2010 Spring

"Amorphous Materials"

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Eun Soo Park

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

Contents for previous class

- **Preparation of amorphous materials**

Sputtering — Surface coating

Chemical vapor deposition

Thermal evaporation

Pulsed laser deposition

electrolytic deposition

Droplet quenching — Bulk type : sphere, rod, plate

Water quenching

Injection casting — **Suction casting**

Squeeze casting — **Strip casting**

Centrifugal casting

Gas atomization — powder

Melt-spinning — thin film

Splat quenching — thin plate

Irradiation

Pressure-induced amorphization

Solid-state diffusional amorphization

Computer simulation

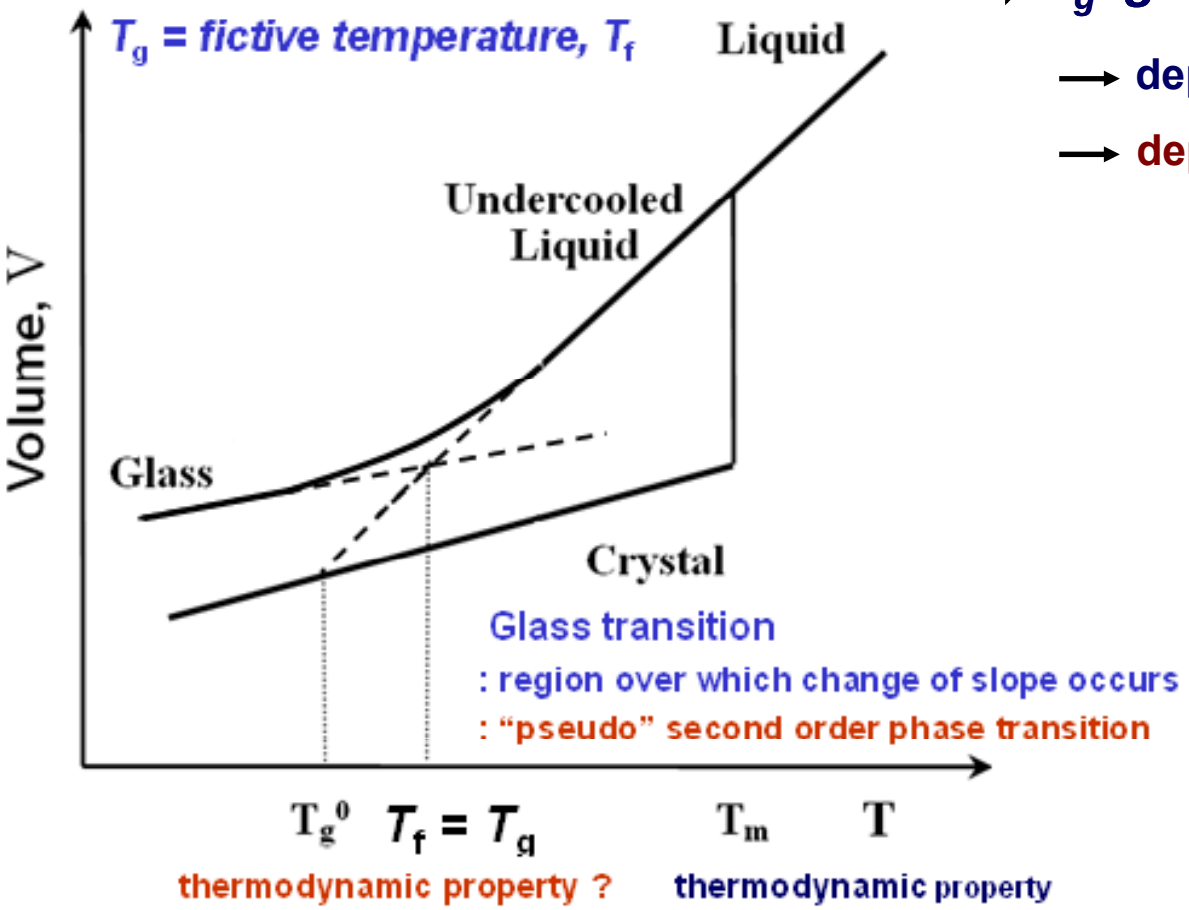
Contents for today's class

- **Bonding in Glasses**
- **Glass transition:** ***Volumetric measurement***

➡ ***T_g glass transition temp.***

→ **depends on cooling rate**

→ **depends on thermal history**



Bonding type: covalent, ionic, metallic, van der waals, hydrogen bond

➡ Glass can be formed by one of those bonding.

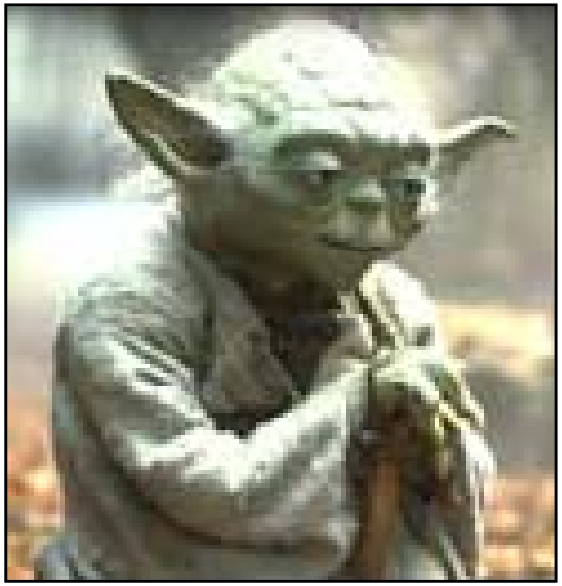
Table 2.1 Examples of glass-formers for the major types of bonding

Type of bond	*Material*
Covalent	As_2Se_3, Se
Ionic	KNO_3–$Ca(NO_3)_2$
Metallic	Zr–Cu, Ni–Nb
Van der Waals'	*ortho* terphenyl
Hydrogen bond	$KHSO_4$, ice, aqueous solution of ionic salts (e.g. LiCl)

➡ Some examples which do not fit into any one category.

Ex) Silica : some ionic + predominant covalent

Review of Chemical Bonds



Most bonds are somewhere in between ionic and covalent.

There are 3 forms of bonding:

- **_____ – complete *transfer* of 1 or more electrons from one atom to another (one loses, the other gains) forming oppositely charged ions that attract one another**
- **_____ – some valence electrons *shared* between atoms**
- **_____ – holds atoms of a metal together**

Type of bond can usually be calculated by finding the difference in electronegativity of the two atoms that are going together.

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
									H 2.1							
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

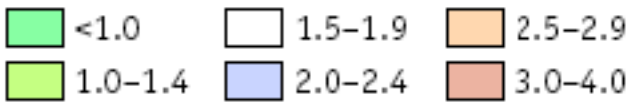


Figure 9.9 Electronegativity values for the elements according to Pauling. Trends for electronegativities are the opposite of the trends defining metallic character. Nonmetals have high values of electronegativity, the metalloids have intermediate values, and the metals have low values.

Electronegativity Difference

- If the difference in electronegativities is between:
  - 1.7 to 4.0: **Ionic**
  - 0.3 to 1.7: **Polar Covalent**
  - 0.0 to 0.3: **Non-Polar Covalent**

1A	2A						8B			1B	2B	3A	4A	5A	6A	7A
							H 2.1									
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	3B	4B	5B	6B	7B						Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
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Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

<1.0 | 1.5–1.9 | 2.5–2.9
1.0–1.4 | 2.0–2.4 | 3.0–4.0

Figure 9.9 Electronegativity values for the elements according to Pauling. Trends for electronegativities are the opposite of the trends defining metallic character. Nonmetals have high values of electronegativity, the metalloids have intermediate values, and the metals have low values.

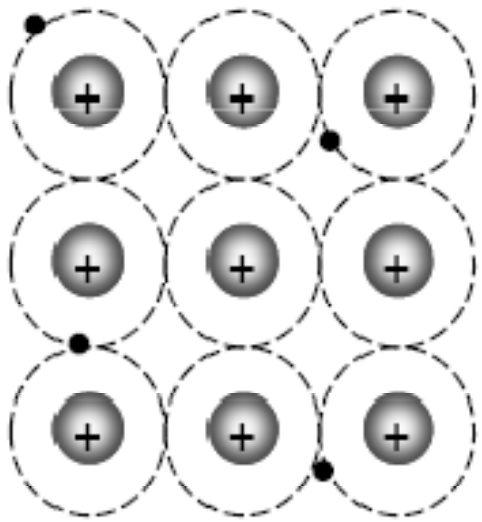
Metallic Solids

- Metallic bonds are generally weaker than ionic or covalent bonds
- The outer electrons in the atoms of a metal are relatively free to move through the material (high mobility)
- The number of such mobile electrons in a metal is large (high carrier density)
- High electrical conductivity (& thermal)

Metallic Solids, cont.

- Valance electrons are relatively bound to the nucleus and therefore they move freely through the metal and they are spread out among the atoms in the form of a low-density electron cloud.

- A metallic bond result from the sharing of a variable number of electrons by a variable number of atoms. A metal may be described as a ***cloud of free electrons.***



- Therefore, metals have high electrical and thermal conductivity.

Metallic Solids, cont.

- All valence electrons in a metal combine to form a "sea" of electrons that *move freely between the atom cores*. The more electrons, the stronger the attraction. This means the melting and boiling points are higher, and the metal is stronger and harder.
- The positively charged cores are held together by these negatively charged electrons.
- The free electrons act as the bond (or as a "glue") between the positively charged ions.
- This type of bonding is nondirectional and is rather insensitive to structure.
- As a result we have a high ductility of metals - the "bonds" do not "break" when atoms are rearranged – metals can experience a significant degree of plastic deformation.

Properties of Metallic Solids

- Light interacts strongly with the free electrons in metals
  - Visible light is absorbed and re-emitted quite close to the surface (reflective)
  - This accounts for the shiny nature of metal surfaces (screening, plasma frequency)
- High electrical conductivity

Bonding type: covalent, ionic, metallic, van der waals, hydrogen bond

➡ **Glass can be formed by one of those bondings.**

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➡ **Some examples which do not fit into any one category.**

Ex) Silica : some ionic + predominant covalent

- **How does glass form?** ➡ **Glass transition (phase transition)**

- **Why does glass form?** ➡ **Better glass former than others**

  ➡ **Glass forming ability**

"Glass transition"

If liquid is cooled, two events can occur.

1) Crystallization (solidification at $T_{m.p.}$)

2) Undercooled below $T_{m.p.}$ (supercooled) ➡ **More viscous**

➡ **Glass**

❖ **The glass transition is 'pseudo' second-order phase transition. And the transition depends on kinetic factors.**

"Phase Transition"

Thermodynamically: what is possible!
Kinetics: speed/rate of the transition.

Thermodynamical classification: first order & second order

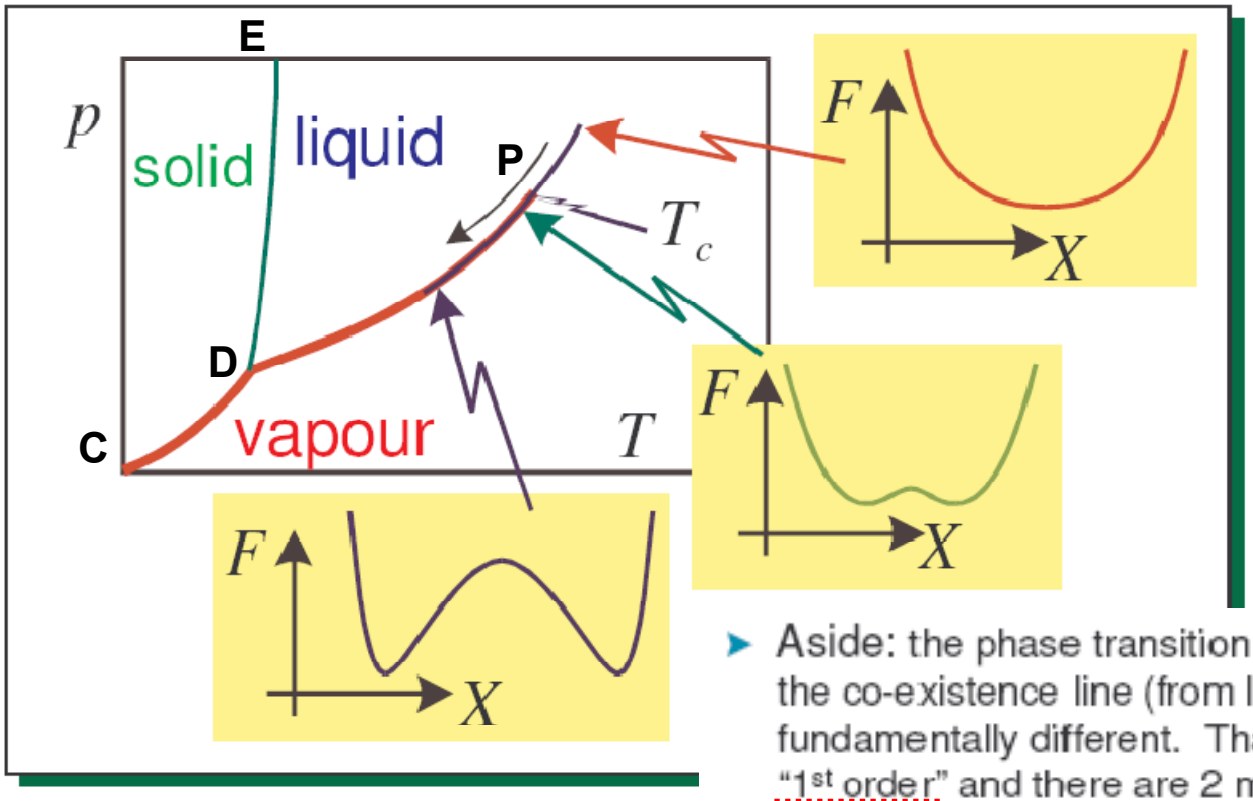
$$\Delta G = \Delta H - T\Delta S = 0$$

- **Order (degree) of transition**

***Continuous phase transitions*:**

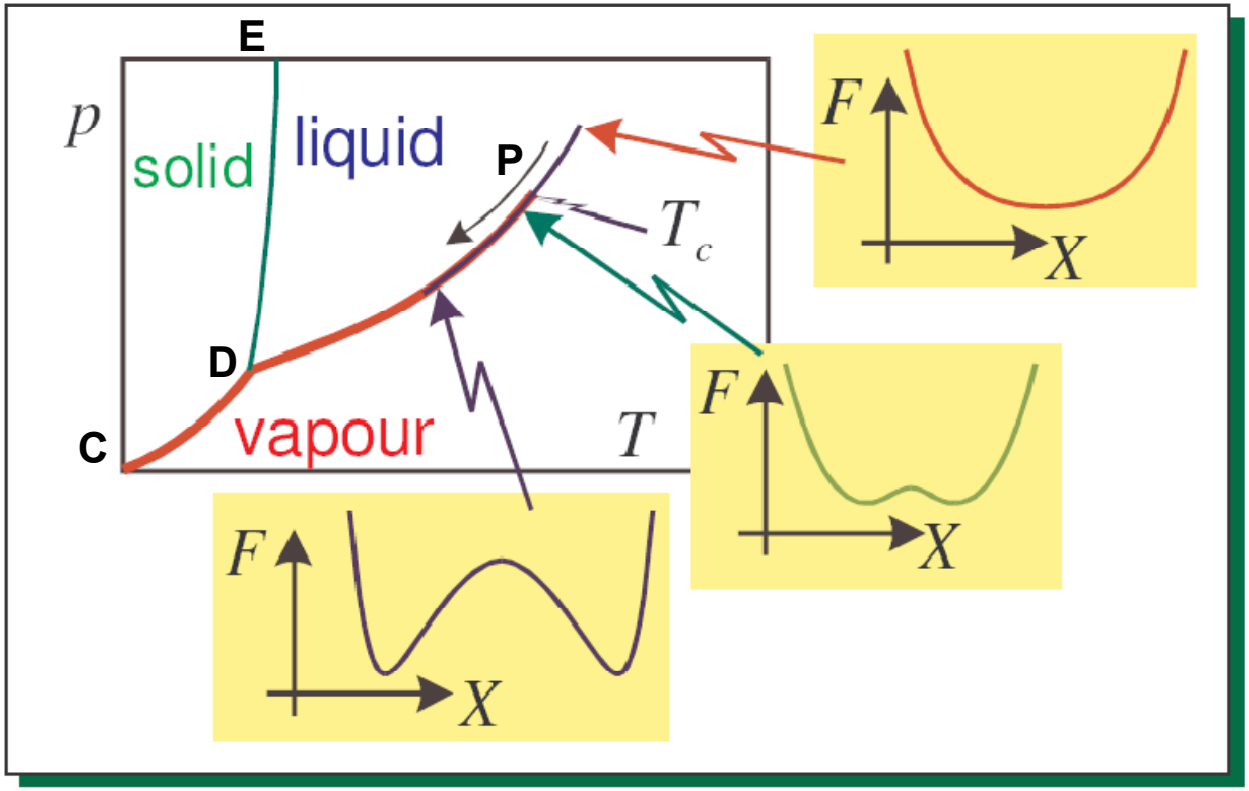
occur when the minimum in the thermodynamic potential evolves smoothly into two equal minima.

An example is seen in the model of phase separation, along the co-existence line.



- Aside: the phase transition as one moves across the co-existence line (from liquid to vapour) is fundamentally different. That transition is known as "1st order" and there are 2 minima in the potential throughout. In the transition the lowest minimum changes from liquid to vapour (and vice-versa).

- **Order (degree) of transition**



- **CD, DE, DP: Equilibrium of 2 phases**
  - → **latent heat**
  - → **Volume change**
  - → **1st order transition**

- **T and P beyond point p**
  : vapor and liquid are indistinguishable.
  - → **Single phase: only property changes.**
  - → **No boiling pt. no latent heat**
  - → **Higher order transition**

First-order transition:
a discontinuity occurs in the first derivative of the free energy with respect to T and P.

Discontinuous enthalpy, entropy and volume

$$\frac{dG}{dT} = -S$$

$$\frac{dG}{dP} = V$$

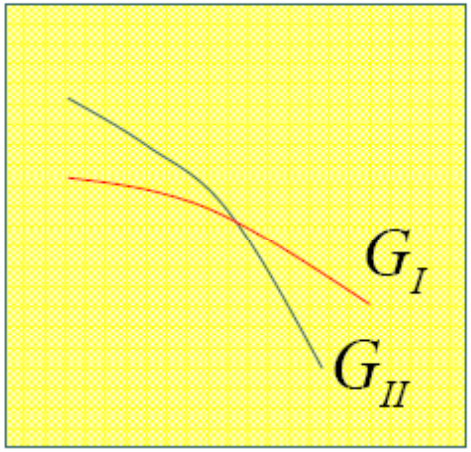
Examples: CsCl structure to NaCl structure; T =479 C.

$$\Delta V = 10.3 cm^3$$

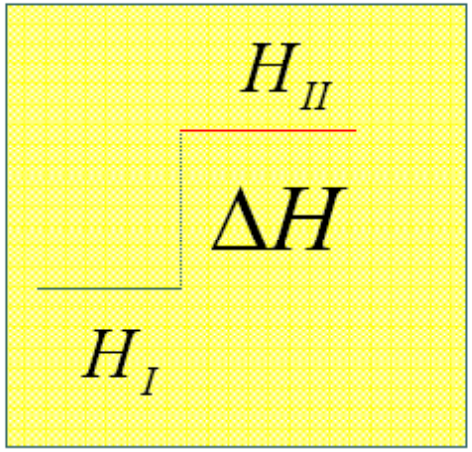
$$\Delta H = 2.424 kJ / mol$$

Melting, freezing, vaporization, condensation…

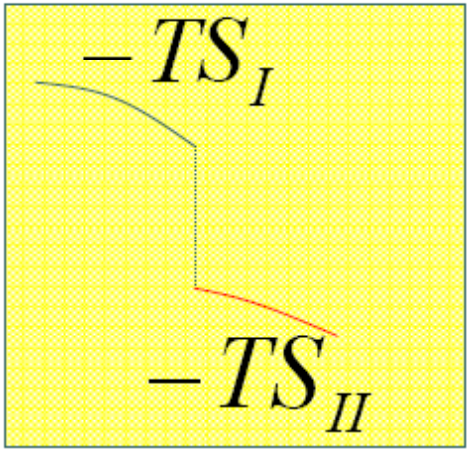
First-order transition:



T_C



T_C



T_C

Second order transition: Discontinuities in the second derivatives of the free energy, i.e. heat capacity, thermal expansion, compressibility.

Enthalpy, entropy and volume, continuous functions of T

$$\frac{\partial^2 G}{\partial P_T^2} = \frac{\partial V}{\partial P_T} = -V\beta(compressibility)$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T_P} = V\alpha(thermal\ \exp ansion)$$

$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T_P} = -\frac{C_p}{T}$$

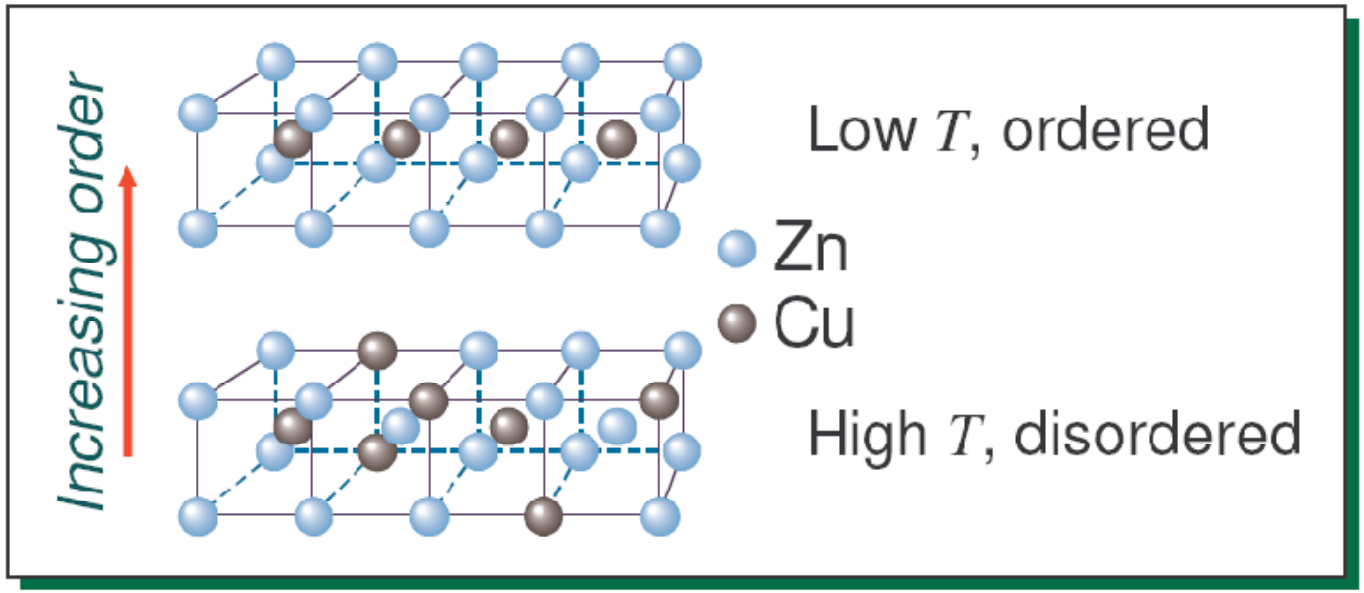
Measurement of heat capacities (calorimetry)

Order-disorder transition: 2nd order transition

- β-brass.

~ Brass is a 50:50, Cu:Zn alloy with a b.c.c structure.

~ At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diagram)



- Two types of site call them: A-sites and B-sites.
- At high T, equal probability for any site to be occupied by Cu or Zn.

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.

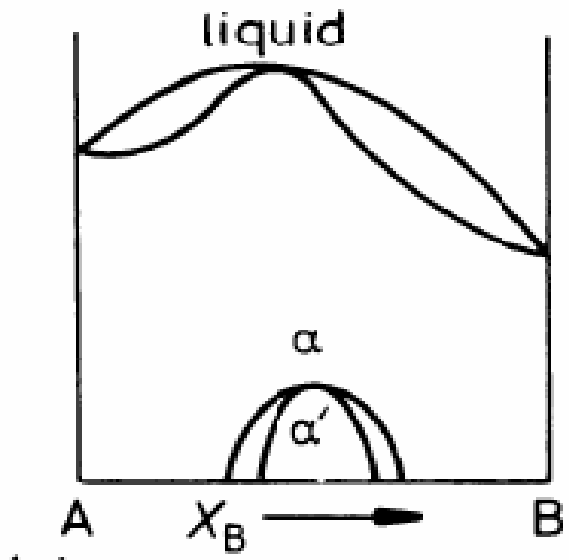
Ordered Alloys $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} < 0$

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

How does the phase diagram differ from the previous case?

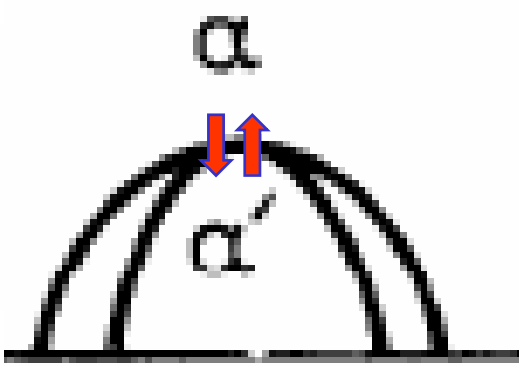
b. What would happen when $\Delta H_{mix} << 0$?

$\rightarrow$ The ordered state can extend to the melting temperature.



(a)

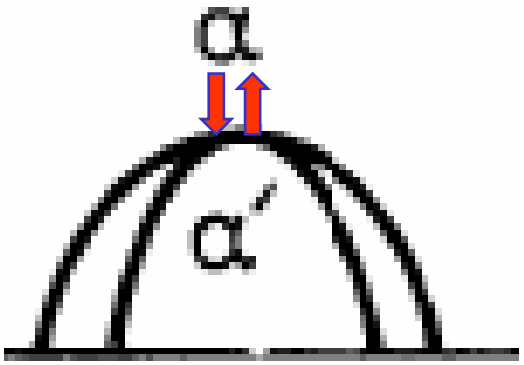
congruent maxima



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

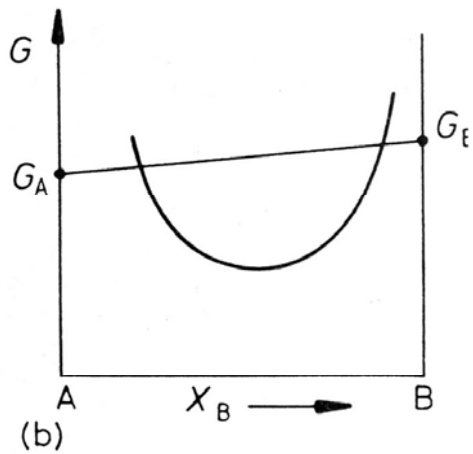
→ entropy ↑

negative enthalpy ↓

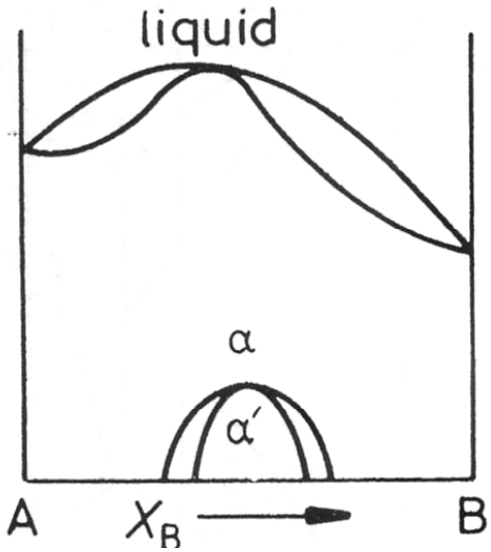
$$\Delta H^{S}_{mix} < 0$$

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 contributio

→ enthalpy more negative ↓

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

Small composition range

➔ G ↓

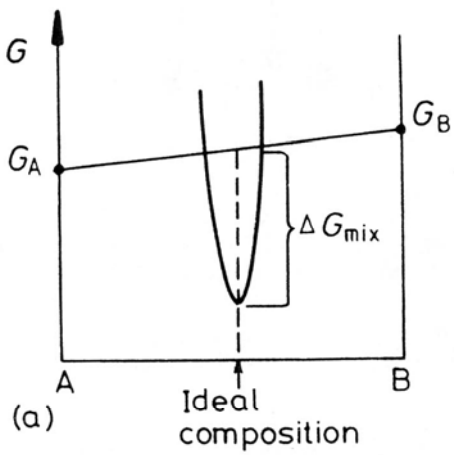
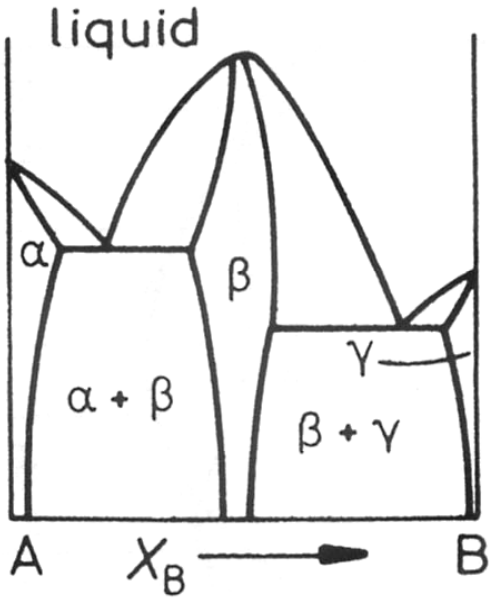
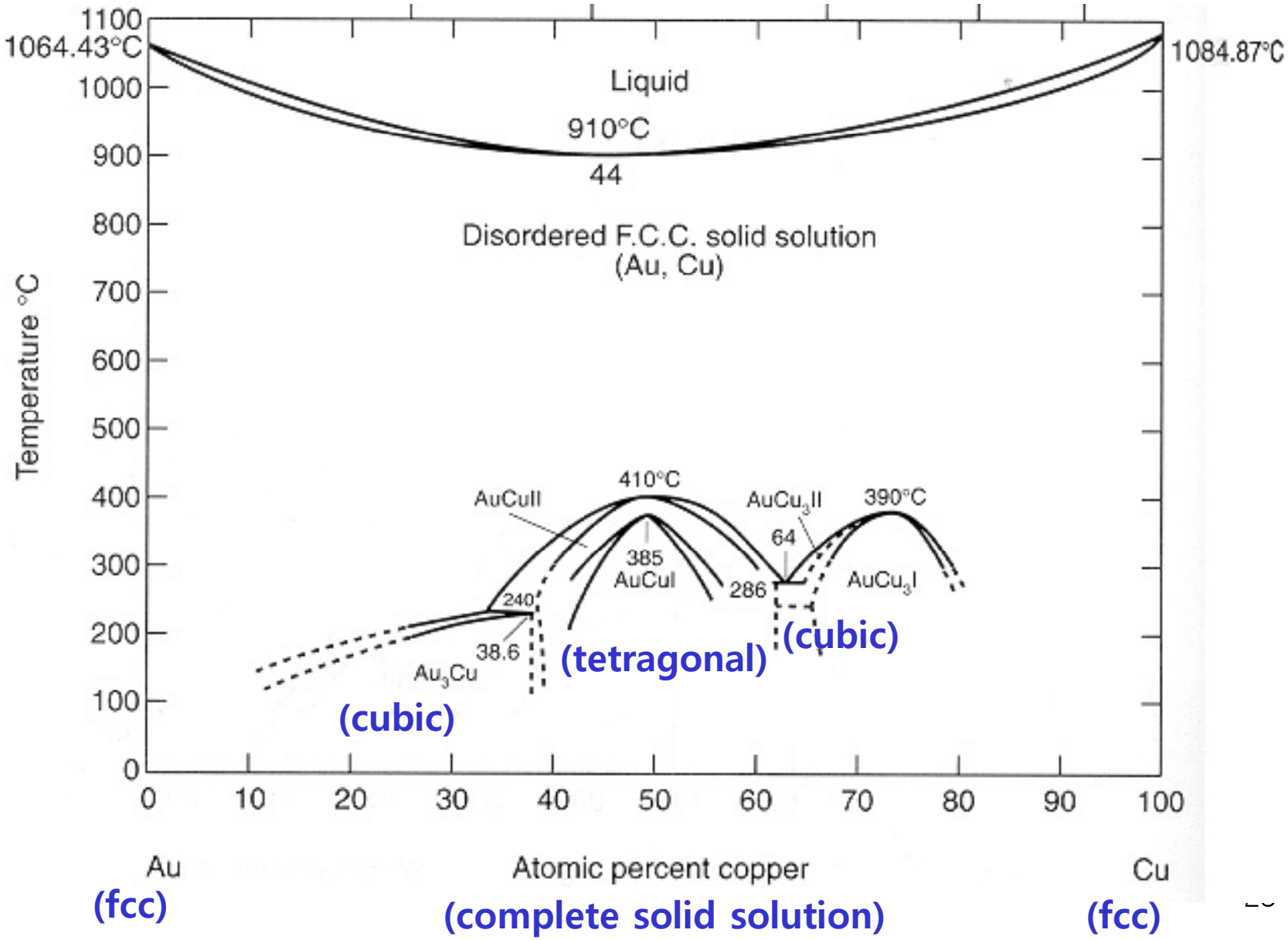


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



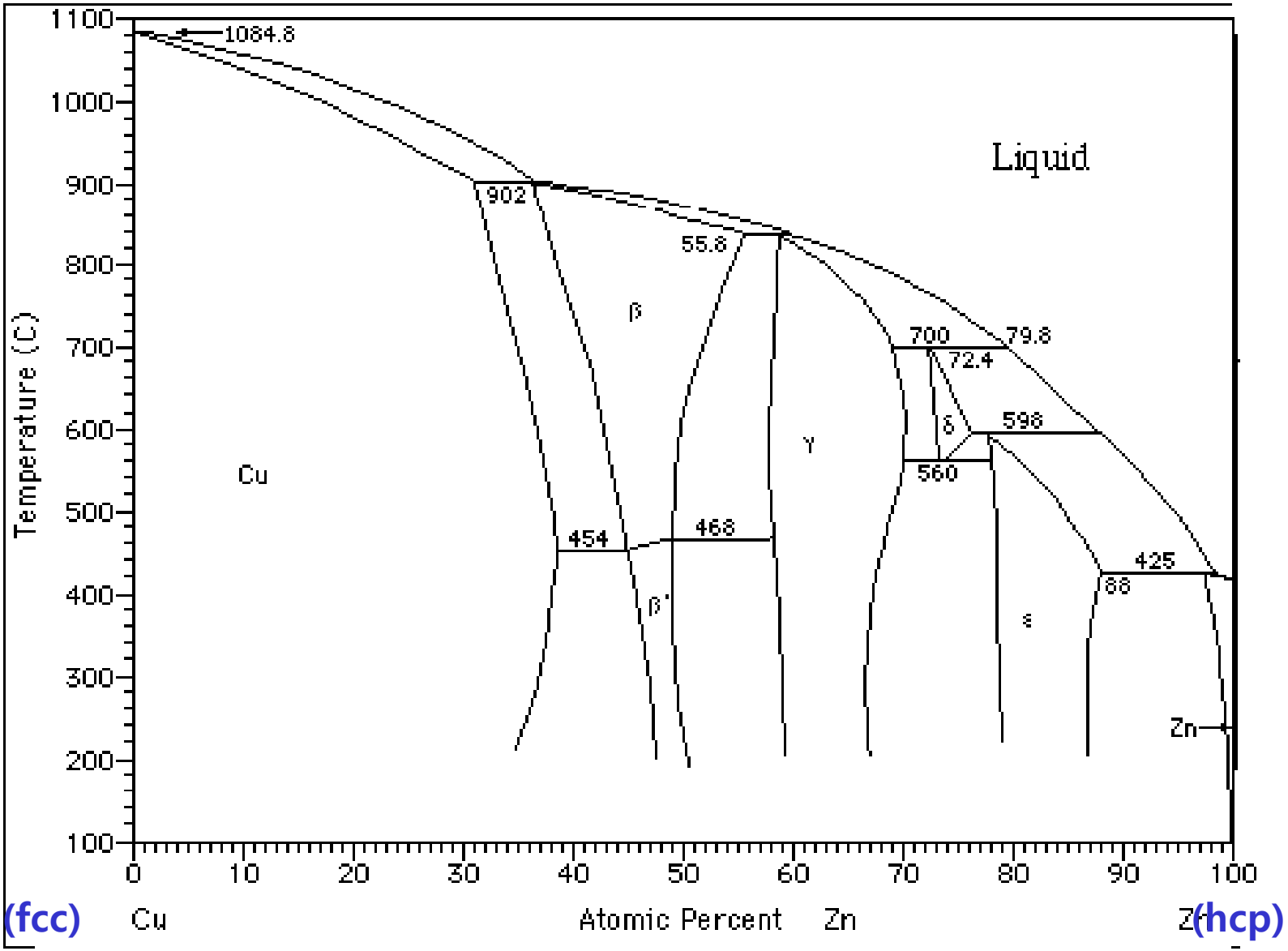
Ordered Phase

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



Intermediate Phase

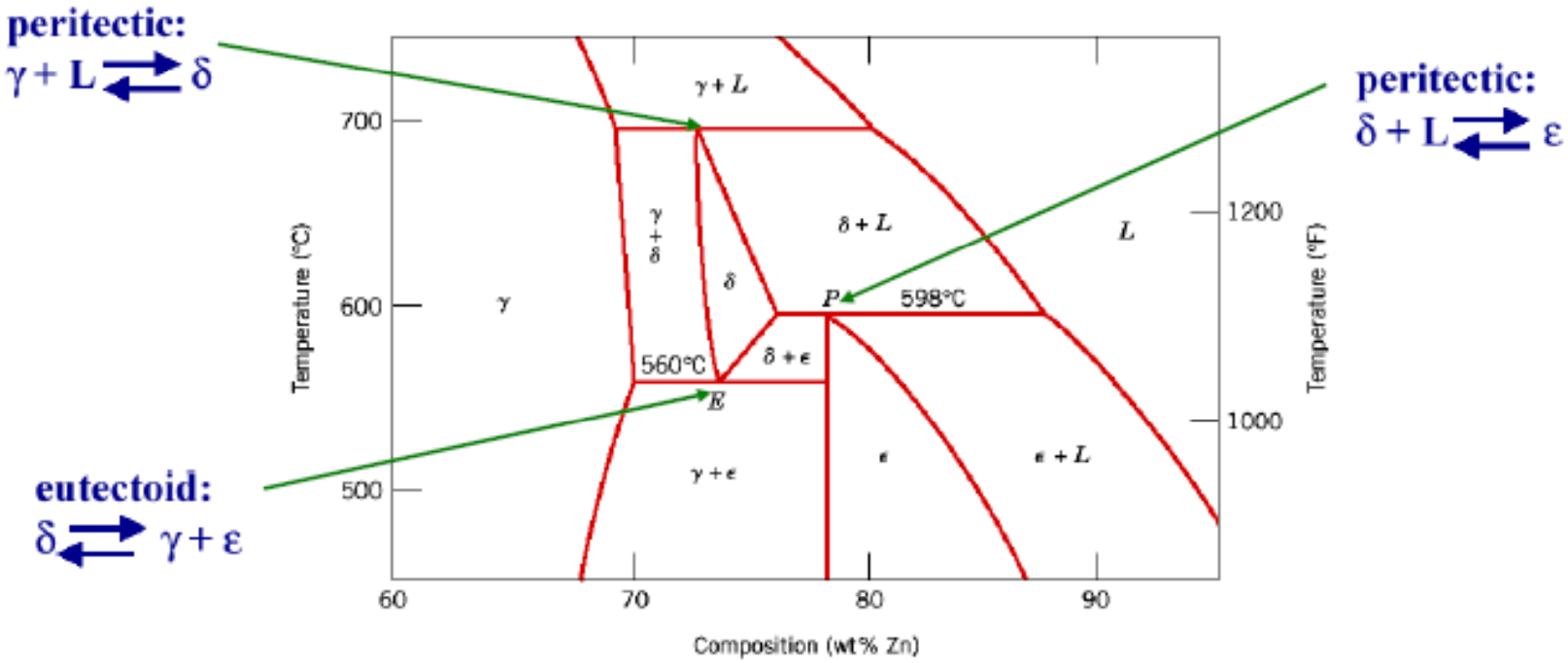
$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim$ -21 kJ/mol



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

Cu-Zn Phase Diagram

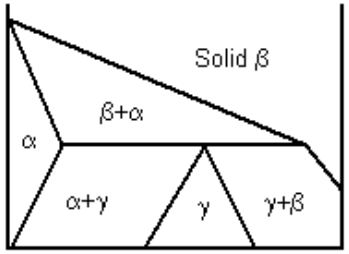
Eutectoid and Peritectic Reactions



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

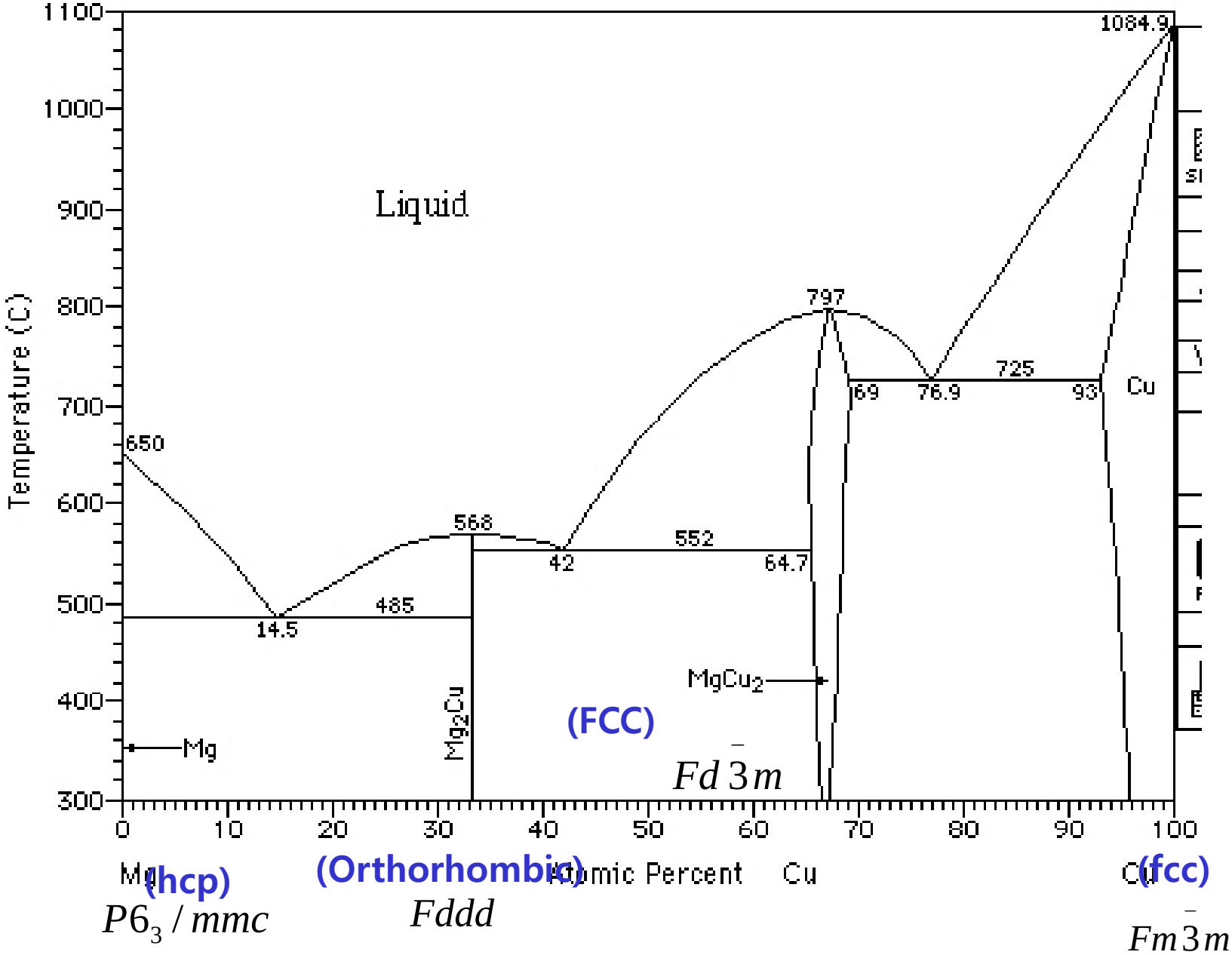
Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

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



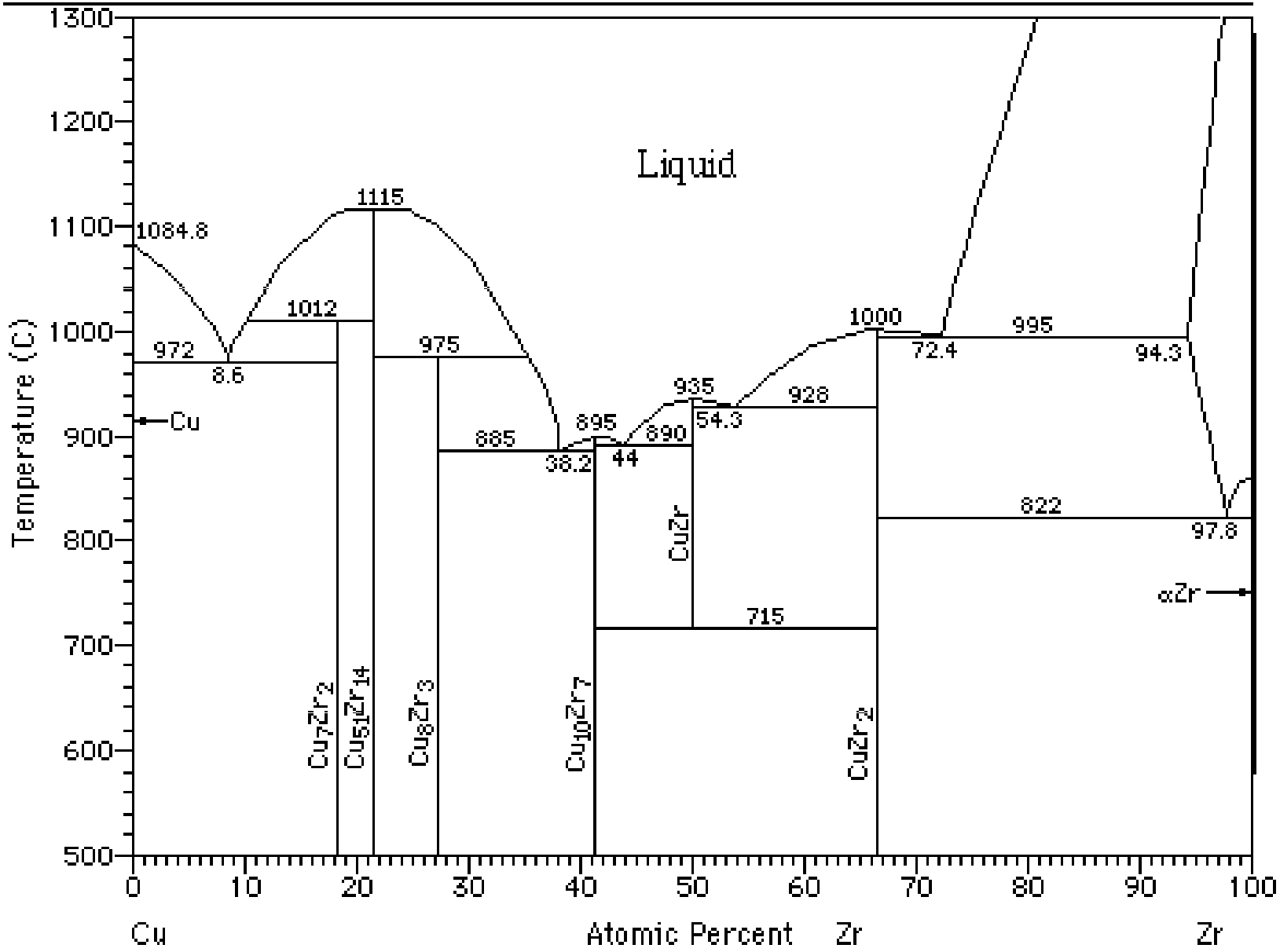
Intermediate Phase

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



Intermediate Phase

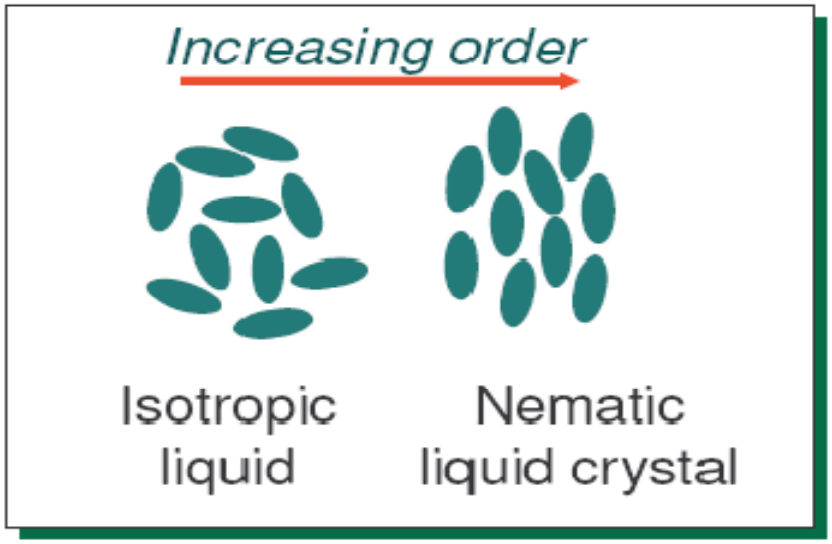
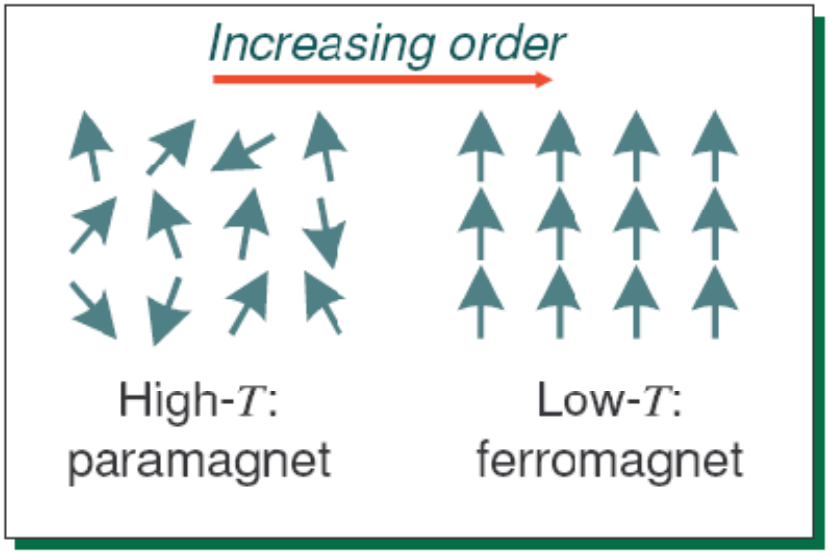
$\varepsilon << 0$, $\Delta H_{mix} << 0$ / $\Delta H_{mix} \sim$ -142 kJ/mol



Order-disorder transition: 2nd order transition

- Other examples (there are many):

- Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).



- Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.