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Phase Transitions in Modulated Structures

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- New mechanisms in 2. order phase transitions.

Introduction

What is basic knowledge on structural phase transitions ?

Introduction

Structural Phase Transition:

A sudden change of the structure symmetry on the variation of thermodynamic parameters.

Classification of structural phase transitions.

- 1. Order Phase Transition.

  at T_c : $\Delta S \neq 0$

  $\Delta V \neq 0$

  Mechanism :
  Nucleation and growth

  Characteristic property:

  Thermal hysteresis

- 2. Order Phase Transition.

  at T_c : $\Delta S = 0$

  $\Delta V = 0$

  Mechanism :
  Continuous Transition

  Characteristic property:

  Landau theory applies

Introduction

Example: $Bi_2Ti_4O_{11}$

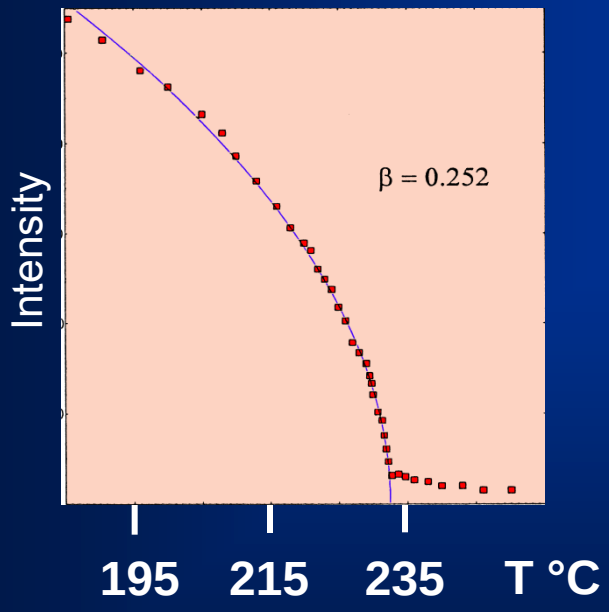
Sequence of phases

α - Phase C2/c

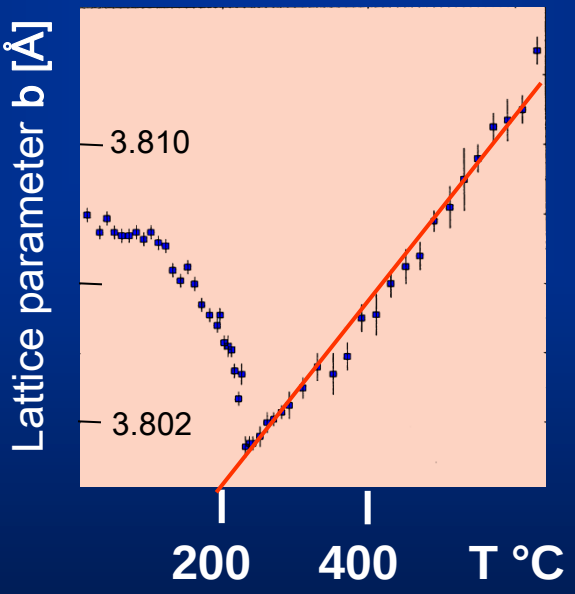
$c_0(\alpha) = 2\ c_0(\beta)$
Tc = 233 °C

β - Phase C2/m

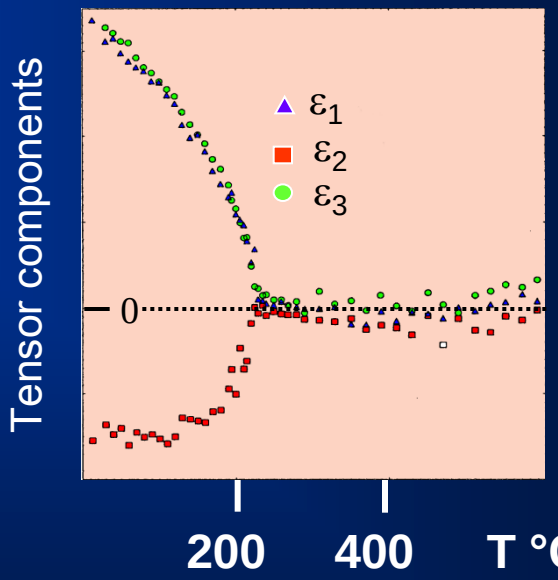
Superstructure reflection



Lattice parameter **b**



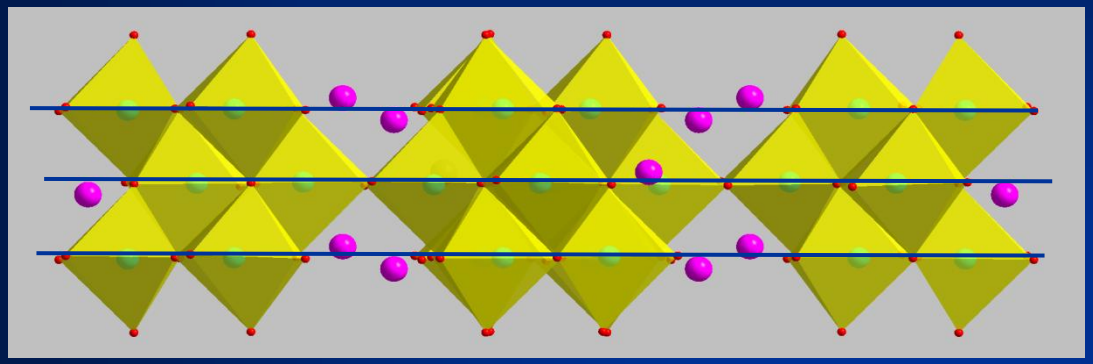
Spontaneous strain



Introduction

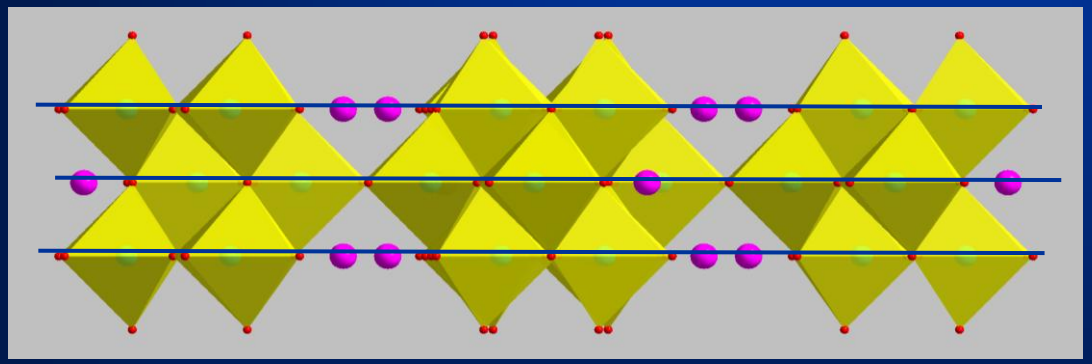
Example: $Bi_2Ti_4O_{11}$

Structure : α-phase



Bi - Atoms

Structure : β-phase



Mechanism:

Continuous shift of Bi-atoms off the mirror plane

Phase transition is triggered by the ordering of the lone pair of Bi.

Structural modulation

What is the basic knowledge on structural modulation ?

Structural modulation

Modulation:
The atomic parameters of a structure are affected by periodic functions of long periods.

The ratio between the periods of the HT-phase and the modulated phase is a small rational number

⇒ Commensurate structure

The ratio between the periods of the HT-phase and the modulated phase is not a small rational number

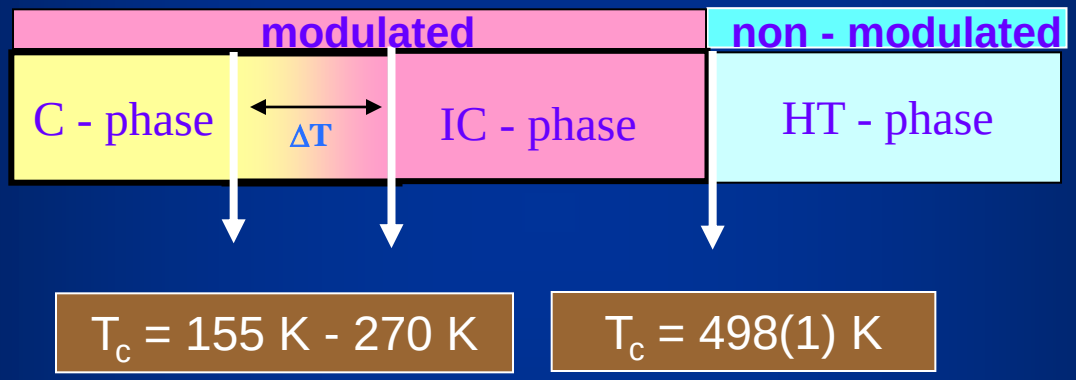
⇒ Incommensurate structure

Typical sequence of phases:

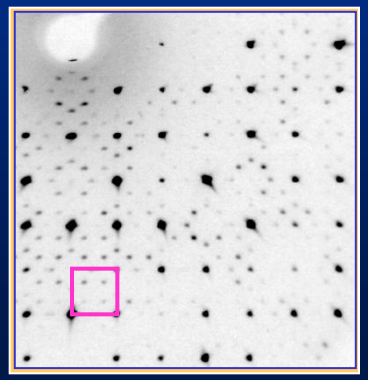
Phase Transitions in modulated structures

Example: $Ca_2CoSi_2O_7$

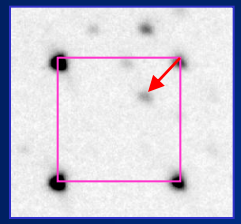
Sequence of phases:



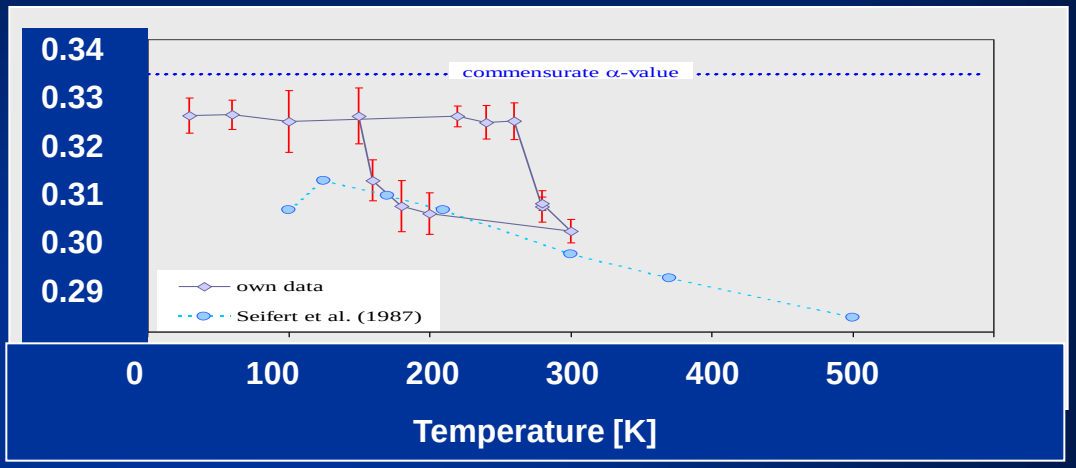
Diffraction pattern at RT:



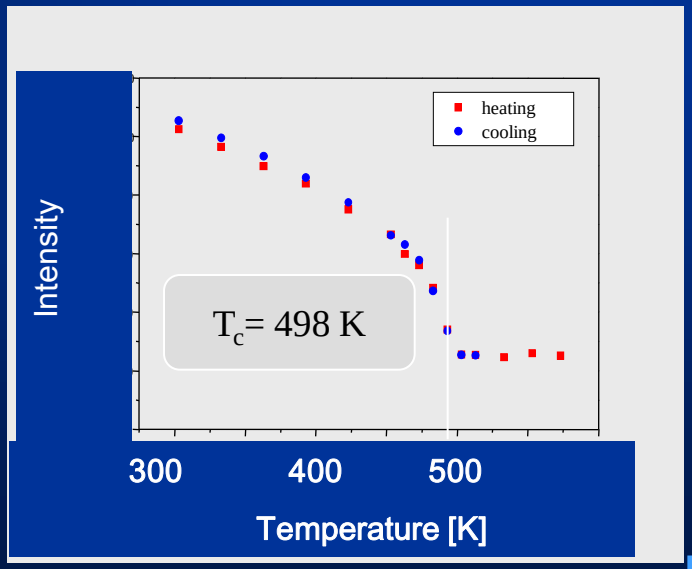
Example: $Ca_2CoSi_2O_7$



Variation of the q-vector

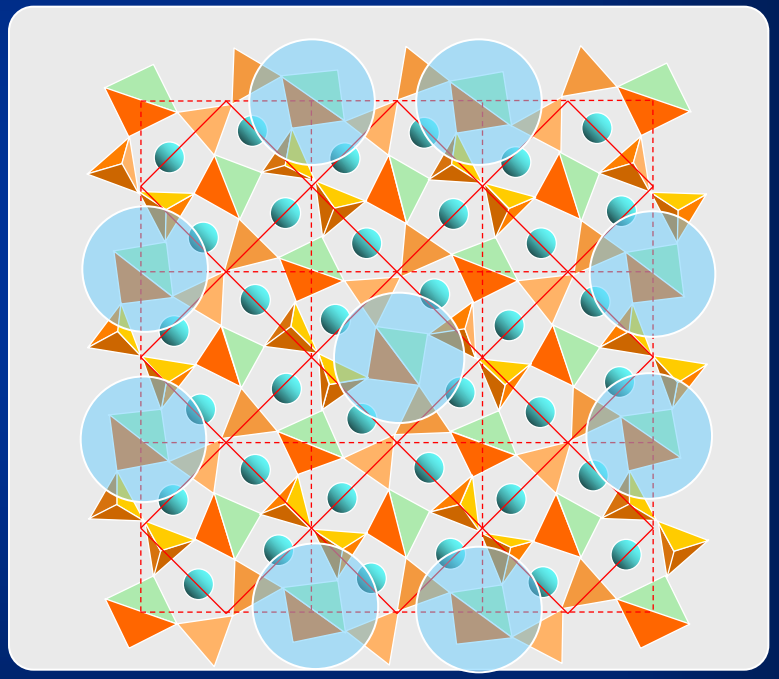


Satellite intensity



Example: $Ca_2CoSi_2O_7$

The structure of the commensurate LT - phase:

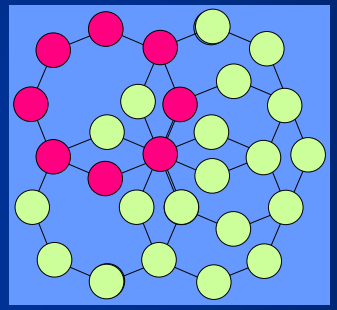


Characteristic feature:
Centers of 6-fold coordinated Calcium are ordered in octagons.

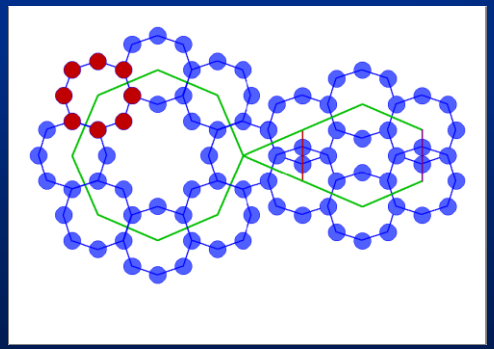
Example: $Ca_2CoSi_2O_7$

Claim: The modulated structures are different degrees of condensations of octagonal clusters with 6-fold coordinated Calcium:

The structure of the commensurate LT - phase:

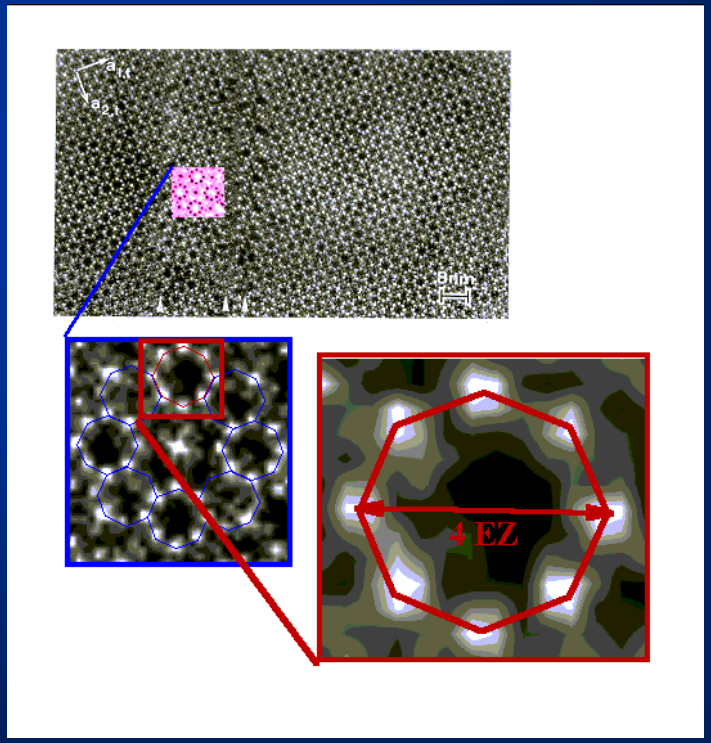


The structure of the incommensurate phase:



Example: $Ca_2CoSi_2O_7$

Proof: TEM pictures of the IC-phase at RT ;
octagonal rings with the size of the rings of 6-fold coordinated Calcium:



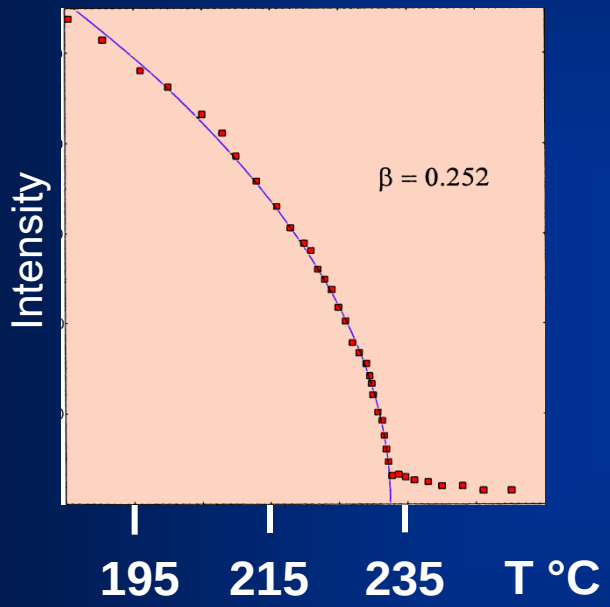
After Van Heurk et al., 1992

New concept

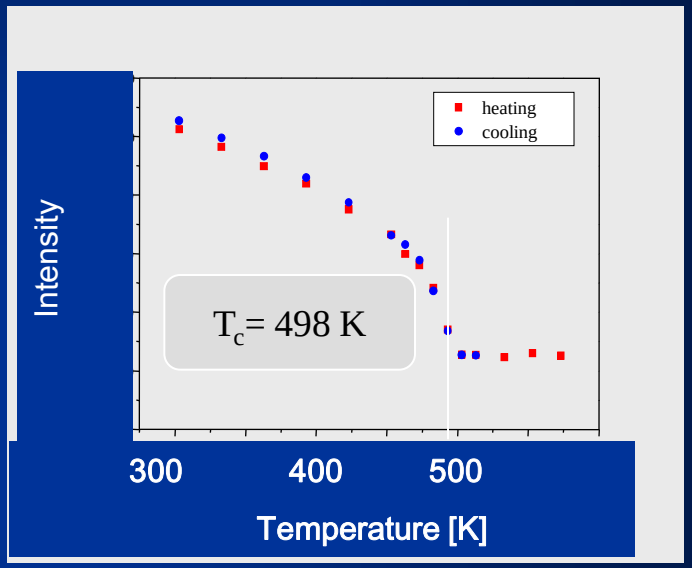
What is new for 2. order phase transitions ?

New mechanisms

Superstructure reflection



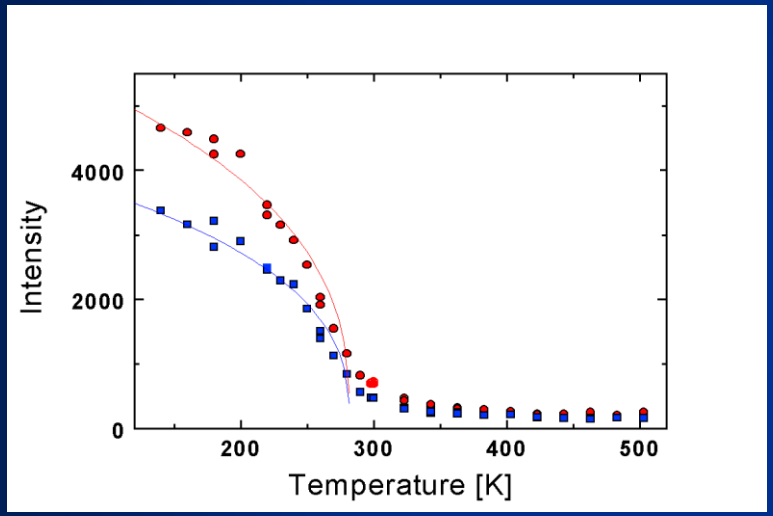
$Bi_2Ti_4O_{11}$

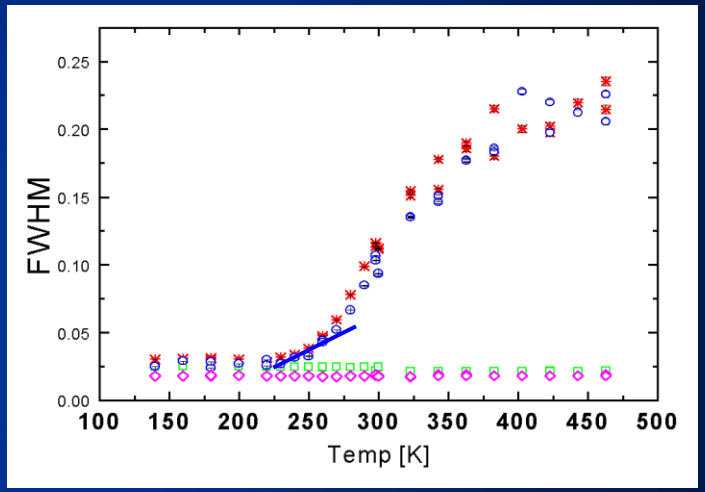


$Ca_2CoSi_2O_7$

New mechanisms

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



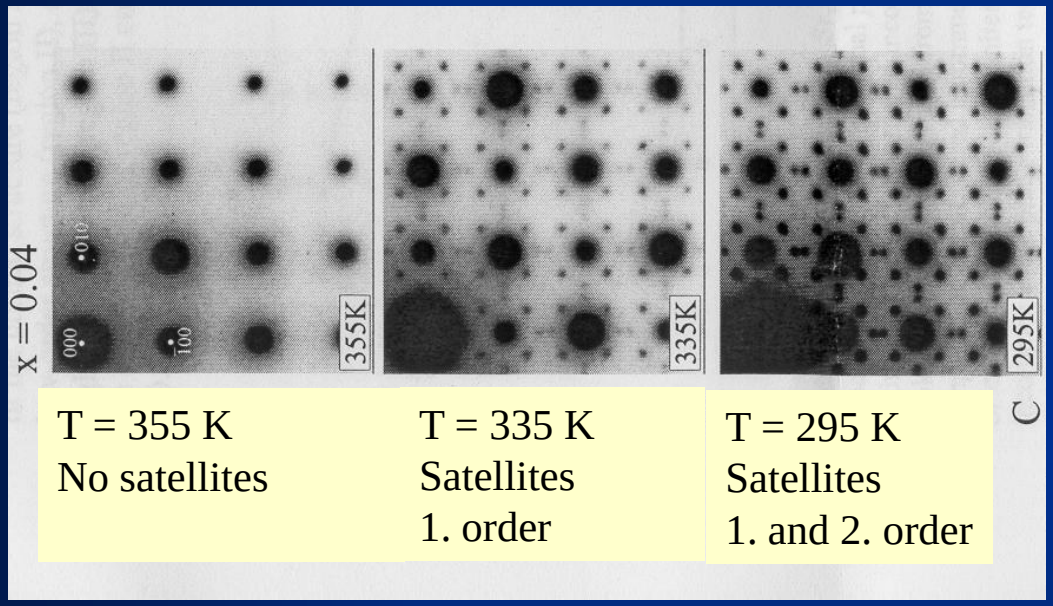


Tc = 277 K ? ⇔ ? Tc = 250 K

Transformation temperature

New mechanisms

TEM diffraction pattern of the incommensurate phase $(Ca_{1-x}Sr_x)_2MgSi_2O_7$.



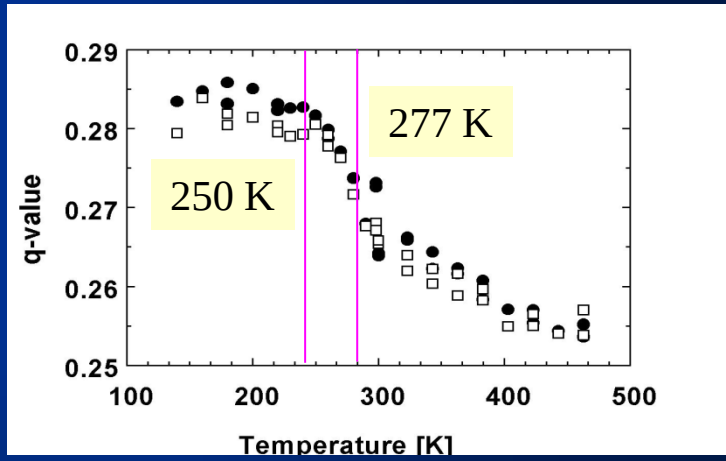
T = 355 K
No satellites

T = 335 K
Satellites
1. order

T = 295 K
Satellites
1. and 2. order

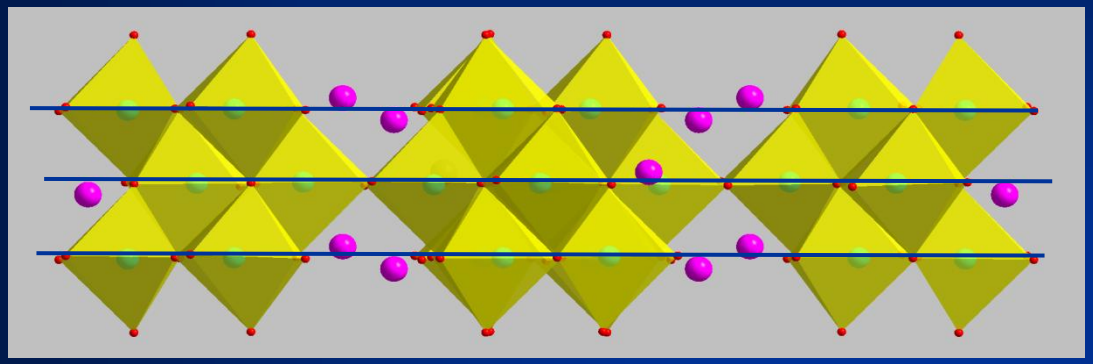
After M. Schosnig et al., 2000

Variation of the q-vector



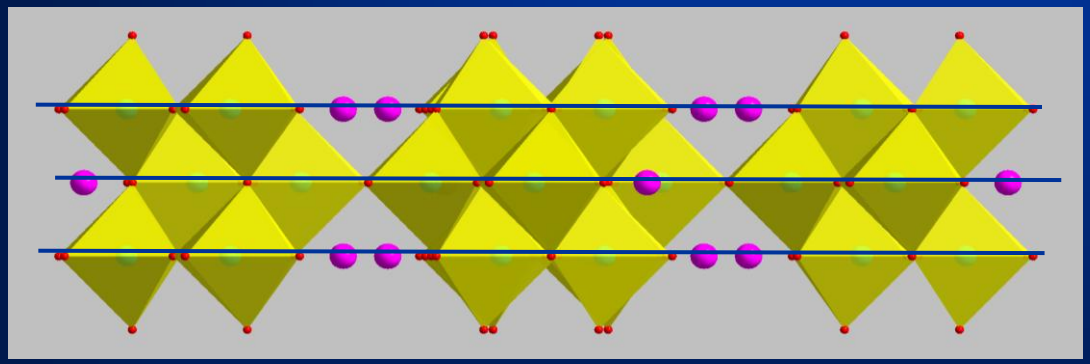
Example: $Bi_2Ti_4O_{11}$

Structure : α-phase



Bi - Atoms

Structure : β-phase



Mechanism:
Continuous shift of Bi-atoms off the mirror plane
Phase transition is triggered by the ordering of the lone pair of Bi.

New mechanisms

The new interpretation of a 2. order phase transition:

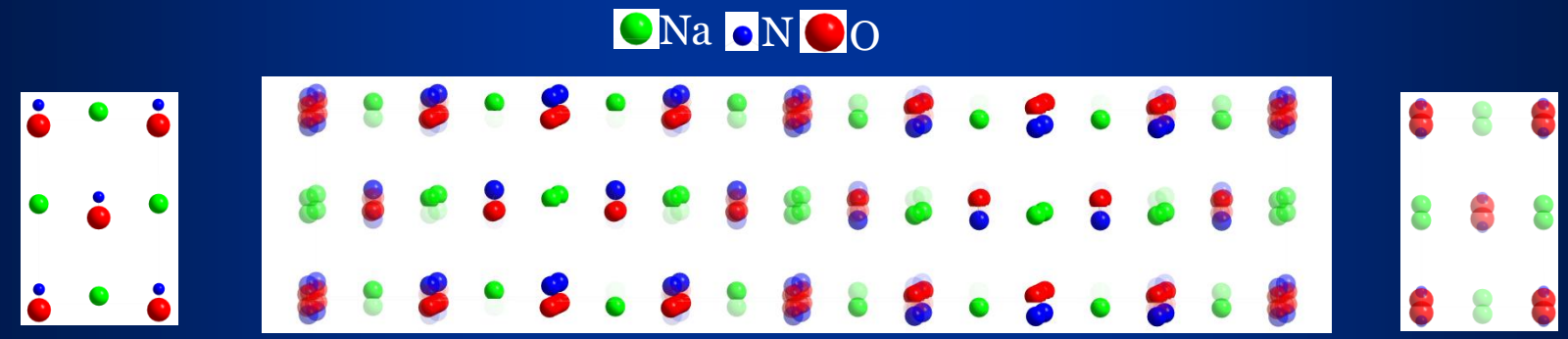
- A 2. order phase transition does not occur at a point,
  the Landau concept is valid far above and far below the transition .
- Fluctuations determine the temperature regime around
  a phase transition.
- Structural motives of the LT phase with short range order
  exist far above the transition as precursors in the HT phase.
  There is a continuous variation of the degree of order with
  temperature.
- The definition of a “transition temperature”
  has some arbitrariness.

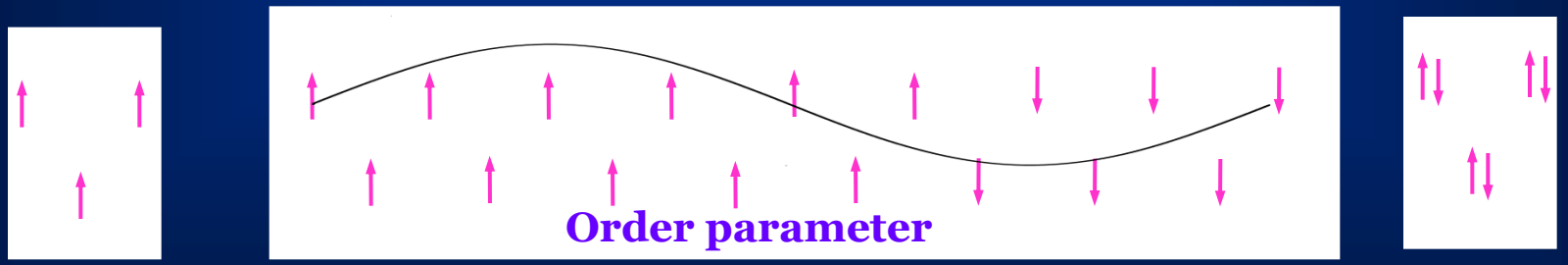
Structural modulation

Example: $NaNO_2$

Sequence of phases:

Ferroelectric phase ⟷ Modulated – phase $\Delta T = 1.2$ ° ⟷ Paraelectric phase





Example: $NaNO_2$

Reciprocal space: