2018 Fall

"Phase Transformation *in* Materials"

09.13.2018

Eun Soo Park

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

Contents for previous class

- 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

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

dn_A~ small enough (∵ μ_A depends on the composition of phase)

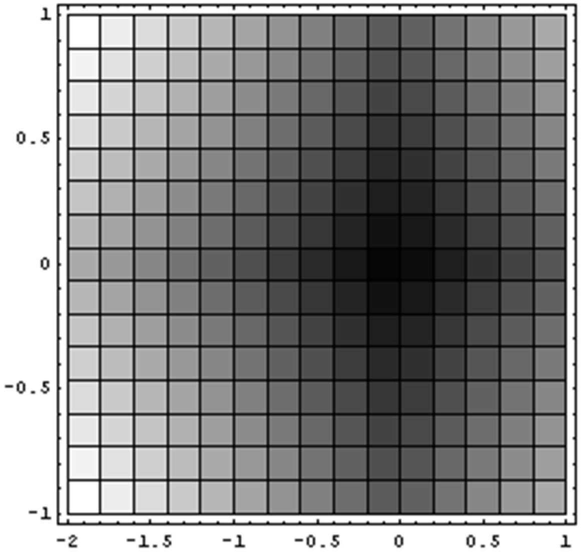
- $\mu_A = G_A + RT\ln a_A$

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

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

1.3 Binary Solutions

1) Ideal solution



$G = H - TS = E + PV - TS$

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to μ_A.

➡ dn_A~ small enough
(∵ μ_A depends on the composition of phase)

$$\boxed{dG' = \mu_A dn_A}$$

(T, P, n_B: constant)

μ_A : **partial molar free energy of A or chemical potential of A**

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

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

1.3 Binary Solutions

1) Ideal solution

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

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

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

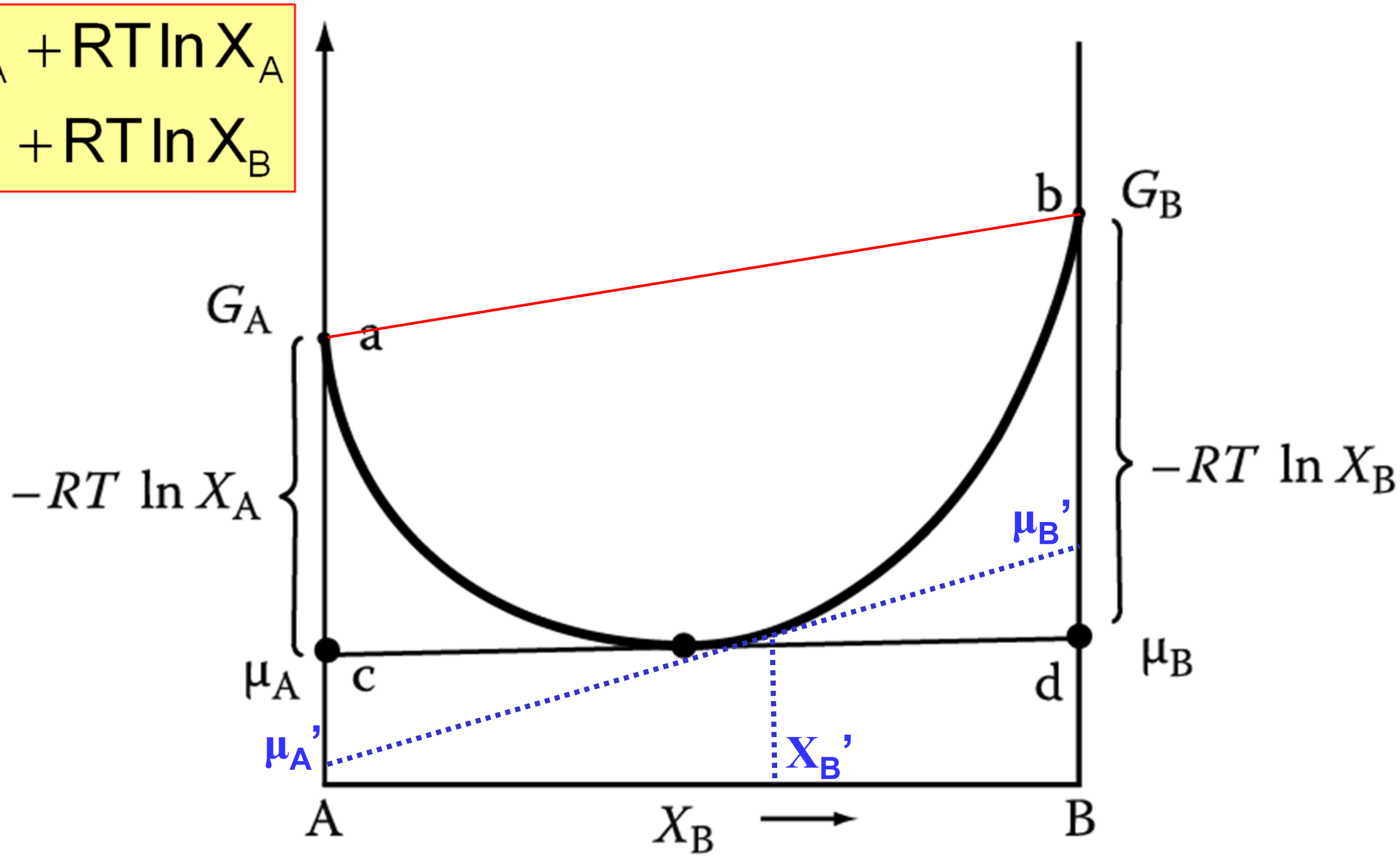


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

Contents for today's class II

- Ideal Solution/ Regular Solution/ Real solution

Q1: What is "Regular Solution"?

1.3 Binary Solutions

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

Regular Solutions

Ideal solution : $\Delta H_{mix} = 0$ ⇨ This type of behavior is exceptional in practice and usually mixing is endothermic or exothermic.

Quasi-chemical model assumes that heat of mixing, ΔH_{mix}, is only due to the bond energies between adjacent atoms.

Assumption: the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are independent of composition.

Structure model of a binary solution

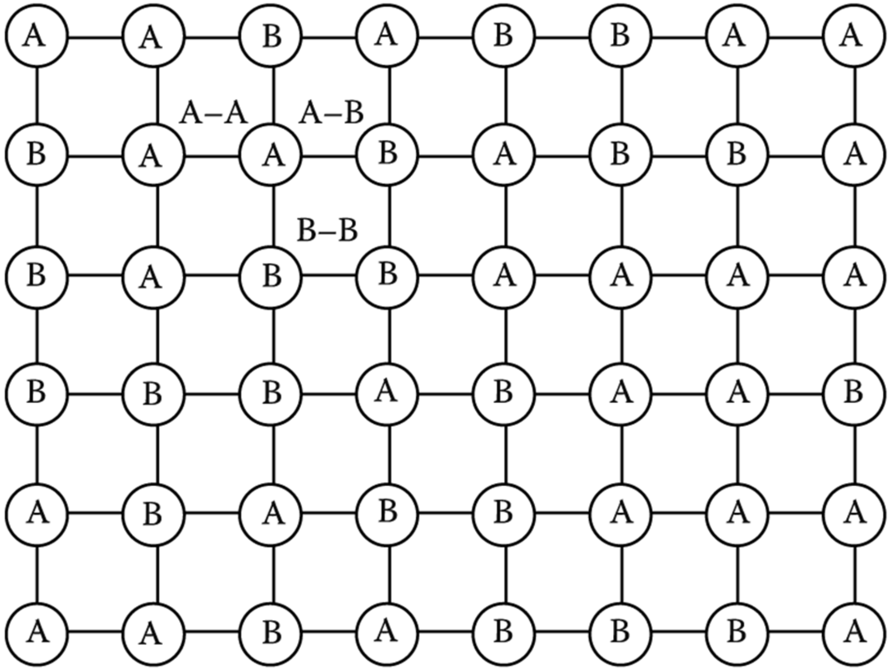


Fig. 1.13 The different types of interatomic bond in a solid solution.

Gibbs Free Energy of Regular Solutions

Q2: How can you estimate "ΔH_{mix} of regular solution"?

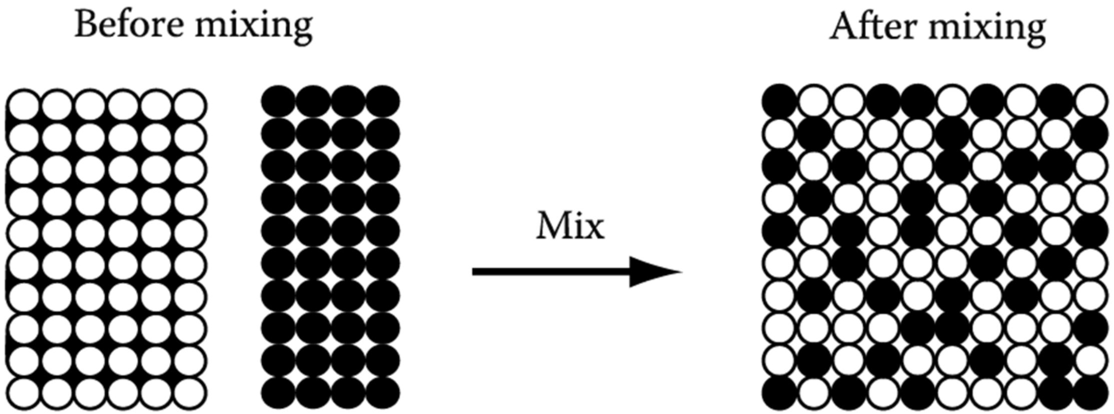
$$\boxed{\Delta H_{mix} = \Omega X_A X_B \quad \text{where} \quad \Omega = N_a z \varepsilon}$$

Regular Solutions

	Bond energy	Number of bond
A-A	ε_{AA}	P_{AA}
B-B	ε_{BB}	P_{BB}
A-B	ε_{AB}	P_{AB}

Internal energy of the solution

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$



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

Regular Solutions

Completely random arrangement

$\varepsilon = 0$ ➡ $\varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

$\Delta H_{mix} = 0$ ideal solution

$\Delta S^{mix} = -R(X_A \ln X_A + X_B \ln X_B)$

$P_{AB} = N_a z X_A X_B$ bonds per mole

N_a : Avogadro's number

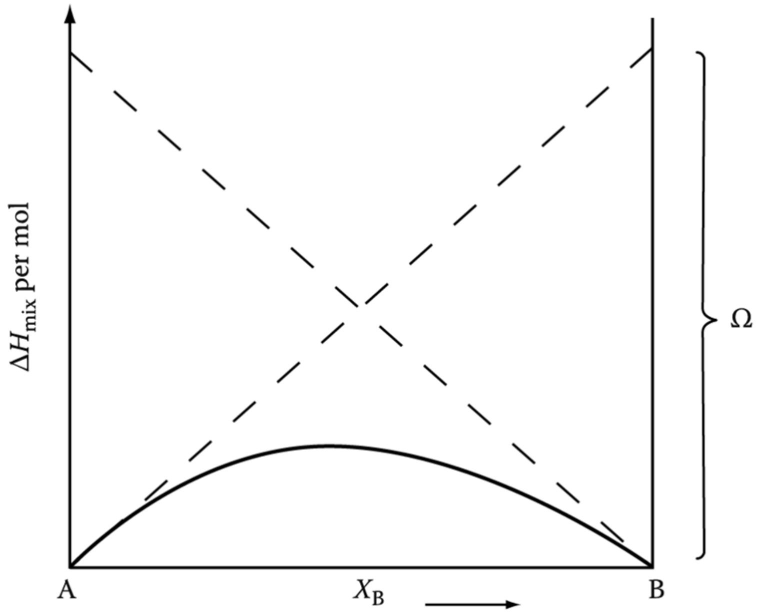
z : number of bonds per atom

(1) $\varepsilon < 0 \rightarrow P_{AB} \uparrow$ (2) $\varepsilon > 0 \rightarrow P_{AB} \downarrow$

(3) $\boxed{\varepsilon \approx 0}$ ➡ $\Delta H_{mix} = P_{AB}\varepsilon$

$$\boxed{\Delta H_{mix} = \Omega X_A X_B \text{ where } \Omega = N_a z \varepsilon}$$

Regular solution



If Ω >0,

Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.

Gibbs Free Energy of Regular Solutions

Q3: How can you estimate
“Molar Free energy for regular solution”?

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

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

Regular Solutions

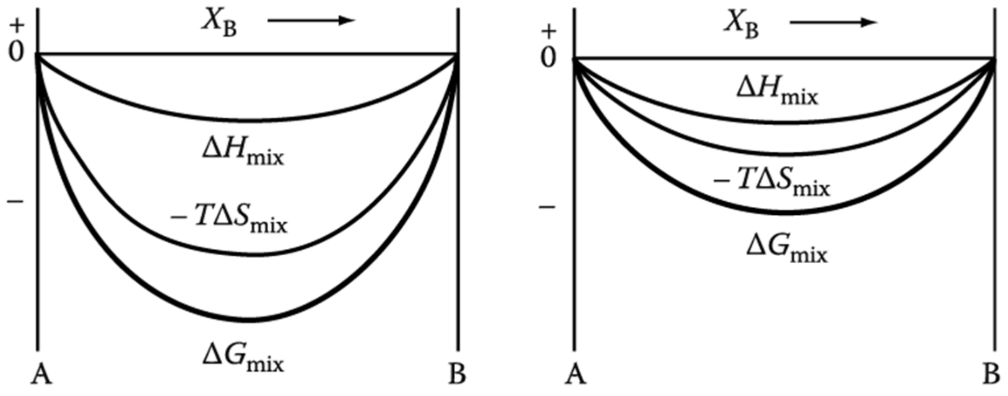
$$G_2 = G_1 + \Delta G_{mix}$$

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

Reference state

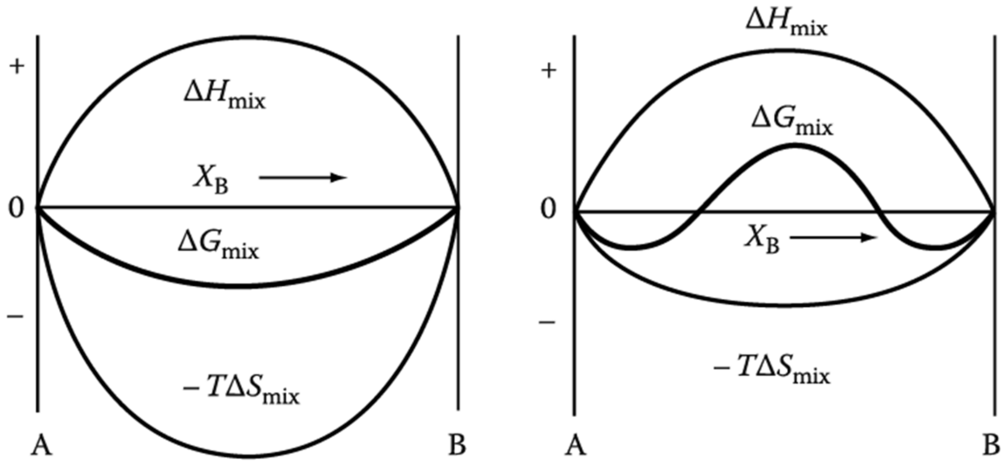
Pure metal $G_A^0 = G_B^0 = 0$

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



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

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



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

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

Q4: “Correlation between chemical potential and free energy”?

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

$G = E + PV - TS$ $$G = \mu_A X_A + \mu_B X_B \quad \mathrm{Jmol}^{-1}$$

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

$$\longrightarrow \quad X_A X_B = X_A X_B (X_A + X_B) = X_A^2 X_B + X_B^2 X_A$$

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

Regular solution

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

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

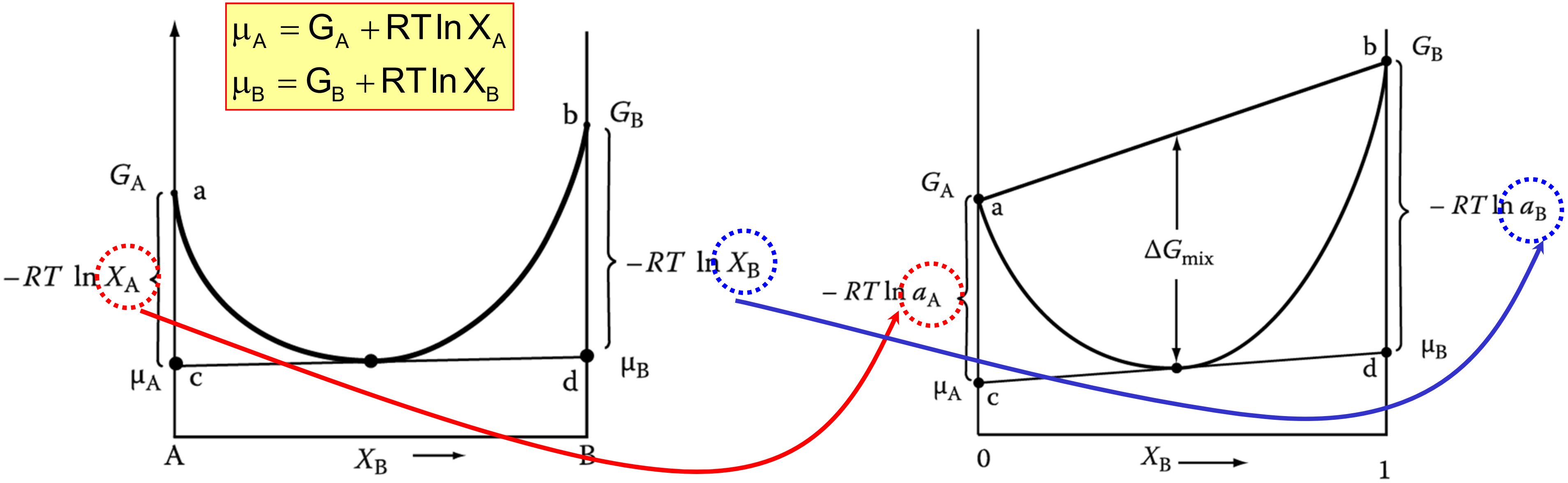
Ideal solution

Q5: What is “activity”?

Activity, a : effective concentration for mass action

ideal solution

regular solution



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

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

$$\mu_B = G_B + RT\ln a_B$$

$$\mu_A = G_A + \Omega\,(1 - X_A)^2 + RT\ \ln\ X_A$$

$$\mu_B = G_B + \Omega\,(1 - X_B)^2 + RT\ \ln\ X_B$$

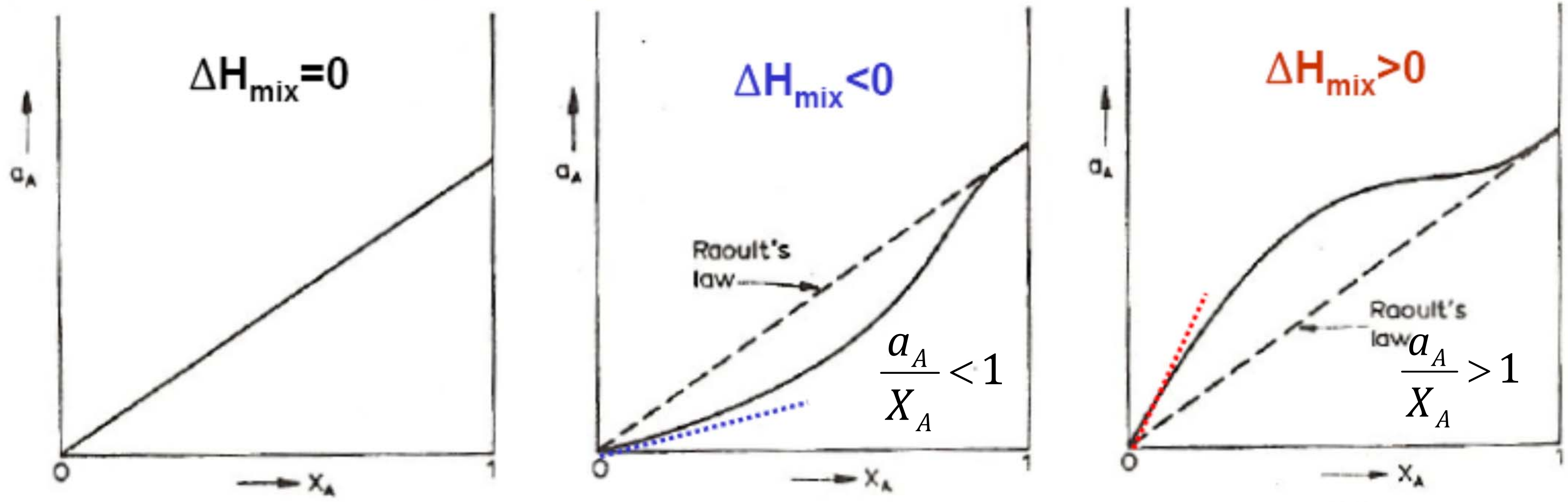
$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

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

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

$$\gamma_B = \frac{a_B}{X_B}$$

Activity-composition curves for solutions



(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
$a_A = a_{Cd}$

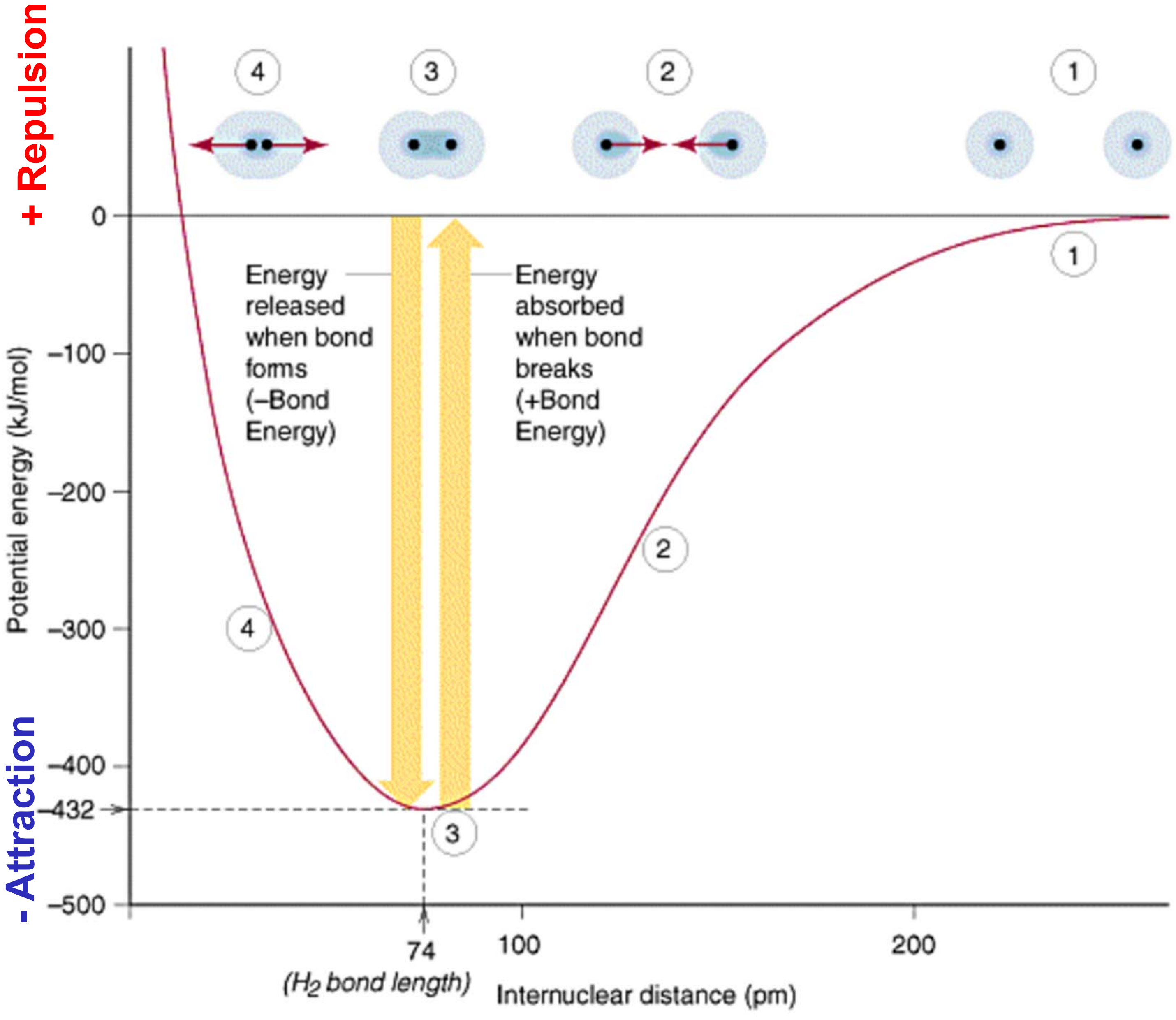
Degree of non-ideality

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

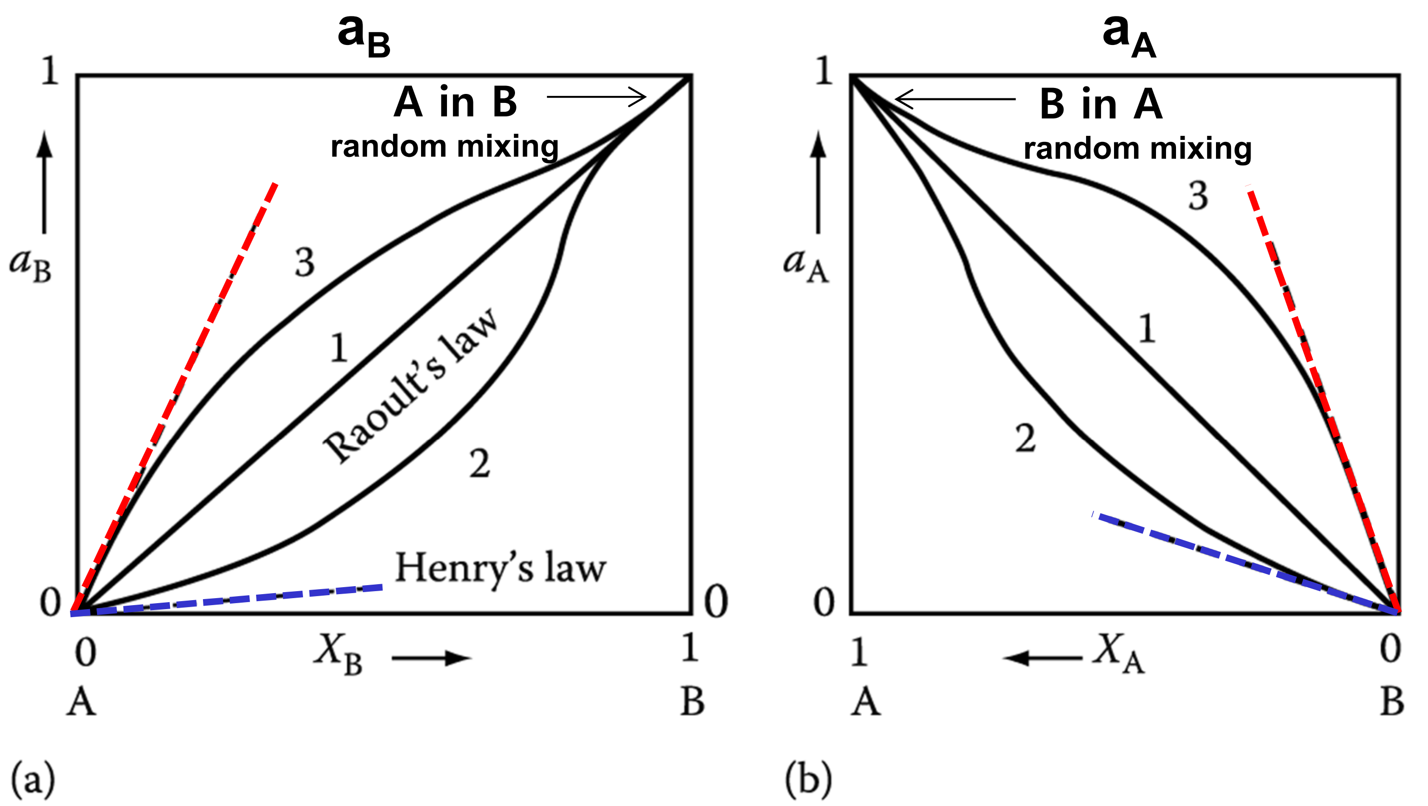
$$\gamma_B = \frac{a_B}{X_B} \cong \text{constant} \quad \text{(Henry's Law)}$$

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

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



Variation of activity with composition (a) a_B, (b) a_A



Line 1 : (a) $a_B=X_B$, (b) $a_A=X_A$ ideal solution…Rault's law

Line 2 : (a) $a_B<X_B$, (b) $a_A<X_A$ $\Delta H_{mix}<0$

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

Line 3 : (a) $a_B>X_B$, (b) $a_A>X_A$ $\Delta H_{mix}>0$

Q6: “Chemical equilibrium of multi-phases”?

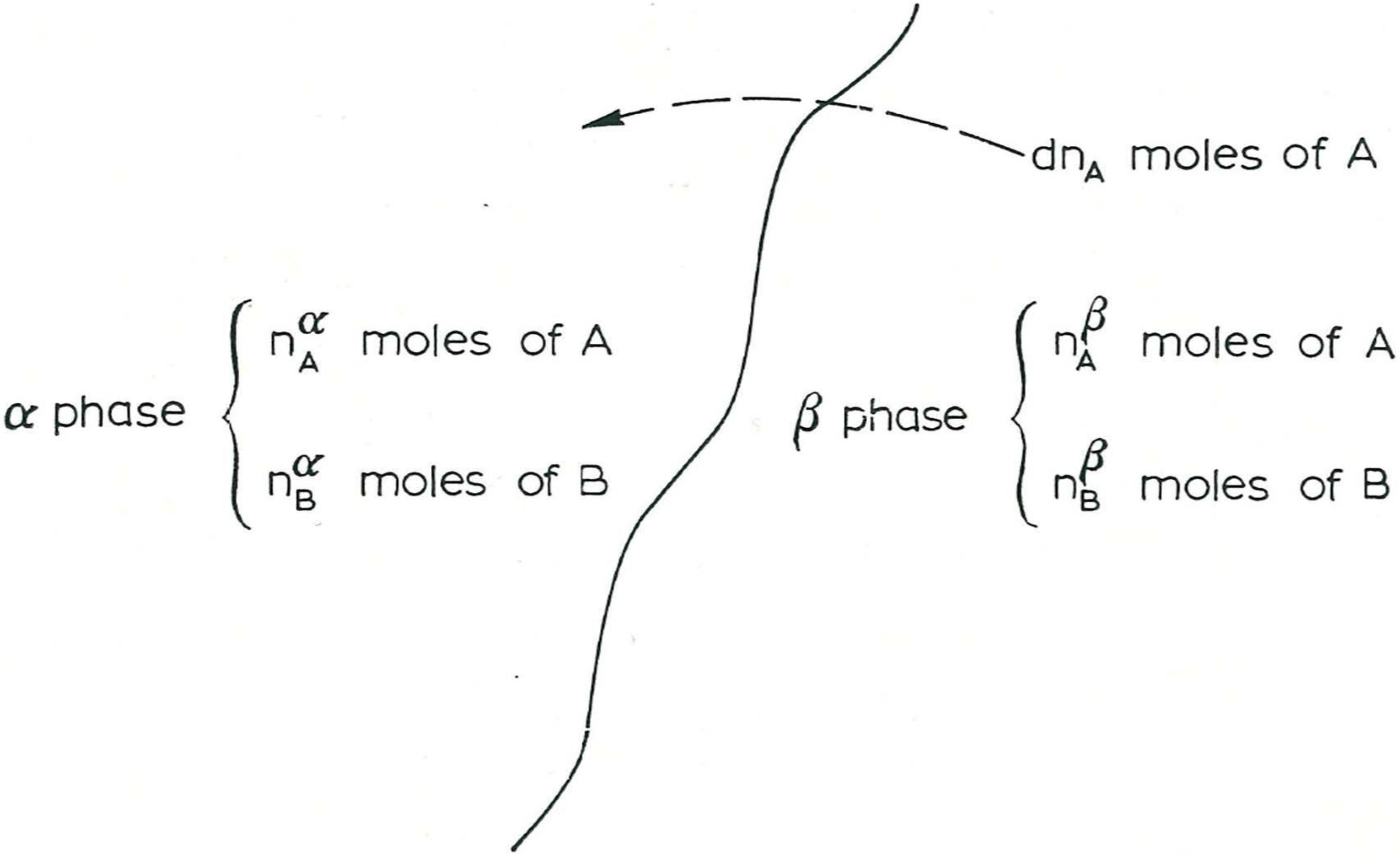


Fig. 10. Transfer of dn_A moles of component A from the β to the α phase.

Activity of a component is just another means of describing the state of the component in a solution.

degree of non-ideality ? $\rightarrow \dfrac{a_A}{X_A}$

$$\frac{a_A}{X_A} = \gamma_A, \quad a_A = \gamma_A X_A$$

γ_A : activity coefficient

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

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

Activity or chemical potential of a component is important when several condensed phases are in equilibrium.

Chemical Equilibrium (μ, a) → multiphase and multicomponent

$$(\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \ldots), (a_i^\alpha = a_i^\beta = a_i^\gamma = \ldots)$$

$$(\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \ldots), (a_A^\alpha = a_A^\beta = a_A^\gamma = \ldots)$$

$$(\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \ldots), (a_B^\alpha = a_B^\beta = a_B^\gamma = \ldots)$$

⋮

- 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

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

μ는 조성에 의해 결정되기 때문에 dn_A가 매우 작아서 조성변화 없어야

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

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

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

Contents for today's class II

- Ideal Solution/ Regular Solution/ Real solution

Q7: What is “Real Solution”?

sufficient disorder + lowest internal E

1.3 Binary Solutions

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

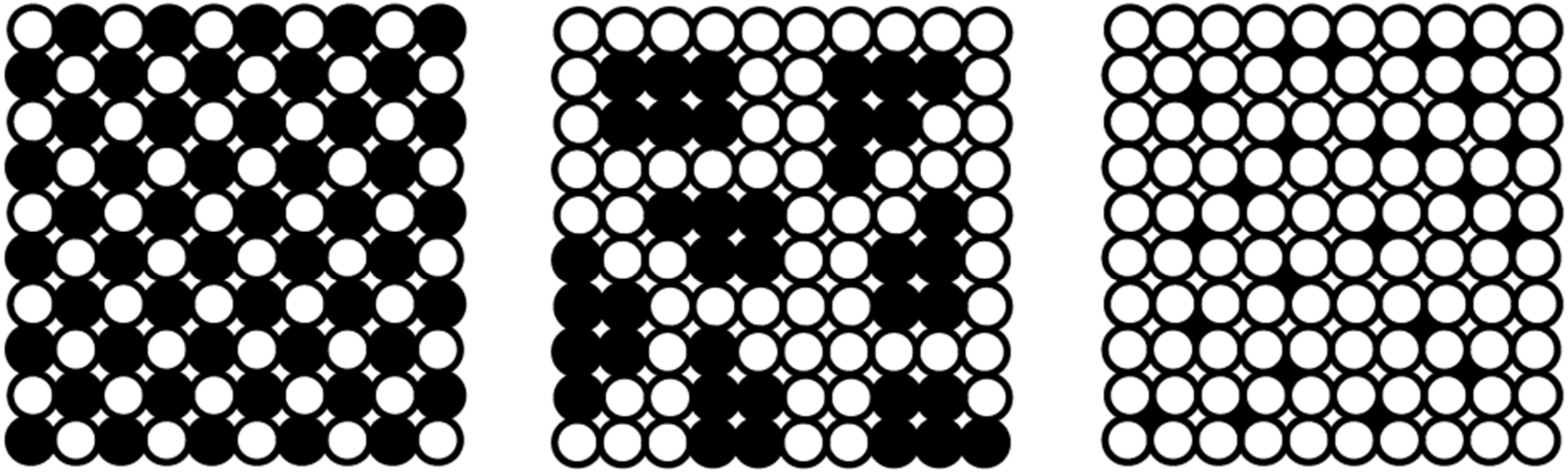
Real solution: sufficient disorder + lowest internal E

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

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

Clustering

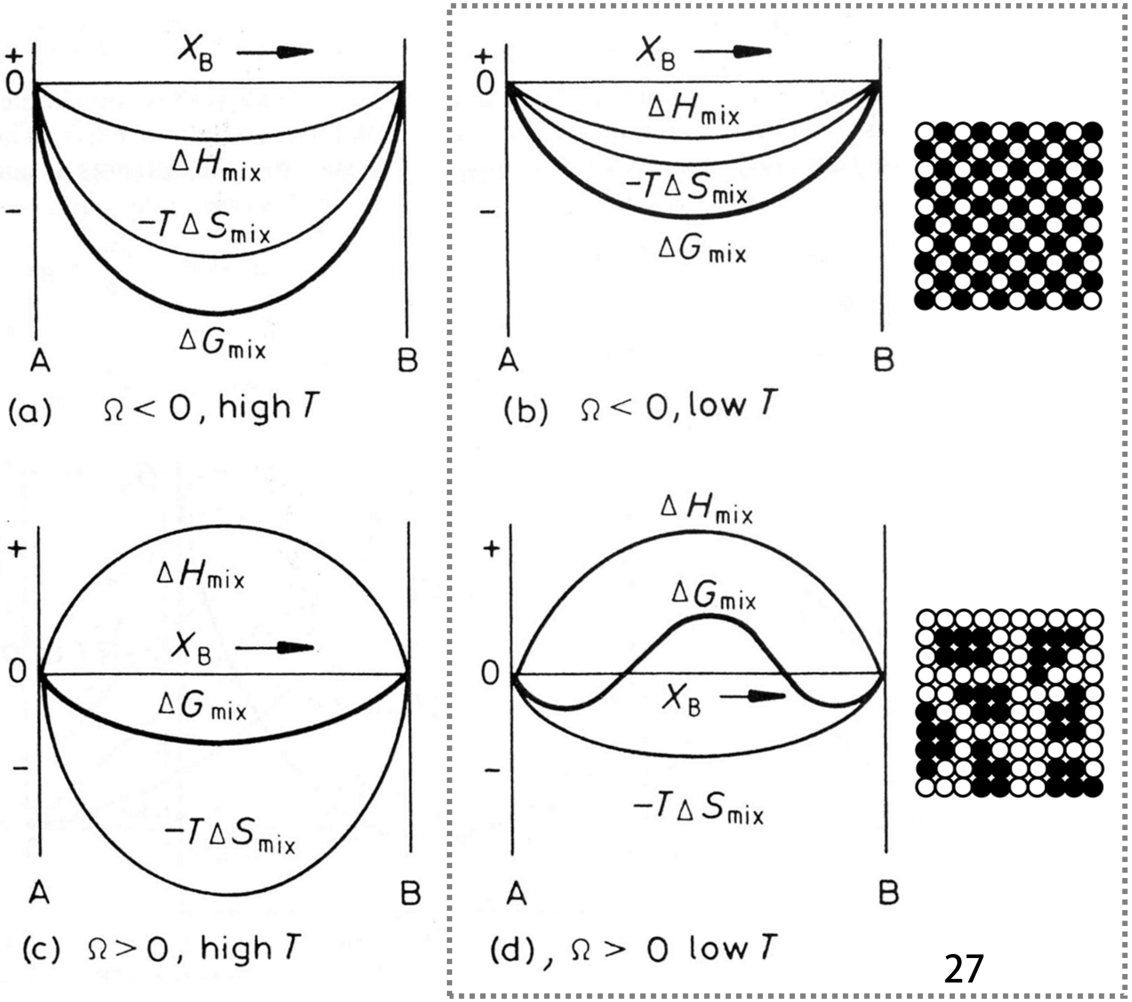
$P_{AA}, P_{BB} \uparrow$

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 ↑

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



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

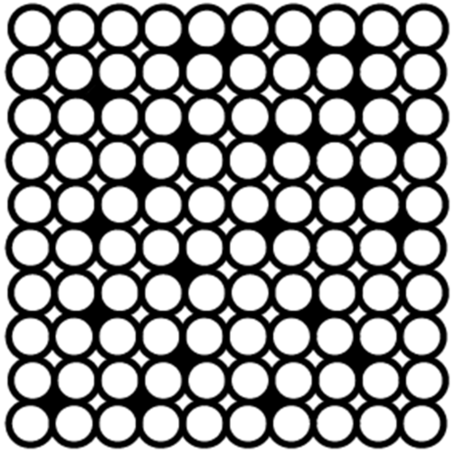
(b) $\Omega < 0$, low T

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

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

Real solution: sufficient disorder + lowest internal E

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



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

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

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

Q8: Ordered phase I:

“Short range order (SRO)” in solution

1.3 Binary Solutions

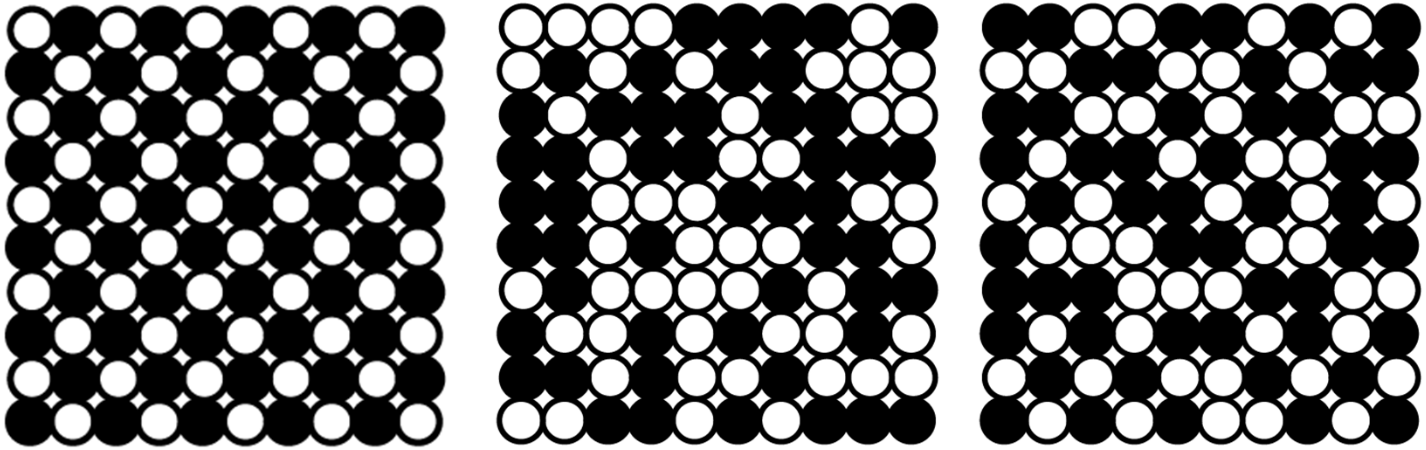
Ordered phase $\varepsilon < 0, \ \Delta H_{mix} < 0$ P_{AB} ↑

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

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

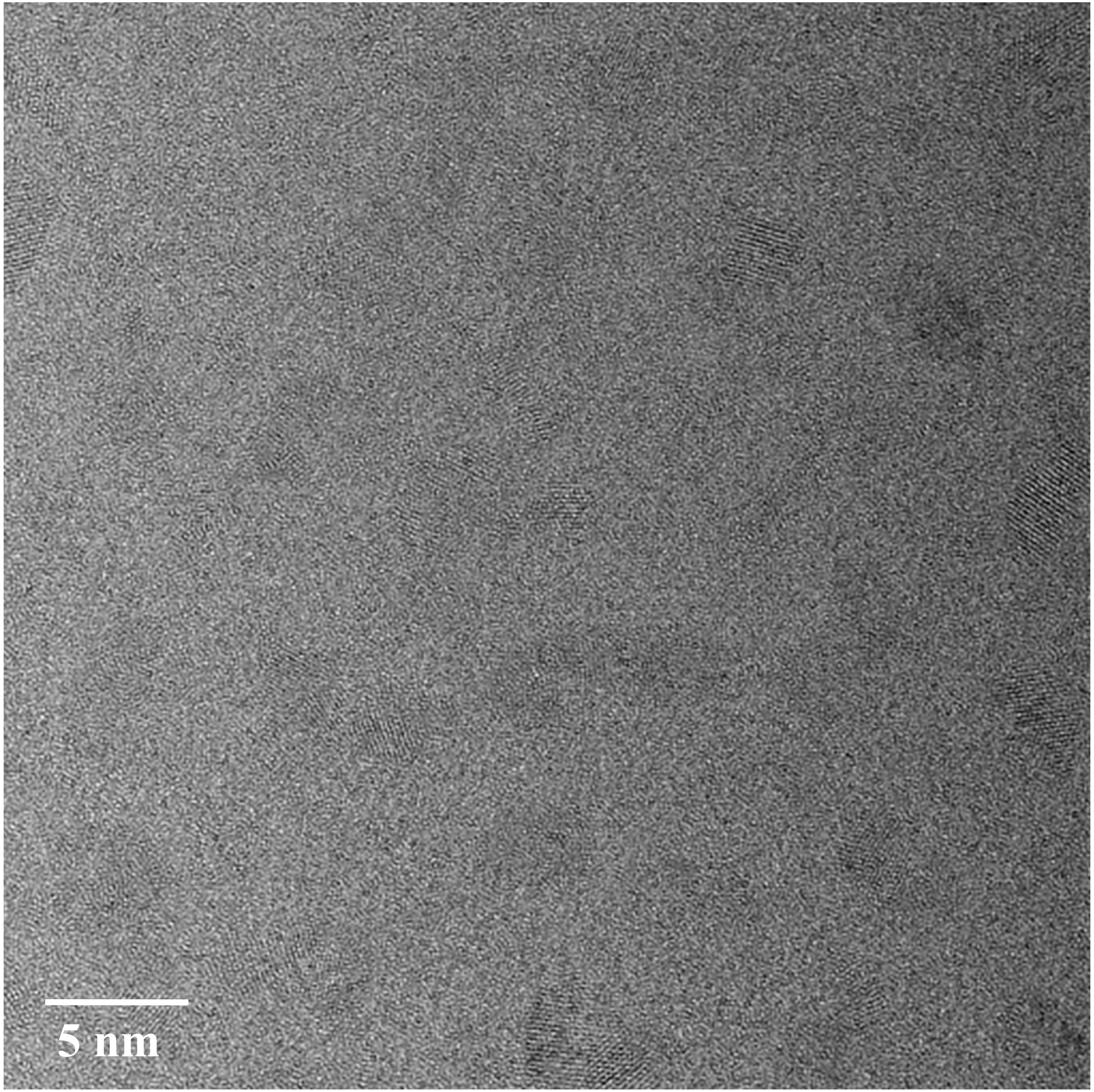
$\Delta\Omega = N_a z\varepsilon$ **SRO parameter = s _ degree of ordering**

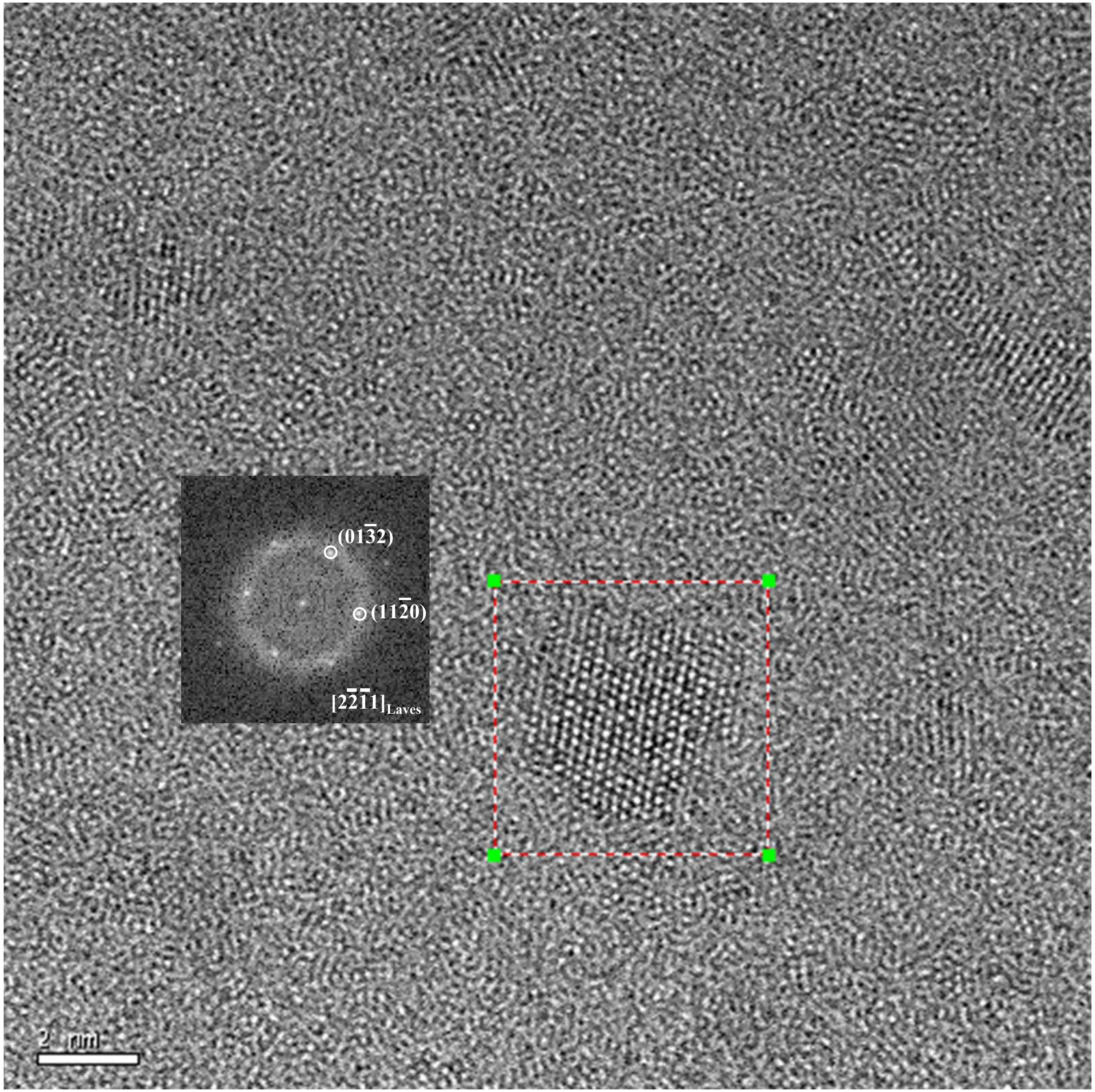
$$s = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$



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}~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}$1]$_{\text{Laves}}$
2 nm

Q9: Ordered phase II:

“Long range order (LRO)”

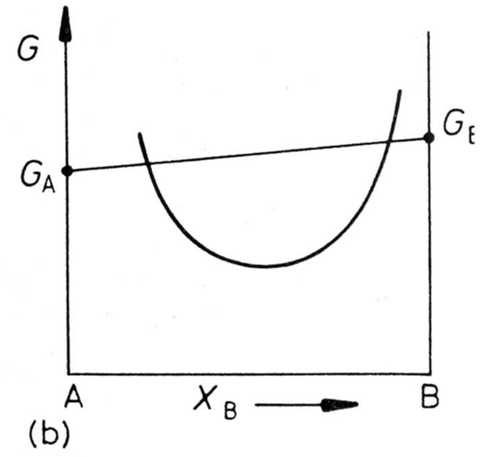
(①superlattice, ②intermediate phase, ③intermetallic compound)

*** Solid solution → ordered phase**

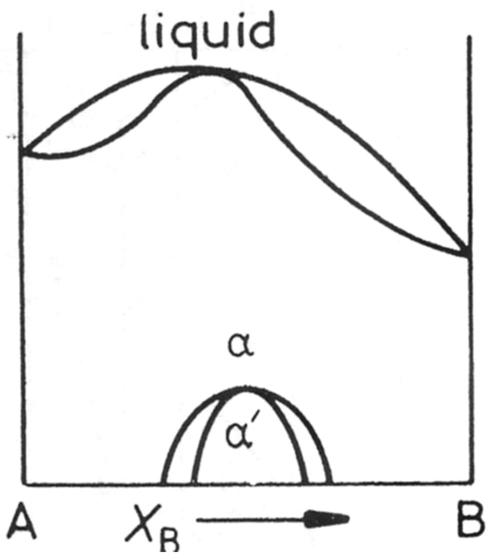
- → random mixing
- → entropy ↑
  negative enthalpy ↓

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

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 ↓

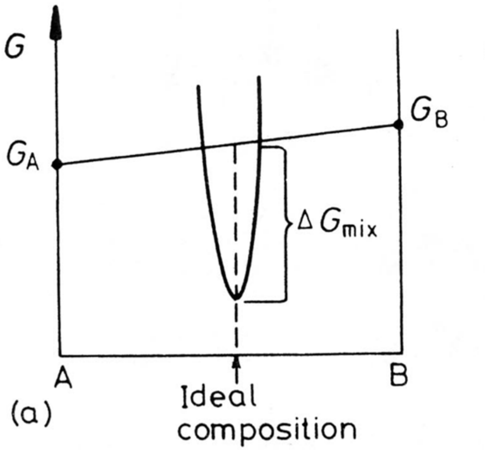
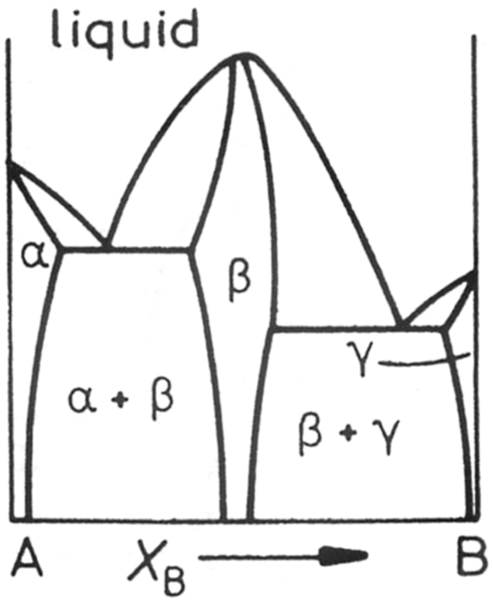


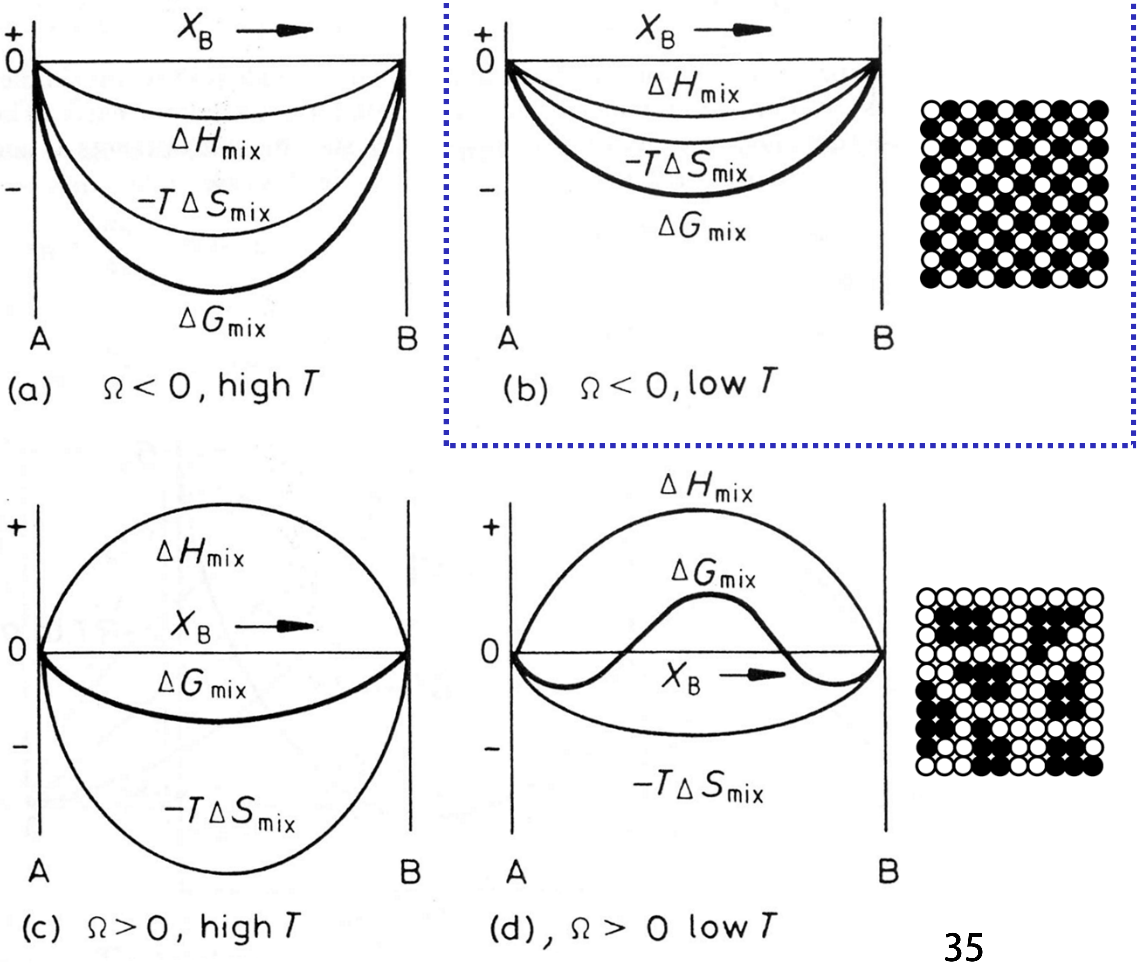
Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



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

High temp. ⟶ Entropy effect ↑ ⟶ Solution stability ↑

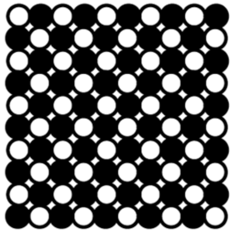
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



Q9-a: Superlattice

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.

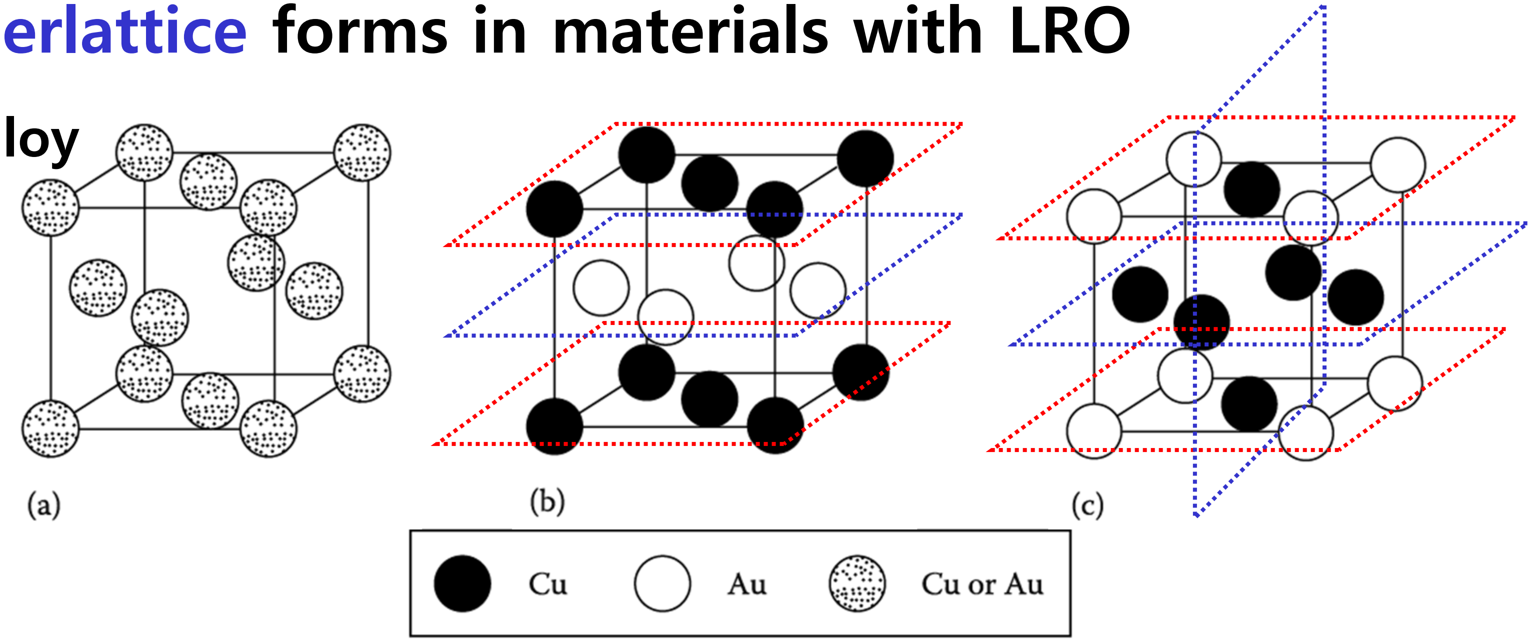


* This is known as **long-range order (LRO)** CuAu, Cu_3Au and many other intermetallics show LRO.

(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

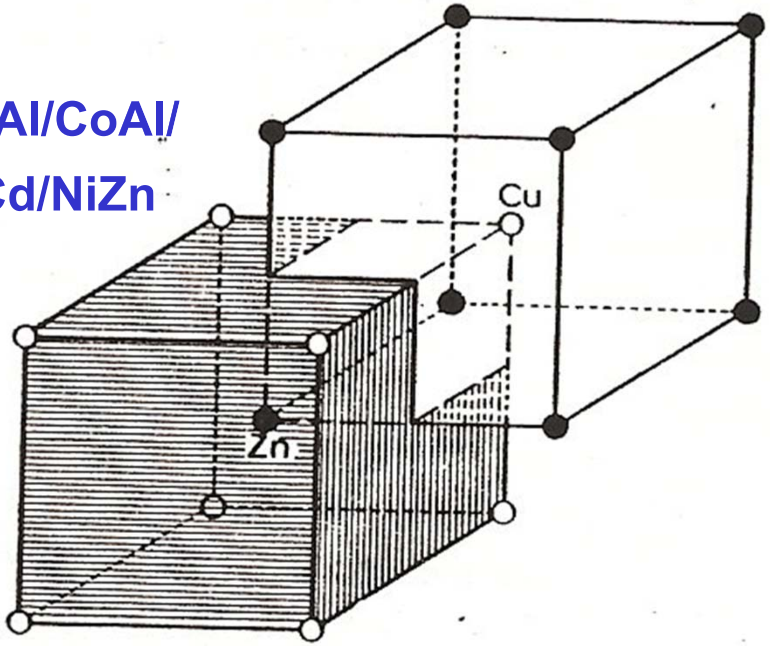
Cu_3Au superlattice

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)$L2_0$:

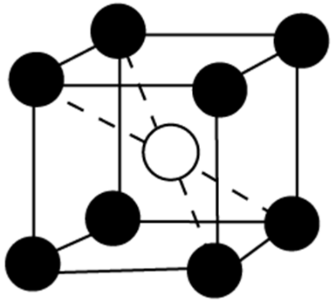
$CuZn/FeCo/NiAl/CoAl/FeAl/AgMg/AuCd/NiZn$

(b) $L1_2$:

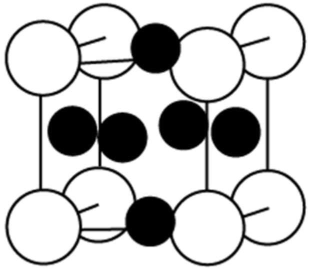
$Cu_3Au/Ni_3Mn/Ni_3Fe/Ni_3Al/Pt_3Fe/Au_3Cd/Co_3V/TiZn_3$

(c) $L1_0$:

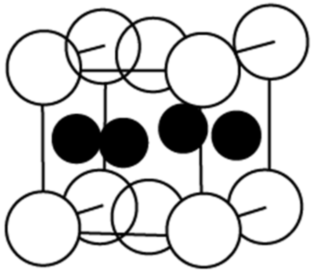
$CuAu/CoPt/FePt$



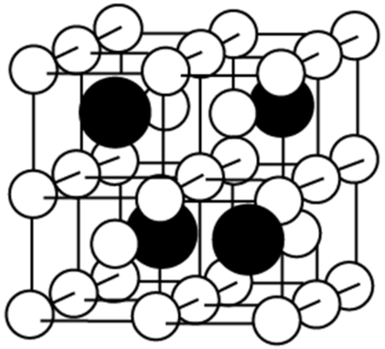
(a) ● Cu ○ Zn



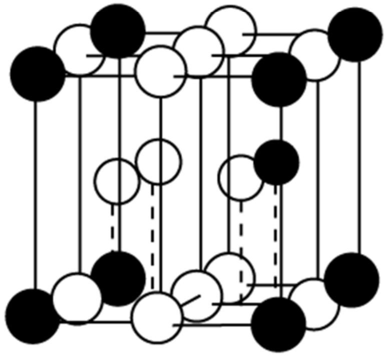
(b) ● Cu ○ Au



(c) ● Cu ○ Au



(d) ● Al ○ Fe



(e) ● Cd ○ Mg

(d) $D0_3$:

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

(e) $D0_{19}$:

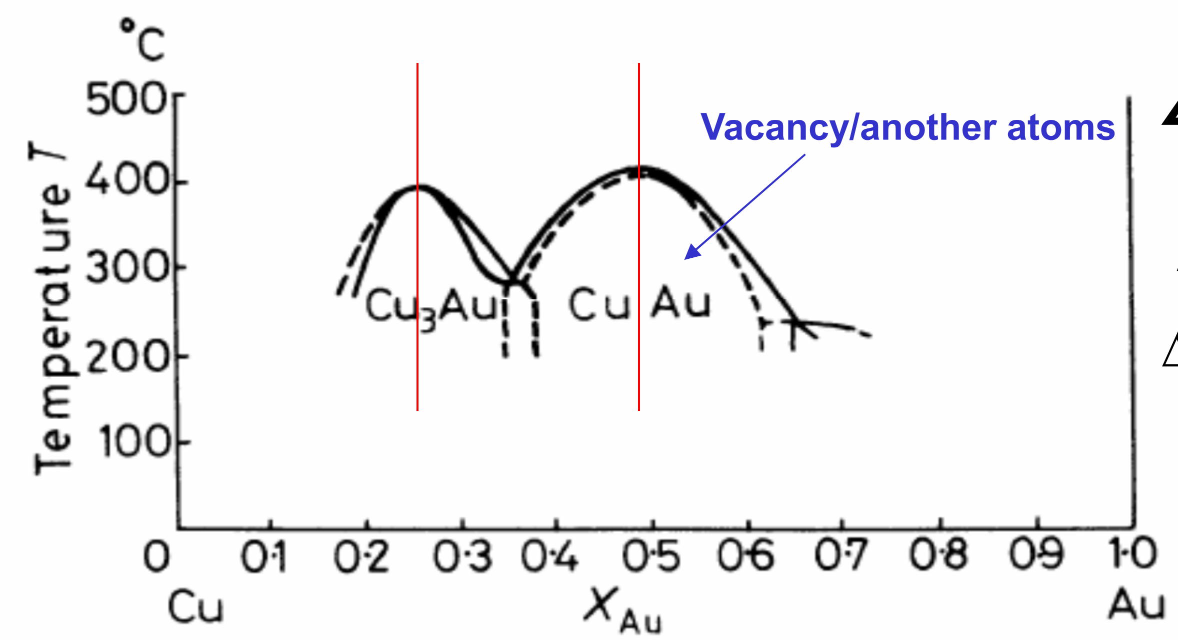
$Mg_3Cd/Cd_3Mg/Ti_3Al/Ni_3Sn/Ag_3In/Co_3Mo/Co_3W/Fe_3Sn/Ni_3In/Ti_3Sn$

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

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.



Vacancy/another atoms

$\Delta S_{mix} \sim small$

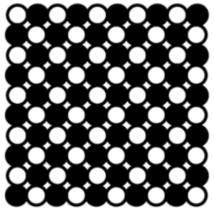
At high Temp.,

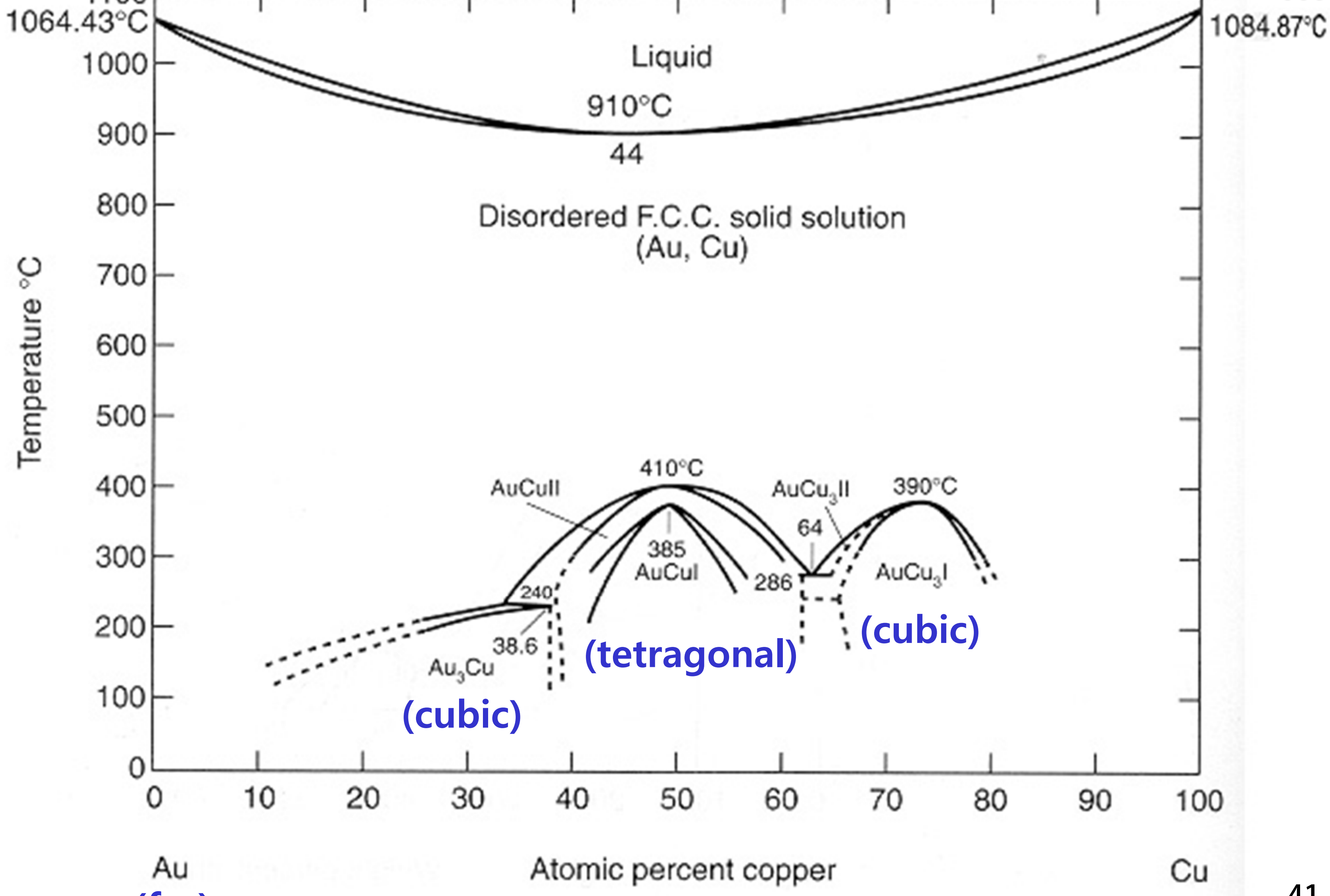
$\Delta G_{mix} \sim large\ (-)$

- **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





(fcc)

(complete solid solution)

(fcc)

Q9-b: Order-disorder transition

Order-disorder phase transformation

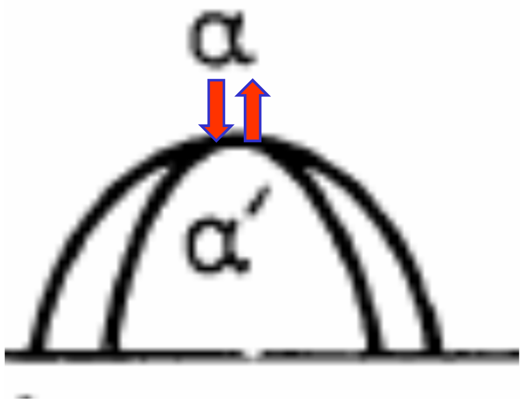
- Not classical phase change=~not depend on diffusion process

- 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

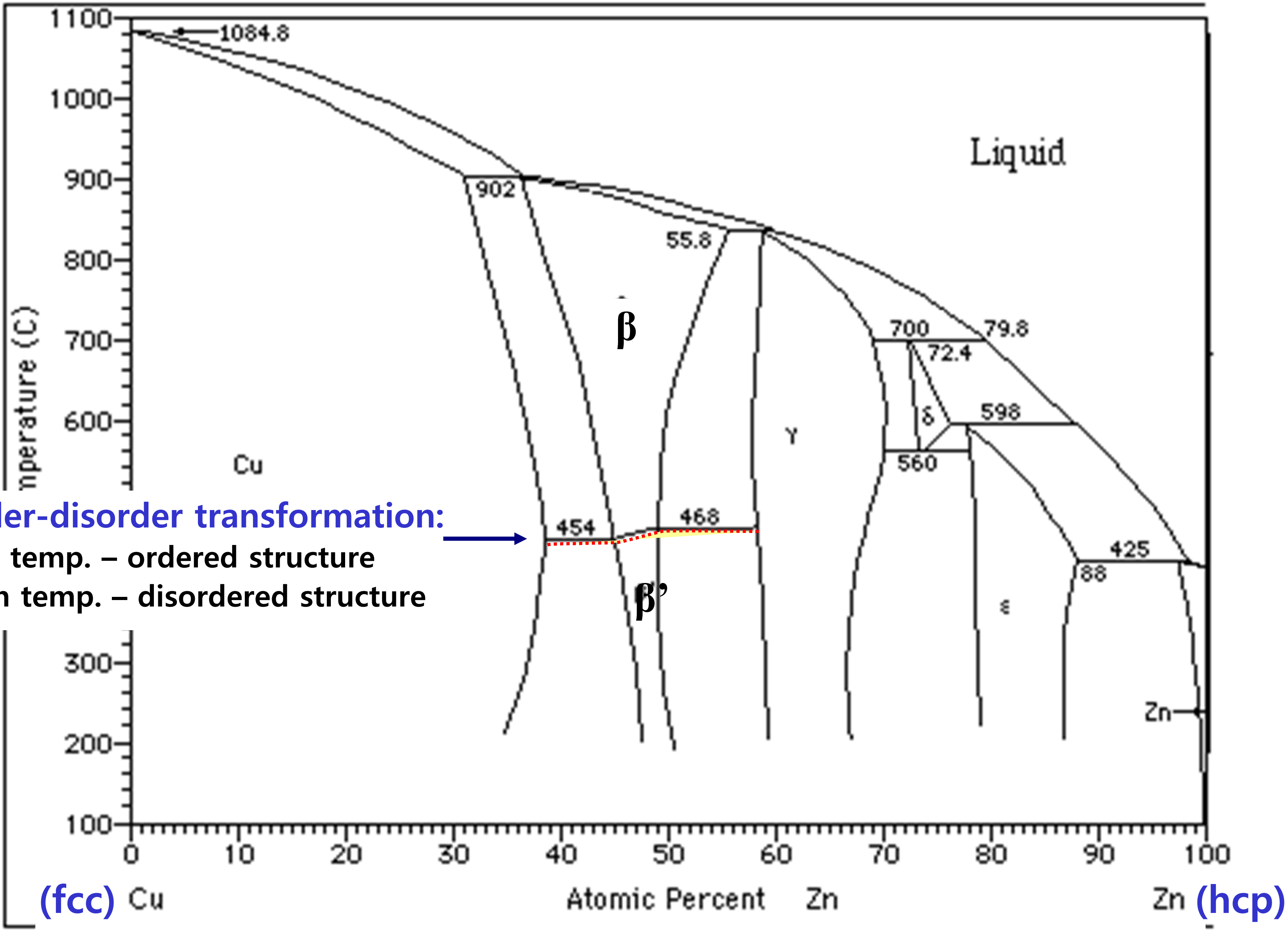
  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.

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



Intermediate Phase

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



Order-disorder transformation:

Low temp. – ordered structure

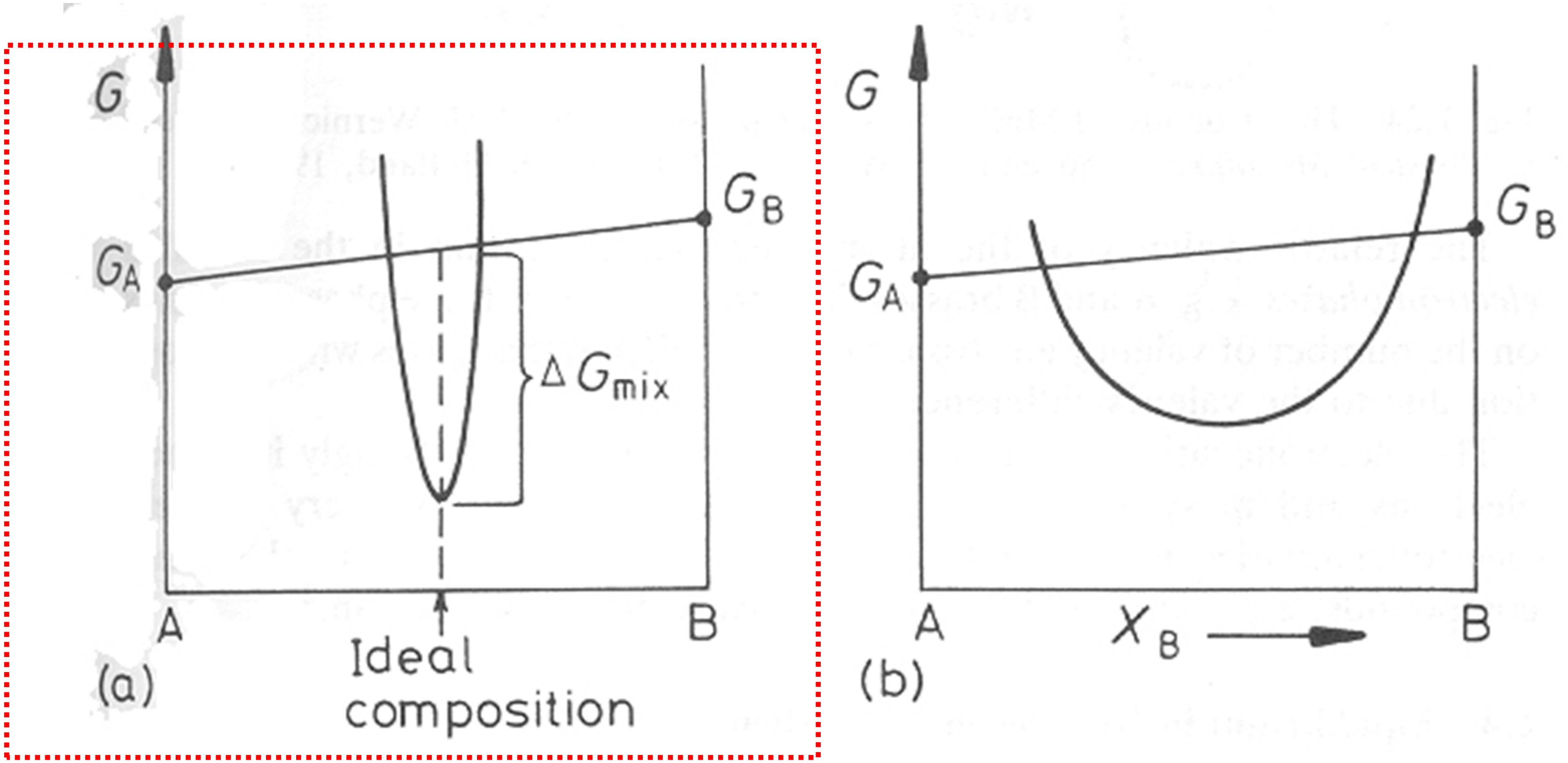
High temp. – disordered structure

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

Q9-c:

Intermediate phase vs Intermetallic compound

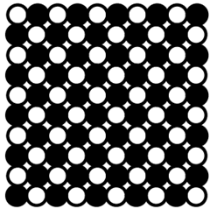
Intermediate Phase



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

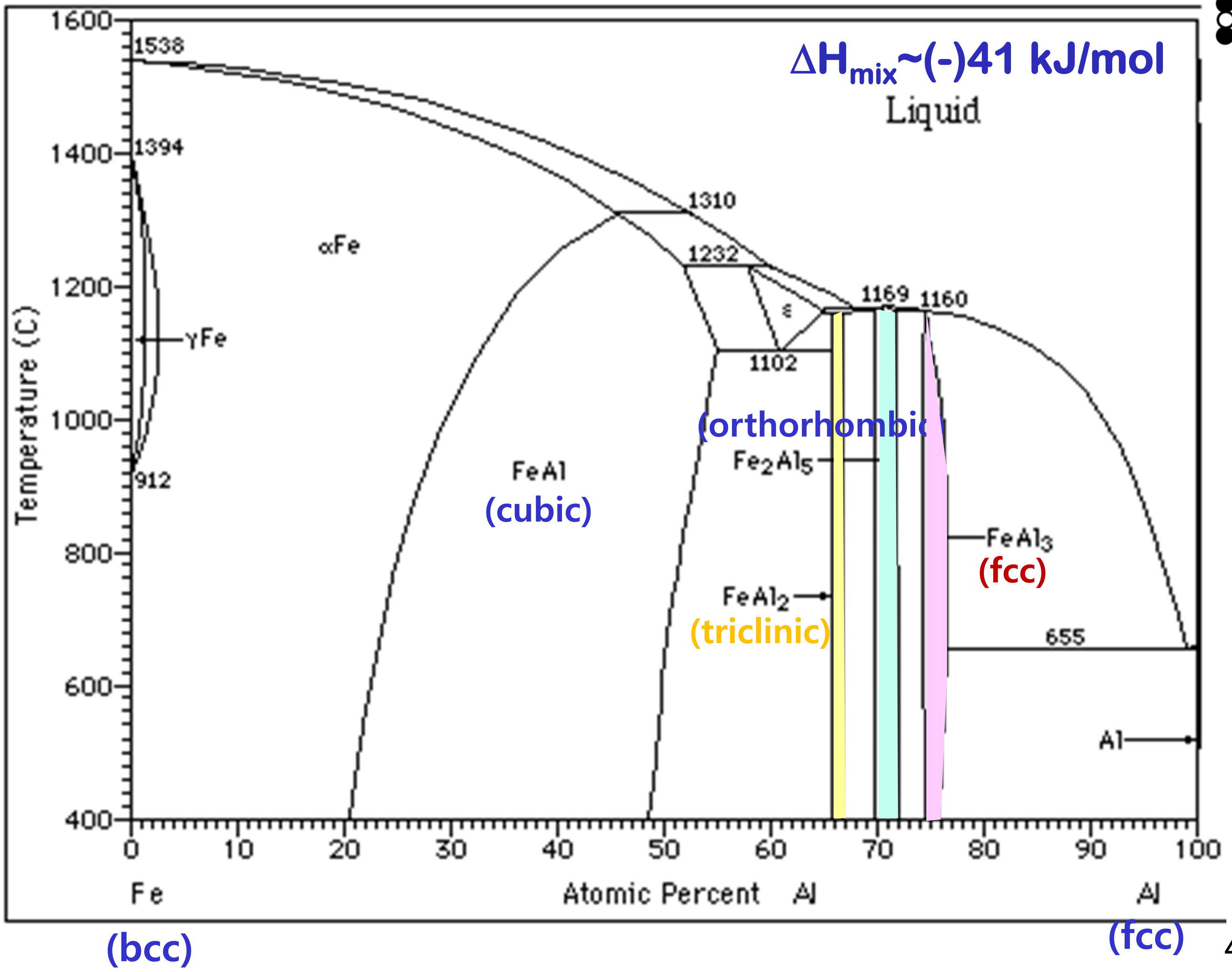
- **In other structure, fluctuations in composition can be tolerated by some atoms occupying 'wrong' position or by atom sites being left vacant, and in these cases the curvature of the G curve is much less, Fig (b).**

Intermediate Phase



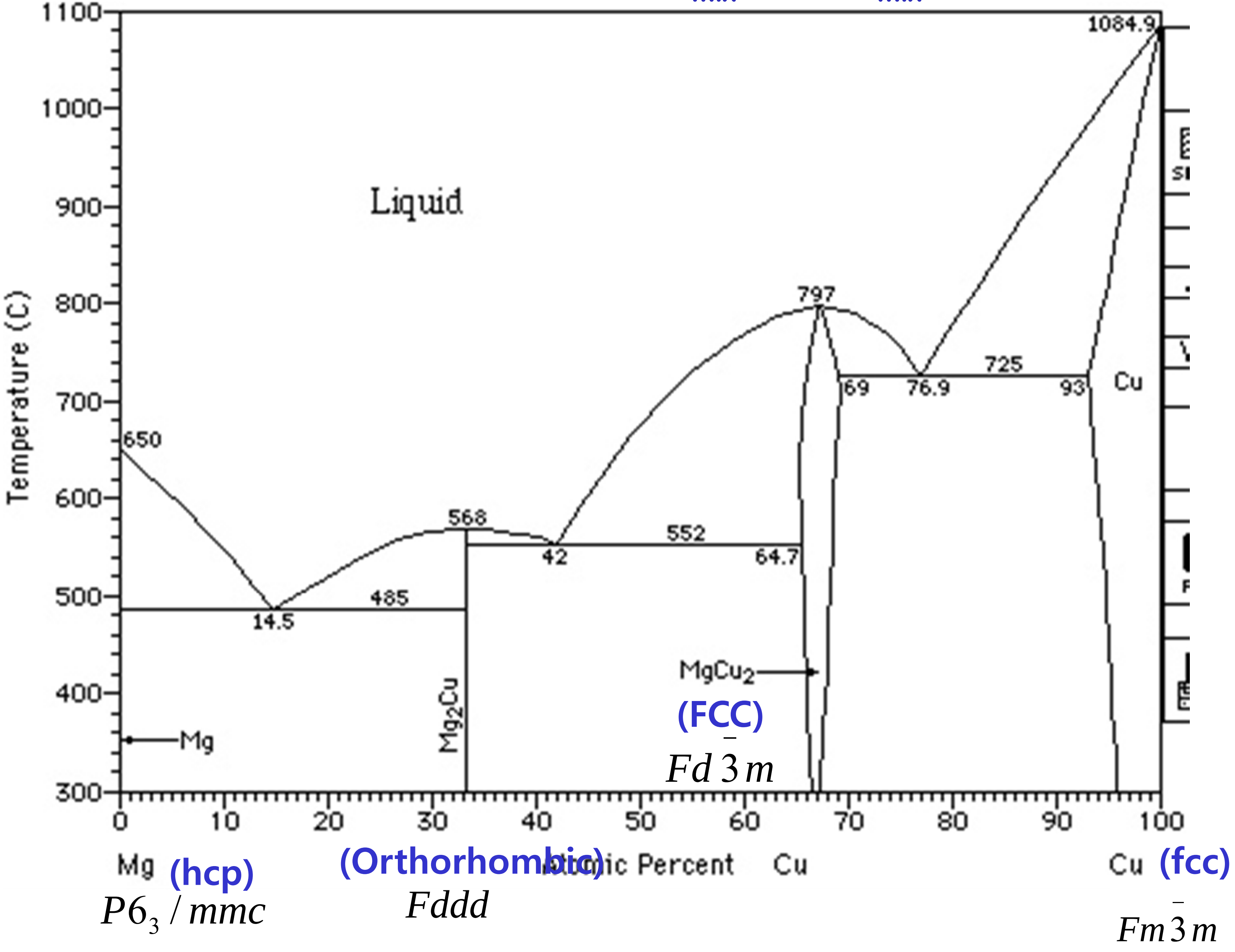
$\varepsilon < 0, \; \Delta H_{mix} < 0$

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



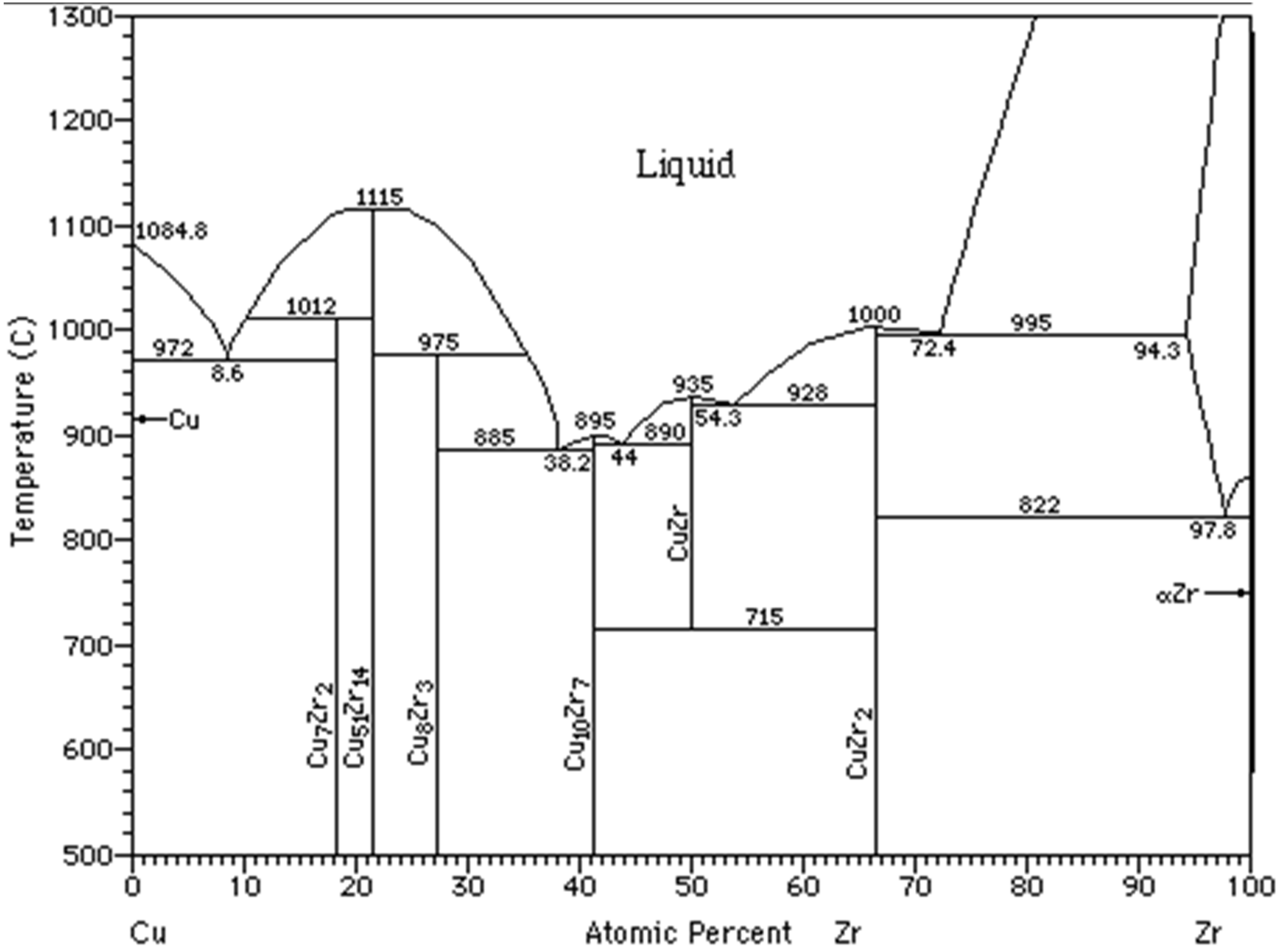
Intermediate Phase

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



Intermediate Phase

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



Intermediate Phase

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

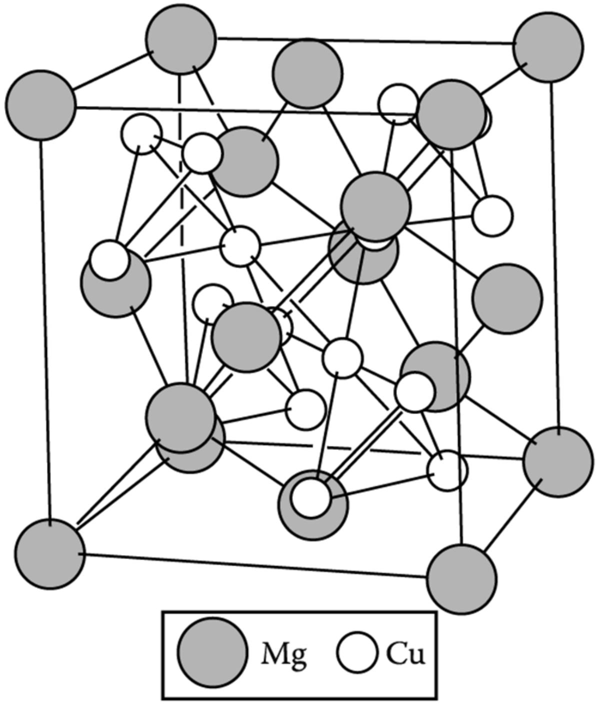
3 main factors
determining the structure of Intermediate phase ?

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

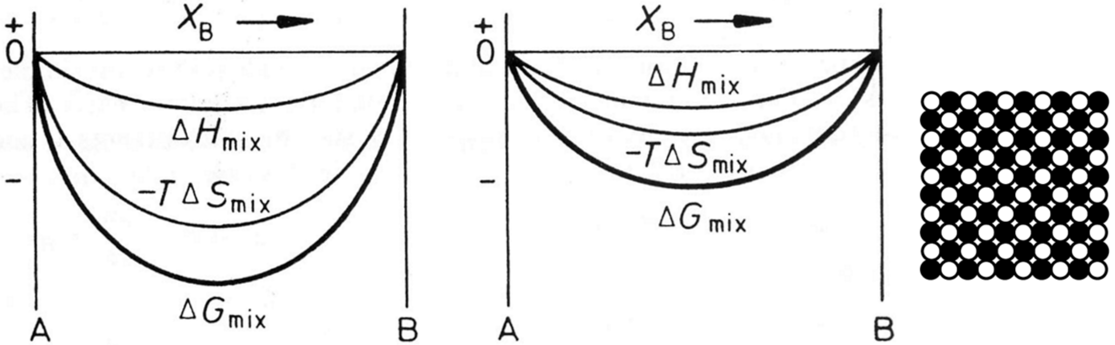
Q10: “Clustering”? → Phase separation

Metastable vs Stable miscibility gap

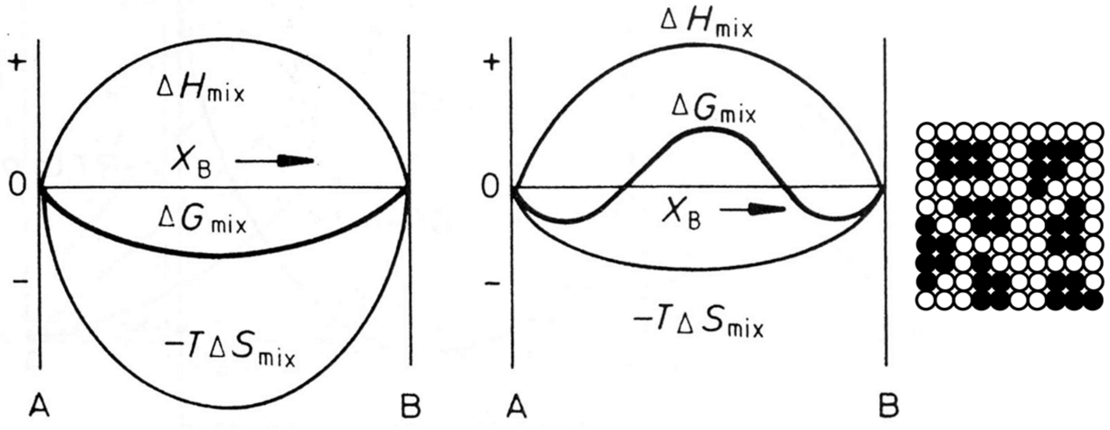
* **The degree of ordering or clustering will decrease as temp. increases due to the increasing importance of entropy.**

High temp. ⟶ Entropy effect ↑ ⟶ Solution stability ↑

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

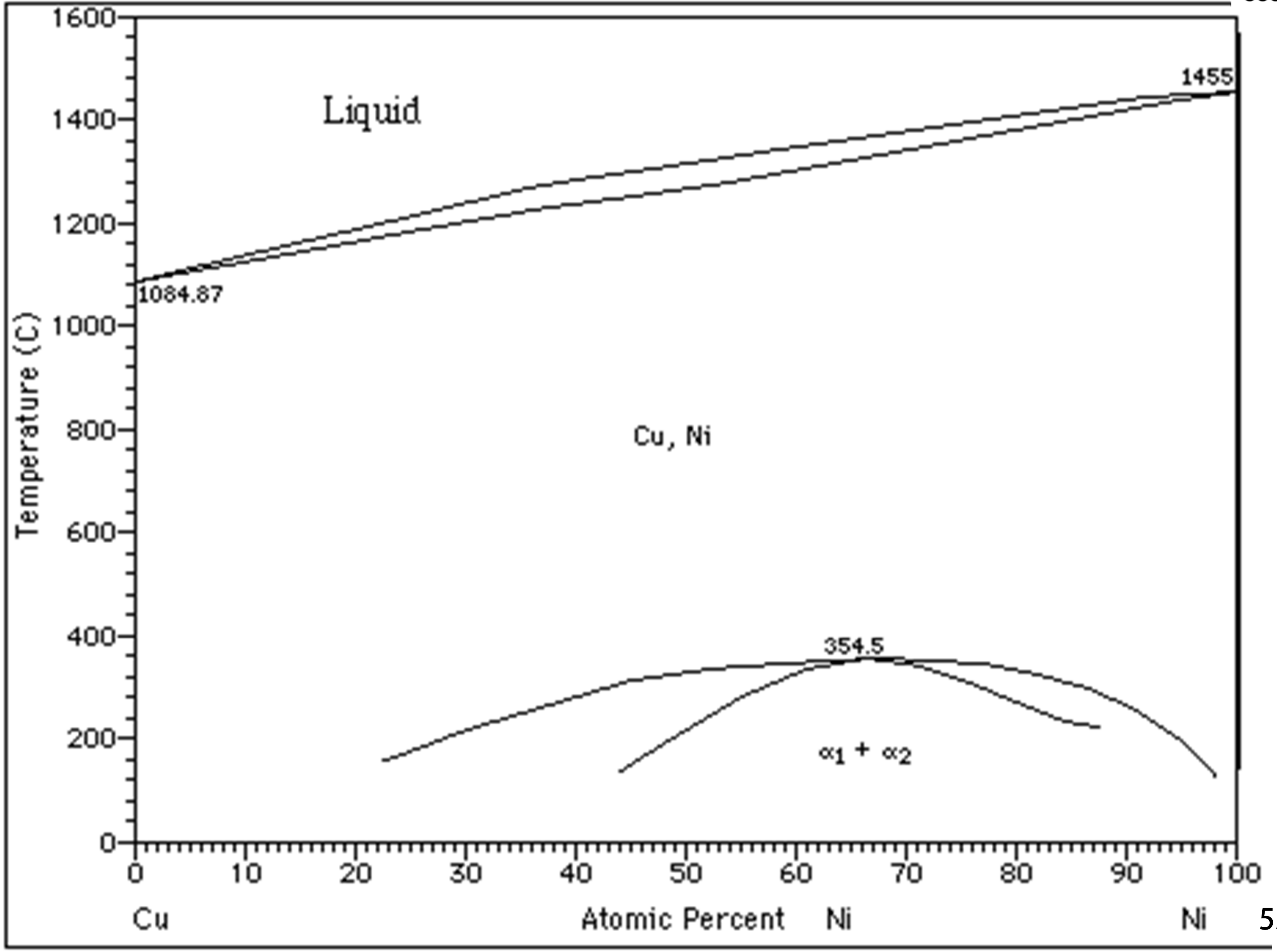


(a) $\Omega < 0$, high T (b) $\Omega < 0$, low T

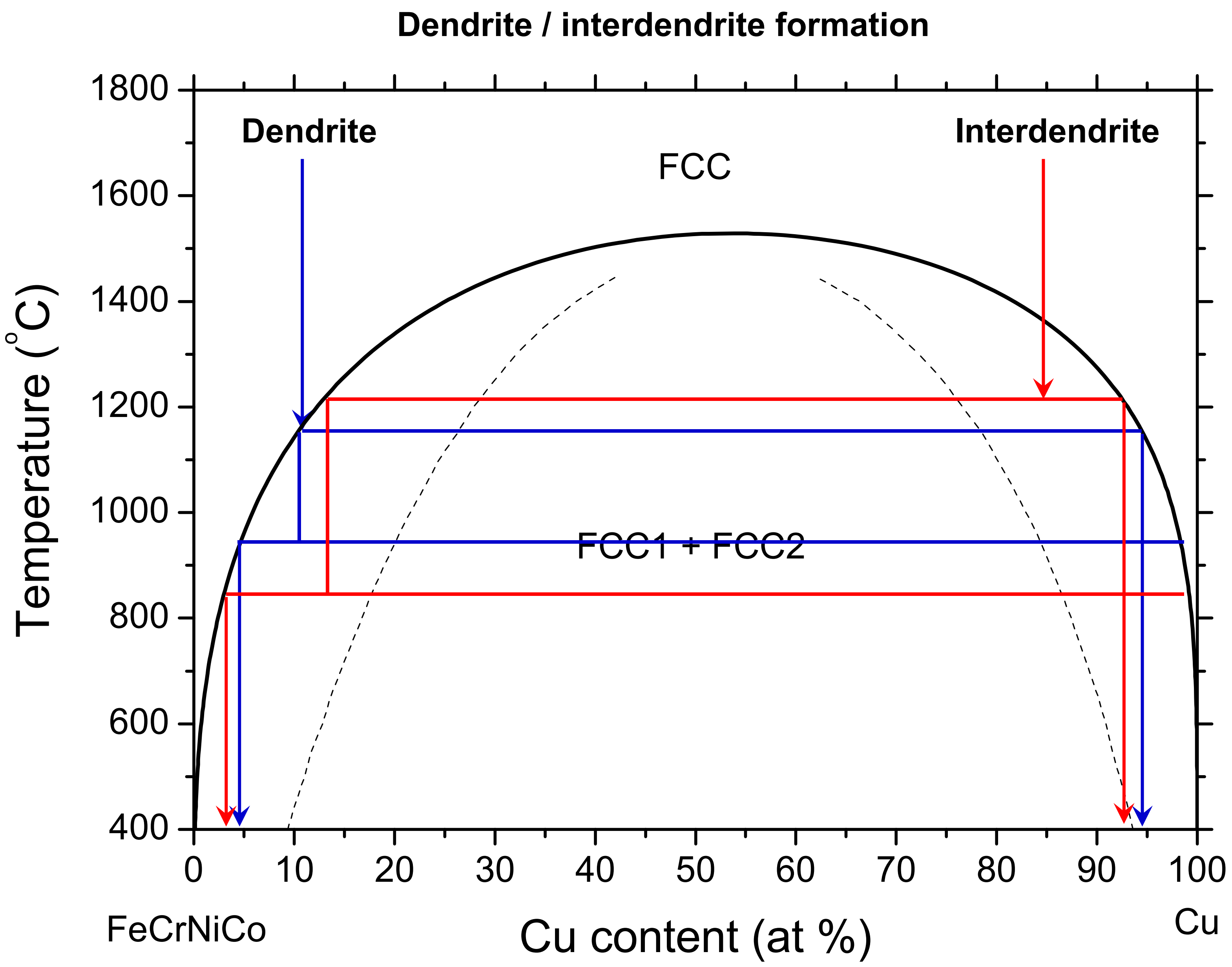


(c) $\Omega > 0$, high T (d), $\Omega > 0$ low T

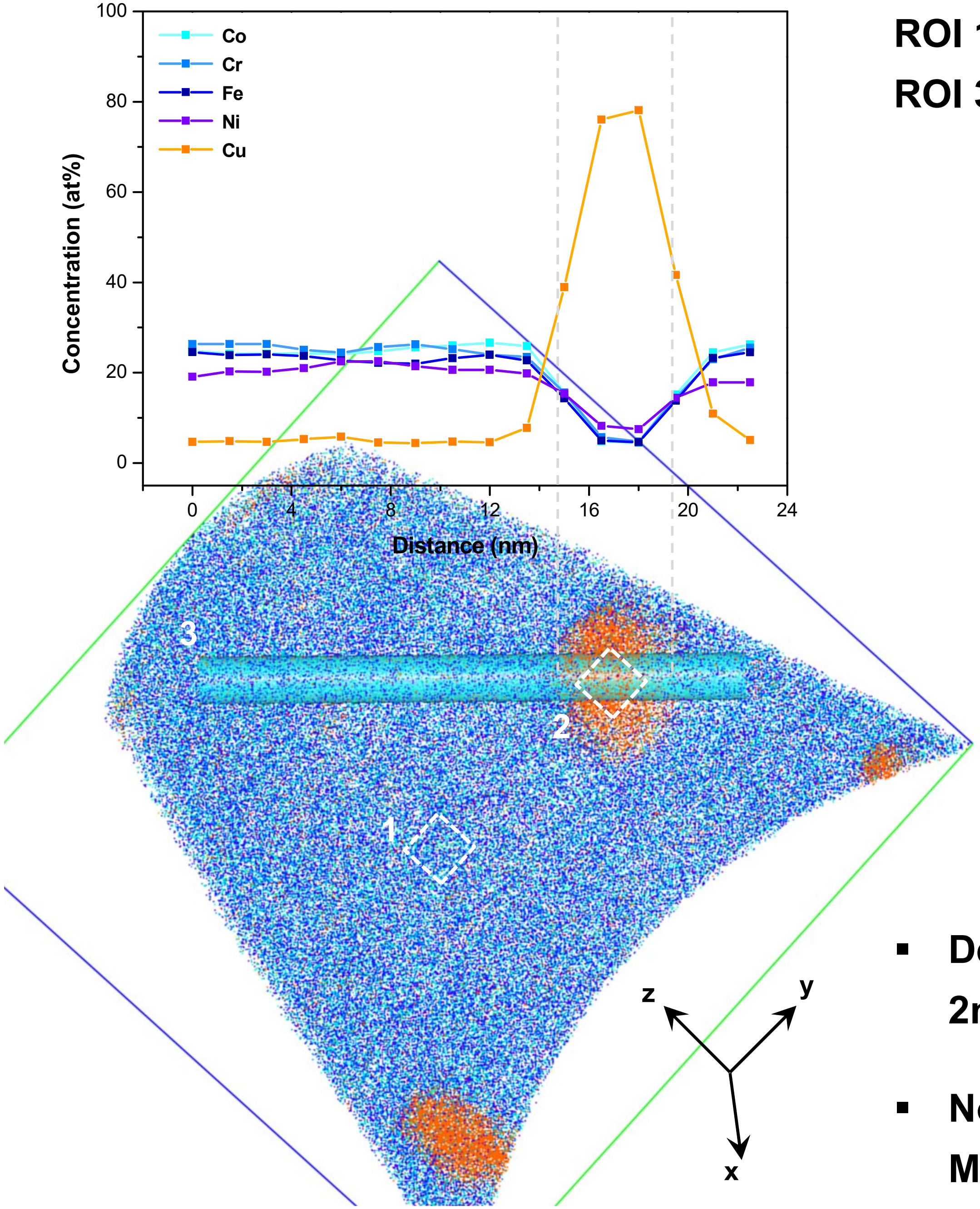
$\varepsilon > 0, \; \Delta H_{mix} > 0 \; / \Delta H_{mix} \sim +26$ kJ/mol



Cooling process in the miscibility gap



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

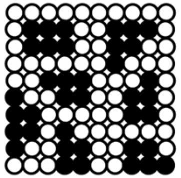
2	at%
Co	0.33
Cr	0.46
Fe	0.39
Ni	5.00
Cu	93.56

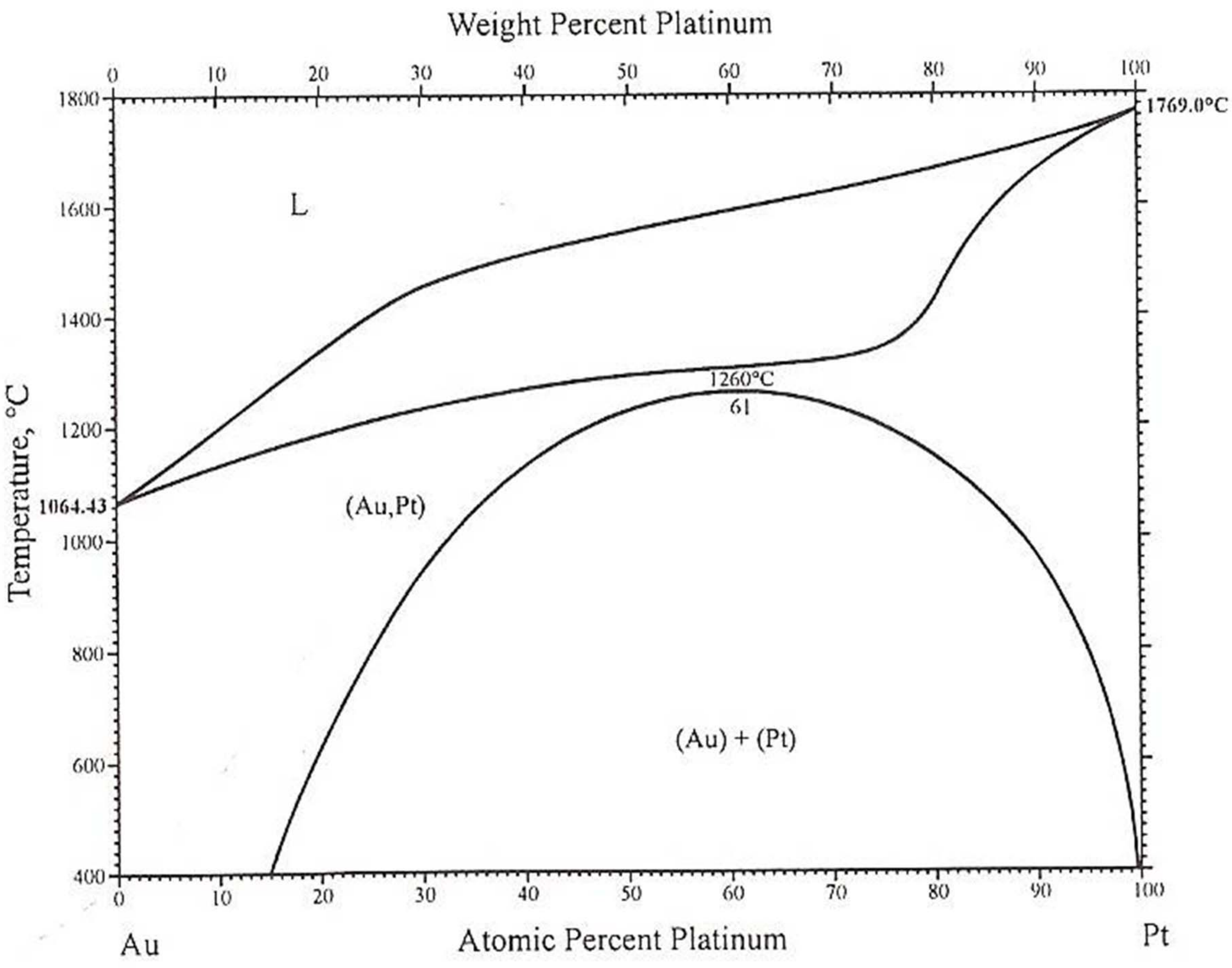
3-1’	at%
Co	25.29
Cr	25.63
Fe	23.63
Ni	20.66
Cu	4.42

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

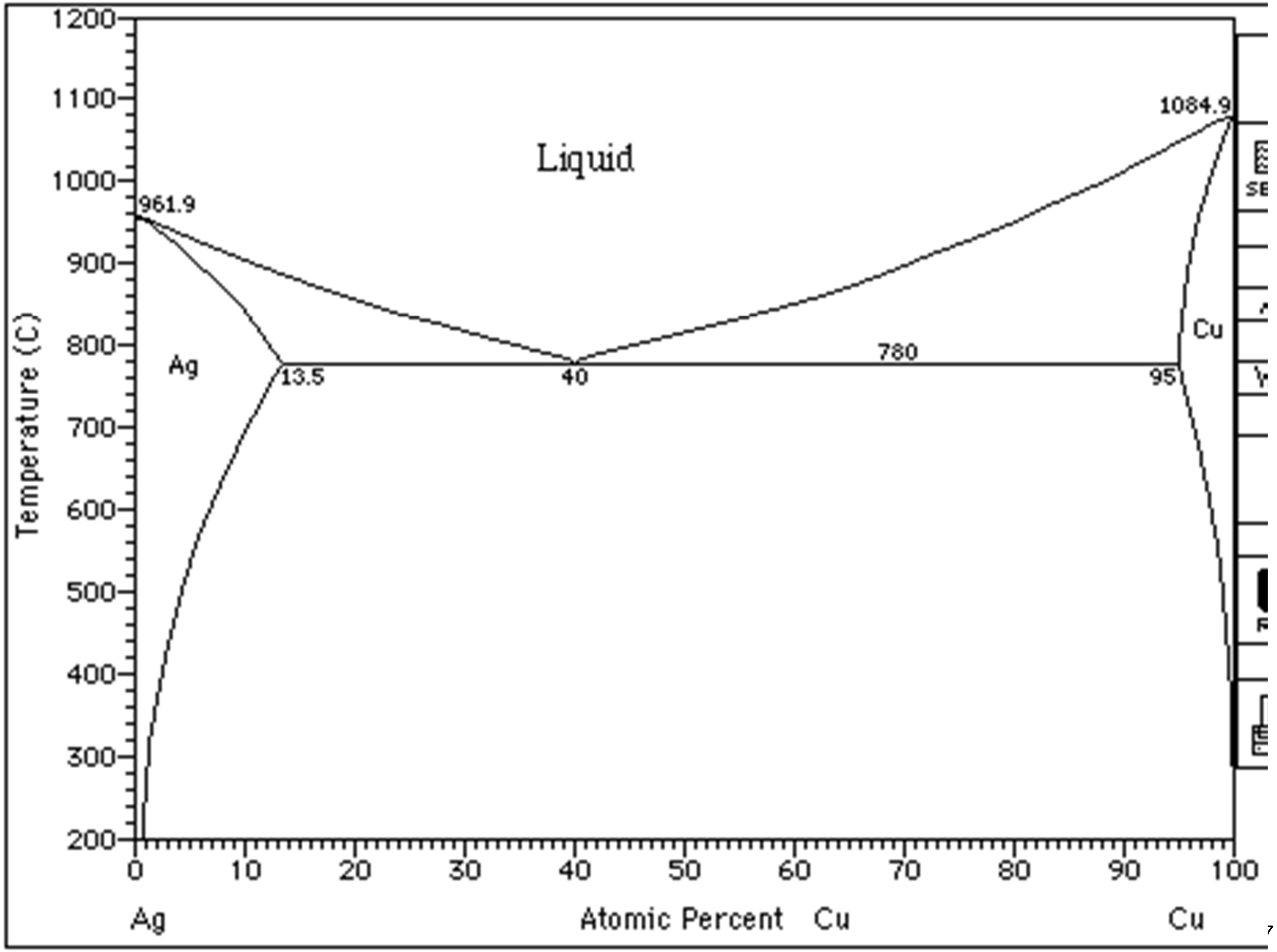
- Dendrite region: matrix (4.74 at%Cu) + 2nd phase (93.56 at%Cu)
- No segregation at the interface between Matrix and 2nd phase

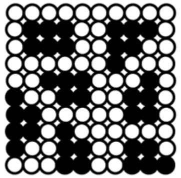
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +17$ kJ/mol



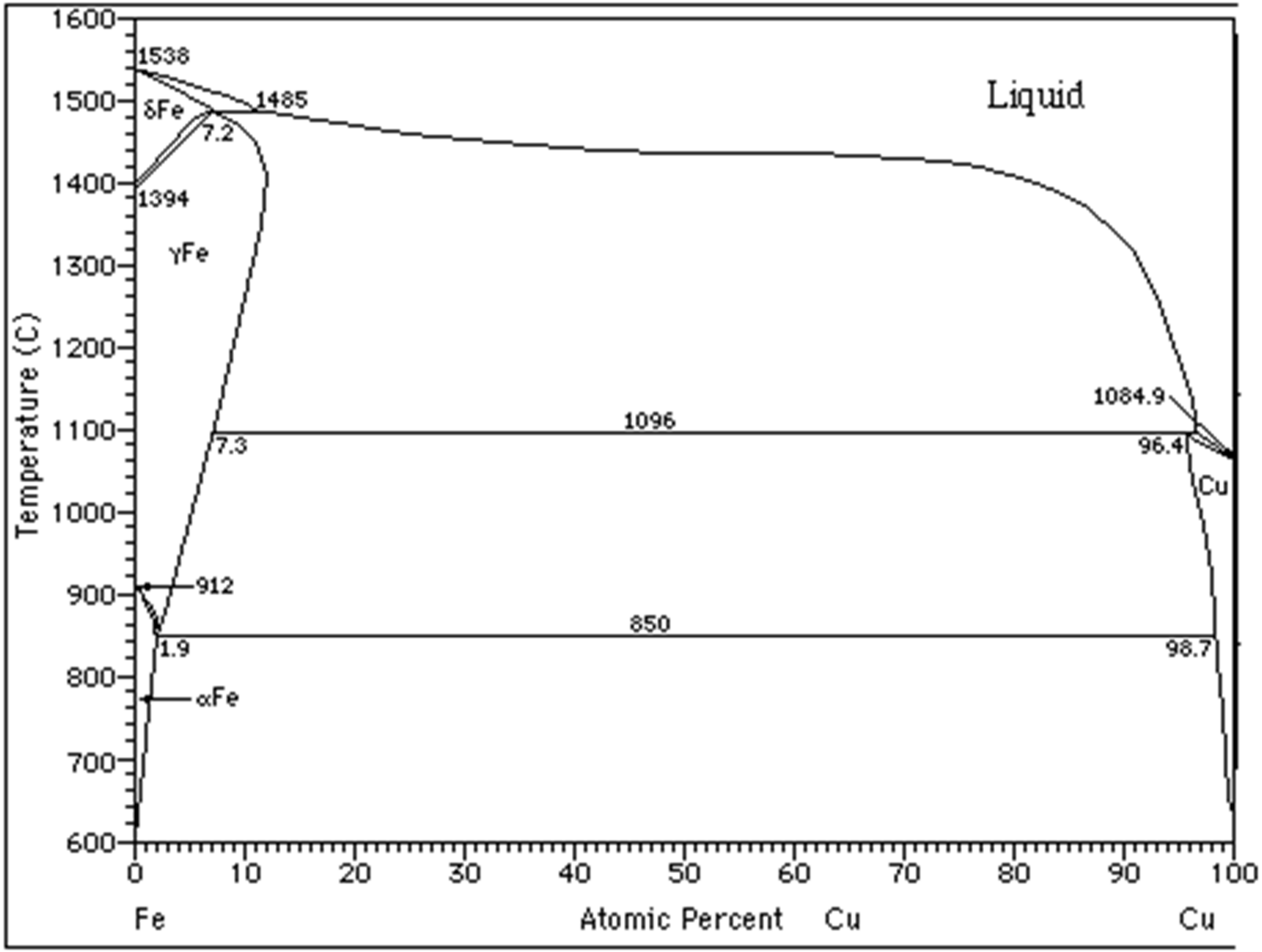


$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol

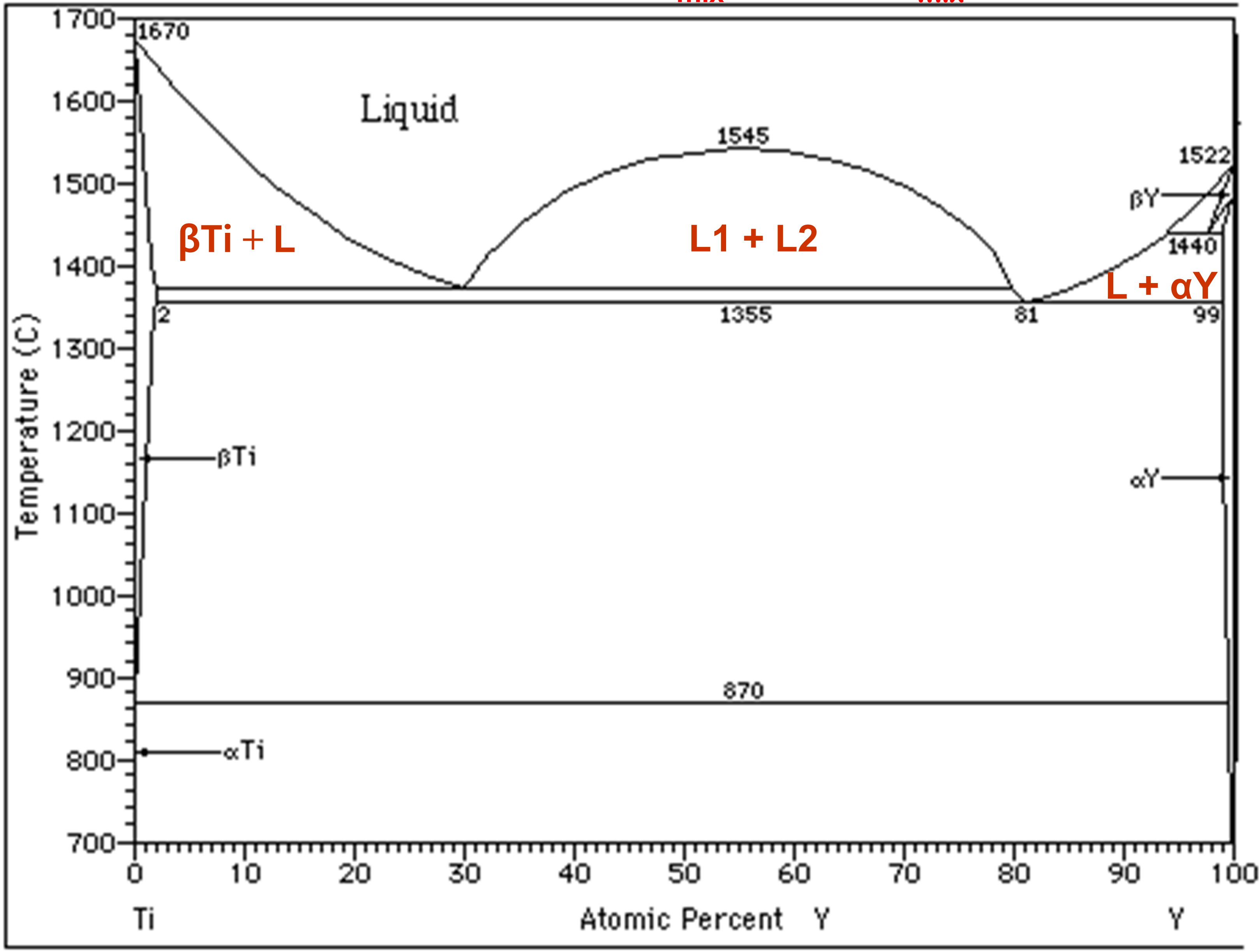




$\varepsilon >> 0$, $\Delta H_{mix} >> 0$ / $\Delta H_{mix} \sim +60$ kJ/mol



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



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

⬇

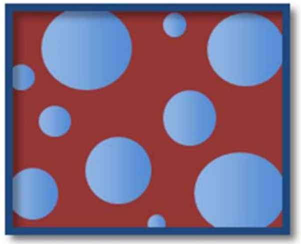
creates (meta)stable miscibility gap in limited composition range

⬇

Phase separation to A-rich & B-rich phase

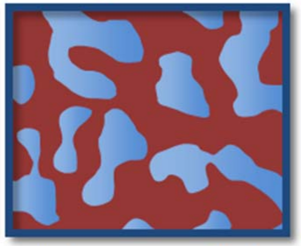
- **Different two-phase structure by initial composition before phase separation**

$C=C_1$



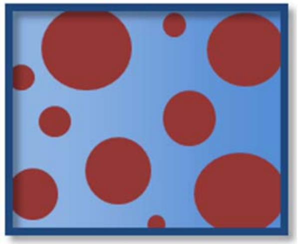
A-rich matrix
B-rich droplet

$C=C_2$

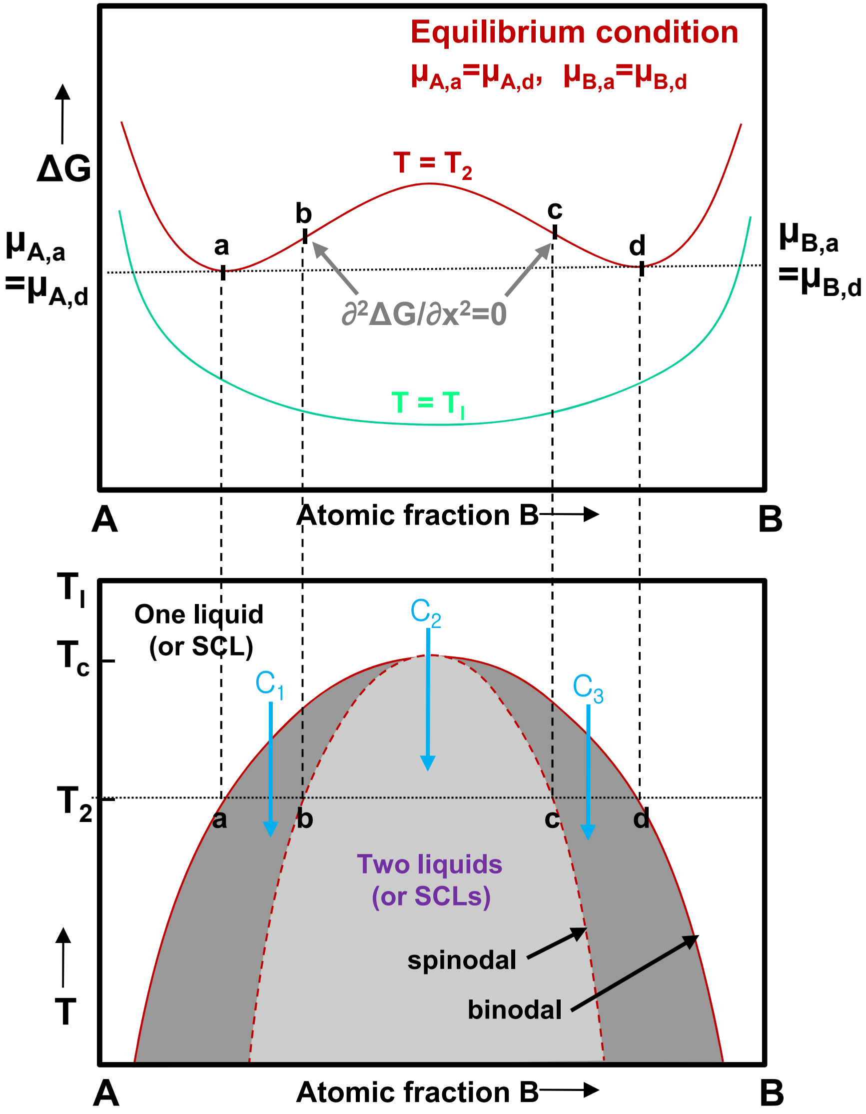


Interconnected
structure

$C=C_3$

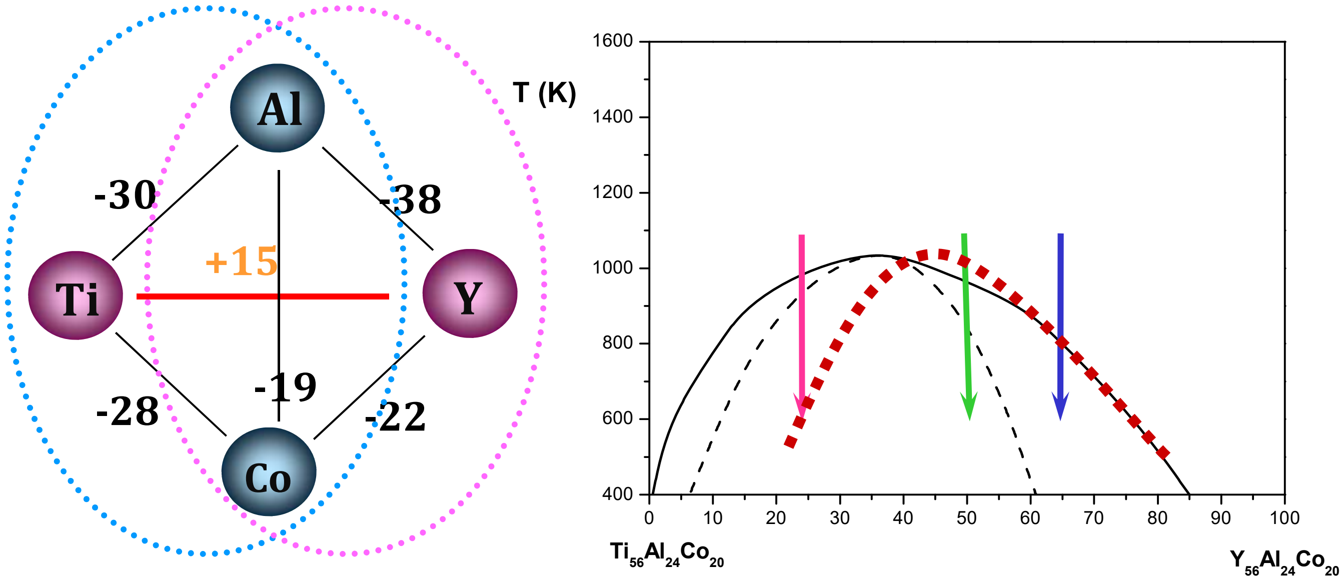


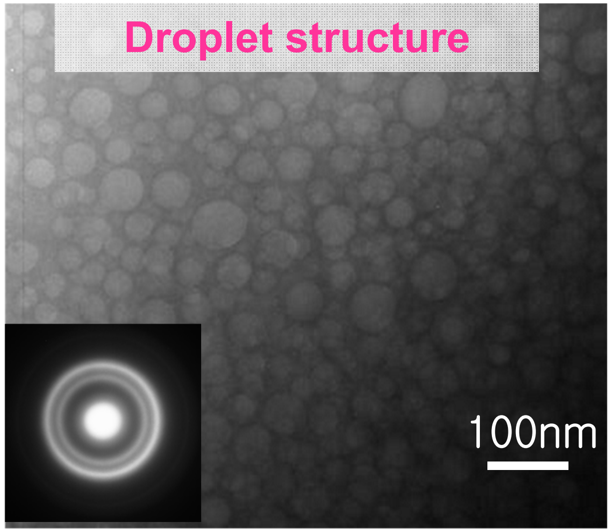
B-rich matrix
A-rich droplet



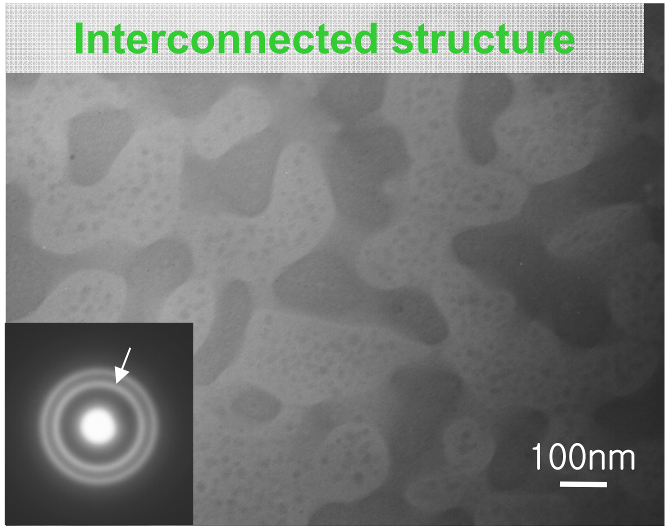
Nucleation and growth ↔ Spinodal decomposition without any barrier to the nucleation process

* Ti-Y-Al-Co system

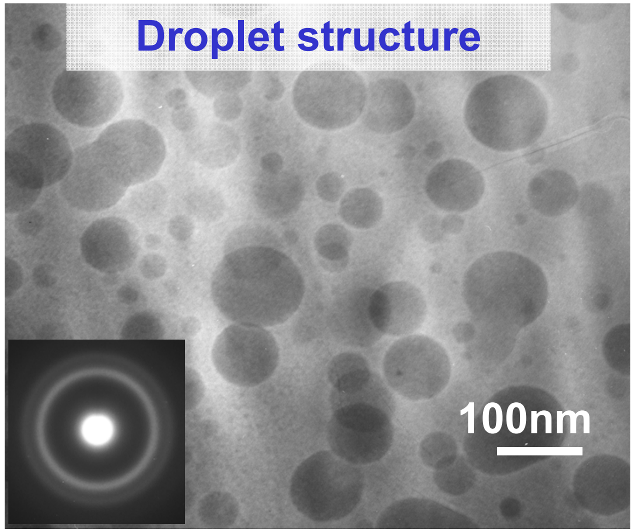




$(Y_{56}Al_{24}Co_{20})_{25}(Ti_{56}Al_{24}Co_{20})_{75}$



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



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

* La-Zr-Al-Cu-Ni system

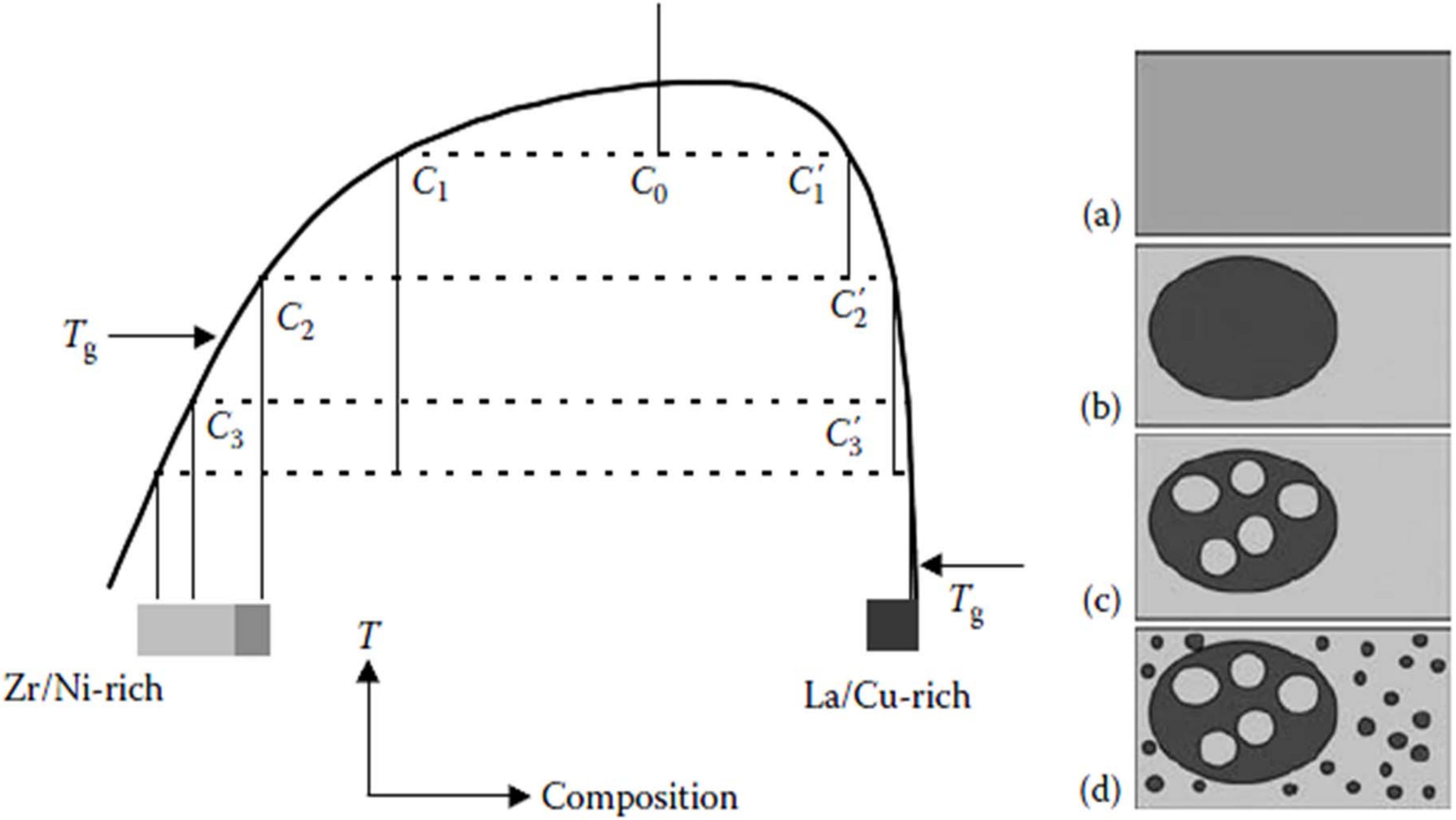
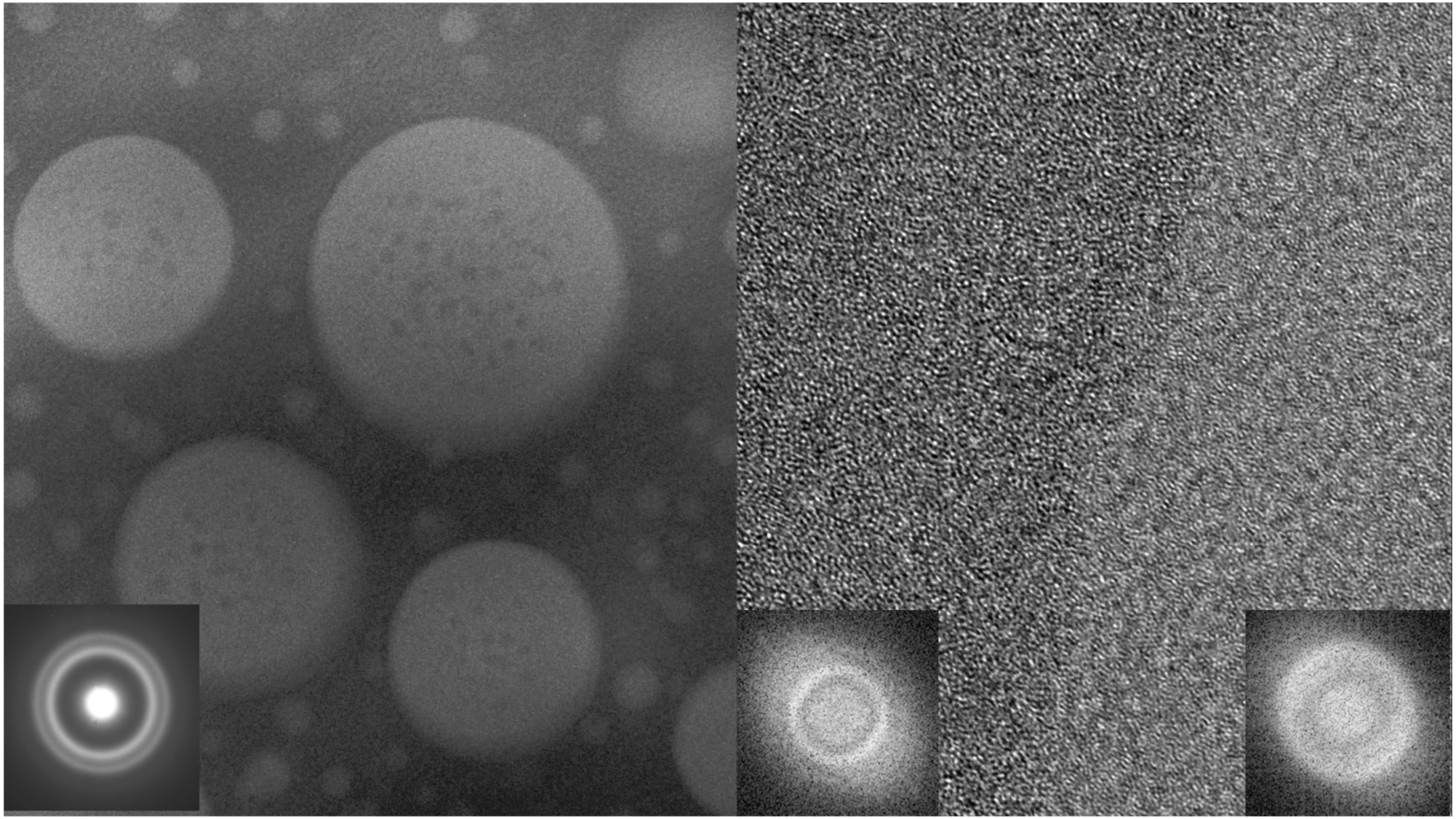


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta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

Phase separation in metallic glasses



- Binary System mixture/ solution / compound

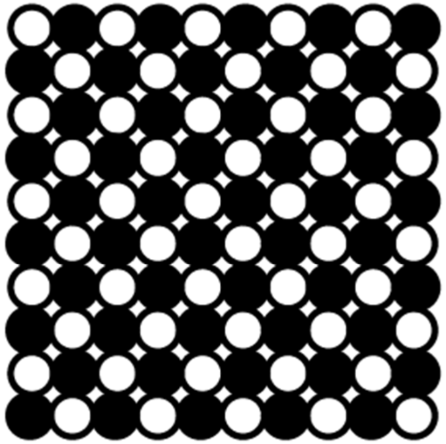
Ideal solution $(\Delta H_{mix}=0)$ **Random distribution**

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

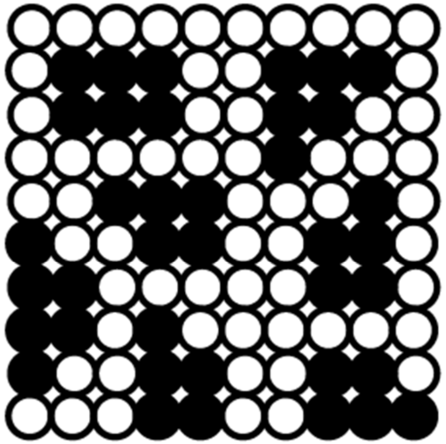
Ordered structure



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

Ordered alloys

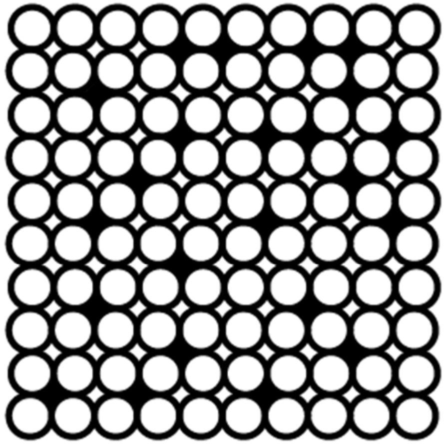
$P_{AB} \uparrow \longrightarrow$ Internal E $\downarrow$



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

Clustering

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

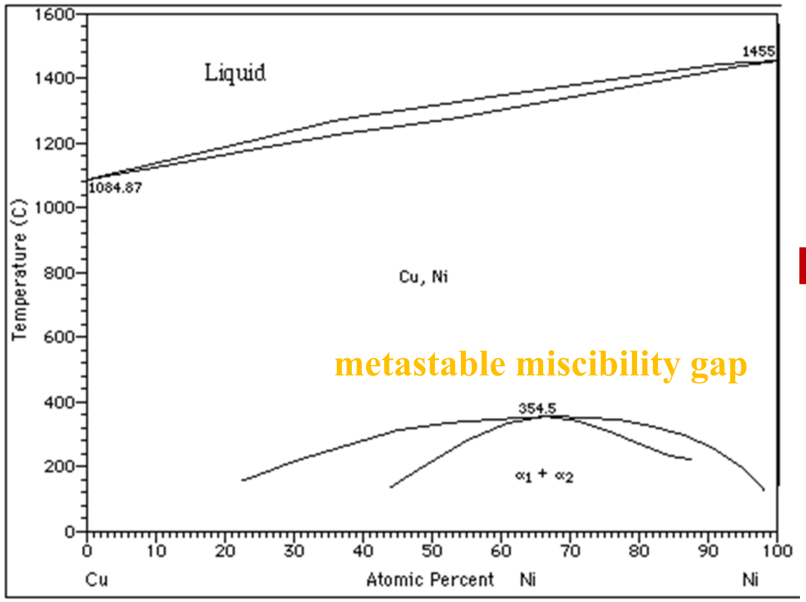


(c) when the size difference is large

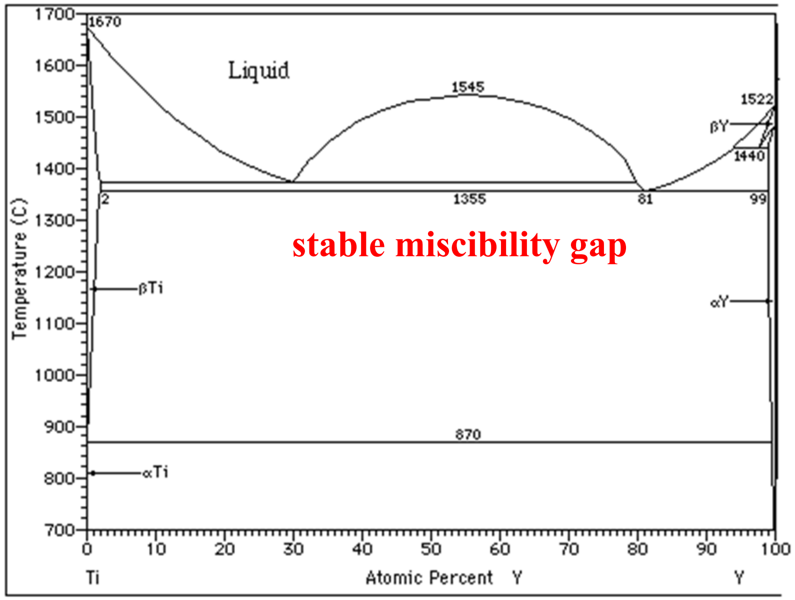
strain effect

Interstitial solution

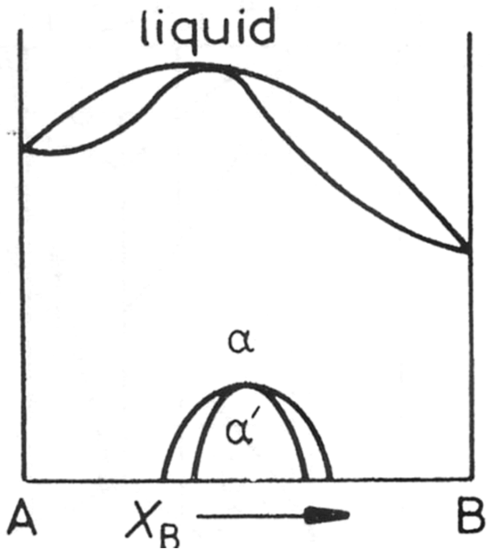
$\Delta H^{S}_{mix} > 0$: Solid solution → solid state phase separation (two solid solutions)

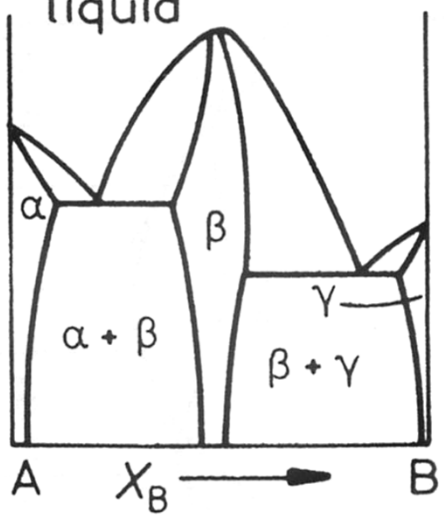


$\Delta H^{S}_{mix} >> 0$: liquid state phase separation (up to two liquid solutions)



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





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