2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

09.22.2009

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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 ($\Delta H_{mix}=0$)

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

Regular solution

$$\Delta H_{mix} = P_{AB}\varepsilon$$

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

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**

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

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

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

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

Contents for today's class

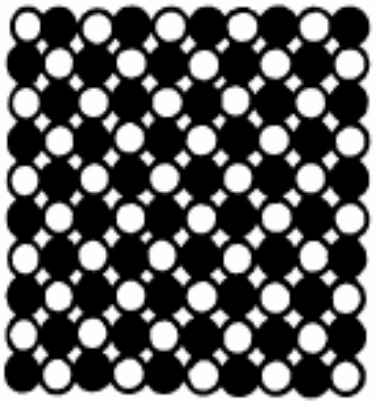
- Binary System mixture/ solution / compound

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

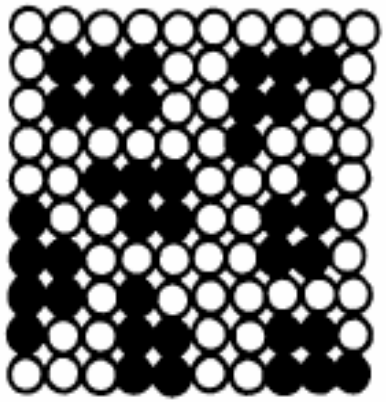
Regular solution $\Delta H_{mix} = P_{AB}\varepsilon$ where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$ $\varepsilon \approx 0$

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

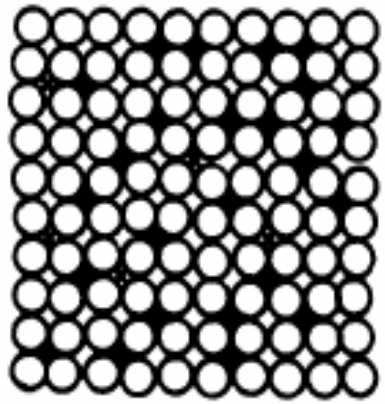
Real solution **Ordered structure**



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



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



(c) when the size difference is large

strain effect

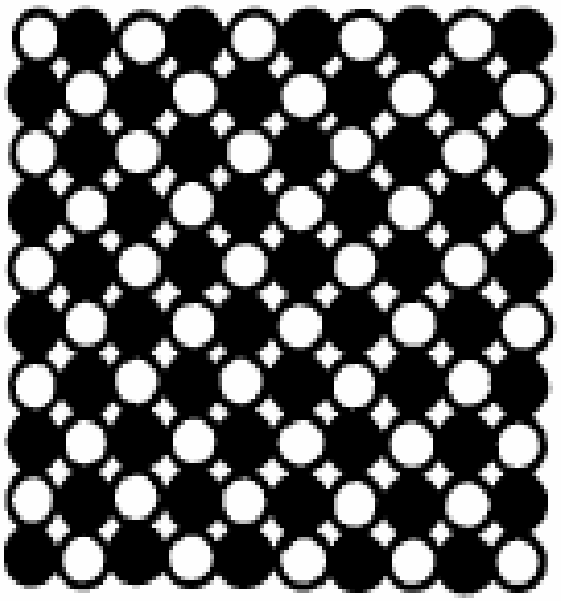
Ordered alloys **Clustering** **Interstitial solution**

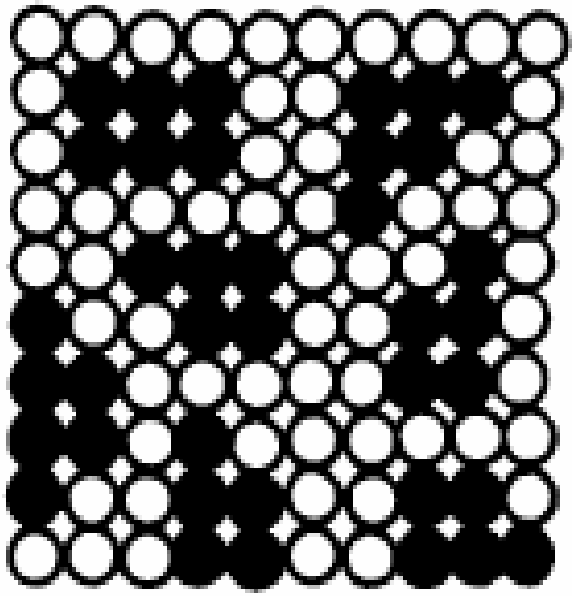
Real solution: $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

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 $\downarrow$

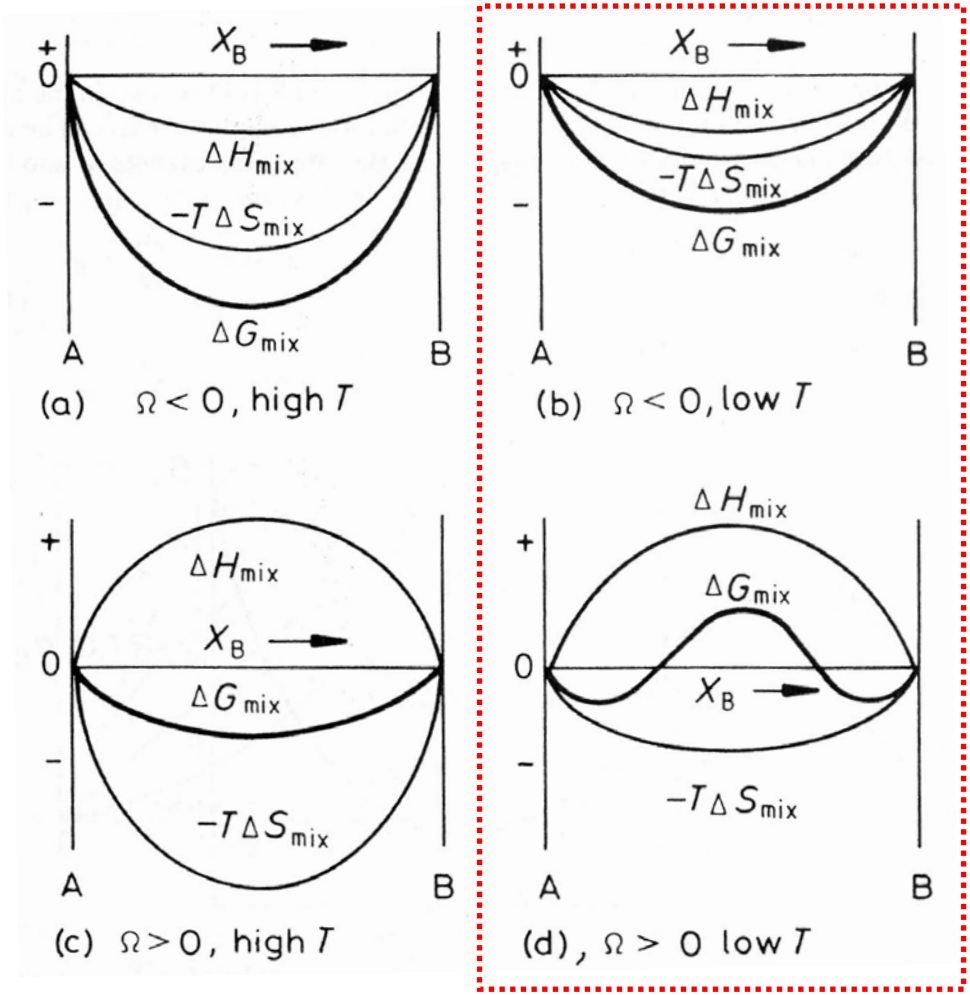
Clustering

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

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

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

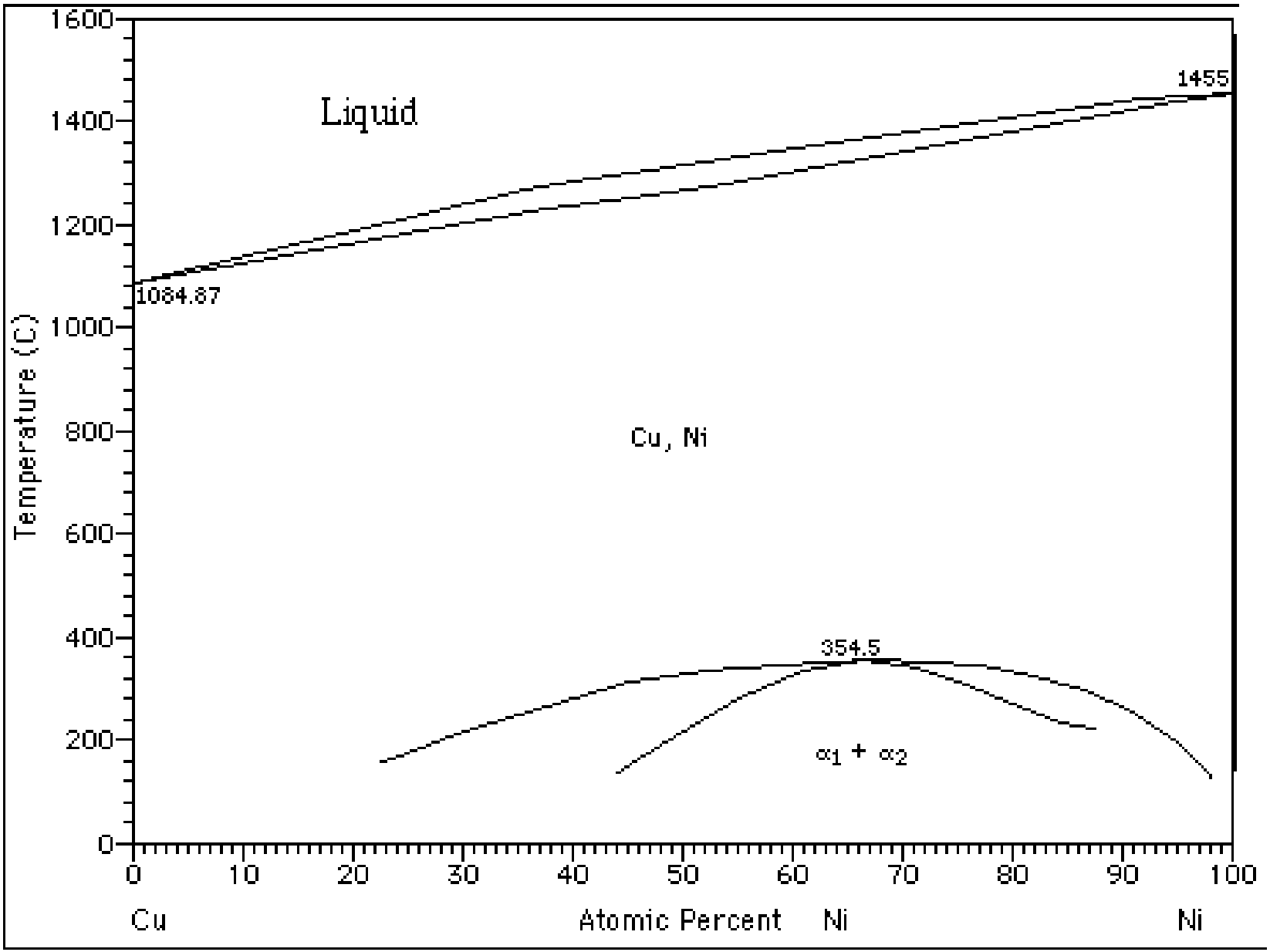
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



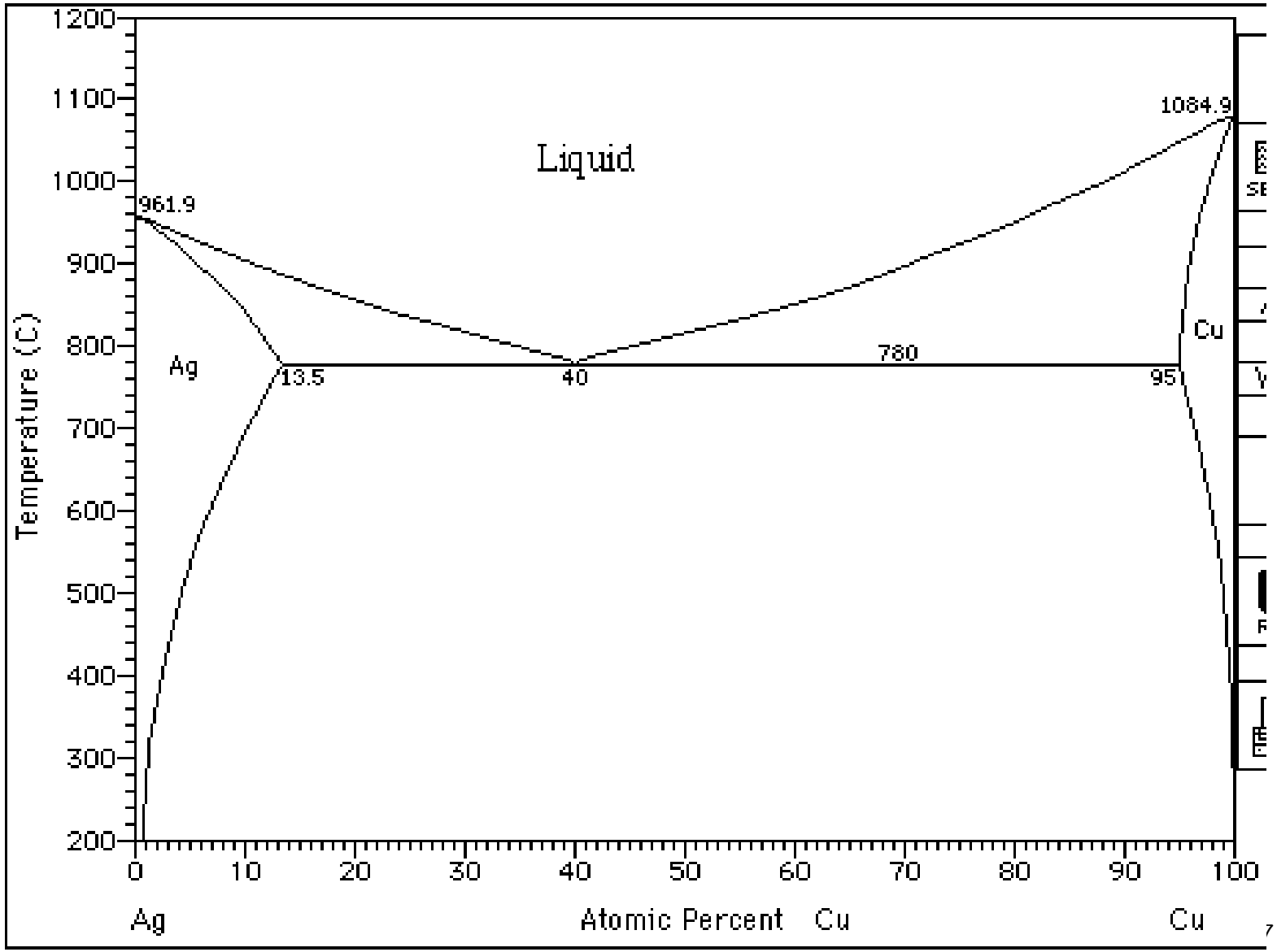
* In systems where there is a size difference between the atom,

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

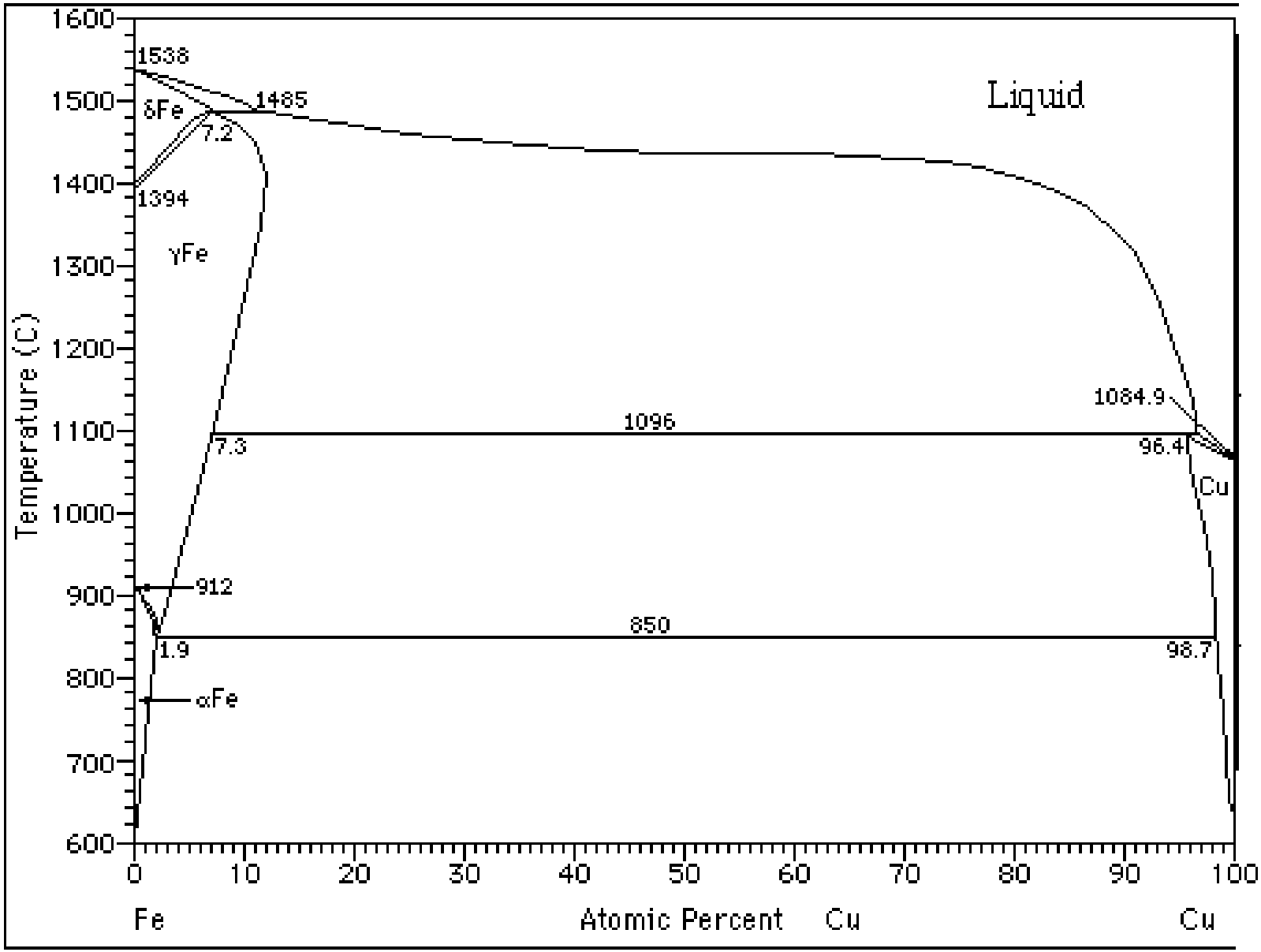
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim$ +26 kJ/mol



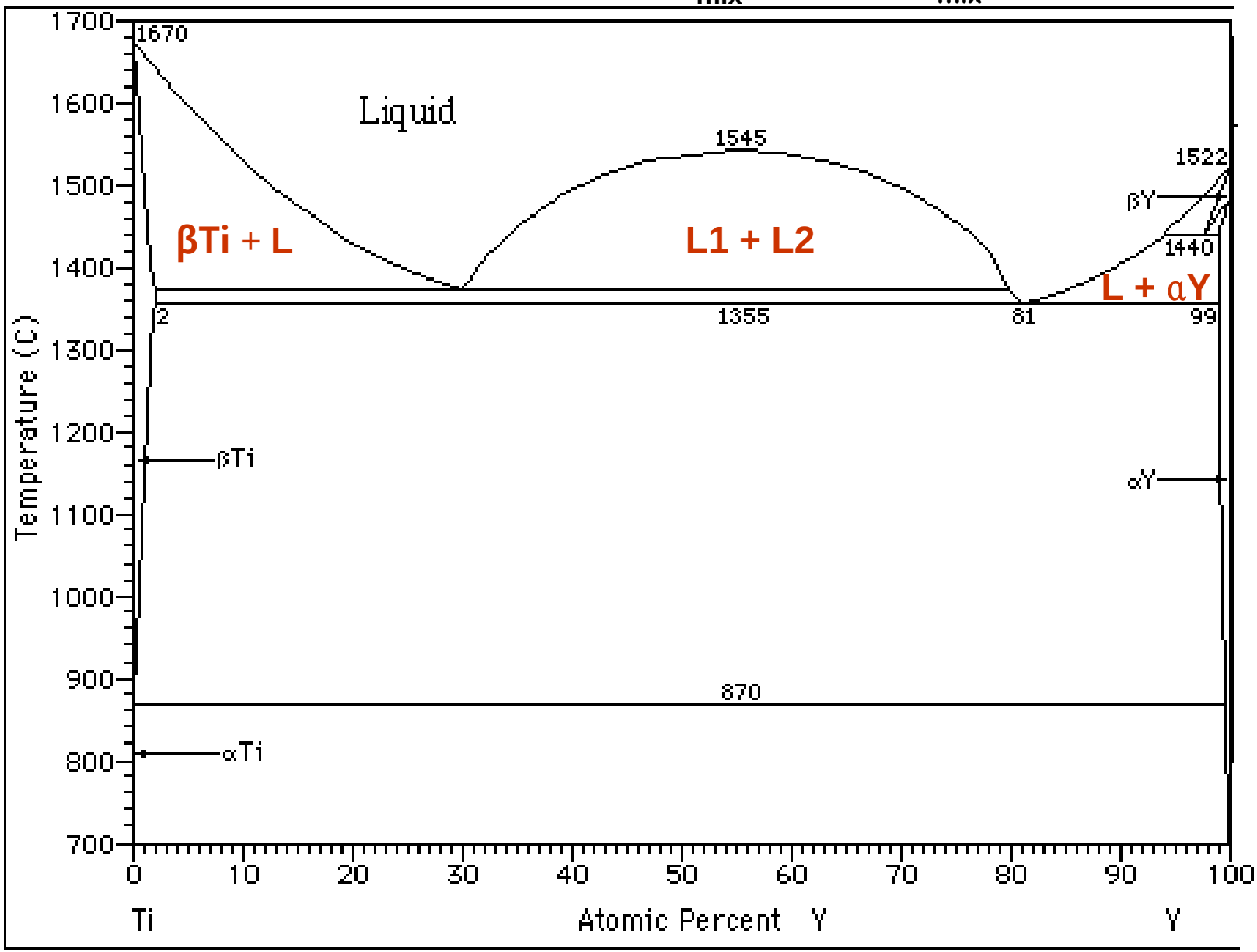
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol



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



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



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

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

$\Delta\Omega = N_a z\varepsilon$

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

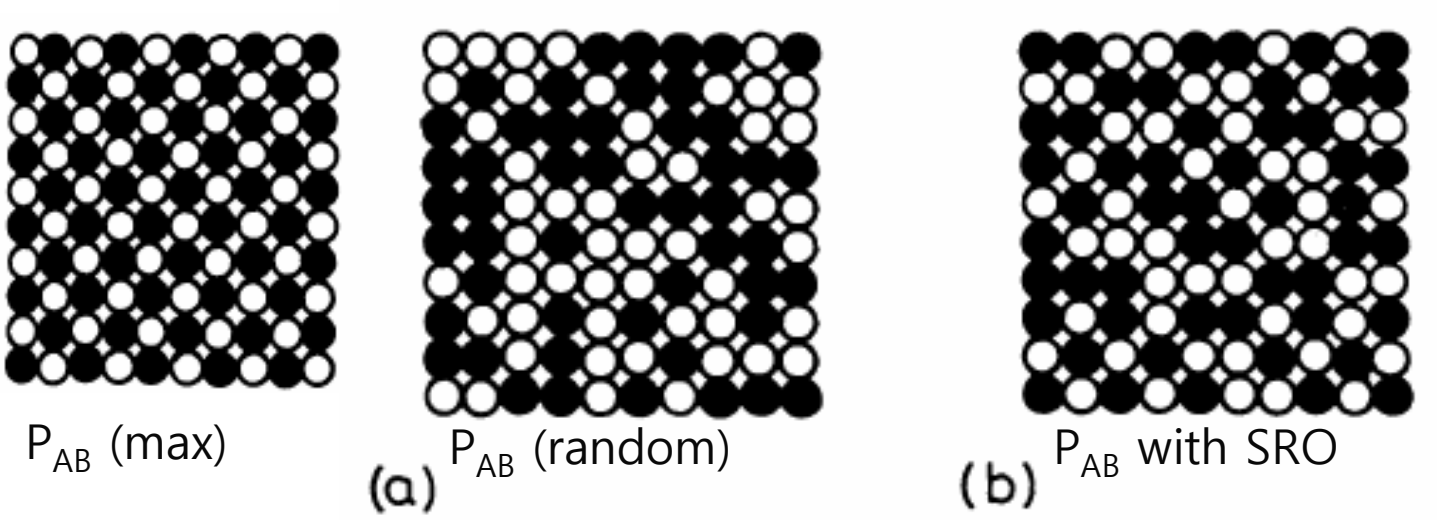
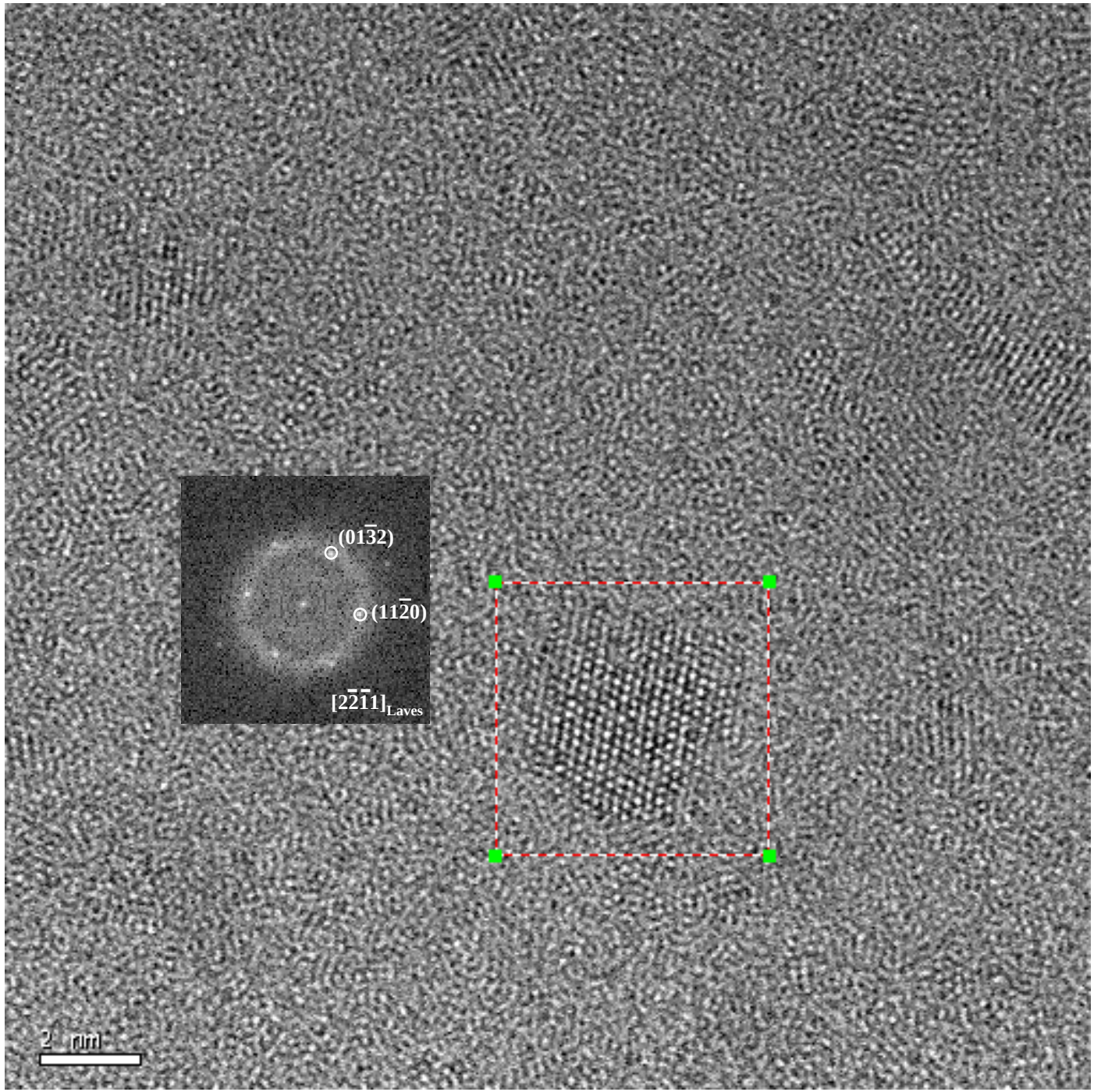
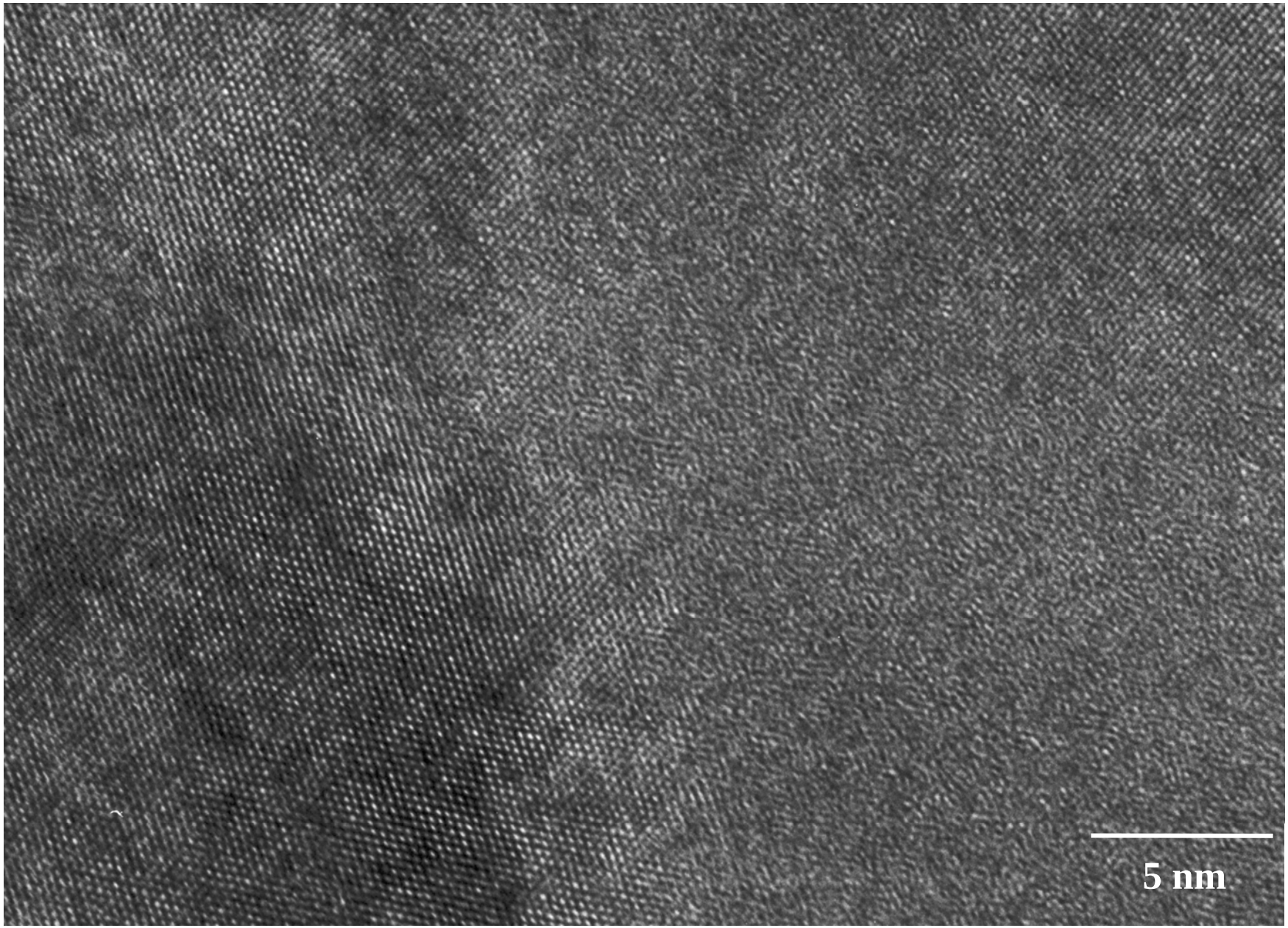


Fig. 1.19 (a) Random A-B solution with a total of 100 atoms and $X_A=X_B=0.5$, P_{AB}~100, S=0. (b) Same alloy with short-range order $P_{AB}=132$, $PAB_{(max)}$~200, S=(132-100)/(200-100)=0.32

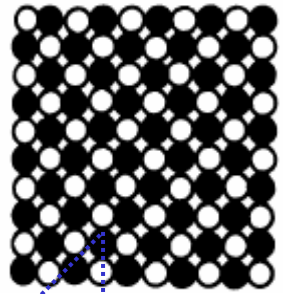

$(01\bar{3}2)$
$(11\bar{2}0)$
$[2\bar{2}\bar{1}1]_{Laves}$
2 nm


5 nm

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

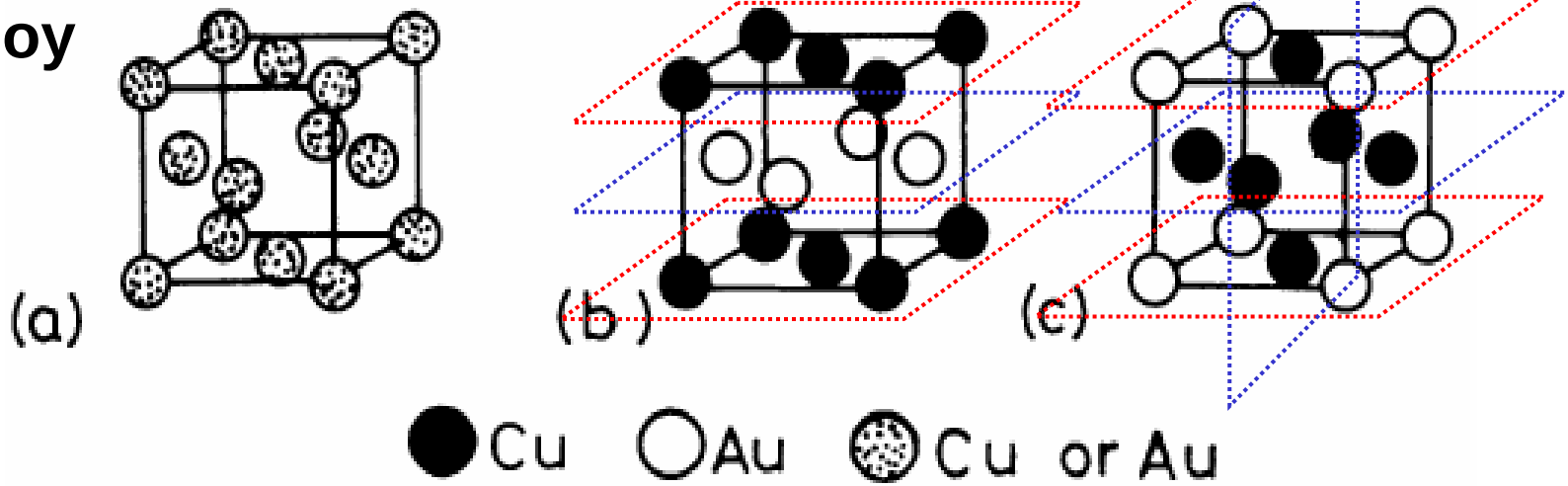
* In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found.

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



* A superlattice forms in materials with LRO

Cu–Au alloy



High temp.
Disordered Structure

Low temp.
CuAu superlattice

Cu_3Au superlattice

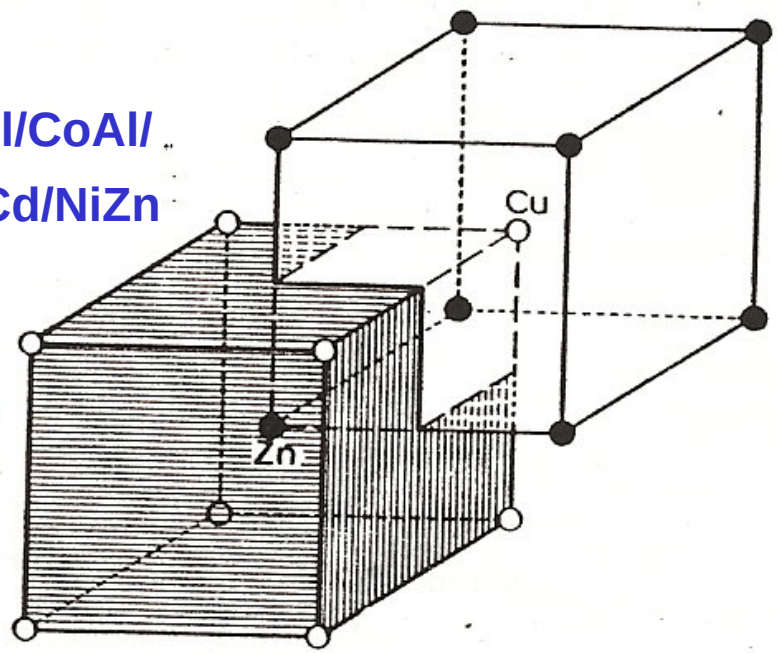
Superlattice formation: order-disorder transformation

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

(a)$L2_0$:

CuZn/FeCo/NiAl/CoAl/

FeAl/AgMg/AuCd/NiZn



β brass superlattice viewed as two inter-penetrating cubic lattices

Five common ordered lattices

(a)$L2_0$:

CuZn/FeCo/NiAl/CoAl/

FeAl/AgMg/AuCd/NiZn

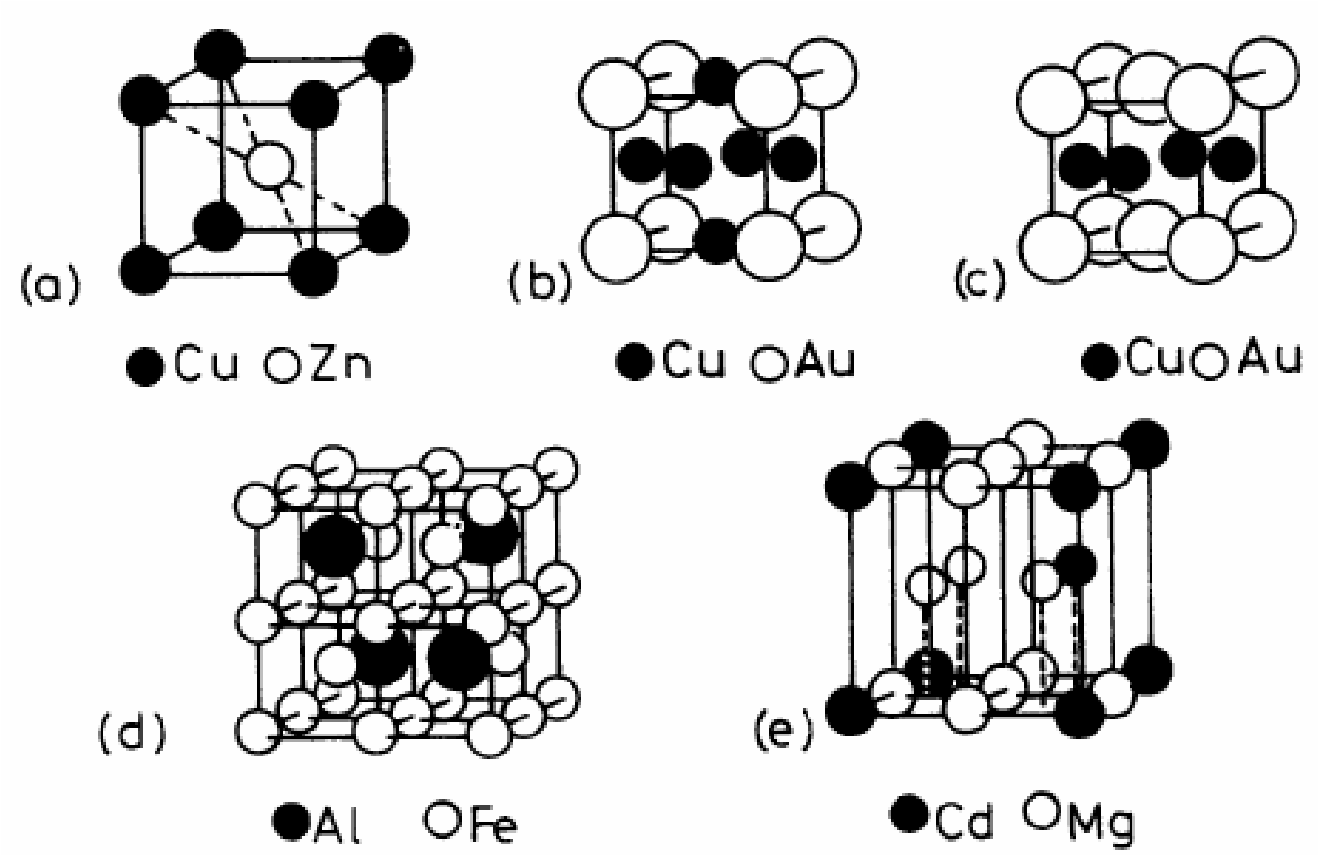
(b) $L1_2$:

$Cu_3Au/Ni_3Mn/Ni_3Fe/Ni_3Al/$

$Pt_3Fe/Au_3Cd/Co_3V/TiZn_3$

(c) $L1_0$:

CuAu/CoPt/FePt



(d) $D0_3$:

$Fe_3Al/Cu_3Sb/Mg_3Li/Fe_3Al/$

$Fe_3Si/Fe_3Be/Cu_3Al$

(e) $D0_{19}$:

$Mg_3Cd/Cd_3Mg/Ti_3Al/Ni_3Sn/Ag_3In/$

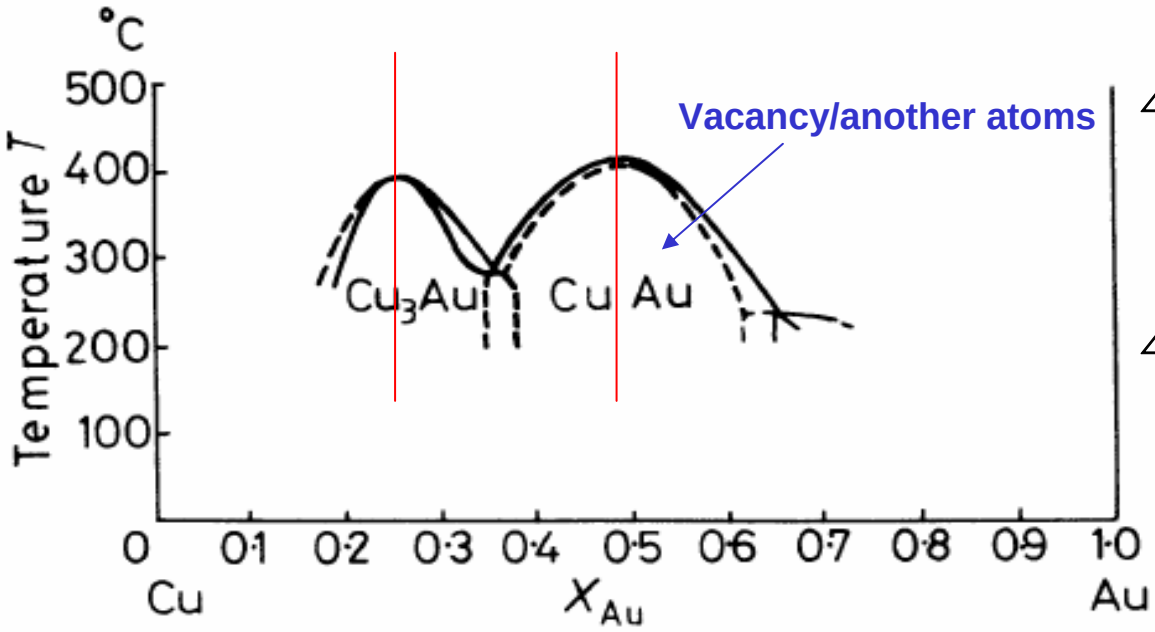
$Co_3Mo/Co_3W/Fe_3Sn/Ni_3In/Ti_3Sn$

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

Ordered phase

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

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

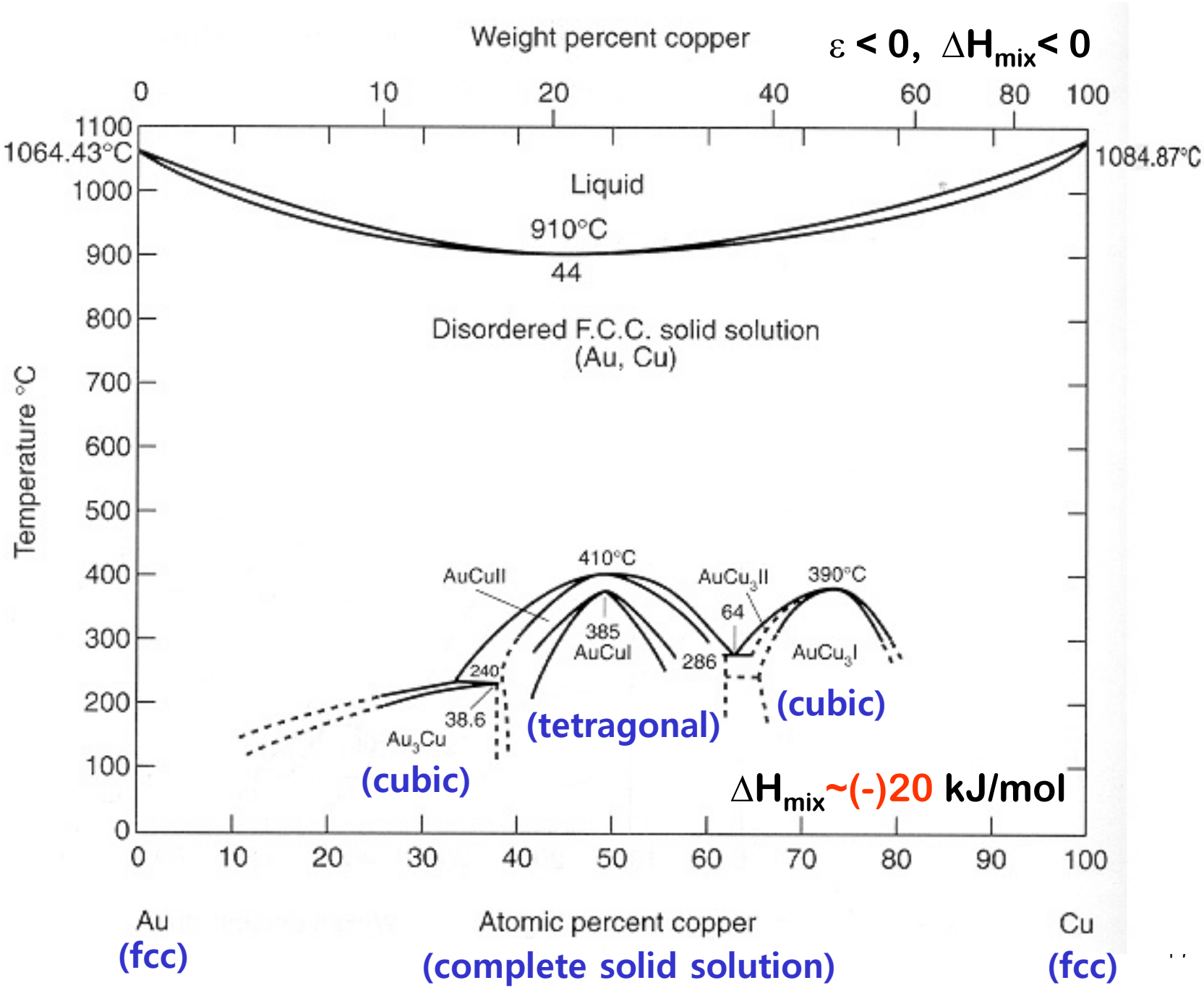


ΔS_{mix}~*small*

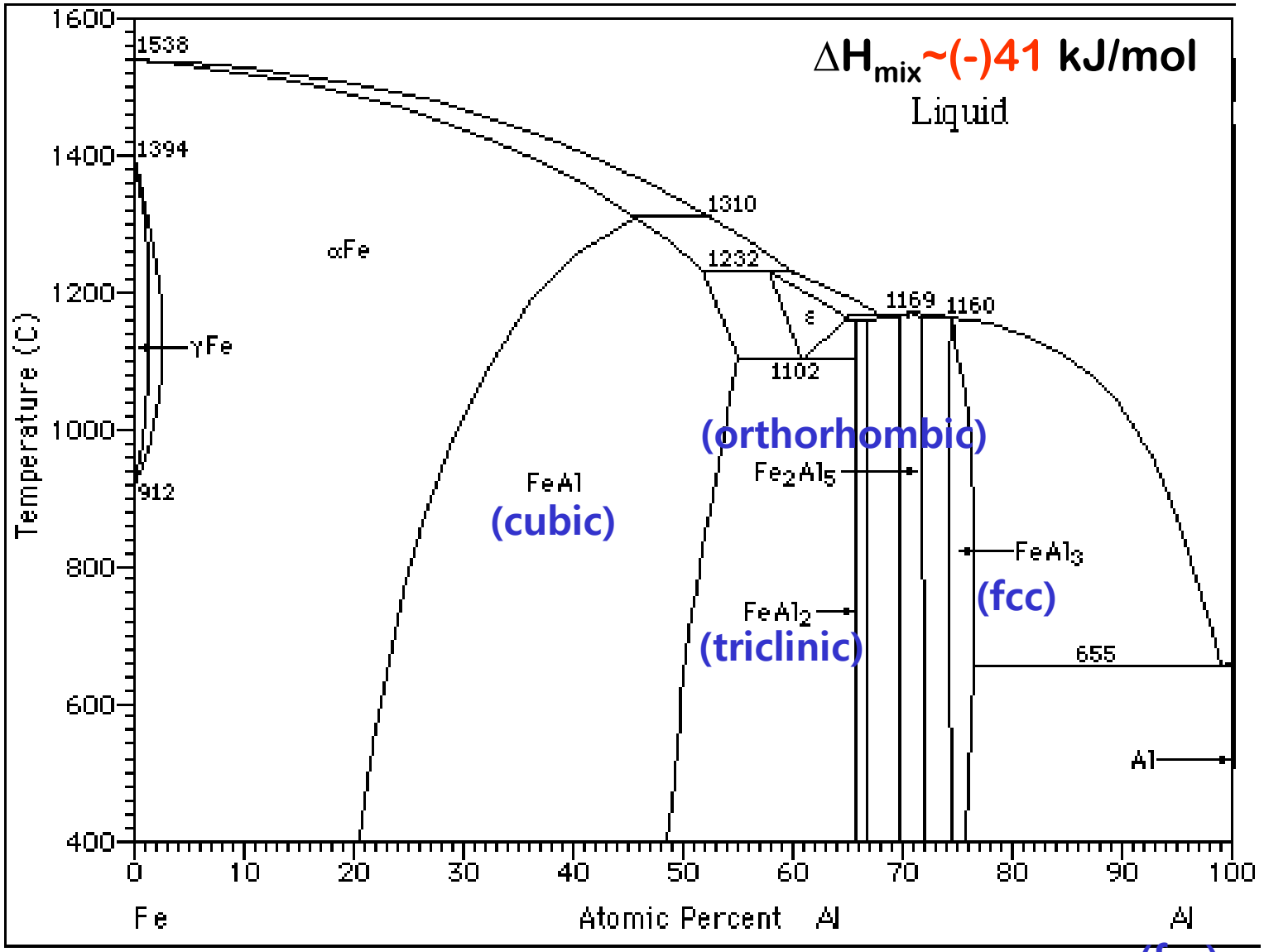
At high Temp.,

ΔG_{mix}~ *large (-)*

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


Weight percent copper
ε < 0, ΔH_mix < 0
0
10
20
40
60
80
100
1100
1064.43°C
1000
900
800
700
600
500
400
300
200
100
0
1084.87°C
Liquid
910°C
44
Disordered F.C.C. solid solution
(Au, Cu)
Temperature °C
AuCuII
410°C
AuCu3II
390°C
64
385
AuCuI
286
AuCu3I
240
38.6
Au3Cu
(tetragonal)
(cubic)
(cubic)
ΔH_mix~(-)20 kJ/mol
0
10
20
30
40
50
60
70
80
90
100
Au
(fcc)
Atomic percent copper
(complete solid solution)
Cu
(fcc)

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



(bcc)

(fcc)

Intermediate Phase

* Often the configuration of atoms that has the minimum free energy after mixing does not have the same crystal structure as either of the pure components. In such cases the new structure is known as an intermediate phase.

* Intermediate phase has crystal structure different from that of either element in pure state. For example, CuZn (bcc) has an ordered body centered structure, different from either Cu (fcc) or Zn (hcp). This particular intermediate phase has some solubility range whereas other intermediate phases may have a very narrow solubility range for the solute element.

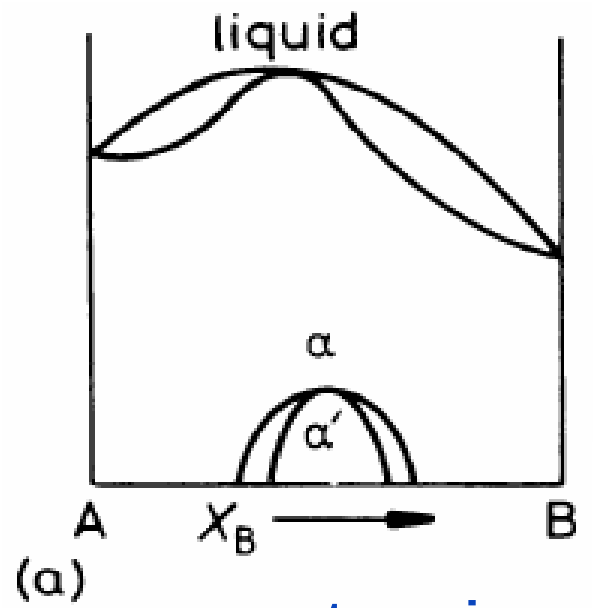
Ordered Alloys $\Delta H_{mix}^{L} = 0$ $\Delta H_{mix}^{S} < 0$

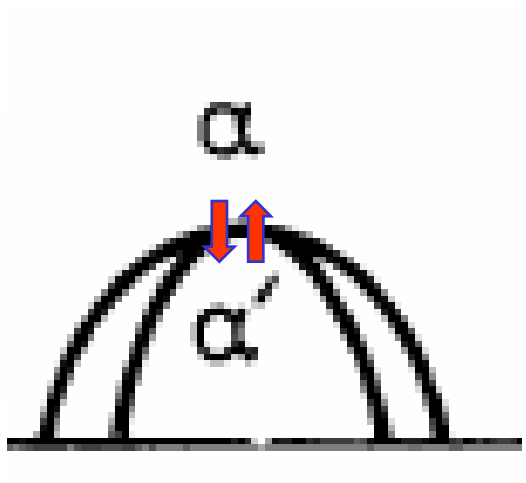
a. **$\Delta H_{mix} < 0 \rightarrow$ A atoms and B atoms like each other.**

How does the phase diagram differ from the previous case?

b. **What would happen when $\Delta H_{mix} << 0$?**

→ The ordered state can extend to the melting temperature.



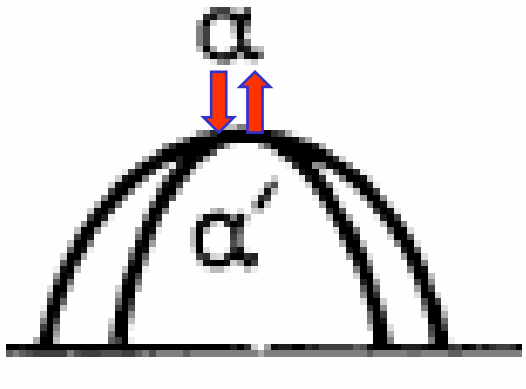


congruent maxima

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
- 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.



*** Solid solution**

→ random mixing

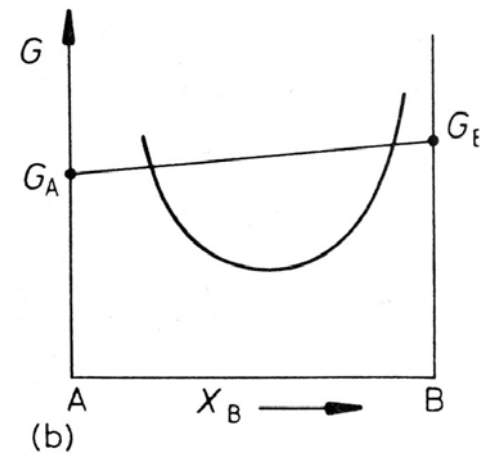
→ entropy ↑

negative enthalpy ↓

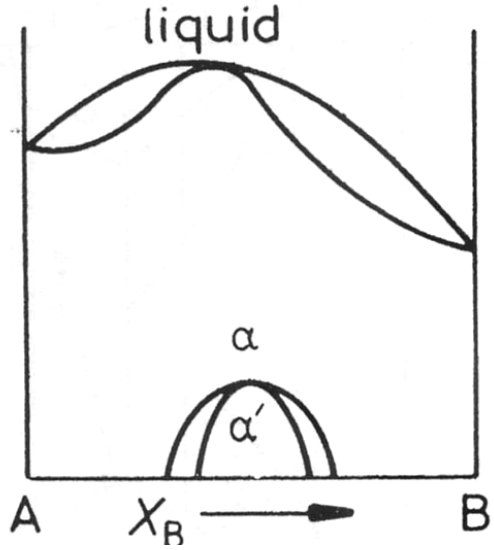
$$\Delta H^{S}_{mix} < 0$$

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 ↓

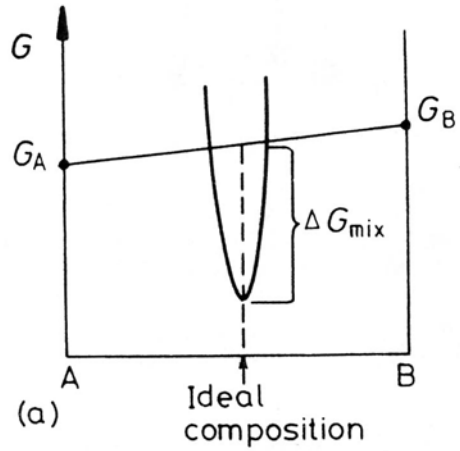
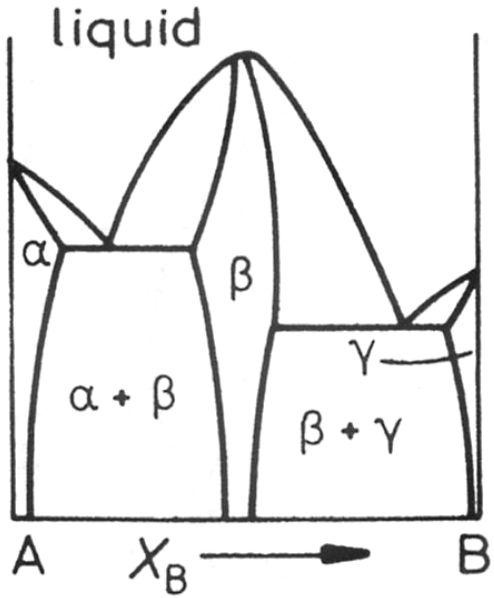
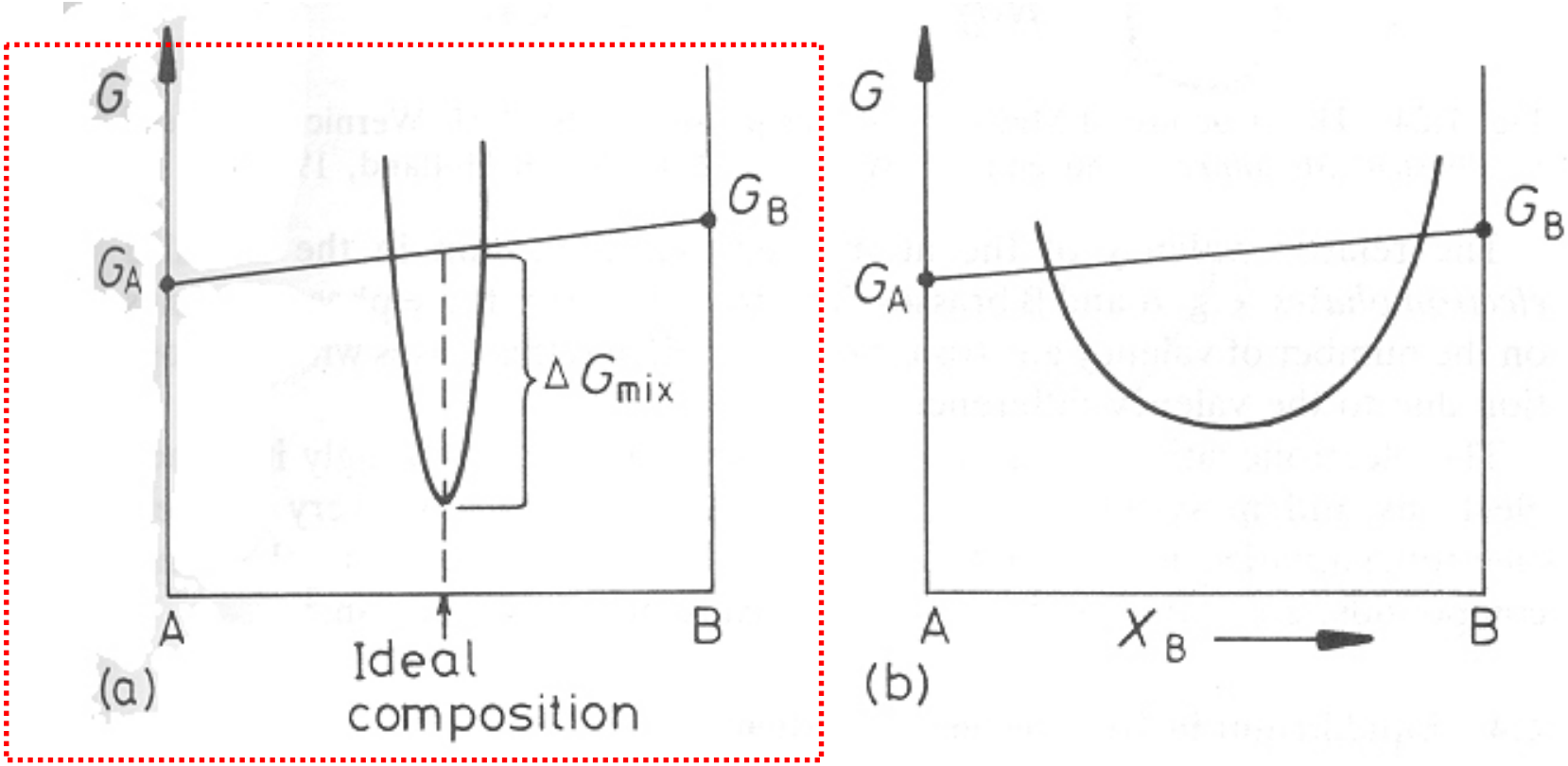


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



Intermediate Phase

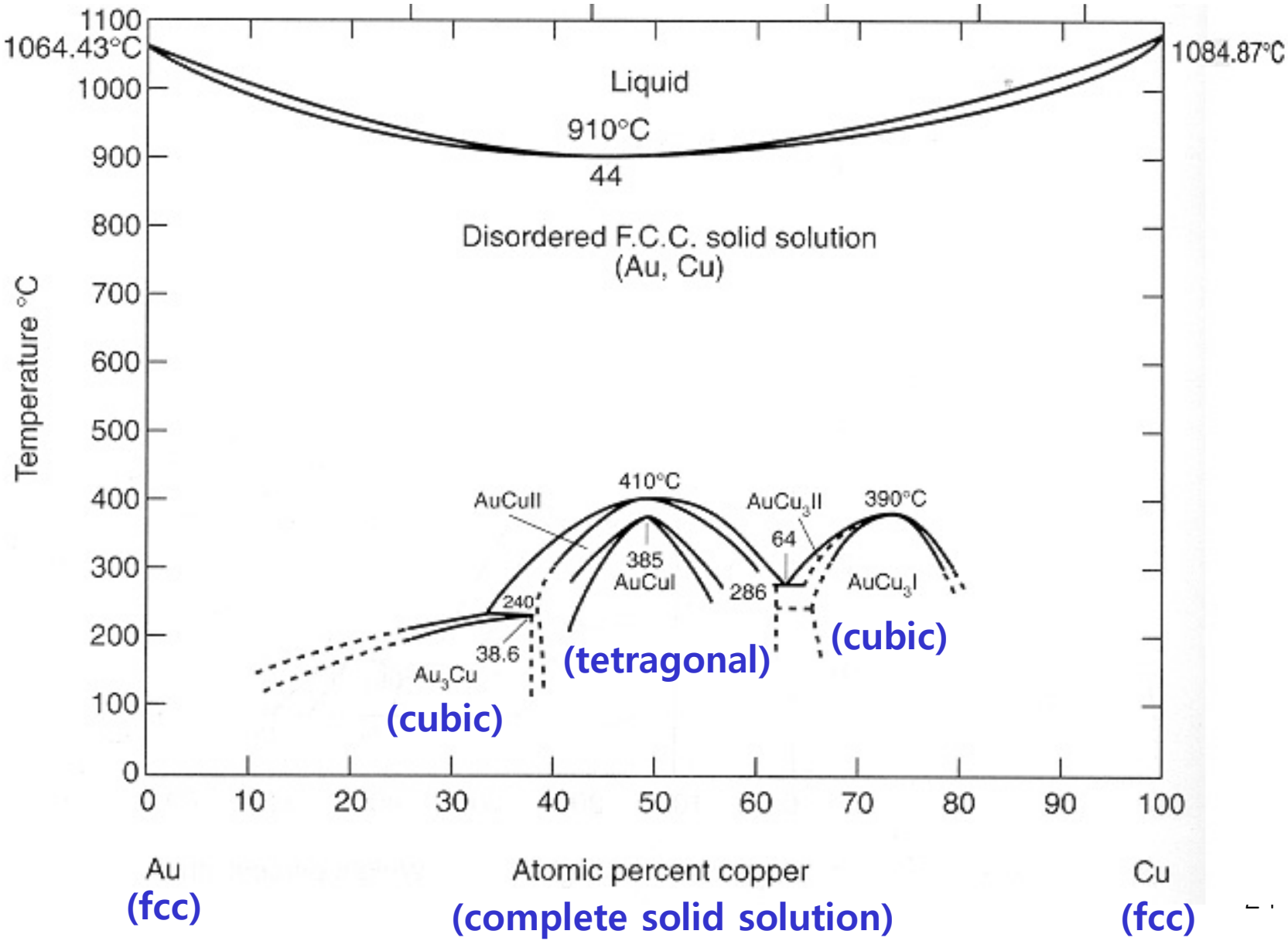


* **Many intermetallic compounds have stoichiometric composition A_mB_n and a characteristic free energy curve as shown in Fig 1.23a.**

* **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. 1.23b**

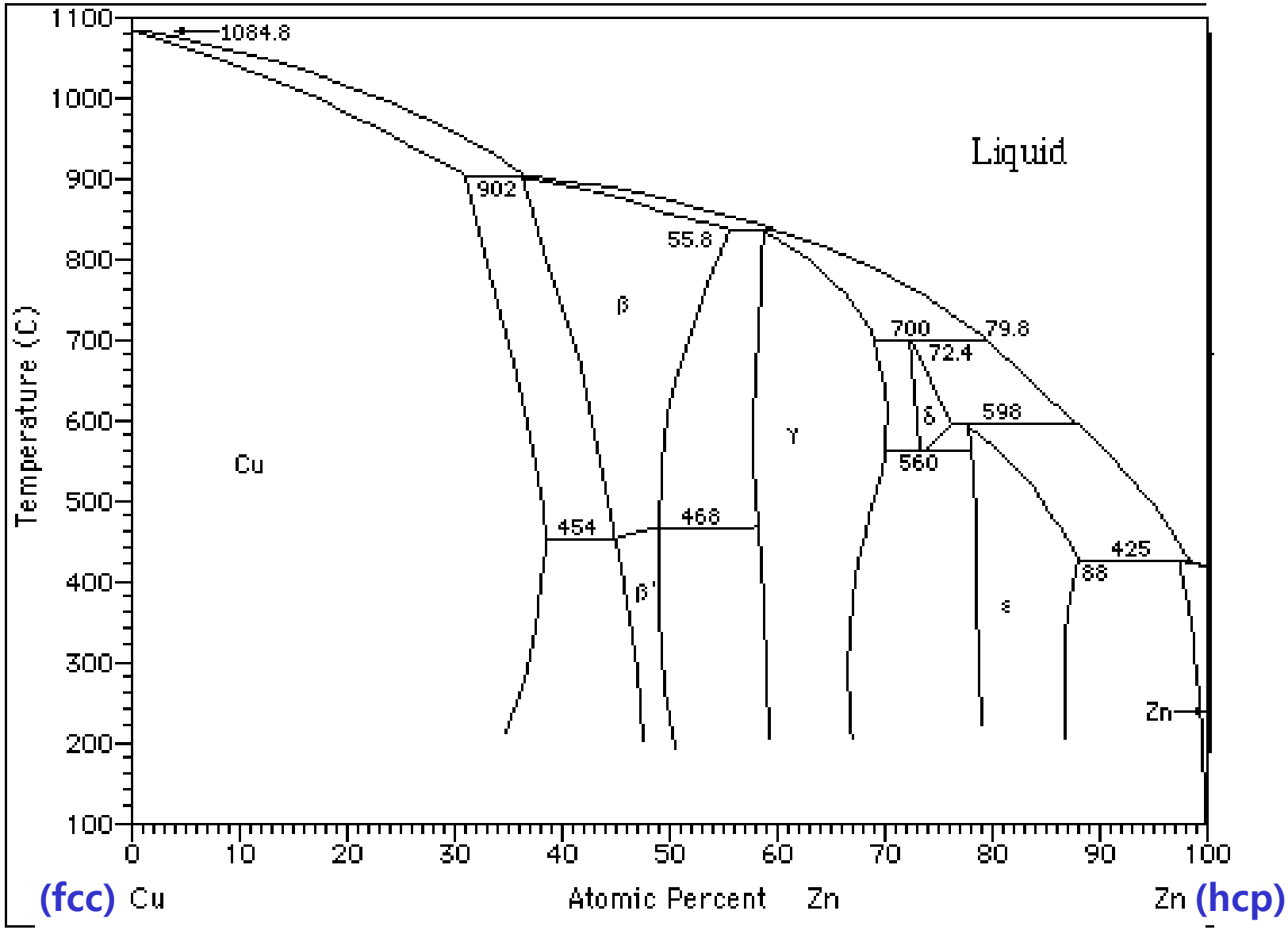
Ordered Phase

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



Intermediate Phase

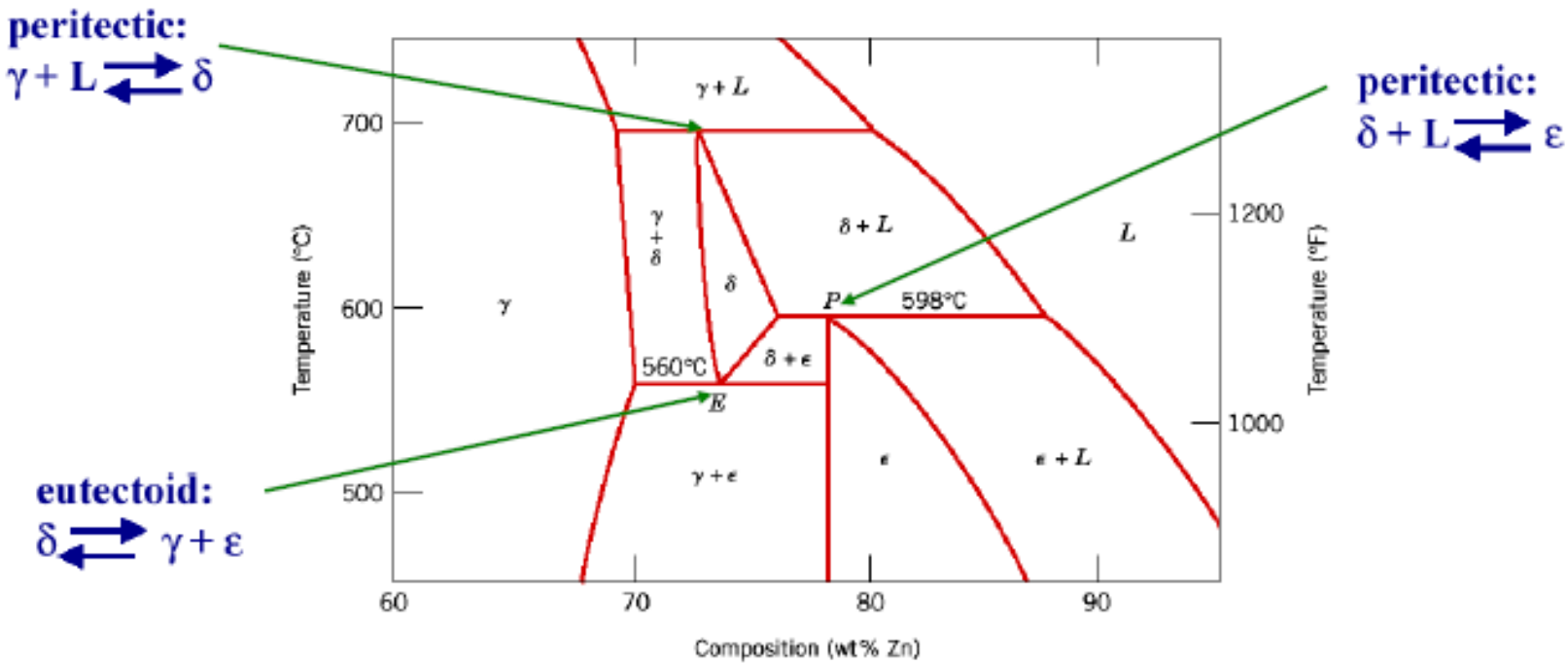
$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim$ -21 kJ/mol



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

Cu-Zn Phase Diagram

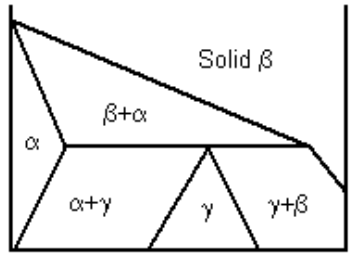
Eutectoid and Peritectic Reactions



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

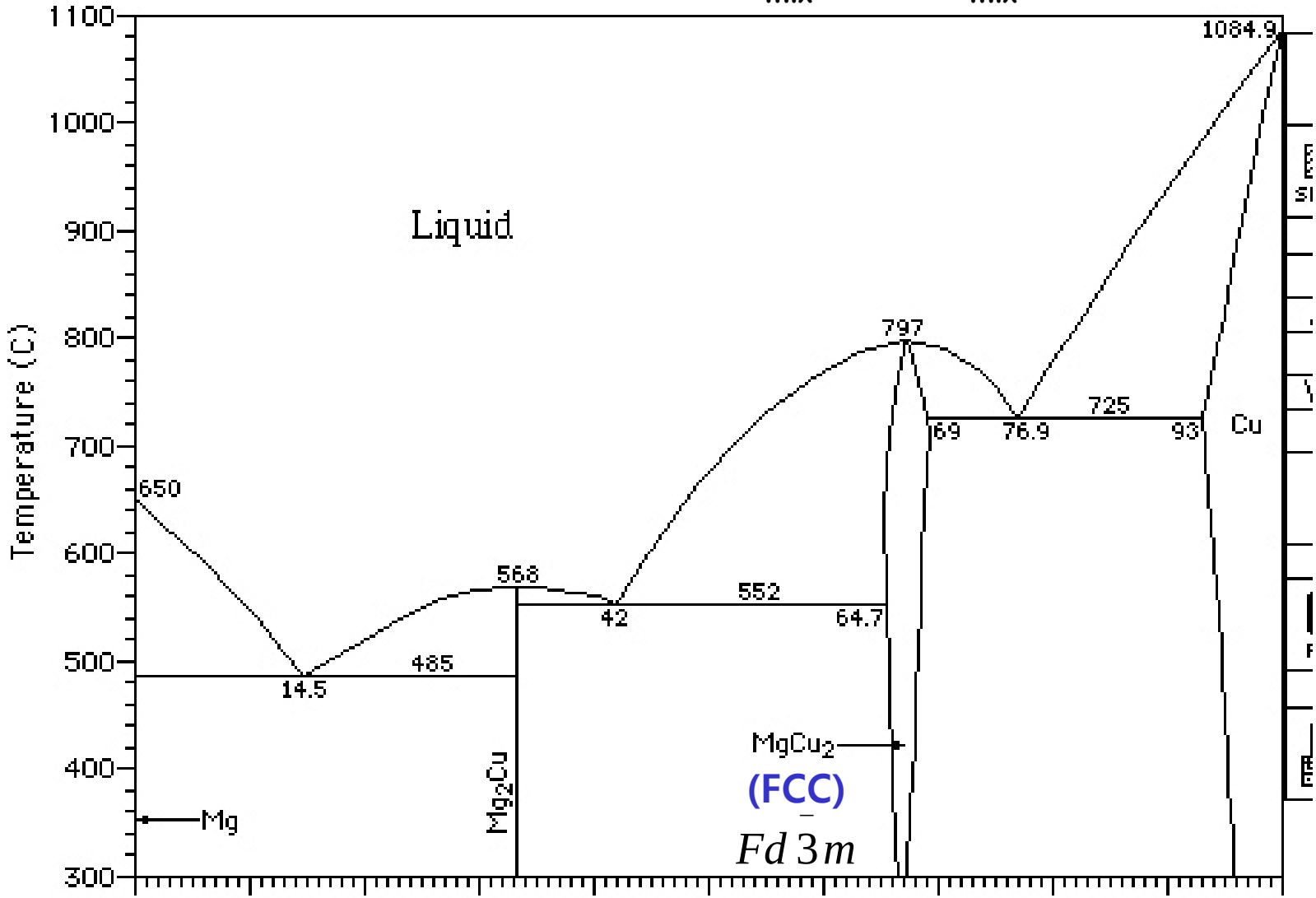
Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

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



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