Advanced Physical Metallurgy
"Amorphous Materials"

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Contents for previous class

- **Preparation of amorphous materials**

Sputtering   Surface coating

Thermal evaporation

Glow-discharge decomposition

Chemical vapor deposition

electrolytic deposition

Injection casting   Bulk type
     : sphere, rod, plate

Suction casting

Squeeze casting

Droplet quenching

Gas atomization   powder

Melt-spinning   thin film

Splat quenching   thin plate

Irradiation

Pressure-induced amorphization

Solid-state diffusional amorphization

Glass

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

➡ Glass has 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

Bonding in Solids

- Bonds in solids can be of the following types
  - Ionic
  - Covalent
  - Metallic

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

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

	1A	2A											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		8B		1B	2B	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

Legend:
- <1.0
- 1.0–1.4
- 1.5–1.9
- 2.0–2.4
- 2.5–2.9
- 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.

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
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

<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.
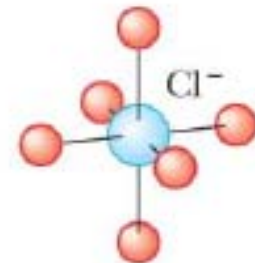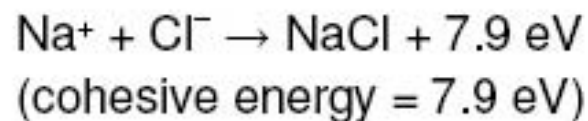
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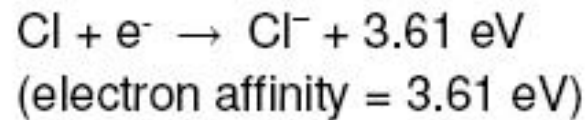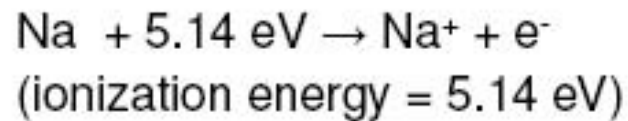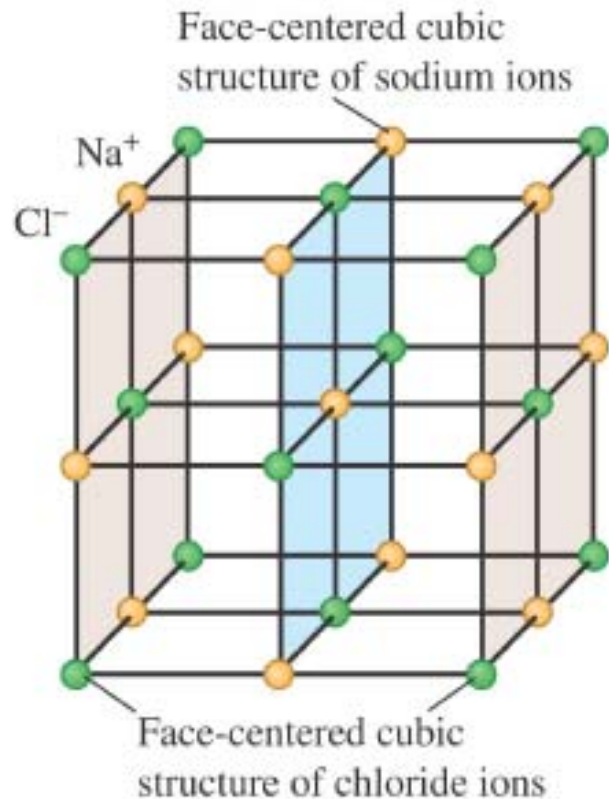# Ionic Bonds, NaCl Example
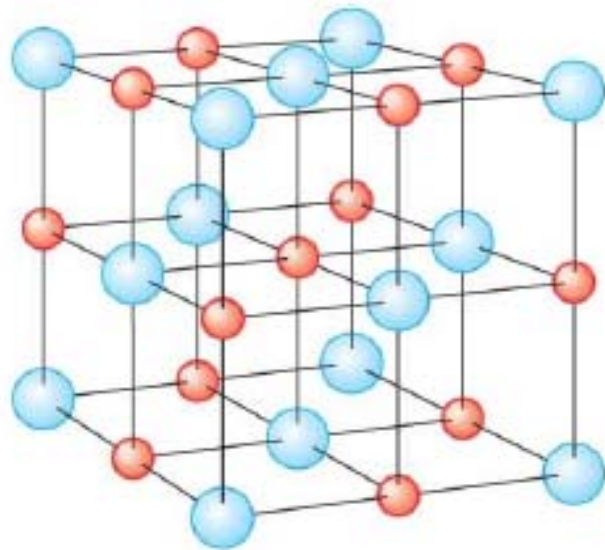
(a)
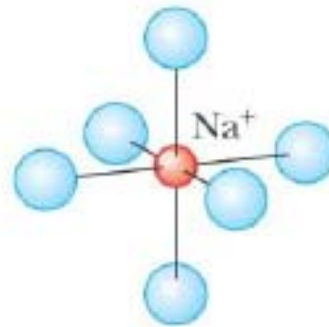
(b)

(c)

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- The crystalline structure is shown (a)
- Each positive sodium ion is surrounded by six negative chlorine ions (b)
- Each chlorine ion is surrounded by six sodium ions (c)

Na-Cl

Face-centered cubic structure of sodium ions

Na$^+$

Cl$^-$

Face-centered cubic structure of chloride ions

Na $+ 5.14$ eV $\rightarrow$ Na$^+$ + e$^-$
(ionization energy $= 5.14$ eV)

Cl + e$^-$ $\rightarrow$ Cl$^-$ + 3.61 eV
(electron affinity $= 3.61$ eV)

Na$^+$ + Cl$^-$ $\rightarrow$ NaCl + 7.9 eV
(cohesive energy $= 7.9$ eV)

i.e. the energy per molecule of NaCl is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms.

More properties of Ionic Crystals

- They form relatively stable, hard crystals
- They are poor electrical conductors
  - They contain no free electrons (filled shells)
  - Each electron is bound tightly to one of the ions
- They have high melting points

Properties of Solids with Covalent Bonds

- Properties include
  - Usually very hard
    - Due to the large atomic cohesive energies
  - High bond energies
  - High melting points
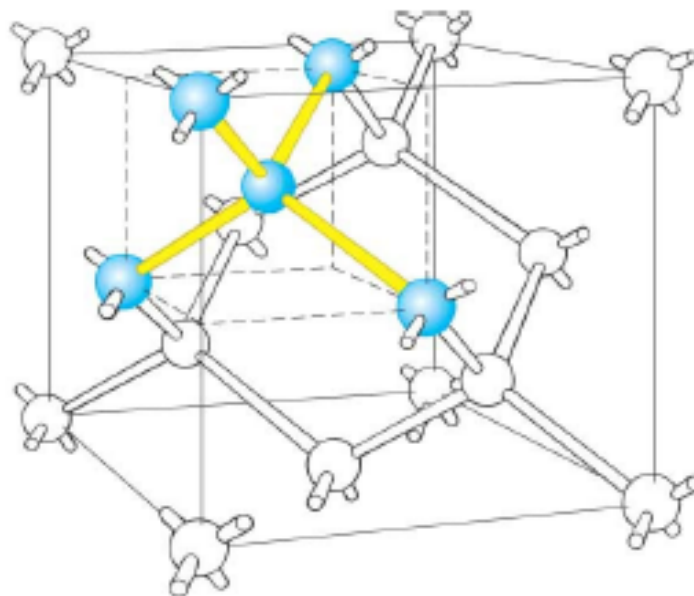 - Good electrical conductors

More about Covalent Bonds

- Share electrons (usually 2 e^-)
- Directional (along orbital that share e^-)
- Electrons tend to localize between atoms
- Perfer anti-parallel spins (Pauli)
- Act as "glue" to atoms
- No clear cut – range to be ionic or covalent

Covalent Bond Example – Diamond
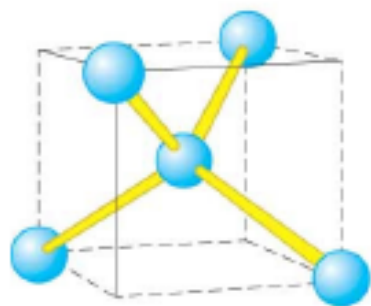
(a)

(b)

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- Each carbon atom in a diamond crystal is covalently bonded to four other carbon atoms
- This forms a tetrahedral structure

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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.
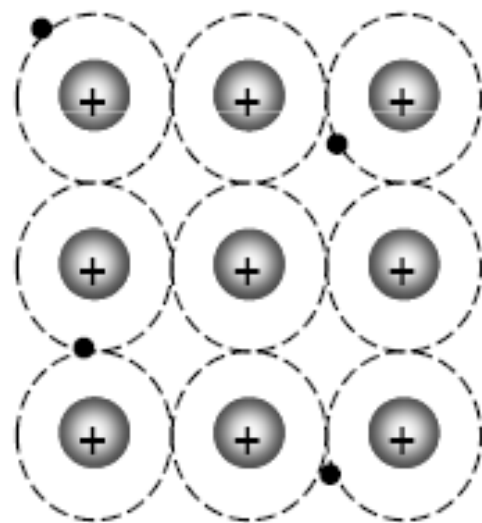
Metallic Solids, cont.

- 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.

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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

Molecular Bonds – Types

- Simplified models of molecular bonding include
  - Ionic
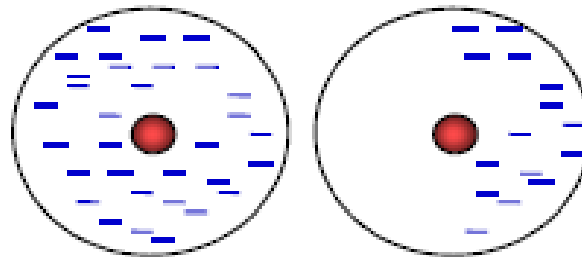 - Covalent
  - van der Waals
  - Hydrogen

Van der Waals Bonding

- It is the weakest bonding mechanism.

- It occurs between neutral atoms and molecules.

- The explanation of these weak forces of attraction is that there are natural fluctuation in the electron density of all molecules and these cause small temporary dipoles within the molecules. It is these temporary dipoles that attract one molecule to another. They are as called van der Waals' forces.

- Such a weak bonding results low melting and boiling points and little mechanical strength.

Van der Waals Bonding, cont.

The dipoles can be formed as a result of _**unbalanced distribution of electrons in asymettrical molecules**_. This is caused by the instantaneous location of a few more electrons on one side of the nucleus than on the other.

symmetric   asymmetric

Therefore atoms or molecules containing dipoles are attracted to each other by electrostatic forces.

Hydrogen Bonding

- In addition to covalent bonds, a hydrogen atom in a molecule can also form a **hydrogen bond** (weak ≤ 0.5 eV)

- Using water (H_2O) as an example
  - There are two covalent bonds in the molecule
  - The electrons from the hydrogen atoms are more likely to be found near the oxygen atom than the hydrogen atoms

Hydrogen bonding between water molecules
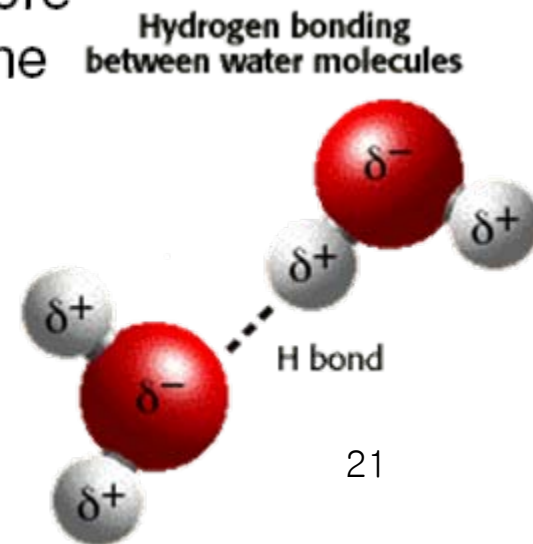
Hydrogen Bonding – H_2O cont.

- This leaves essentially bare protons at the positions of the hydrogen atoms
- The negative end of another molecule can come very close to the proton
- This bond is strong enough to form a solid crystalline structure

Hydrogen Bonding, Final

- The hydrogen bond is relatively weak compared with other electrical bonds

- Hydrogen bonding is a critical mechanism for the linking of biological molecules and polymers

- DNA is an example

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Glass

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- **How does glass form?** ➡ **Glass 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 $T_{m.p.}$** ➡ **More viscous**
   (supercooled) ➡ **Glass**

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Liquid to Crystal Transition vs. Liquid to Glass Transition

- Crystallization (liquid to crystal transition) is defined from a thermodynamic standpoint by a number of changes in the materials properties at the transition temperature T_C :

    – a change in enthalpy (a latent heat of crystallization ΔH_C)

    – a change in specific volume or density (V_C, V_A, ρ_A, ρ_C)

    – a change in isobaric coefficient of thermal expansion (α_C, α_A)

    – a change in isothermal compressibility (β_C, β_A)

    – a change in heat capacity $C_{P(A)}$, $C_{P(B)}$

- Such changes in material properties at a phase transformation is characteristic of what one calls a First Order Phase Transformation.

- Liquid to Glass Transition is also a transition from the liquid to the solid state. What can be said about the characterisitic changes in state functions (ρ or V, H) for the liquid to glass transformation.

Ehrenfest Classification of Phase Transitions

- First Order Phase Transition at T_T:
  - G is <u>continuous</u> at T_T
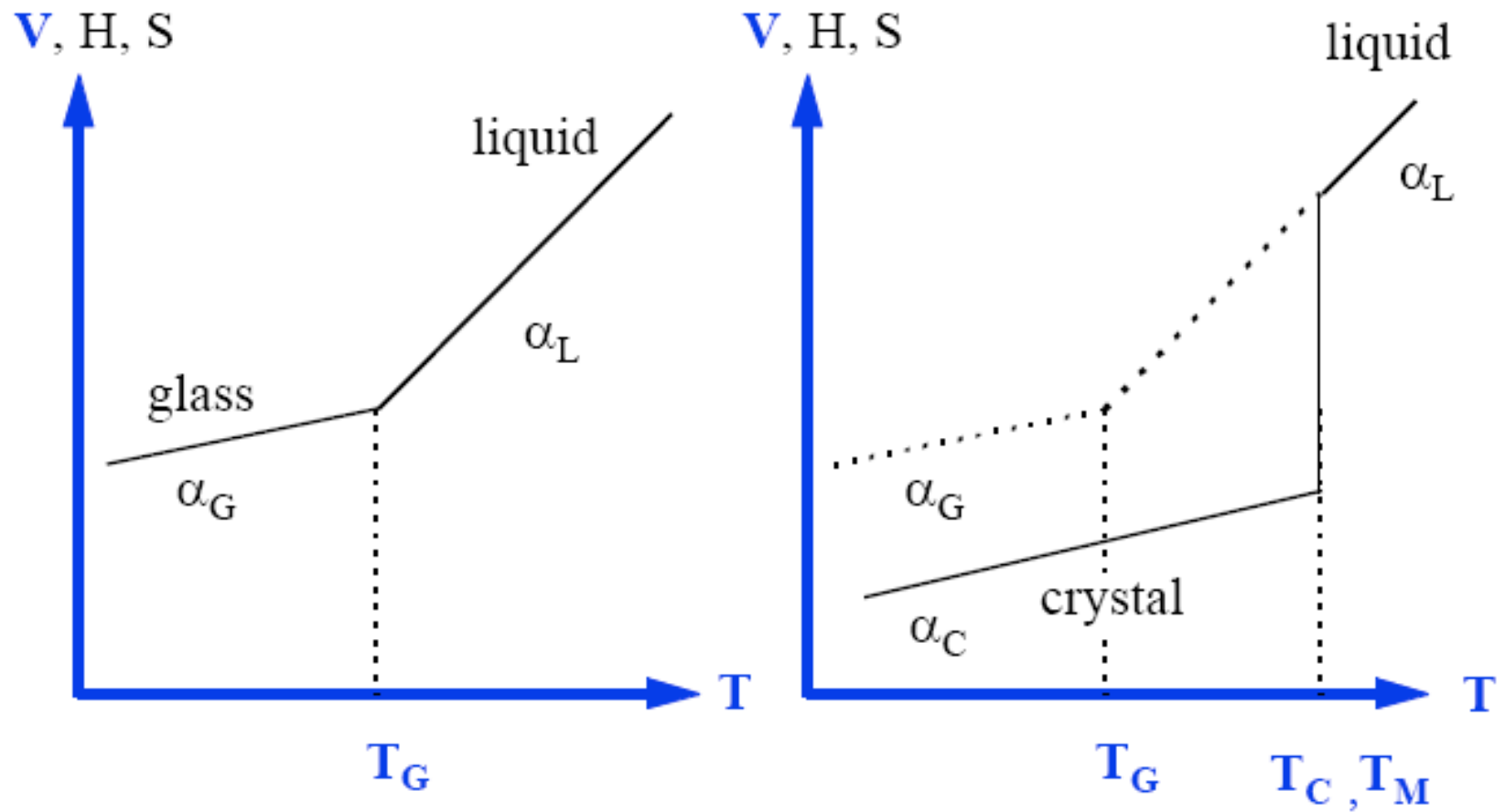 - First derivatives of G (V, S, H) are <u>discontinuous</u> at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are <u>discontinuous</u> at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

- Second Order Phase Transition at T_T:

  - G is <u>continuous</u> at T_T

  - First derivatives of G (V, S, H) are <u>continuous</u> at T_T

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$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Experimental Evidence: Dilatometry $V = f(T, P)$

Liquid to Glass Transition
"Second Order" Transition

Liquid to Crystal Transition
First Oder Transition

- Second Order Phase Transition at T_T:

    - G is <u>continuous</u> at T_T

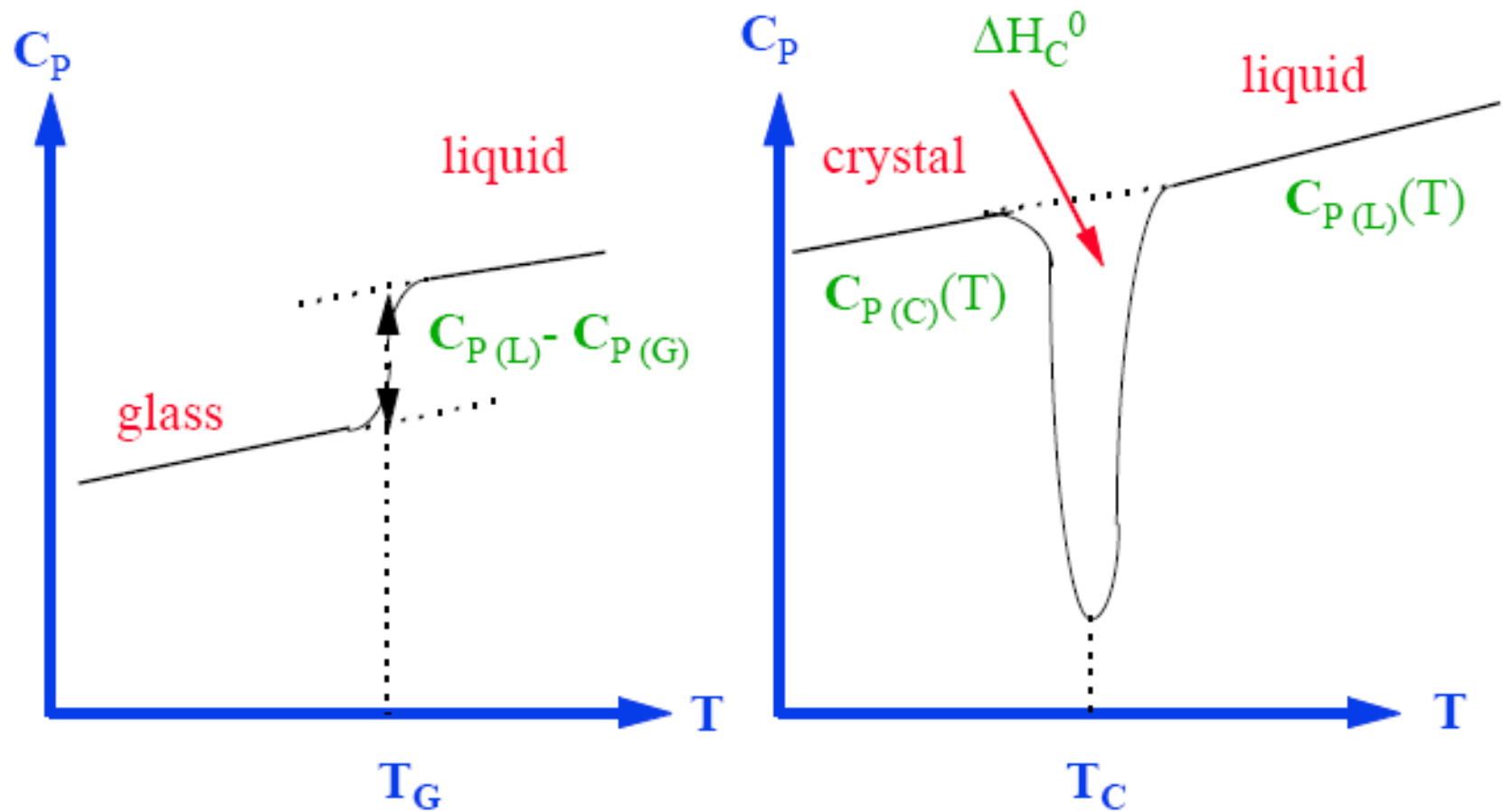   - First derivatives of G (V, S, H) are <u>continuous</u> at T_T

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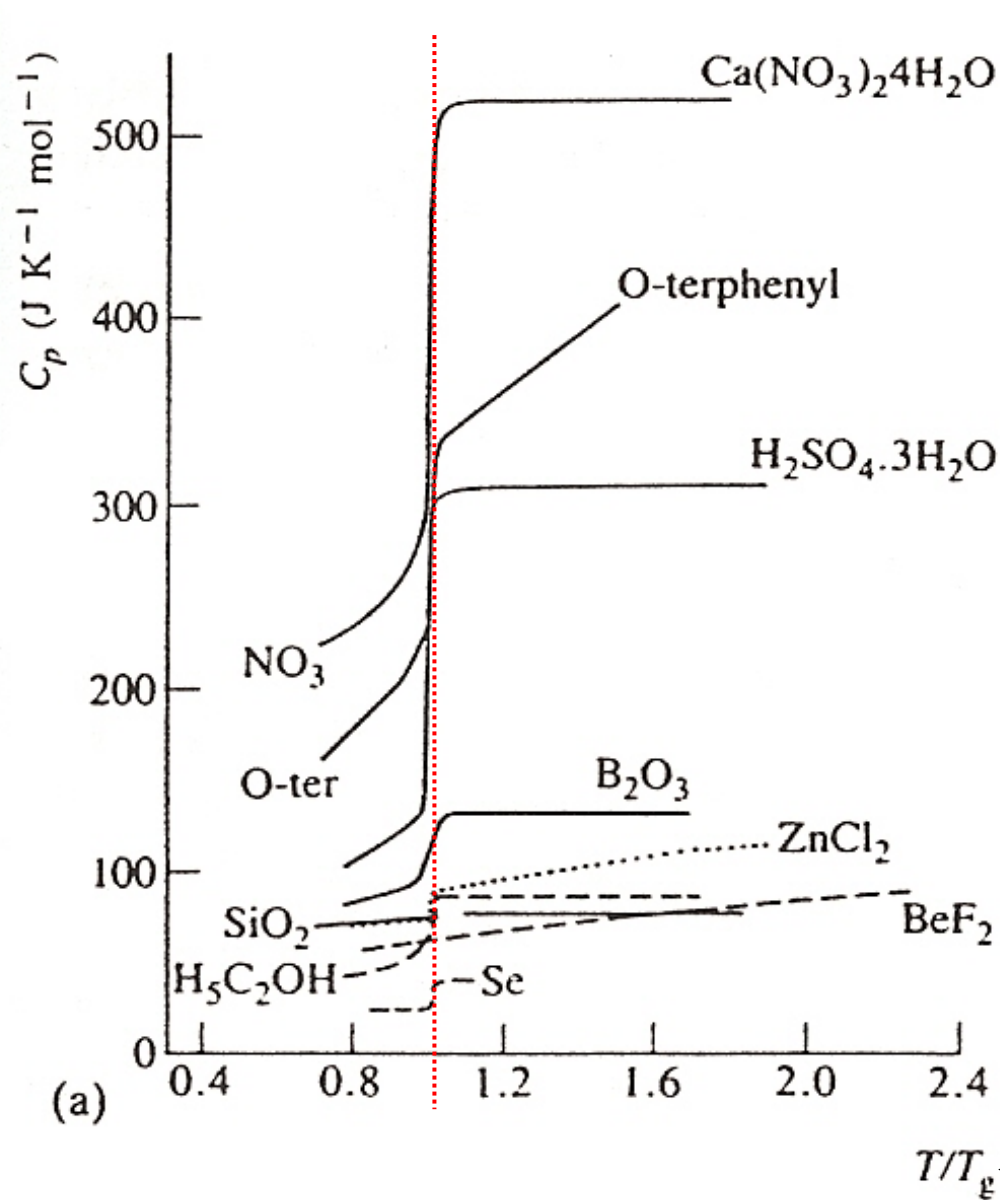
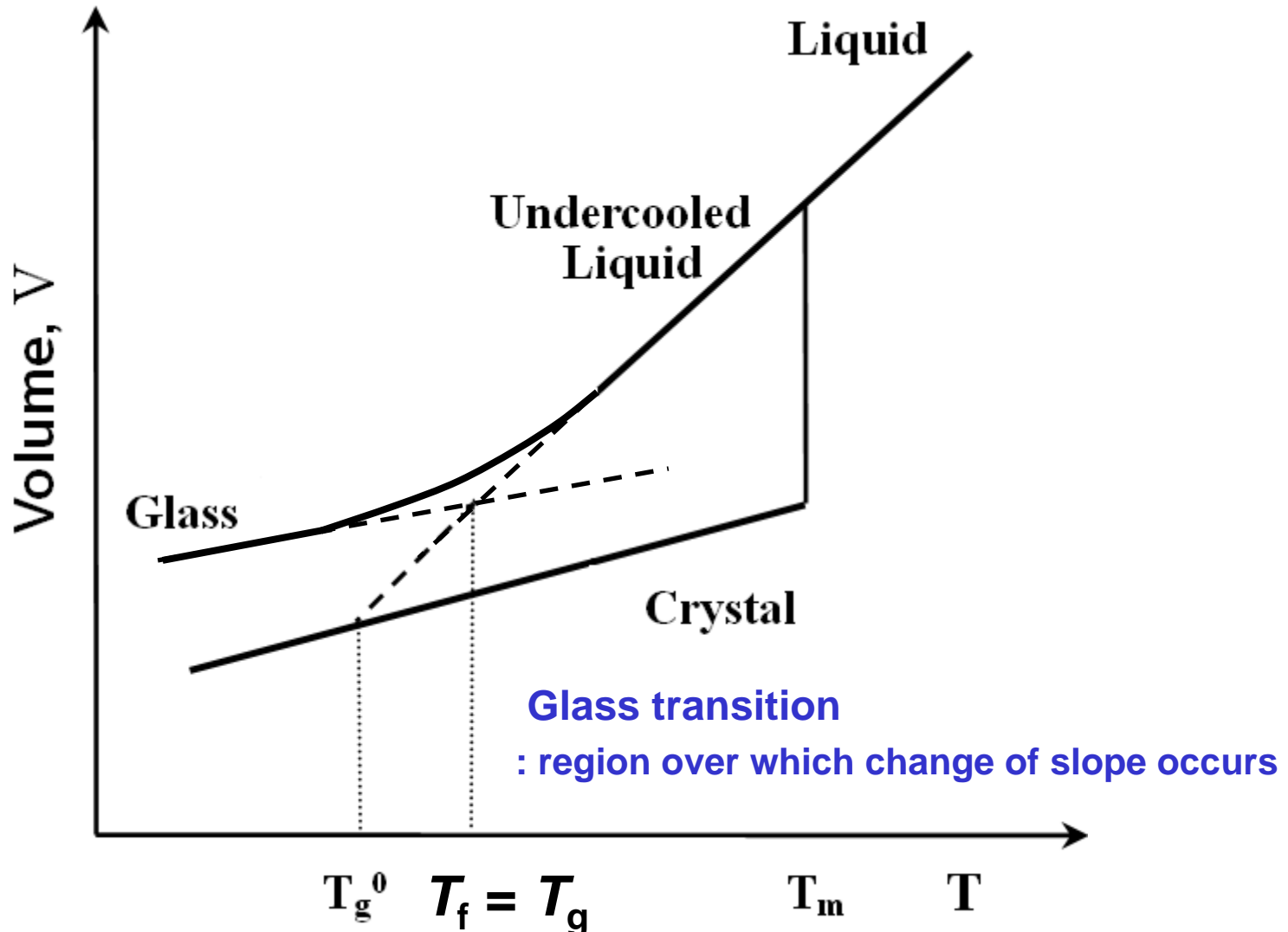# Experimental Evidence: Calorimetry $C_p = f(T)$

Liquid to Glass Transition
"Second Order" Transition

Liquid to Crystal Transition
First Order Transition
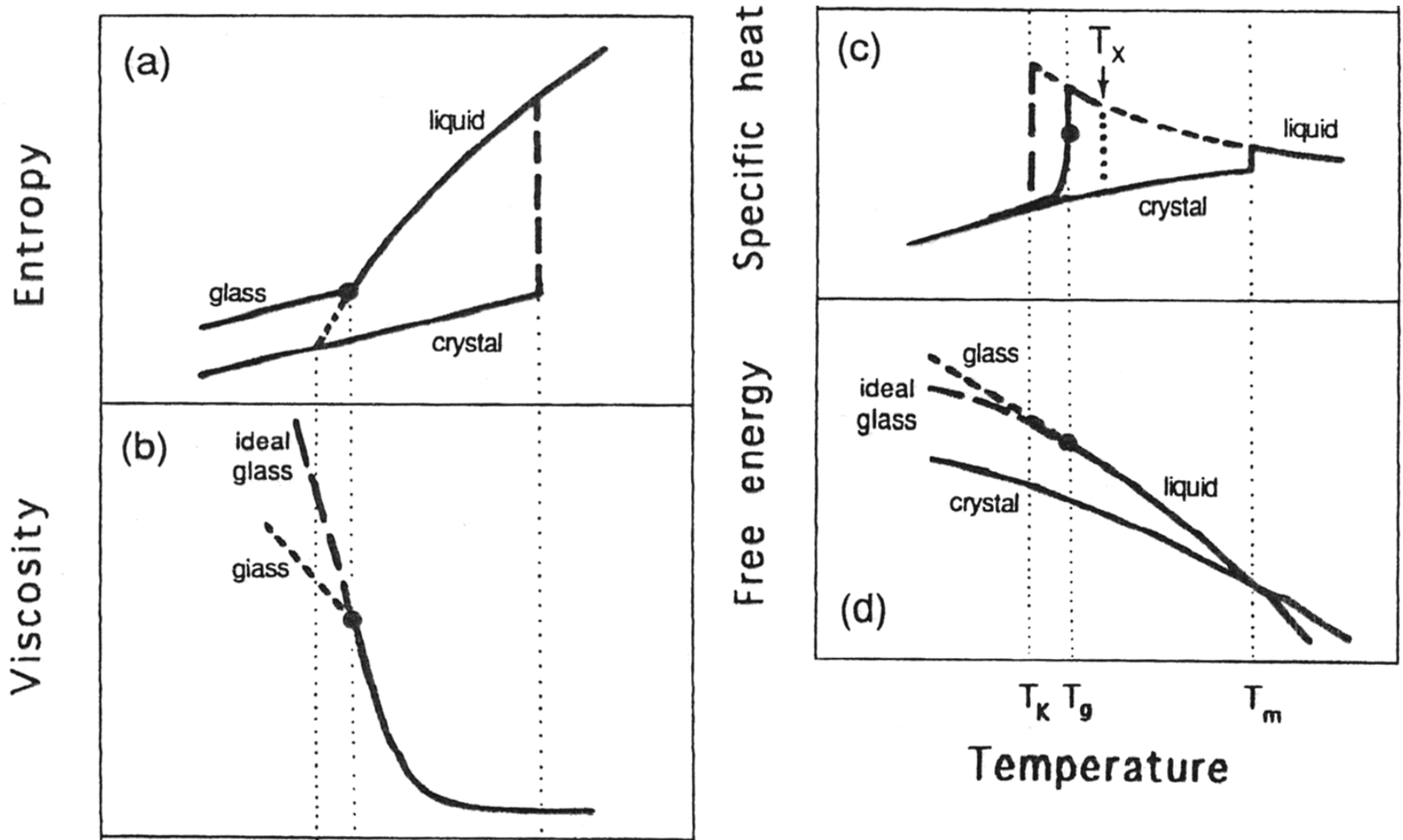
Difference of C$_p$ at T$_g$ depending on materials

(a)

Normalizing as T_g

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T_g = fictive temperature, T_f

Volume, V

Liquid

Undercooled Liquid

Glass

Crystal

T_g^0 $T_f = T_g$ T_m T

Glass transition

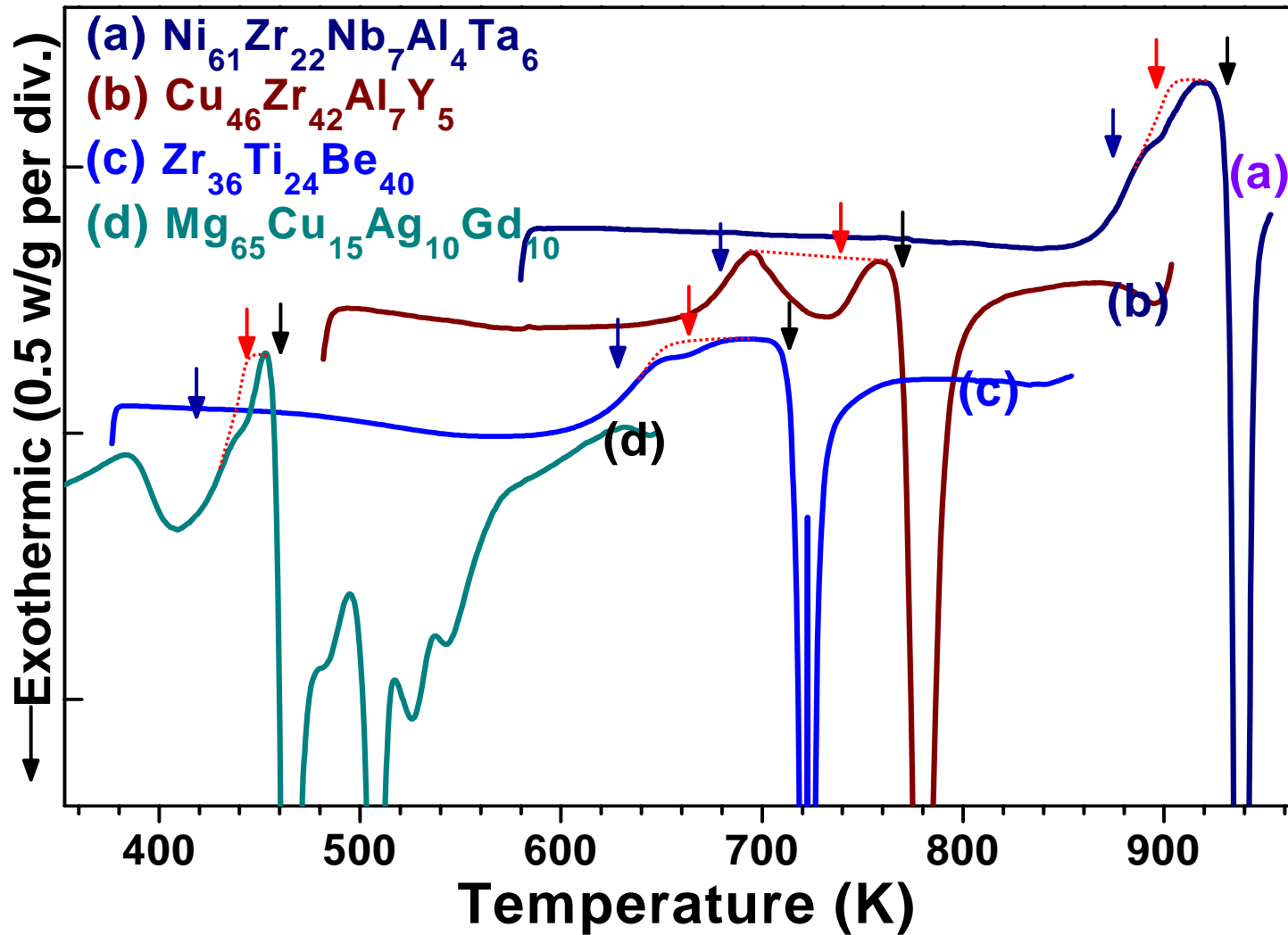**: region over which change of slope occurs**

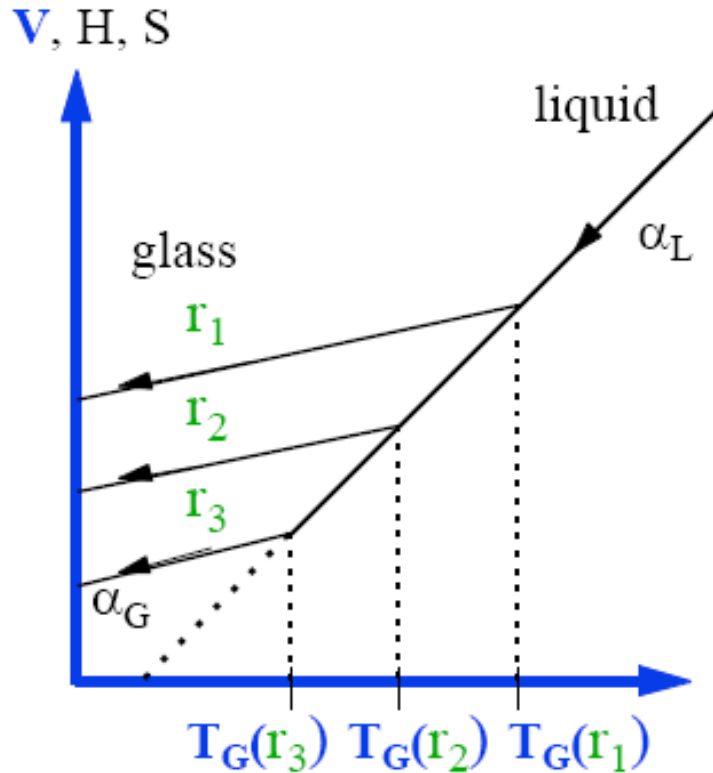**thermodynamic property ?**   **thermodynamic property**

Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

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Change of T_gs depending on alloy compositions

(a) $Ni_{61}Zr_{22}Nb_7Al_4Ta_6$
(b) $Cu_{46}Zr_{42}Al_7Y_5$
(c) $Zr_{36}Ti_{24}Be_{40}$
(d) $Mg_{65}Cu_{15}Ag_{10}Gd_{10}$

Exothermic (0.5 w/g per div.)

Temperature (K)

• T_g *depends on thermal history.*

Kinetic Nature of the Glass Transition

V, H, S

liquid

glass

α_L

r_1

r_2

r_3

α_G

$T_G(r_3)$ $T_G(r_2)$ $T_G(r_1)$

Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$
if $r_3 < r_2 < r_1$

- T_g vs. cooling speed (v)

: $v = v_o \exp[-1/C(1/T_g - 1/T_m)]$

--*from free-volume theory*

i.e., slower v → lower T_g

T_g **(bulk : melt-quenched)**

< T_g **(film : vacuum vapor-deposited)**

DSC results
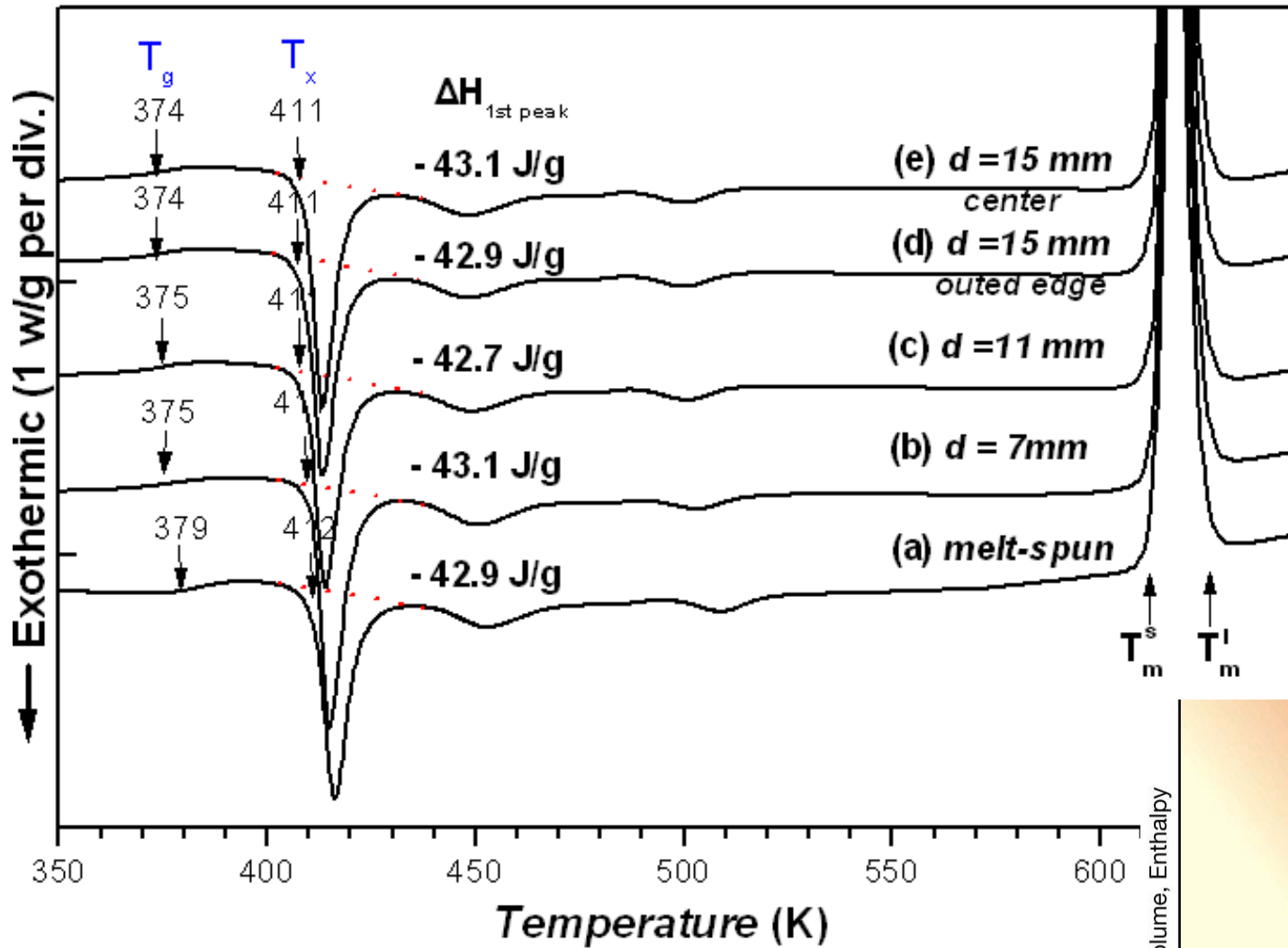
- T_g depends on thermal history even in same alloy composition.