2009 fall

Phase Transformation of Materials

09.10.2009

Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for today's 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

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

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

- **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 Solution
  - Ideal solution and Regular solution
  - Real solution
  - Ordered phases: SRO & LRO, superlattice
  - Intermediate phase (intermetallic compound)
- Equilibrium in heterogeneous system

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

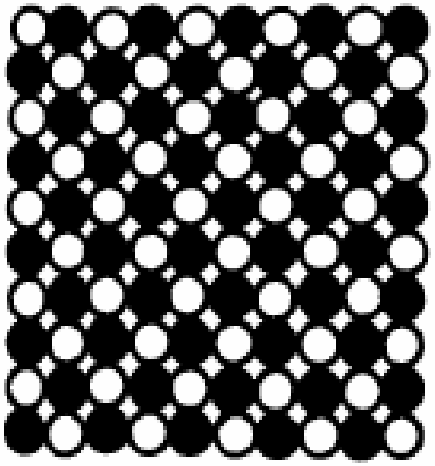
Real solution: 충분한 무질서도 + 가장 낮은 내부 E

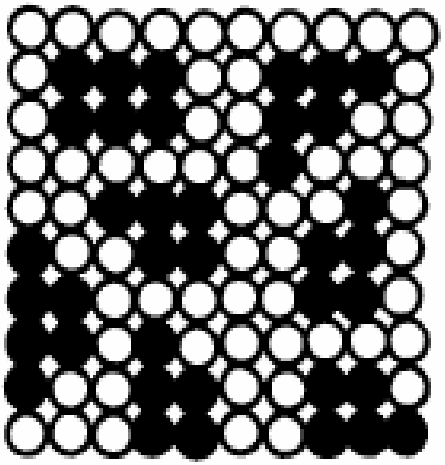
Ideal or Regular solution : over simplification of reality

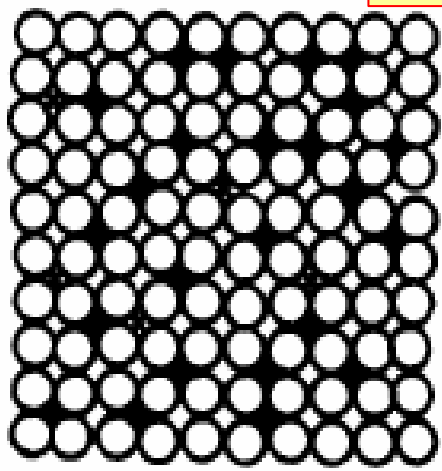
배열 Entropy $S = k \ln w$ + 원자간 결합의 효과 $\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$

$S_{thermal} = 0$

$\varepsilon \approx 0$







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

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

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

P_{AB} ↑ ⟶ 내부 E ↓

P_{AA}, P_{BB} ↑

Real solution: 충분한 무질서도 + 가장 낮은 내부 E

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

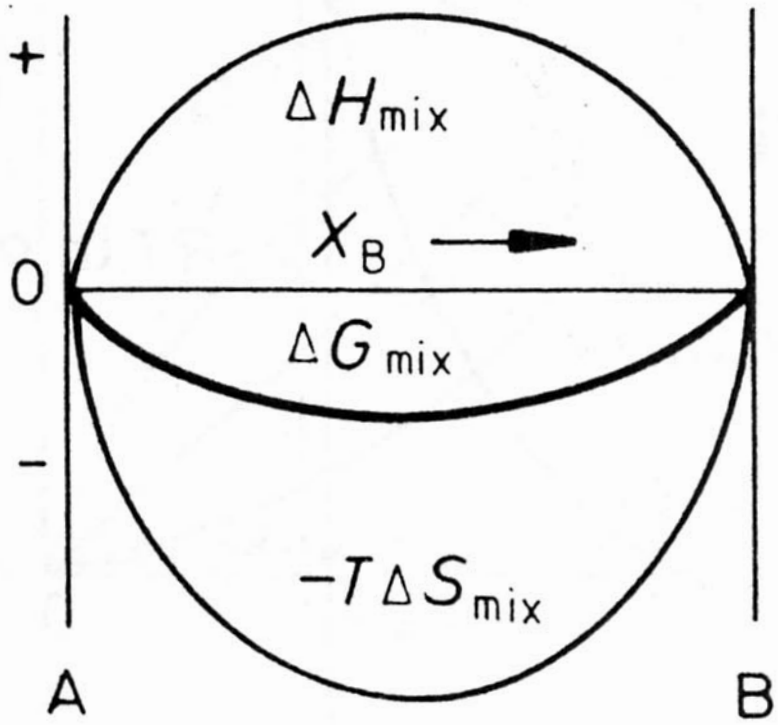
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

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

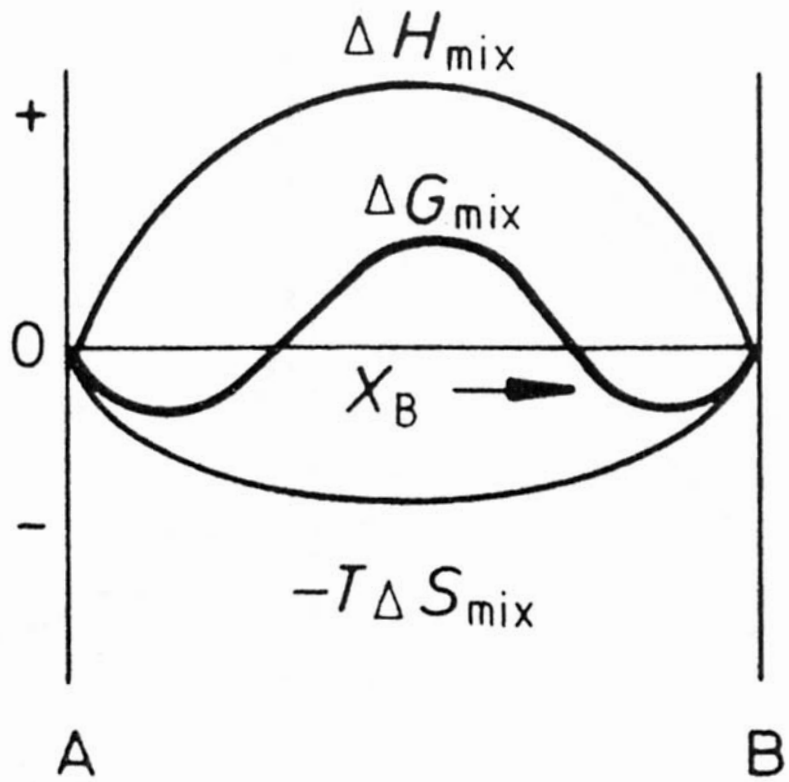
$\Delta E = \Delta H_{mix}$ + elastic strain

➡ quasi- chemical model 에서 단지 ΔH_{mix} 만 고려

정확한 내부 E 변화 알기 위해선 새로운 수학적 모델 요망



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



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

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

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

$\Delta\Omega = N_a z\varepsilon$

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

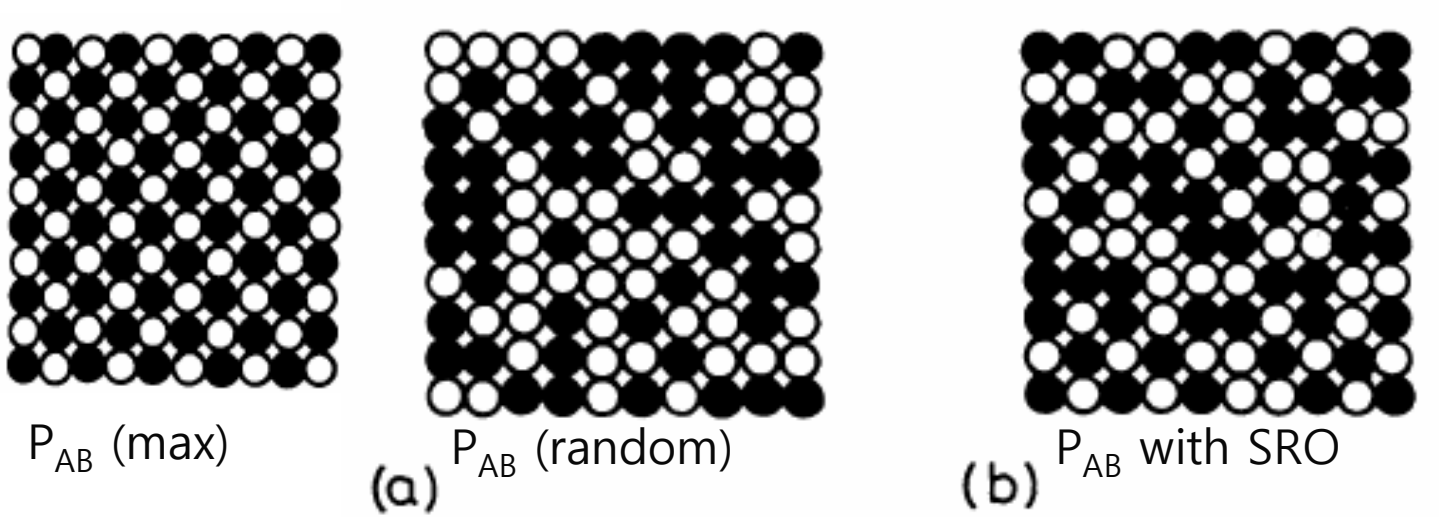
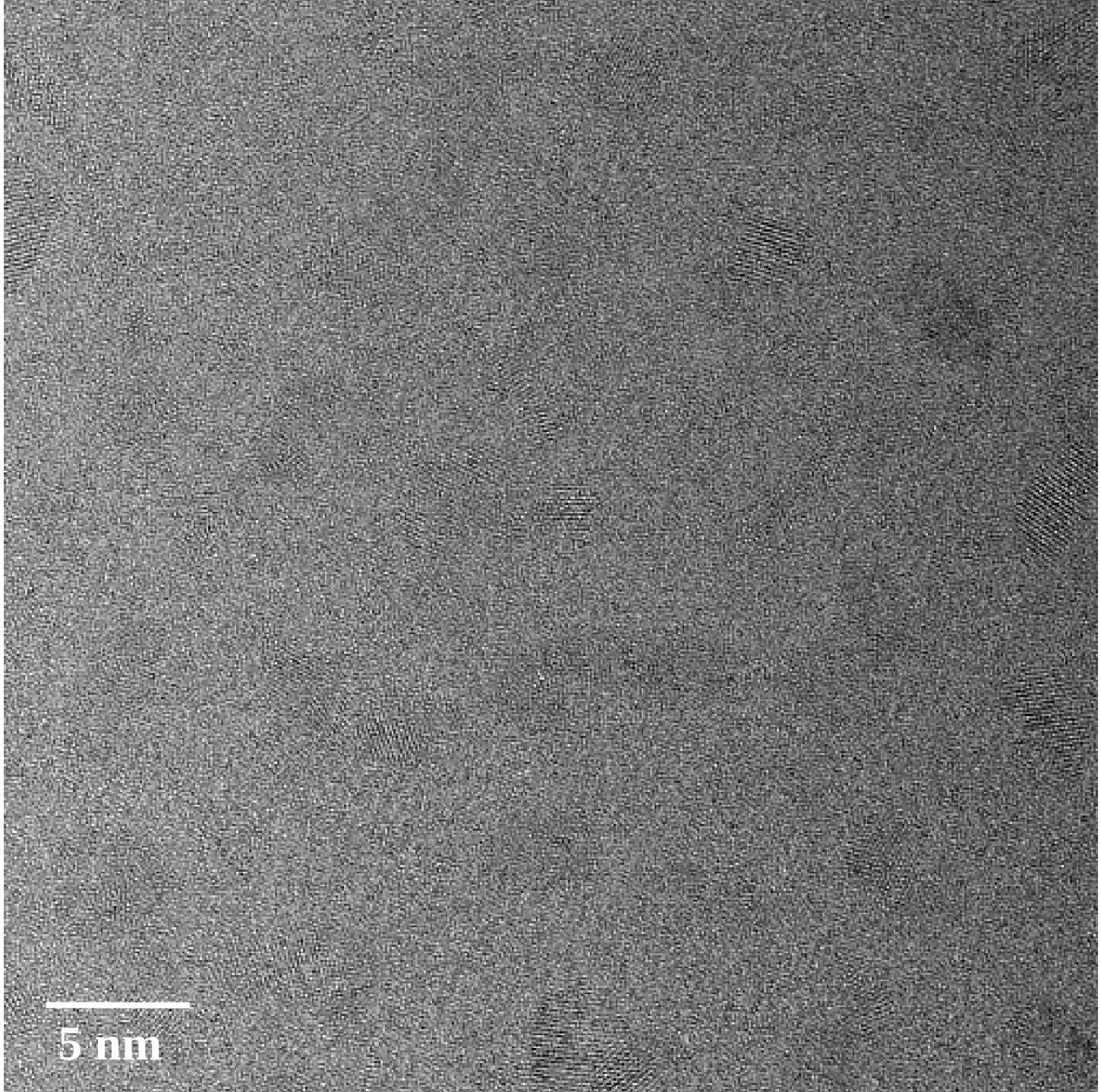
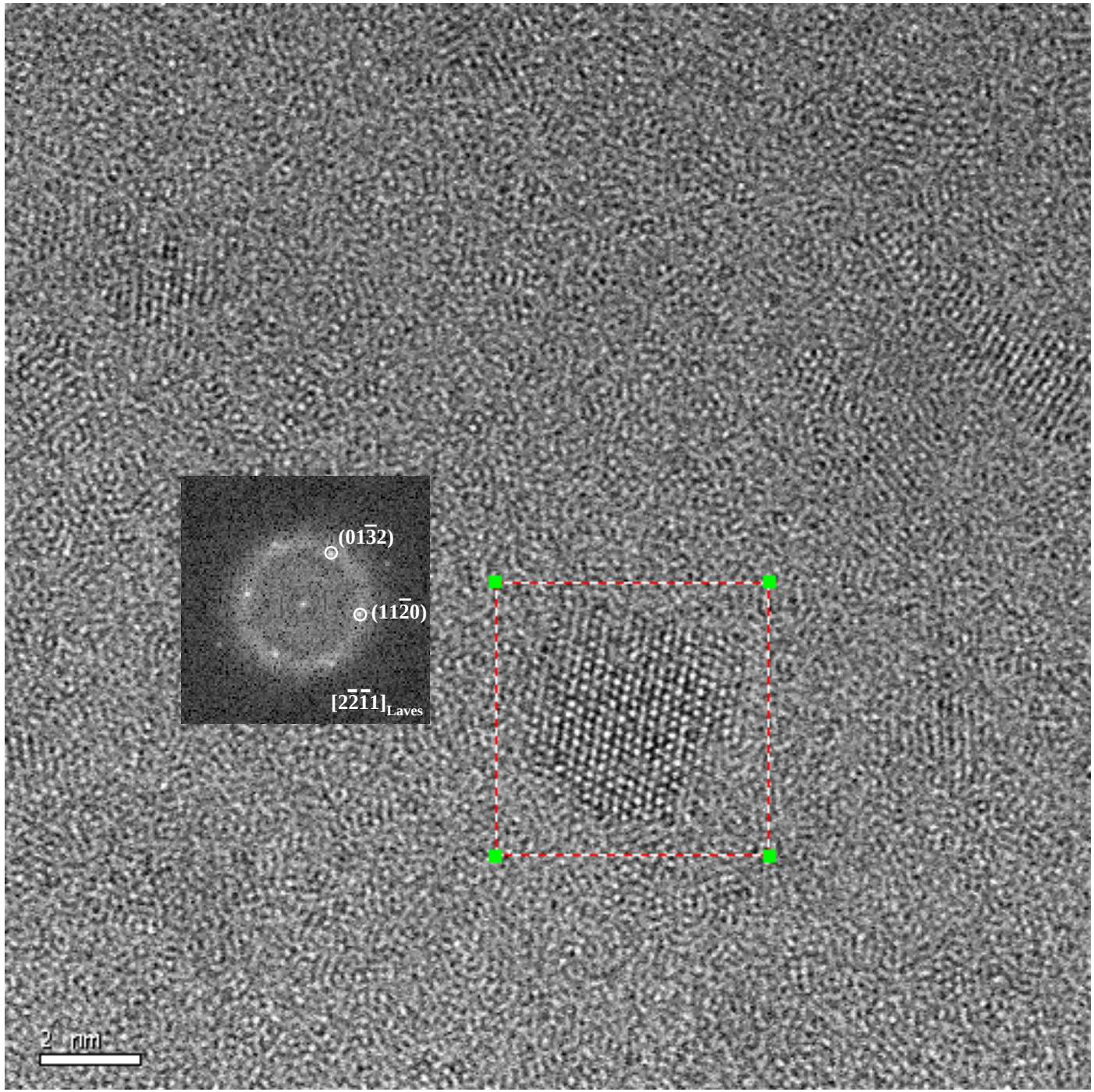


Fig. 1.19 (a) Random A-B solution with a total of 100 atoms and $X_A=X_B=0.5$, P_{AB}~100, S=0. (b) Same alloy with short-range order P_{AB}=132, $PAB_{(max)}$~200, S=(132-100)/(200-100)=0.32

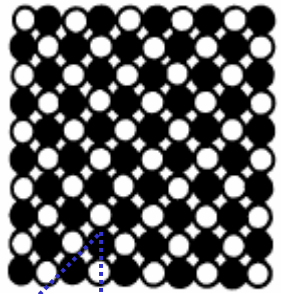

5 nm


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

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

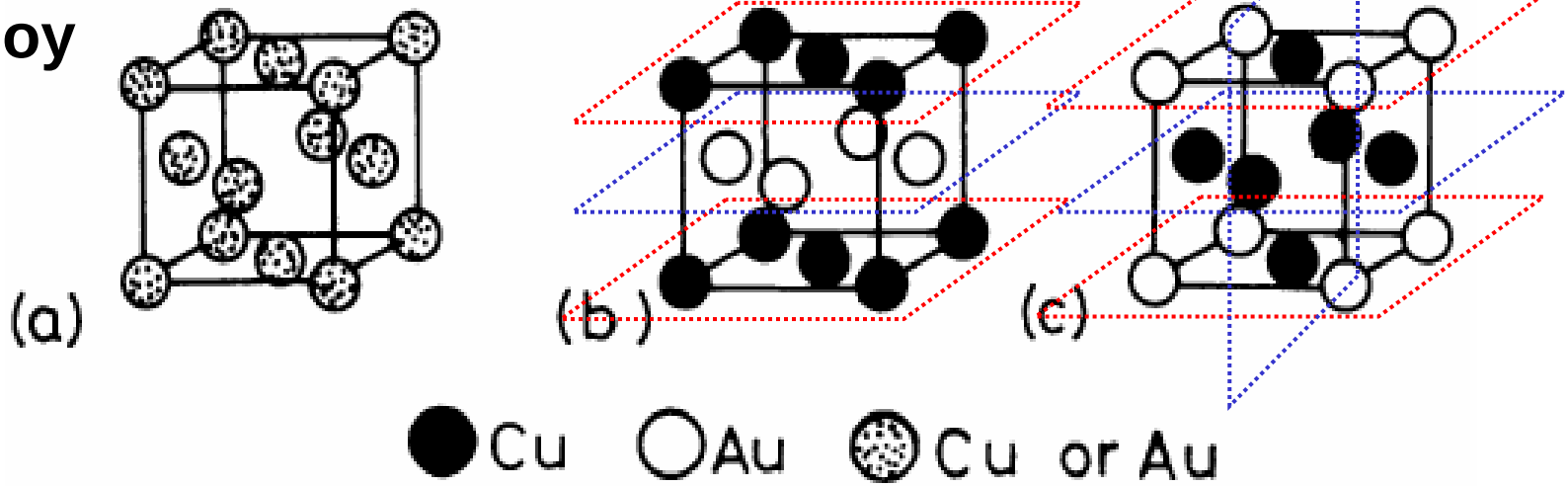
* In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found.

* 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

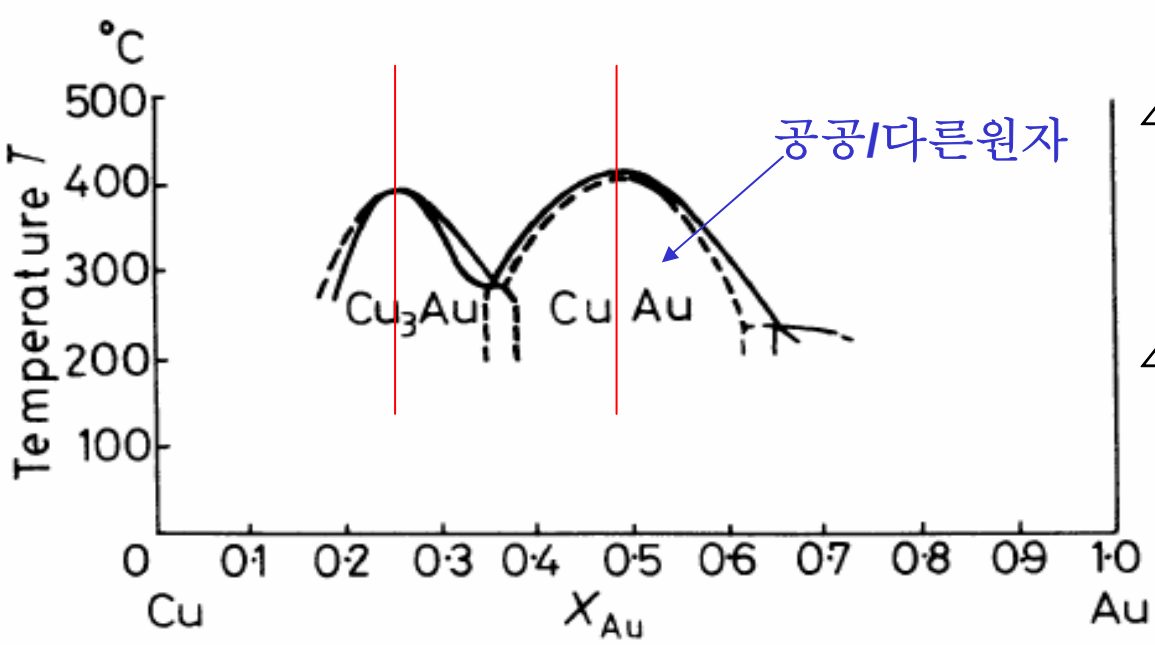
Cu_3Au superlattice

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

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.

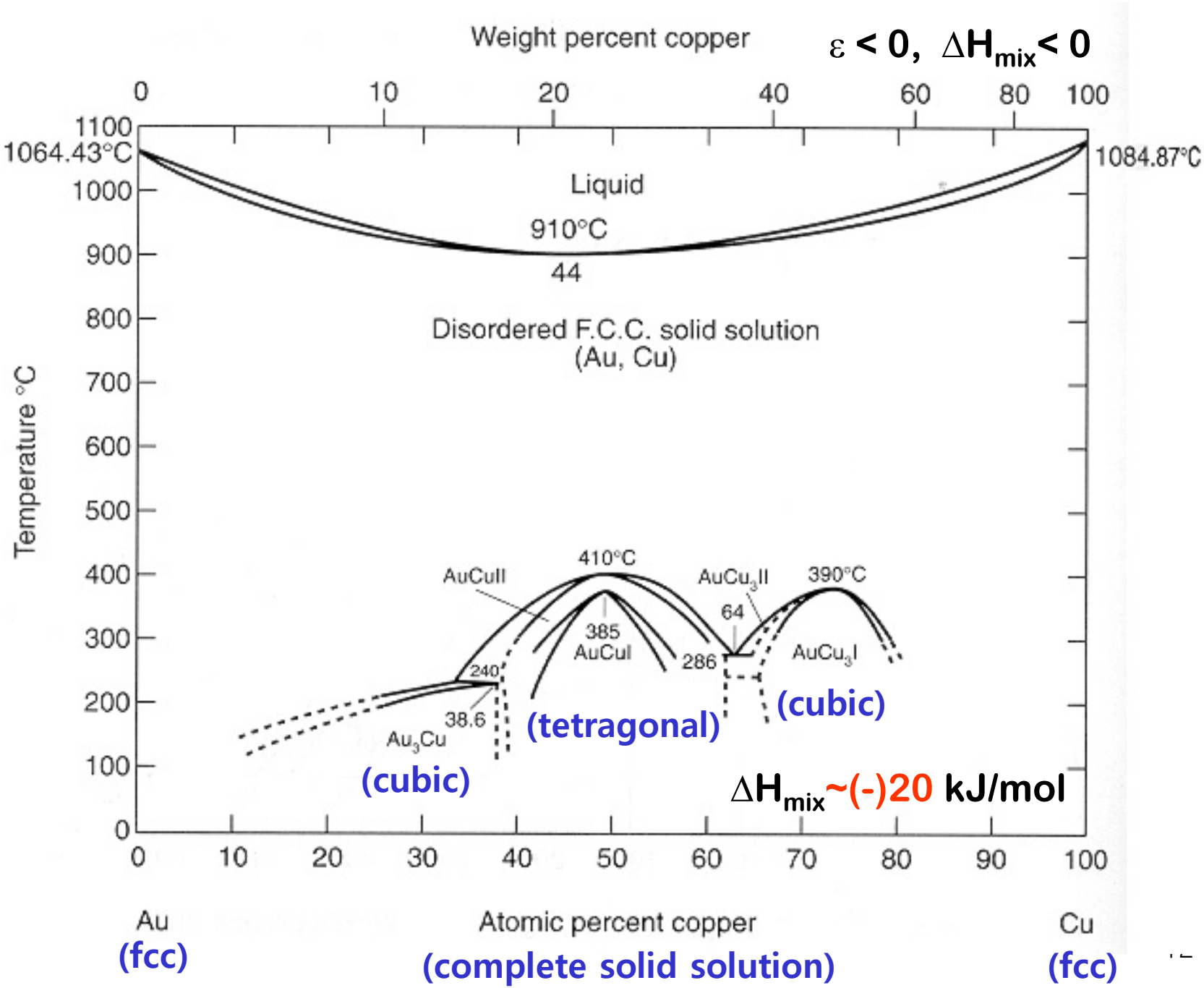


ΔS_{mix}~small

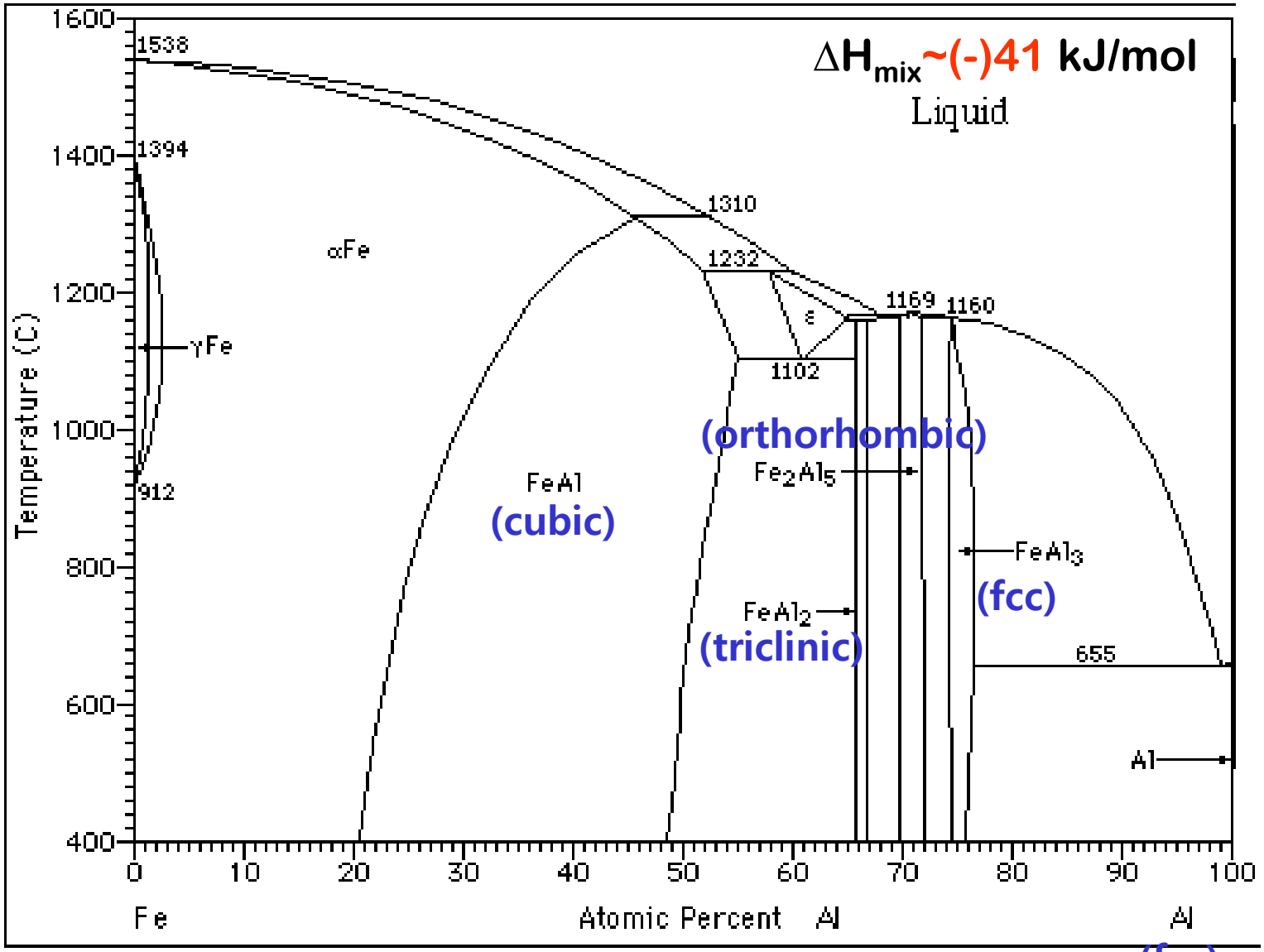
At high Temp.,

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.
- LRO 파괴되는 임계 온도는 Ω 혹은 Δh_{mix} (결합에너지)가 증가함에 따라 상승.
- 대부분의 계에서 규칙상은 용융점까지 안정하다.


Weight percent copper
$\varepsilon < 0$, $\Delta H_{mix} < 0$
0
10
20
40
60
80
100
1100
1064.43°C
1084.87°C
1000
900
800
700
600
500
400
300
200
100
0
Liquid
910°C
44
Disordered F.C.C. solid solution
(Au, Cu)
Temperature °C
AuCuII
410°C
$AuCu_3$II
390°C
64
385
AuCuI
286
240
$AuCu_3$I
38.6
Au_3Cu
(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)

Five common ordered lattices

(a)$L2_0$:

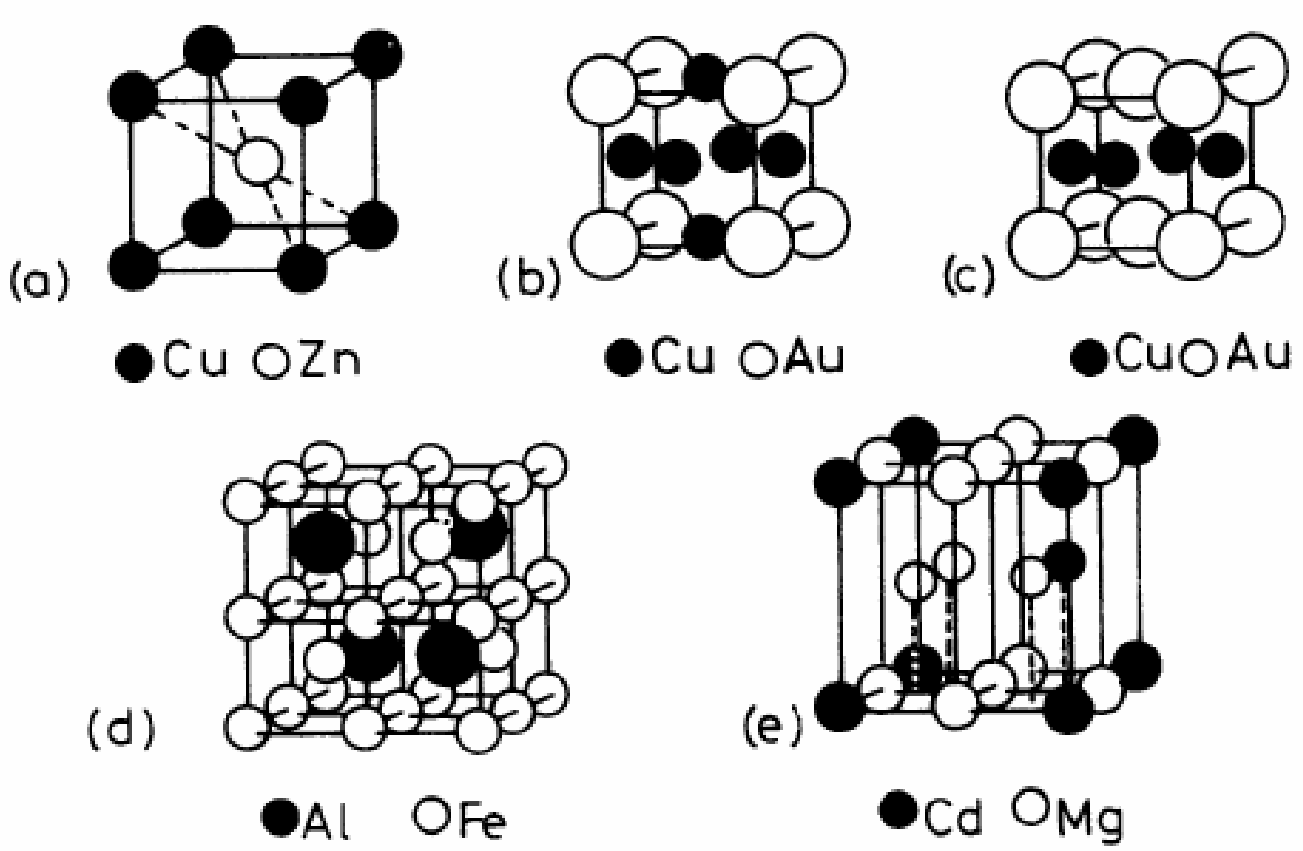
CuZn/FeCo/NiAl/CoAl/
FeAl/AgMg/AuCd/NiZn

(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

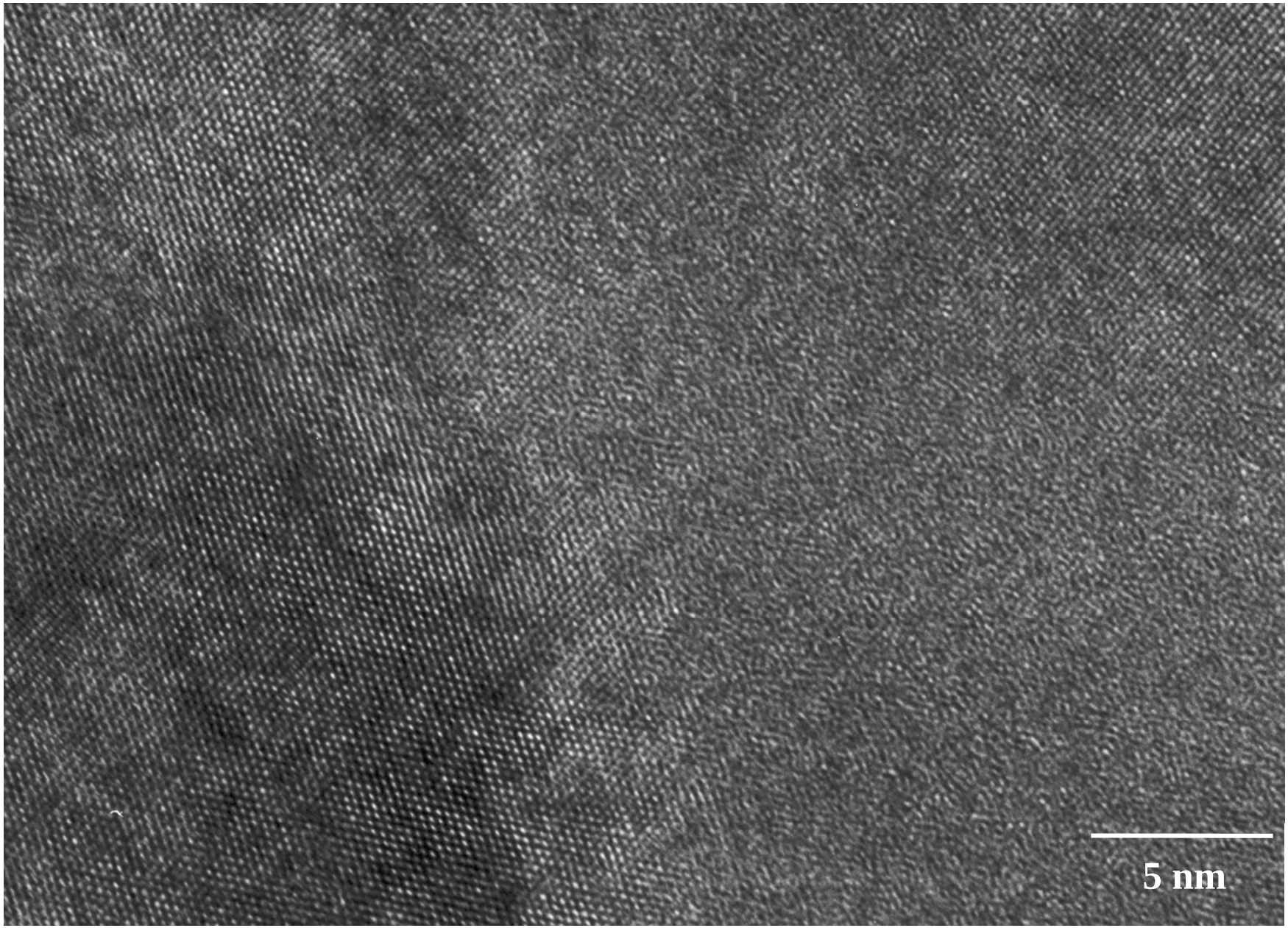


(d) $D0_3$:

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

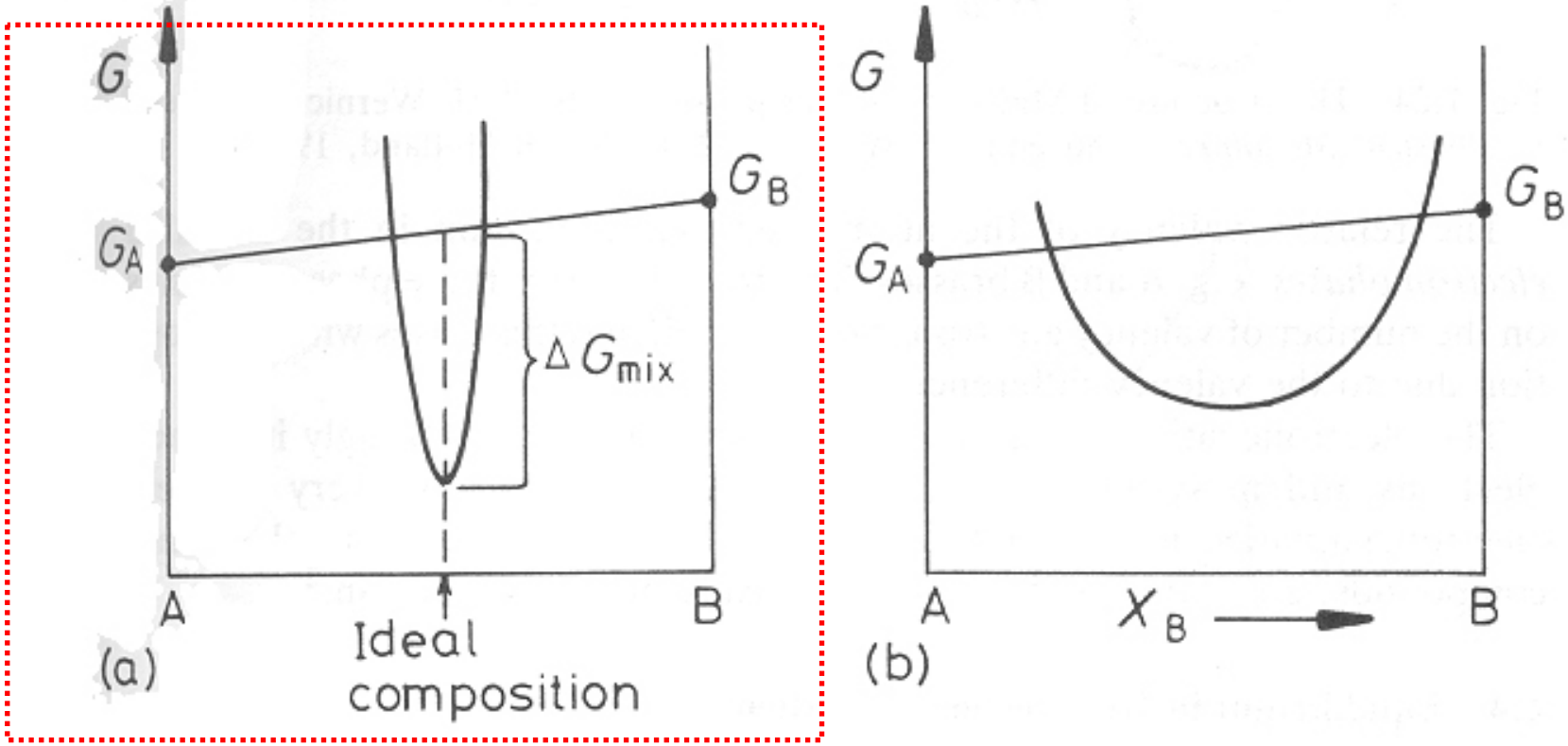

5 nm

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.

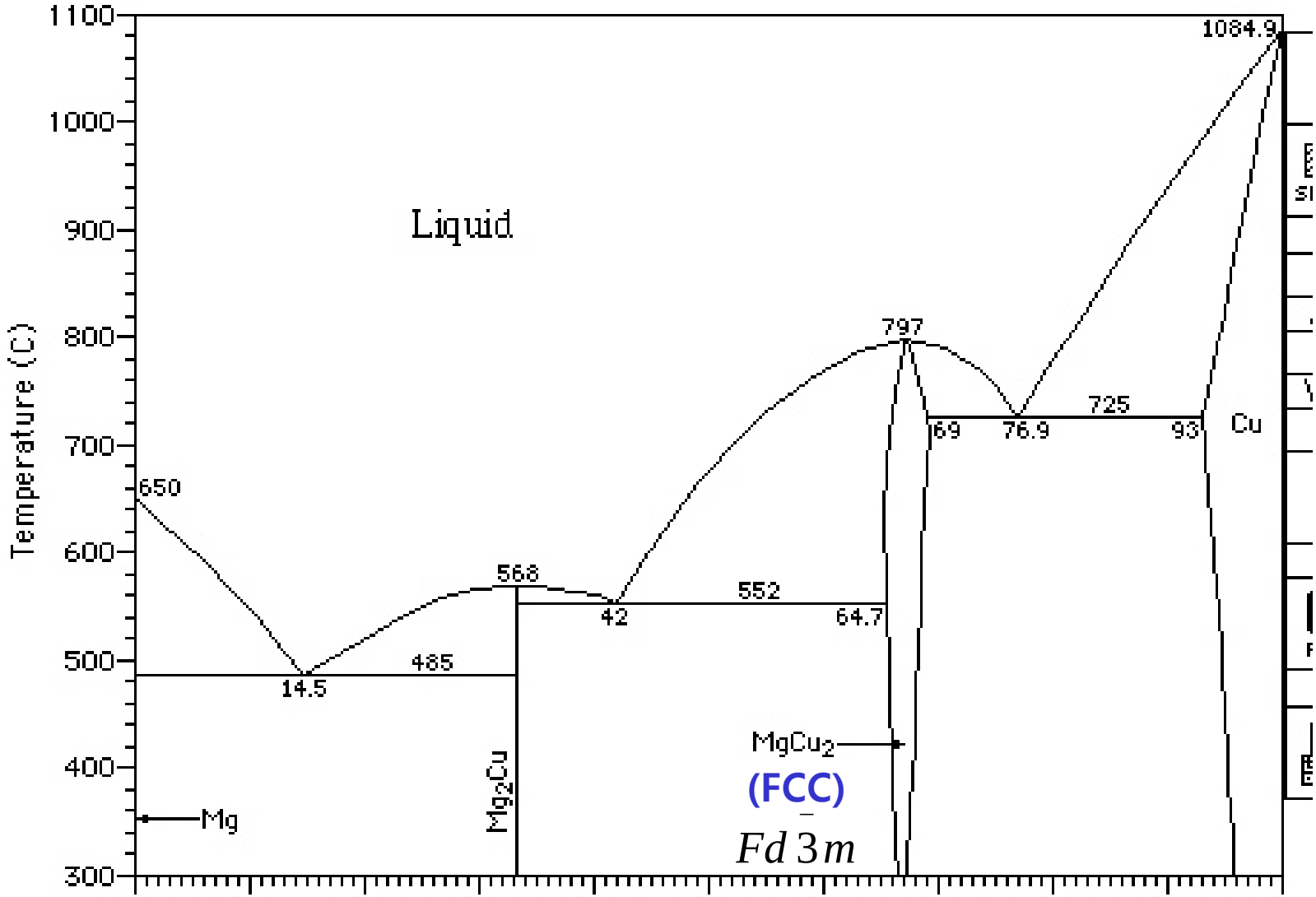
Intermediate Phase



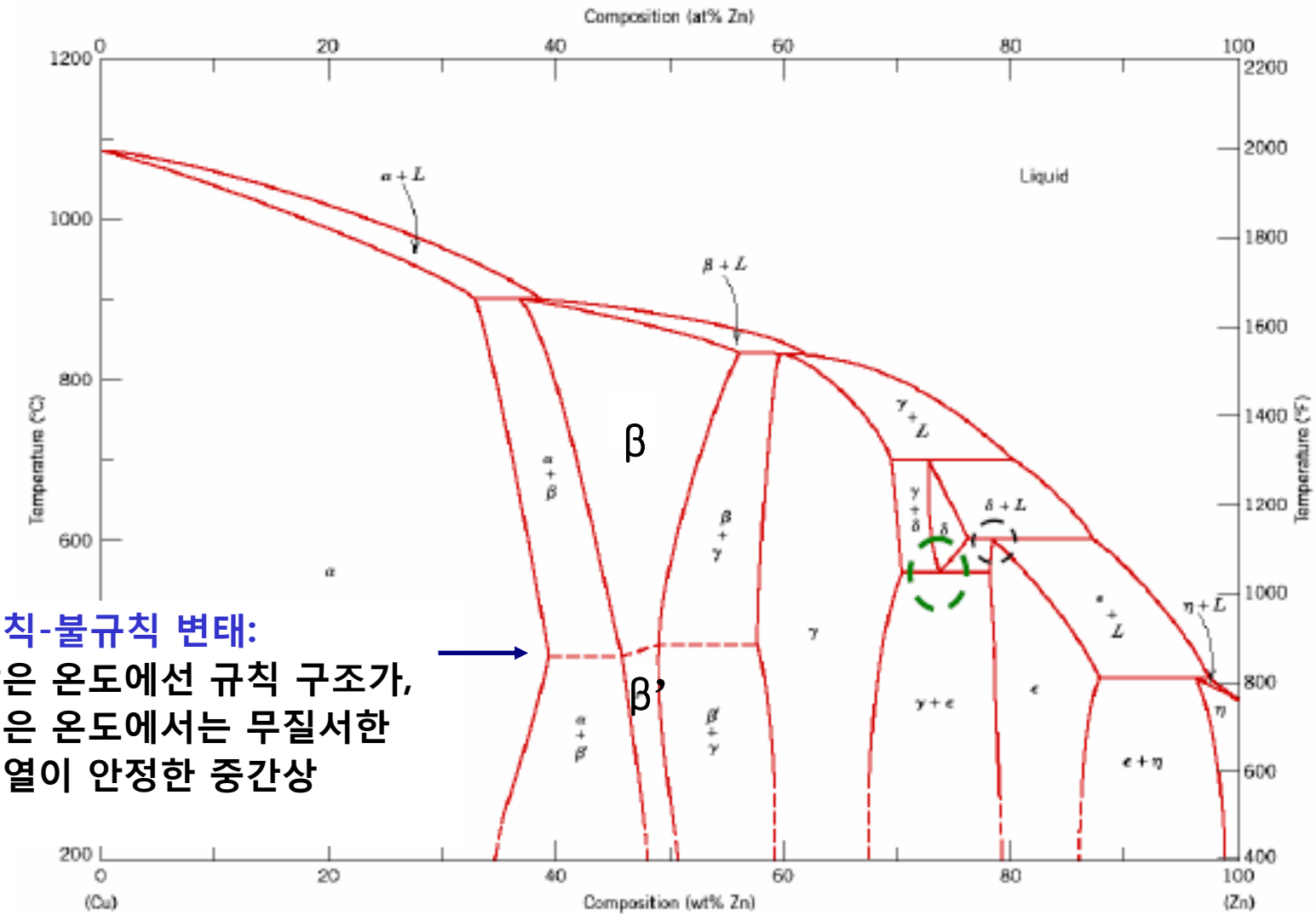
* **Many intermetallic compounds have stoichiometric composition A_mB_n and a characteristic free energy curve as shown in Fig 1.23a.**

* **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**

Intermediate Phase



Cu-Zn Phase Diagram



규칙-불규칙 변태:
낮은 온도에선 규칙 구조가,
높은 온도에서는 무질서한
배열이 안정한 중간상

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

Intermediate Phase

3 main factors

determining the structure of Intermediate phase ?

1) Relative atomic size

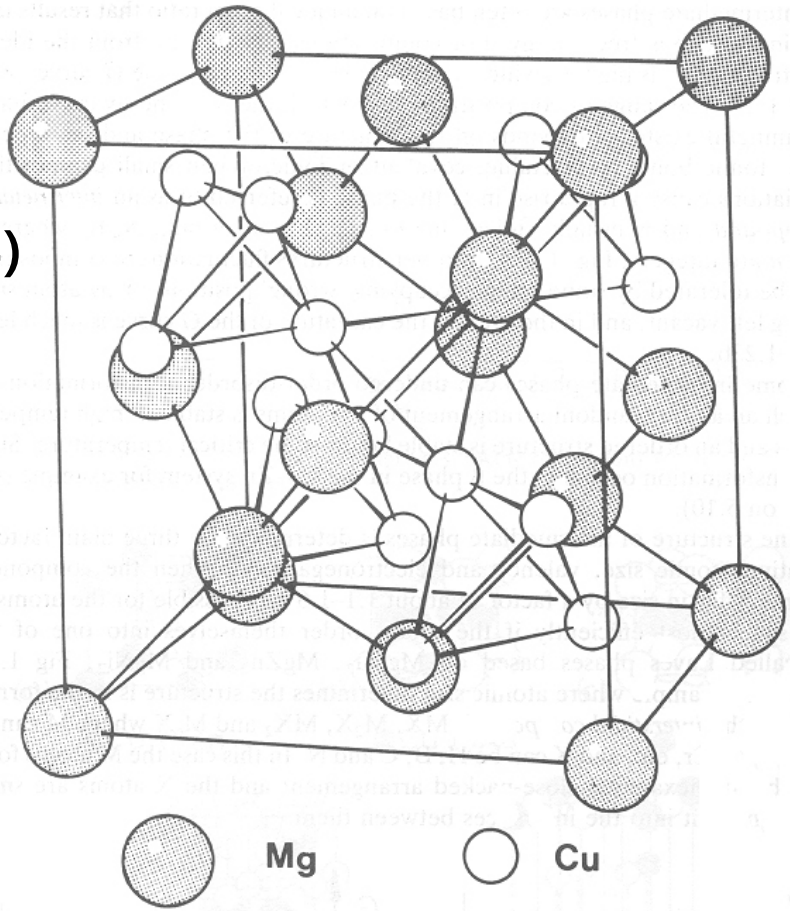
- **Laves 상 (원자크기비가 1.1~1.6인 경우)**
- **침입형 화합물: MX, M_2X, MX_2, M_6X**

2) Valency Electron

- **전자상이 형성되는 경우 ex_α & β 황동**

3) Electronegativity

- **이온결합에 의한 화합물 Mg_2Sn**



$MgCu_2$ (A Laves phase)