재 료 상 변 태

Phase Transformation of Materials

2008.09.11.

박 은 수

서울대학교 재료공학부

Contents for previous class

- **Ideal solution**과 **regular solution**의 이해
- 이상 용액과 규칙 용액에서 **Gibbs Free Energy**
- **Chemical potential**과 **Activity** 의 이해

Contents for today's class

- **Review for last class**
- **Real solutions**
- **Ordered phases: SRO & LRO, Superlattice**
- **Intermediate phase (intermetallic compound)**
- **Equilibrium in heterogeneous system**

* **Single component system** **One element (Al, Fe), One type of molecule (H_2O)**

: 평형 상태 압력과 온도에 의해 결정됨

* **Binary System (two component)** → A, B

: 평형 상태 온도(T)와 압력(P) 이외에도 조성의 변화(X)를 고려

- **Mixture ; A – A, B – B ;** → 각각의 성질 유지, **boundary**는 존재,

  A **B** 섞이지 않고 기계적 혼합

- **Solution ; A – A – A ;** → **atomic scale**로 섞여 있다. **Random distribution**

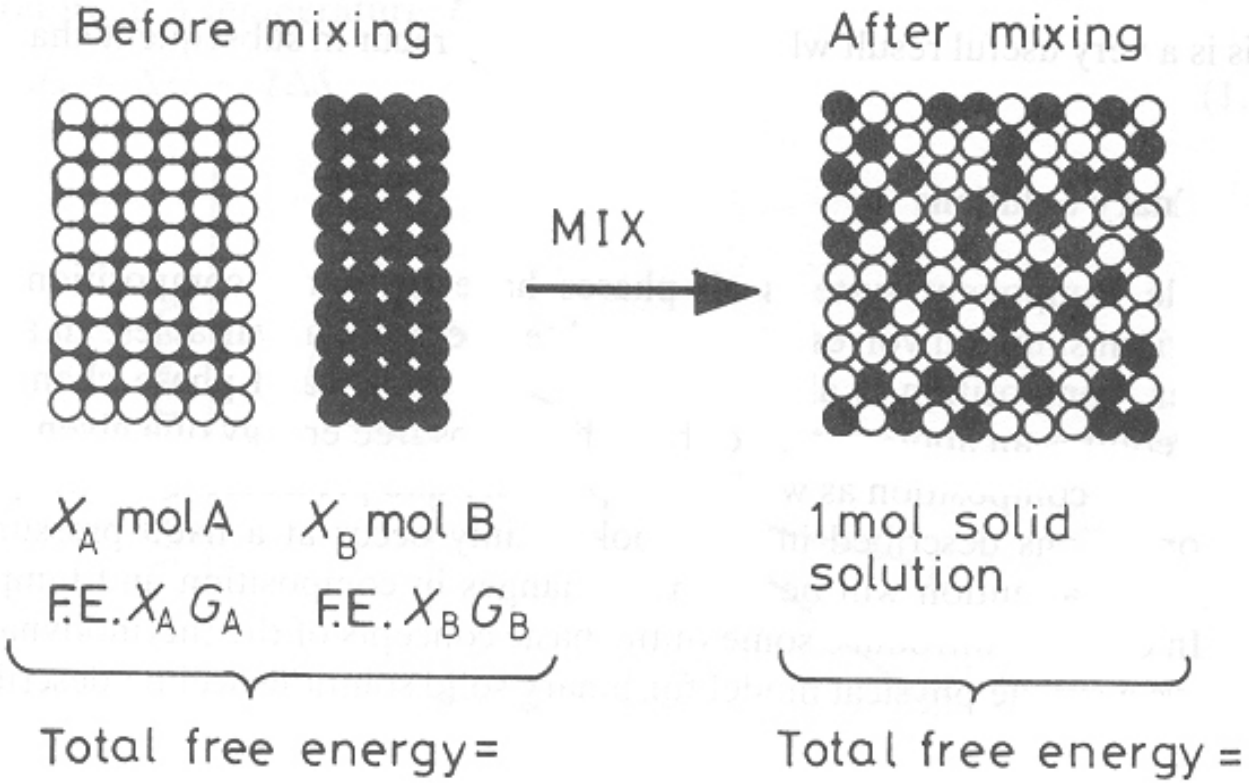
  A – B – A **Solid solution : substitutional or interstitial**

- **compound ; A – B – A – B ;** → **A, B**의 위치가 정해짐, **Ordered state**

  B – A – B – A

Gibbs Free Energy of Binary Solutions

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



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

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

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

➡ ***How can you estimate ΔH_{mix} and ΔS_{mix} ?***

Mixing free energy ΔG_{mix}

1) Ideal solution

가정1 ; $\Delta H_{mix}=0$:

; A와 B가 complete solid solution

(A,B ; same crystal structure)

; no volume change

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

$$\Delta G_{mix} = -T\Delta S_{mix}\ J/mol$$

Entropy can be computed from randomness by Boltzmann equation,

$$S = k \ln w$$

w : degree of randomness, k: Boltzman constant

$$S = S_{th} + S_{config}$$

→ thermal; vibration (no volume change)

→ Configuration; atom 의 배열 방법 수 (distinguishable)

If there is no volume change or heat change,

$$\Delta S^{mix} = S^{after} - S^{before} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!} - k \ln 1$$

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

Mixing free energy ΔG_{mix}

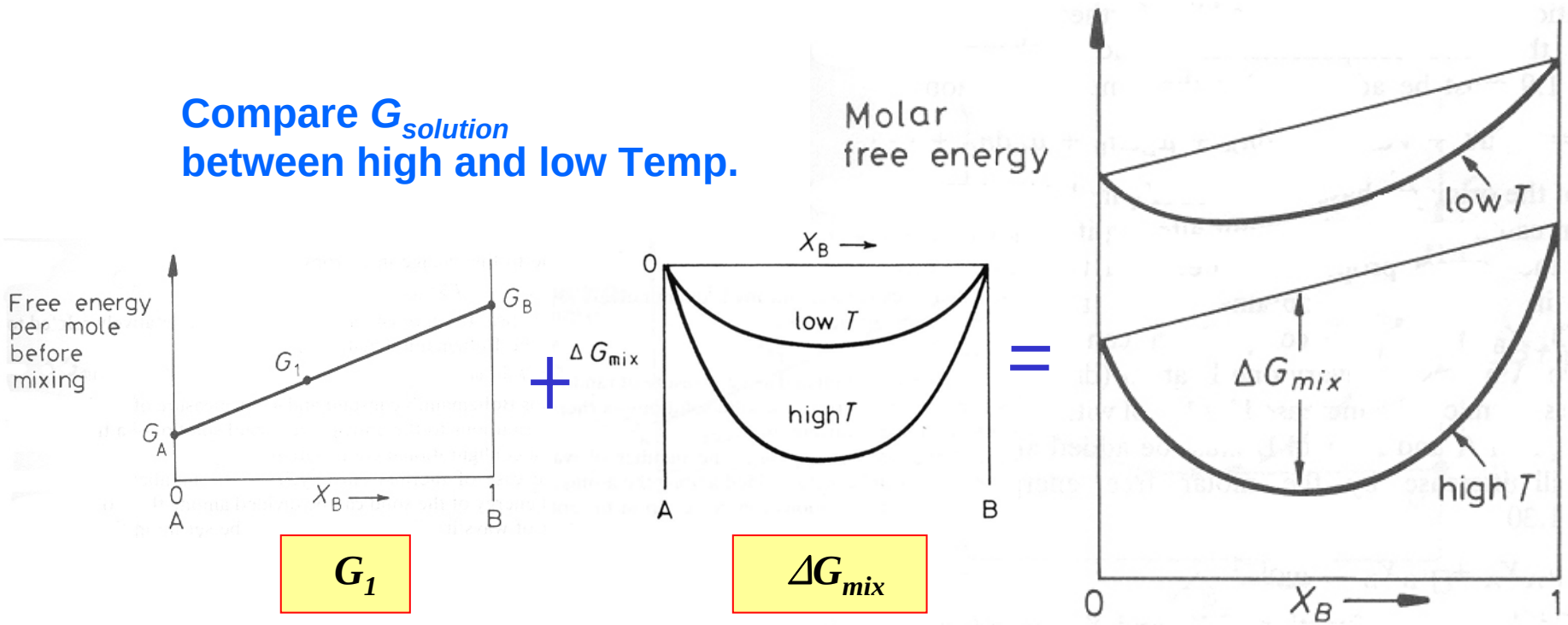
1) Ideal solution (ΔH_{mix}=0)

$$\Delta G_{mix} = -T\Delta S_{mix} \Rightarrow \Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

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

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

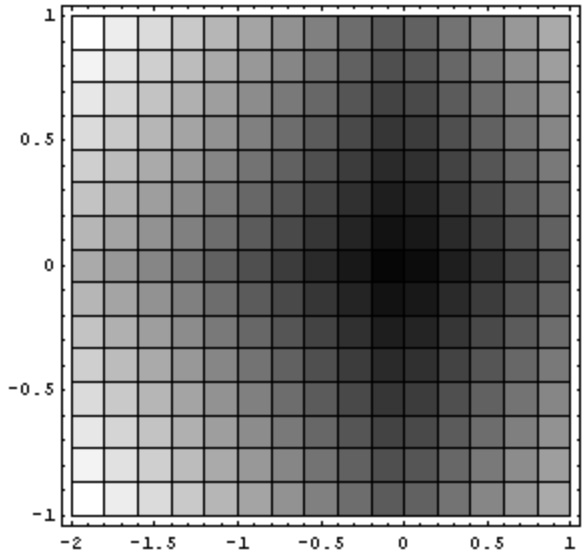
Compare $G_{solution}$ between high and low Temp.



G_1 + ΔG_{mix} =

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

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 dn_A.

➡ 소량 첨가에 의한 내부 에너지 변화 계산

$$dG' = \mu_A\, dn_A$$ **(T, P, n_B: constant)**

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

For variable T and P

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

Chemical potential 과 Free E와의 관계

1) Ideal solution

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

G = E+PV-TS

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

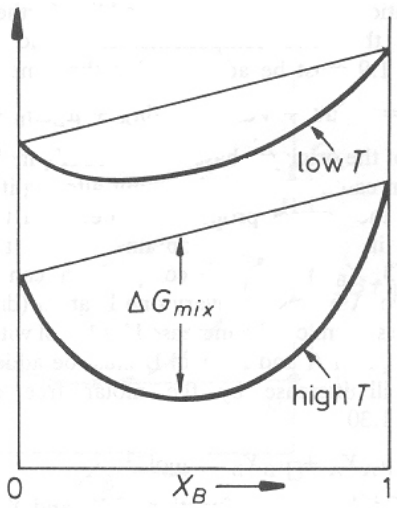
G = H-TS

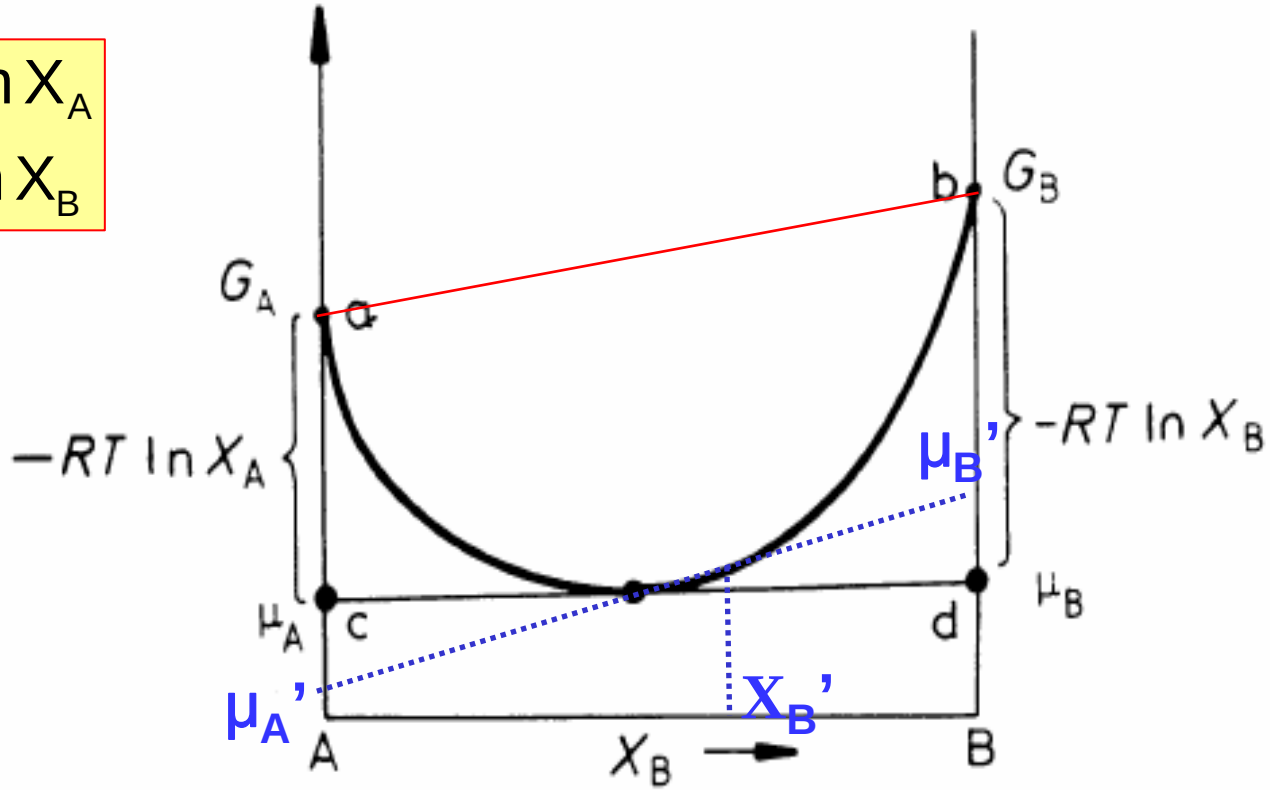
$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

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

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

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





For 1 mole of the solution

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

$$dG = \mu_A dX_A + \mu_B dX_B$$

$$\frac{dG}{dX_B} = \mu_B - \mu_A$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$G = \left(\mu_B - \frac{dG}{dX_B}\right) X_A + \mu_B X_B$$

$$= \mu_B X_A - \frac{dG}{dX_B} X_A + \mu_B X_B$$

$$= \mu_B - \frac{dG}{dX_B} X_A$$

$$= \mu_B - \frac{dG}{dX_B}(1 - X_B)$$

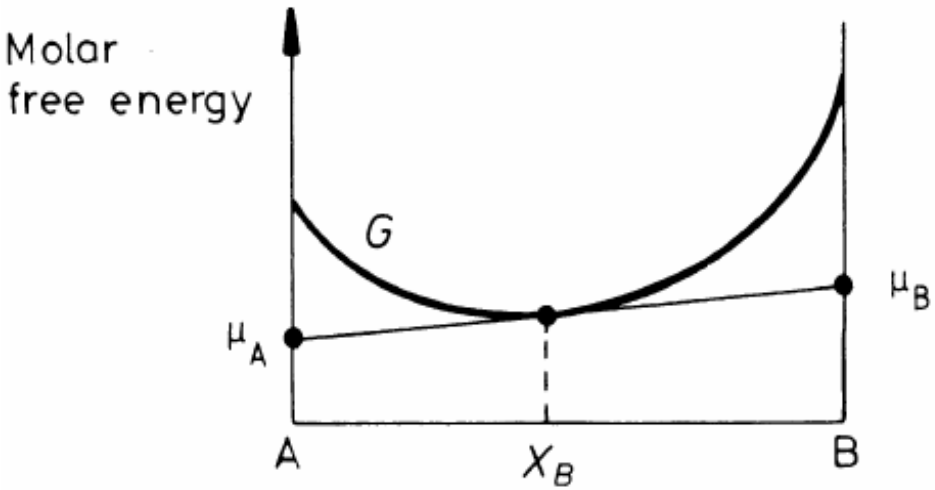


Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

2) Regular solution : $\Delta H_{mix} \neq 0$

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

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

$\Delta H_{mix} = P_{AB}\varepsilon$ = **(# of bond)X(bond E)**

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

N_a : Avogadro's number

z : number of bonds per atom

$\varepsilon \approx 0$

Regular solution $\Delta H_{mix} = \Omega X_A X_B$ **where** $\Omega = N_a z \varepsilon$

$$G_2 = G_1 + \Delta G_{mix} \qquad \Delta G_{mix} = \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

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

Regular Solutions

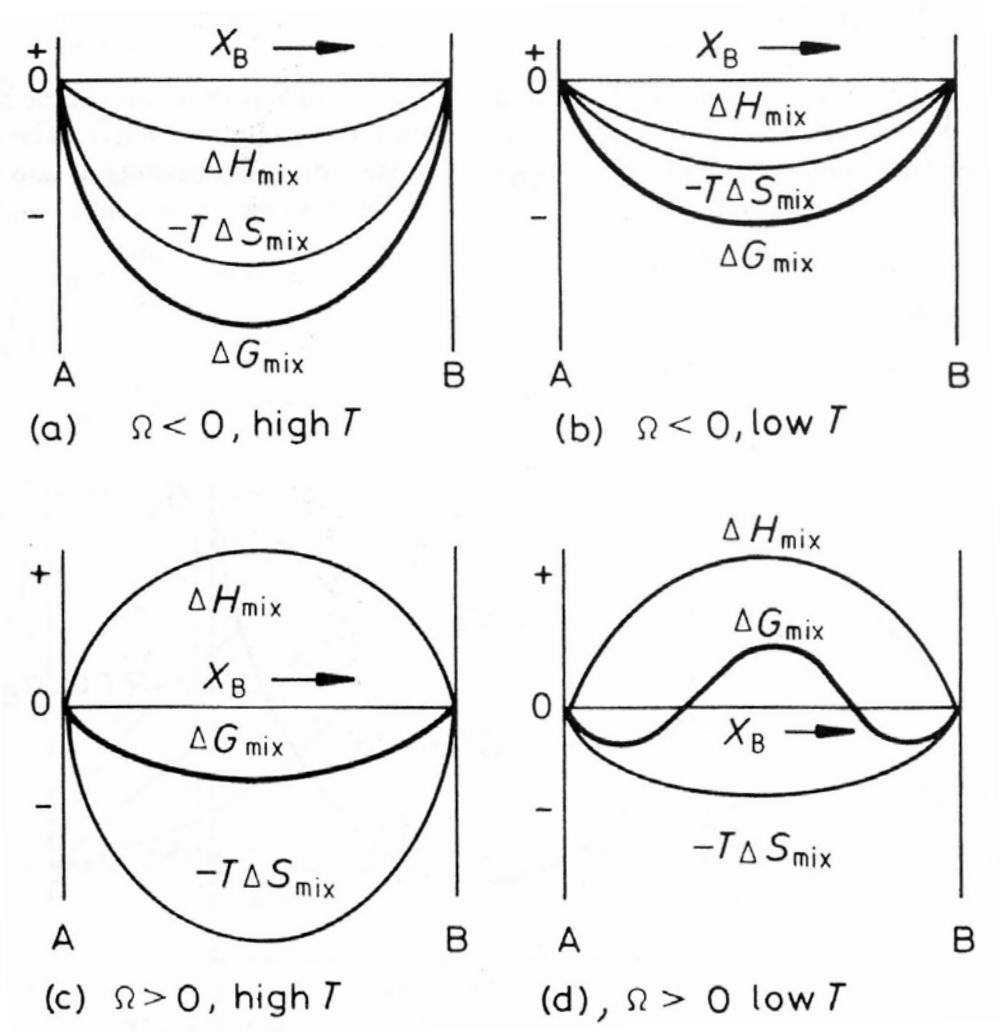
$$G_2 = G_1 + \Delta G_{mix}$$

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

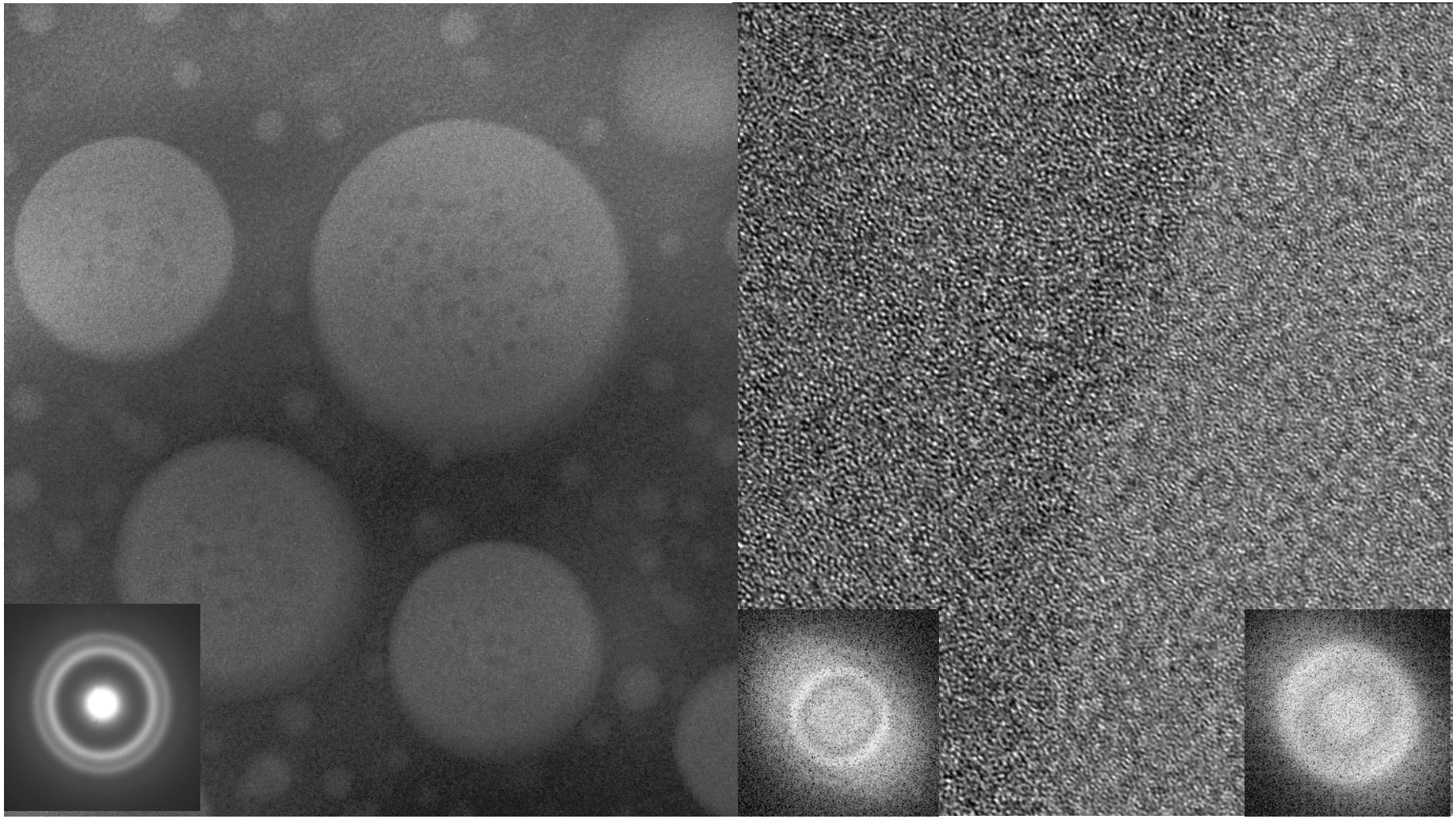
Reference state

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

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



Phase separation in metallic glasses



Chemical potential 과 Free E와의 관계

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

G = E+PV-TS

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

G = H-TS

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

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

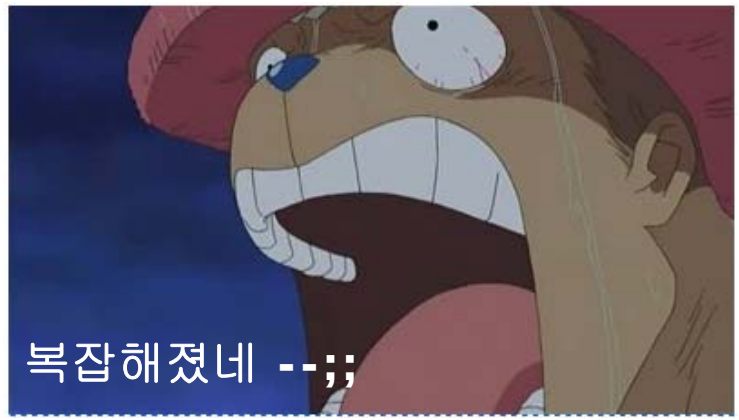
$$= \mu_A(G_A + \Omega(1-X_A)^2 + RT \ln X_A) + \mu_B(G_B + \Omega(1-X_B)^2 + RT \ln X_B)$$

Regular solution

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

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

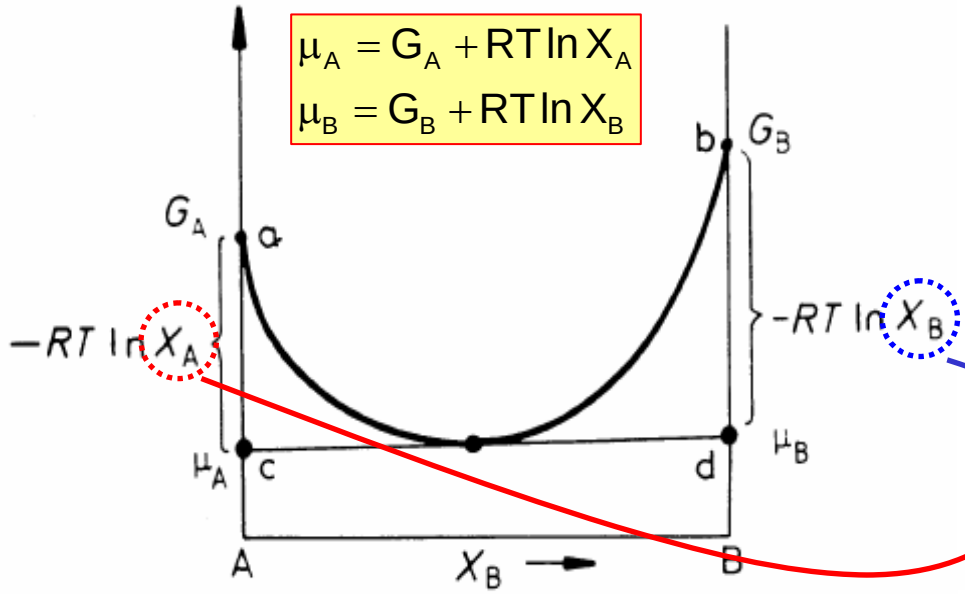
Ideal solution



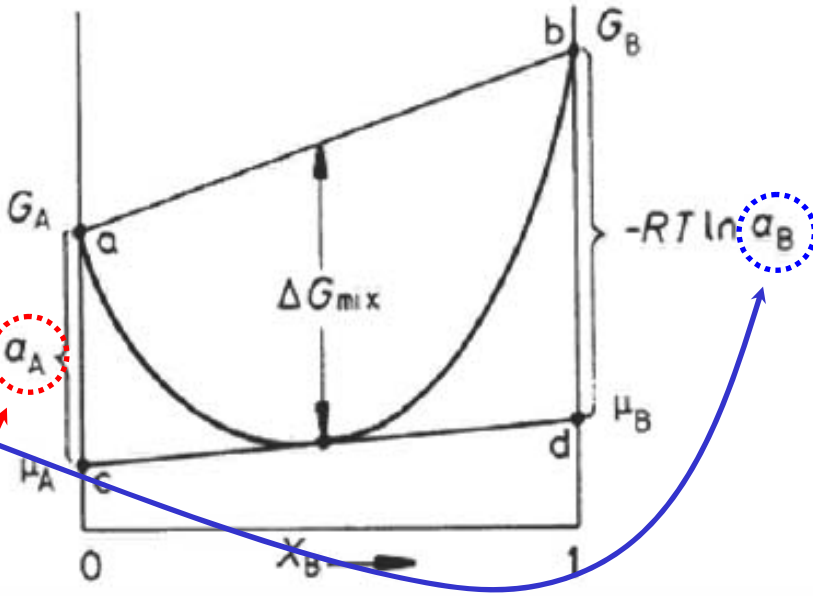
Activity, a : mass action을 위해 effective concentration

ideal solution

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



regular solution



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

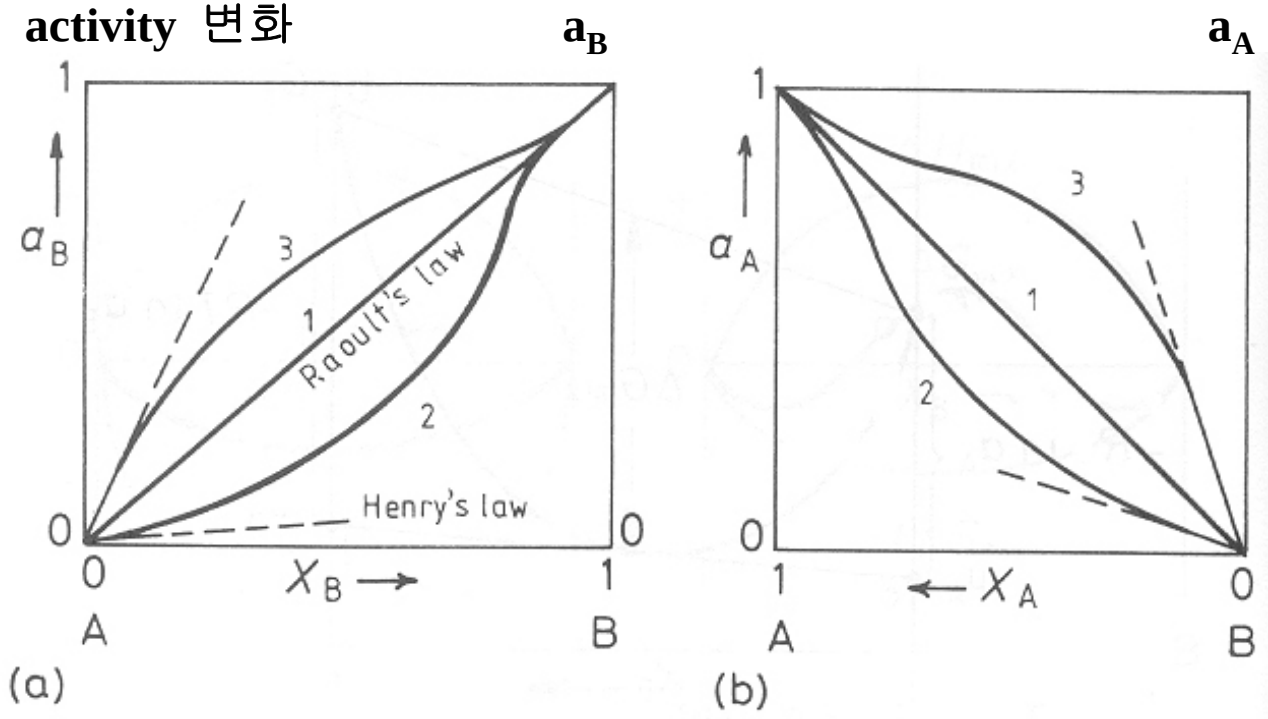
$$\mu_A = G_A + \Omega(1-X_A)^2 + RT\ln X_A \qquad \mu_B = G_B + \Omega(1-X_B)^2 + RT\ln X_B$$

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

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

Solution에서 a와 X와의 관계

조성 따른 **activity** 변화



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) $a_A>X_A$ — **$\Delta H_{mix}>0$**

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

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

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

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

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

γ_A : activity coefficient

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

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

Activity는 **solution**의 상태를 나타내는
조성 과 **Chemical potential** 과 상관관계 가짐.

Chemical Equilibrium (μ, a) → multiphase and multicomponent

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

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

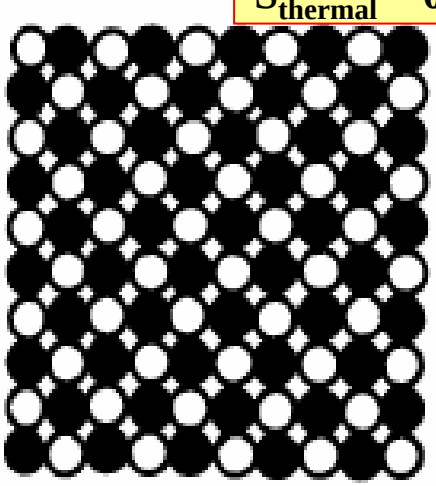
Real solution: 충분한 무질서도 + 가장 낮은 내부 E

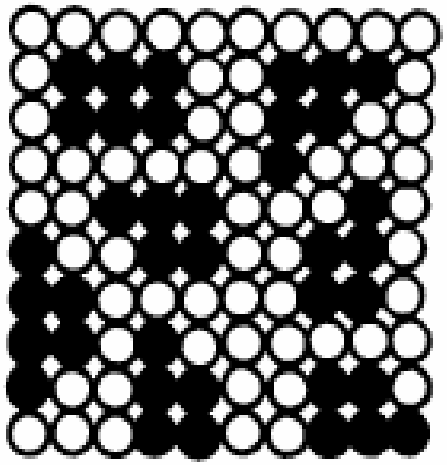
Ideal or Regular solution : over simplification of reality

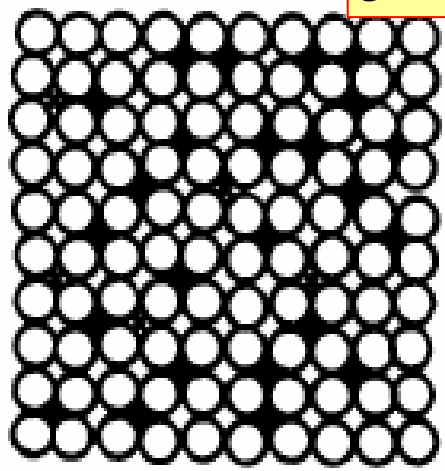
배열 Entropy $S = k \ln w$ + 원자간 결합의 효과 $\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z\varepsilon$

$S_{thermal} = 0$

$\varepsilon \approx 0$







(a) $\varepsilon < 0$, $\Delta H_{mix} < 0$ (b) $\varepsilon > 0$, $\Delta H_{mix} > 0$ (c) when the size difference is large

Ordered alloys

P_{AB} ↑ ⟶ 내부 E ↓

Clustering

P_{AA}, P_{BB} ↑

Random interstitial strain effects

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,**

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

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

➡ 정확한 내부 **E** 변화 알기 위해선 새로운 수학적 모델 요망

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

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

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

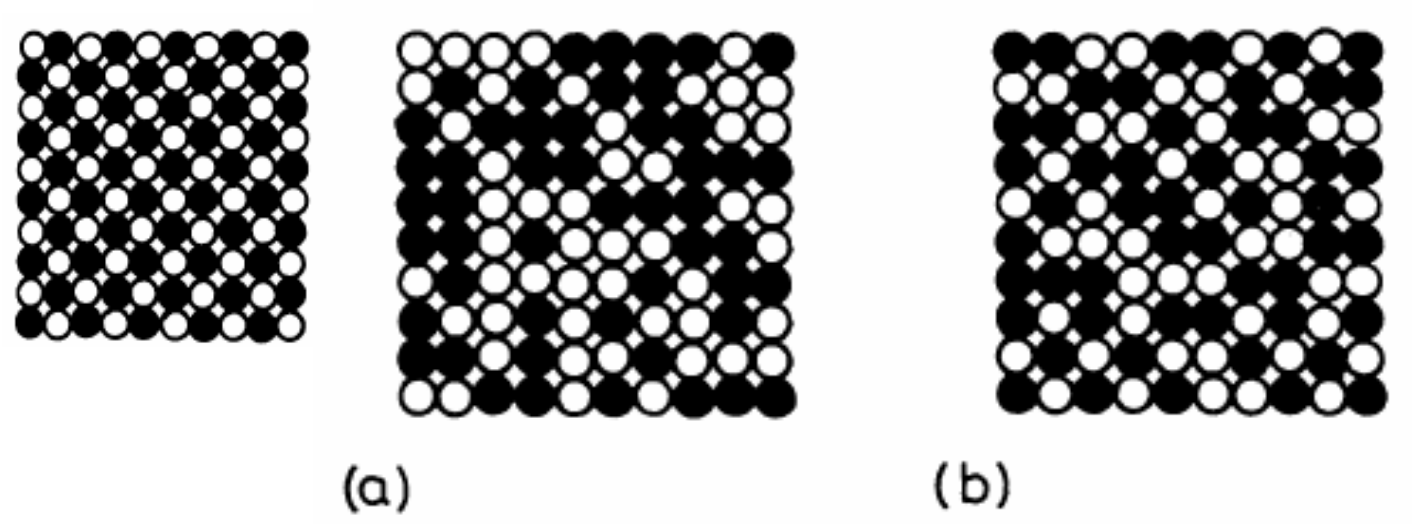
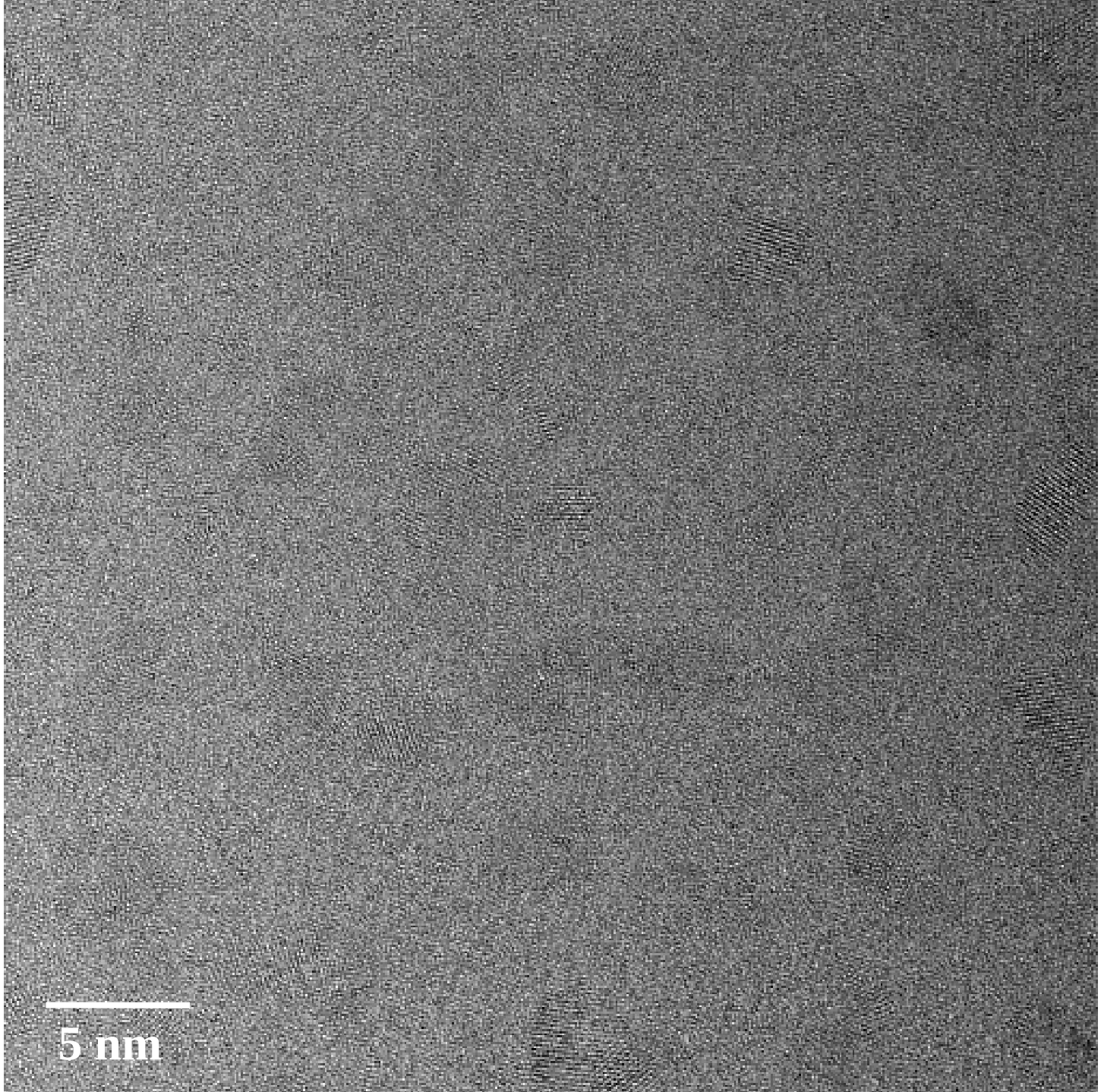
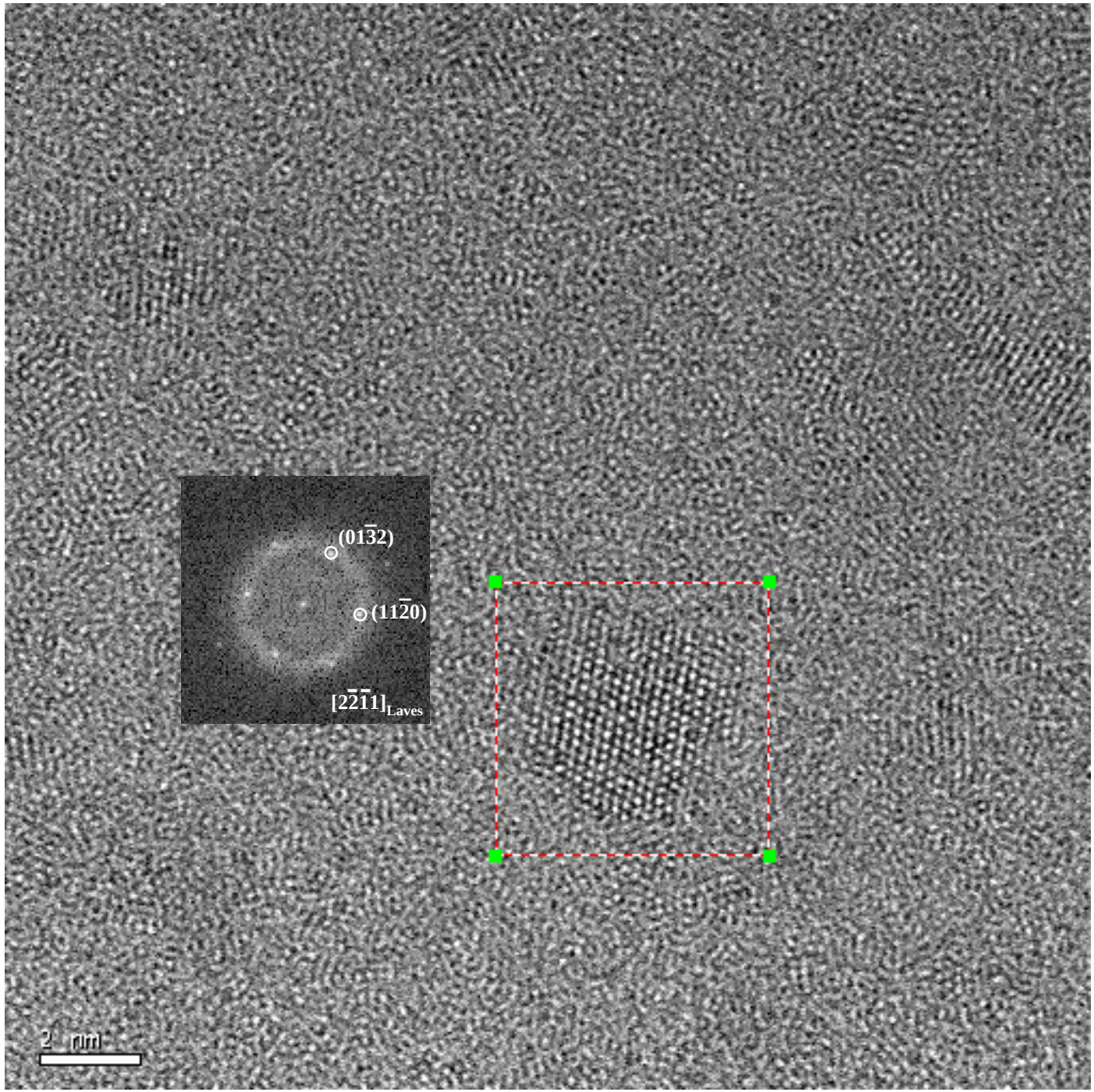


Fig. 1.19 (a) Random A-B solution with a total of 100 atoms and $X_A=X_B=0.5$, P_{AB}~100, S=0. (b) Same alloy with short-range order P_{AB}=132, $PAB_{(max)}$~200, S=(132-100)/(200-100)=0.32


5 nm


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

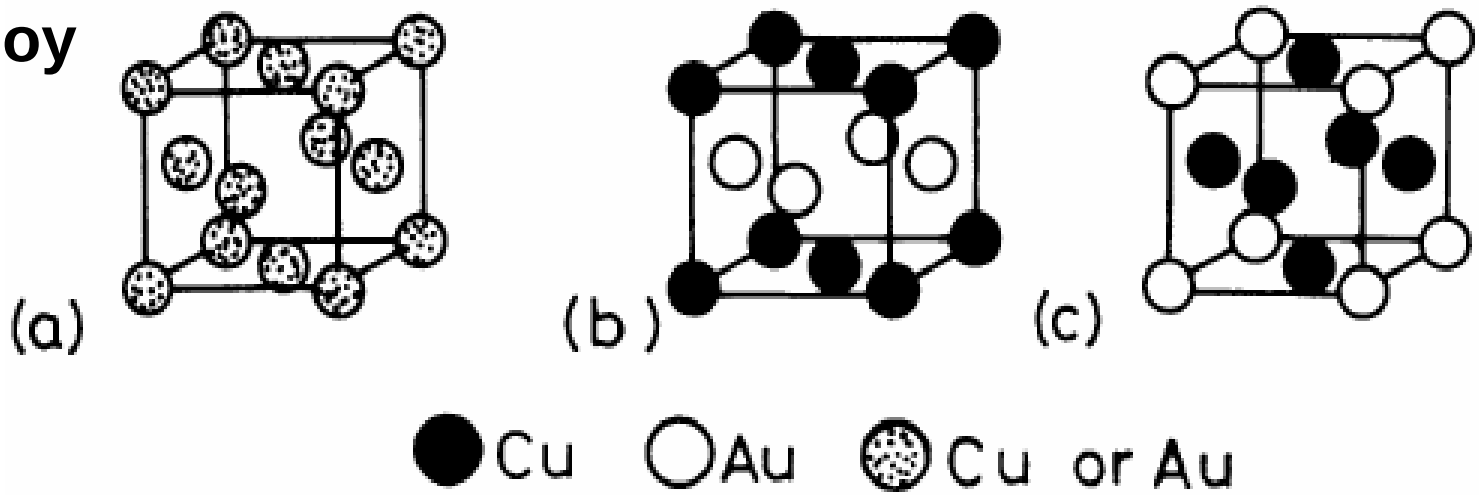
Ordered phase $\varepsilon < 0$, $\Delta H_{mix} < 0$

* 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



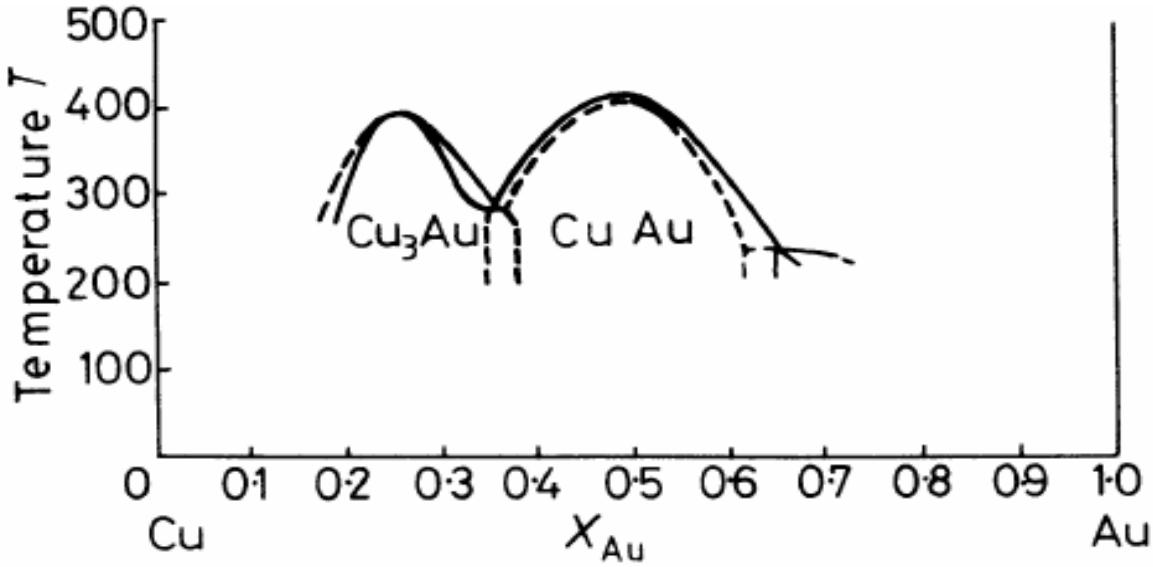
High temp.
Disordered Structure

Low temp.
CuAu superlattice

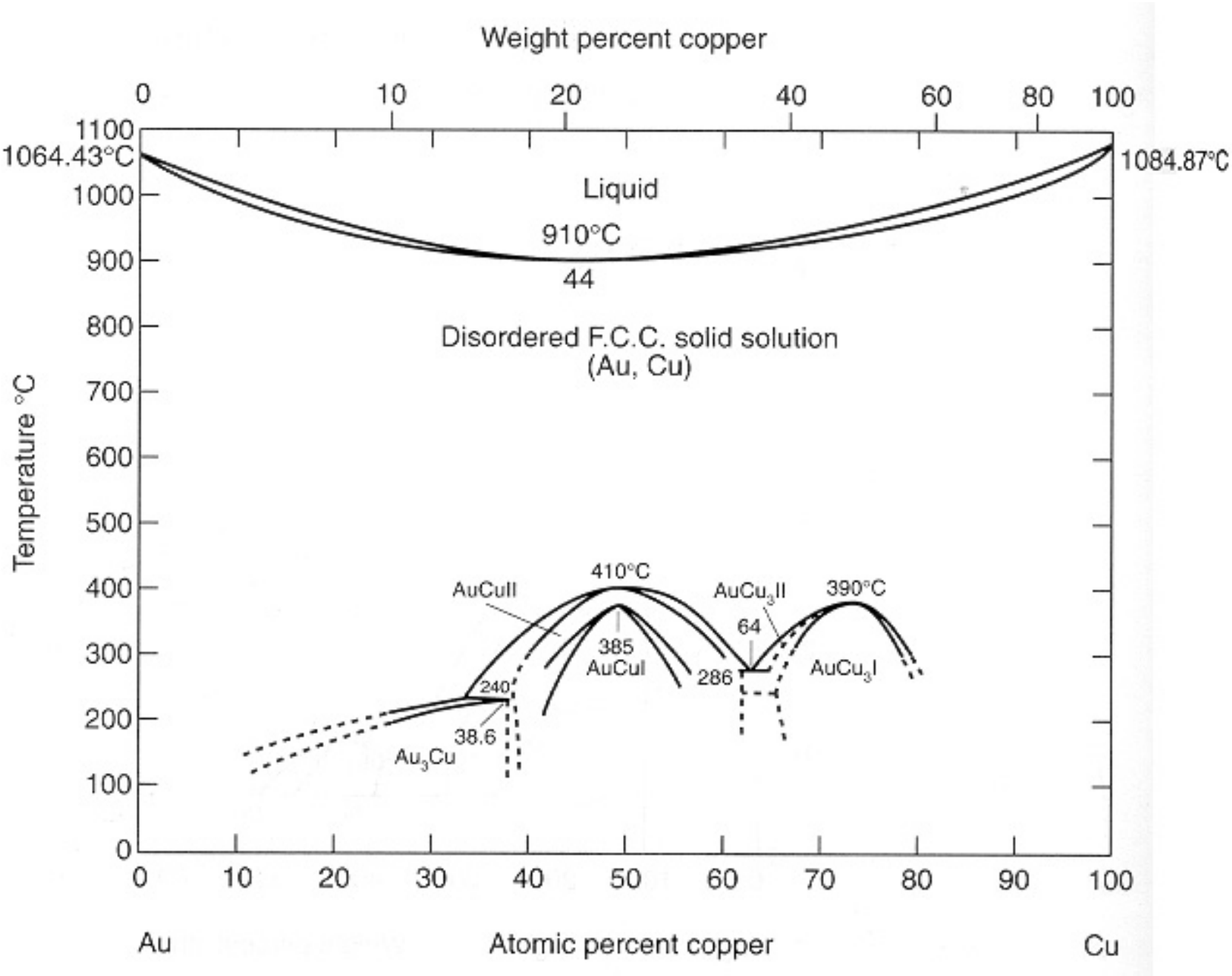
Cu_3Au superlattice

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



- **The entropy of mixing of structure with LRO is extremely small and with increasing temperature the degree of order decrease 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**.**

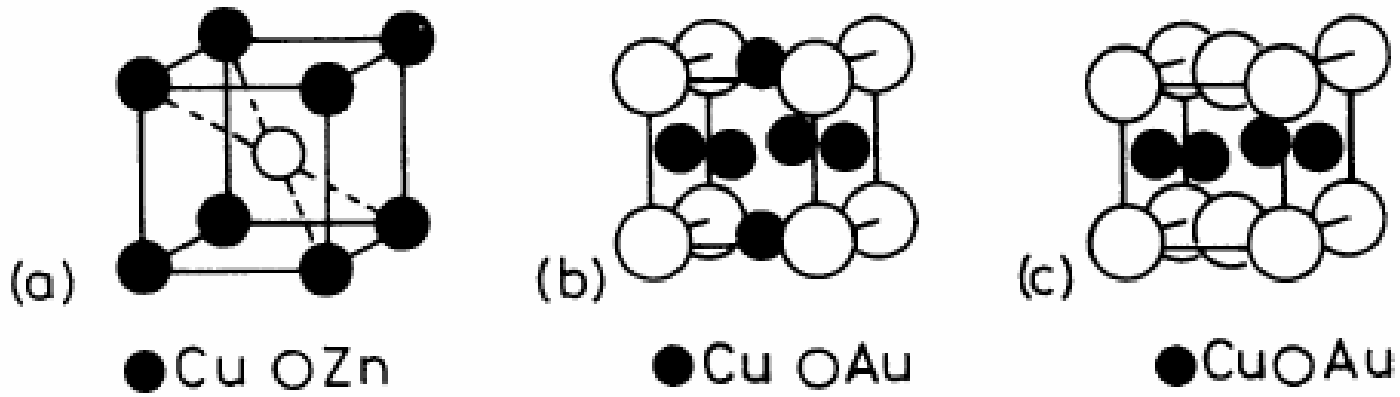

Weight percent copper
0
10
20
40
60
80
100
1100
1064.43°C
1084.87°C
1000
900
800
700
600
500
400
300
200
100
0
Liquid
910°C
44
Disordered F.C.C. solid solution
(Au, Cu)
Temperature °C
410°C
AuCuII
AuCu3II
390°C
64
385
AuCuI
286
AuCu3I
240
38.6
Au3Cu
0
10
20
30
40
50
60
70
80
90
100
Au
Atomic percent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

Five common ordered lattices

(a) $L2_0$: CuZn

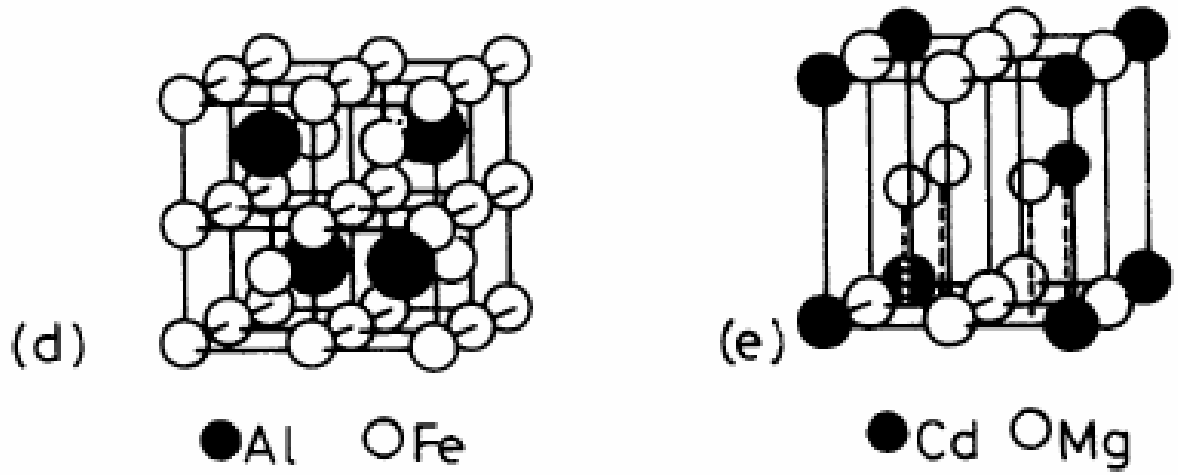
(b) $L1_2$: Cu_3Au

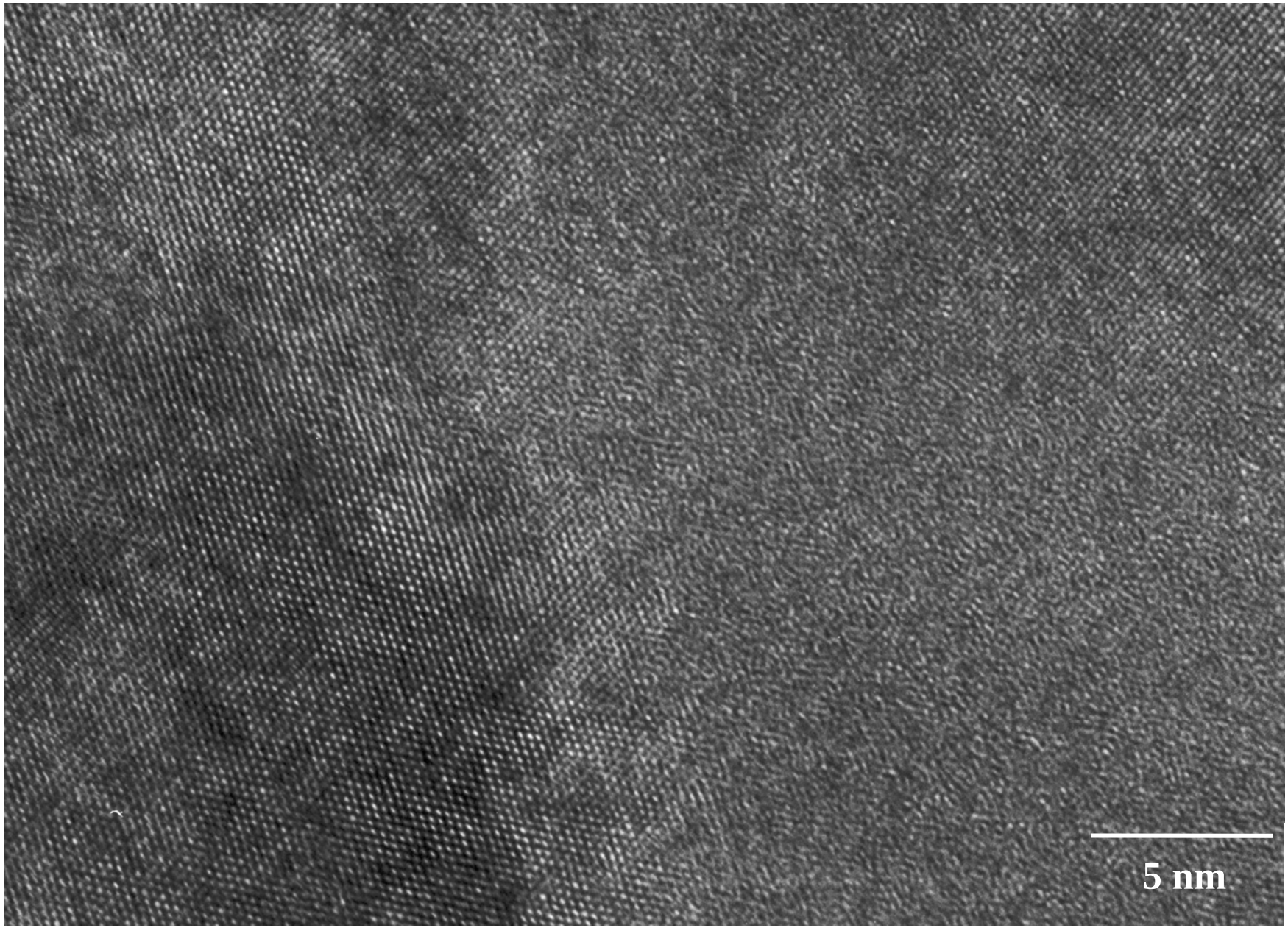
(c) $L1_0$: Cu_3Au



(d) $D0_3$: Fe_3Al

(d) $D0_{19}$: Mg_3Cd



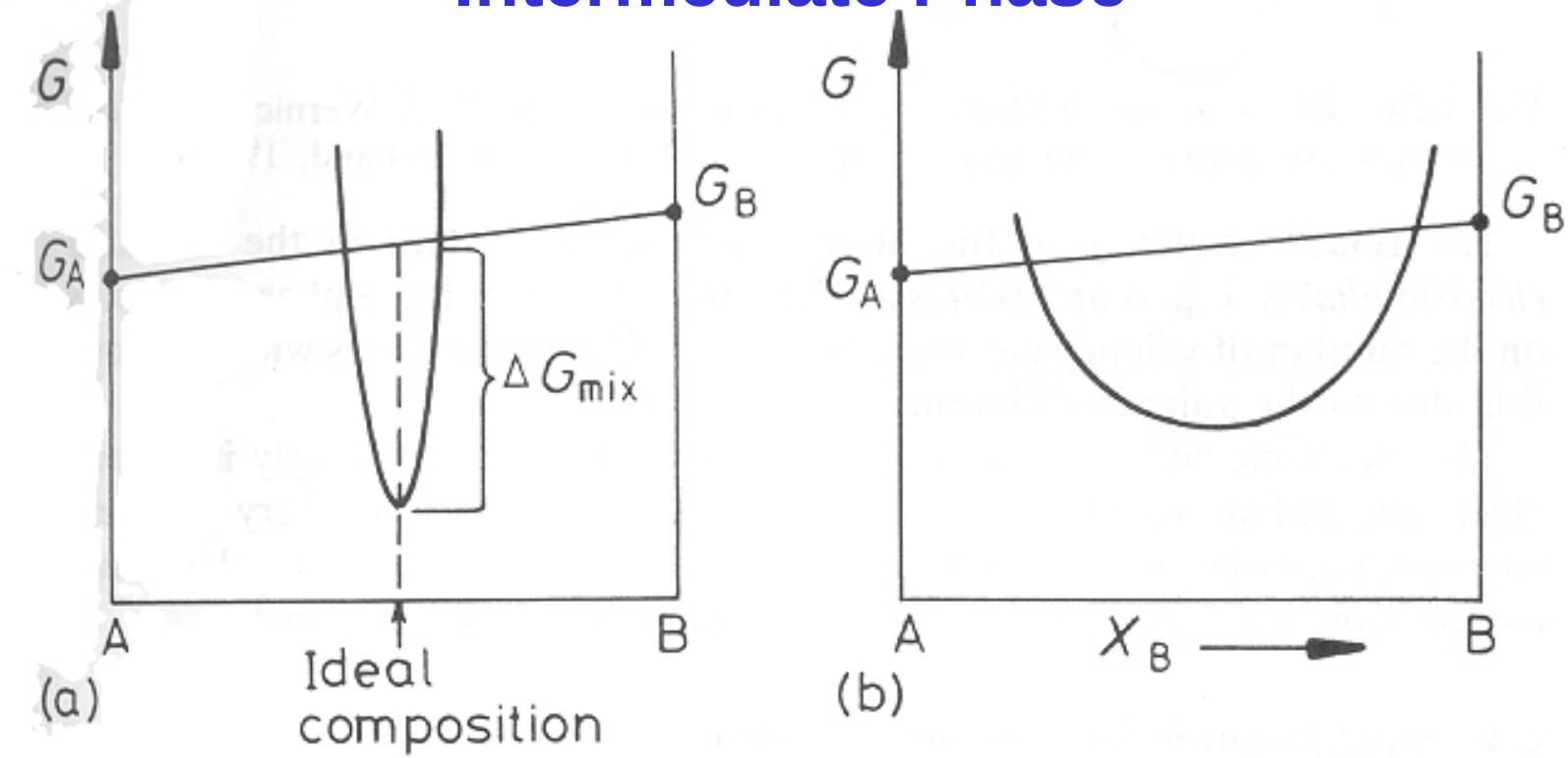

5 nm

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 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.**

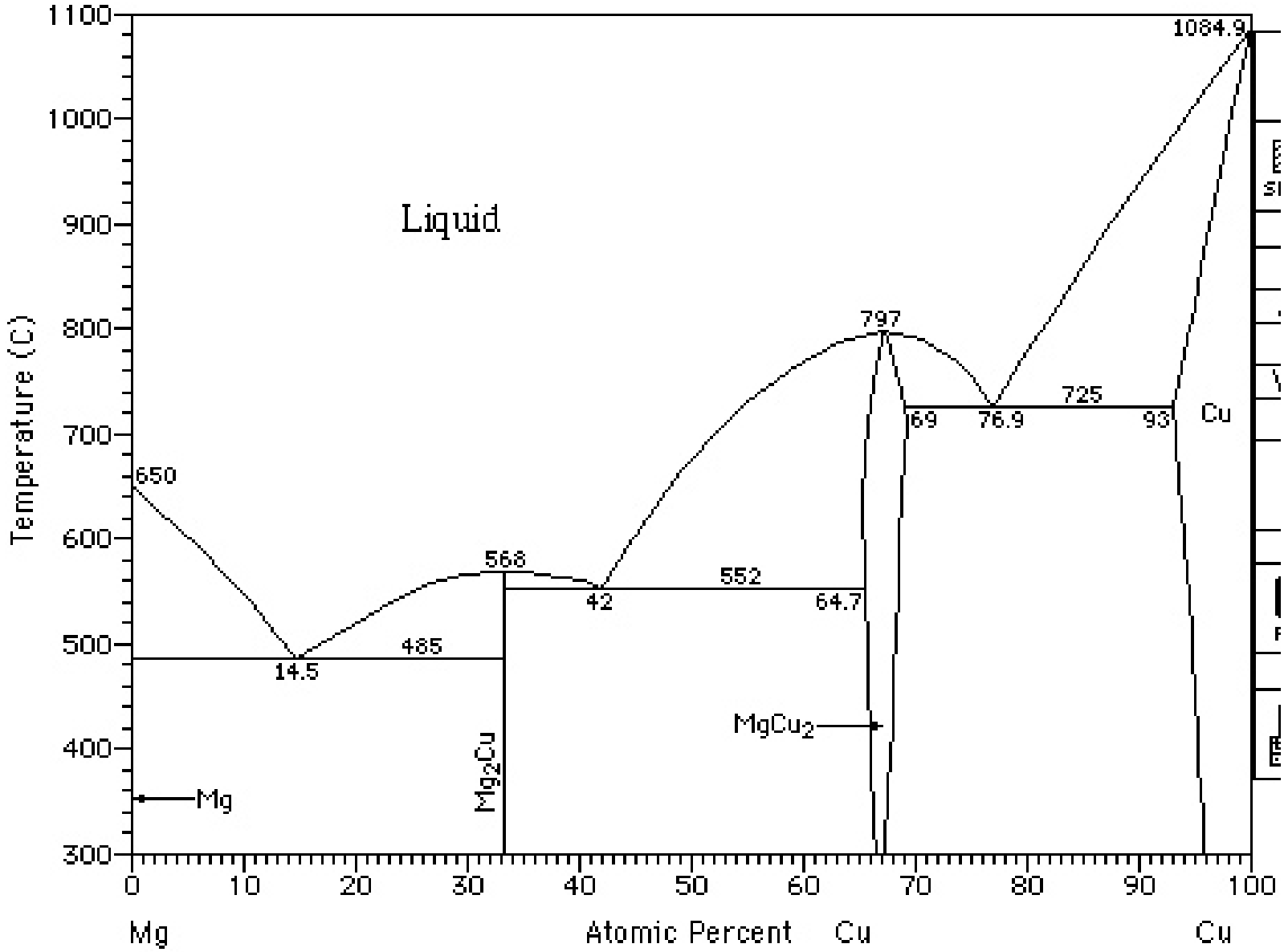
Intermediate Phase



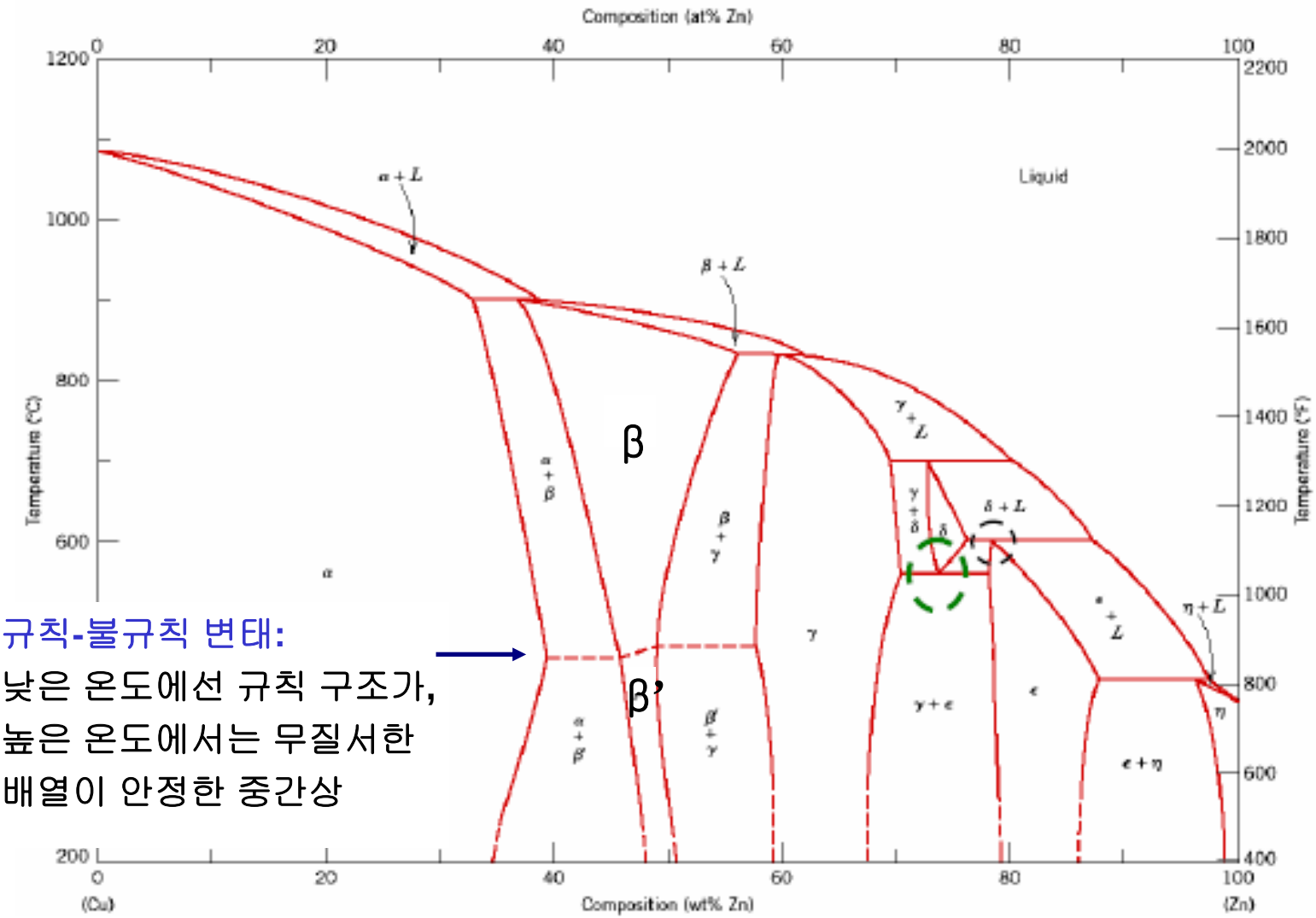
* Many **intermetallic compounds** have **stoichiometric composition** A_mB_n and a characteristic free energy curve as shown in Fig 1.23a.

* 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

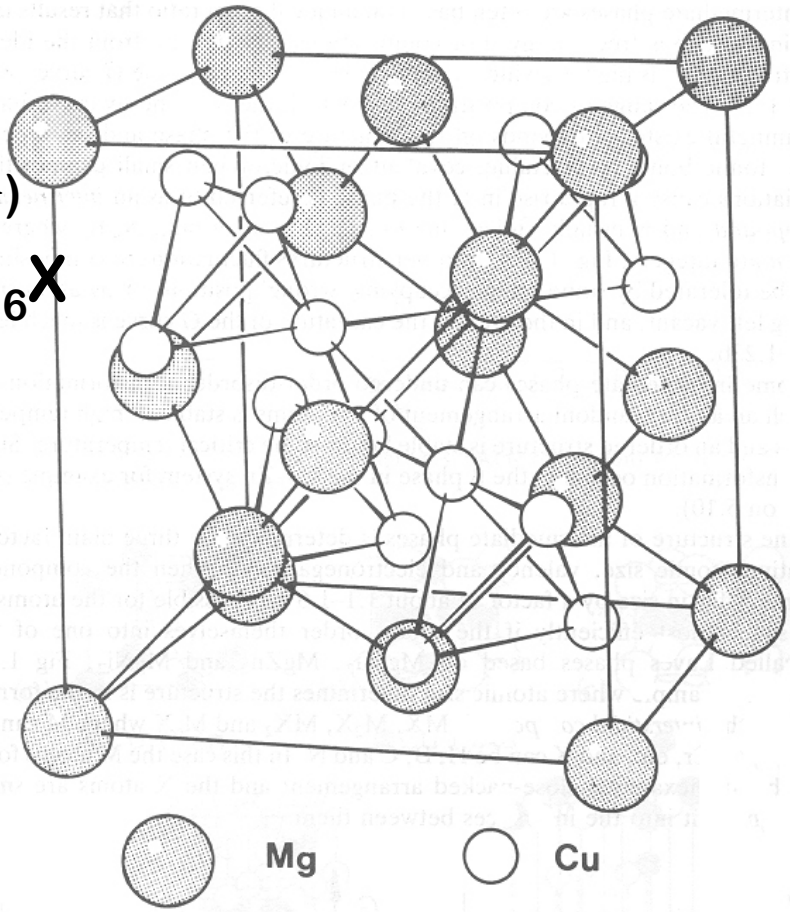
- **Laves** 상 (원자크기비가 **1.1~1.6**인 경우)
- 침입형 화합물: **MX, M_2X, MX_2, M_6X**

2) Valency Electron

- 전자상이 형성되는 경우

3) Electronegativity

- 이온결합에 의한 화합물 **Mg_2Sn**



$MgCu_2$ (A Laves phase)