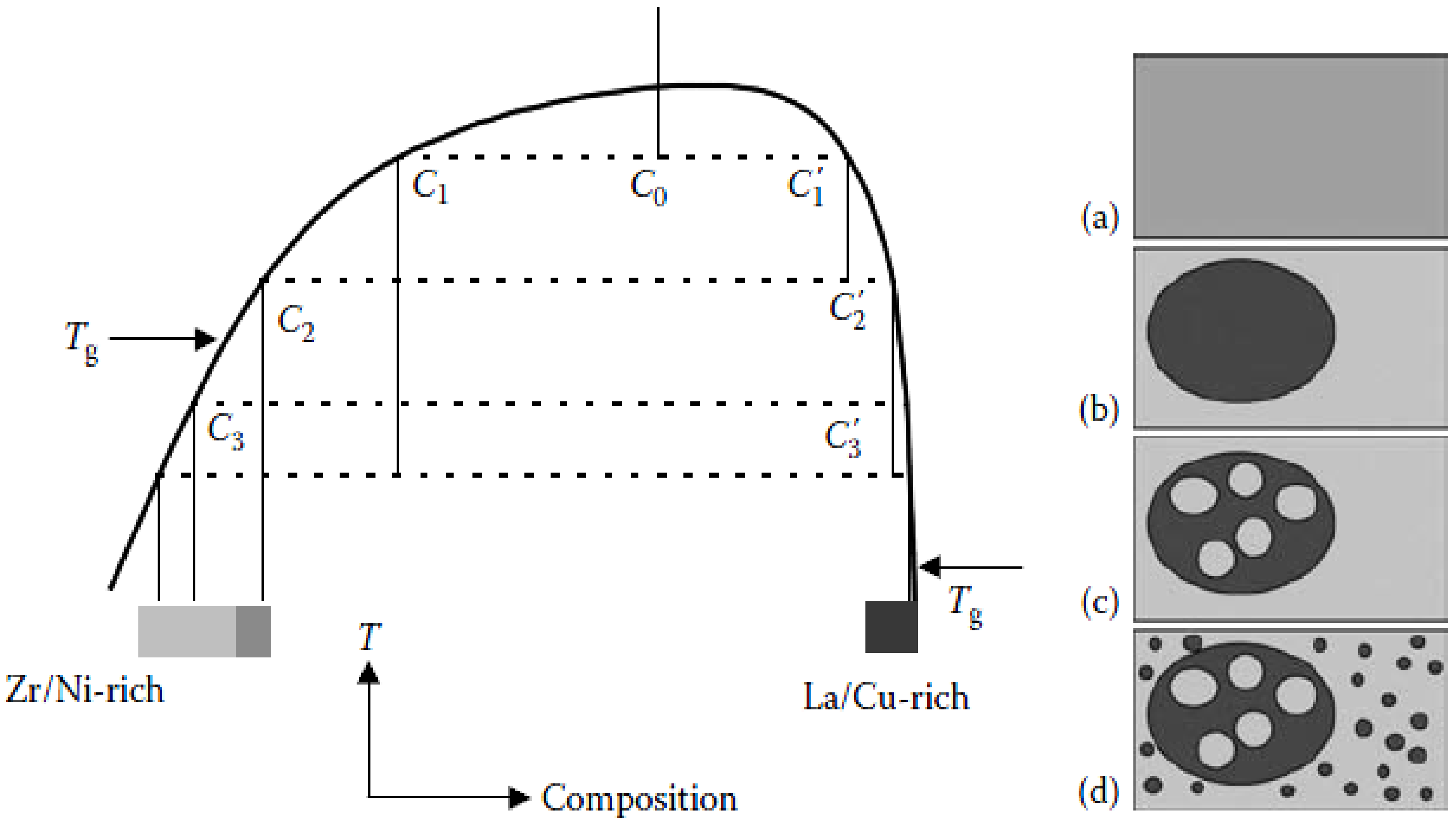


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta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

Q: 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

Contents for today's class

CHAPTER 3
Binary Phase Diagrams_Two-Phase Equilibrium

- Equilibrium in Heterogeneous Systems

- Binary phase diagrams

1) Simple Phase Diagrams

2) Variant of the simple phase diagram

a. $\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$ **Systems with miscibility gab**

b. $\Delta H_{mix} < 0 \quad \Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

c. **Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions**

Q1: How can we define equilibrium in heterogeneous systems?

1.4

Equilibrium in Heterogeneous Systems

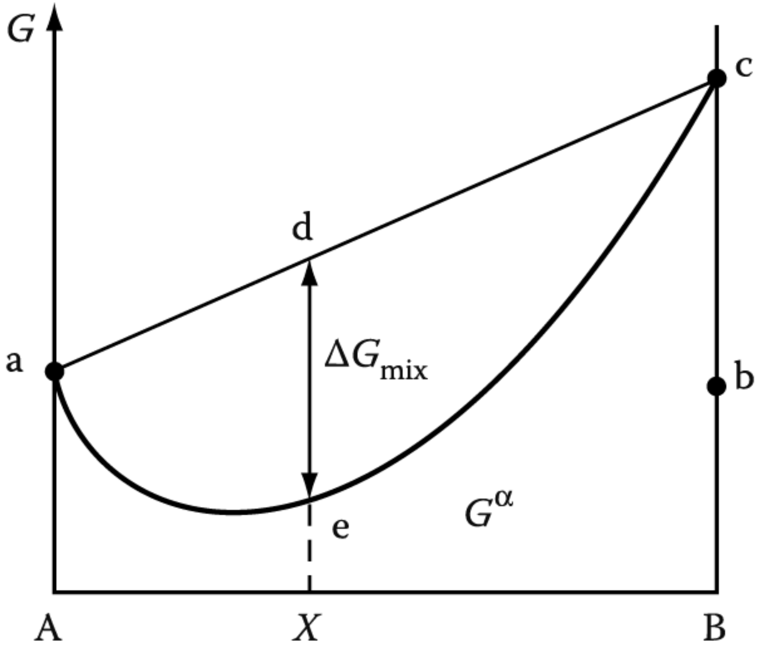
A, B different crystal structure → two free energy curves must be drawn, one for each structure.

We have dealt with the case where the components A and B have the same crystal structure.

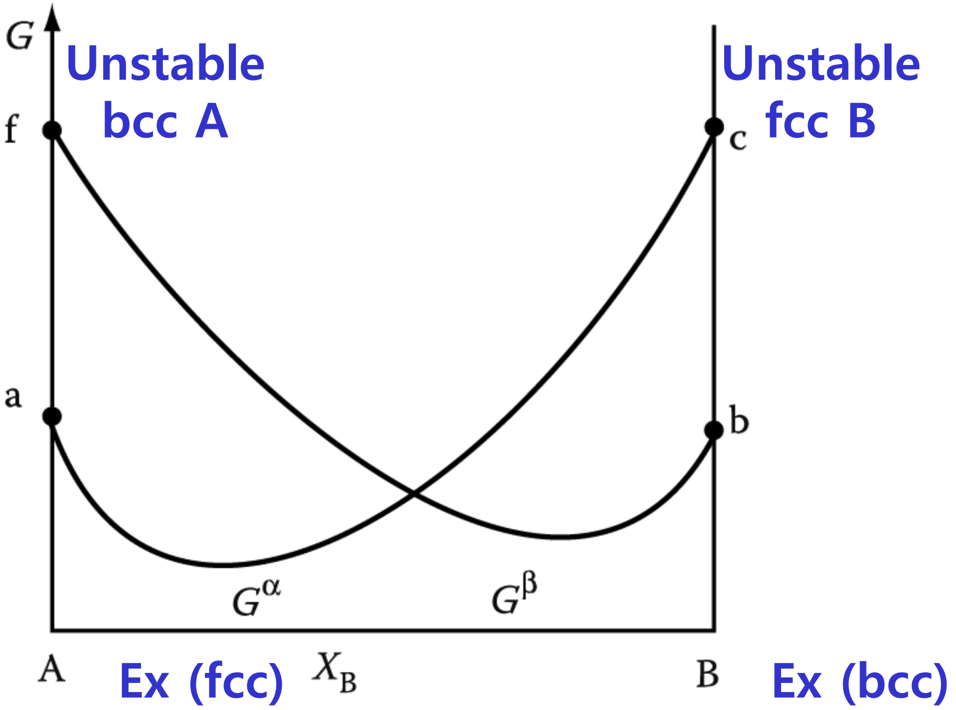
$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

What would happen when the components A and B have a different crystal structure?

→ **heterogeneous system**



(a)



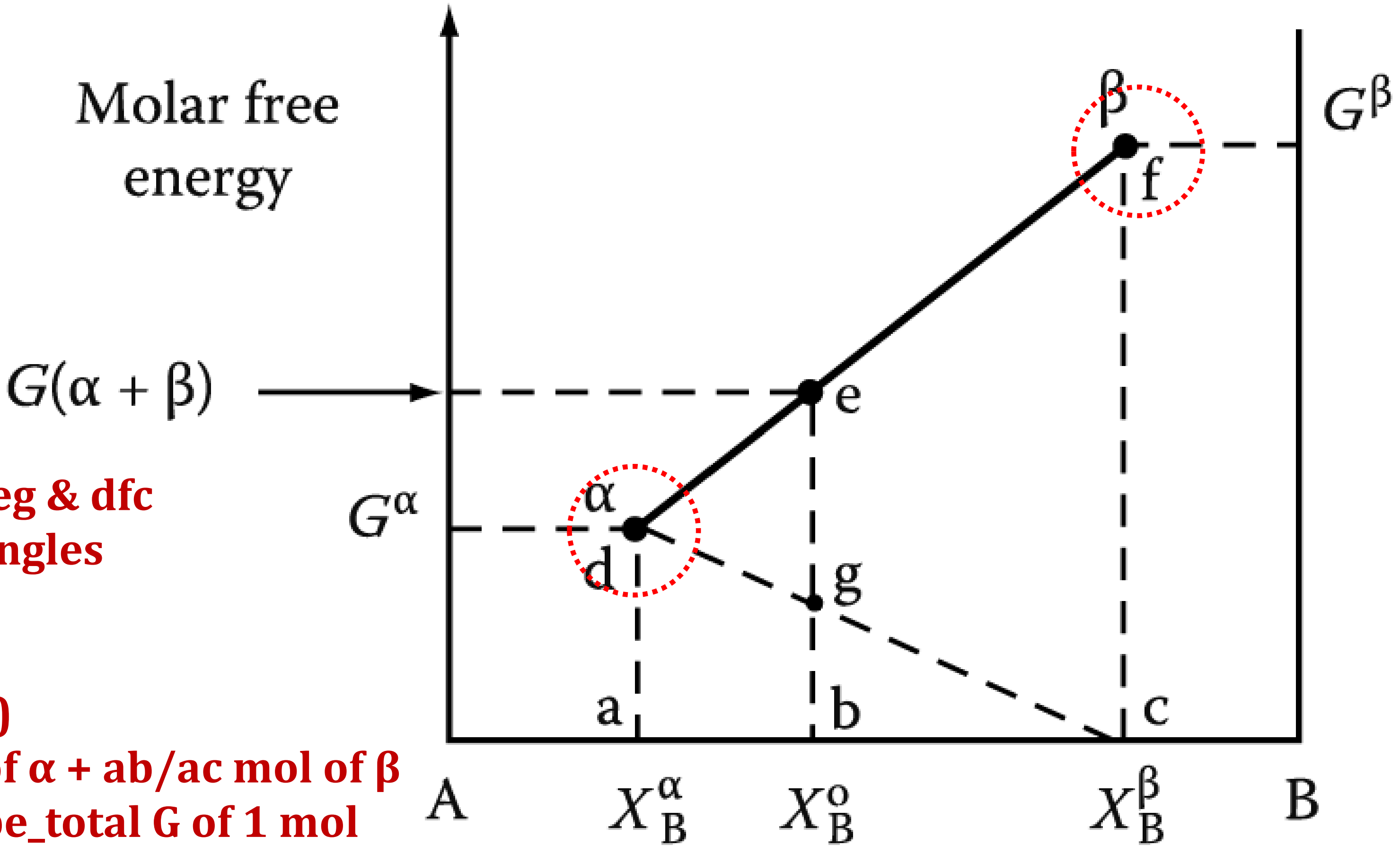
(b)

1.4

Equilibrium in Heterogeneous Systems

If $G^{\alpha}(X_B^{\alpha})$ and $G^{\beta}(X_B^{\beta})$ are given,

what would be $G(\alpha+\beta)$ *at* $X_B^o = ?$



- bcg & acd, deg & dfc
: similar triangles

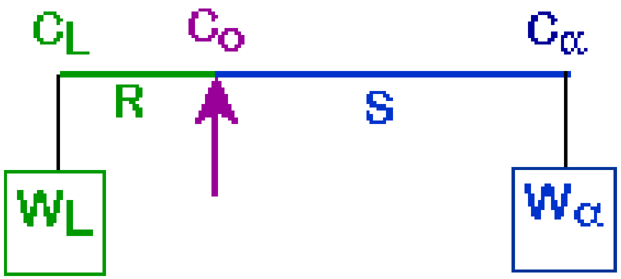
- Lever rule

- 1 mole (α+β)
: bc/ac mol of α + ab/ac mol of β
→ bg + ge = be_total G of 1 mol

Fig. 1.26 The molar free energy of a two-phase mixture (α+β)

Lever rule

A geometric interpretation:



moment equilibrium:

$$\boxed{W_L} R = W_\alpha S$$

$$\boxed{1 - W_\alpha}$$

solving gives Lever Rule

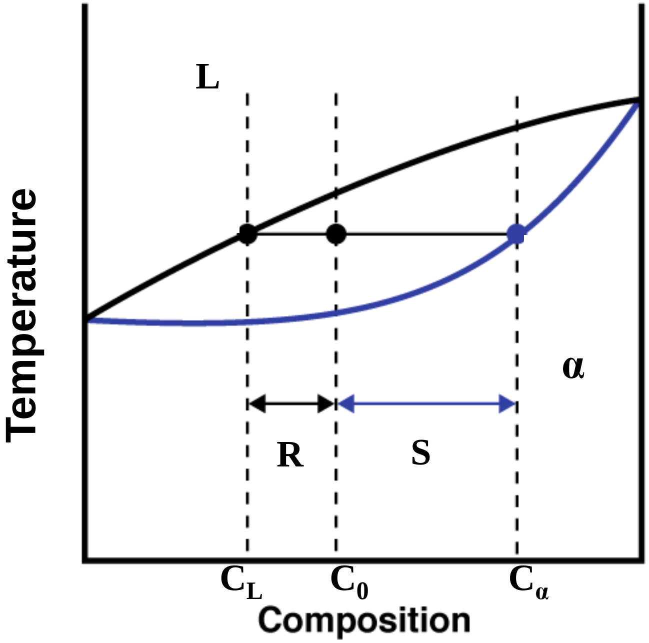
Sum of weight fractions: $W_L + W_\alpha = 1$

Conservation of mass (Ni): $C_o = W_L C_L + W_\alpha C_\alpha$

Combine above equations:

$$\boxed{W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{S}{R + S}}$$

$$\boxed{W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = \frac{R}{R + S}}$$



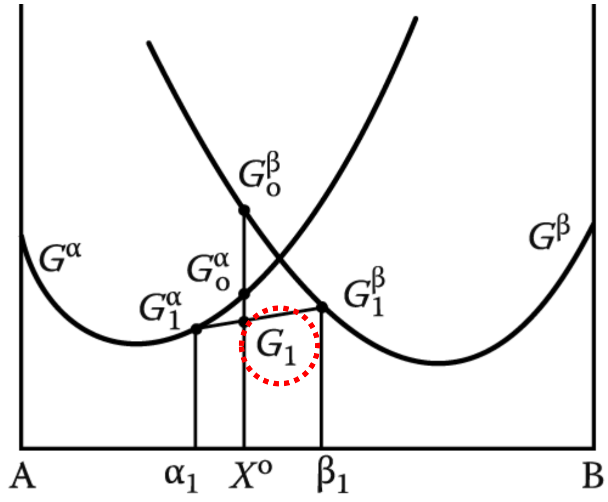
1.4

Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$

Exchange of A and B atoms

→ **$\alpha + \beta$ phase separation**

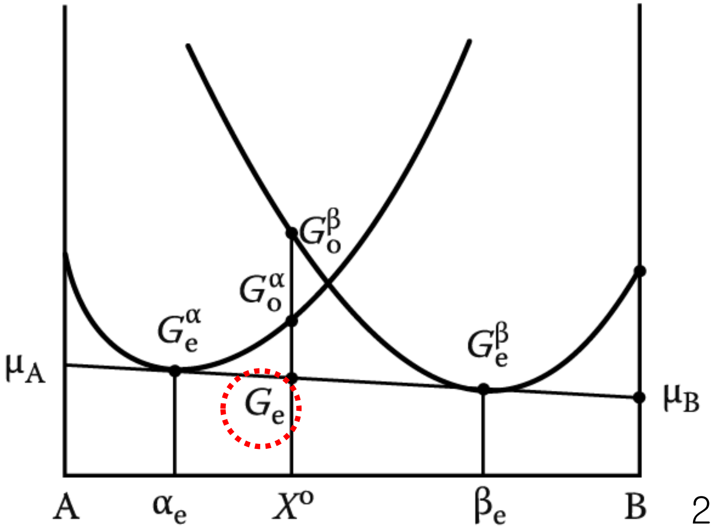


(a)

Chemical Equilibrium (μ, a)
→ multiphase and multicomponent
($\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \ldots$), ($a_i^\alpha = a_i^\beta = a_i^\gamma = \ldots$)

$$\mu_A^\alpha = \mu_A^\beta \qquad \mu_B^\alpha = \mu_B^\beta$$

Unified Chemical potential of two phases



(b)

Variation of activity with composition

Activity, a : effective concentration for mass action

The most stable state,
with the lowest free energy,
is usually defined as the
state in which the pure
component has unit activity
of A in pure α.

$$when\ X_A = 1 \rightarrow a_A^{\alpha} = 1$$

$$when\ X_B = 1 \rightarrow a_B^{\beta} = 1$$

when α and β in equil.

$$a_A^{\alpha} = a_A^{\beta}$$

$$a_B^{\alpha} = a_B^{\beta}$$

Unified activity of two phase

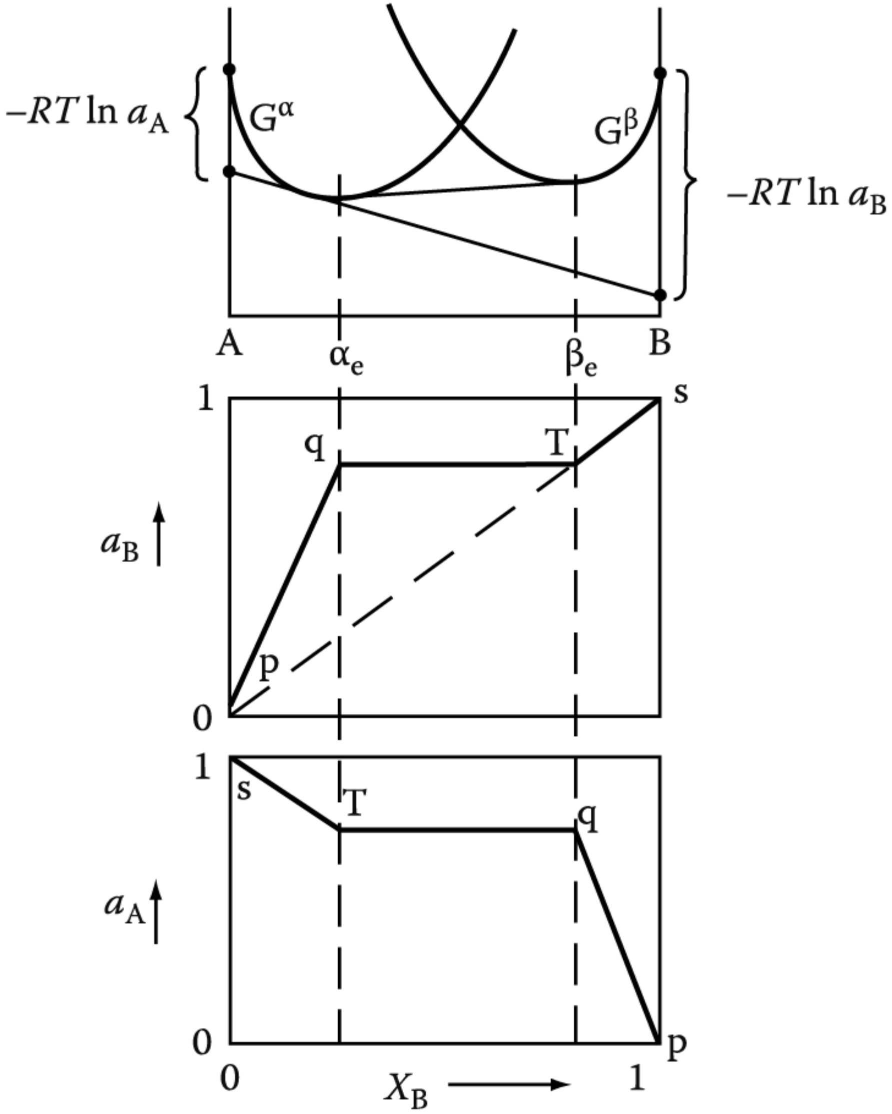
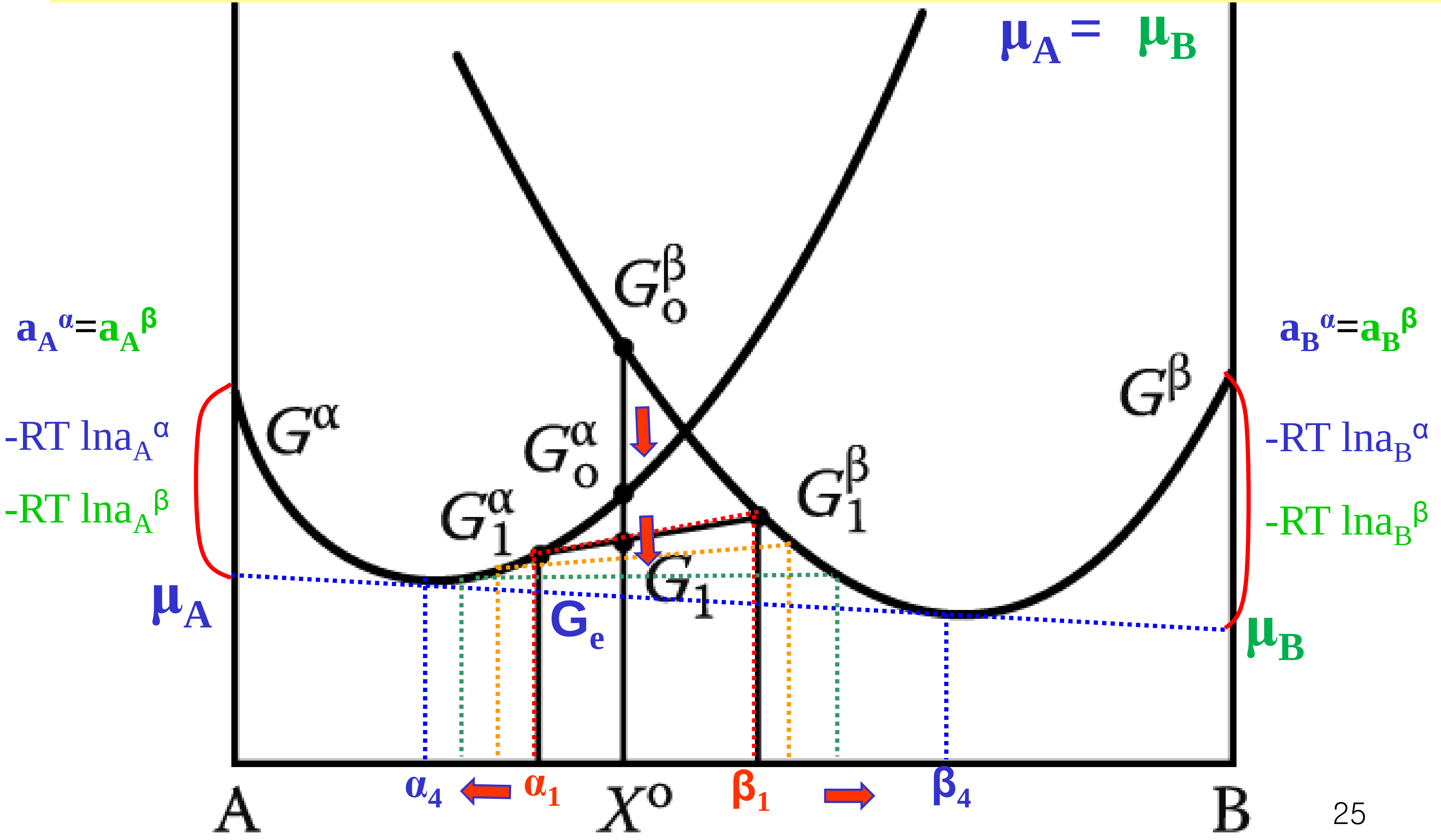


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β

Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ ➡ α + β separation ➡ unified chemical potential



Q2: How equilibrium is affected by temperature in complete solid solution?

- Two-Phase Equilibrium

1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.

(2) Both are ideal soln.

$$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$$

(3) $T_m(A) > T_m(B)$

$$dG^s = V^s\,dP - S^s\,dT + \mu^s_A\,dX^s_A + \mu^s_B\,dX^s_B$$
$$dG^l = V^l\,dP - S^l\,dT + \mu^l_A\,dX^l_A + \mu^l_B\,dX^l_B.$$

At equilibrium

$$dG^s = dG^l, \quad \mu^s_A = \mu^l_A \quad \text{and} \quad \mu^s_B = \mu^l_B.$$

At constant P

$$-(S^s - S^l)\,dT = (\mu_A - \mu_B)(dX^l_A - dX^s_A).$$

Differentiating with respect to X_A,

$$(S^s - S^l)\frac{dT}{dX_A} = (\mu_A - \mu_B)\left(\frac{dX^s_A}{dX_A} - \frac{dX^l_A}{dX_A}\right). \tag{102}$$

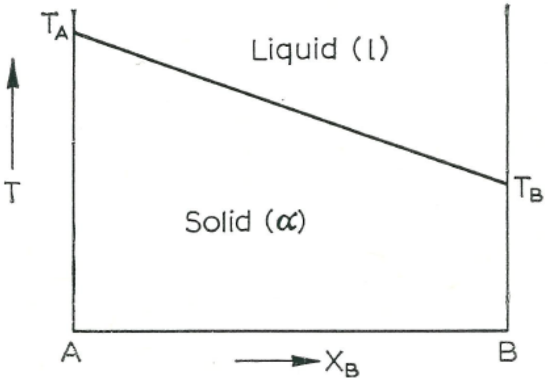


Fig. 22.

If the boundary between liquid and solid were as shown in Fig. 22, then $X^s_A = X^l_A$ (the liquid and solid would have the same composition when in equilibrium at a point on the line $T_A T_B$). From eqn. (102)

$$(S^s - S^l)\frac{dT}{dX_A} = 0.$$

From eqn. (102)

$$(S^s - S^l)\,\frac{\mathrm{d}T}{\mathrm{d}X_A} = 0.$$

Since $S^s \neq S^l$, then $\mathrm{d}T/\mathrm{d}X_A = 0$. Thus the condition $X_A^s = X_A^l$ is only associated with $\mathrm{d}T/\mathrm{d}X_A = 0$, *i.e.* with a minimum or a maximum in the line $T_A T_B$ of Fig. 22. Except for this particular case therefore $X_A^s \neq X_A^l$. There is a difference between the composition of the liquid and solid phase in the general case.

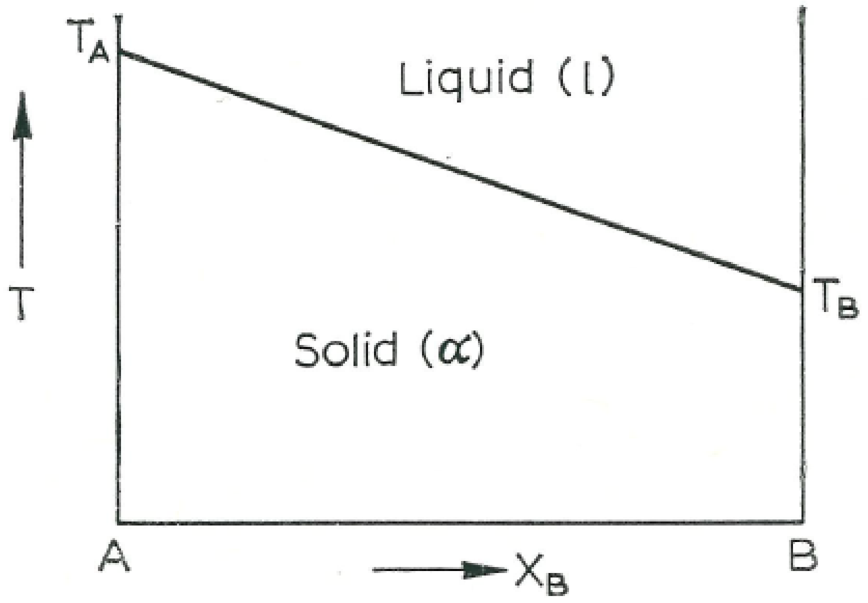
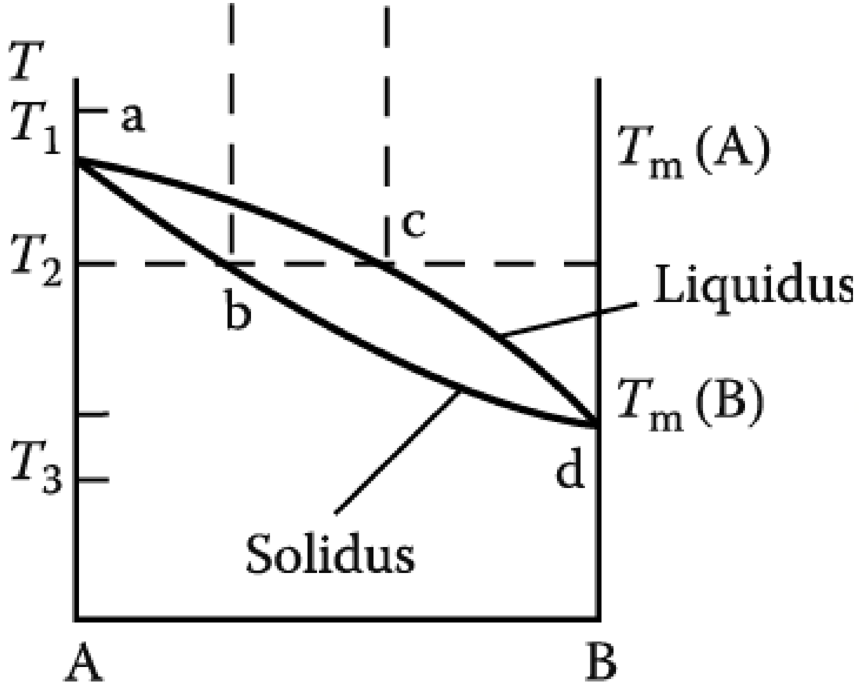


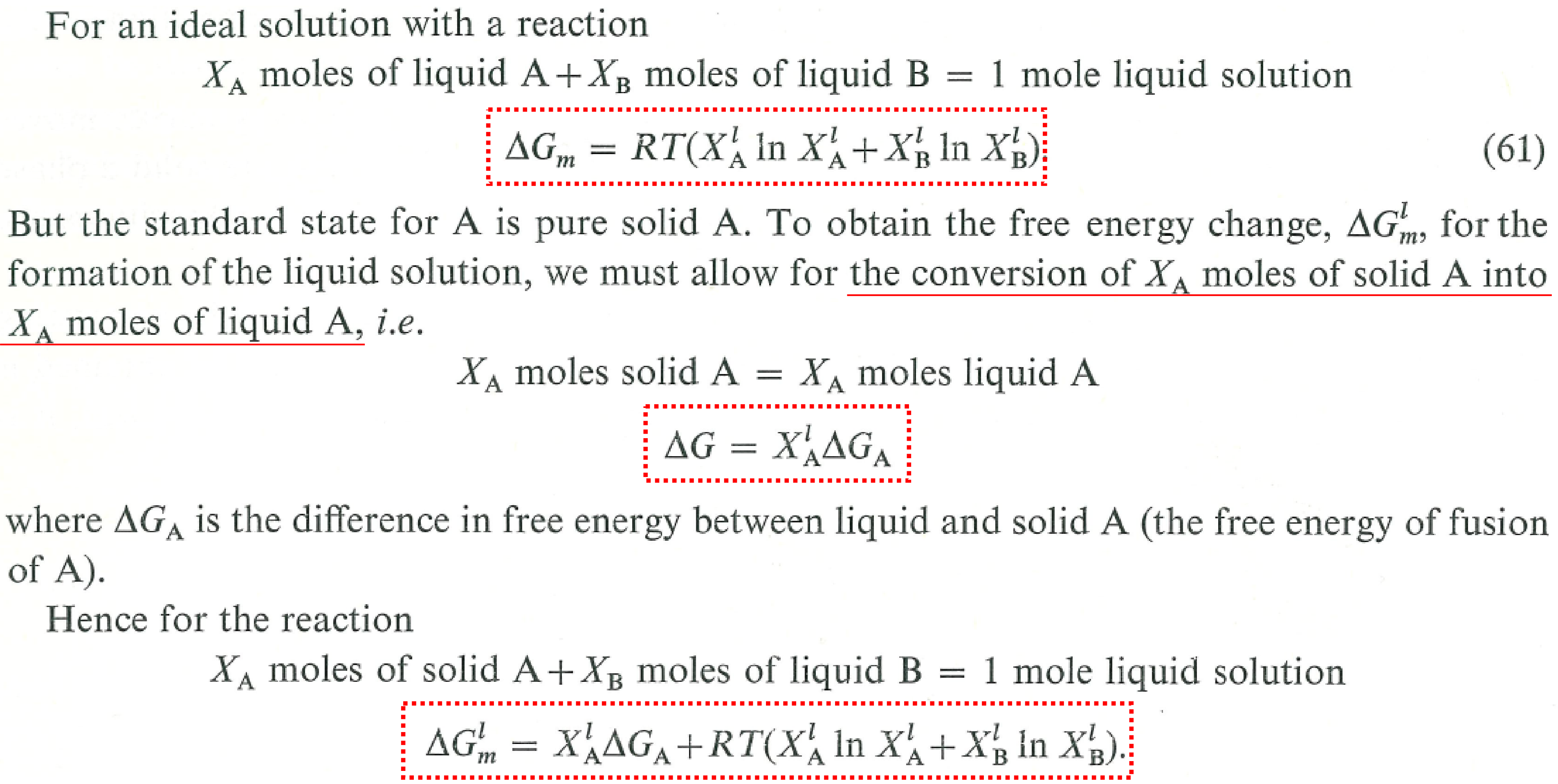
Fig. 22.



(f)

*** Consider the free energy curves for liquid and α phase at a temperature T, where $T_A>T>T_B$. The standard states are pure *solid* A and pure *liquid* B at temperature T. → Derive the free energy curves for the liquid and α phases.**

1) Free energy curve for the liquid phase



For an ideal solution with a reaction

$$X_A \text{ moles of liquid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m = RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l)} \qquad (61)$$

But the standard state for A is pure solid A. To obtain the free energy change, ΔG_m^l, for the formation of the liquid solution, we must allow for the conversion of X_A moles of solid A into X_A moles of liquid A, *i.e.*

$$X_A \text{ moles solid A} = X_A \text{ moles liquid A}$$

$$\boxed{\Delta G = X_A^l \Delta G_A}$$

where ΔG_A is the difference in free energy between liquid and solid A (the free energy of fusion of A).

Hence for the reaction

$$X_A \text{ moles of solid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m^l = X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).}$$

2) Free energy curve for α phase

For an ideal solid solution formed according to the equation

$$X_A \text{ moles of solid A} + X_B \text{ moles of solid B} = 1 \text{ mole } \alpha \text{ solid solution}$$

$$\boxed{\Delta G_m = RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

Since the standard state for B is pure *liquid* B, allowance must be made for the free energy change on transforming X_B moles of liquid B to X_B moles of solid B, *i.e.*

$$\boxed{\Delta G = -X_B^s \Delta G_B}$$

where ΔG_B is the difference in free energy between liquid and solid B. It is a negative quantity since the liquid phase is the more stable at temperature T.

For the reaction

$$X_A \text{ moles of solid A} + X_B \text{ moles of liquid B} = 1 \text{ mole } \alpha \text{ solid solution}$$

$$\boxed{\Delta G_m^s = -X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

At temperature T the chemical potential of component B is identical in the α and liquid phases. Therefore

$$\boxed{\frac{\partial \Delta G_m^s}{\partial X_B} = \frac{\partial \Delta G_m^l}{\partial X_B}}$$

$$\frac{\partial \Delta G_m^s}{\partial X_B} = -\Delta G_B + RT \ln \frac{X_B^s}{X_A^s} \qquad \text{and} \qquad \frac{\partial \Delta G_m^l}{\partial X_B} = -\Delta G_A + RT \ln \frac{X_B^l}{X_A^l}.$$

Therefore

$$\Delta G_A - \Delta G_B = RT \left(\ln \frac{X_B^l}{X_A^l} - \ln \frac{X_B^s}{X_A^s} \right)$$

or,

$$\Delta G_A - \Delta G_B = RT \left(\ln \frac{X_A^s}{X_A^l} - \ln \frac{X_B^s}{X_B^l} \right).$$

We can relate ΔG_A and ΔG_B to ΔH_A and ΔH_B, T_A and T_B, *i.e.* to the respective molar heats of fusion of pure A and B, and their melting points. For example, for component B at T_B:

$$\Delta G_B = \Delta H_B - T_B \Delta S_B = 0$$

or,

$$\boxed{\Delta S_B = \frac{\Delta H_B}{T_B}.}$$

At a temperature T,

$$\Delta G_B = \Delta H_B - T \Delta S_B \neq 0.$$

Therefore

$$\begin{aligned}\Delta G_{\mathrm{B}} &= \Delta H_{\mathrm{B}} - T\,\frac{\Delta H_{\mathrm{B}}}{T_{\mathrm{B}}}\\ &\boxed{= \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right).}\end{aligned}$$

$$\Delta G_{\mathrm{A}} - \Delta G_{\mathrm{B}} = RT\left(\ln \frac{X^s_{\mathrm{A}}}{X^l_{\mathrm{A}}} - \ln \frac{X^s_{\mathrm{B}}}{X^l_{\mathrm{B}}}\right)$$

Substituting,

$$\Delta H_{\mathrm{A}}\left(1 - \frac{T}{T_{\mathrm{A}}}\right) - \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right) = RT\left(\ln \frac{X^s_{\mathrm{A}}}{X^l_{\mathrm{A}}} - \ln \frac{X^s_{\mathrm{B}}}{X^l_{\mathrm{B}}}\right)$$

or,

$$\ln \frac{X^s_{\mathrm{A}}}{X^l_{\mathrm{A}}} - \ln \frac{X^s_{\mathrm{B}}}{X^l_{\mathrm{B}}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right) - \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).$$

As the temperature approaches T_{A} the quantities X^s_{A} and X^l_{A} will approach unity, and $1/T$ will approach $1/T_{\mathrm{A}}$.

Hence near T_{A}:

$$\boxed{\ln \frac{X^s_{\mathrm{B}}}{X^l_{\mathrm{B}}} = \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).} \qquad (103)$$

Similarly, if the temperature approaches T_{B}, $X^s_{\mathrm{B}} \simeq X^l_{\mathrm{B}} \to 1$ and $1/T \to 1/T_{\mathrm{B}}$. Near T_{B}:

$$\boxed{\ln \frac{X^s_{\mathrm{A}}}{X^l_{\mathrm{A}}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right).} \qquad (104)$$

Knowing ΔH_{A}, ΔH_{B}, T_{A} and T_{B}, the above two equations can be used to determine the compositions of co-existing phases at a series of temperatures, T, between T_{A} and T_{B}. → **Fig. 23*f***

1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.

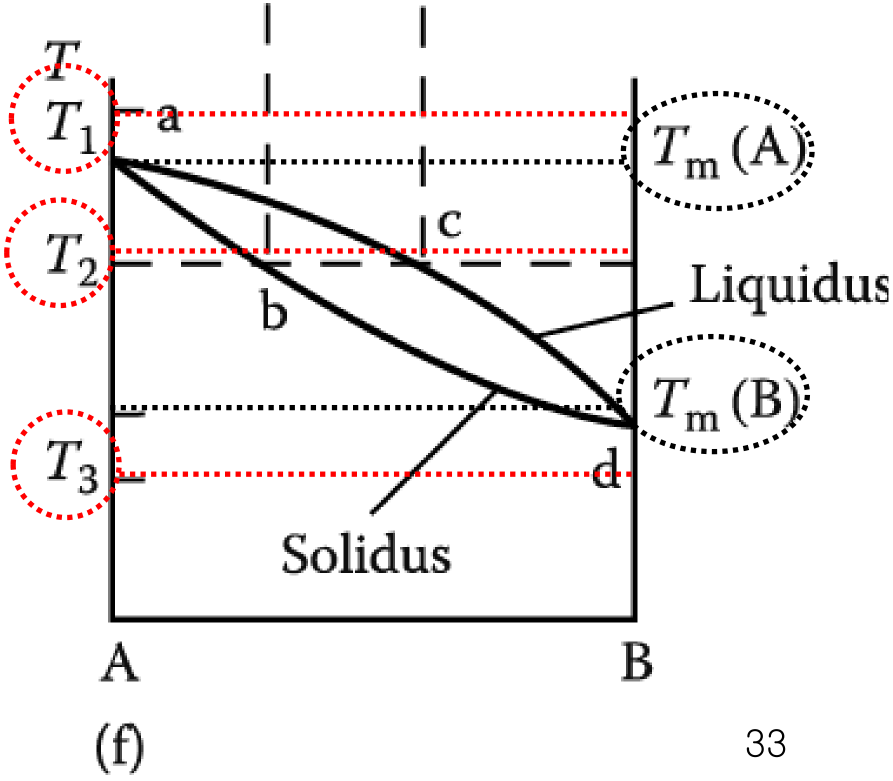
(2) Both are ideal soln.

$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$

(3) $T_m(A) > T_m(B)$

(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$

Draw G^L and G^S as a function of composition X_B at T_1, $T_m(A)$, T_2, $T_m(B)$, and T_3.

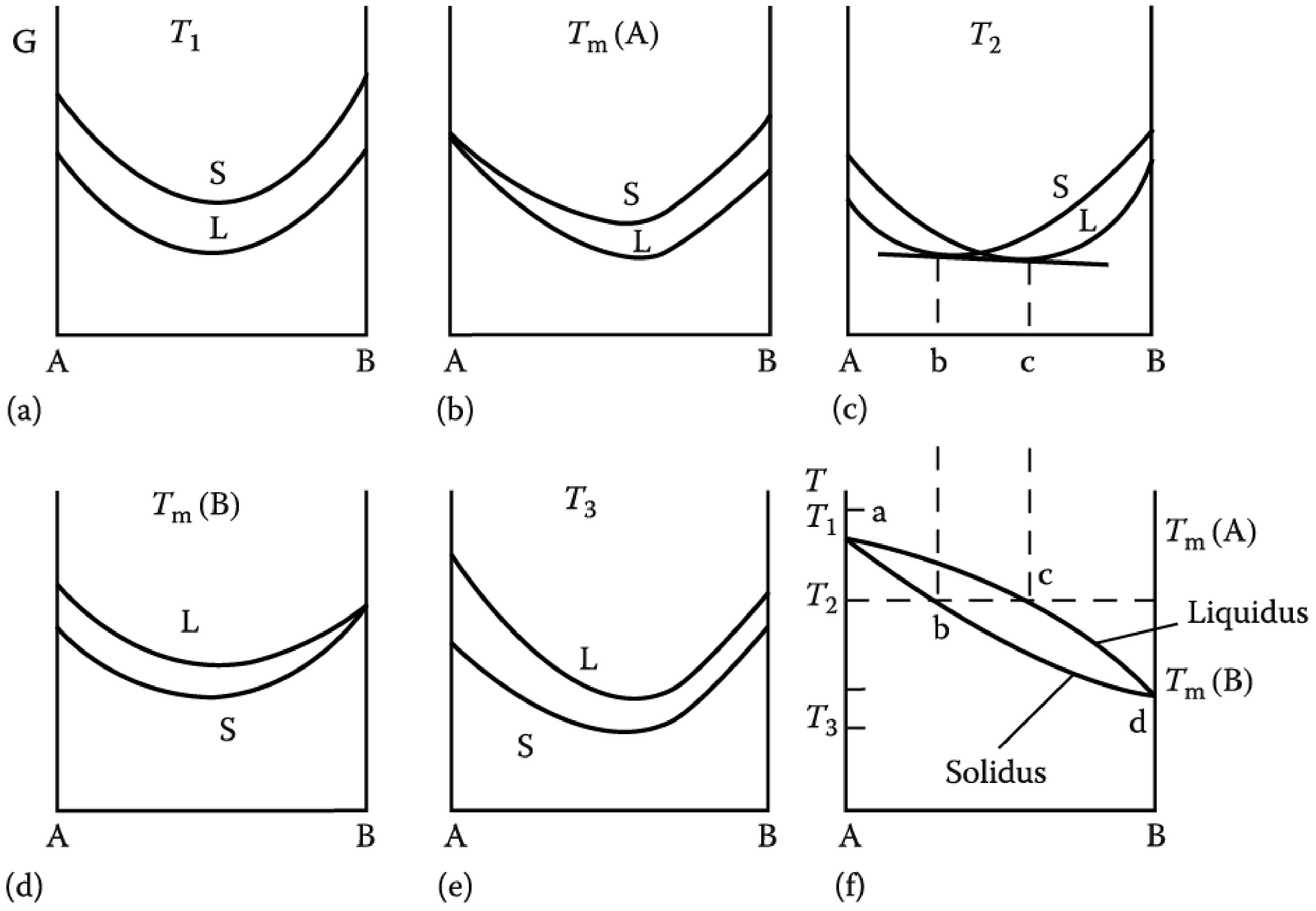


1.5 Binary phase diagrams

1) Simple Phase Diagrams

Assumption:

- **(1) completely miscible in solid and liquid.**
- **(2) Both are ideal soln.**
- **(3) $T_m(A) > T_m(B)$**
- **(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$**



* Consider actual (or so-called regular) solutions

in which $\Delta H_m \neq 0$, but $\Delta S_m = \Delta S_{m,\mathrm{ideal}}$.

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

Since

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

then,

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta H_A - X_A^l T\Delta S_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

The free energy curve for the solid phase is:

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s)$$

or,

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta H_B + X_B^s T\Delta S_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).$$

1) Simple Phase Diagrams

a) Variation of temp.: $G^L > G^s$

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

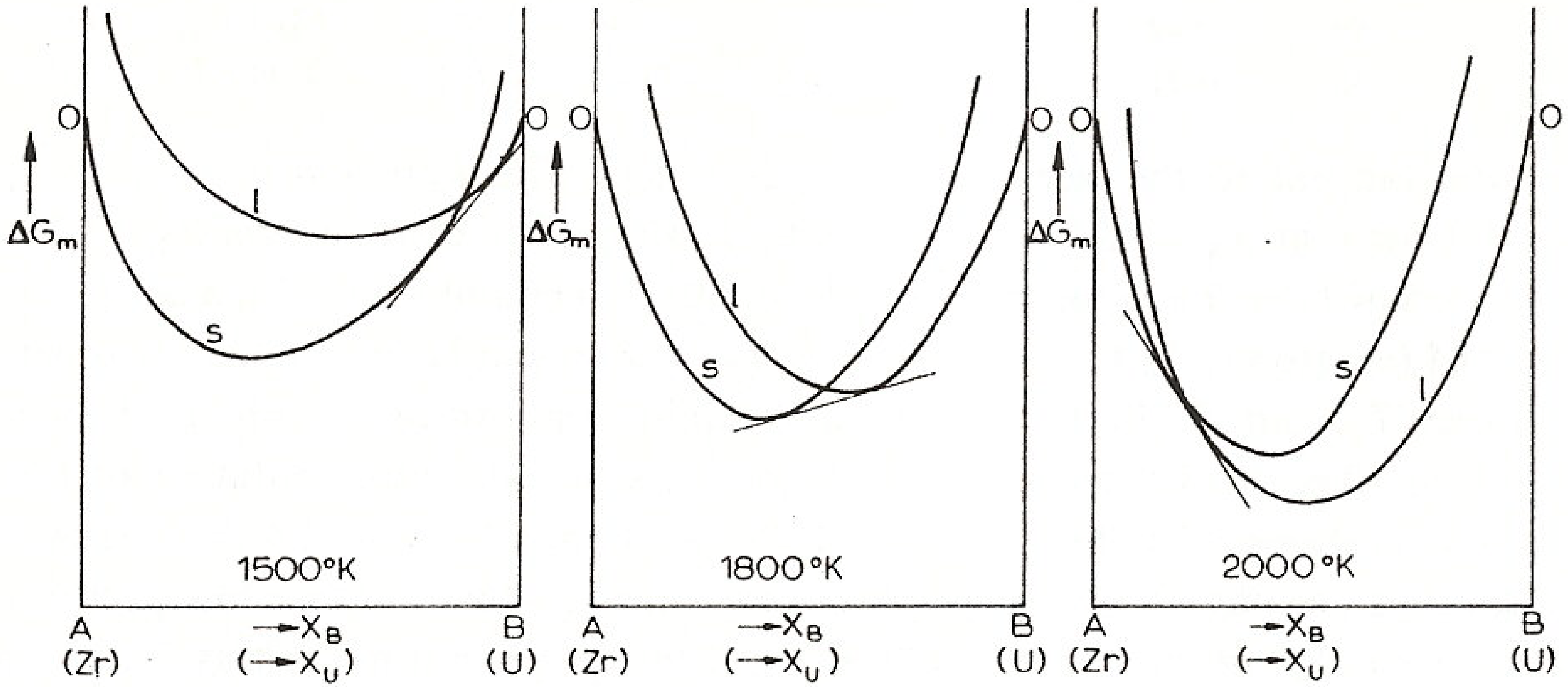


Fig. 26. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

It was assumed that $\Delta H_m^l = \Delta H_m^s$

1.5 Binary phase diagrams

1) Simple Phase Diagrams

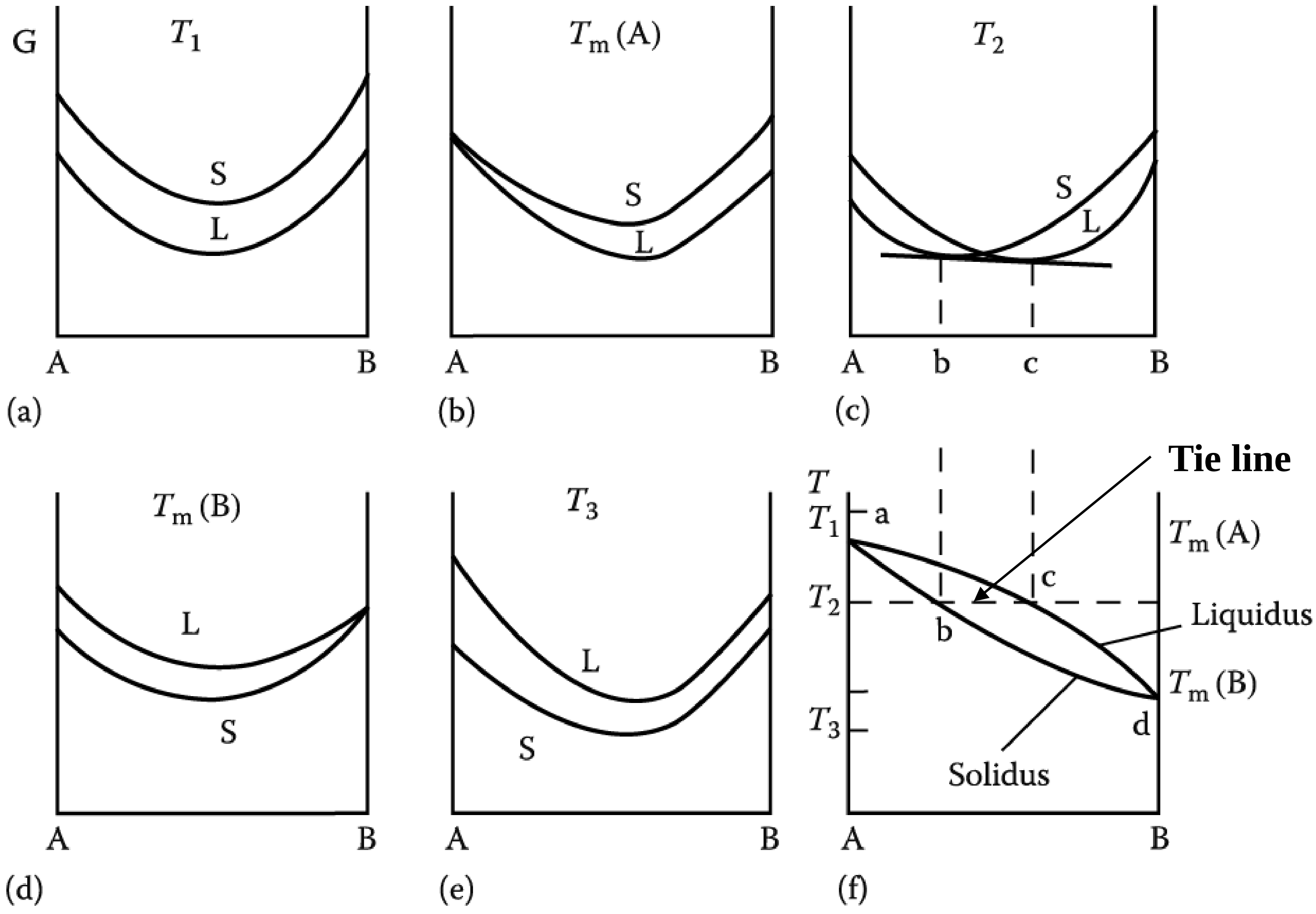
a) Variation of temp.: $G^L > G^s$

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

Assumption:

- (1) completely miscible in solid and liquid.
- (2) Both are ideal soln.
- (3) $T_m(A) > T_m(B)$
- (4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



Referring to Fig. 23f, if A is regarded as the solvent, for very dilute solutions of B in A we can write

$$X_{\mathrm{A}} \rightarrow 1 \quad \text{and} \quad -\ln X_{\mathrm{A}} \simeq X_{\mathrm{B}}.$$

In terms of eqn. (104):

$$X_{\mathrm{A}}^{l} - X_{\mathrm{A}}^{s} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}} - T}{T T_{\mathrm{A}}}\right).$$

Since $X_{\mathrm{A}}^{l} = 1 - X_{\mathrm{B}}^{l}$ and $X_{\mathrm{A}}^{s} = 1 - X_{\mathrm{B}}^{s}$

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}} - T}{T T_{\mathrm{A}}}\right). \tag{105}$$

As T approaches T_{A} (in dilute solutions of B in solvent A), the denominator on the right-hand side of eqn. (105) can be written RT_{A}^{2}. Therefore

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}(T_{\mathrm{A}} - T) \tag{106}$$

or,

$$\left(\frac{\mathrm{d}X_{\mathrm{B}}^{s}}{\mathrm{d}T} - \frac{\mathrm{d}X_{\mathrm{B}}^{l}}{\mathrm{d}T}\right)_{T=T_{\mathrm{A}}} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}. \tag{107}$$

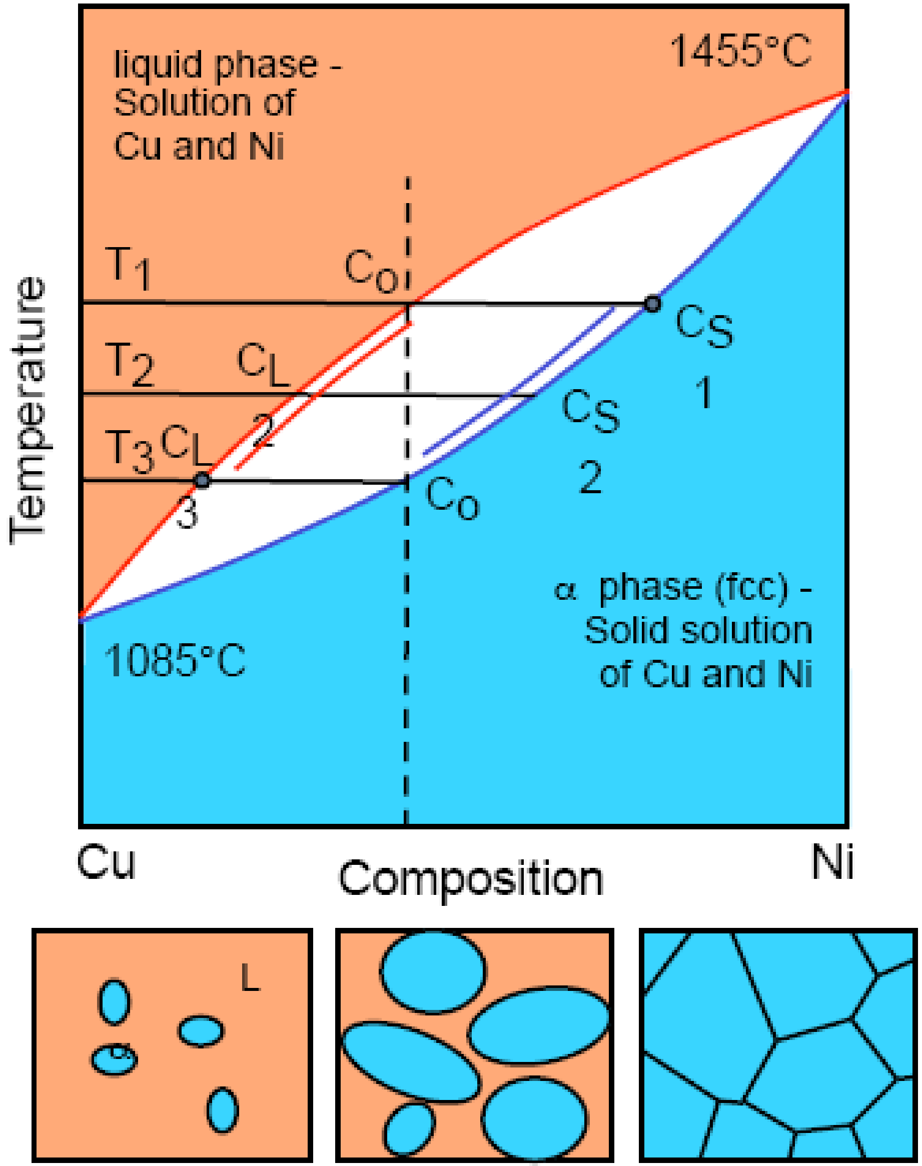
Equations (106) and (107) are referred to as the Van't Hoff relation. They give the depression of the freezing point for a liquid solution in equilibrium with a solid solution. The difference in initial slopes of the solidus and liquidus curves, the slopes at $T = T_{\mathrm{A}}$ and $X_{\mathrm{A}} = 1$, are dependent on the latent heat of fusion of pure A (ΔH_{A}) but independent of the nature of the solute.

1.5 Binary phase diagrams

1) Simple Phase Diagrams

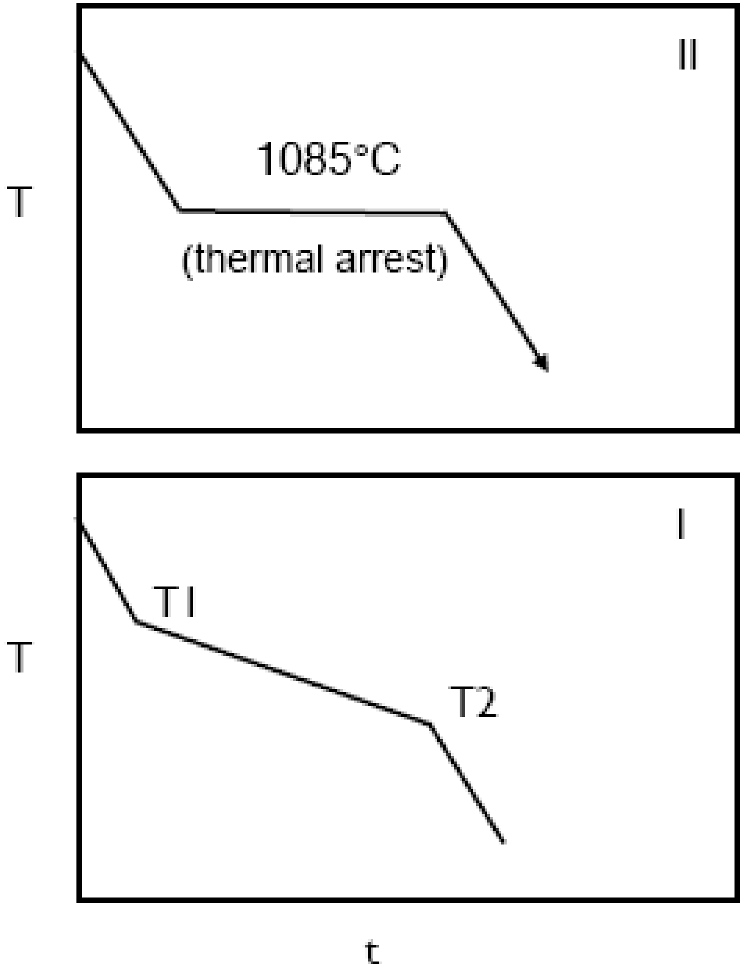
The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

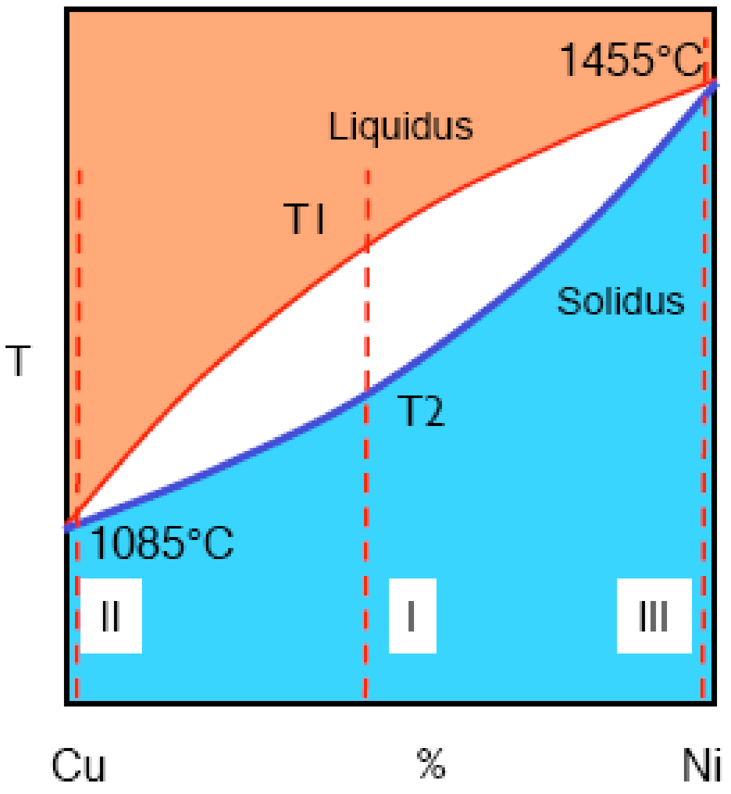
Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes its composition from C_o to C_{L3} following the liquidus. The solidification completes at T_3.



Cooling Curves

determination of Phase diagrams



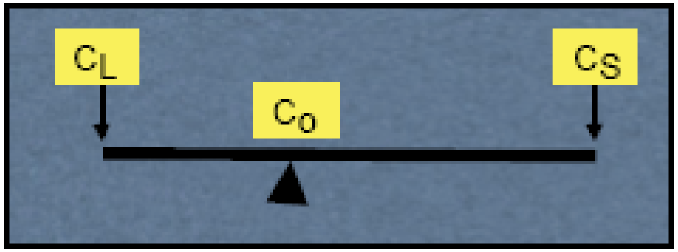


1.5 Binary phase diagrams

Example

At temperature T_1, alloy C_o is in the dual phase region, comprising the liquid phase and the α-phase.

(i) Determine the compositions of the two phases;
(ii) Determine the weight fractions of the two phases



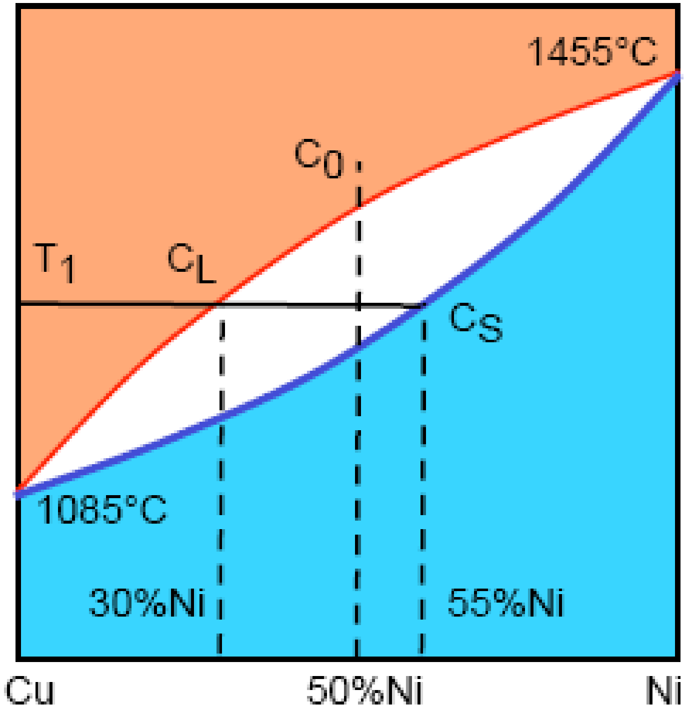
Read from the tie line:
Liquid phase: Cu-30%Ni
α-phase: Cu-55%Ni

$$W_L = \frac{C_s - C_o}{C_s - C_L} = \frac{55-50}{55-30} = 0.2 = 20\%$$

$$W_\alpha = \frac{C_o - C_L}{C_s - C_L} = \frac{50-30}{55-30} = 0.8 = 80\%$$

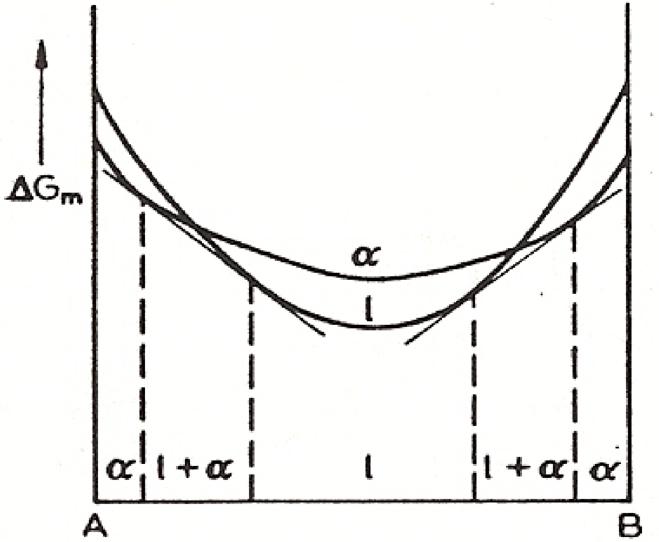
or

$$W_\alpha = 1 - W_L = 1 - 0.2 = 0.8 = 80\%$$

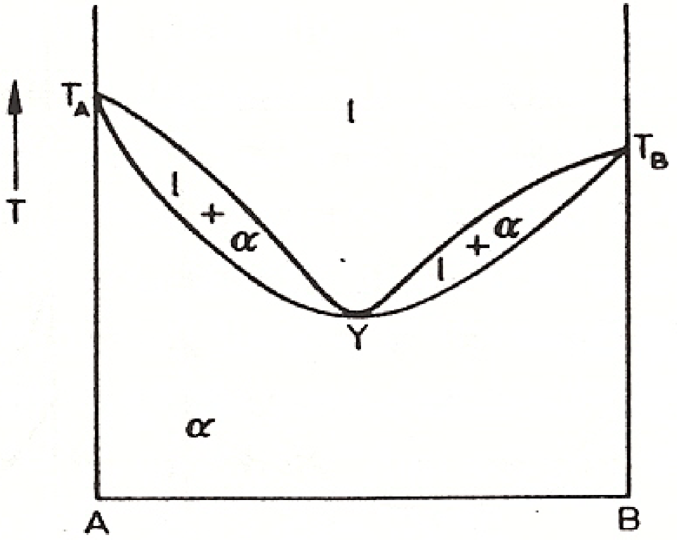


2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$$



(a)



(b)

2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$$

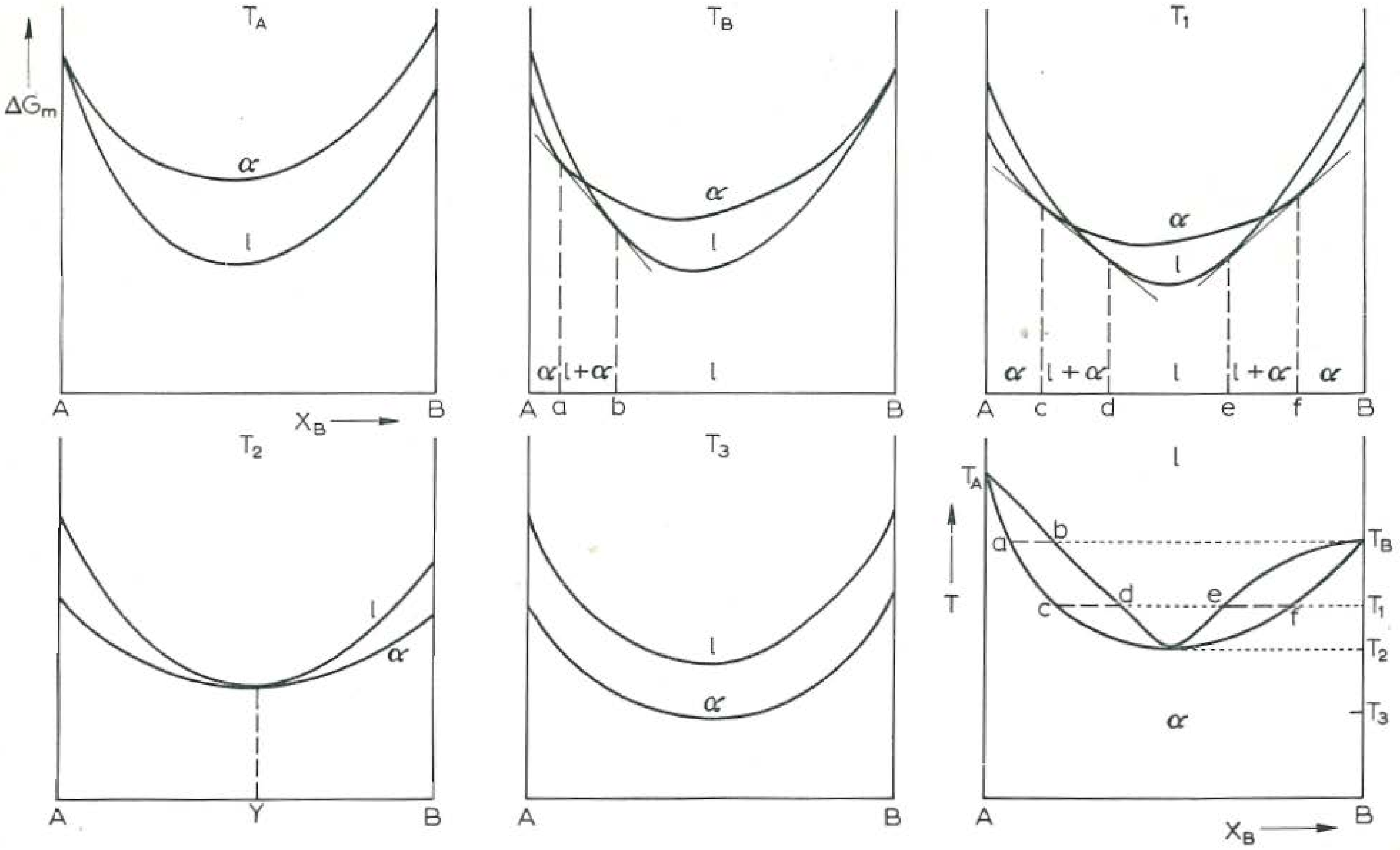
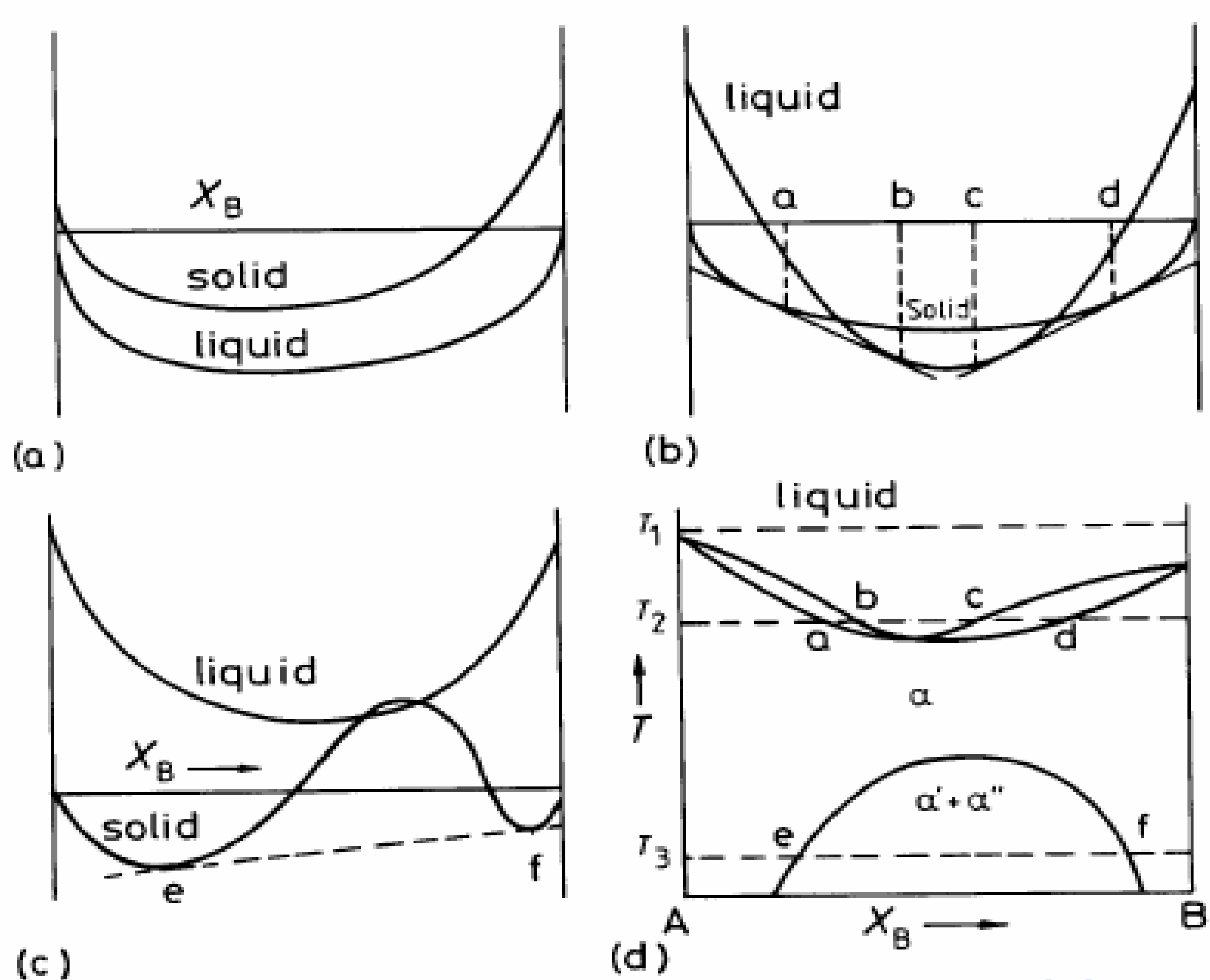


Fig. 30. Derivation of the phase diagram (Fig. 29b) from free energy curves for the liquid and solid phases. $T_A > T_B > T_1 > T_2 > T_3$.

2) Variant of the simple phase diagram

Systems with miscibility gab $\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$



congruent minima

2) Variant of the simple phase diagram

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

$$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$$

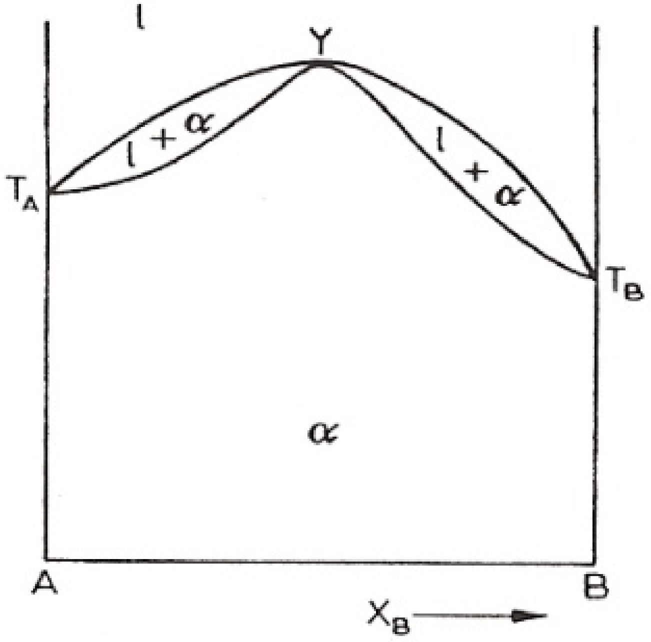


Fig. 32. Phase diagram with a maximum in the liquidus.

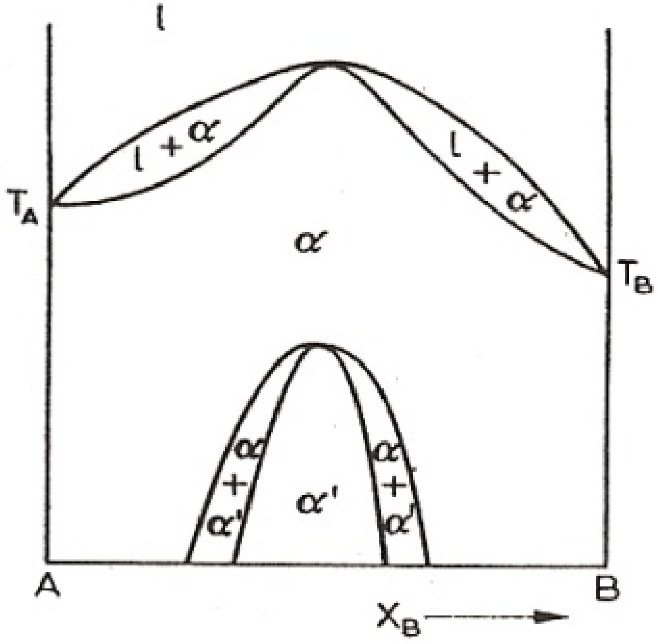


Fig. 33. Appearance of an ordered α′ phase at low temperatures.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

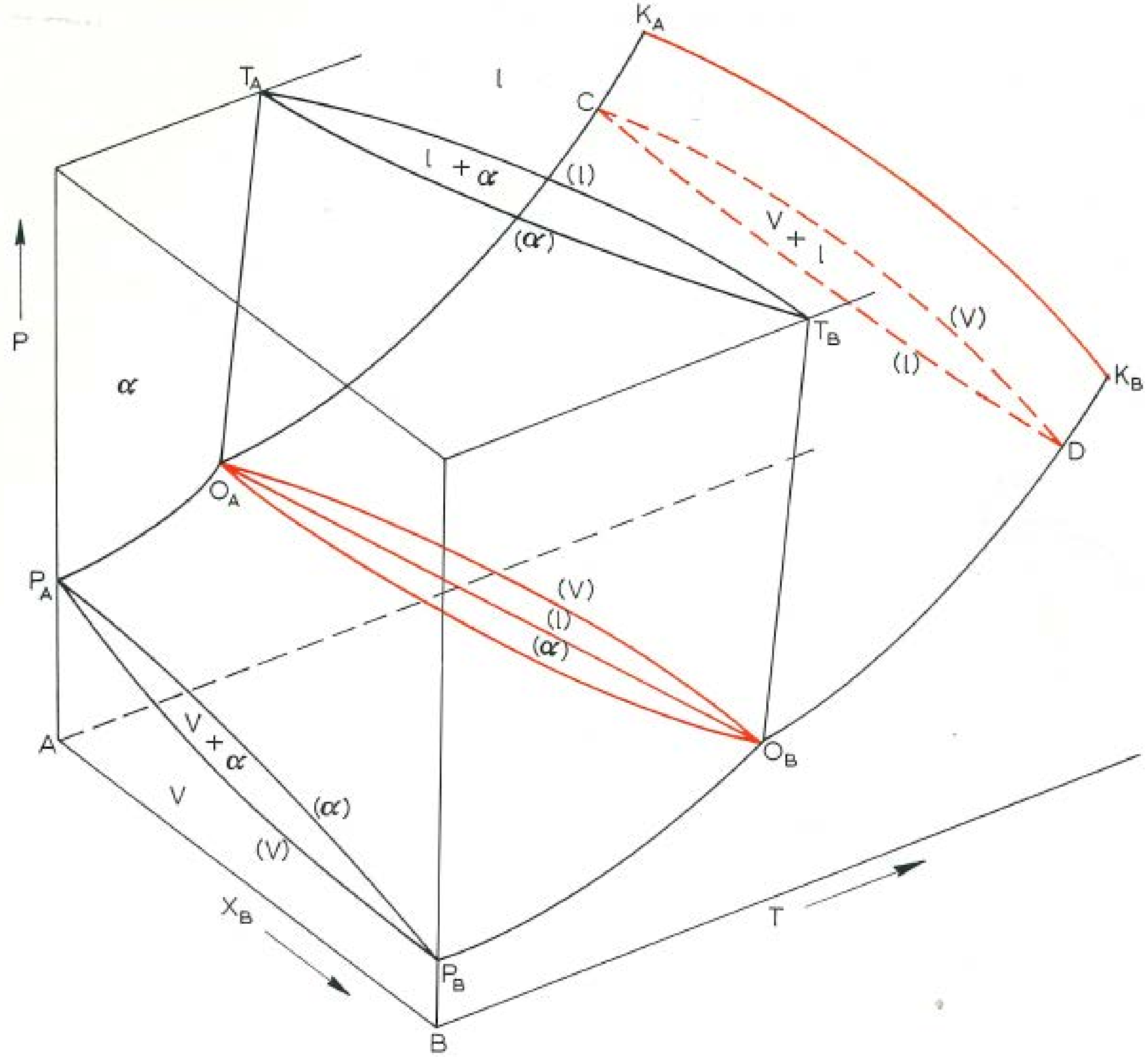


Fig. 35. Pressure–temperature–composition phase diagram for a system with continuous series of solutions

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

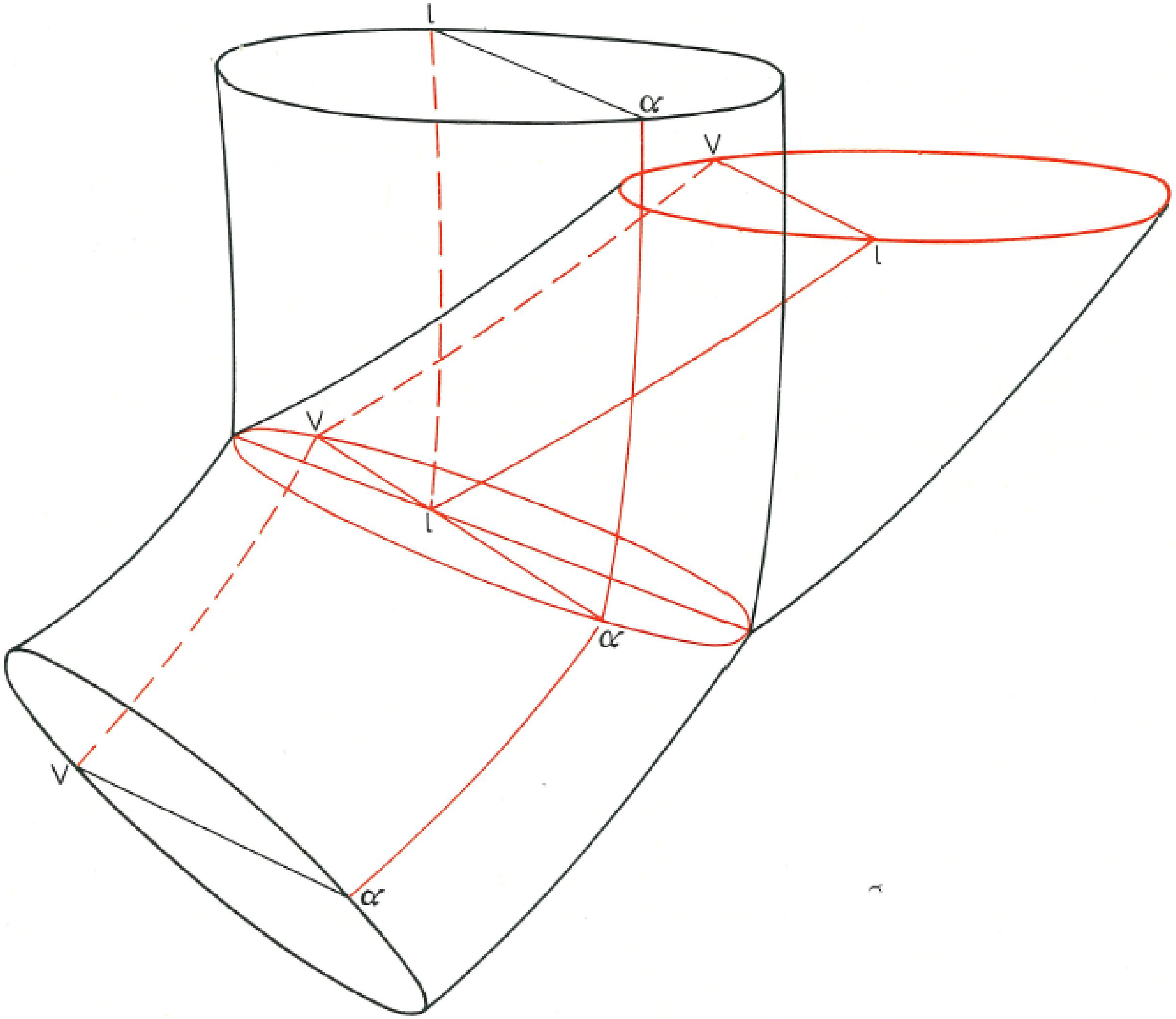


Fig. 36. Formation of a three-phase tie line *Vlα*.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

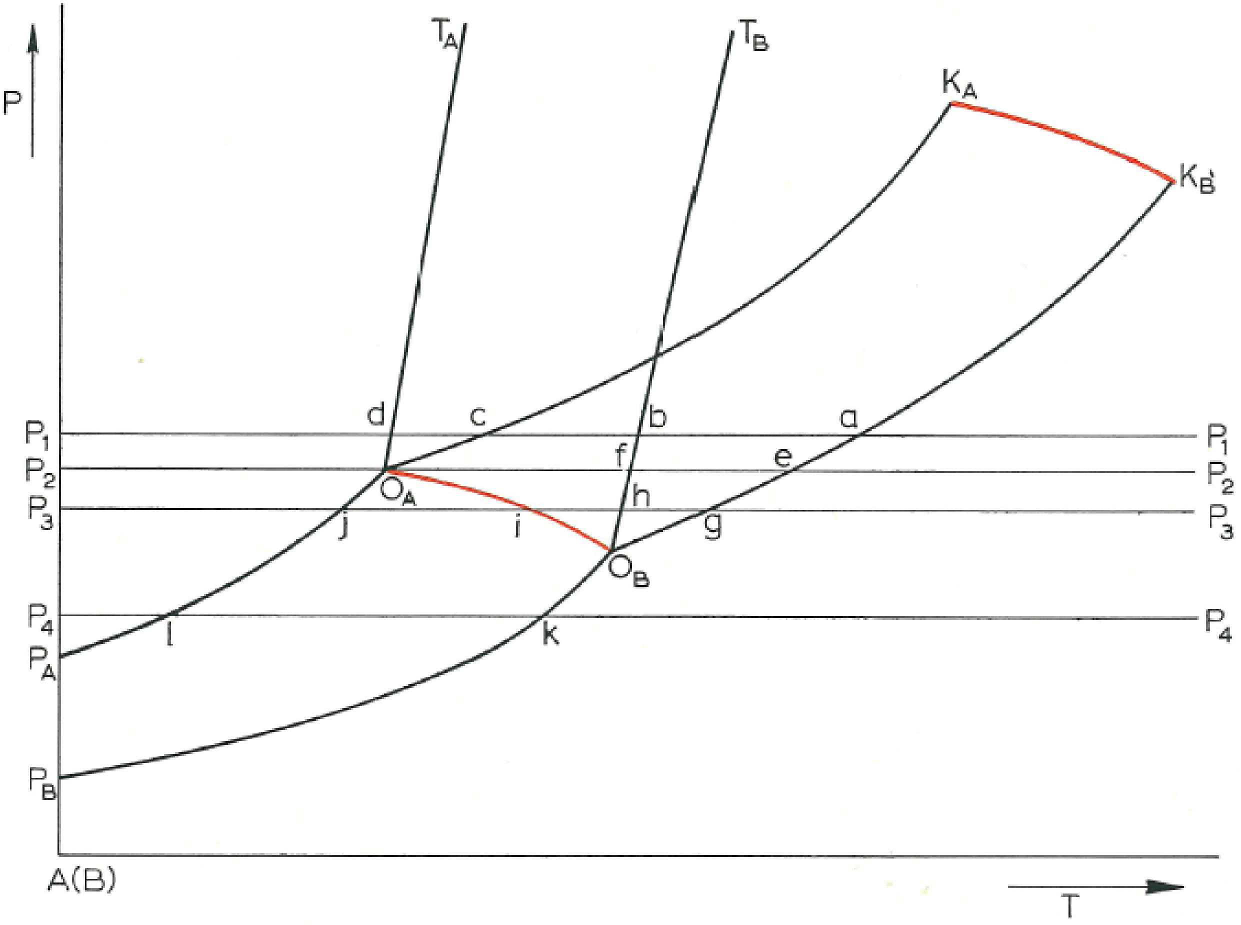


Fig. 37. Two-dimensional projection of Fig. 35 on the P–T plane for component A. P_AO_A — equilibrium between V_A and α_A; P_BO_B — V_B and α_B; O_AT_A — l_A and α_A; O_BT_B — l_B and α_B; O_AK_A — V_A and l_A; O_BK_B — V_B and l_B; O_AO_B — V_{AB}, l_{AB} and α_{AB}; O_A — V_A, l_A and α_A; O_B — V_B, l_B and α_B; K_AK_B — $V_{AB} = l_{AB}$.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

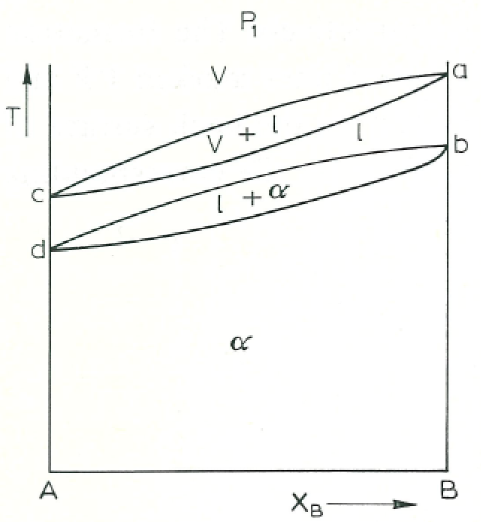


Fig. 38. *T–X* section through Fig. 35 at a pressure P_1 where $K_B > P_1 > O_A$.

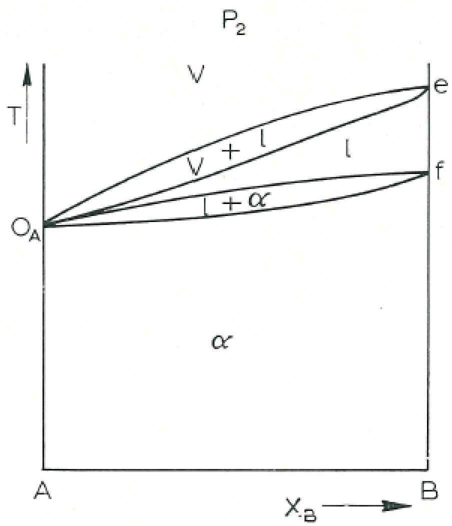


Fig. 39. *T–X* section through Fig. 35 at a pressure P_2 where $P_2 = O_A$

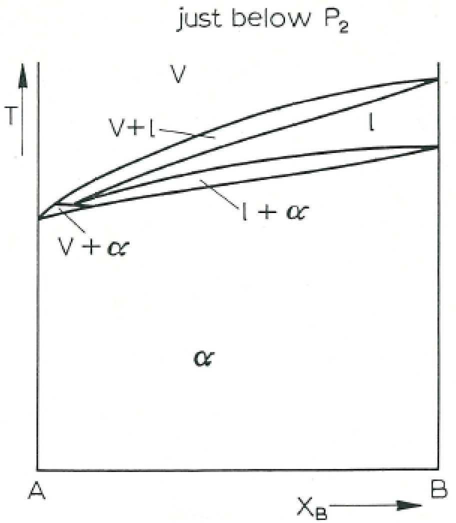


Fig. 40. *T–X* section through Fig. 35 at a pressure just below P_2.

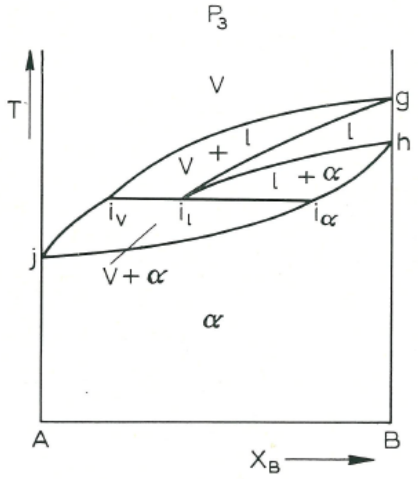


Fig. 41. *T–X* section through Fig. 35 at a pressure P_3 where $O_A > P_3 > O_B$.

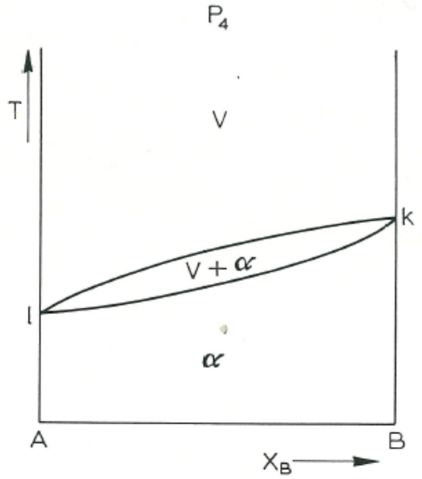


Fig. 42. *T–X* section through Fig. 35 at a pressure P_4 where $O_B > P_4 > P_B$.

Contents for today's class

- Equilibrium in Heterogeneous Systems

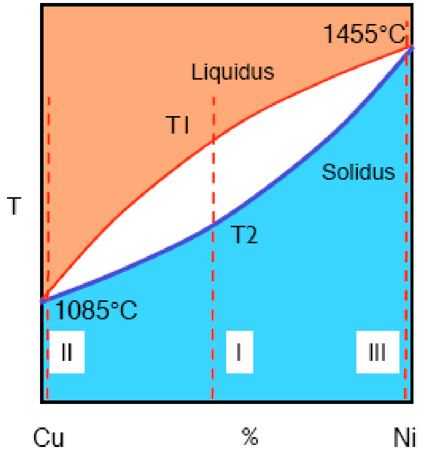
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ ⇨ **α + β separation** ⇨ **unified chemical potential**

- Binary phase diagrams

1) Simple Phase Diagrams

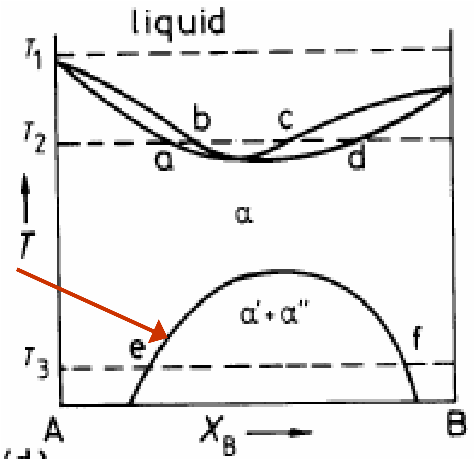
$\Delta H^{L}_{mix} = 0 \ \Delta H^{S}_{mix} = 0$

Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$



miscibility gab

$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

Ordered phase