Mechanisms at Structural Phase Transitions

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Definition

Structural Phase Transition:

It occurs in a crystalline solid with a sudden change in symmetry because of a change of pressure and/or temperature.

A change of the symmetry is associated with the change of the structure.

classification

- First order phase transitions.

  at the temperature T_c : $\Delta S \neq 0$

  $\Delta V \neq 0$

  Mechanisms:

  nucleation and growth,

  range of coexisting phases

  characteristic features:

  thermal hysteresis

classification

- Second order phase transitions.

  at the temperature T_c : $\Delta S = 0$

  $\Delta V = 0$

  Mechanisms:

  continuous transition

  characteristic feature:

  no thermal hysteresis;

  Landau Theory is applied

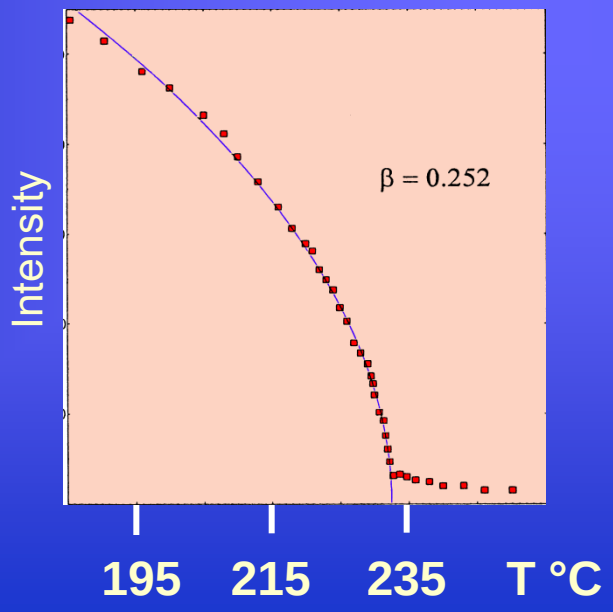
Example $Bi_2Ti_4O_{11}$

Sequence of phases

α - Phase
C2/c

$c_0(\alpha) = 2\, c_0(\beta)$
Tc = 233 °C

β - Phase
C2/m



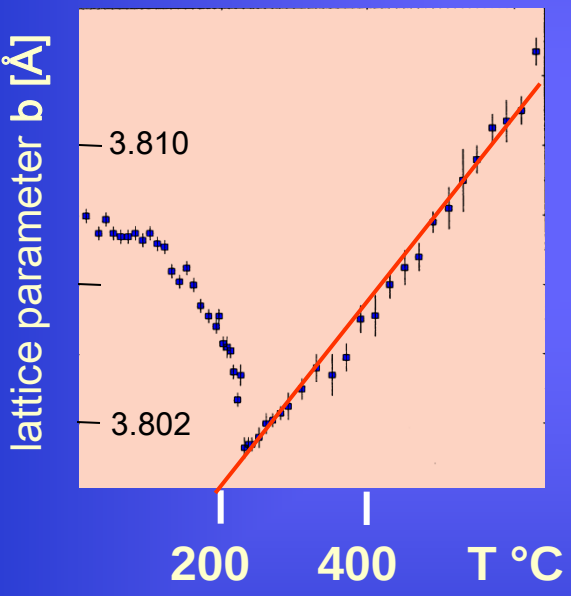
$$\sqrt{I} \sim \eta = \eta_0 (T_c - T)^{\beta}$$

η = order parameter

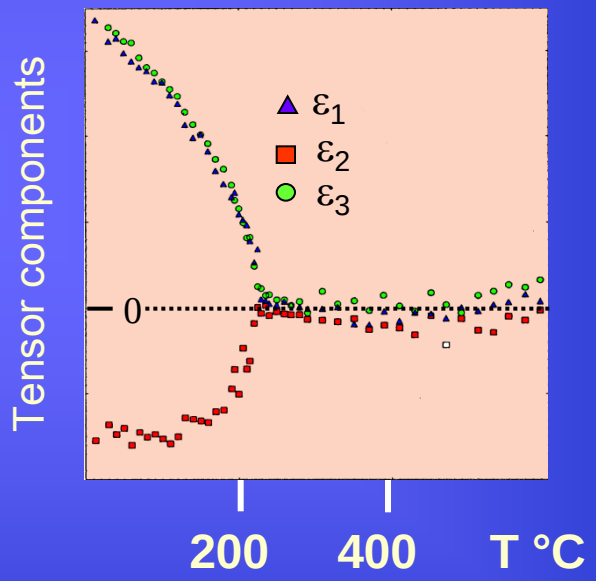
Superstructure reflection

continued $Bi_2Ti_4O_{11}$

Lattice parameter **b**



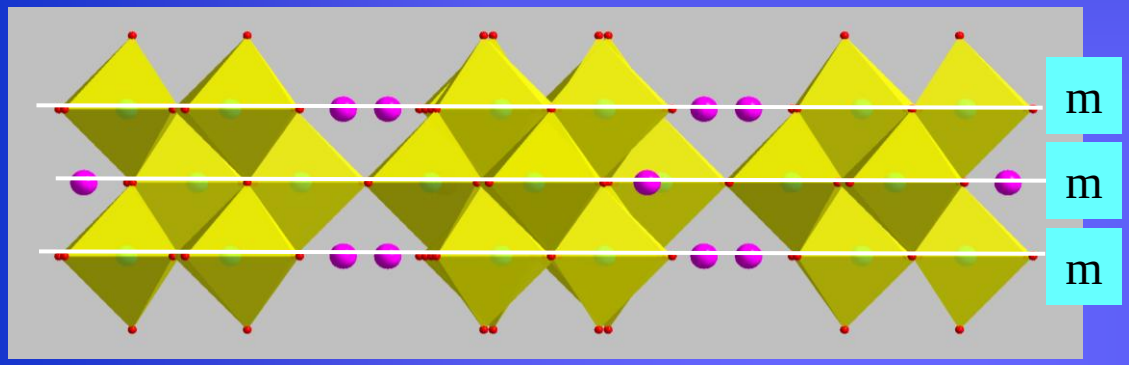
Spontaneous strain



No thermal hysteresis:
2.nd order phase transition ,
coupling between η and the spontaneous strain

continued $Bi_2Ti_4O_{11}$

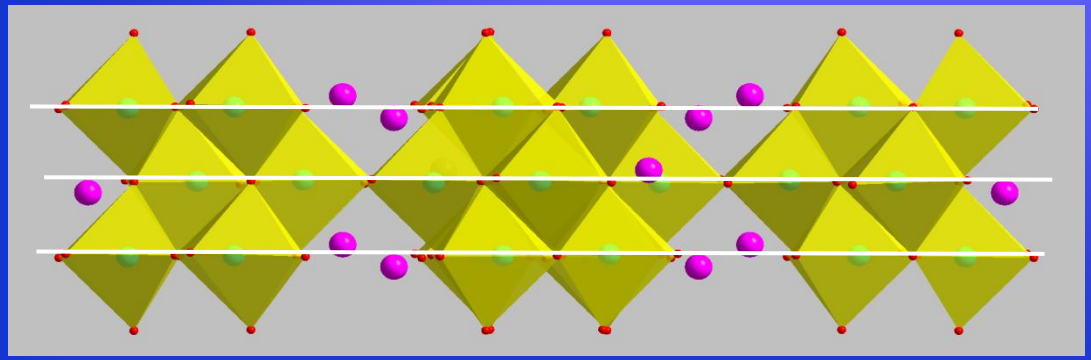
structure : β-Phase



Interpretation in terms of the Landau Theory:
At Tc a continuous shift of the Bi-atoms begins off the mirror plane.

structure : α-Phase

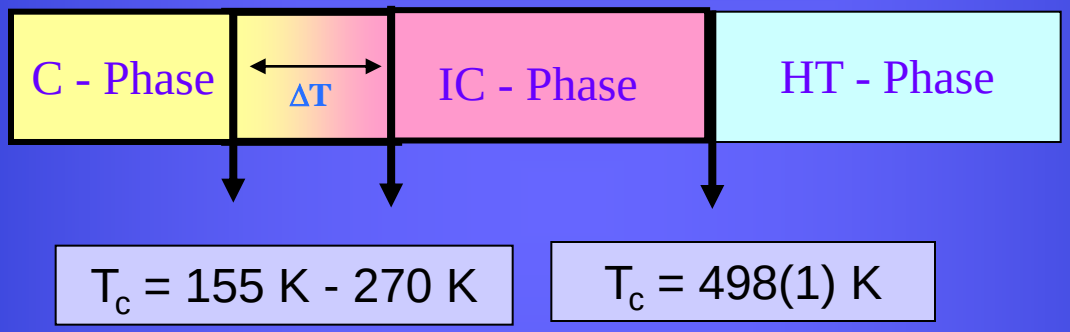
Bi - Atome



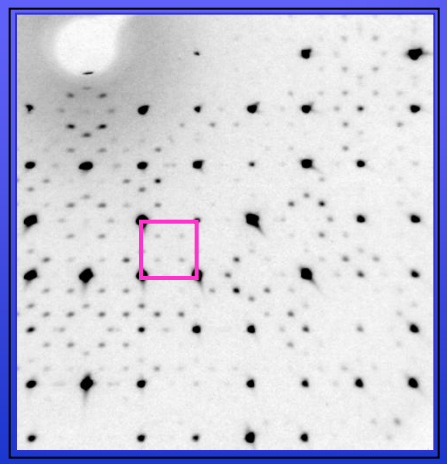
Comment:
The transition is triggered by the ordering of the lone electron pair of Bi.

Example $Ca_2CoSi_2O_7$

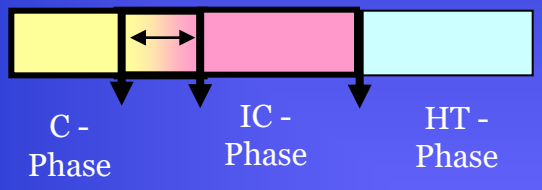
Sequence of phases:

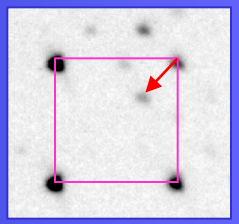


Diffraction pattern at RT:

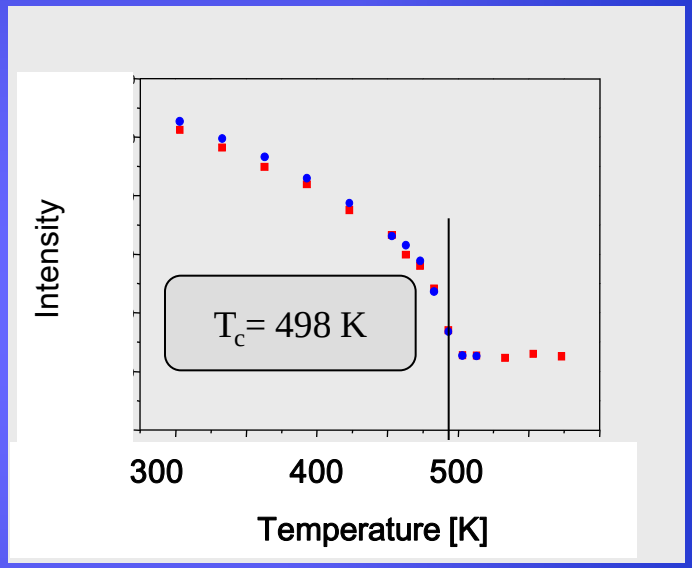


continued $Ca_2CoSi_2O_7$





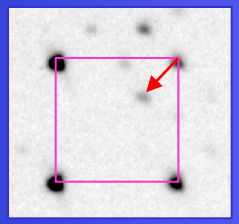
Satellite-Intensity

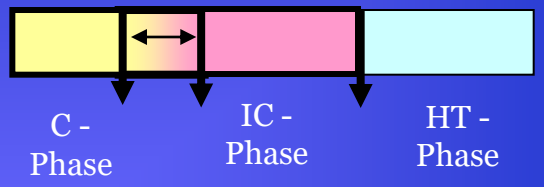


Phase transition at about 500 K

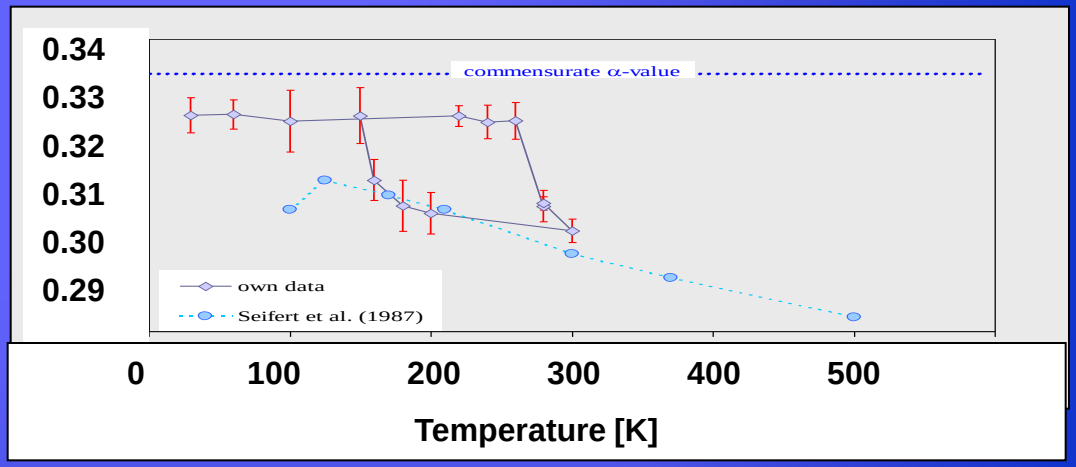
No thermal hysteresis:
2.nd order phase transition

continued $Ca_2CoSi_2O_7$





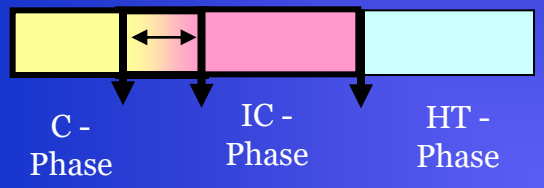
Variation of the q-vector
(incommensurate phase)



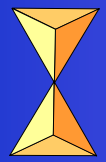
Phase transition
between 155 K und 270 K

Thermal hysteresis:
1. order phase transition

$Ca_2CoSi_2O_7$ continued

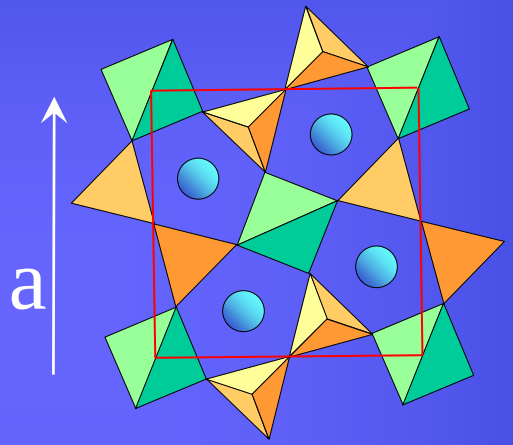


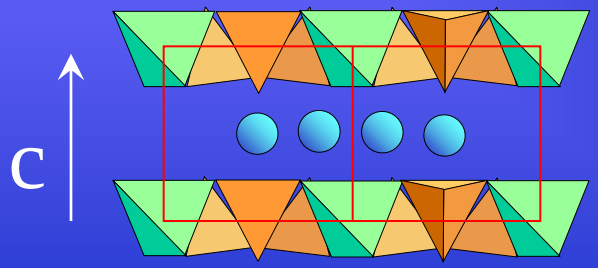
 = CoO_4

 = Si_2O_7

 = Ca

HT - Phase

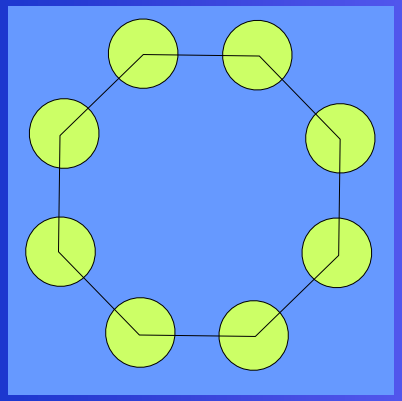


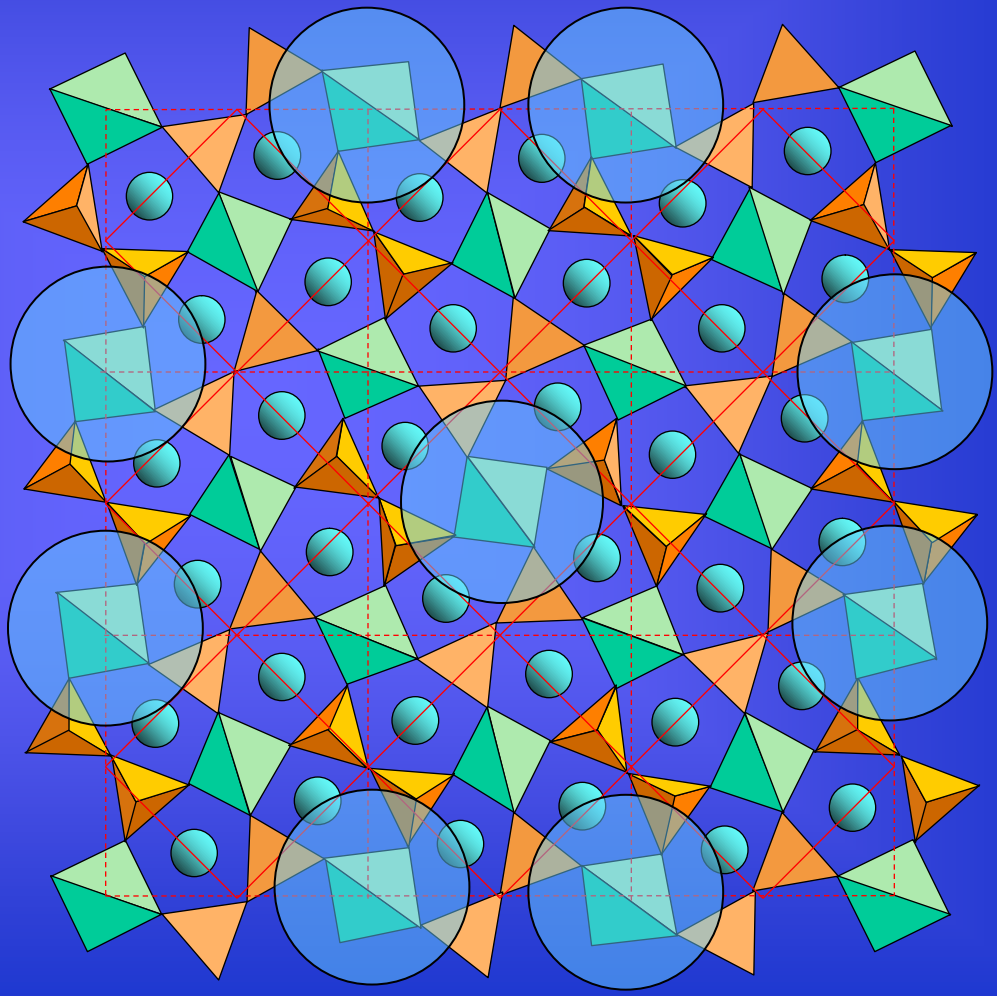


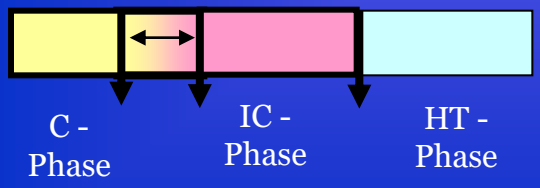
continued

$Ca_2CoSi_2O_7$

C - Phase

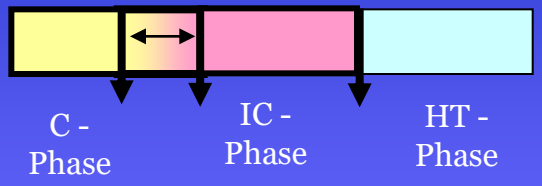






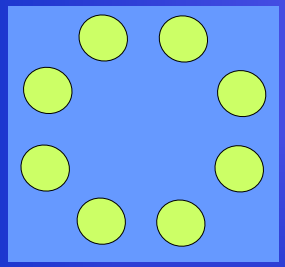
continued

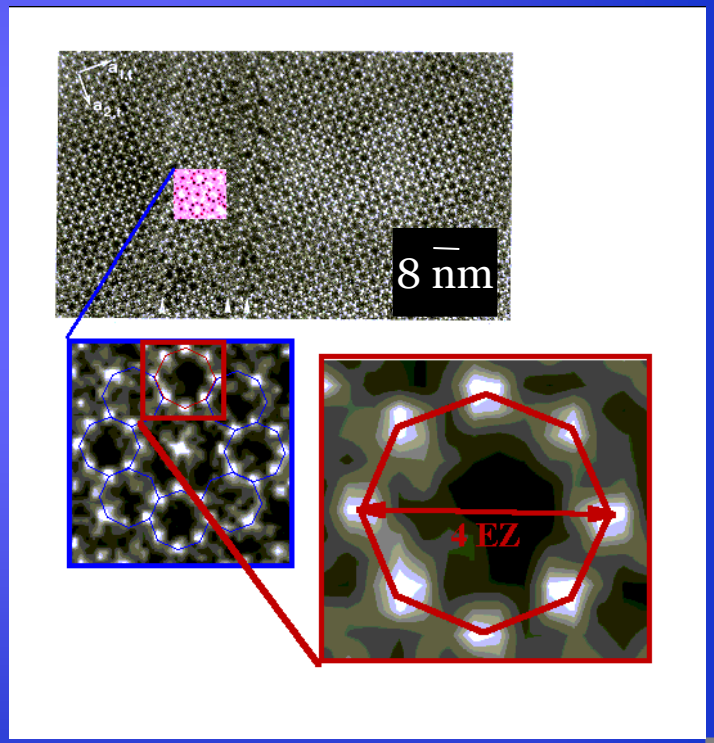
$Ca_2CoSi_2O_7$



IC - Phase

HRTEM picture at RT:
Octagonal rings.



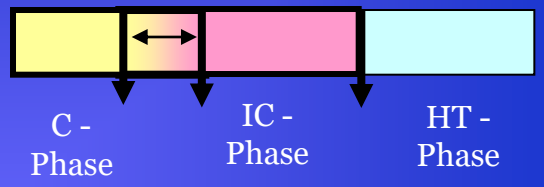


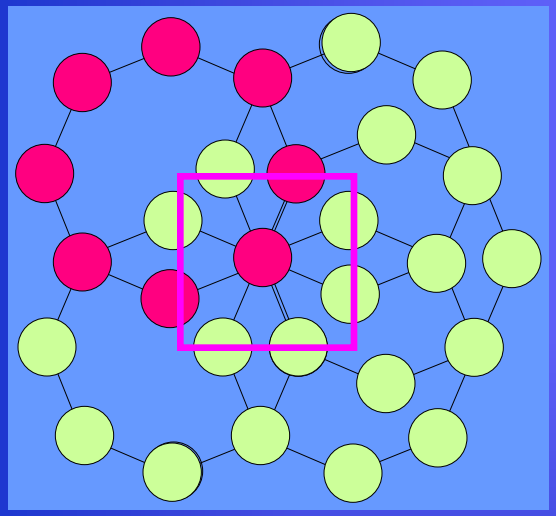
Van Heurk et al., 1992

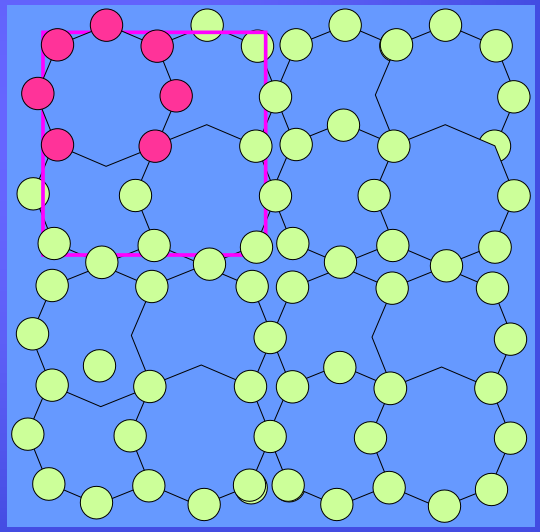
continued

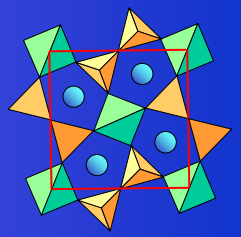
$Ca_2CoSi_2O_7$

Relationship between the phases







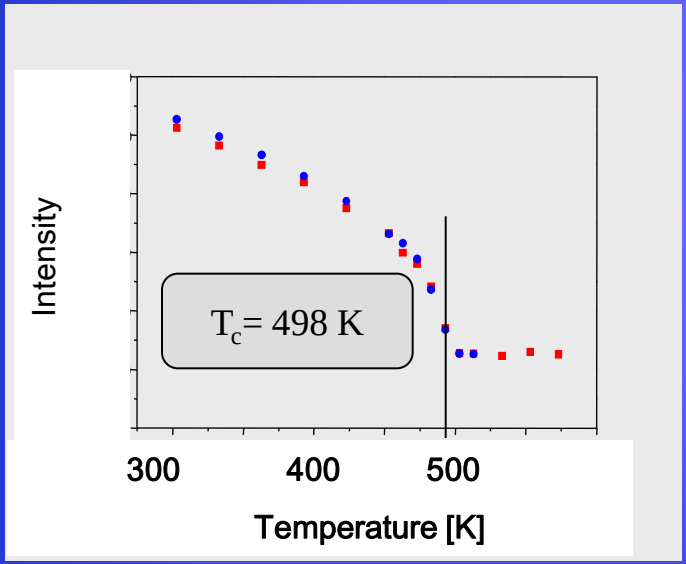


C-Phase:
An ordered superposition of octagonal rings.

IC-Phase:
An arbitrary superposition of octagonal rings.

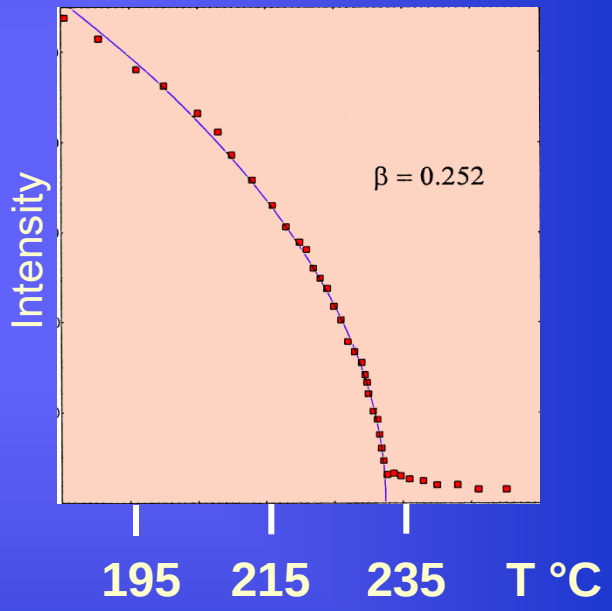
Mechanisms

$Ca_2CoSi_2O_7$



Satellite reflection

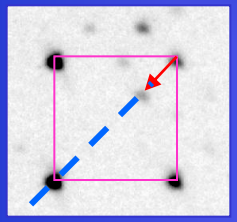
$Bi_2Ti_4O_{11}$

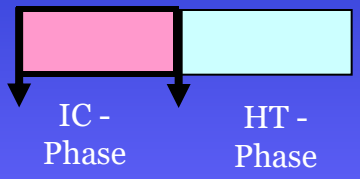


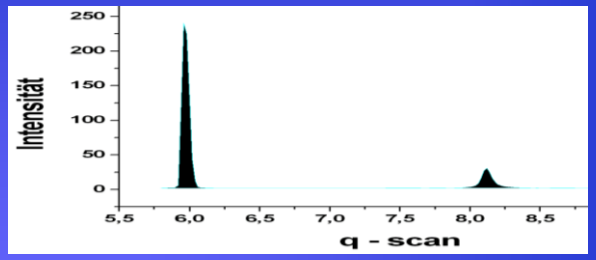
Superstructure reflection

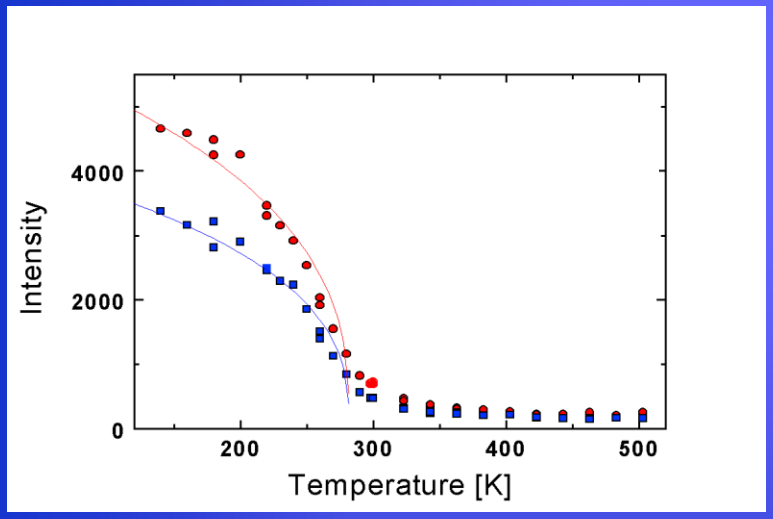
Mechanisms

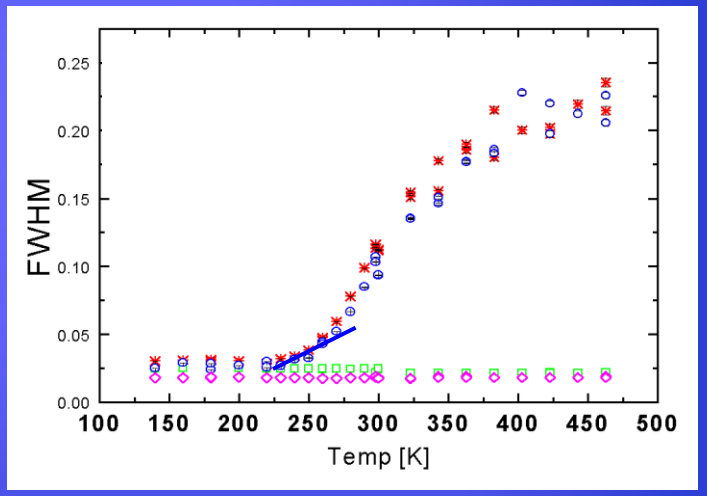
$(Ca_{1-x}Sr_x)_2MgSi_2O_7$; $x = 0.16$









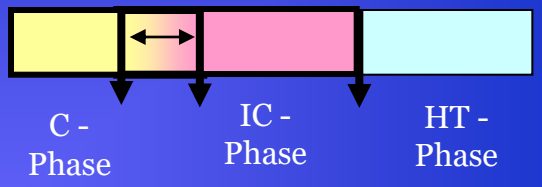


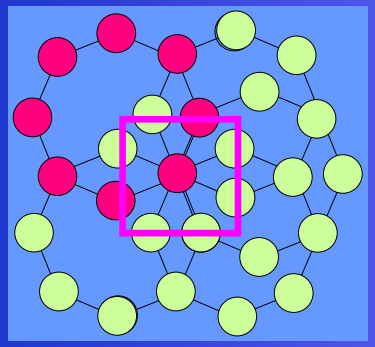
$T_c = 277$ K ? ⇔ ? $T_c = 250$ K

Transformation temperature

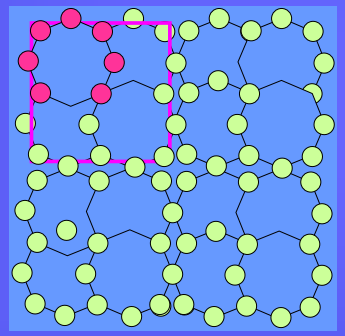
continued $Ca_2CoSi_2O_7$

Relationship between the phases

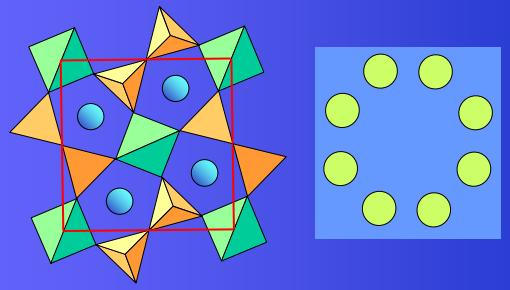




C-Phase:
An ordered superposition of octagonal rings.



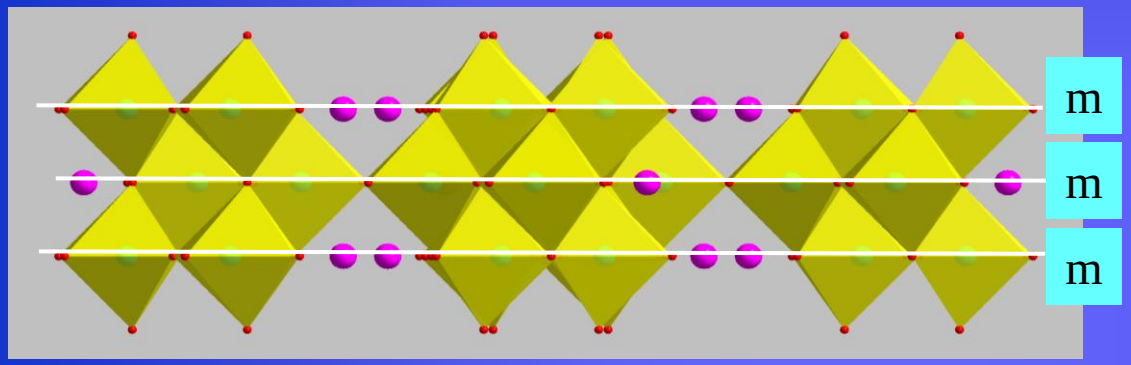
IC-Phase:
An arbitrary superposition of octagonal rings.



HT-Phase:
Domains of octagonal rings with short range order.

continued $Bi_2Ti_4O_{11}$

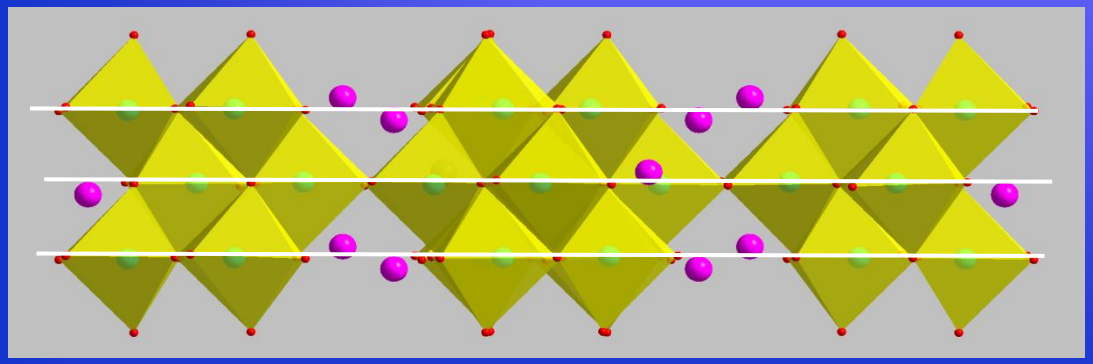
structure : β-Phase



Interpretation :
Above T_c the lone pair of Bi-atoms begins to order in domains with short range order.

structure : α-Phase

Bi - Atome



Long range order is attained at the transition point

Final question

What characterizes a continuous phase transition ?

Answer:
The continuous increase of the range of order until long range order is achieved
(not a continuous shift of atomic positions).