

# PHY2002: Thermodynamics and Phase Transitions

Marty Gregg

## **Possible Books**

*'Phase Transformations in Metals and Alloys'*, Porter and Easterling, Van Nostrand Reinhold.

*'Phase Transitions in Solids'*, Rao and Rao, M<sup>c</sup>Graw-Hill.

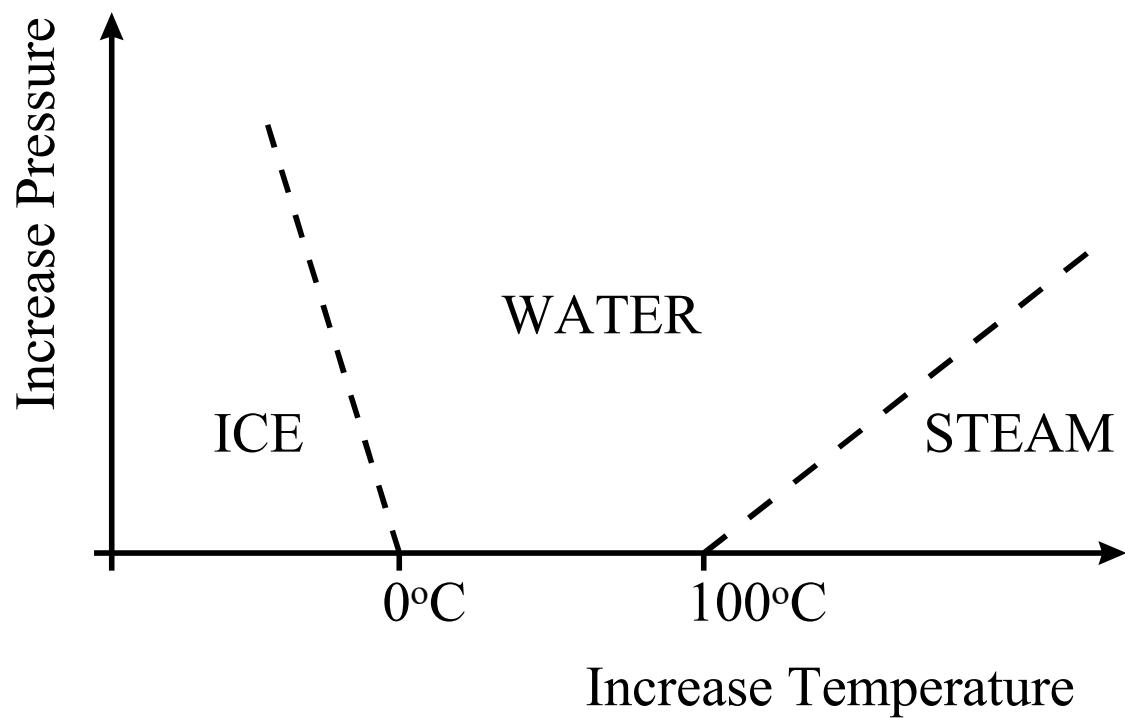
*'Introduction to Mineral Sciences'*, Putnis, C. U. P. 1992.



The Physical Properties of Materials are not Fixed.

e.g. Rubber @ Room Temp – elastic @ 77K - inelastic and brittle

e.g. H<sub>2</sub>O >0°C, @1atm – liquid; <0°C, @1atm - brittle crystalline solid  
<0°C, Pressure >> 1atm – liquid

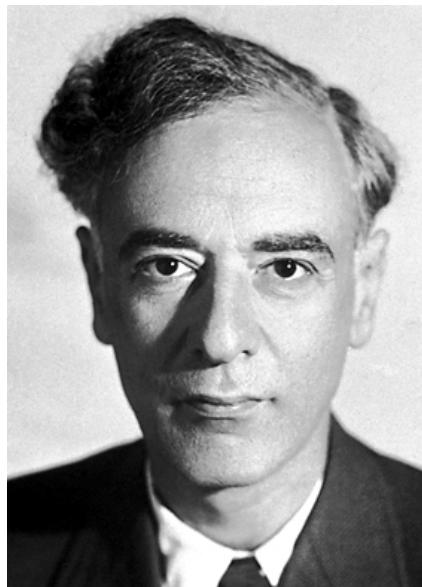


## Nobel Prize in Physics 2003: Abrikosov, Ginzburg, Legget



*"for pioneering contributions to the theory of superconductors and superfluids"*

## Nobel Prize in Physics 1962: Landau



*"for his pioneering theories for condensed matter, especially liquid helium"*

## Nobel Prize in Physics 1982: Wilson



*"for his theory for critical phenomena in connection with phase transitions"*

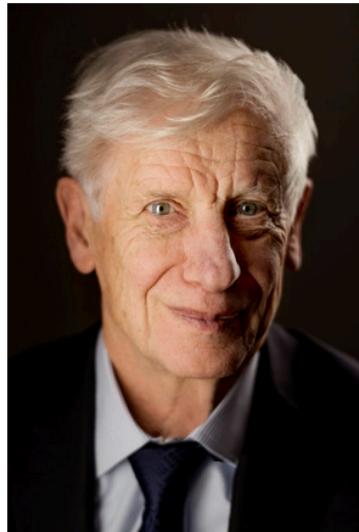
## Nobel Prize in Physics 1991: de Gennes



*"for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers".*

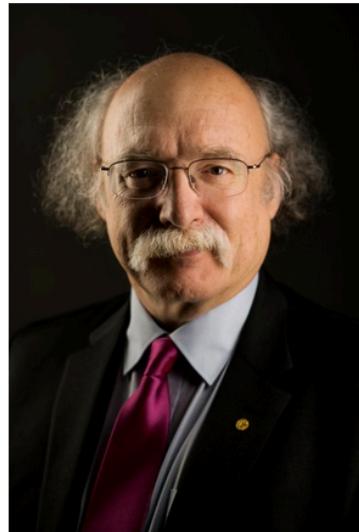
# The Nobel Prize in Physics 2016

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© Nobel Media AB. Photo: A.  
Mahmoud

**David J. Thouless**  
Prize share: 1/2



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**F. Duncan M.  
Haldane**  
Prize share: 1/4



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**J. Michael Kosterlitz**  
Prize share: 1/4

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The Nobel Prize in Physics 2016 was divided, one half awarded to David J. Thouless, the other half jointly to F. Duncan M. Haldane and J. Michael Kosterlitz "for theoretical discoveries of topological phase transitions and topological phases of matter."

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Changes in properties are manifestations of more fundamental changes at atomic level -

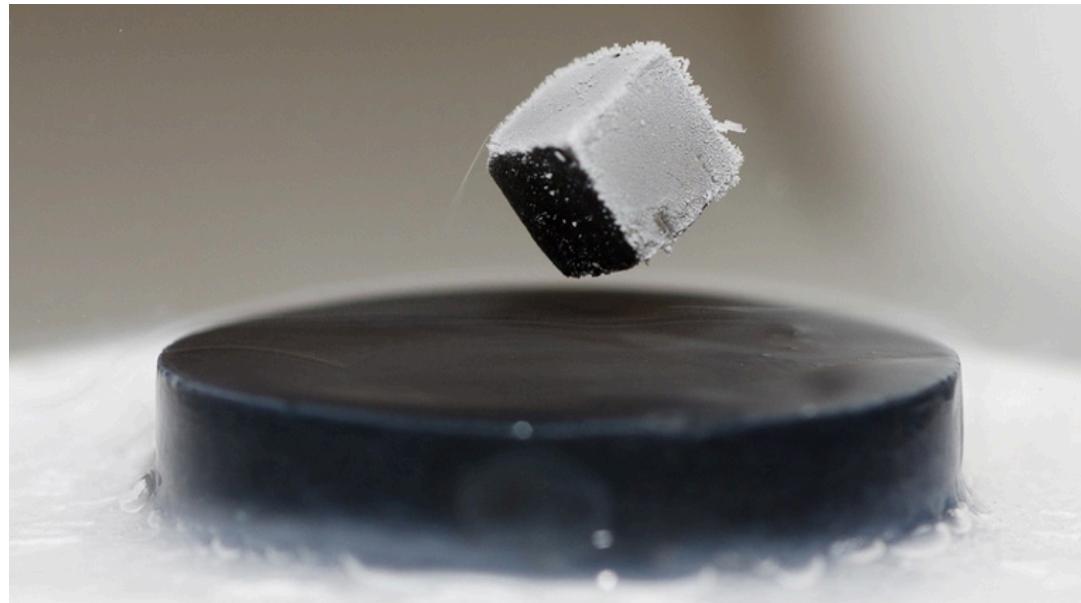
## **Phase Changes / Phase Transformations**

Commonly observed phase transformations are the changes of state:

Solid  $\longleftrightarrow$  Liquid  $\longleftrightarrow$  Gas

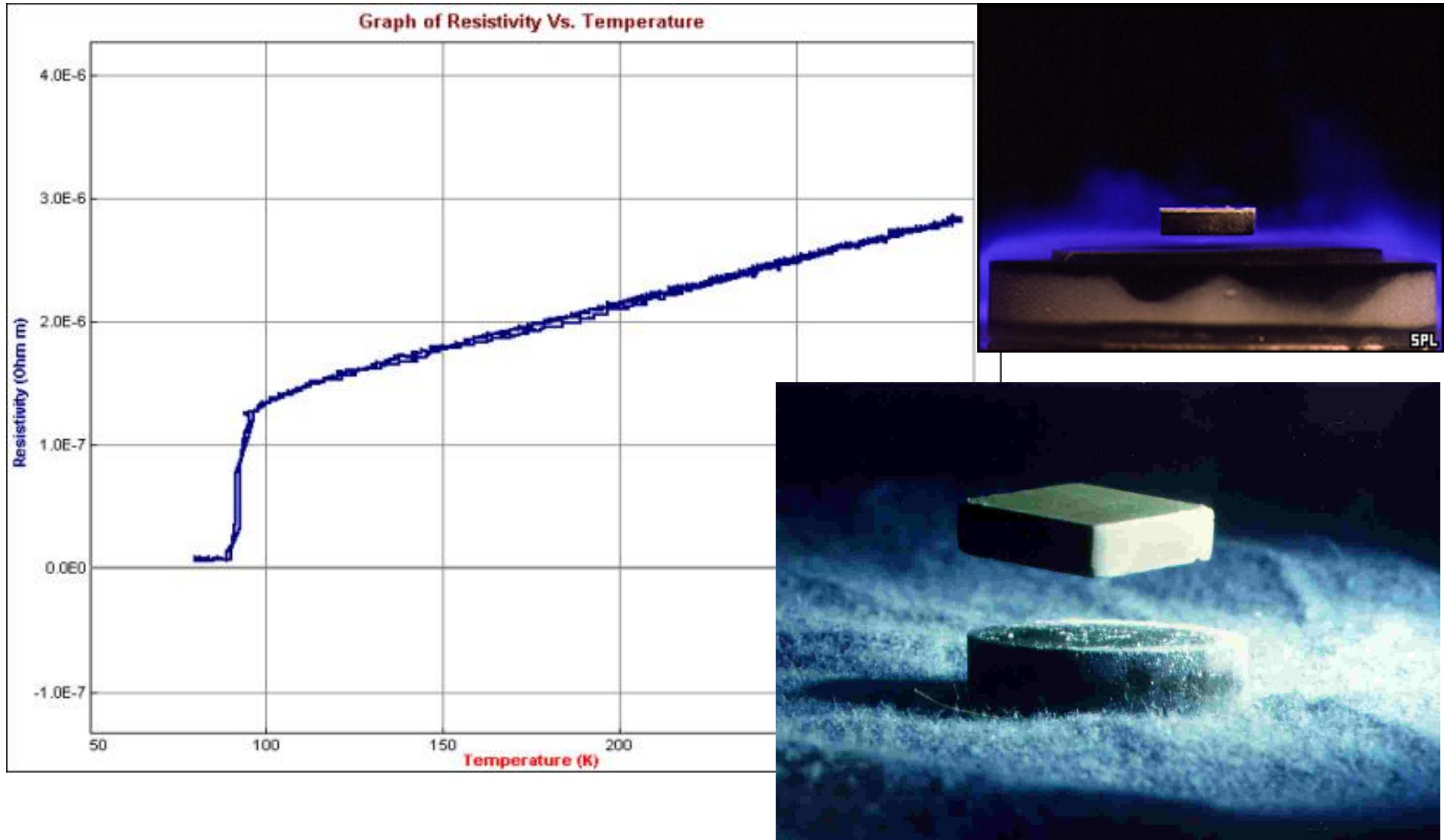
However, many more subtle phase transformations occur, particularly between different structures within the solid state.

The Properties of Materials are not Fixed – even  
within the solid state

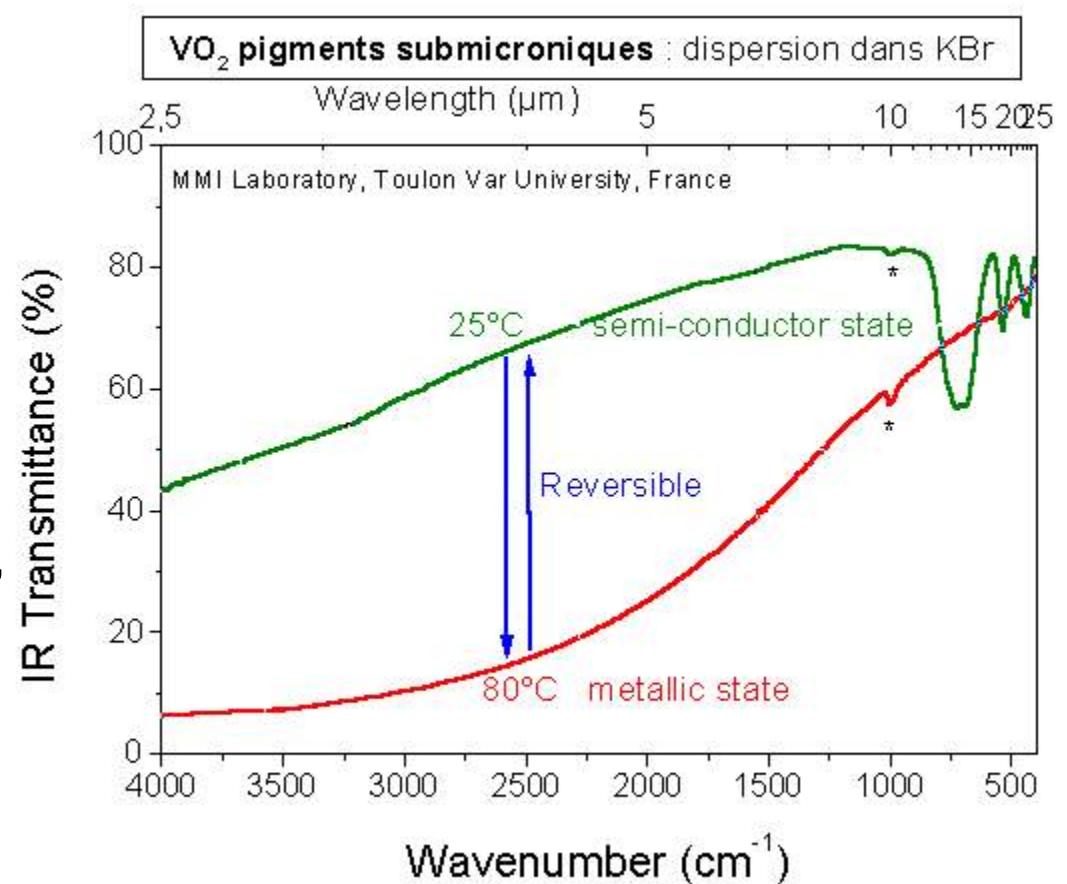
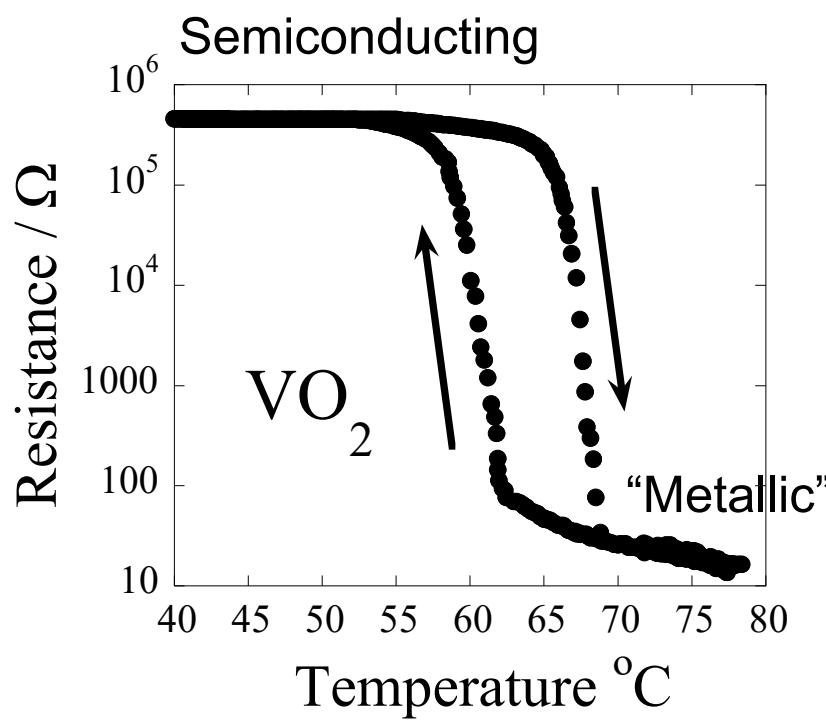


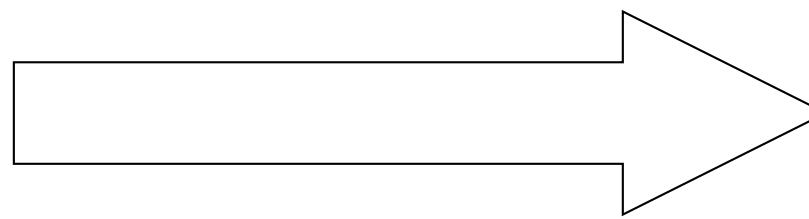
<https://www.youtube.com/watch?v=HRLvVkkq5GE>

# Nobel Prize in Physics 2003: Abrikosov, Ginzburg, Legget



# Vanadium Dioxide – metal-semiconductor transitions

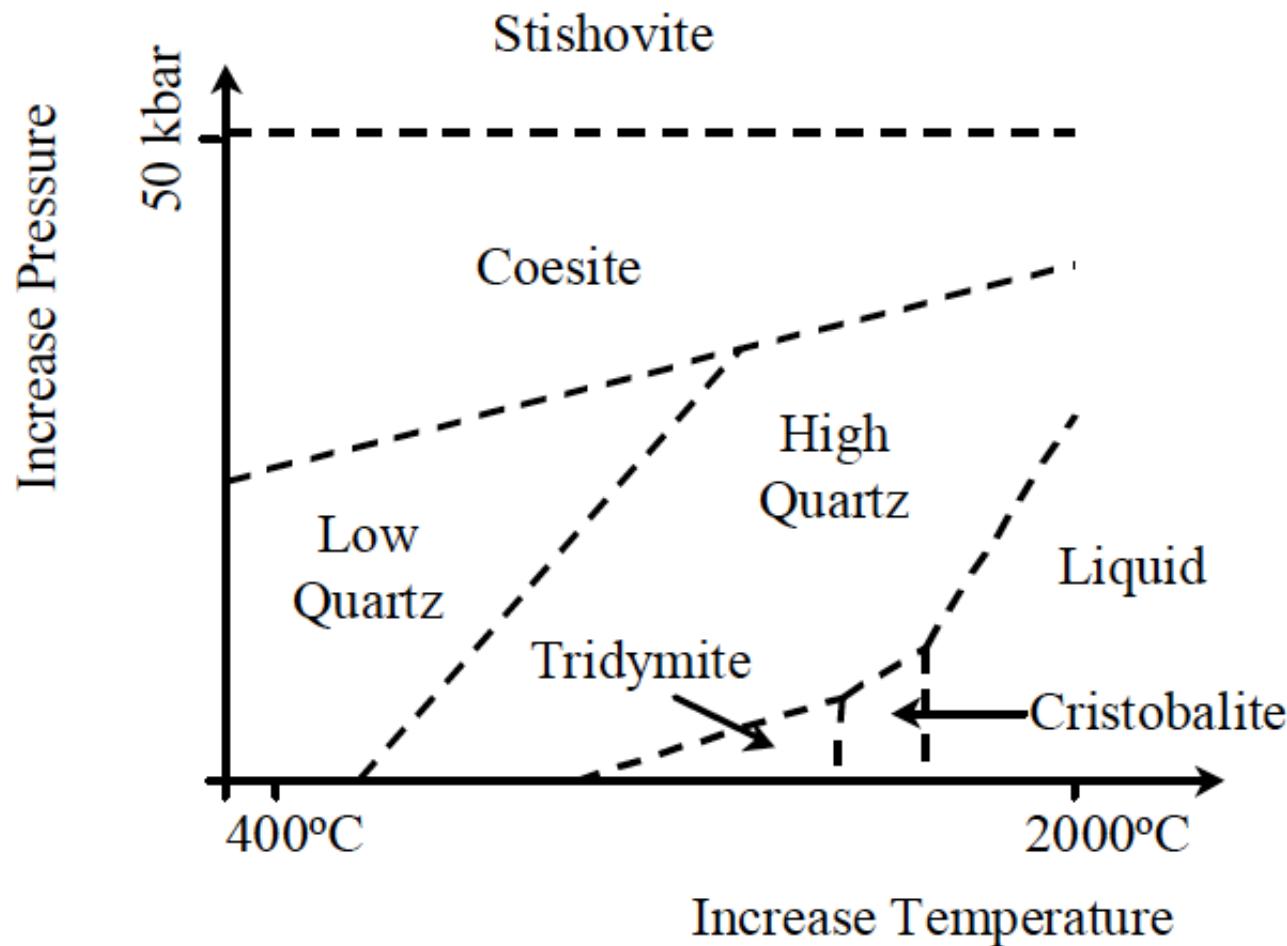




Room heats up; semi-conductor → metal

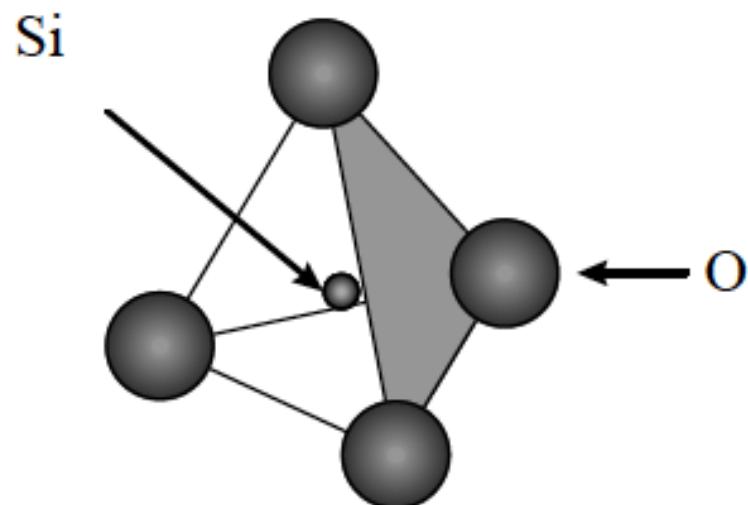
e.g. Quartz -  $\text{SiO}_2$

Common refractory (high temperature use) material - BUT it exists in many forms:

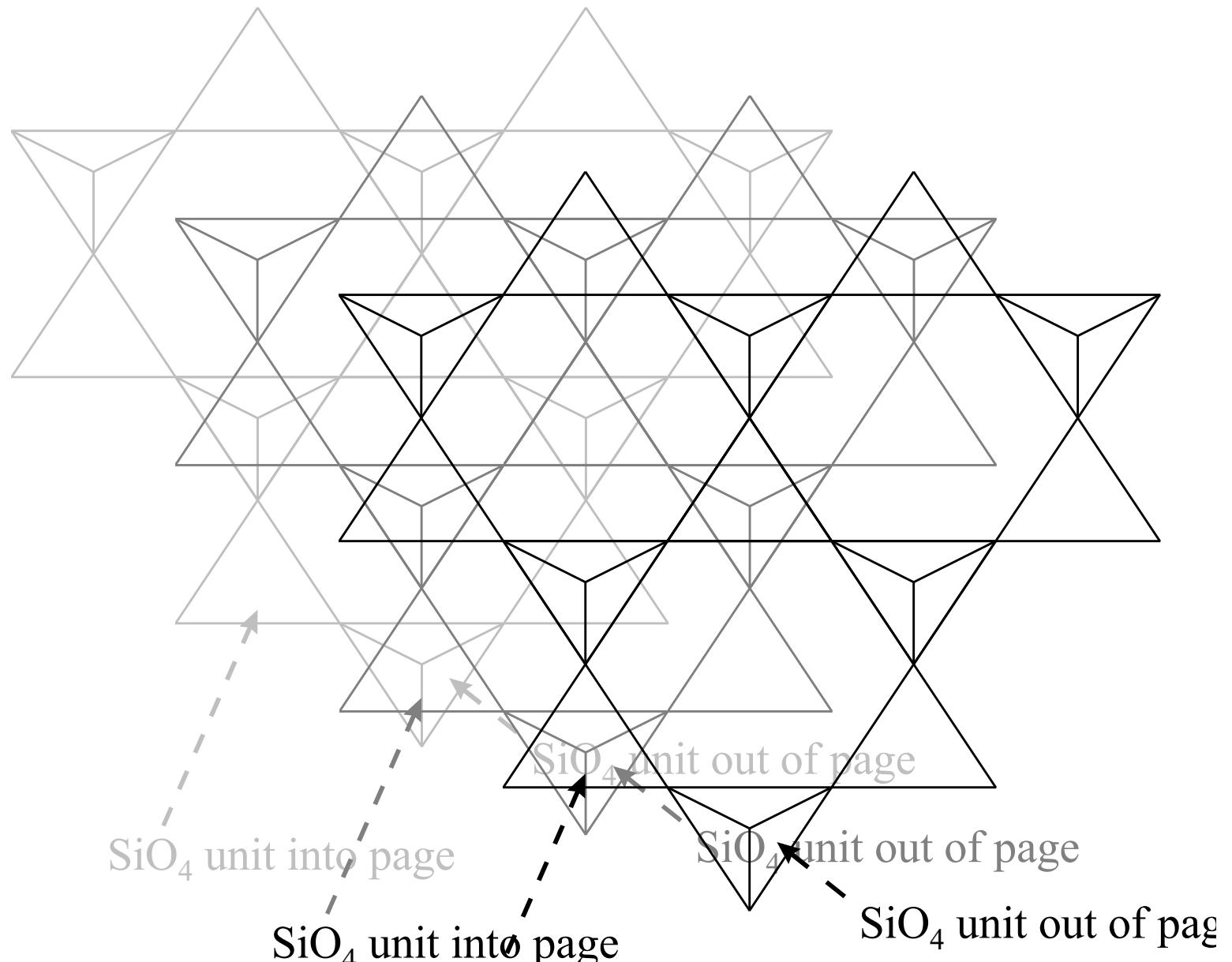


## **Details|of the Quartz Structures:**

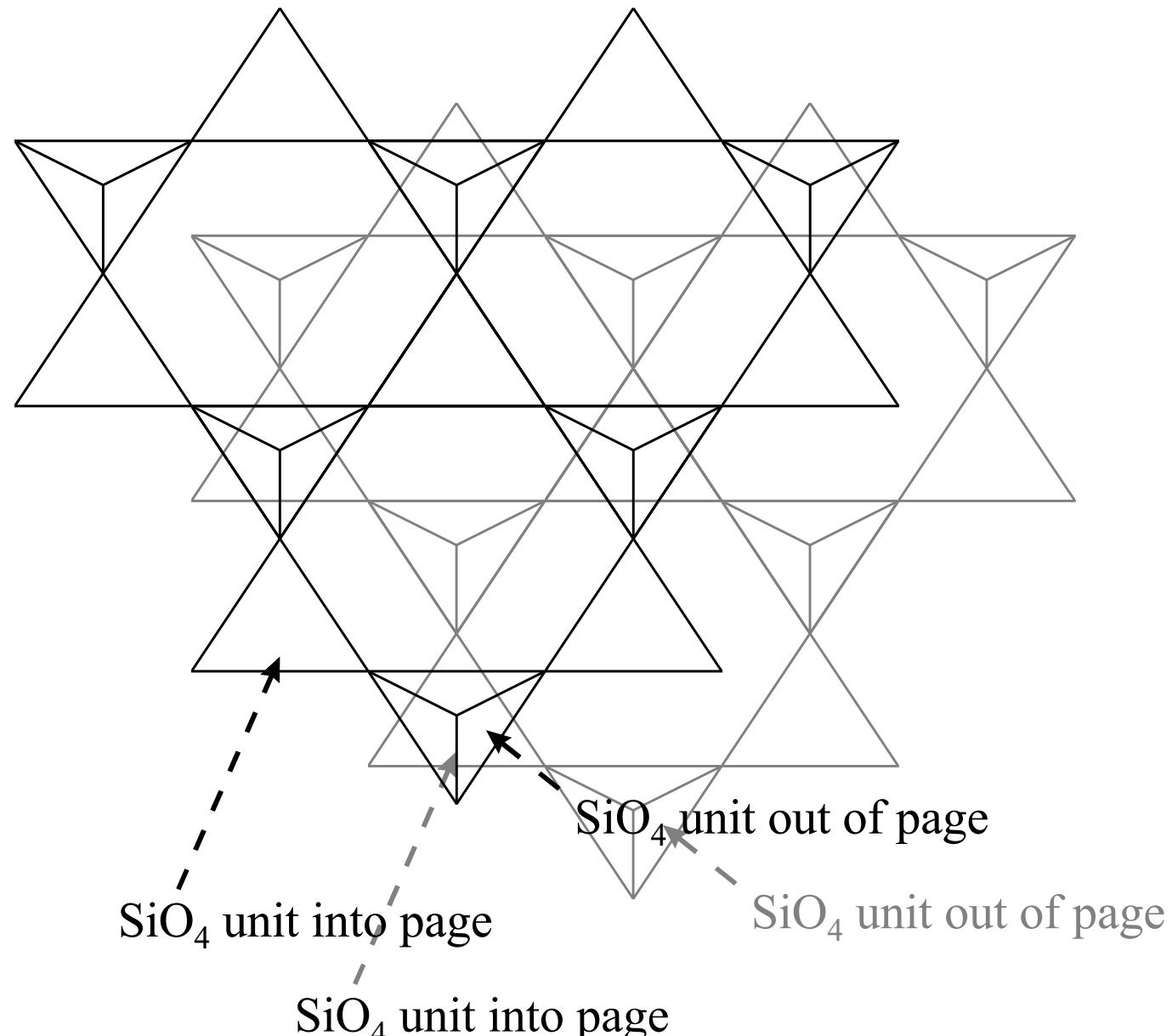
The basic building block of most quartz polymorphs is the  $\text{SiO}_4$  tetrahedral unit:



*Cristobalite and Tridymite:* These structures can be described as sheets of corner sharing  $\text{SiO}_4$  units. Each sheet looks like the schematic below:



*Cristobalite and Tridymite:* These structures can be described as sheets of corner sharing  $\text{SiO}_4$  units. Each sheet looks like the schematic below:



In successive layers, the oxygens on the tetrahedra pointing up from the lower layer are shared by tetrahedra of the upper layer pointing down.

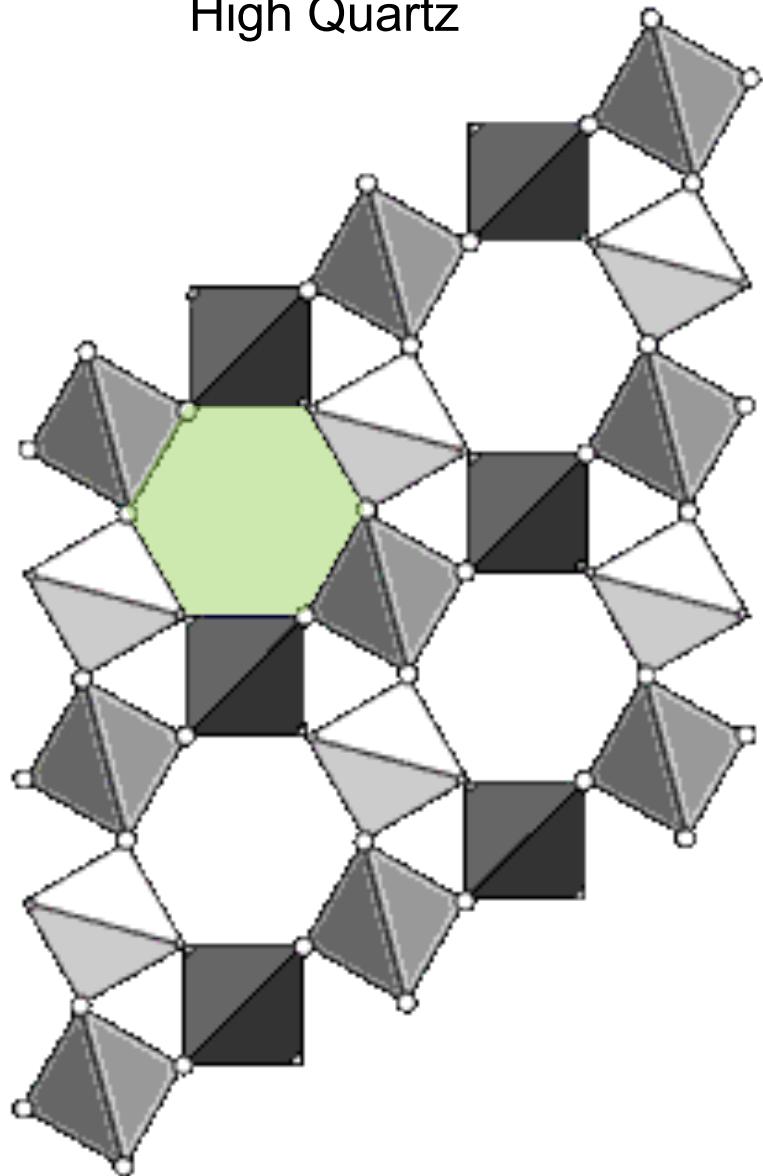
There are options to layer stacking.

A repeat sequence ....ABABAB.... gives the Tridymite structure (hexagonal crystal)

.....ABCABCABC..... gives the cristobalite structure (cubic crystal - ideally).

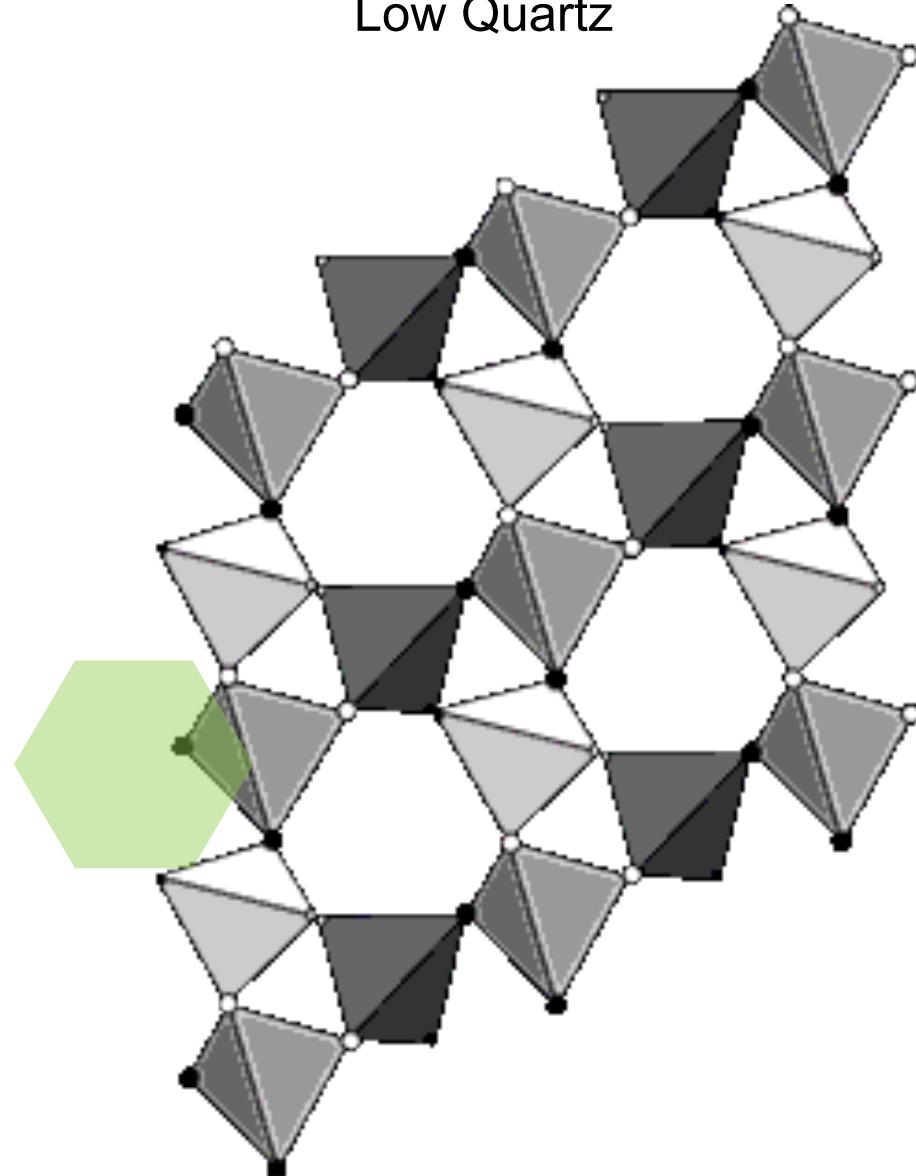
Cristobalite and tridymite are the structures adopted by quartz at relatively high temperatures, and relatively low pressures.

High Quartz



(a)

Low Quartz



(b)

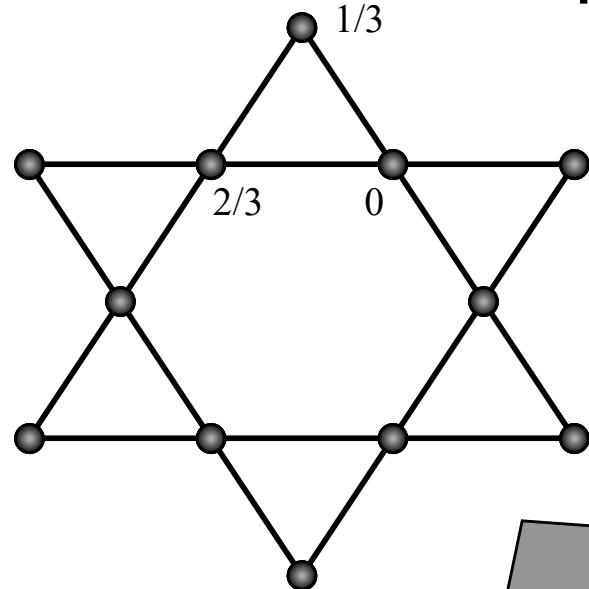
### *High and Low Quartz:*

These structures are more complex than cristobalite and tridymite, but still form from corner sharing  $\text{SiO}_4$  tetrahedra.

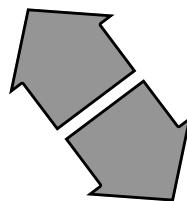
Low Quartz is a distortion of the higher temperature High Quartz caused by structural collapse as thermal vibrations of atoms lessen. High and low quartz are stable over a great range of temperatures and pressures.

In considering their structures look at a projection of Si atoms only:

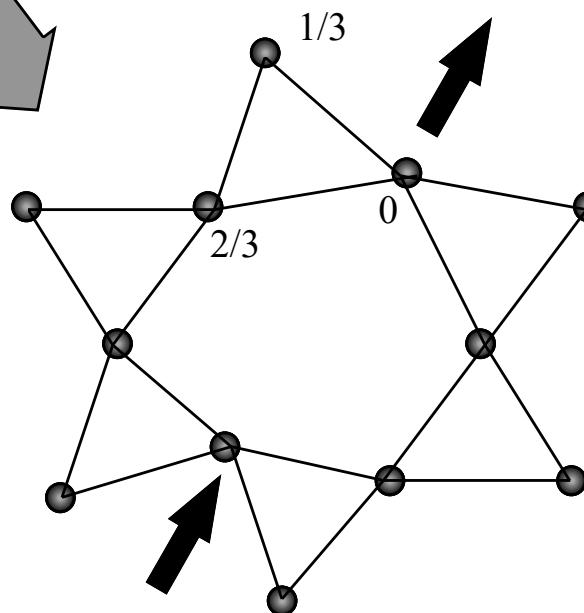
## Plotting Just the Si Atoms



High Quartz

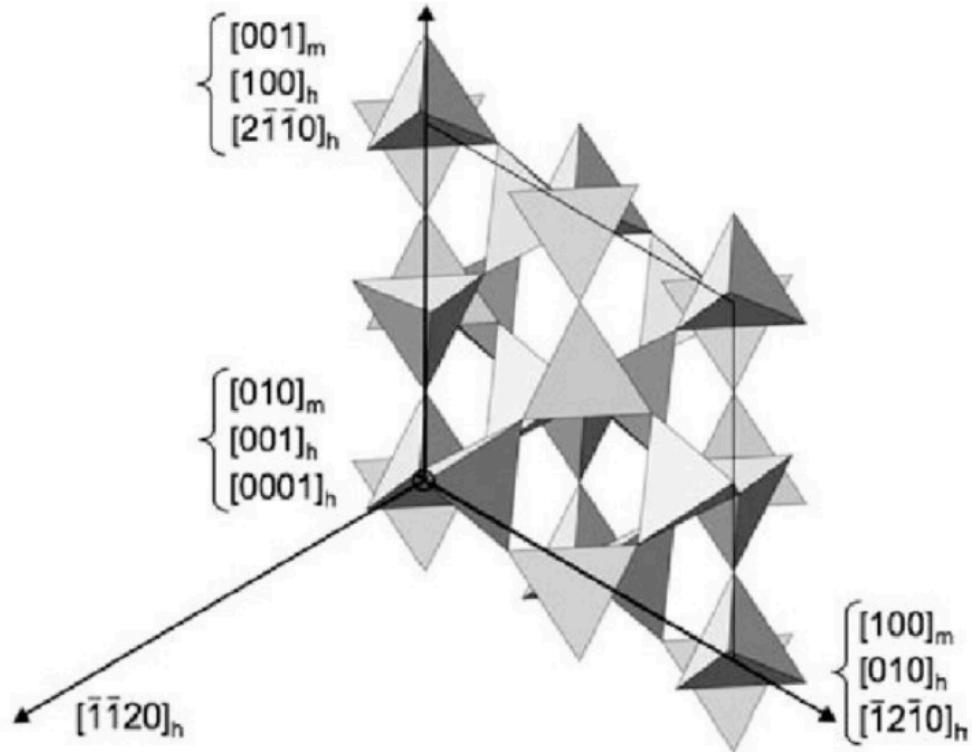


Low Quartz



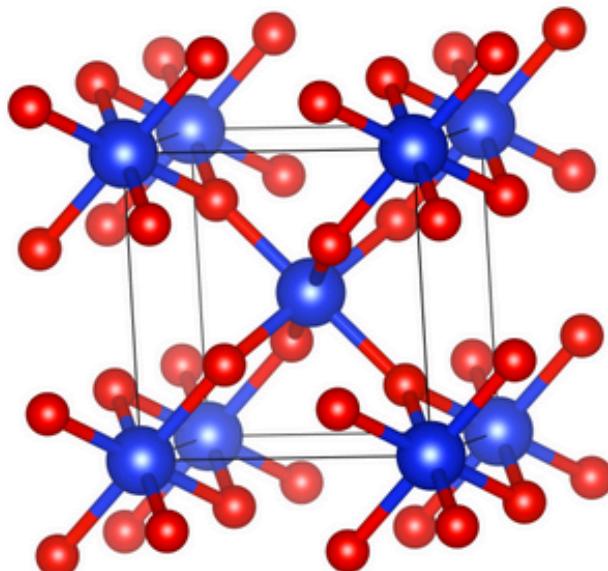
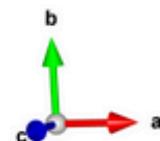
Deformation





**Coesite:** complex corner sharing  
network of  $\text{SiO}_4$  tetrahedra

**Stishovite:** corner sharing  
network of  $\text{SiO}_6$  octahedra



### *Coesite and Stishovite:*

Coesite and stishovite are the high pressure polymorphs of quartz, different in structure from any of the above forms. They have been observed naturally as a result of meteor impacts.

Using quartz as an example we see that solid systems show preferences for existing in different forms depending on external factors such as Temperature and Pressure.

In quartz the physical and optical properties are different for each structure e.g. low and high quartz are optically active (rotate the plane of polarisation of light); stishovite has a density about twice that of the other forms (4.28 g / cm)

Clearly it is important to understand and describe why such preferences for particular atomic arrangements in materials occur.

# MATERIALS ADOPT DIFFERENT STRUCTURES DEPENDING ON EXTERNAL FORCES SUCH AS TEMPERATURE AND PRESSURE

## WHY ?

### Concept of *Free Energy*

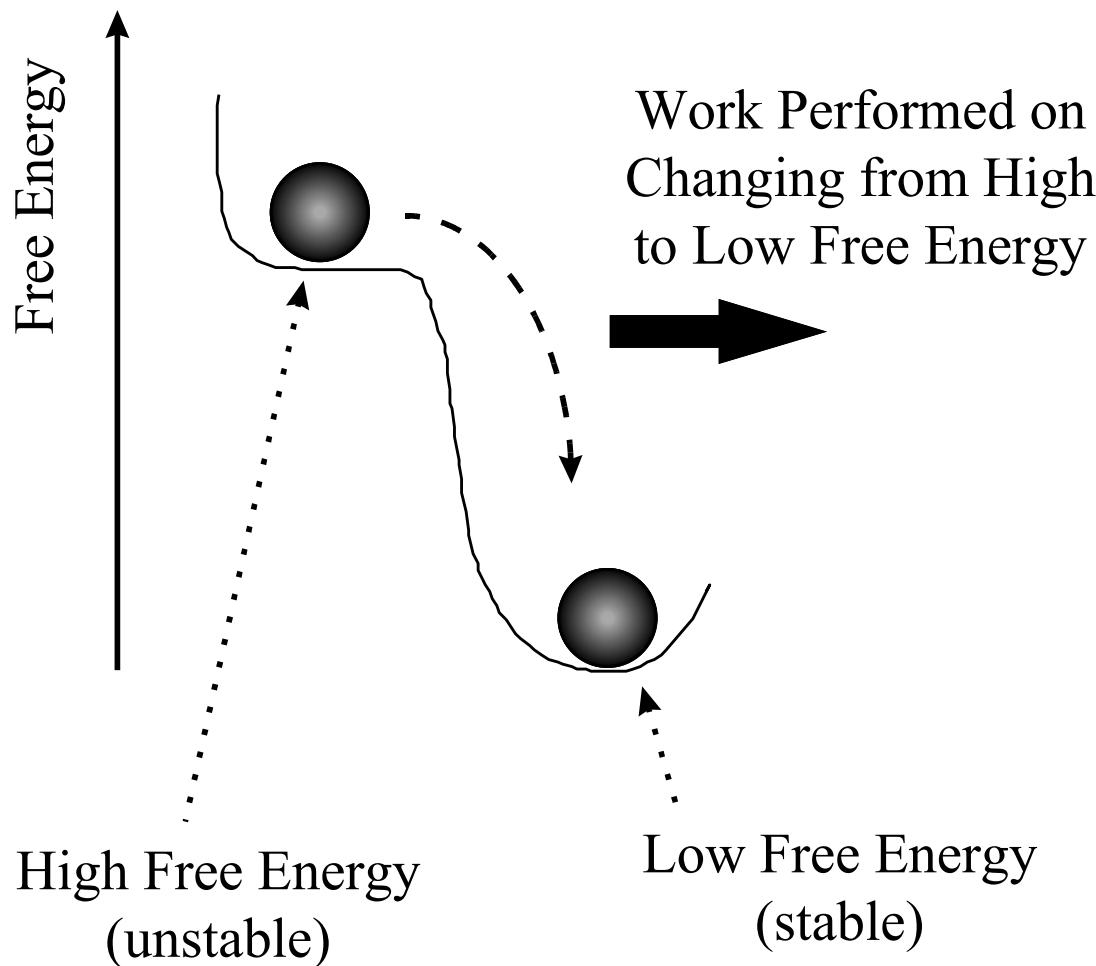
*High Energy* - *Able to do WORK*

*Low Energy* - *Unable to do WORK*

Because high energy systems can perform work, they have an innate ability to change, whereas low energy systems do not.

Hence low free energy tends to preclude change, and impose *stability*. High free energy, and the associated ability to change, leads to *instability*.

If dynamic systems alter  
they do so such that free energy is reduced.



## How to Express Free Energy

Since stability = low free energy

We observe:

- (i) gas/liquids stable at high temperatures  
∴ have low free energy at high temperature
- (ii) solids/crystals stable at low temperatures  
∴ have low free energy at low temperature

Expression for free energy must satisfy both these observations.

*Properties of gas/liquid:*

No interatomic bonds; Atoms arranged randomly.

*Properties of solid/crystal:*

Atoms form bonds; Atoms arranged in regular array.

making

Call energy associated with ~~breaking~~ bonds -  $H$

Call energy | associated with disorder -  $S$

related term

## **Formal Description of $G$ , $H$ and $S$ .**

Gibb's Free Energy  $G$  (at constant temperature and pressure) is given by:

$$G = H - TS$$

Where  $H$  is **enthalpy**,  $S$  is **entropy** and  $T$  is absolute temperature.

**OR**

Helmholtz Free Energy  $F$  (at constant temperature and volume) is given by:

$$F = U - TS$$

Where  $U$  is **internal energy** rather than **enthalpy**.

Because:

$G$  - Constant Pressure

$F$  - Constant Volume

$G$  is used by experimentalists and  $F$  by modellers ( $U$  easier to calculate than  $H$ ).

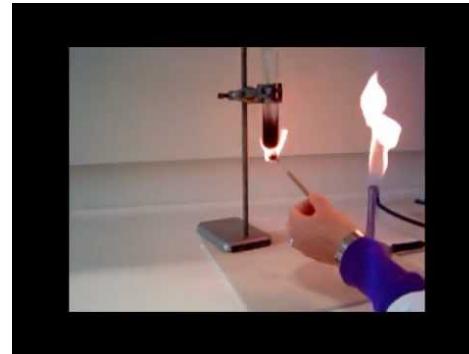
## Internal Energy

Internal energy ( $U$ ) is the innate potential energy of the system, plus kinetic energy associated with heat.

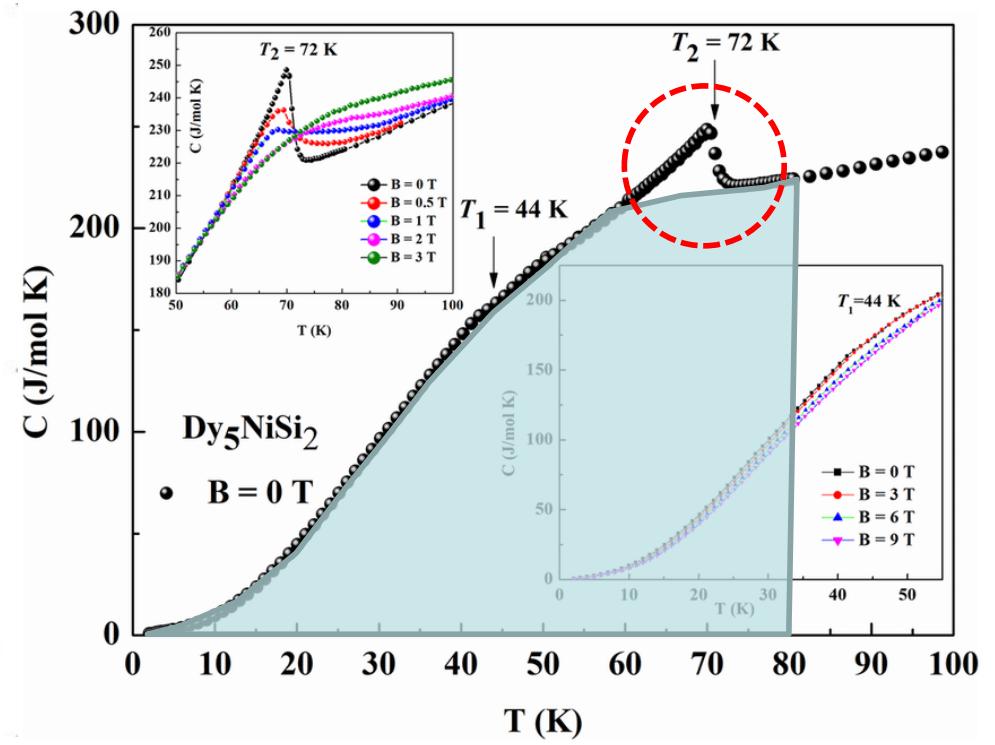
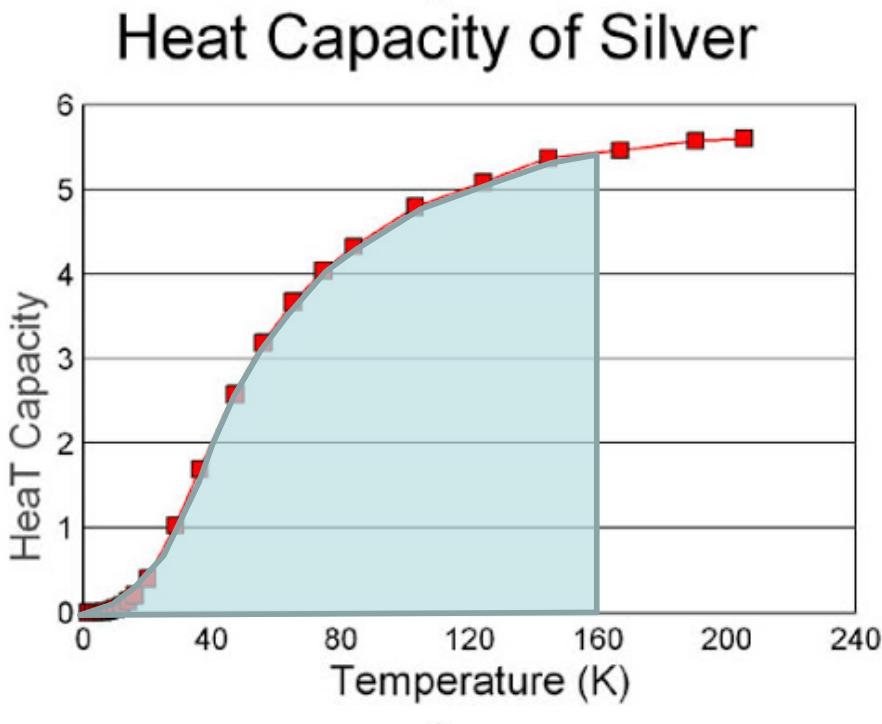
Heat Capacity :

$$C = \frac{\delta U}{\delta T}$$

@ constant volume:  $\delta U = C_V \delta T$



Additional areas superposed onto smooth heat capacity function deemed “latent heat” and traditionally added as a separate component to the internal energy.....but.....it is a little unnecessary (could just integrate heat capacity recognizing that anomalies also should be integrated).



## **Enthalpy**

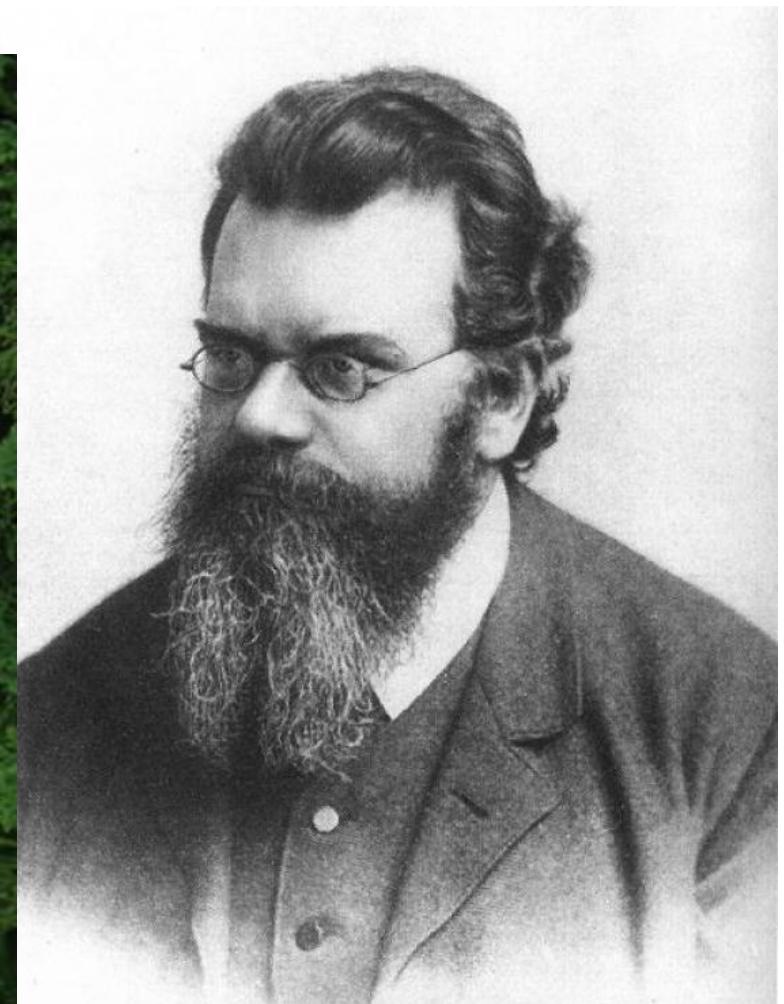
Similar treatment of the internal energy of a system at constant pressure rather than volume gives enthalpy:

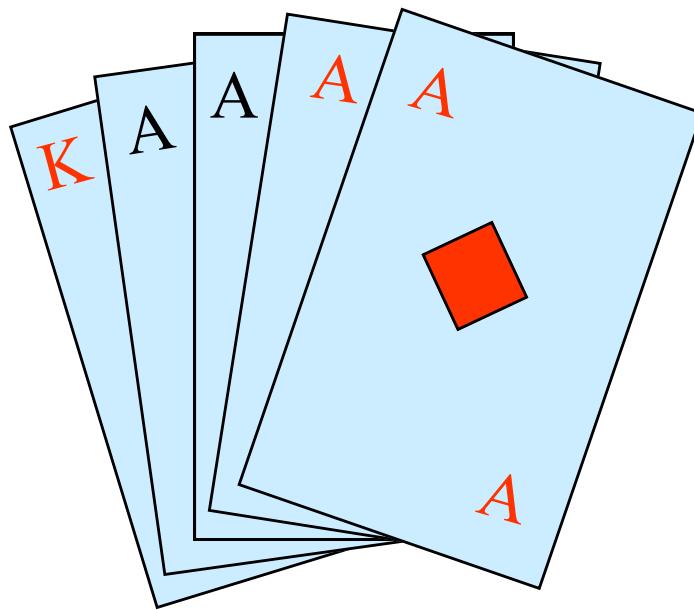
$$H = H_0 + \int_0^{T_1} C_P dT + \sum_i L_i$$

where  $C_P$  is the heat capacity at constant pressure.

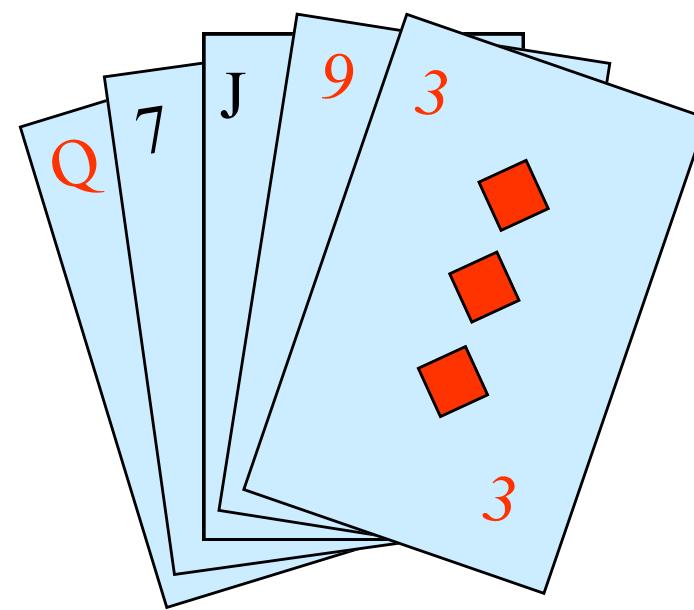
# Ludwig Boltzmann

$$S = k \ln W$$





Probability of this hand  
is relatively low -  
LOW ENTROPY



Probability of a hand  
*like this* is relatively high -  
HIGH ENTROPY



Formally entropy is defined as:

$$S = k \ln W$$

where  $k$  is the Boltzmann constant, and  $W$  is the number of states indistinguishable from that being considered.

It may be measured at constant pressure as follows:

$$G = H - TS \rightarrow dG = dH - TdS - SdT$$

$$C_p = \frac{dH}{dT} \therefore dH = C_p dT$$

Equilibrium:  $dG = 0$

$$dH = TdS$$

$$dS = \frac{dH}{T}$$

At fixed temperature:  $dT = 0$

therefore

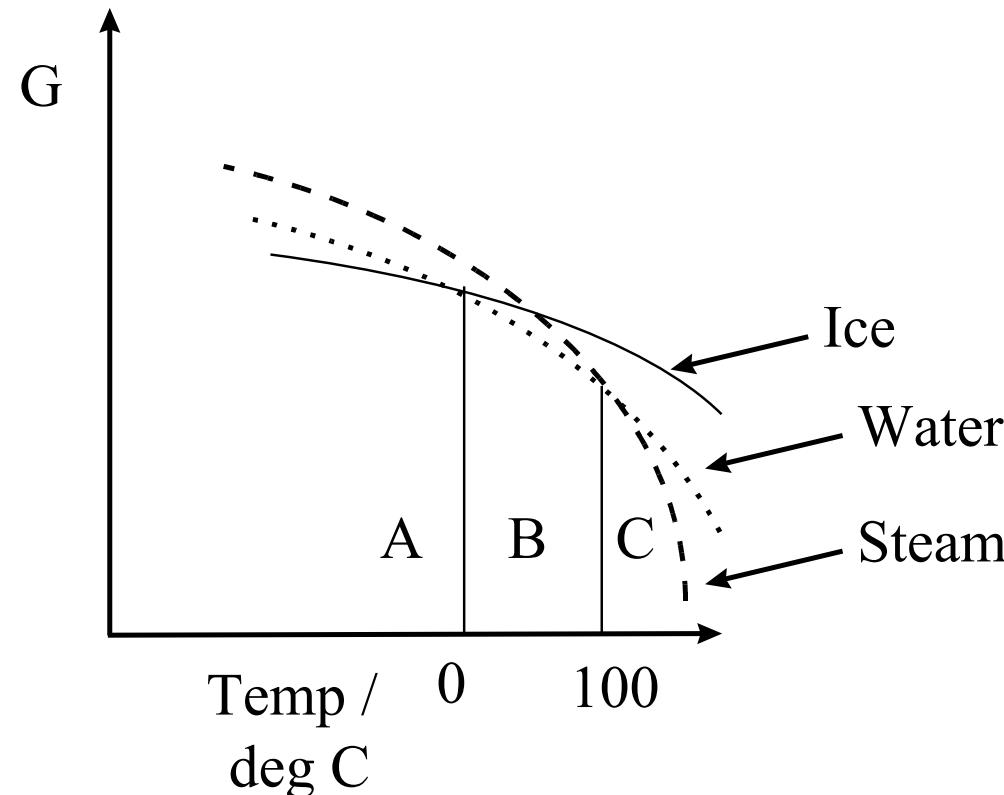
$$S = S_0 + \int_0^{T_1} \left( \frac{C_P}{T} \right) dT + \sum_i \frac{L_i}{T}$$

Same slightly artificial separation of  
“latent heat”

where  $L_i$  is the latent heat of any phase transformations.

## **MODELLING FREE ENERGY TO UNDERSTAND PHASE TRANSFORMATIONS AND PHASE DIAGRAMS:**

*Ice - Water - Steam*

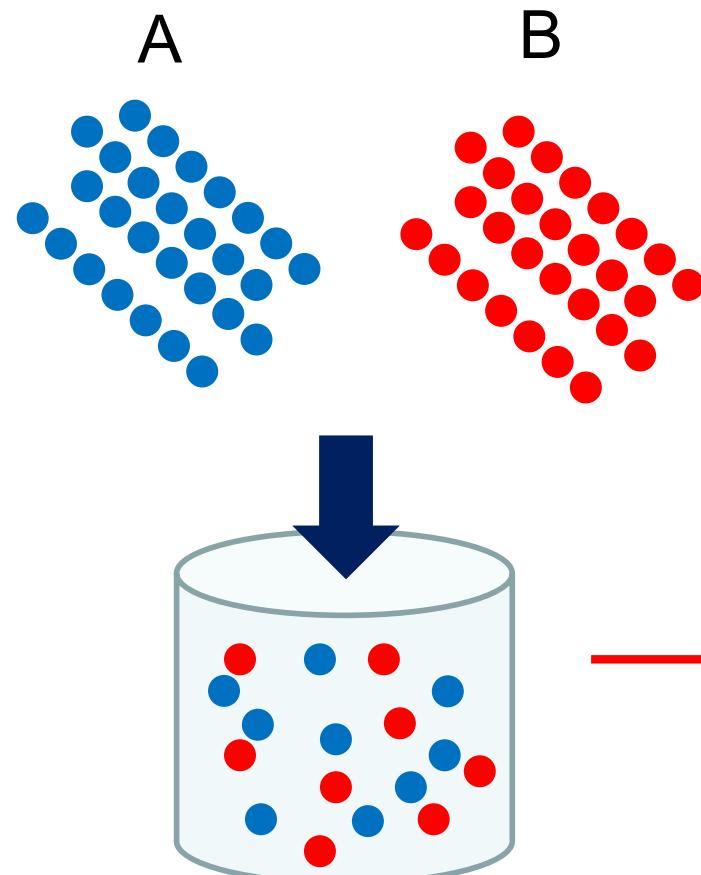


### Note 3 Regions:

- A - Below 0°C Ice has the lowest free energy
- B - Between 0°C and 100°C water has lowest free energy
- C - Above 100°C steam has lowest free energy

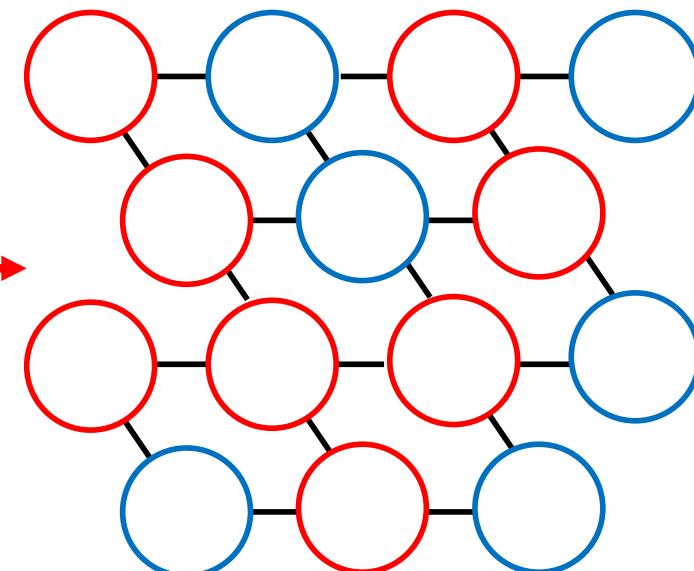
Schematic free energy plot therefore gives information about *regions of stability* of different phases.

Pellets or grains of two different elements: “A” and “B”



$$\Delta G_{mix} =$$

## Solid Solution



## Mechanical Mixture

Individual “A” and “B” atoms  
bonded together randomly

## **GENERATING FREE ENERGY PLOT FOR A MORE COMPLEX SYSTEM (TWO PHASE MIXTURE) TO FIND REGIONS OF STABILITY**

Mechanical mixture of two phases, pure A and pure B. Mixture is transformed by annealing into a single solution phase - A and B distributed randomly over atomic sites. There will be:

- an enthalpy change associated with interactions between A and B atoms -  $\Delta H_{mix}$
- an entropy change,  $\Delta S_{mix}$  associated with the increase in randomness of A and B positions
- a resultant free energy of mixing -  $\Delta G_{mix}$  such that:

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

The following treatment assumes  $N$  atoms;  $x_A N$  of A and  $x_B N$  of B, where:

$x_A$ = fraction of A atoms

$x_B = (1 - x_A)$  = fraction of B atoms.

## Enthalpy of Mixing - $\Delta H_{mix}$

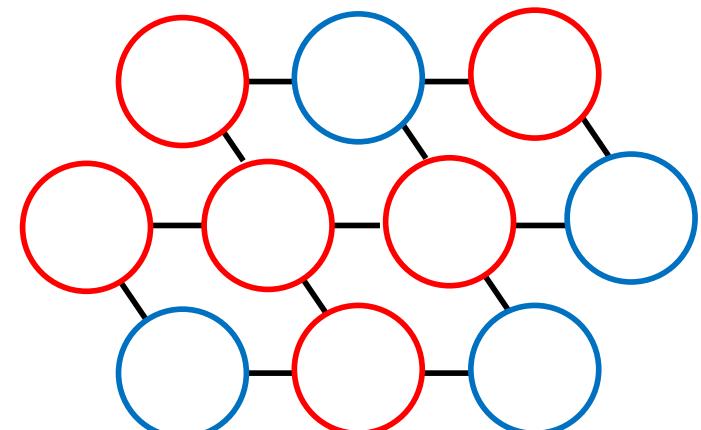
Let:

$w_{AA}$  = interaction energy A-A

$w_{BB}$  = interaction energy B-B

$w_{AB}$  = interaction energy A-B

Let A and B have coordination number  $z$  ( $z$  nearest neighbours). For  $N$  atoms  
total number of nearest neighbour pairs =  $\frac{1}{2} Nz$



Total number of bonds

Mean bond energy (probability of each bond times its specific energy)

For solid solution (random A-B distribution):

$$H_{sol.} = \frac{Nz}{2} (x_A^2 w_{AA} + x_B^2 w_{BB} + 2x_A x_B w_{AB})$$

The change of enthalpy due to forming a solid solution of A and B is therefore:

$$\Delta H_{mix} = \frac{N_z}{2} \left( \underbrace{x_A^2 w_{AA} + x_B^2 w_{BB} + 2x_A x_B w_{AB}}_{\text{Enthalpy term from ss}^n} - \underbrace{x_A w_{AA} - x_B w_{BB}}_{\text{Enthalpy term from mech mix}} \right)$$

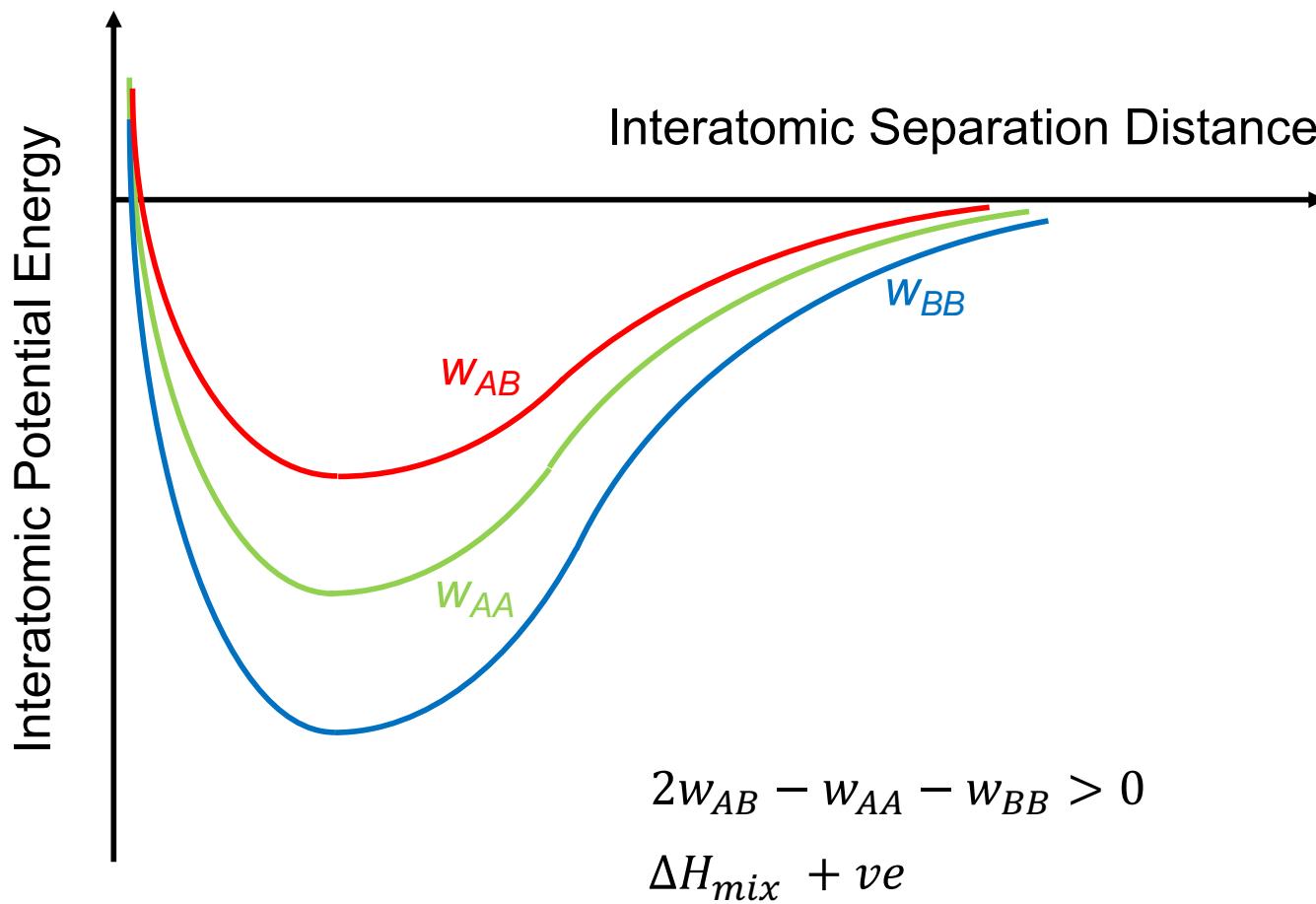
We define a quantity

$$W_H = \frac{N z}{2} (2w_{AB} - w_{AA} - w_{BB})$$

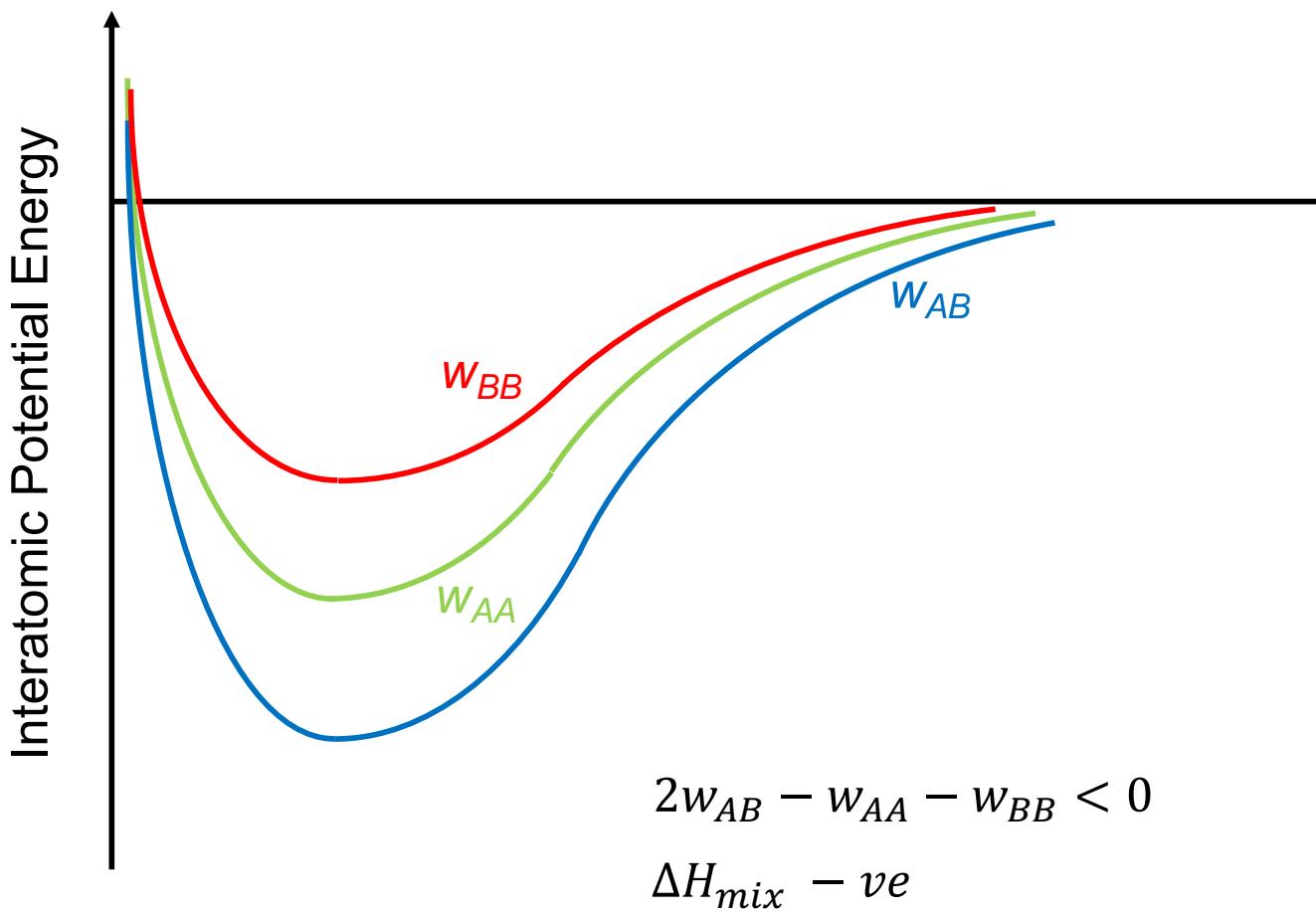
*Determines sign of  $\Delta H_{\text{mix}}$*

and rewrite the enthalpy of mixing per mole as

$$\Delta H_{\text{mix}} = x_A x_B W_H$$



In this example of relative bond energies, it's clear that the enthalpic energy pay-off (reduction) in forming a mechanical mixture of A-A and B-B bonds is much greater than that of forming A-B bonds....expect exsolution (at low temperatures).



In this example I've swapped the labels on the interatomic potential energy curves, such that now the enthalpic energy pay-off in forming A-B bonds is obviously greater than the combination of A-A and B-B (much more advantageous to form A-B bonds).....expect ordering to occur.

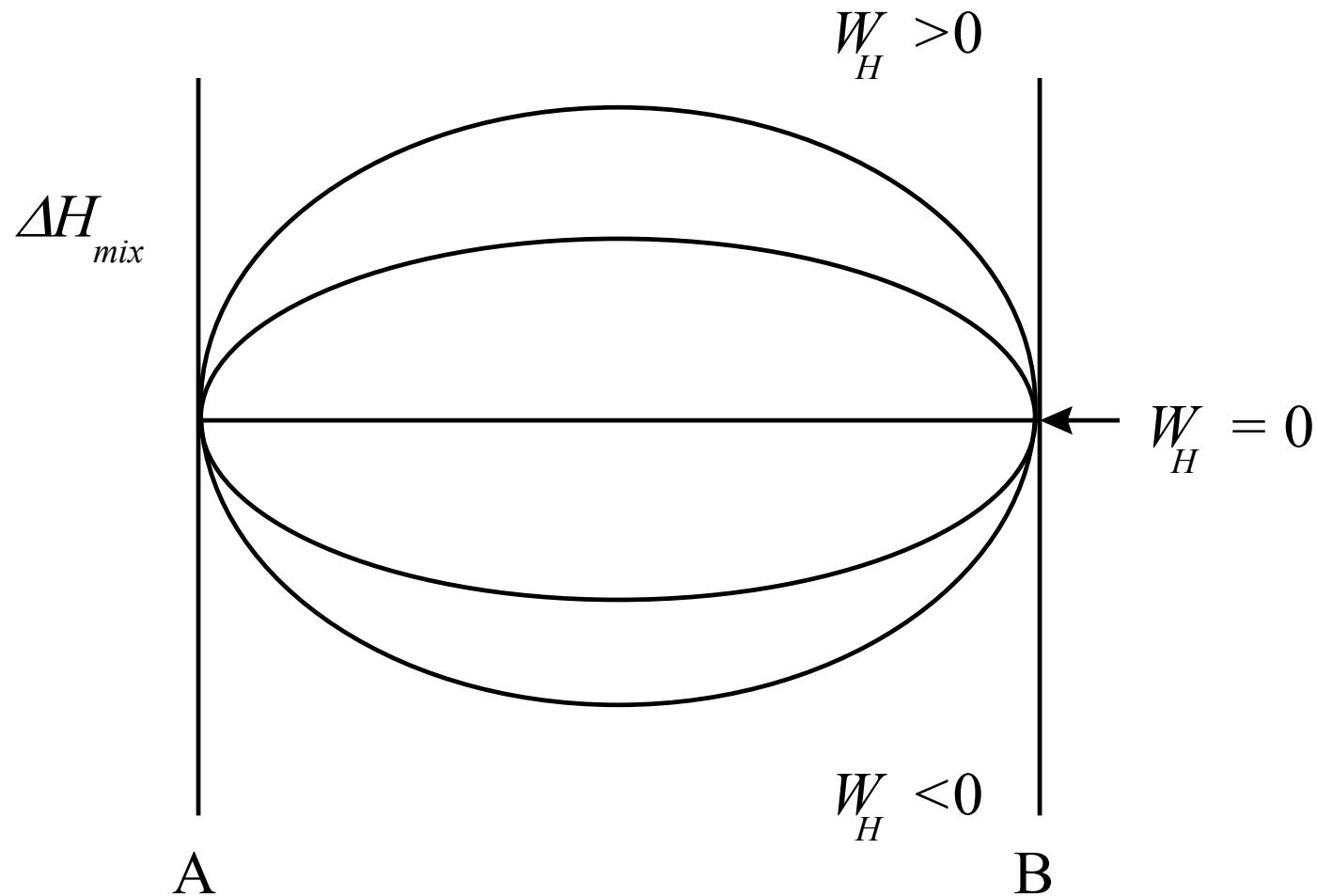
Consider three possible cases:

(i) If  $W_H = 0$ ; A-B interactions are energetically equivalent to B-B and A-A interactions. Hence  $\Delta H_{mix} = 0$  - the ideal solution.

(ii) If  $W_H > 0$ ; A-A, B-B interactions are more favourable than A-B. Hence  $\Delta H_{mix} > 0$ , giving a tendency for the solution to segregate into A-rich and B-rich regions (**exsolution**).

(iii) If  $W_H < 0$ ; A-B interactions are more favourable than A-A, B-B.  $\Delta H_{mix} < 0$ , giving tendency for ordering of the solution into A-B-A-B-A type structures (**ordering**).

$$W_H = \frac{Nz}{2} (2w_{AB} - w_{AA} - w_{BB}) \quad \Delta H_{mix} = \frac{Nz}{2} x_A x_B (2w_{AB} - w_{AA} - w_{BB})$$



## Entropy of Mixing (Configurational)

Thermal vibrations of atoms contribute to entropy, but here we will consider **configurational entropy** alone.

For a mechanical mixture of A and B atoms, there is only one possible atomic configuration (all A atoms on sites in phase A, all B atoms in sites in phase B).

Hence:  $S_{mech} = k \ln(1) = 0$

For a solution of A and B atoms in a mixed A-B phase there are:

$$\frac{N!}{\{x_A N\}! \{(1 - x_A) N\}!}$$

Permutations and Combinations  
(here combinations)

ways of distributing the A and B atoms.

solid

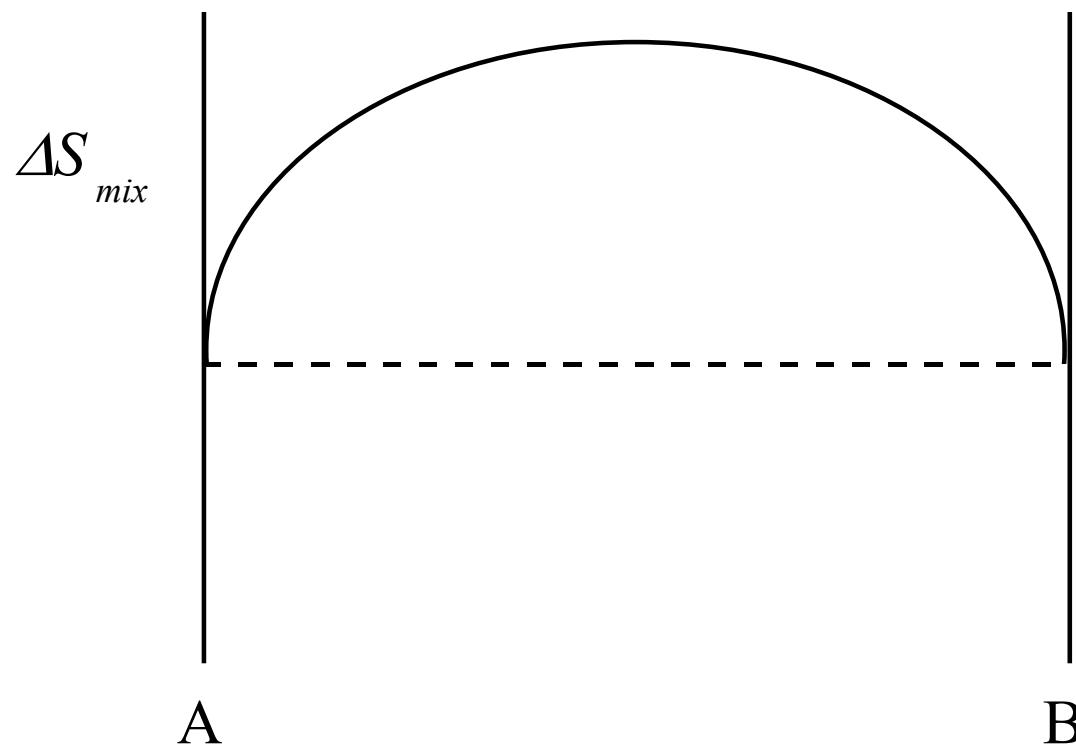
So, the configurational entropy of the solution is

$$\therefore S_{sol} = k \ln \left[ \frac{N!}{\{x_A N\}! \{(1-x_A)N\}!} \right]$$

$$\Delta S_{mix} = S_{sol} - S_{mech}$$

For  $N$  = Avagadro's Number,  $kN = R$  (gas constant), and hence per mole of sites on which mixing occurs:

$$\Delta S_{mix} = -R(x_A \ln x_A + x_B \ln x_B)$$



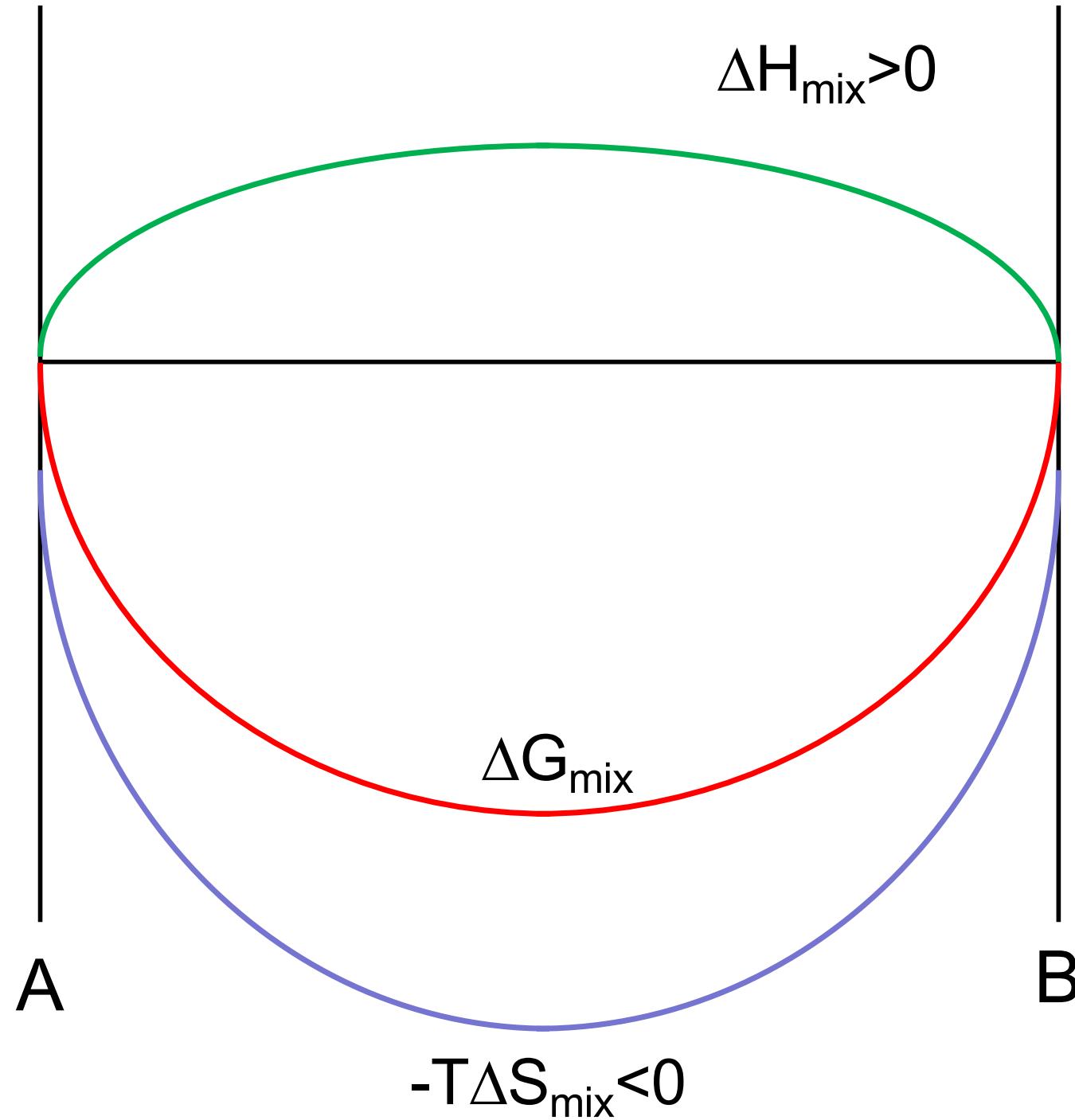
## Free Energy of Mixing

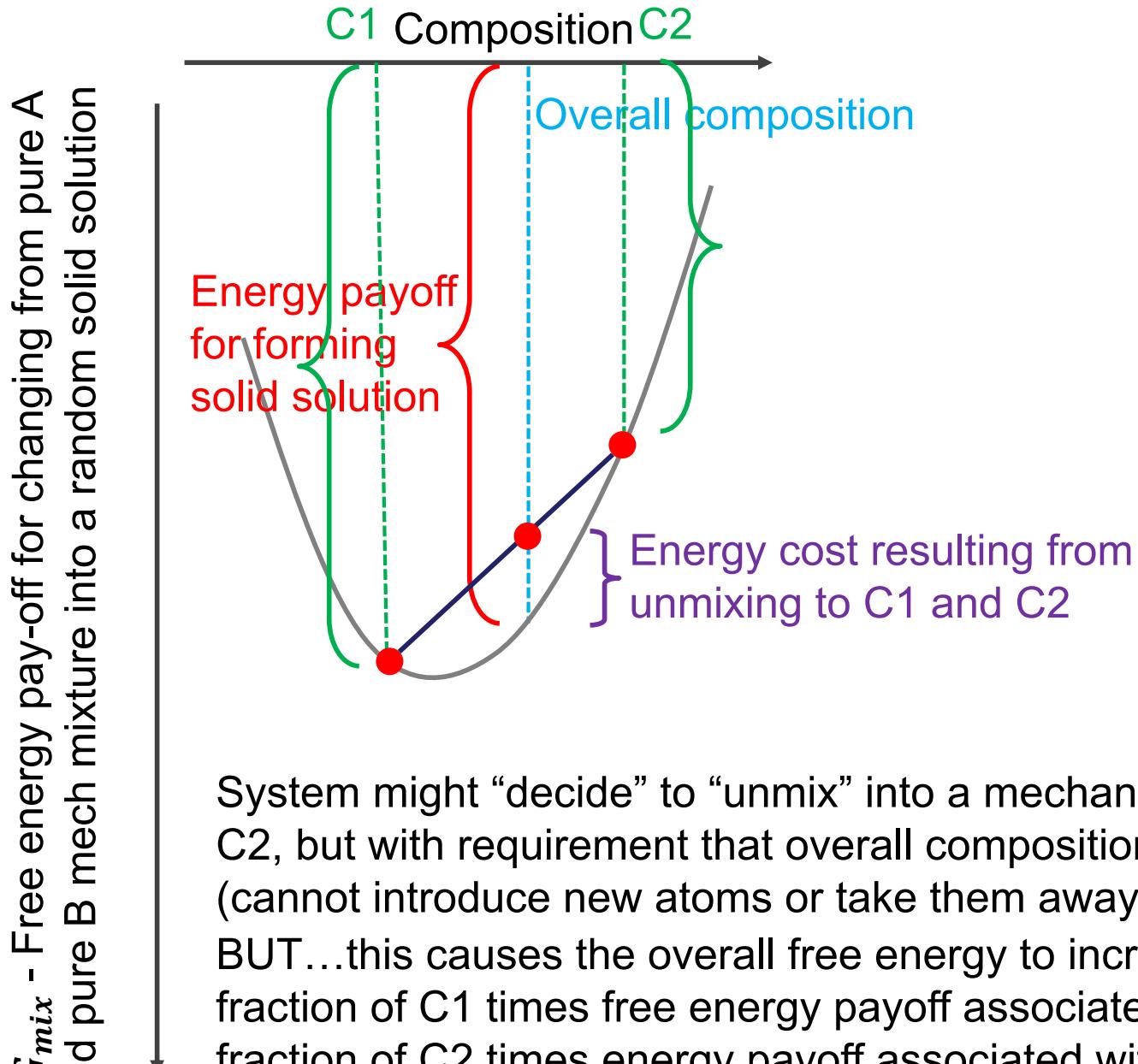
Combining the two results above for enthalpy and entropy of mixing we obtain:

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

$$\Rightarrow x_A x_B W_H + RT(x_A \ln x_A + x_B \ln x_B)$$

(Joules / mol)

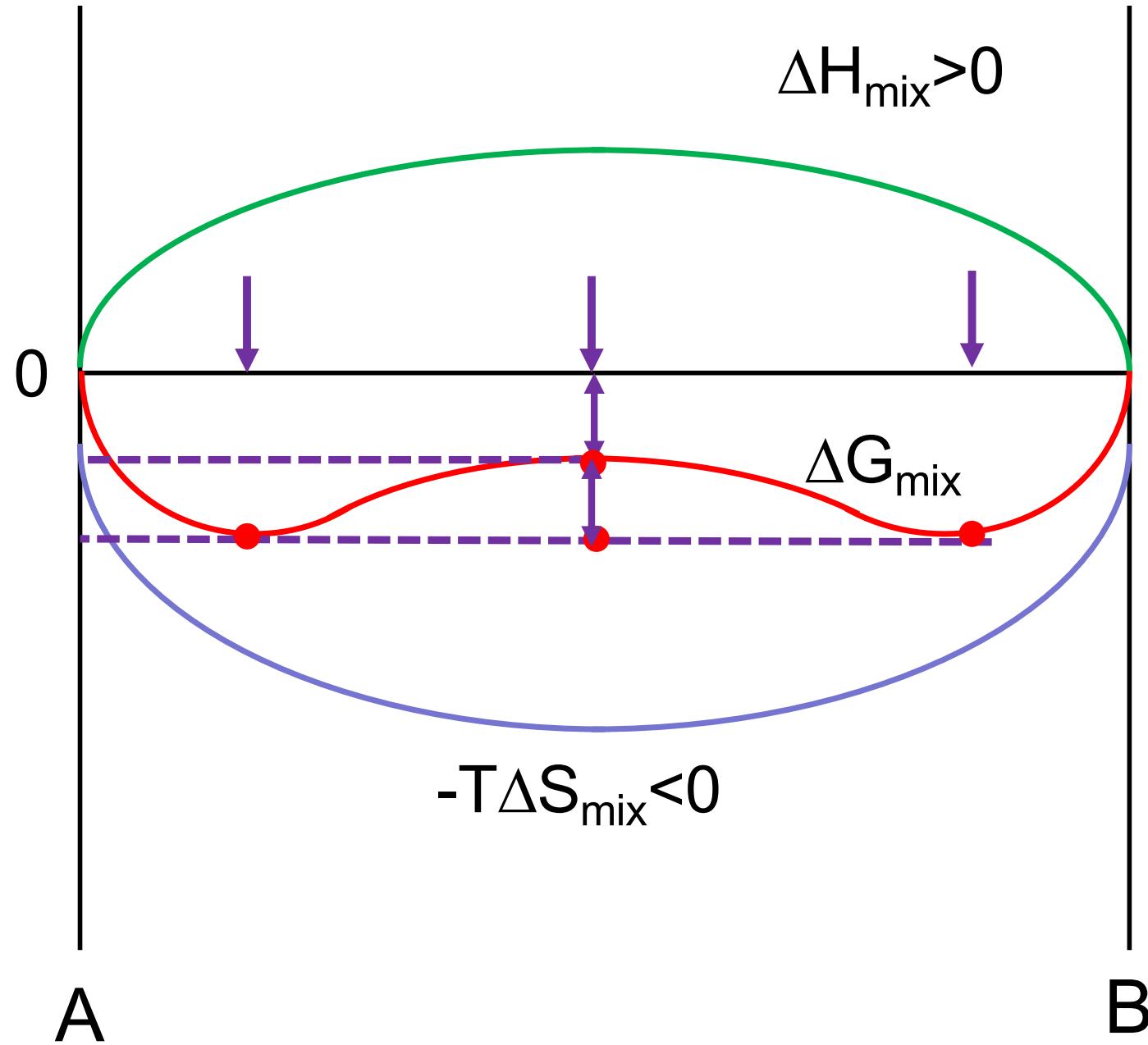




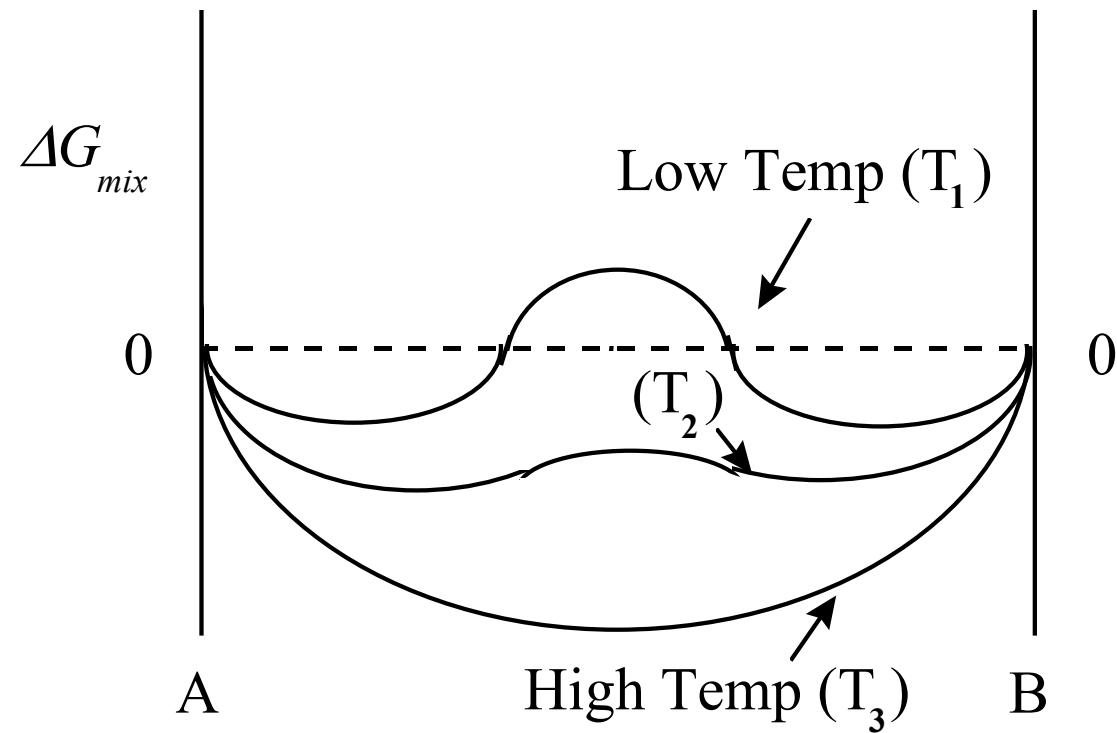
System might “decide” to “unmix” into a mechanical mixture of C1 and C2, but with requirement that overall composition is unchanged (cannot introduce new atoms or take them away)

BUT...this causes the overall free energy to increase – given by fraction of C1 times free energy payoff associated with C1, plus fraction of C2 times energy payoff associated with C2

So.....here exsolution into two solid solution C1 and C2 NOT thermodynamically favourable

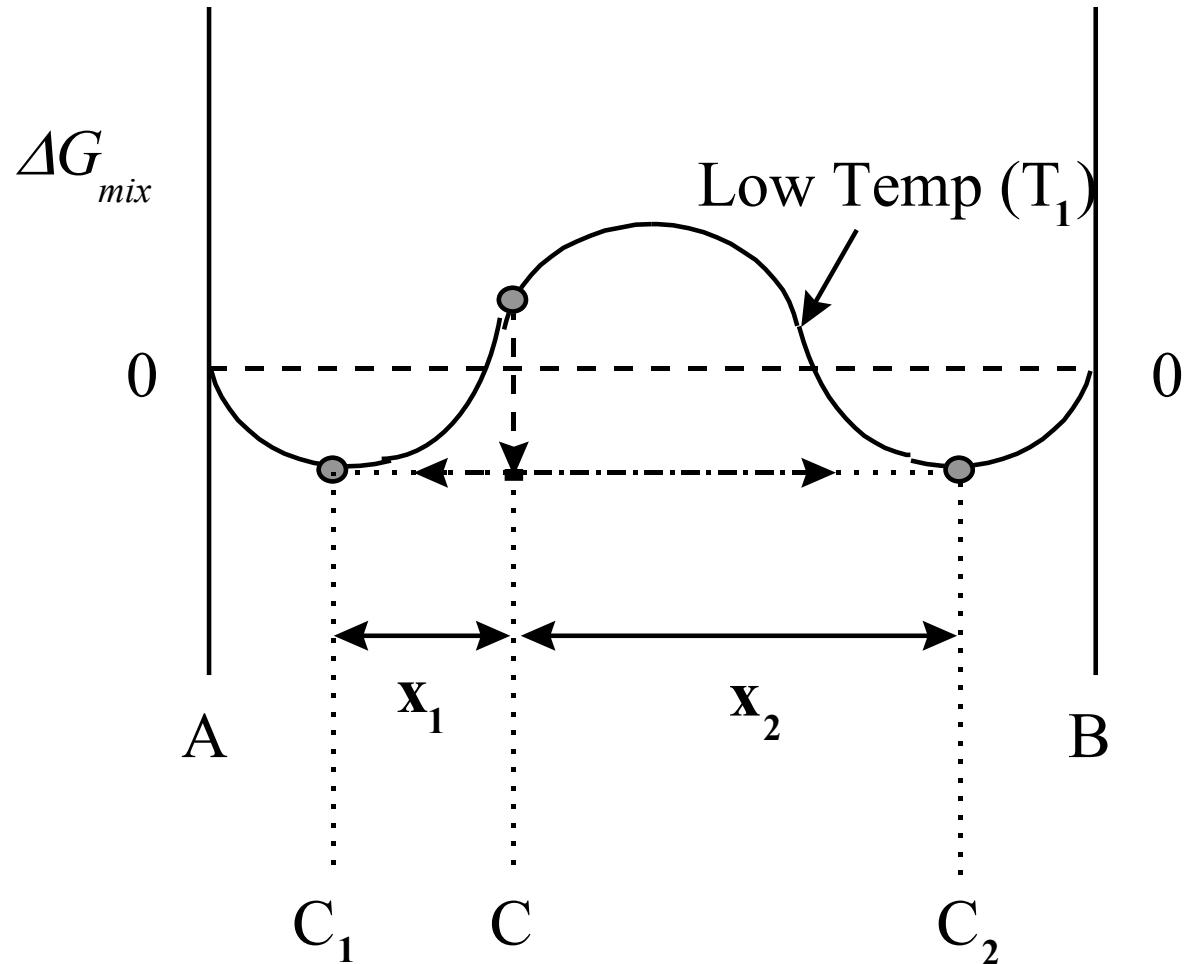


If  $W_H > 0$ ,  $\Delta H_{mix}$  and  $\Delta S_{mix}$  are both positive -  $\Delta G_{mix}$  is a more complex function of Temperature:



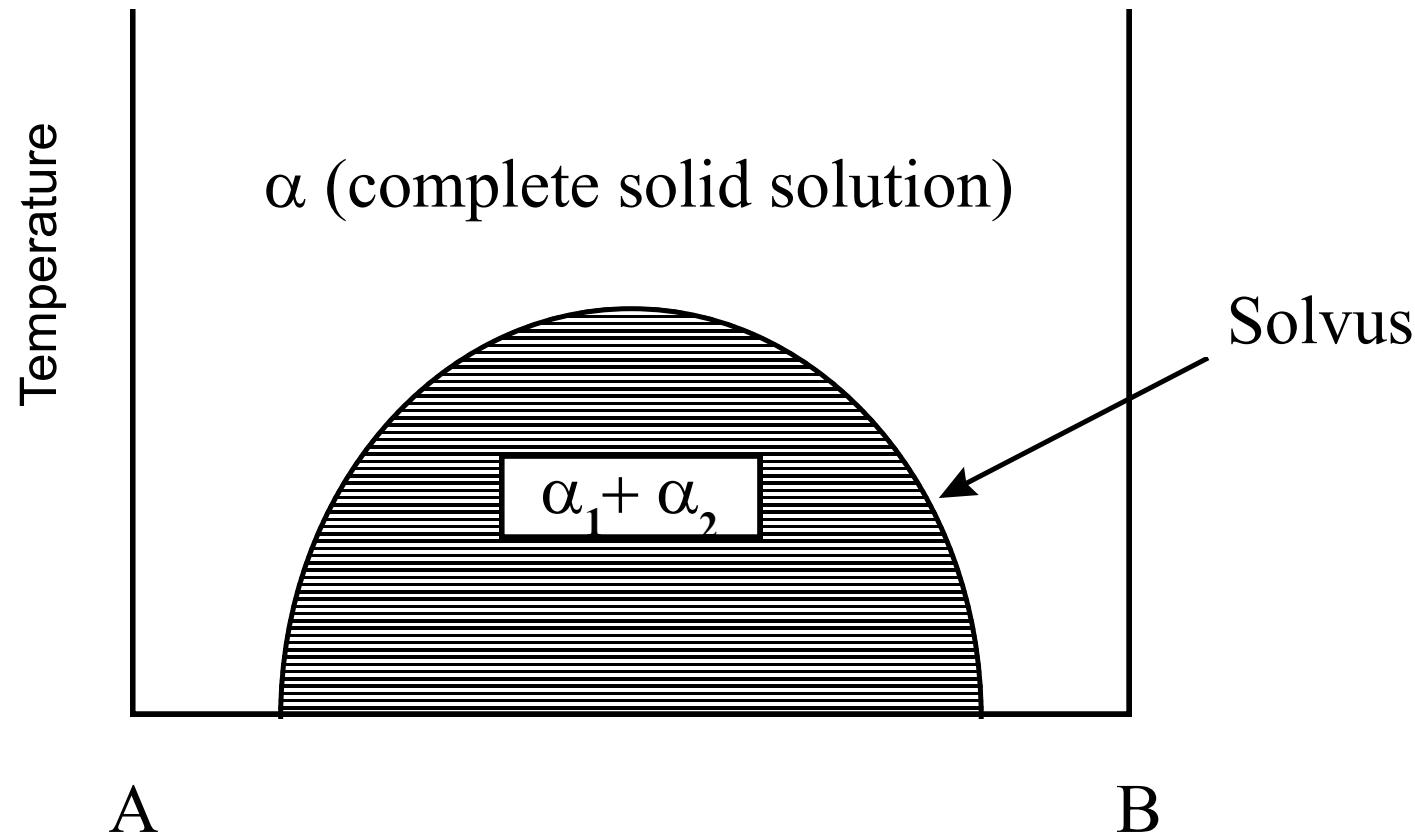
Note:

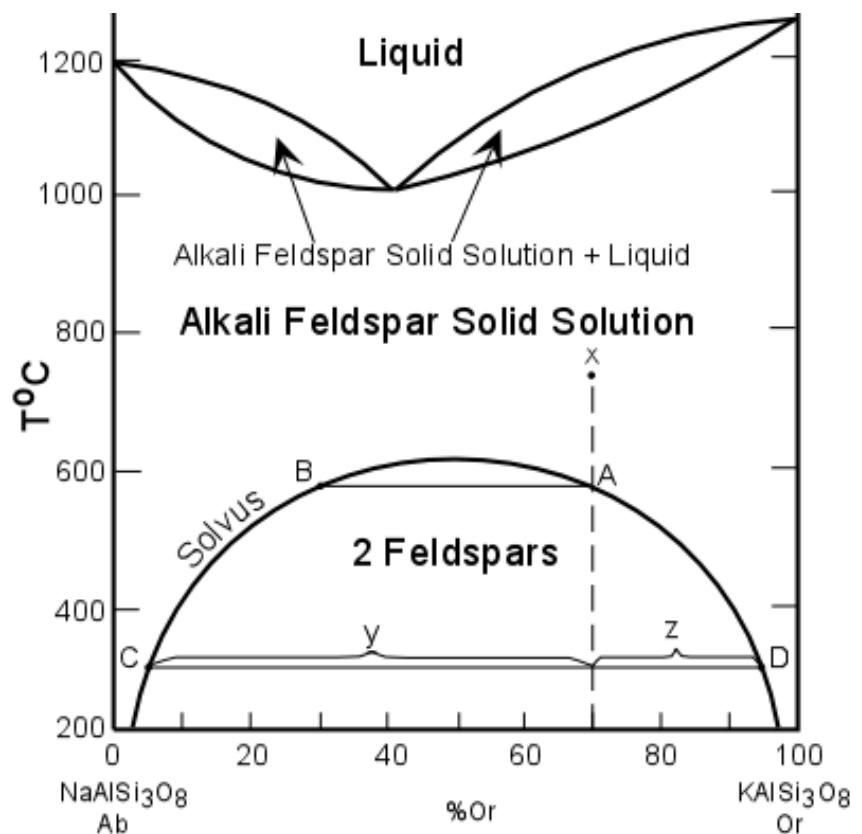
- At high temperature ( $T_3$ ) there is complete solid solution between A and B
- At lower temperature ( $T_1$ ) the +ve enthalpy begins to change the shape of the free energy curve. Now for the compositions between minima, total energy can be reduced by splitting of the phases into a mechanical mixture of an A-rich phase and a B-rich phase.



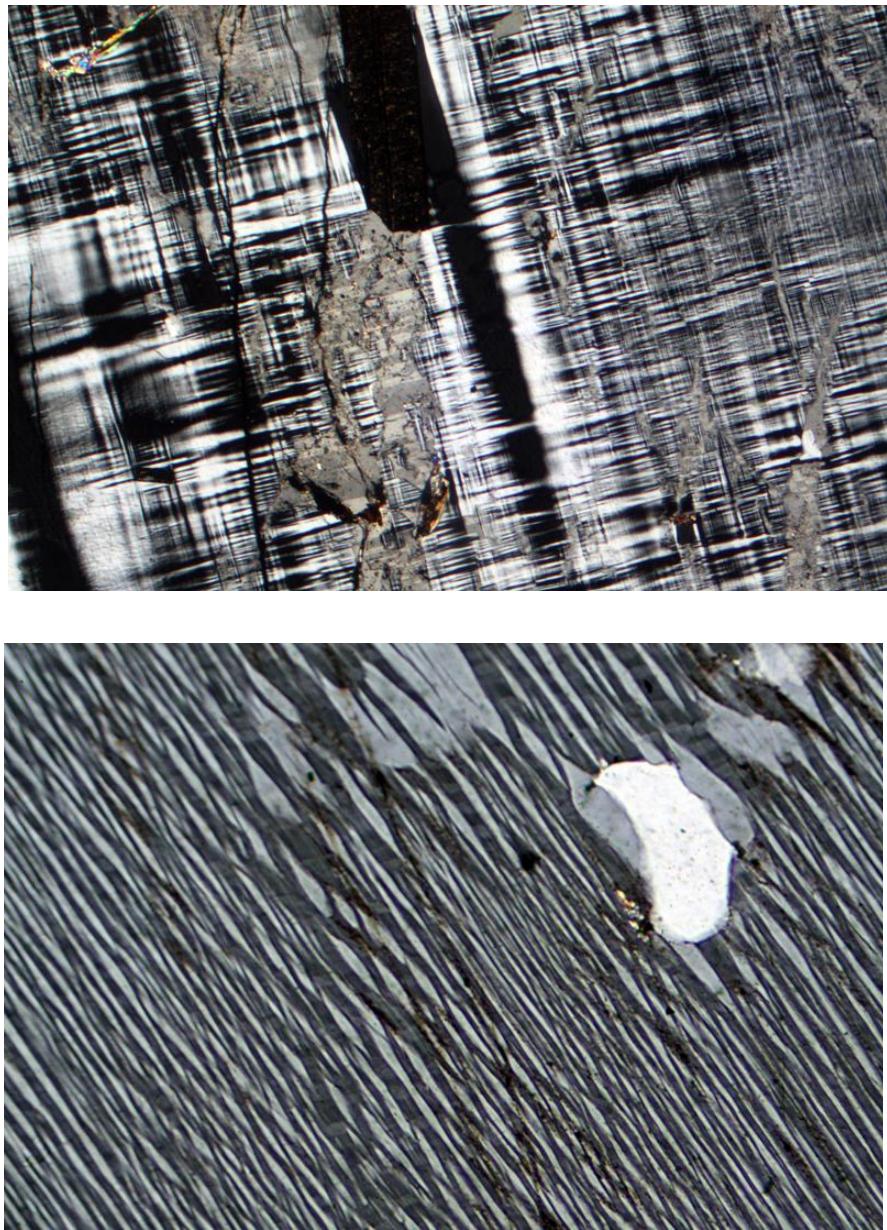
Composition C at temperature  $T_1$  may lower its free energy by splitting into two parts:  
one at composition  $C_1$  and the other at  $C_2$ .

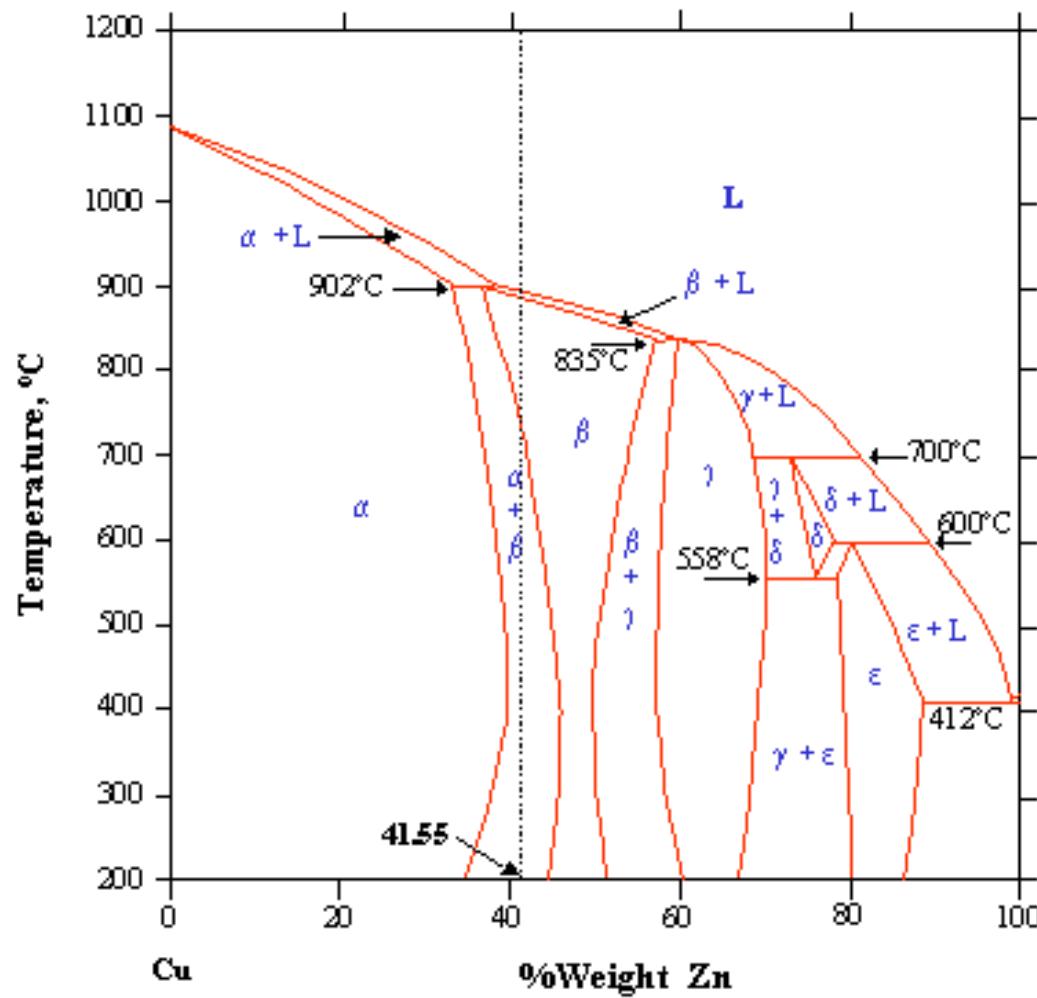
Diagram of the locus of the compositions which give the minimum overall free energy for various temperatures:





**Figure 4**





## ORDER-DISORDER TRANSFORMATIONS

REMINDER: The enthalpy of mixing may be given by:

$$\Delta H_{mix} = x_A x_B W_H$$

where  $W_H$  defined as:

$$W_H = \frac{Nz}{2} (2w_{AB} - w_{AA} - w_{BB})$$

Note 3 situations:

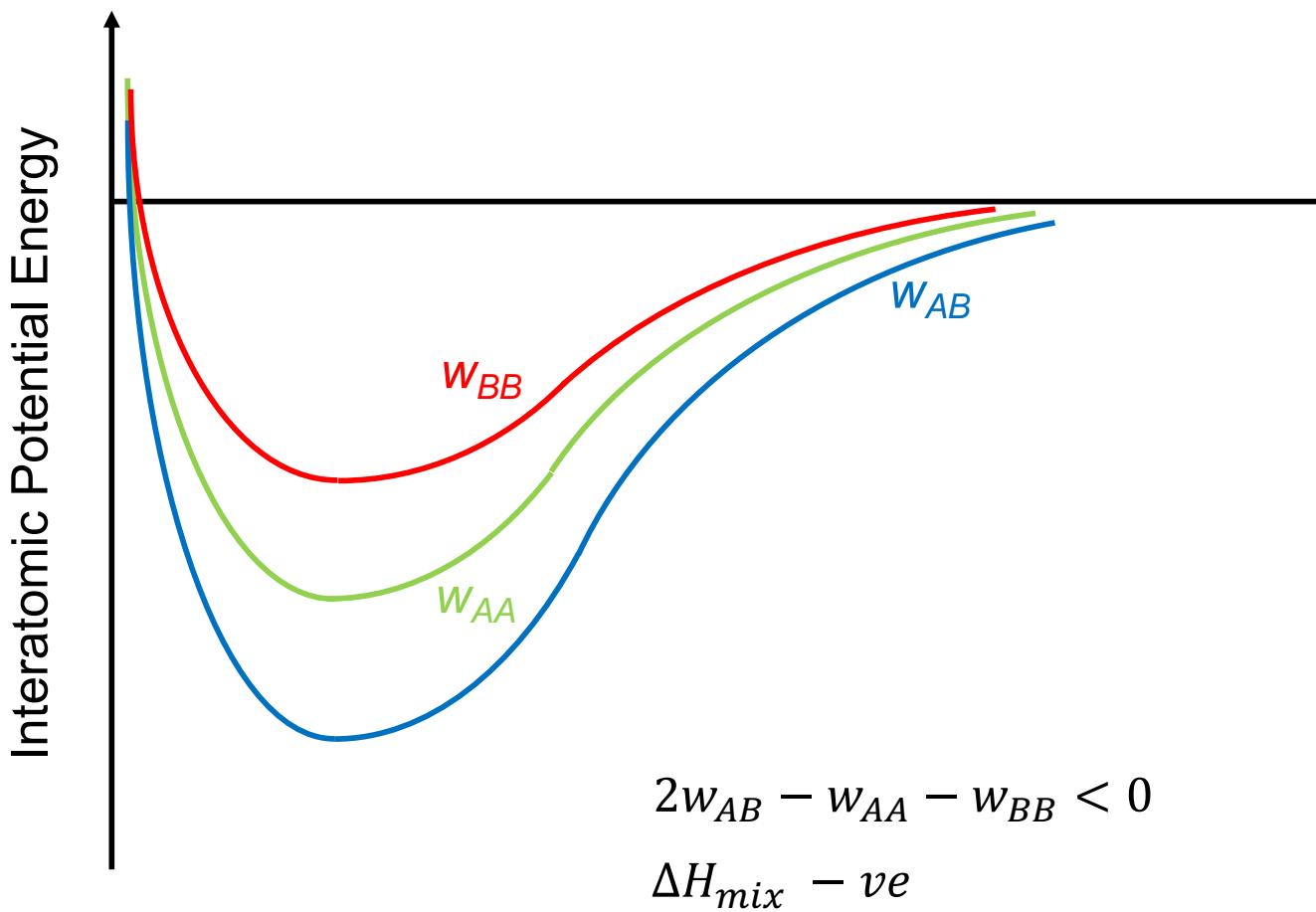
- (i)  $w_{AB} = \frac{w_{AA} + w_{BB}}{2}$ ; i.e. AB bonds have the same stability as the average AA and BB = IDEAL SOLUTION - COMPLETE MIXING

(i)  $w_{AB} > \frac{w_{AA} + w_{BB}}{2}$ ; i.e. AA and BB bonds are more stable than AB bonds =  
EXSOLUTION AT LOW TEMPERATURES

(ii)  $w_{AB} < \frac{w_{AA} + w_{BB}}{2}$ ; i.e. AB bonds are more stable than AA and BB bonds =  
ORDERING AT LOW TEMPERATURES

So far dealt with a cooling system changing such that EXSOLUTION occurs at low temperature.

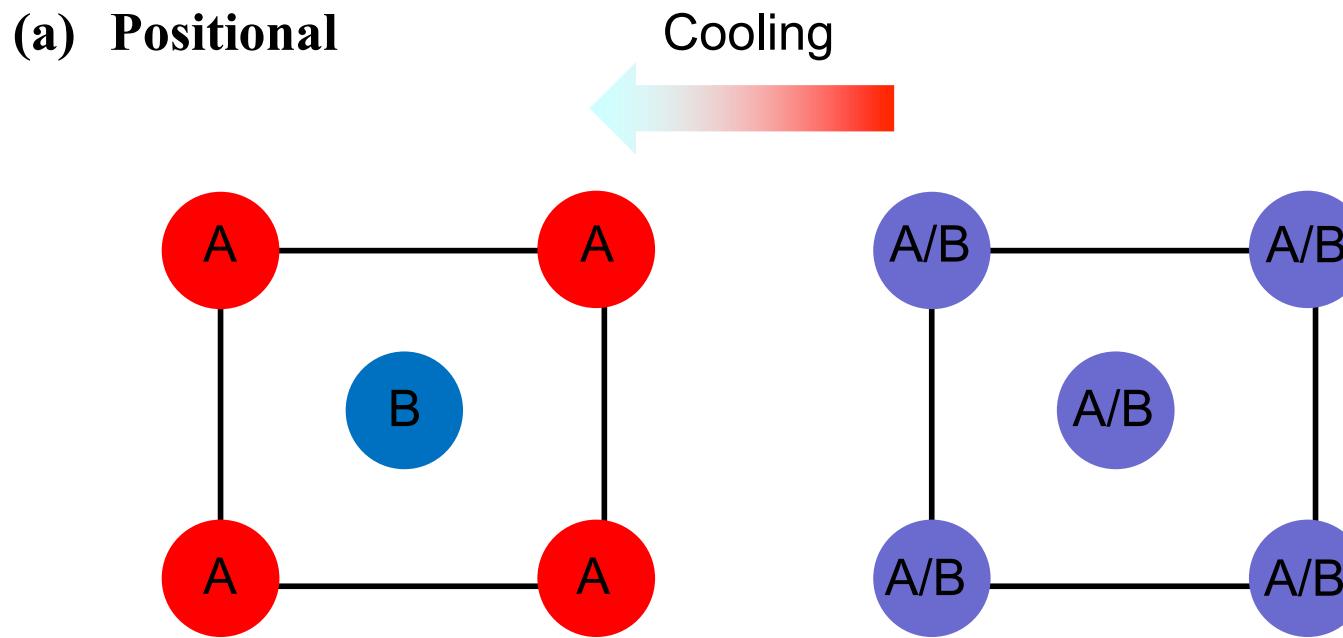
Now consider ORDERING transformation on cooling:



In this example I've swapped the labels on the interatomic potential energy curves, such that now the enthalpic energy pay-off in forming A-B bonds is obviously greater than the combination of A-A and B-B (much more advantageous to form A-B bonds).....expect ordering to occur.

Order-Disorder Transformations may be divided into 3 groups:

- (a) *Positional*
- (b) *Orientational*
- (c) *Spin State*



In ordered state A atoms only occur on A-lattice sites, and B atoms only occur on B-lattice sites.

In disordered state lattice sites are randomly occupied by A and B atoms.

## EXAMPLE of Positional Order-Disorder

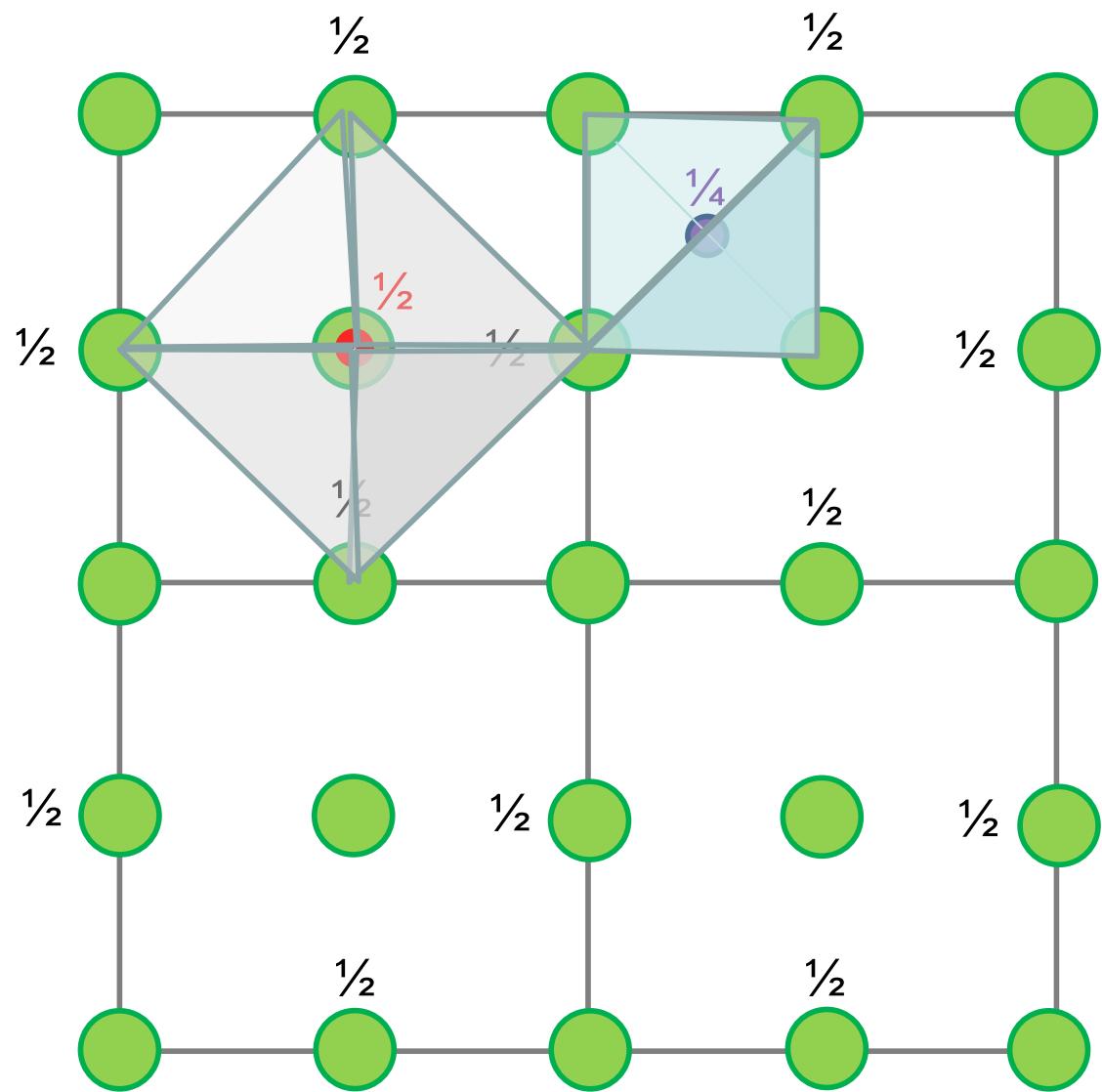
### Magnetite ( $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ )

Member of Spinel series of Oxides - Commercial Importance for Magnets.

- Spinel
- Close Packed Array of Oxygen Ions.
  - Gaps between oxygens partially filled by  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions.

2 types of gaps:

- (i) Ones surrounded by 6 oxygens - *Octahedral sites*
- (ii) Ones surrounded by 4 oxygens - *Tetrahedral sites*



General Spinel Formula =  $\text{AB}_2\text{O}_4$

*Normal Spinel:* A atoms occupy tetrahedral sites

B atoms occupy octahedral sites

*Inverse Spinel:*  $\text{B}/2$  atoms occupy tetrahedral sites

$\text{A}+\text{B}/2$  atoms occupy octahedral sites

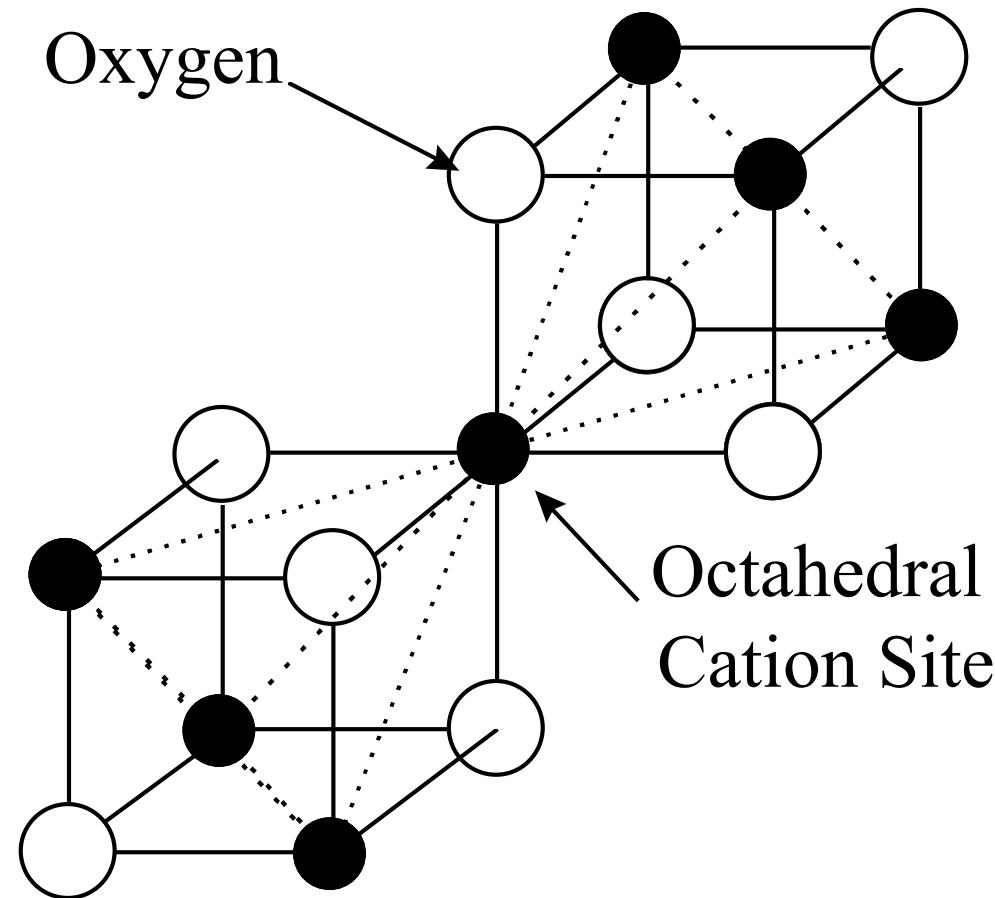
Magnetite is an Inverse Spinel.

i.e. half of  $\text{Fe}^{3+}$  ions occur on tetrahedral sites; the  $\text{Fe}^{2+}$  ions and half of the  $\text{Fe}^{3+}$  ions occupy octahedral sites.

>120K -  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  randomly distributed on octahedral sites.

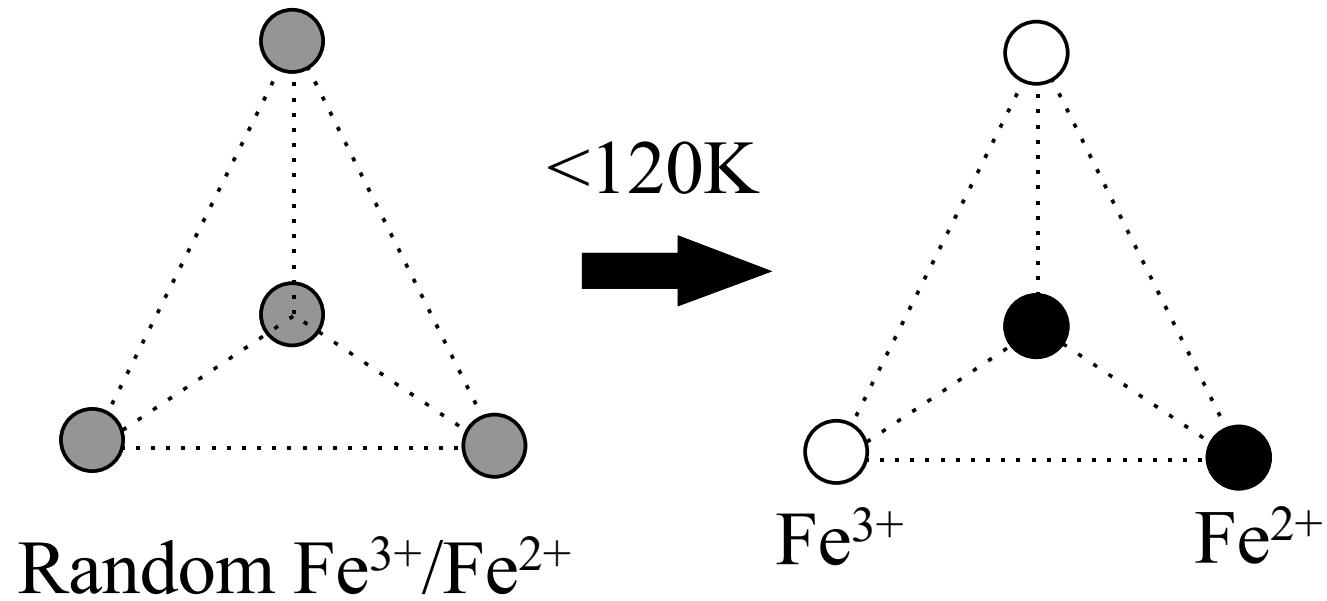
<120K -  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  order into specific arrangements on the octahedral sites.

This ordering is known as the Verwey Transition.



**Arrangement of Octahedral Sites in Spinel.**

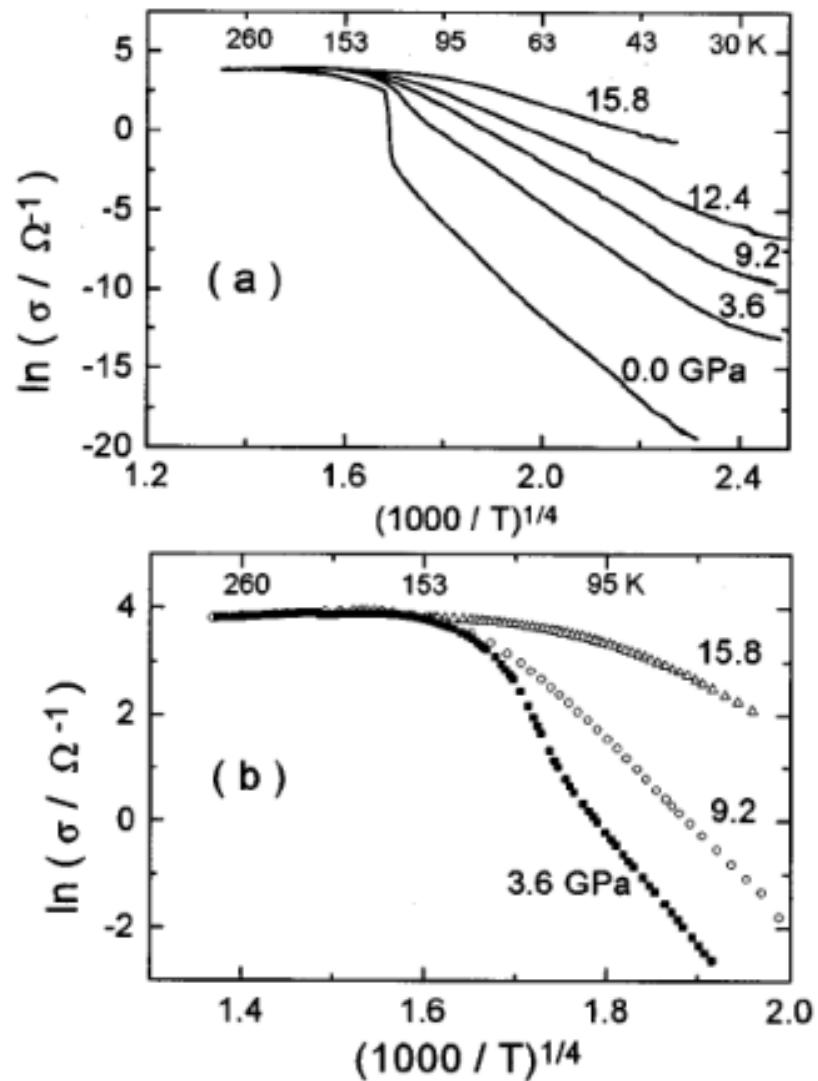
Octahedral sites may be linked as elongated tetrahedra.



Verwey transition creates a low temperature phase of reduced electrical conductivity.

# Conductivity vs reciprocal temperature

(Rozenberg et al. PRB 53,  
6482 (1996))



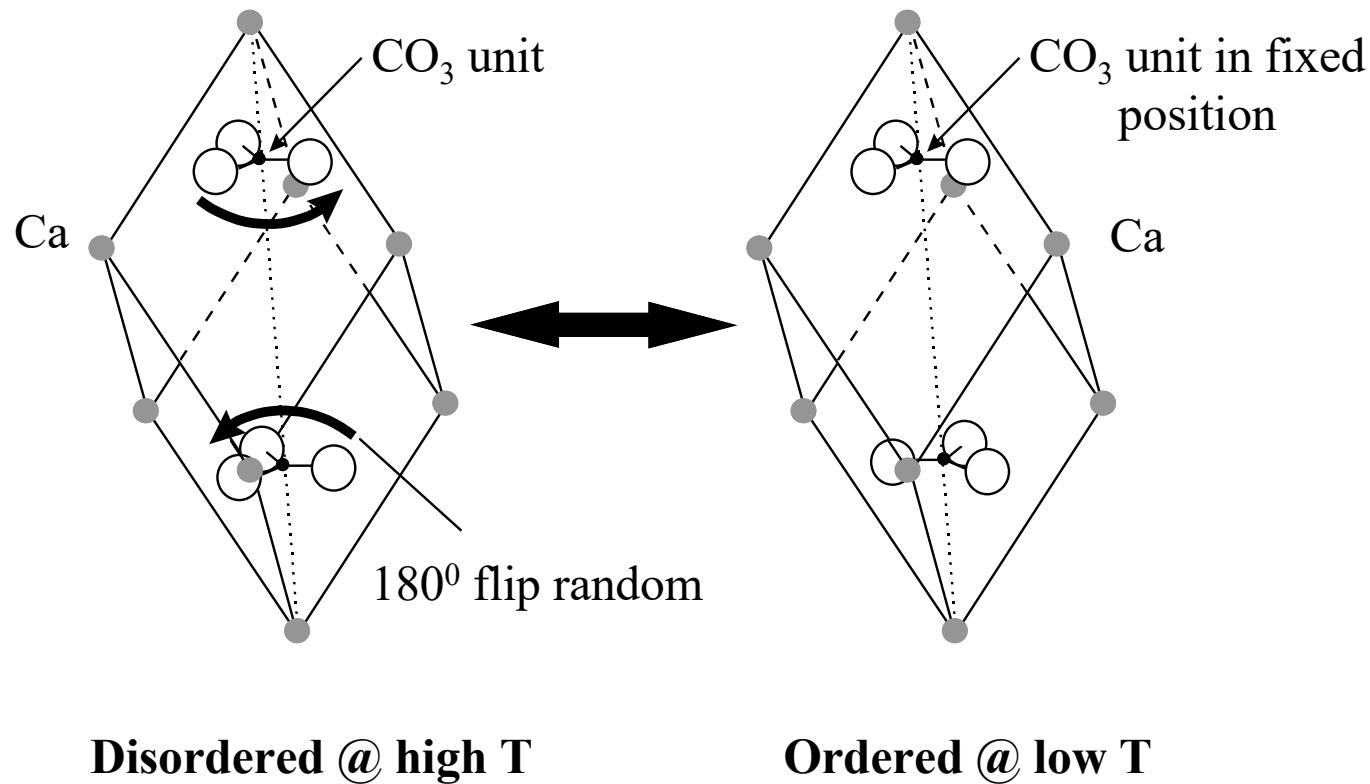
## **(b) Orientational**

Any crystalline solid consisting of nonmonatomic ions or molecules in the lattice can exhibit orientational randomisation unless its melting point is very low and interaction in the lattice is highly asymmetric.

System examples are: cyanides ( $\text{CN}^-$  group may adopt various orientations); nitrates ( $\text{NO}_3^-$  ions); carbonates ( $\text{CO}_3^-$  ions).

## EXAMPLE of Orientational Order-Disorder

**Calcite ( $\text{CaCO}_3$ ):**



In disordered state  $\text{CO}_3$  units randomly adopt either of two orientational possibilities.

In ordered state alternate  $\text{CO}_3$  units are constrained to adopt 180° rotations relative to each other.

### (c) Spin

Crystalline compounds of transition metal ions exhibit spin disorder at high temperatures.

On cooling the spins may couple in two ways:

- (i) Parallel
- (ii) Antiparallel

If parallel alignment occurs - *ferromagnetic*.

If antiparallel alignment occurs between ions of equal magnetic moment, no net magnetisation - *antiferromagnetic*.

If antiparallel alignment occurs between ions of unequal magnetic moment, then net magnetisation results - *ferrimagnetic*.

# Lodestone

From Wikipedia, the free encyclopedia

For a general description of the mineral itself, see [Magnetite](#).

For other uses, see [Lodestone \(disambiguation\)](#).

A **lodestone** is a naturally magnetized piece of the mineral [magnetite](#).<sup>[1][2]</sup> They are naturally occurring [magnets](#), which can attract [iron](#). The property of [magnetism](#) was first discovered in [antiquity](#) through lodestones.<sup>[3]</sup> Pieces of lodestone, suspended so they could turn, were the first [magnetic compasses](#),<sup>[3][4][5][6]</sup> and their importance to early [navigation](#) is indicated by the name [lodestone](#), which in [Middle English](#) means 'course stone' or 'leading stone'.<sup>[7]</sup> from the now-obsolete meaning of [lode](#) as 'journey, way'.<sup>[8]</sup>

Lodestone is one of the few minerals that is found naturally magnetized.<sup>[1]</sup> Magnetite is black or brownish-black, with a metallic [luster](#), a [Mohs hardness](#) of 5.5–6.5 and a black [streak](#).



## **EXAMPLE of Spin Order-Disorder**

### **Magnetite ( $\text{Fe}_3\text{O}_4$ ):**

Seen already the Verwey transition in magnetite. It also undergoes a spin order-disorder transformation at  $585^\circ\text{C}$ , resulting in a *ferrimagnet*:

Two types of sites for iron cations in magnetite:

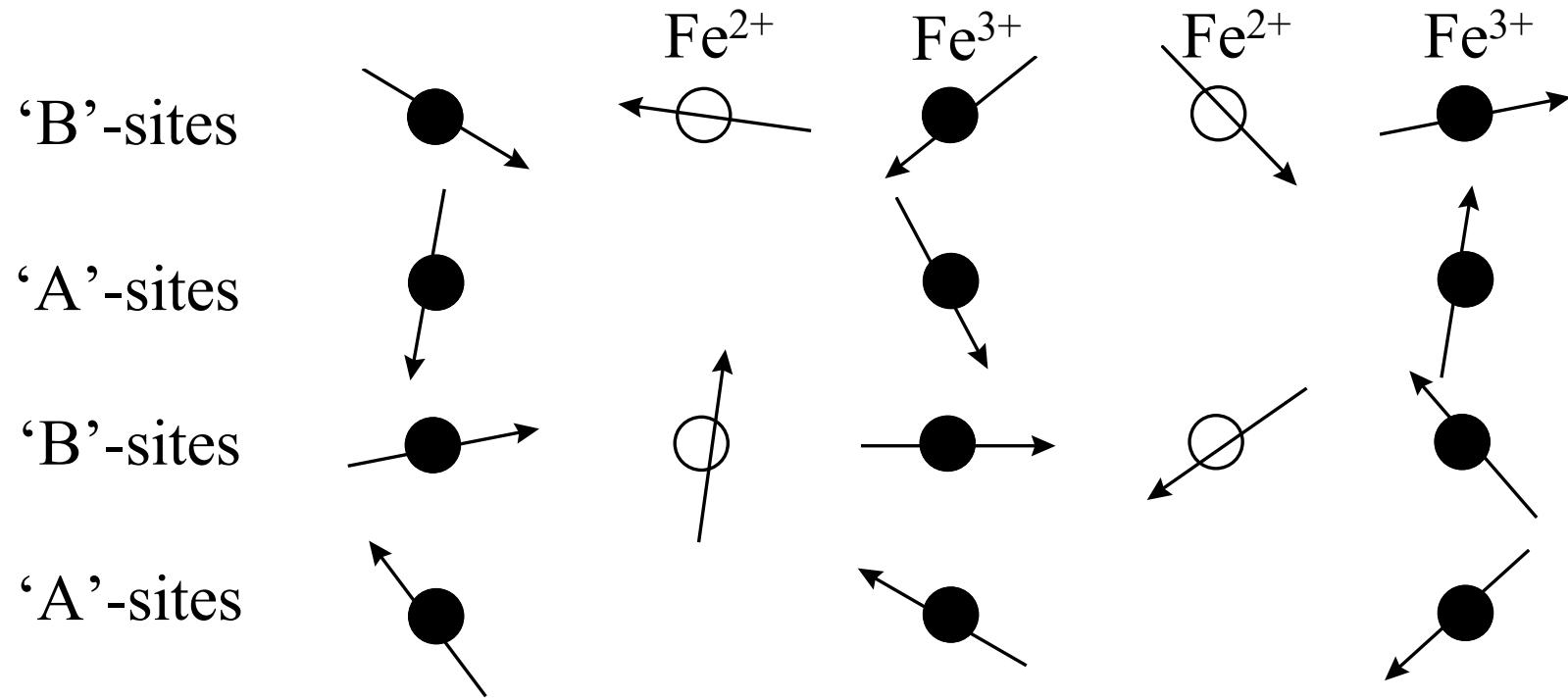
- (i) ‘A’-sites (tetrahedrally surrounded by oxygen)
- (ii) ‘B’-sites (octahedrally surrounded by oxygen).

Seen before that half of  $\text{Fe}^{3+}$  occupies ‘A’-sites.  $\text{Fe}^{2+}$  and other half of  $\text{Fe}^{3+}$  occupy ‘B’-sites. Above  $585^\circ\text{C}$  magnetic moments point in random directions - *paramagnetic*.

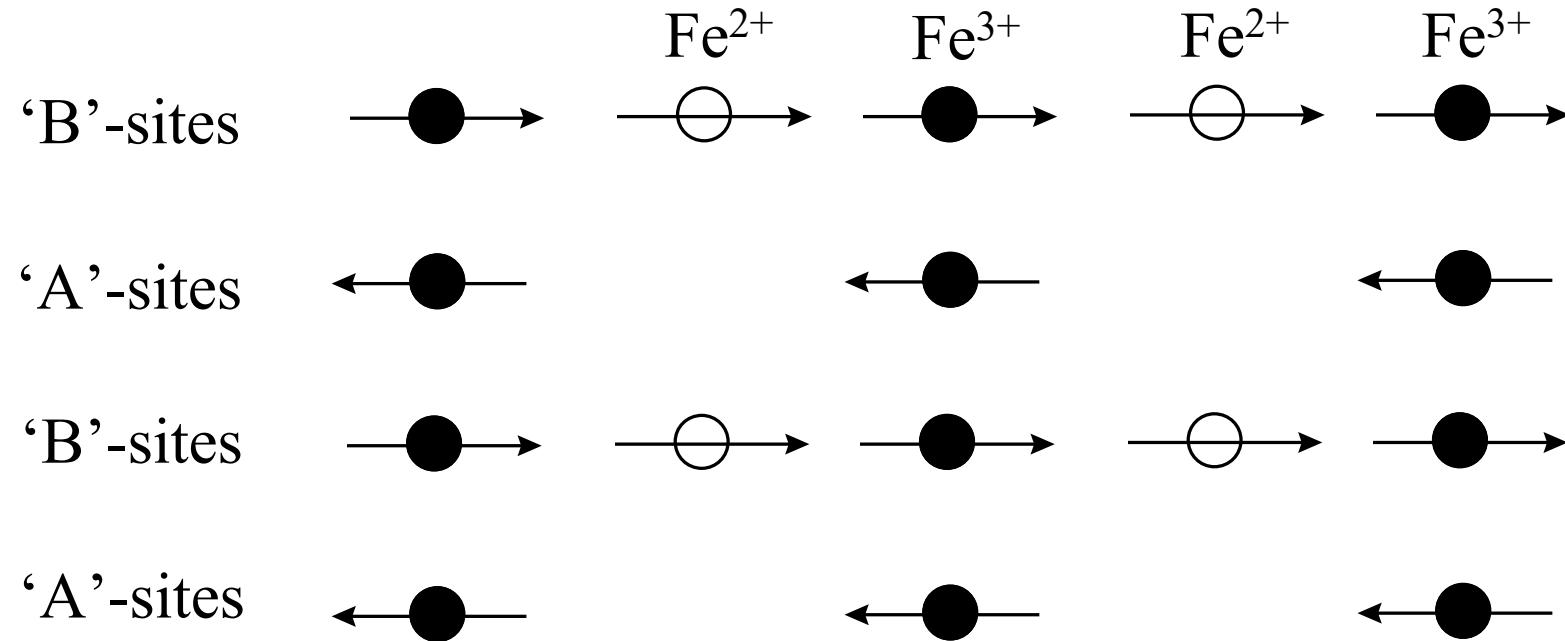
Below  $585^{\circ}\text{C}$  phenomenon known as *superexchange* causes magnetic ions to couple antiparallel across oxygen ions. Strength of coupling depends on the cation $\wedge$ oxygen $\wedge$ cation angle. Largest coupling strength occurs for  $180^{\circ}$ .

In spinels A $\wedge$ O $\wedge$ B angle is  $125^{\circ}$  and is the closest to  $180^{\circ}$ . Therefore antiparallel coupling between ‘A’ and ‘B’ sites occurs.

Magnetic moments of  $\text{Fe}^{3+}$  on ‘A’ cancel with those on ‘B’. The moment of  $\text{Fe}^{2+}$  on ‘B’-sites remains.



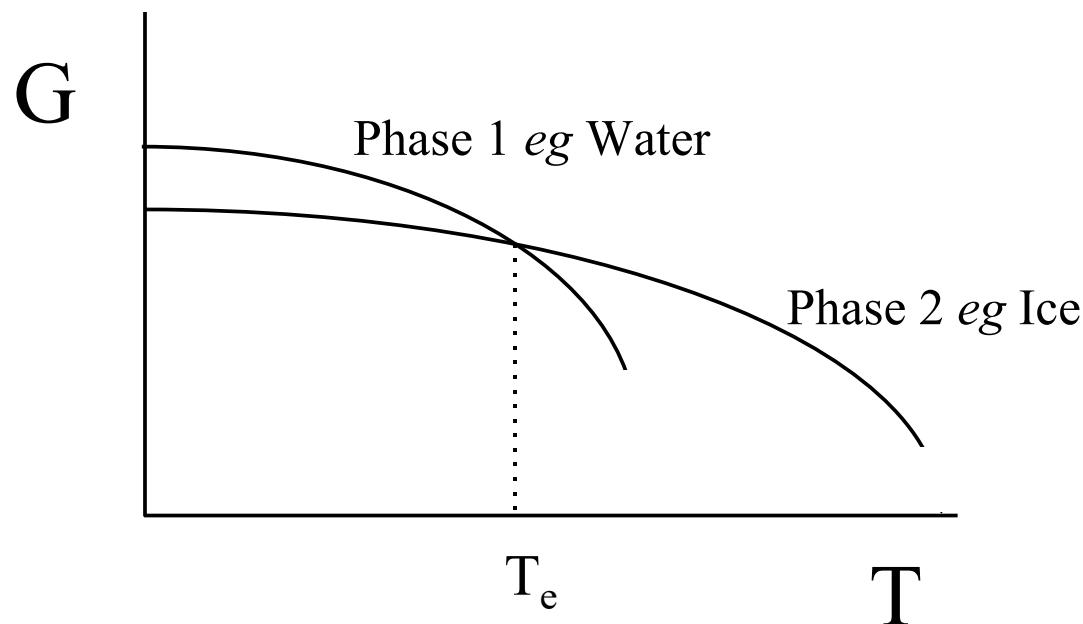
$>585^\circ\text{C}$  - Paramagnetic



$<585^\circ\text{C}$  - Ferrimagnetic

## THE PROCESS OF TRANSFORMATION

Phase Transformations are grouped depending on behaviour of Free Energy across transformation:



In the phase transformation between water and ice, across  $T_e$  (equal free energies):

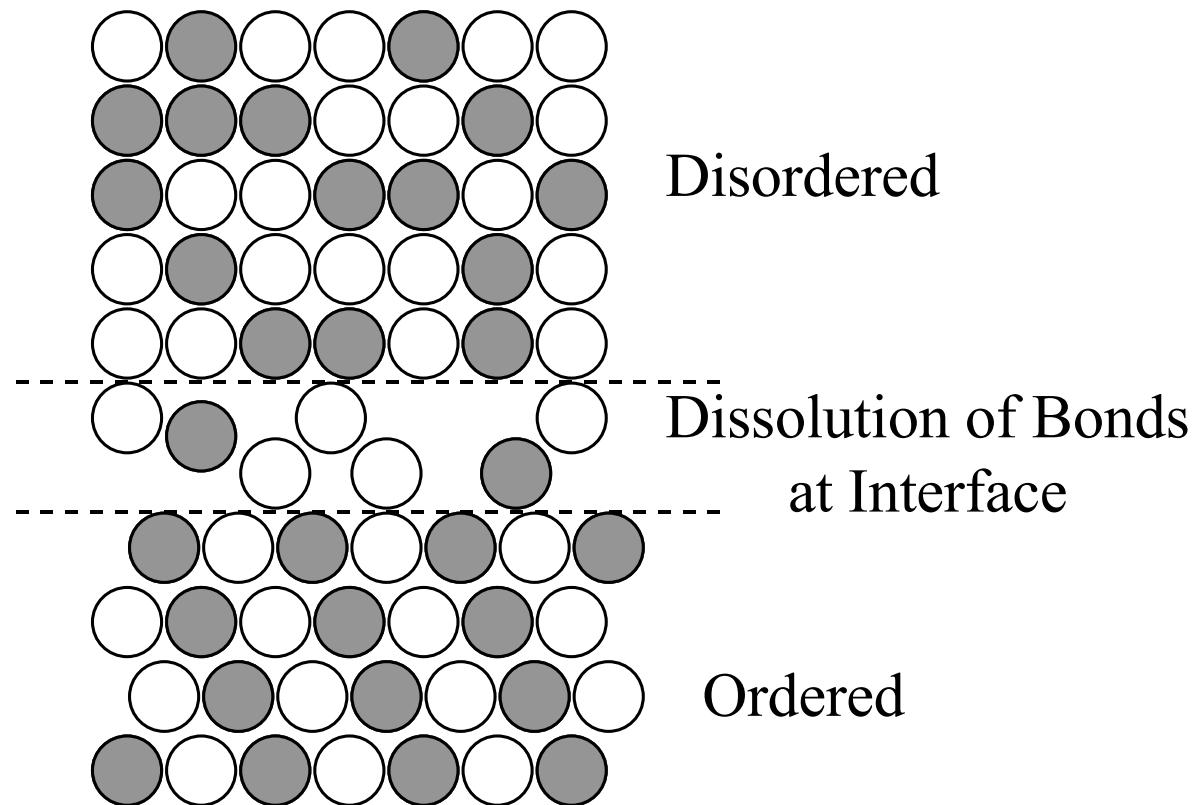
$$\frac{dG}{dT} = \text{discontinuous}$$

Because the first order derivative of the free energy is discontinuous, this type of transformation is called **first order**.

The radical nature of Free Energy change in first order transitions implies a distinct difference in the structures of parent and daughter phases.

Often (but not always) first order behaviour implies a reconstructive mechanism.

## Reconstructive Transformation



Changes of state need not be so radical. Small, but coordinated atomic shifts may occur which change the symmetry of a solid.

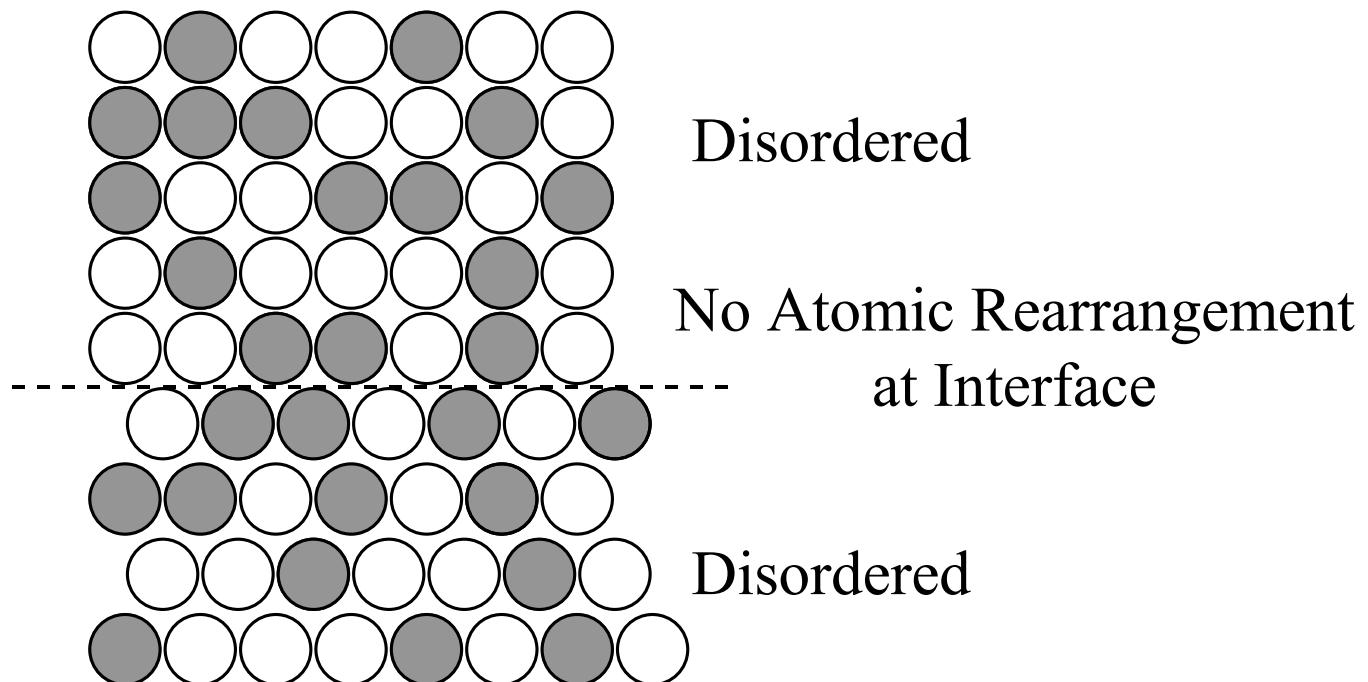
New phases are produced with different properties from the parent phases, but the free energy change is continuous.

In fact it is the second derivative of the free energy which is discontinuous. Such transformations of state are therefore known as **second order**.

$$\frac{d^2 G}{dT^2} = \text{discontinuous}$$

The tendency for small atomic displacements to cause second order transformations has led to a general link between **displacive phase transformations** and second order transformations.

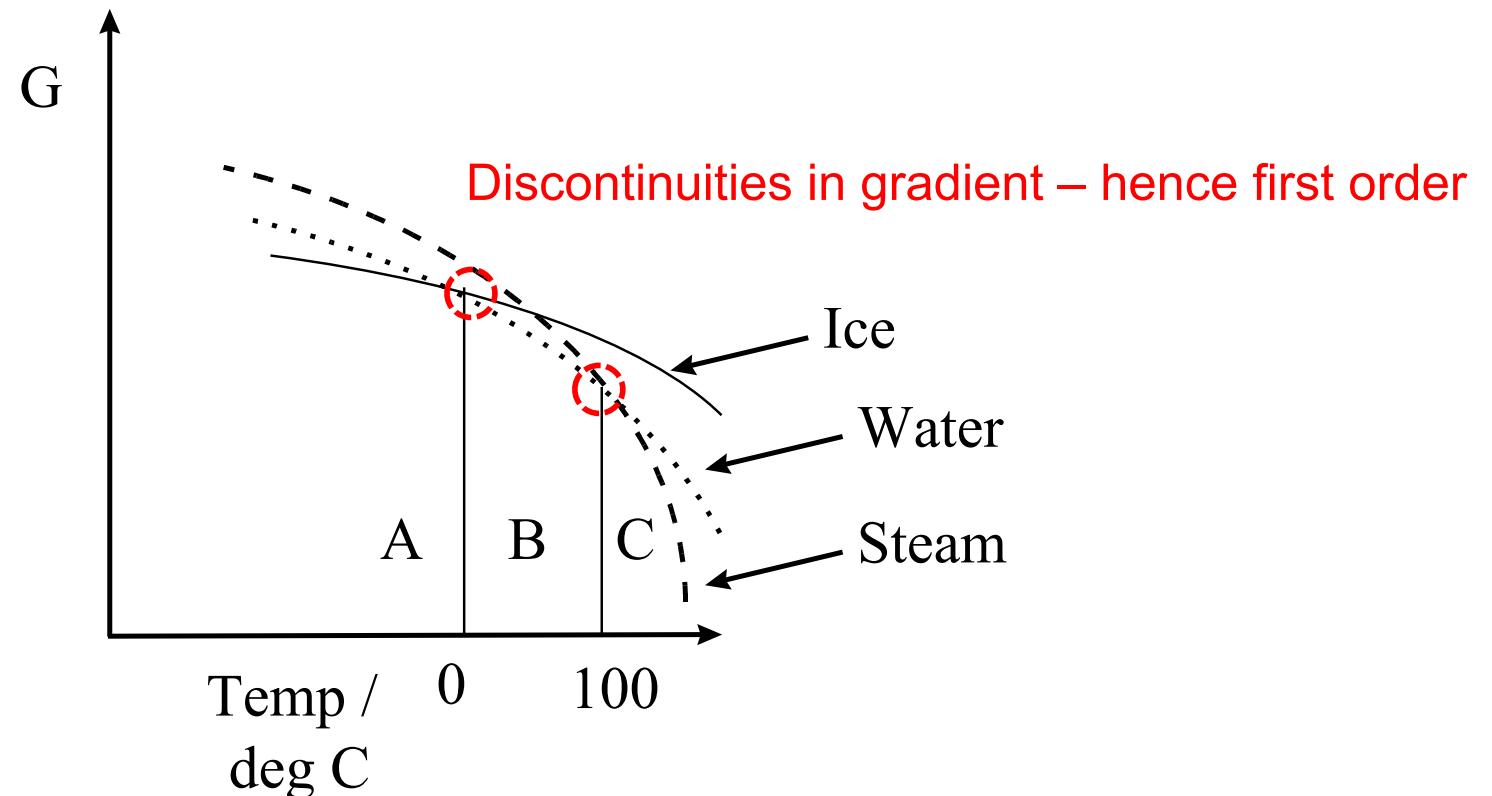
## Displacive Transformation



Many phase transformations in nature do not conform to either of the above descriptions - the changes in free energy are not completely discontinuous, but are only just continuous - such intermediate transformation behaviour is termed **tricritical**.

## MODELLING FREE ENERGY TO UNDERSTAND PHASE TRANSFORMATIONS AND PHASE DIAGRAMS:

*Ice - Water - Steam*



## **GENERAL DESCRIPTION OF TRANSFORMATION PROCESS**

### **The Order Parameter: Q**

To describe the dynamics of transformation the concept of the order parameter is used. Initially this parameter referred to order-disorder transitions (hence the name). Now it is used more generally.

Completely High Temp Phase -  $Q=0$

Complete Low Temp Phase -  $Q=1$

For intermediate system states the order parameter should reflect the extent of transformation:

e.g. Alloy system AB. A atoms belong to A sites; B atoms to B sites. As Temp rises some A atoms wrongly occupy B sites and an equal number of B atoms wrongly occupy A sites.

Let  $R$  denote number of right atoms, and  $W$  denote the number of wrong atoms of a particular kind. Then:

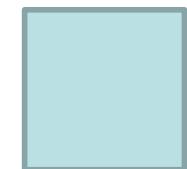
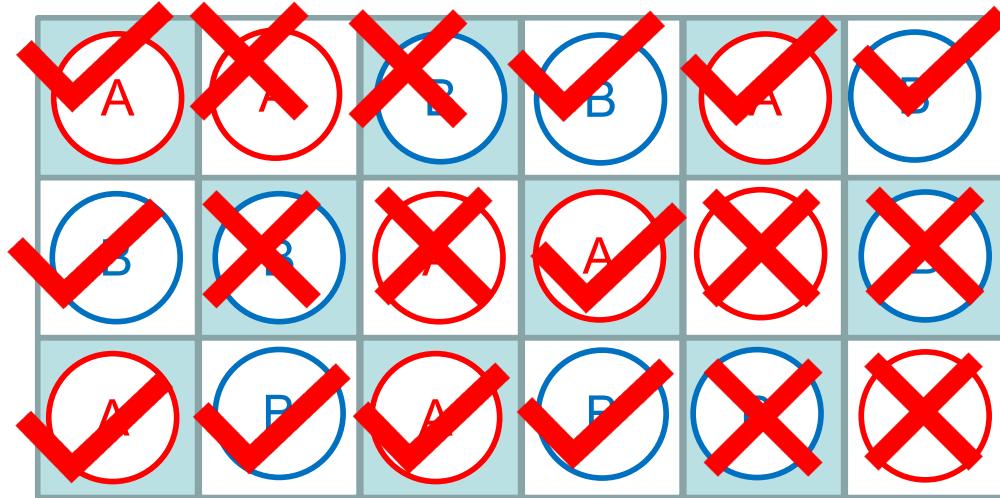
$$R + W = \text{total no. of atoms of particular kind}$$

Highest Order:  $W = 0; Q = 1$

Lowest Order:  $R = W; Q = 0$

General Order Parameter Expression may therefore be given as:

$$Q = \frac{R - W}{R + W}$$



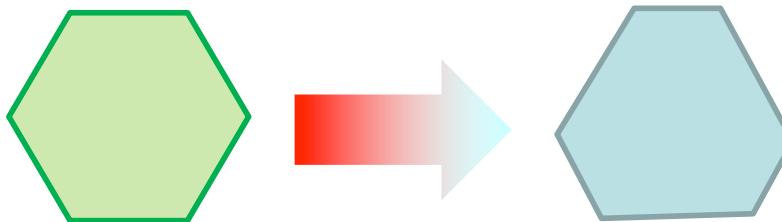
“A”-Site



“B”-Site

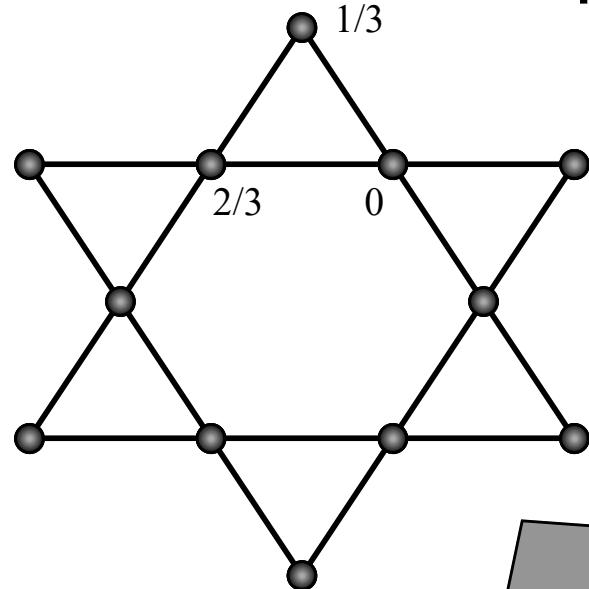
$$Q = \frac{R - W}{R + W} = \frac{2}{18} = 0.1$$

OR....let's instead consider a phase transition involving structural collapse (like high-low quartz):



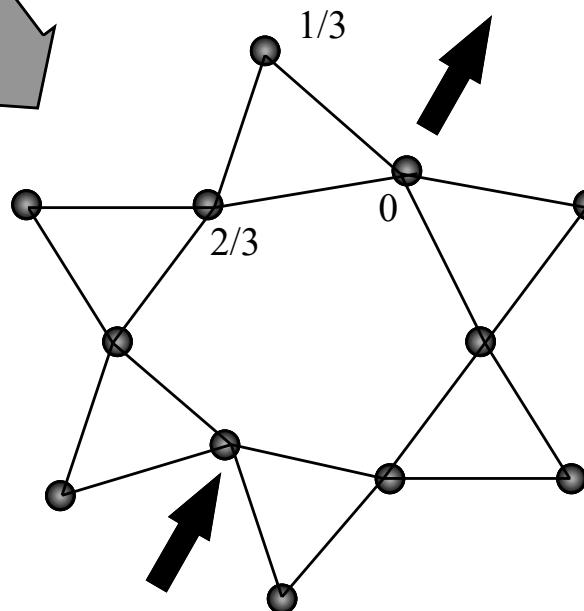
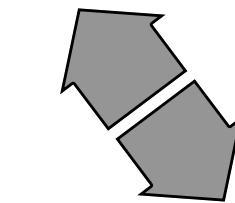
Here the order parameter would reflect the extent to which the full distortion to low quartz had occurred.

## Plotting Just the Si Atoms

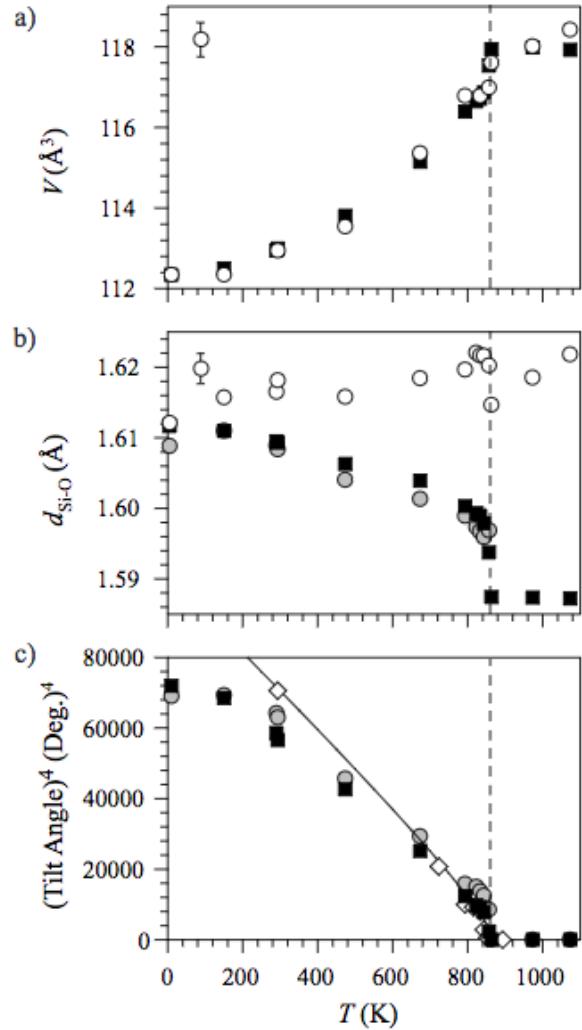


High Quartz

Low Quartz

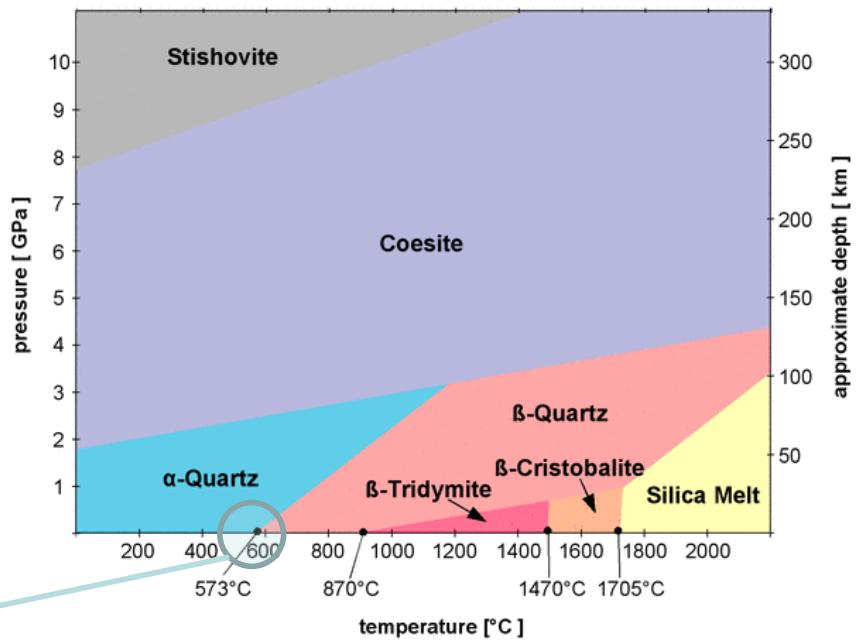


Deformation



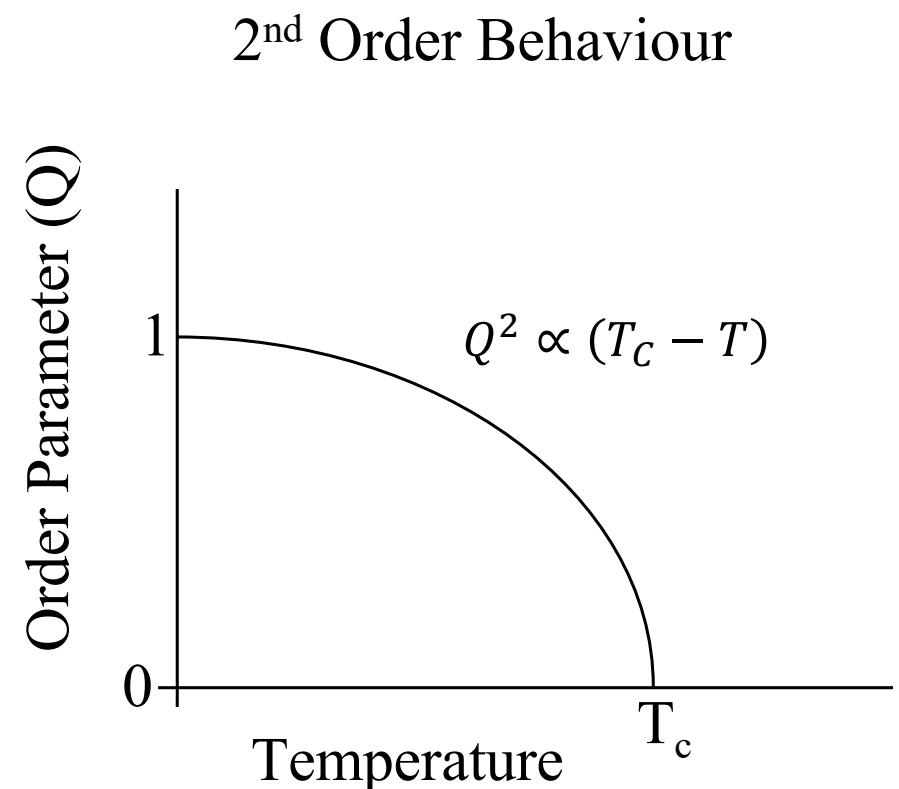
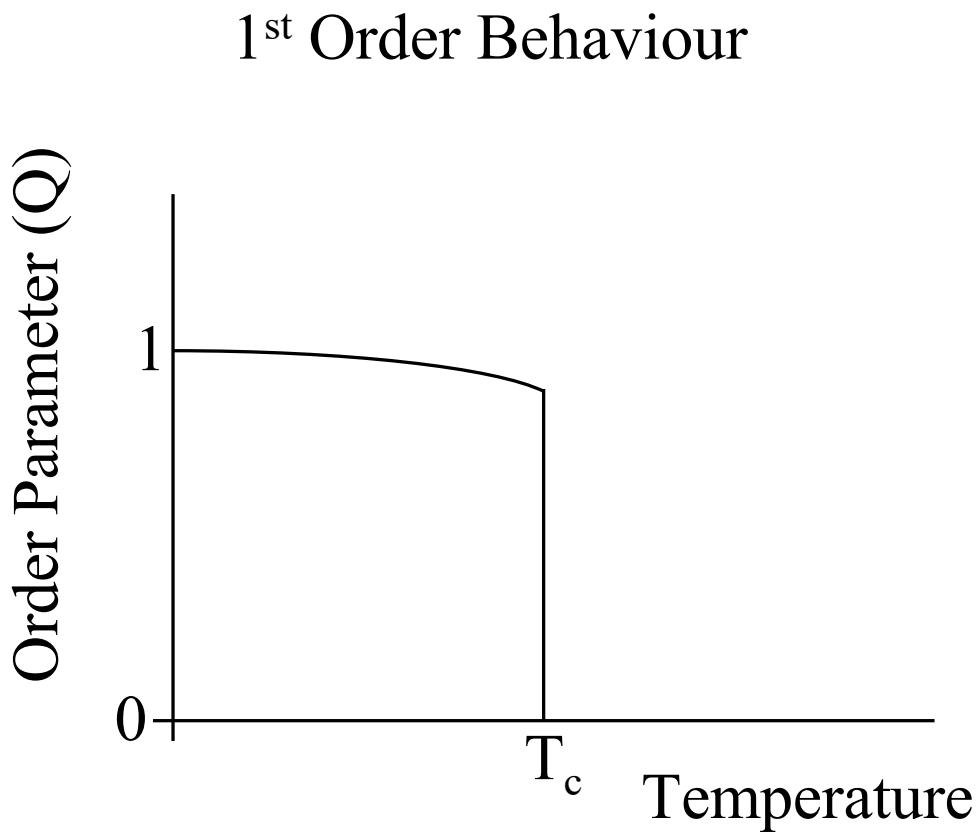
**Figure 2.** Temperature dependence of the (a) unit cell volume, (b) Si–O distance, and (c) fourth power of the average  $\text{SiO}_4$  tetrahedral tilt angle. The vertical dashed line shows  $T_c$ . In (a) data from the Rietveld refinement and the 17  $\text{\AA}$  peak in  $T(r)$  are given by squares and open circles respectively. In (b) squares and filled circles represent the distances between average positions,  $(\text{Si})-(\text{O})$  given by Rietveld refinement and the RMC respectively, and the open circles represent the average values of the instantaneous bond length,  $\langle \text{Si}-\text{O} \rangle$  from RMC. In (c) squares and filled circles represent data from Rietveld refinements and RMC respectively, and diamonds and line represent experimental x-ray diffraction data and results of a fitted Landau free-energy function [8]. In (a) and (b) we show the maximum non-sytemmatic errors on one set of data by drawing an error bar in the top left corner of each plot; in all other cases the non-sytemmatic errors are smaller than the sizes of the points.

## Introduction to the “Order Parameter” Concept

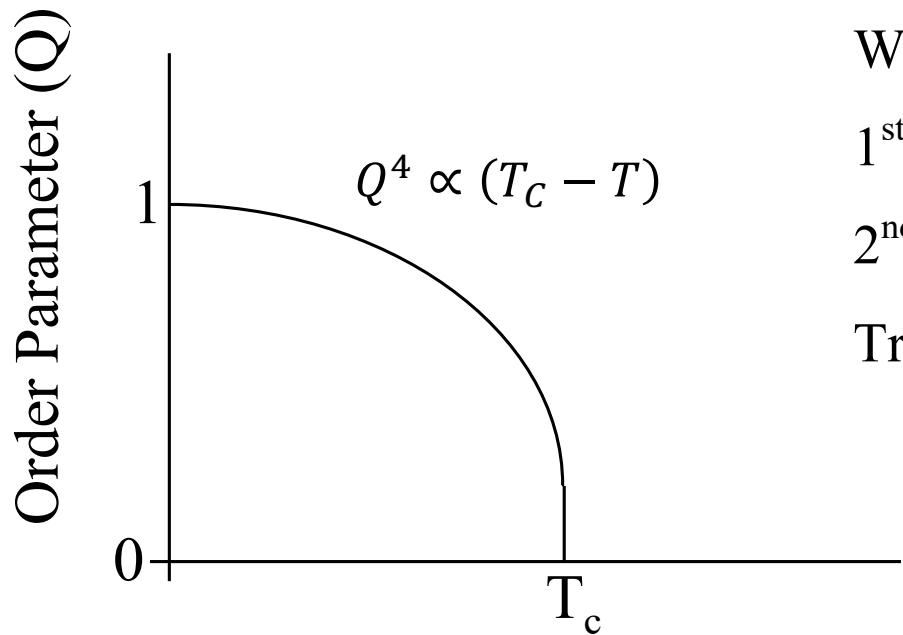


Here, the order parameter is the angle of tilt of the  $\text{SiO}_4$  corner-sharing tetrahedra

Consideration of the order parameter as a function of temperature illustrates the differences between 1<sup>st</sup> Order, 2<sup>nd</sup> Order and Tricritical transitions:



## Tricritical Behaviour



We will see later that:

1<sup>st</sup> Order  $Q$  is complex function of  $T$

2<sup>nd</sup> Order  $Q^2$  proportional to  $(T-T_c)$

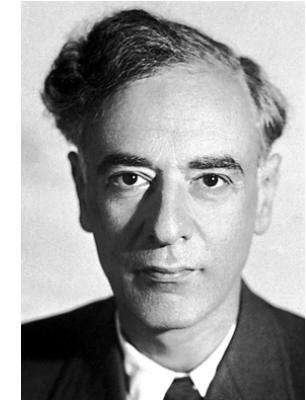
Tricritical  $Q^4$  proportional to  $(T-T_c)$ .

## LANDAU THEORY OF PHASE TRANSFORMATIONS

Consider the Long Range Order Parameter once more:

General Order Parameter Expression given as:

$$Q = \frac{R - W}{R + W}$$

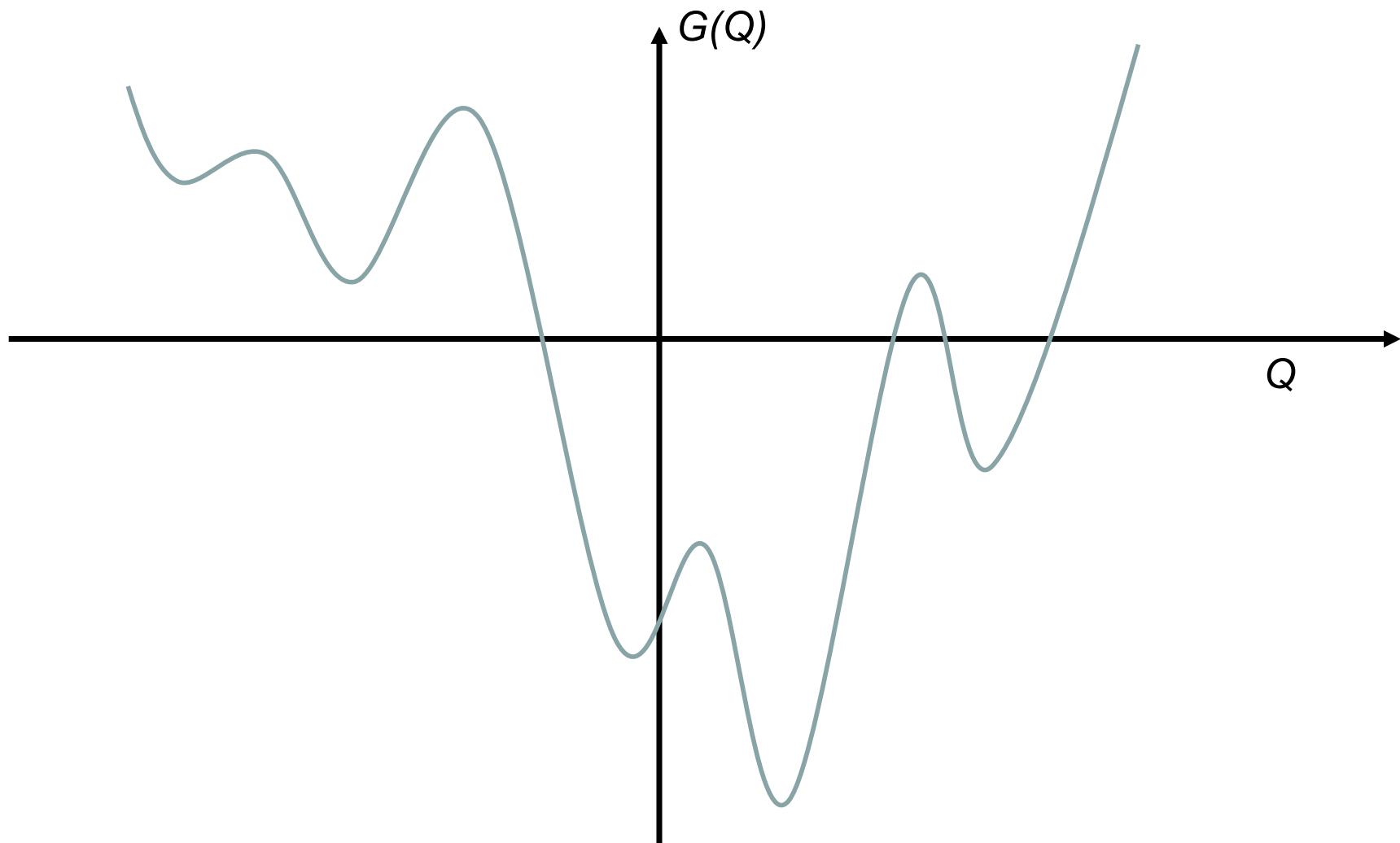


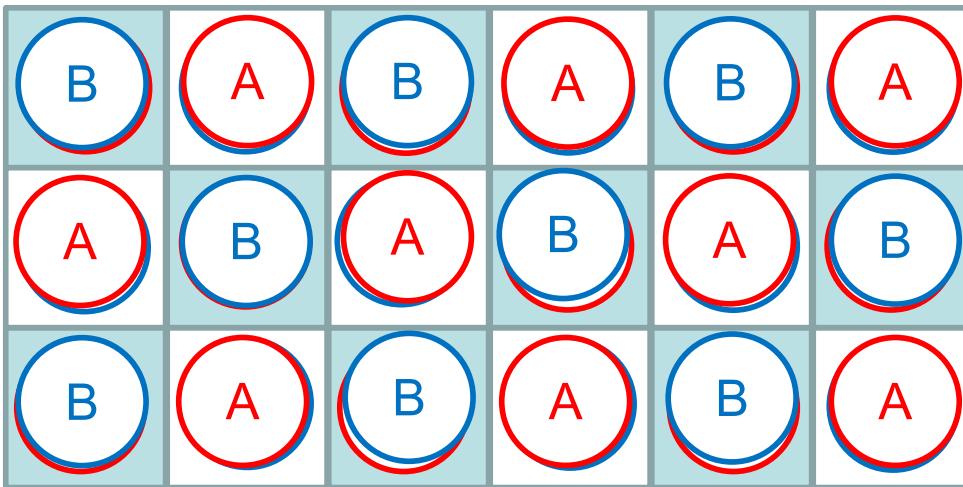
**Important to note:** If lattice had been defined such that  $R$  and  $W$  were interchanged then:

Highest Order:  $R = 0; Q = -1$

Lowest Order:  $W = R; Q = 0$

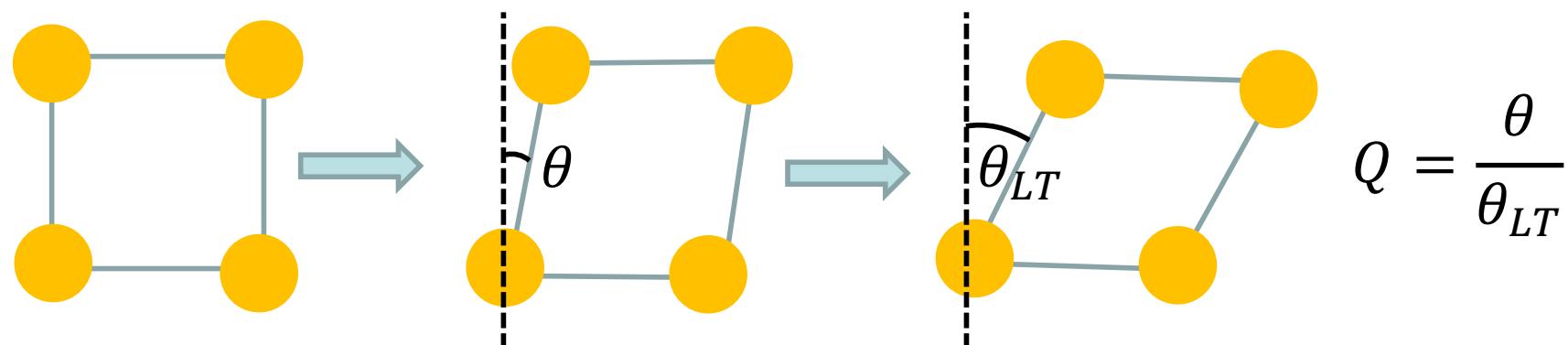
So  $Q$  would equal  $-1$  for complete order, rather than  $+1$ . Both expressions of the order parameter represent the same state. Therefore any full description of order parameter behaviour must show  $+$ / $-$  symmetry.



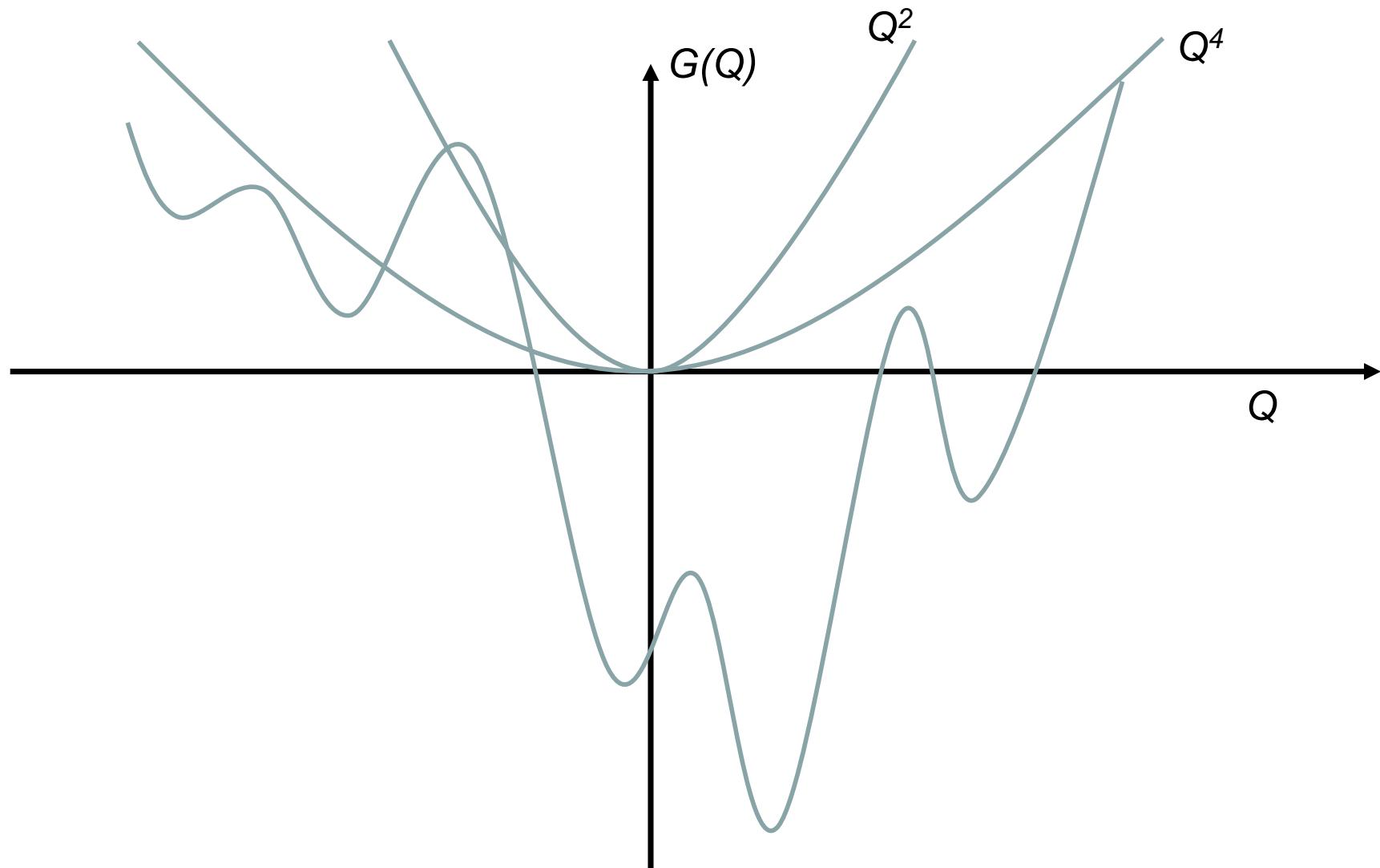


$$Q = \frac{R - W}{R + W} = \frac{18_1 8}{18_8} = 1 - 1$$

OR....let's instead consider a phase transition involving structural collapse:



Viewed from behind the computer screen, clockwise fractional angle of distortion becomes negative.



## **Landau**

Landau describes the Free Energy as a function of the Order Parameter near the transition temperature  $T_c$  by a general polynomial (may describe any function in this way):

$$G(P, T, Q) = G_0(P, T) + aQ + bQ^2 + cQ^3 + dQ^4 + \dots$$

HOWEVER, as seen above expression involving order parameter MUST BE SYMMETRIC (no terms in odd powers):

$$\therefore G(P, T, Q) = G_0(P, T) + bQ^2 + dQ^4 + fQ^6 \dots$$

For Equilibrium state Free Energy is a minimum:

$$(i) \quad \frac{dG}{dQ} = 0$$

and

$$(ii) \quad \frac{d^2G}{dQ^2} > 0$$

Hence

$$(i) \quad Q(b + 2dQ^2) = 0$$

$$(ii) \quad b + 6dQ^2 > 0$$

From (i) find solutions for Q:  $Q = 0$  and  $Q^2 = -b/2d$

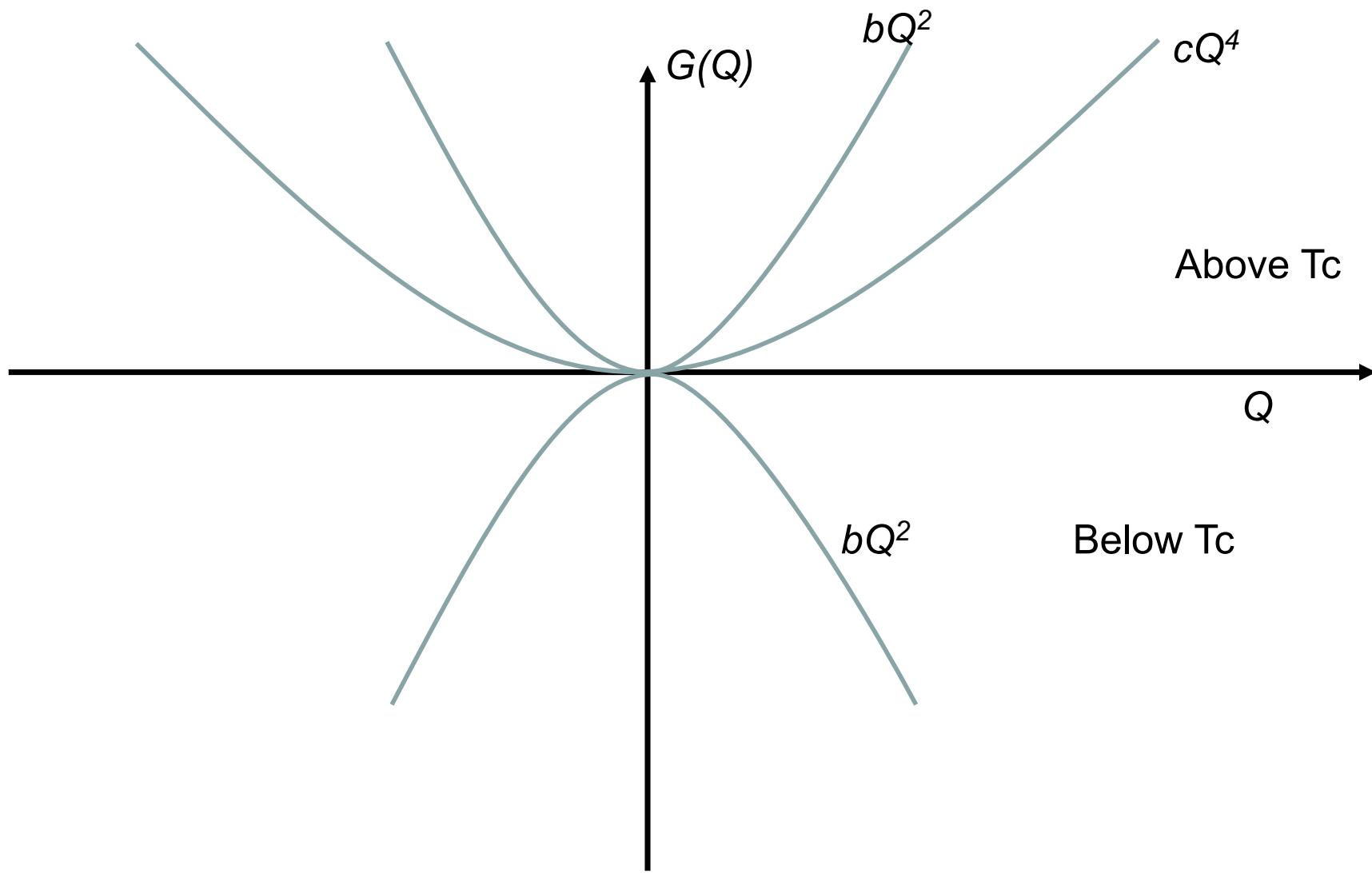
$Q = 0 \equiv$  disordered state or high symmetry state  
eq<sup>n</sup> (ii) gives  $b > 0$ .

$Q^2 = -b/2d$  must be ordered state or low symmetry state  
eq<sup>n</sup> (ii) gives  $b < 0$ .

So.... parameter  $b$  must change sign through the transformation. Assuming  $b$  to vary linearly with temperature we find near transition:

$$b(T) = B(T - T_c)$$

$T_c$  is the ‘critical’ or transition temperature.



Therefore the Landau Free Energy may be given more explicitly:

$$\therefore G = G_0 + \frac{a}{2}(T - T_c)Q^2 + \frac{b}{4}Q^4 + \frac{c}{6}Q^6 \dots$$

where constant parameters  $\frac{a}{2}, \frac{b}{4}$  etc. are used in order to make differentiated expressions simpler.

Often the Landau Free Energy is not used to examine the total free energy, but instead looks at the difference in free energy between two transitional states.

Hence:

$$\Delta G = \frac{a}{2}(T - T_c)Q^2 + \frac{b}{4}Q^4 + \frac{c}{6}Q^6 \dots$$

This is the simplest form of the Landau Expression, or Landau Potential.

For equilibrium behaviour, the order parameter adopted by the system obeys:

$$\frac{dG}{dQ} = 0$$

$$\therefore 0 = Q[a(T - T_c) + bQ^2 + cQ^4]$$

Solutions are:

$Q = 0$  (disordered / high temperature phase)

**OR:**

Let  $b$  be positive;  $c=0$

$$Q^2 = \frac{a}{b}(T_c - T) \text{ (2}^{\text{nd}} \text{ Order Behaviour)}$$

**OR:**

Let  $b$  be negative;  $c$  non zero

$$Q^2 = \frac{1}{c} \left[ -\frac{1}{2}b + \sqrt{\frac{b^2}{4} - ac(T - T_c)} \right]$$

(1<sup>st</sup> Order Behaviour)

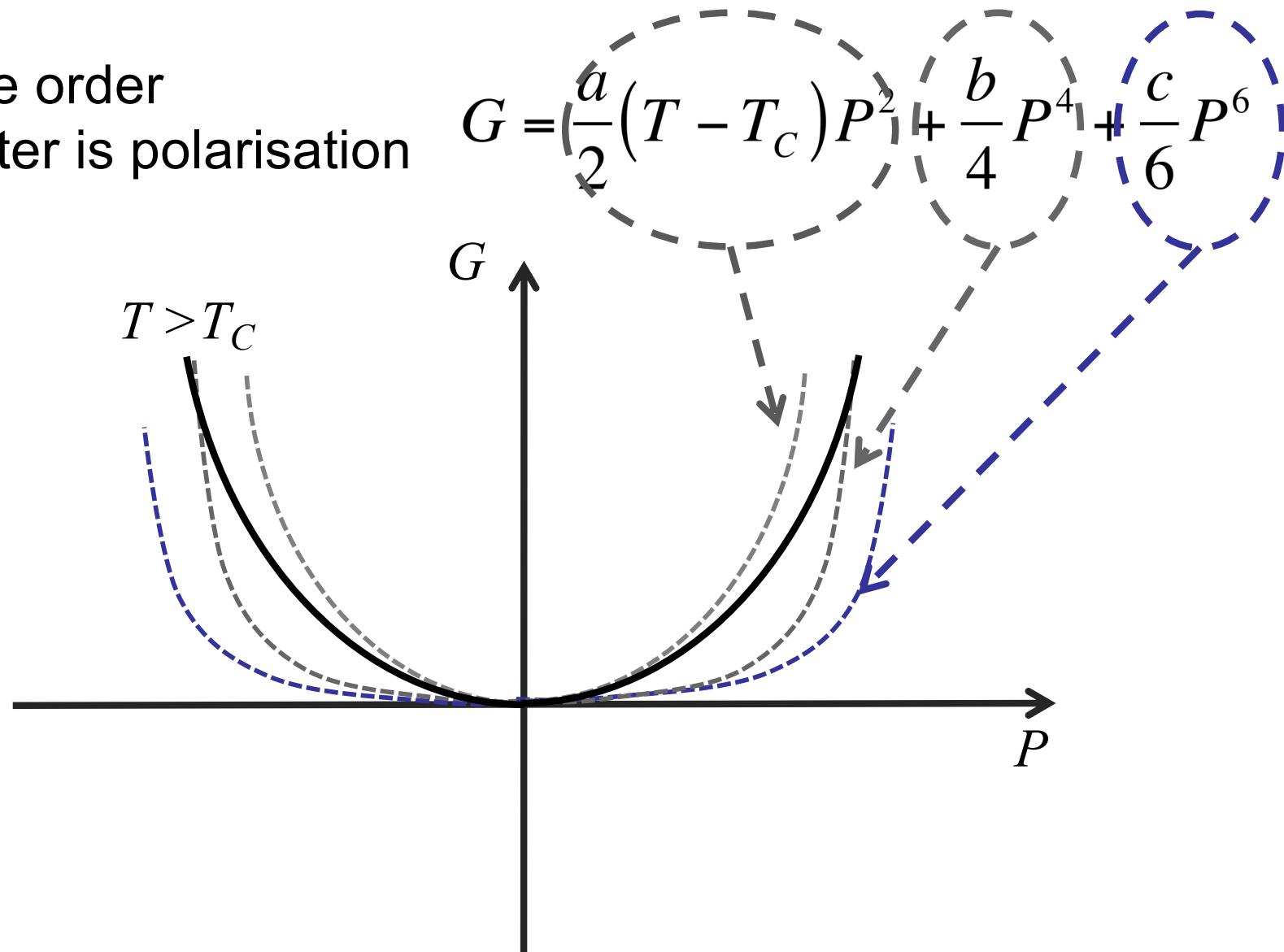
**OR:**

Let  $b = 0$

$$Q^4 = \frac{a}{c}(T_c - T) \quad (\text{Tricritical Behaviour})$$

# Landau-Ginzburg-Devonshire (LGD) Theory

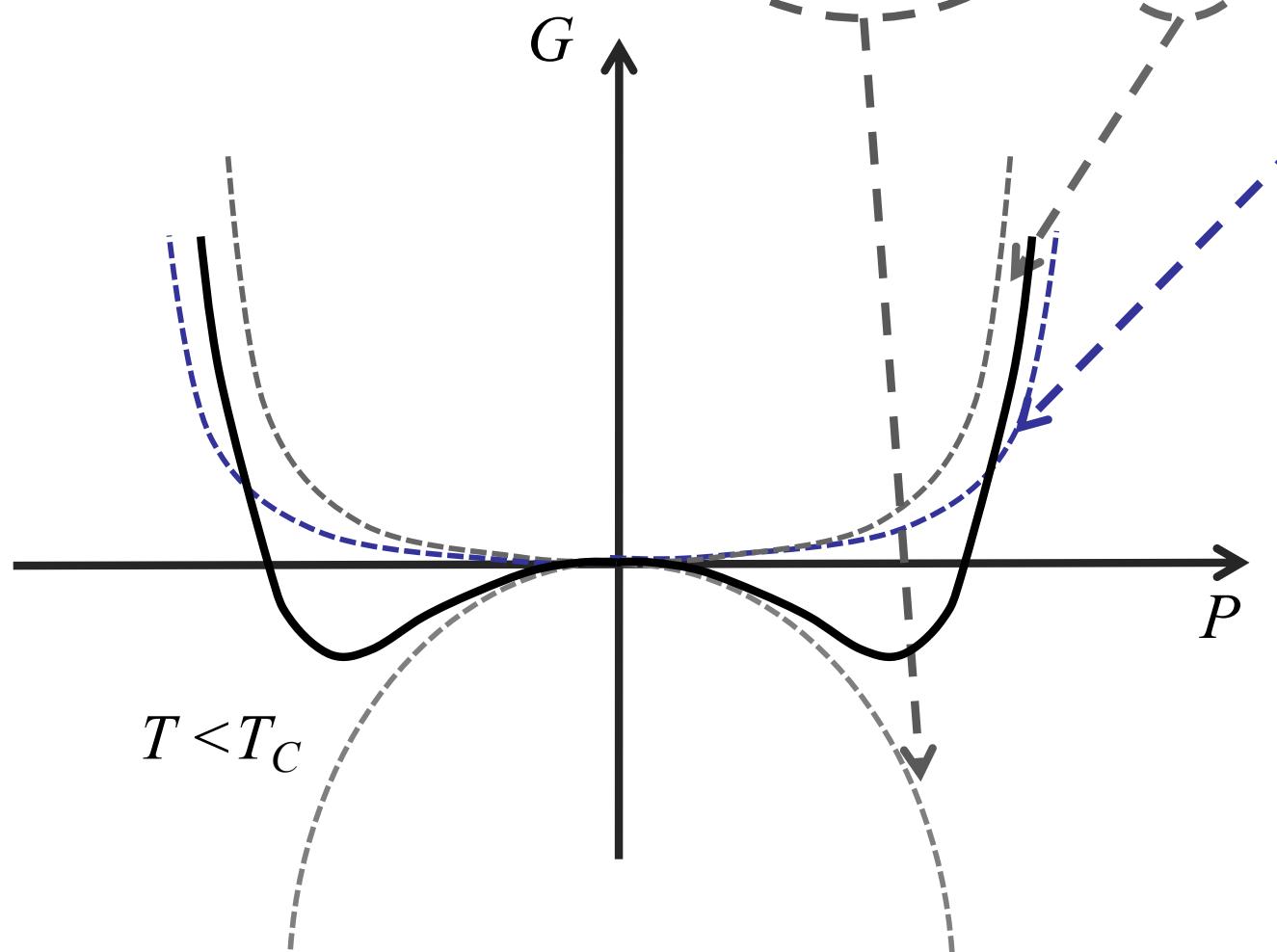
Here the order parameter is polarisation (P):



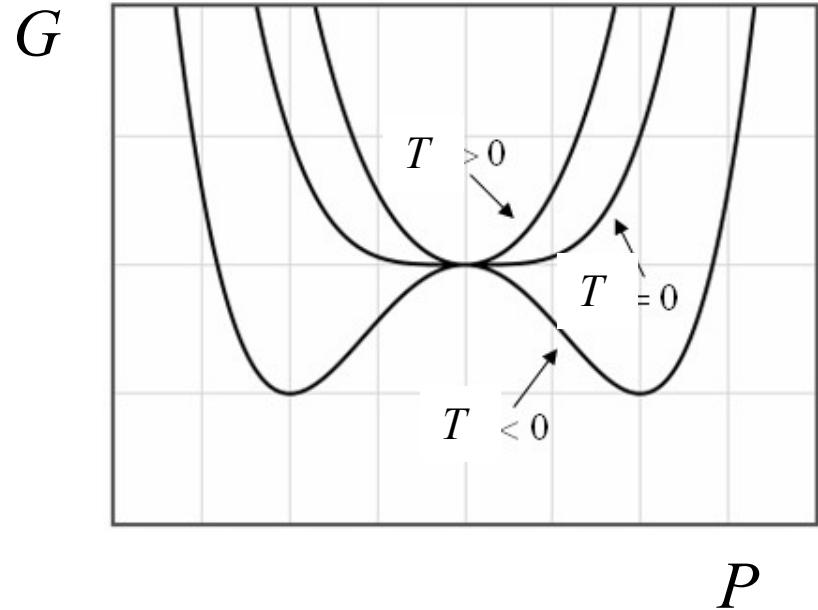
# Landau-Ginzburg-Devonshire (LGD) Theory

Order parameter is  $P$ :

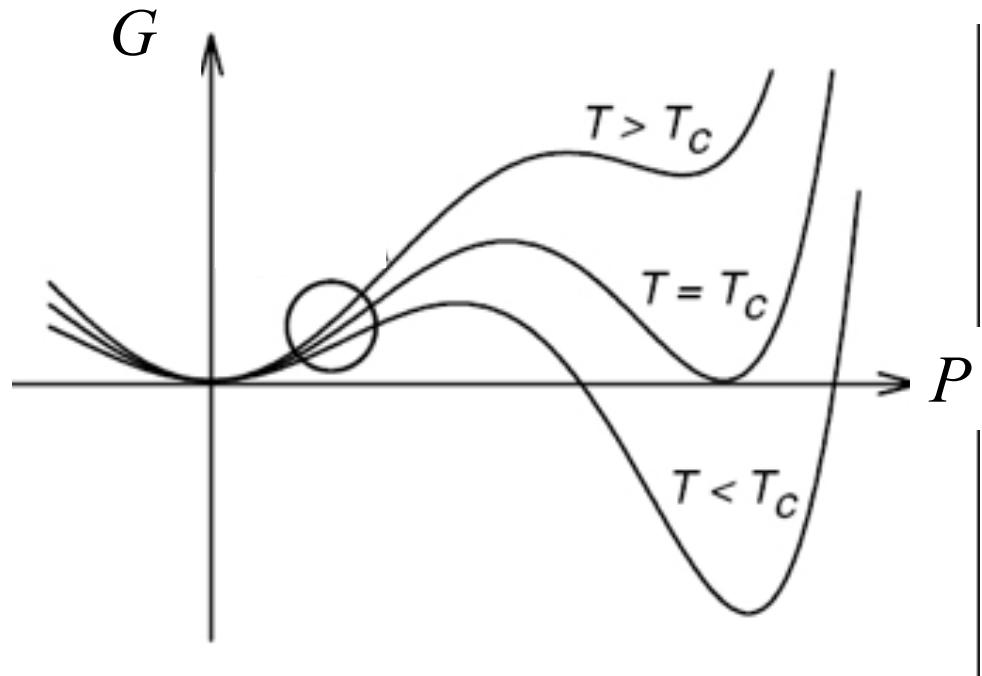
$$G = \frac{a}{2}(T - T_c)P^2 + \frac{b}{4}P^4 + \frac{c}{6}P^6$$



# Landau-Ginzburg-Devonshire (LGD) Theory



**2<sup>nd</sup> Order** – continuous development of polarisation on cooling; 1 minimum (high T, P=0) develops into 2 minima at finite values of P below  $T_c$ .



**1st Order** – discontinuous development of polarisation on cooling; 1 minimum (high T, P=0) develops 2 additional local minima. At  $T_c$ , three equal minima exist. Below  $T_c$ , still have metastable P=0.

# Transformation Plasticity

Define the *susceptibility* of a system  $\chi$ .

Susceptibility is simply how easily affected the system's properties are under the influence of an external field.

We consider a general field  $H$ .

And assign an order parameter to the property that  $H$  will affect.

Then: 
$$\chi = \frac{\delta Q}{\delta H}$$

Work done by applied field ( $H$ ) =  $H.Q$

So general free energy when system under an applied field  $H$ :

$$G = \frac{a}{2}(T - T_C)Q^2 + \frac{b}{4}Q^4 - H.Q$$

under equilibrium :

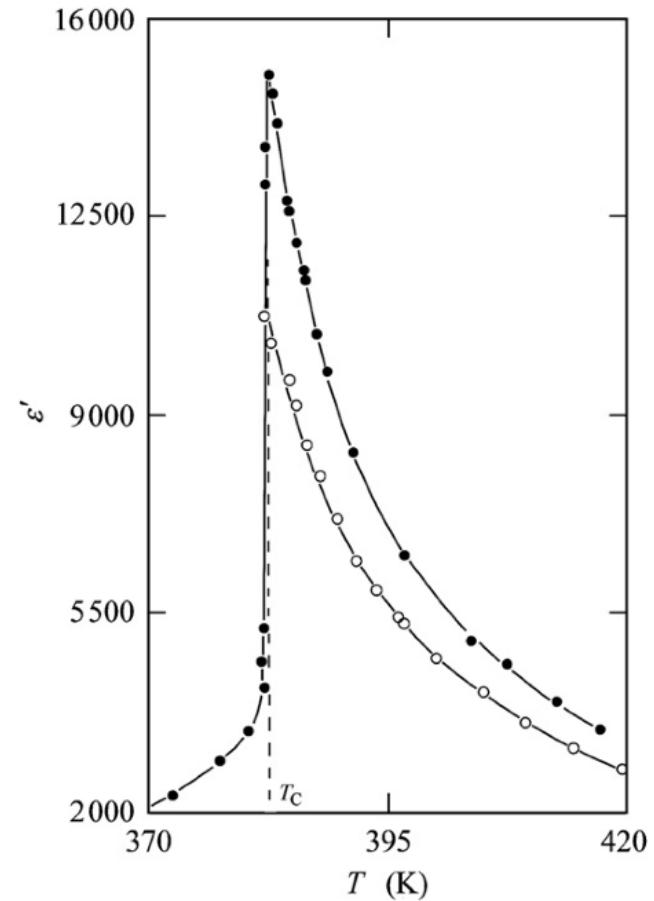
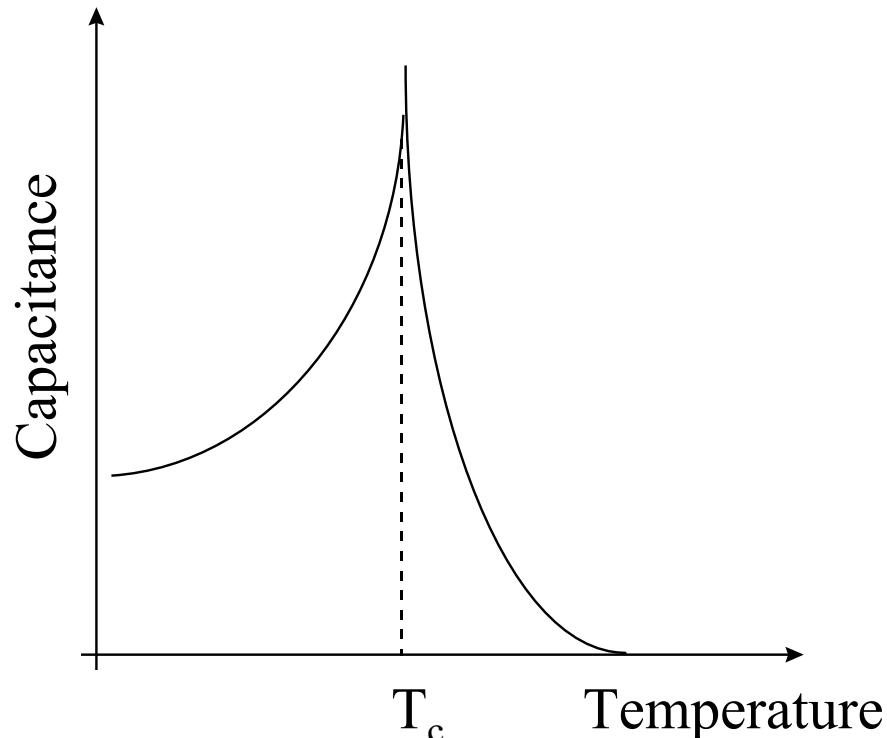
$$\frac{dG}{dQ} = 0 \quad \therefore H = a(T - T_C)Q + bQ^3$$

## **Another Example of Transformation Plasticity: Ferroelectrics.**

Here

$C = \frac{q}{V}$ , charge per unit volt applied. Capacitance **is** a susceptibility. Therefore at the Curie Temperature Landau Theory predicts that it tends to infinity.

This is experimentally observed:



**Figure 2.** ‘Static’ permittivity  $\epsilon(0)$  of two  $\text{BaTiO}_3$  single crystals at 30 kHz measured as a function of temperature  $T$  using a resonant circuit [83]. Symbols identify the crystals. The dashed line shows the Curie temperature  $T_c$ . In the paraelectric region ( $T > T_c$ ) the lines are graphs of the universal Curie–Weiss law  $\epsilon(0, T) = C/(T - T_0)$ , with individual parameters  $C$  and  $T_0$  ( $< T_c$ ).

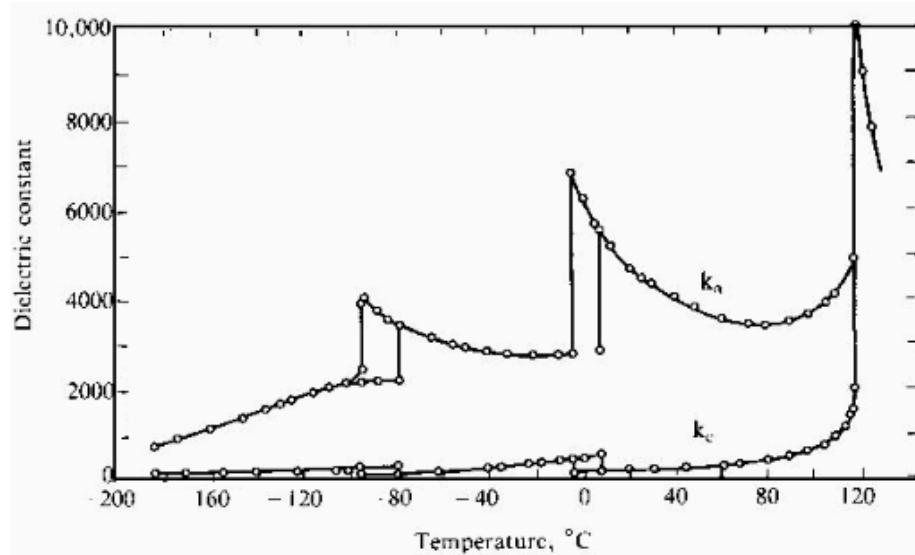


Figure 3. Dielectric constants of BaTiO<sub>3</sub> as a function of temperature <sup>[11]</sup>.

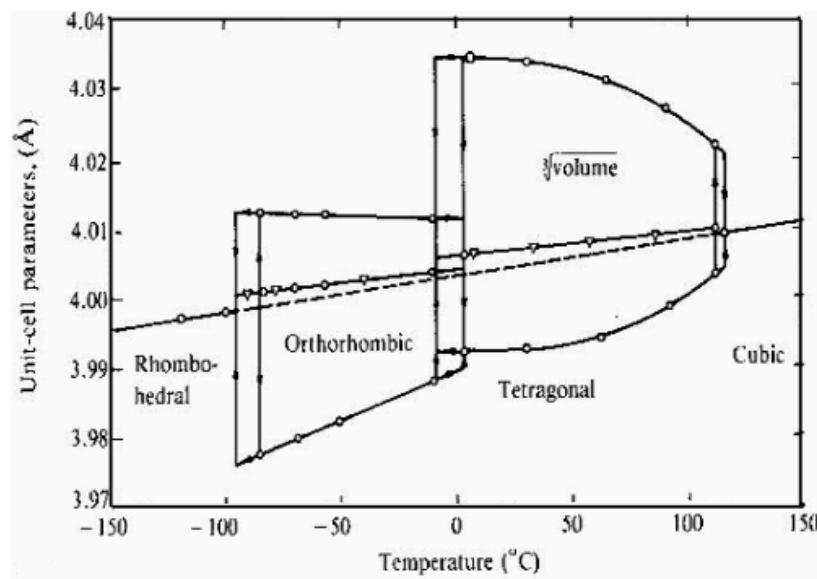


Figure 2. Lattice parameters of BaTiO<sub>3</sub> as a function of temperature <sup>[11]</sup>.

There are a number of phase transitions in BaTiO<sub>3</sub>, all of which show permittivity anomalies (susceptibility peaks in polarizability predicted by Landau theory).

However, it is not just polarization that develops when the phase transitions occur.

The polarization is associated with a spontaneous distortion of the BaTiO<sub>3</sub> crystal itself: spontaneous strain occurs which is intimately linked to the spontaneous polarization.

## Implications of Landau Theory when Elastic Coupling Occurs

For this analysis we assume terms above the quadratic in  $Q$  can be ignored.

$$\Delta G = \frac{a}{2}(T - T_c)Q^2 + \lambda Q e_s + \frac{1}{2} C e_s^2$$

In thermodynamic equilibrium:

$$\frac{dG}{dQ} = 0$$

So:

$$0 = a(T - T_c)Q + \lambda e_s$$

$$Q = -\frac{\lambda e_s}{a(T - T_c)}$$

Substitute back into free energy expression:

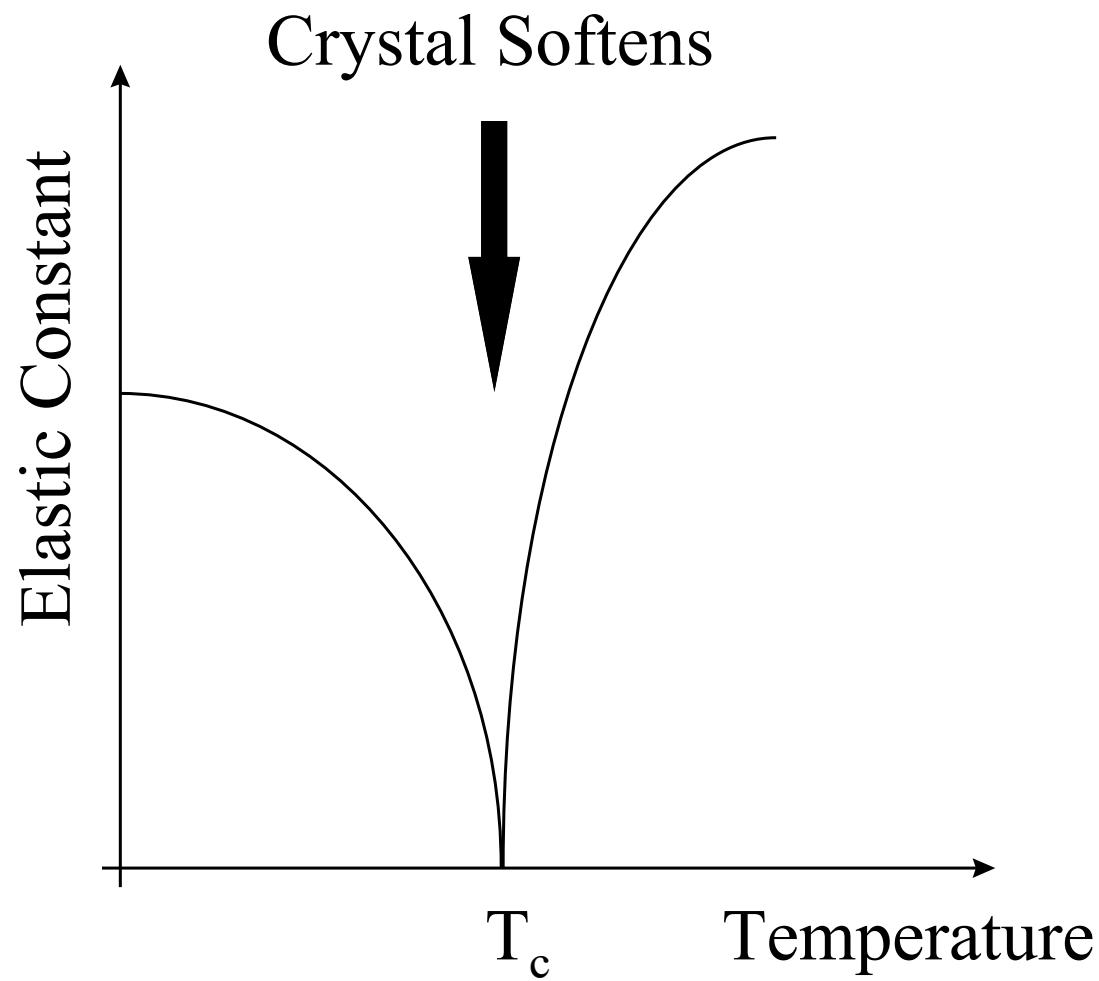
$$\Delta G = \frac{1}{2} \frac{\lambda^2 e_s^2}{a(T - T_c)} - \frac{\lambda^2 e_s^2}{a(T - T_c)} + \frac{1}{2} C e_s^2$$

$$\begin{aligned}\Delta G &= -\frac{1}{2} \frac{\lambda^2 e^2}{a(T - T_c)} + \frac{1}{2} C e_s^2 = \frac{1}{2} e_s^2 \left( C - \frac{\lambda^2}{a(T - T_c)} \right) \\ &= \frac{1}{2} e_s^2 C' \text{ where } C' = \left( C - \frac{\lambda^2}{a(T - T_c)} \right)\end{aligned}$$

The free energy change associated with transformation is now considered purely by an elastic energy, with renormalised elastic constants.  $C'$  is the effective elastic constant in the transforming system.

Consider around transition:  $T = T_c$

$$C' \rightarrow 0$$



This physical softening is a commonly observed phenomenon around  $T_c$ . Known as *Transformation Plasticity*.