Introduction to Structural Phase Transitions

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Definition

Structural Phase Transition:

In a crystalline solid distortions may occur when thermodynamical variables are changed. A consequence of such distortions is a change of symmetry at discrete values of these variables.

Thermodynamical variables:

temperature [T],
pressure [p],
chemical composition (molar fraction) [X].

Two regions α and β in the thermodynamical space differ by the sets of symmetry elements.

Thermodynamical Principles

An isotropic, homogeneous substance is specified by the **Gibbs Potential** (Gibbs' Free Energy):

$G = U - TS + pV$

Consider a system with the variables: p, T, N_j

N_j : number of molecules of the species j.

$G(p, T, N_j)$

$$dG = \frac{\partial G}{\partial p}\,dp + \frac{\partial G}{\partial T}\,dT + \sum_i \frac{\partial G}{\partial N_i}\,dN_i$$

$$\frac{\partial G}{\partial T} = -S \qquad \frac{\partial G}{\partial p} = V$$

Thermodynamical Principles

For the system with the variables: p, T, N_j
we get:

$$dG = Vdp - SdT + \sum_i \mu_i dN_i$$

$\frac{\partial G}{\partial N_i} = \mu_i$ = chemical potential of the molecule of type i

Consider a homogeneous and isotropic substance
which consists of two components A and B (e.g. solid solution).

Asumption:

There are two phases α and β, which are described in the variables T, p, X.

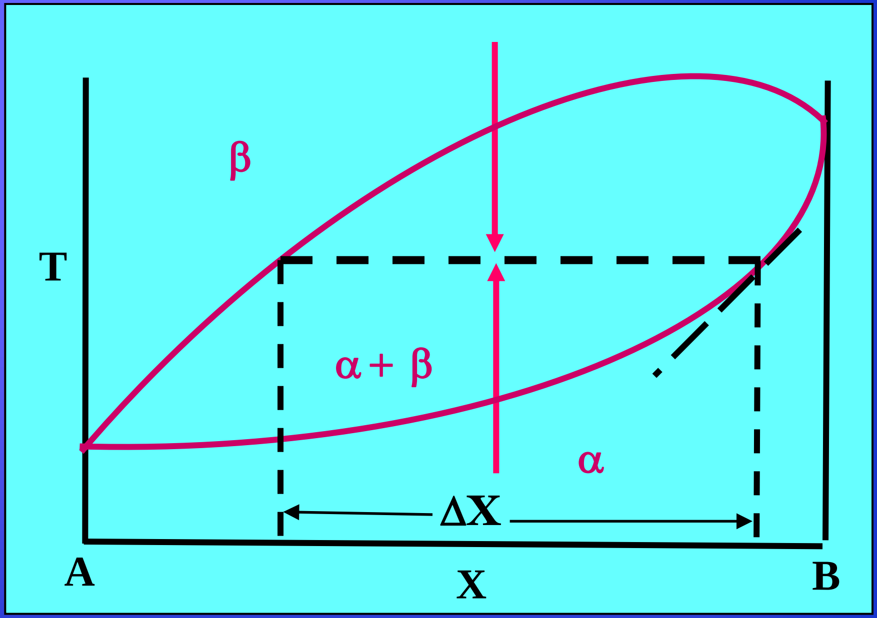
Thermodynamical Principles

The transition from one state to the other can be described in a phase diagram (e. g. with p=const.):

⇒ T – X diagram (if p=const.):

Reversible change from state α to state β. Two different ways of transition from state α to state β are observed.

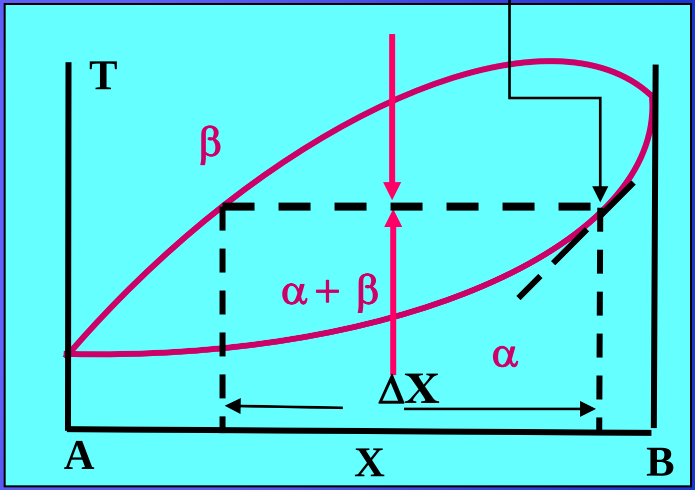
a) A general observation:
There are two border lines, which separate the region of the pure phases α and β from a region α + β.



Thermodynamical Principles

The boarder lines in this diagram are described by the **Gibbs – Konovalow Equation**.

$$slope = \frac{\partial T}{\partial X^{\alpha}}\Big|_p$$



$$\frac{\partial T}{\partial X^{\alpha}}\Big|_p = -\frac{\left[\left(\frac{\partial \mu_A^{\alpha}}{\partial X_A}\right)_{T,p} + \left(\frac{\partial \mu_B^{\alpha}}{\partial X_B}\right)_{T,p}\right]\Delta X}{\Delta S + (S_A^{\alpha} - S_B^{\alpha})\,\Delta X}$$

$$\frac{\partial T}{\partial X^{\alpha}}\Big|_p = boarder\ line\ \ of\ \ \ state\ \ \alpha$$

$$\left(\frac{\partial \mu_A^{\alpha}}{\partial X_A}\right)_{T,p} =$$ mole fraction partial derivative of the chemical potential of phase α of component A

S_A^{α} = partial molar entropy of component A

$\Delta S = S^{\alpha} - S^{\beta}$ = molar entropy difference

Thermodynamical Principles

Discussion:

Transition from state α to state β.
In phase α a small nucleus with symmetry β is formed. It grows at the expense of α.

Since $\Delta X \neq O \Rightarrow \Delta S \neq O$

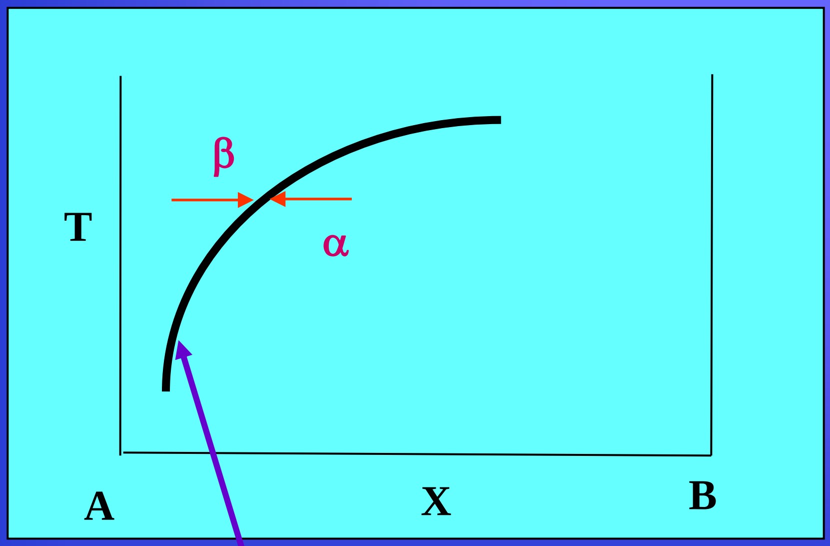
$$\frac{\partial T}{\partial X^{\alpha}}\Big|_p = -\frac{\left[\left(\frac{\partial \mu_A^{\alpha}}{\partial X_A}\right)_{T,p} + \left(\frac{\partial \mu_B^{\alpha}}{\partial X_B}\right)_{T,p}\right]\Delta X}{\Delta S + (S_A^{\alpha} - S_B^{\alpha})\,\Delta X}$$

Remember:
The mechanism of the phase transition, if $\Delta S \neq O$, is nucleation and growth.

Thermodynamical Principles

b)

Continuous and reversible change from state α to state β with $\Delta X = O$ at the phase boundary. However, a discontinuous change of symmetry.

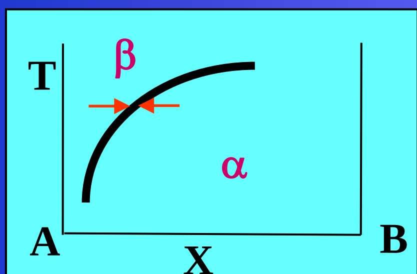


phase boundary

Thermodynamical Principles

Discussion:

At the transition from state α to state β.



$$\left.\frac{\partial T}{\partial X^{\alpha}}\right|_{p} \neq 0$$

$$\left.\frac{\partial T}{\partial X^{\alpha}}\right|_{p} = -\frac{\left[\left(\frac{\partial \mu_A^{\alpha}}{\partial X_A}\right)_{T,p} + \left(\frac{\partial \mu_B^{\alpha}}{\partial X_B}\right)_{T,p}\right]\Delta X}{\Delta S + (S_A^{\alpha} - S_B^{\alpha})\,\Delta X}$$

Since ΔX = O ⇒ ΔS = O

A similar discussion in a **p – X diagram** (if T=const.):

If ΔX = O ⇒ ΔV = O

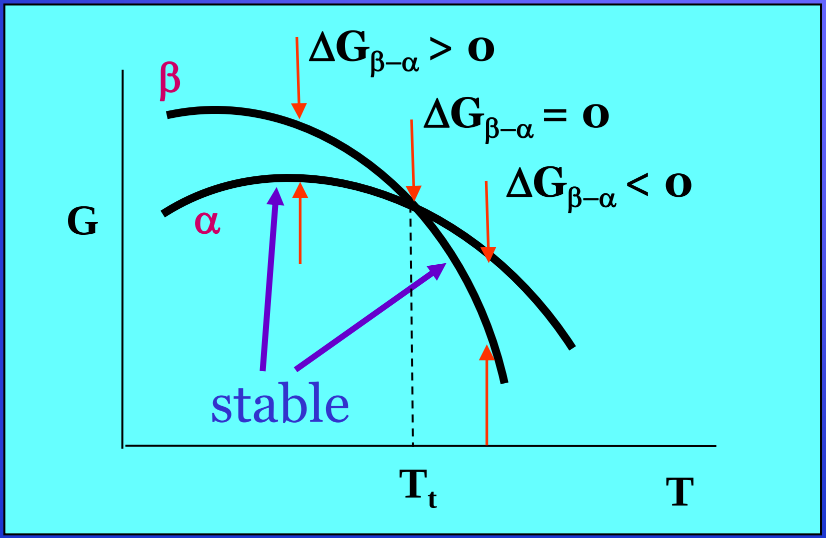
Remember:
The mechanism of the phase transition is a continuous change in entropy and volume.

Discussion of the Gibbs Potential

We discuss a phase transition when T is varied.

⇒ G – T diagram (if p,X=const.):

$$G_\beta - G_\alpha = \Delta G_{\beta-\alpha}$$



At the transition from state α to state β:

$$\Delta G = o$$

T_t = transition temperature

Discussion of the Gibbs Potential

What is common to both forms of a phase transition:
The Gibbs potential is a continuous function.

$\mathbf{G_\alpha < G_\beta}$	α phase is stable
$\mathbf{\Delta G = 0}$	At T_t:
$\mathbf{G_\beta < G_\alpha}$	β phase is stable

At T_t: $\frac{\partial G}{\partial T} = -S$ $\quad \Delta S \neq O$

This is a transition of type a)

In a **G – p** diagram :

$\frac{\partial G}{\partial p} = V$ $\quad \Delta V \neq O$

Discussion of the Gibbs Potential

Properties of the G – T diagram (if p,X=const.):

We expand G(T) in a series about the point T_t:

$$G(T) = G(T_t) + \frac{\partial G}{\partial T}\Big|_{T=T_t}(T - T_t) + \tfrac{1}{2}\frac{\partial^2 G}{\partial T^2}\Big|_{T=T_t}(T - T_t)^2 + \ldots\ldots$$

Using the relations:

$$\frac{\partial G}{\partial T} = -S$$

$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T} = -{c_p}/{T}$$

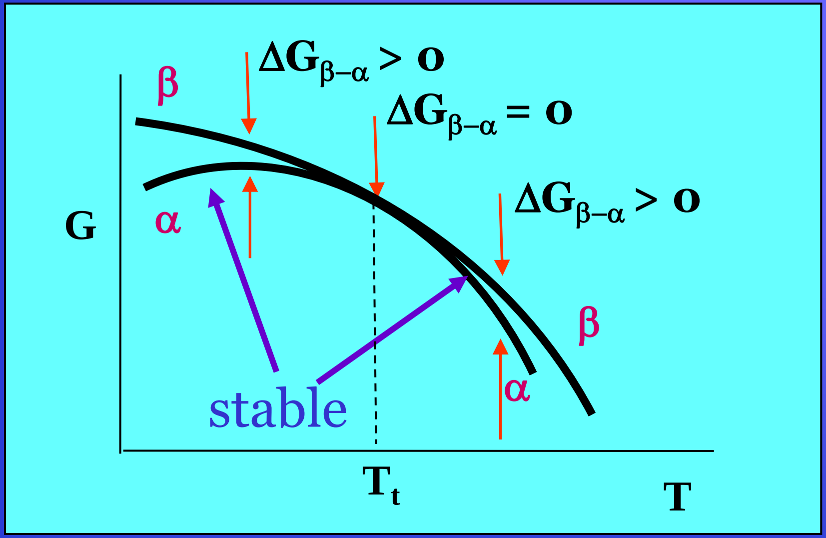
$$G(T) = G(T_t) - S(T_t)(T - T_t) - \tfrac{1}{2}\frac{c_p}{T_t}(T - T_t)^2 + \ldots\ldots$$

Discussion of the Gibbs Potential

We discuss now the case b) $\Delta S = O, \Delta V = O$

$$\Delta G(T) = G_\alpha - G_\beta - \tfrac{1}{2}\frac{\Delta c_p}{T_t}(T - T_t)^2 + \ldots\ldots$$

(an even function in T)

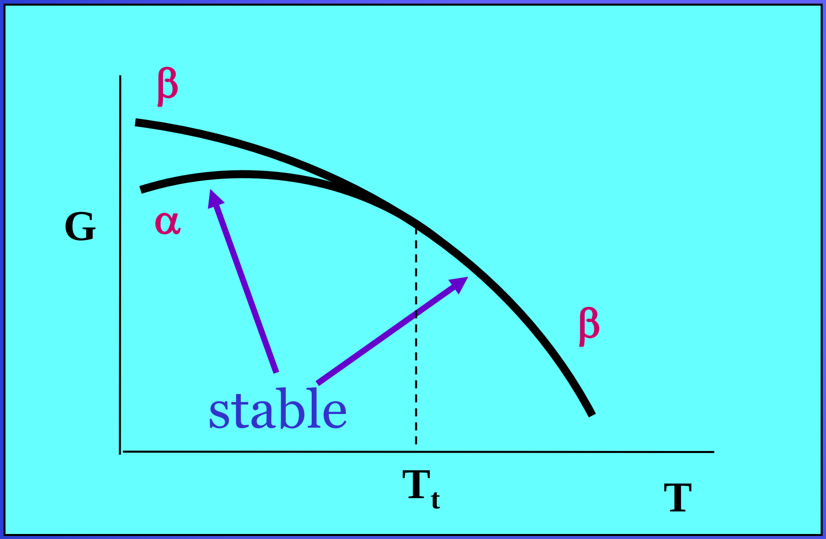


α phase is stable
for $T<T_t$ and $T> T_t$

This is no phase transition !!

Discussion of the Gibbs Potential

Solution: symmetry α is not possible above T_t



At $T=T_t$:
$\Delta S=0$ means the curves have the same slope but different curvatures

Classification

- 1. Order phase transition (after Ehrenfest)

At the temperature T_t :

$$\Delta G(T \to T_t) = 0$$

$$\frac{\partial \Delta G}{\partial T} = -\Delta S(T \to T_t) \neq 0$$

$$\frac{\partial \Delta G}{\partial p} = \Delta V(T \to T_t) \neq 0$$

$$\frac{\partial^2 \Delta G}{\partial T^2} = -\frac{c_p}{T_t}(T \to T_t) \neq 0$$

useful properties:

$$\frac{\partial^2 G}{\partial p^2} = \left(\frac{\partial V}{\partial p}\right)_T = -\beta V$$

β=compressibility

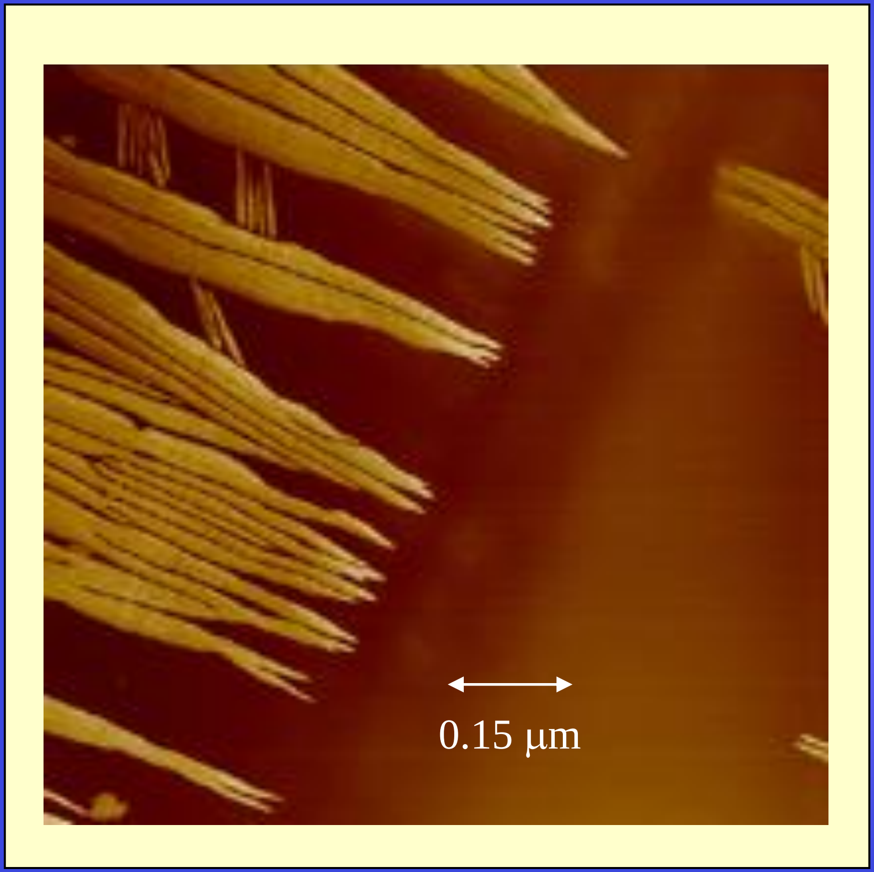
$$\frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

α=thermal expansion coefficient

Mechanism: nucleation and growth

Typical property: thermal hysteresis

Example



Atomic Force Microscope (AFM) picture of the transition of Polydiethylsiloxane (PDES) at T = –6 °C

Classification

- 2. Order phase transition (after Ehrenfest)

At the temperature T_t :

$$\Delta G(T \rightarrow T_t) = 0$$

$$\frac{\partial \Delta G}{\partial T} = -\Delta S(T \rightarrow T_t) = 0$$

$$\frac{\partial \Delta G}{\partial p} = \Delta V(T \rightarrow T_t) = 0$$

$$\frac{\partial^2 \Delta G}{\partial T^2} = -\frac{c_p}{T_t}(T \rightarrow T_t) \neq 0$$

useful properties:

$$\frac{\partial^2 G}{\partial p^2} = \left(\frac{\partial V}{\partial p}\right)_T = -\beta V$$

β=compressibility

$$\frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

α=thermal expansion coefficient

Mechanism: continuous phase transition

Typical property: Landau theory applies

Introduction to 2. order phase transition

Properties of a 2. order phase transition:

- A continuous change of the structure at the phase boundary, but a discontinuous change of the symmetry.
  At the phase boundary both structures become indistinguishable

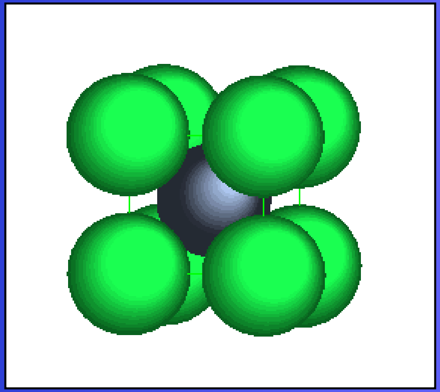
- The phase transition occurs without the co-existence of two phases.
  i.e. no nucleation and growth

- Typical mechanisms:
  - Order – Disorder processes
  - Displacive deformations

Introduction to 2. order phase transition

Examples:

a) The ß – ß‘ transition of CuZn.



At low temperatures:
CsCl-type, cubic P-lattice.

At higher temperatures:
statistical occupation of both sites by Cu and Zn, cubic I-lattice.

Degree of order is given by an **order parameter**:

$$\eta = 2q_{Cu} - 1$$

q_{Cu}= fraction of (000)-sites occupied by Cu-atoms

Introduction to 2. order phase transition

q_{Cu} =1 ⇒ **η=1** complete order P-lattice

q_{Cu} =0.5 ⇒ **η=0** complete disorder I-lattice

We can see the essential properties:

(i) A continuous variation of η between 0.......1

(ii) A discontinuous change of translational symmetry at the transformation temperature.

(ii) No co-existence of two phases.

This is a typical example of an order – disorder transformation.

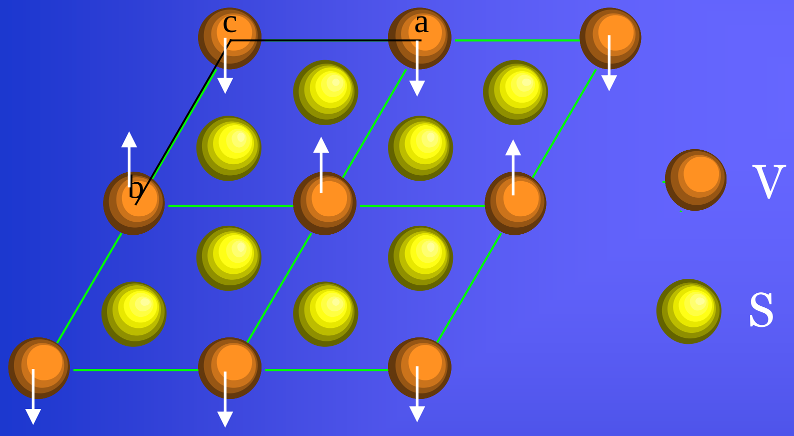
Introduction to 2. order phase transition

MnP-Type	NiAs-Type
Pcmn	P63/mmc

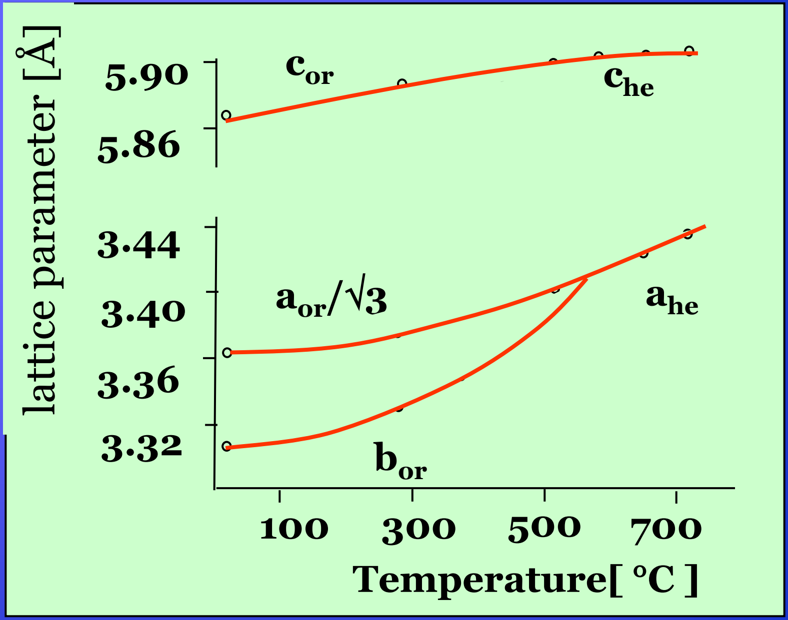
580 °C

b) The transition of VS.

Order parameter = shift of Vanadium



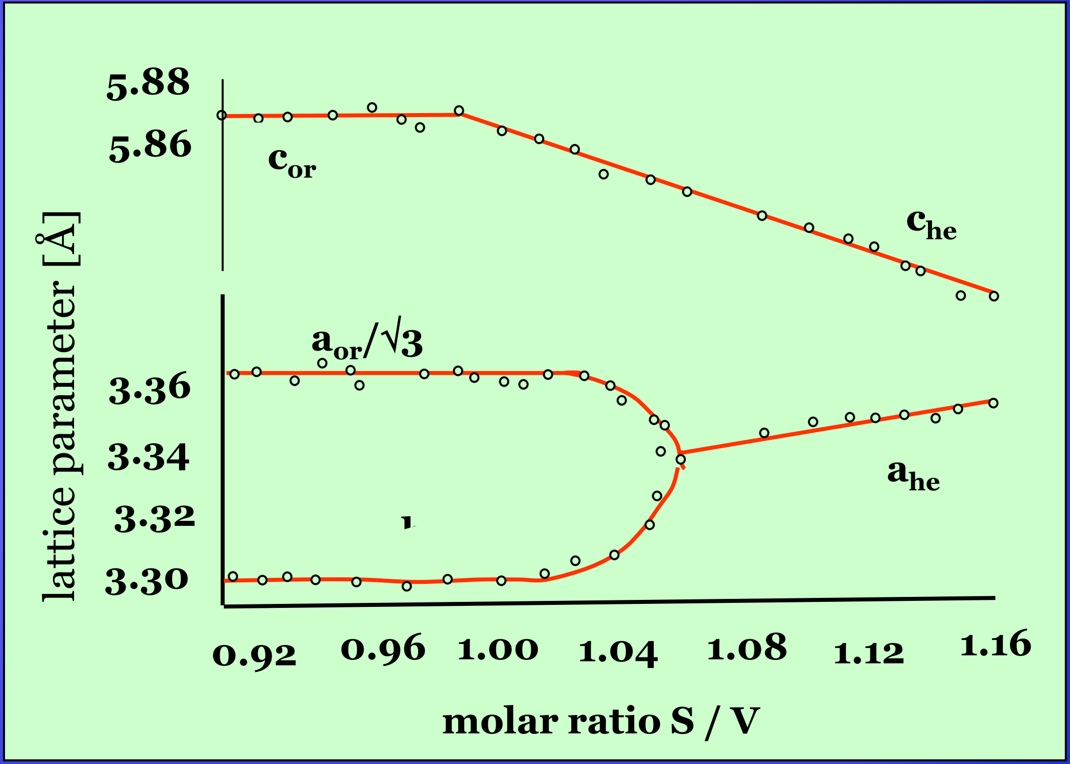
Variation of T



This is a typical example of a displacive transformation.

Introduction to 2. order phase transition

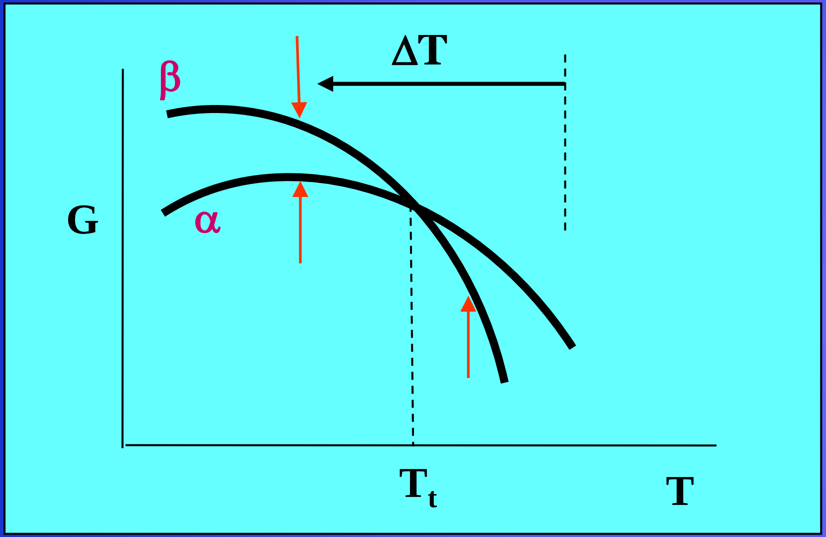
b) The transition of VS.



Variation of X

The NiAs-type is only stable with a deficiency of Vanadium.

Comments



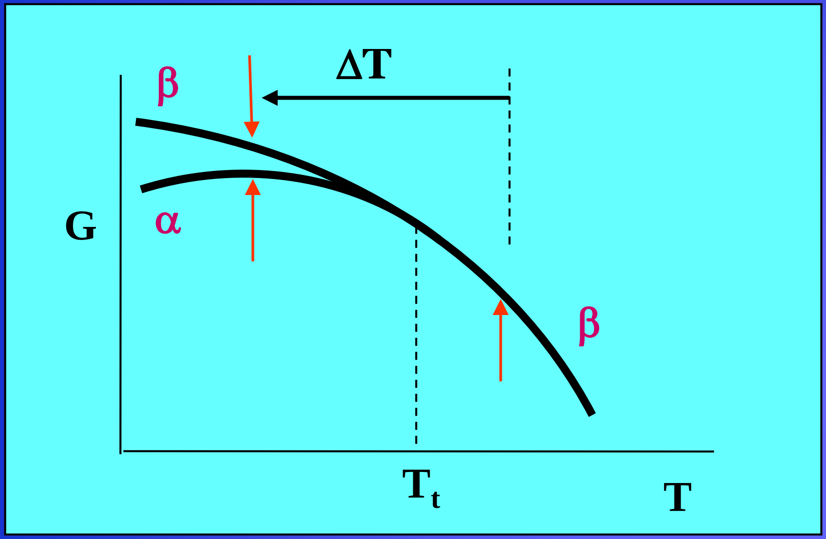
Quenching from a temperature above T_t for a 1. order phase transition.

(i) The β phase might be metastable below T_t.

(ii) Or a nucleus of phase α is formed.

(iii) No state between the curves is possible

Comments



Quenching from a temperature above T_t for a 2. order phase transition.

(i) The β phase cannot be quenched below T_t for a displacive transformation.

(ii) The β phase can be quenched below T_t for a order – disorder (diffusive) transformation.

(iii) Any state between the curves is possible

<u>Last comment</u>: The continuous variation of η or the lack of a thermal hysteresis are indicative for a 2. order phase transition

However, the experimental verification of these criteria might be difficult !!

Gibbs Potential and Landau theory

Consider G = G(T, p, X):

Each equilibrium state in α is characterized by $\eta_{eq} \neq 0$,
each equilibrium state in β is characterized by $\eta_{eq} = 0$

Consider G as a power series expansion of η :

$$G(\eta) = G^0 + \alpha\eta + A\eta^2 + B\eta^3 + C\eta^4 + ...$$

For each equilibrium state $G(\eta_{eq.})$ has a minimum, it must hold:

$$\left.\frac{\partial G}{\partial \eta}\right|_{\eta=\eta_{eq.}} = 0$$

Since $\left.\frac{\partial G}{\partial \eta}\right|_{\eta=0} = 0$ and $\left.\frac{\partial^2 G}{\partial \eta^2}\right|_{\eta=0} > 0$

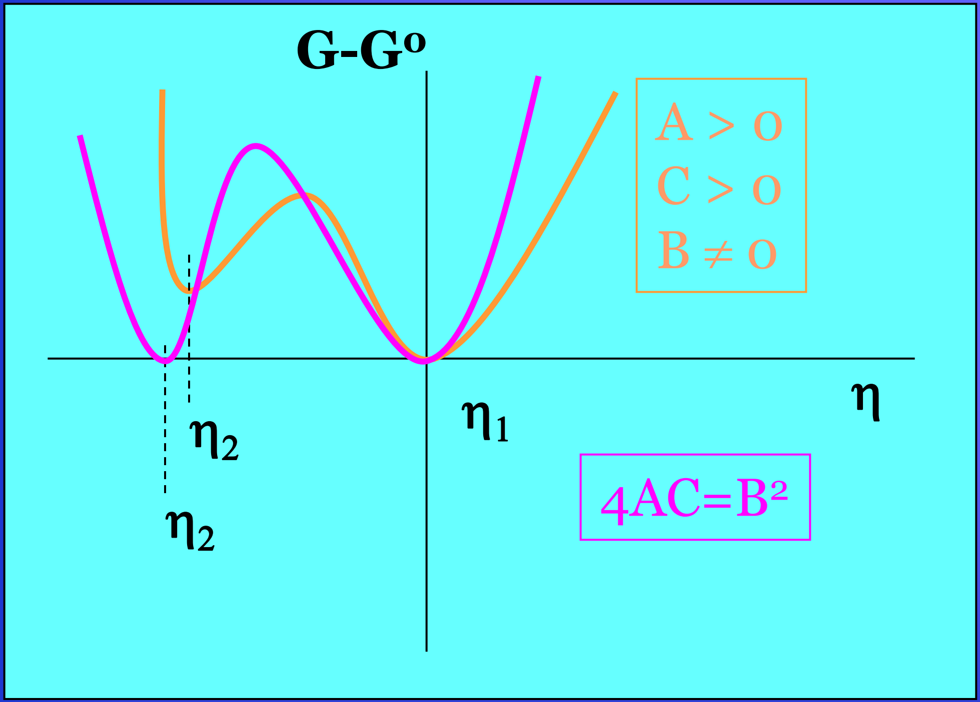
for the equilibrium state of β, it must hold:

$\alpha = 0$ $\quad$ $A > 0$

Gibbs potential and Landau theory

$$G(\eta) = G^0 + A\eta^2 + B\eta^3 + C\eta^4 + ...$$

(A > 0 and C > 0)



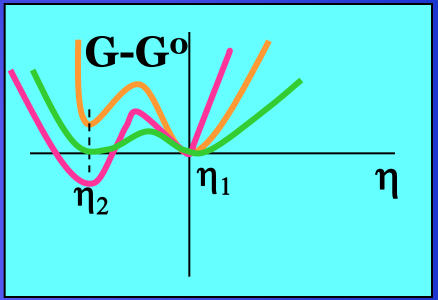
<u>Here:</u>
η_1=0 stable state
$\eta_2 \neq 0$ metastable state
(or vice versa)

<u>Here:</u>
η_1=0 stable state
$\eta_2 \neq 0$ stable state
co-existence of two stable states

All coefficients are functions of T, p, X.

Gibbs potential and Landau theory

Result:



General case:

η_1=0 (i.e. β) is the stable state and $\eta_2 \neq 0$ (i.e. α) is a metastable state

or

η_1=0 (i.e. β) is the metastable state and $\eta_2 \neq 0$ (i.e. α) is a stable state

Special case: $4AC=B^2$

η_1=0 (i.e. β) is the stable state **and** $\eta_2 \neq 0$ (i.e. α) is a stable state

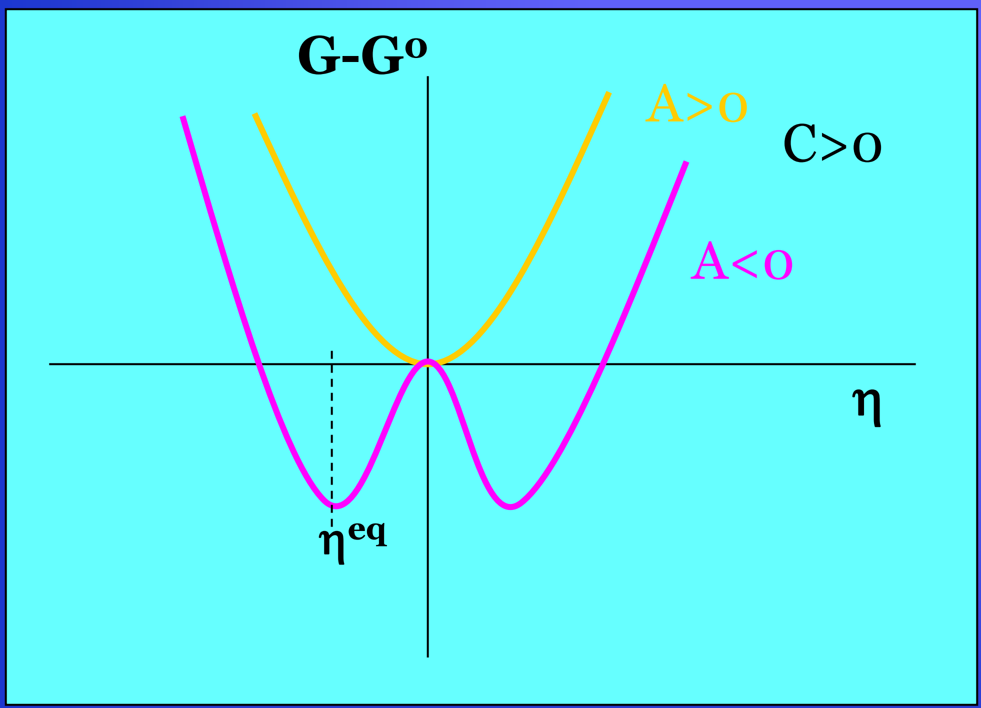
⇒ coexistence of α **and** β.

- This is the case of a 1. order phase transition !

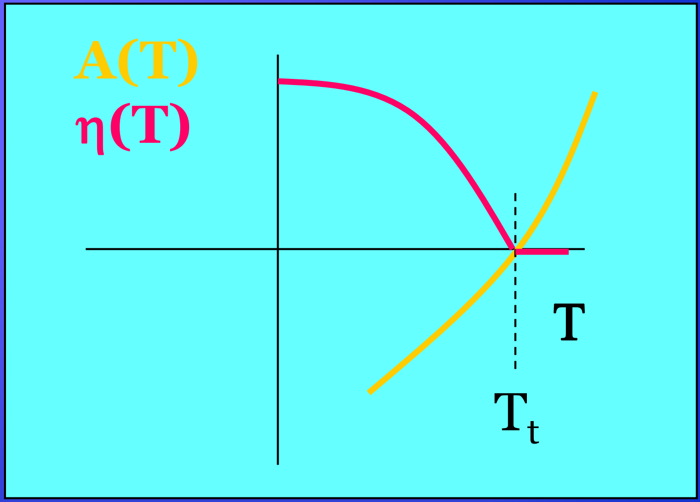
Gibbs potential and Landau theory

Consequence:

For a 2. order phase transition, B must be identical zero, it must vanish by symmetry, B≡0.



$$G(\eta) = G^0 + A\eta^2 + C\eta^4 + \ldots\ldots$$



$A = \mu(T - T_t)$

Landau theory

Density

The symmetry group of the β state be $\mathcal{G}^0$
the density be ρ^o (η=0).
At the transformation to the α phase symmetry is lost,
the density be ρ ($\eta \neq 0$) .

The density change at the phase transition is

$$\Delta\rho = \rho - \rho^o$$

From group theory it is known, that for each group $\mathcal{G}^0$ there exists a set of basis functions $\{\Phi_i\}$ which remain invariant under the symmetry operations of $\mathcal{G}^0$.

$$\Delta\rho = \Sigma \mathbf{c}_i \mathbf{\Phi}_\mathbf{i}$$

Example: P4

	1	4^1	4^2	4^3
	x	-y	-x	y
	y	x	-y	-x
	z	z	z	z

basis functions {Φi}

$\Phi_1 = x^2+y^2$

$\Phi_2 = x^2- y^2$

$\Phi_3 = xz$

$\Phi_4 = yz$

	1	4^1	4^2	4^3
	Φ_1	Φ_1	Φ_1	Φ_1
	Φ_2	$-\Phi_2$	Φ_2	$-\Phi_2$
	Φ_3	$-\Phi_4$	$-\Phi_3$	Φ_4
	Φ_4	Φ_3	$-\Phi_4$	$-\Phi_3$

$\{\Phi_i\}$ are transformed into itself.
They form 3 groups which remain invariant:
$\{\Phi_1\}, \{\Phi_2\}, \{\Phi_3,\Phi_4\}$

Landau theory

Criteria as postulated by Landau:

- <u>First presumption</u>:

  The symmetry group $\mathcal{G}$ of the state α is a subgroup of $\mathcal{G}^0$.

The symmetry group $\mathcal{G}$ is a subgroup of $\mathcal{G}^0$ if the symmetry elements of $\mathcal{G}$ are a subset of the symmetry elements of $\mathcal{G}^0$,
i.e. the multiplication table of $\mathcal{G}^0$ contains the elements of $\mathcal{G}$.

Reminder: Group Theory

Example

$\mathcal{G}^0 = mm2$

$\mathcal{G} = m$

	1	m_x	m_y	2_z
1	1	m_x	m_y	2_z
m_x	m_x	1	2_z	m_y
m_y	m_y	2_z	1	m_x
2_z	2_z	m_y	m_x	1

Reminder: Group Theory

The maximal non-isomorphic subgroups $\mathcal{G}$ of the space group $\mathcal{G}^0$ are divided into two types.

I. „translationengleiche" or „***t*** subgroups"

II. „klassengleiche" or „***k*** subgroups"

isomorphic means: they have the same abstract multiplication table

The maximal non-isomorphic subgroups $\mathcal{G}$ of the space group $\mathcal{G}^0$ are listed in the „International Tables"

Example: P422

$\mathcal{G}^0$

CONTINUED — No. 89 — $P\,4\,2\,2$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates				Reflection conditions
					General:
8 p 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
	(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	

Maximal non-isomorphic subgroups

I [2]$P\,4\,1\,1\,(P\,4)$ 1; 2; 3; 4
[2]$P\,2\,2\,1\,(P\,2\,2\,2)$ 1; 2; 5; 6
[2]$P\,2\,1\,2\,(C\,2\,2\,2)$ 1; 2; 7; 8

IIa none

IIb [2]$P\,4_2\,2\,2\,(\mathbf{c}'=2\mathbf{c})$; [2]$C\,4\,2\,2_1\,(\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b})(P\,4\,2_1\,2)$; [2]$F\,4\,2\,2\,(\mathbf{a}'=2\mathbf{a},\mathbf{b}'=2\mathbf{b},\mathbf{c}'=2\mathbf{c})(I\,4\,2\,2)$

If k^o is the order of $\mathcal{G}^0$ and k is the order of $\mathcal{G}$, then **[i]** = k^o/k is the index of the subgroup

Landau theory

- Second presumption:

  The distortions at the phase transition correspond to a single irreducible representation of the group of the wave vector.

Two terms must be explained:

- What is an irreducible representation ?
- What is the group of the wave vector ?

Representation

Definition:

τ is a representation of of the group $\mathcal{G}$, if there exists an matrix operator $\tau(g)$ for each element $g \in \mathcal{G}$, so that for each multiplication

$$g_1 \cdot g_2 = g_3$$

there is an equivalent multiplication

$$\tau(g_1) \cdot \tau(g_2) = \tau(g_3)$$

If the matrix consists of small blocks on the diagonal, it is called irreducible.

$$\tau(A) = \begin{pmatrix} \tau_1(A) & 0 \\ 0 & \tau_2(A) \end{pmatrix}$$

Example: 4

	1	4^1	4^2	4^3
τ	$\left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$	$\left(\begin{array}{cc|c} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$	$\left(\begin{array}{cc|c} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$	$\left(\begin{array}{cc|c} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$

τ_1	1	1	1	1
τ_2	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ \bar{1} & 0 \end{pmatrix}$
τ_3	1	-1	1	-1

	1	4^1	4^2	4^3
τ_1	Φ_1	Φ_1	Φ_1	Φ_1
τ_3	Φ_2	$-\Phi_2$	Φ_2	$-\Phi_2$
τ_2	Φ_3	$-\Phi_4$	$-\Phi_3$	Φ_4
	Φ_4	Φ_3	$-\Phi_4$	$-\Phi_3$

The representations describe how the symmetry operators effect the basis functions

e. g.

$$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \Phi_3 \\ \Phi_4 \end{pmatrix} = \begin{pmatrix} -\Phi_4 \\ \Phi_3 \end{pmatrix}$$

The dimension of the irreducible representation corresponds to the number of basis functions

Wave vector

The phase transition occurs in the crystal space, however, it may become evident in the reciprocal space:
by the appearance of superstructure reflections or satellite reflections.

Therefore the symmetry elements must also leave the vector (so called wave vector $\boldsymbol{k}$) invariant at which the transformation occurs.

The group of the wave vector not only leaves the structure invariant but also the wave vector.

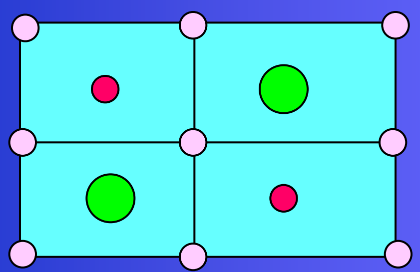
Note : The wave vector might be $\boldsymbol{k}$=(0 0 0); the transition occurs at a main reflection. The group $\mathcal{G}^0$ contains all symmetry elements of the space group.

Example: Pmm2

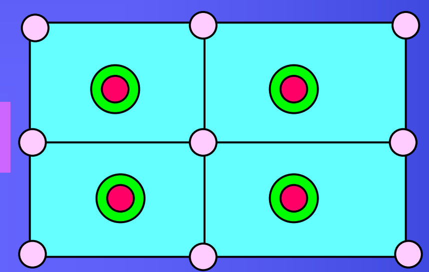
Consider a simple orthorhombic structure:

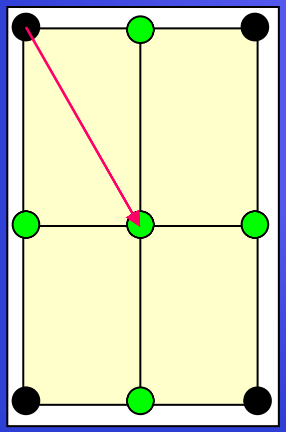
Atom A

Atom B

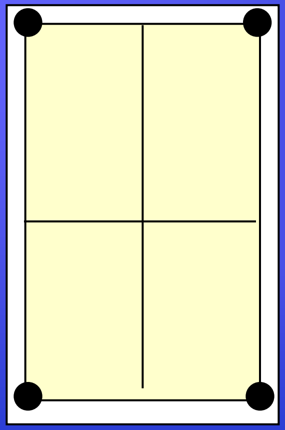


Order ⇔ Disorder

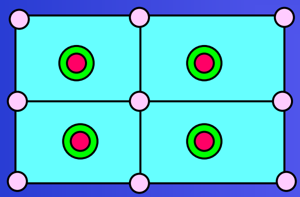




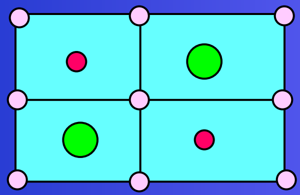
k=1/2(a*+b*)



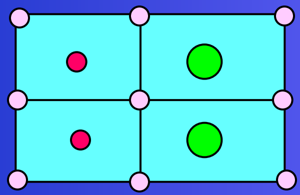
Example: Pmm2



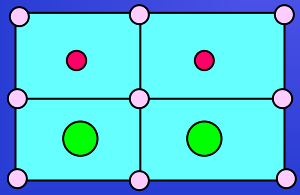
→ τ_1



→ τ_2



→ τ_3

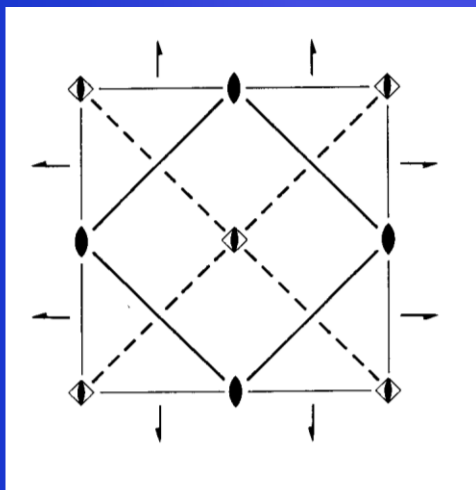


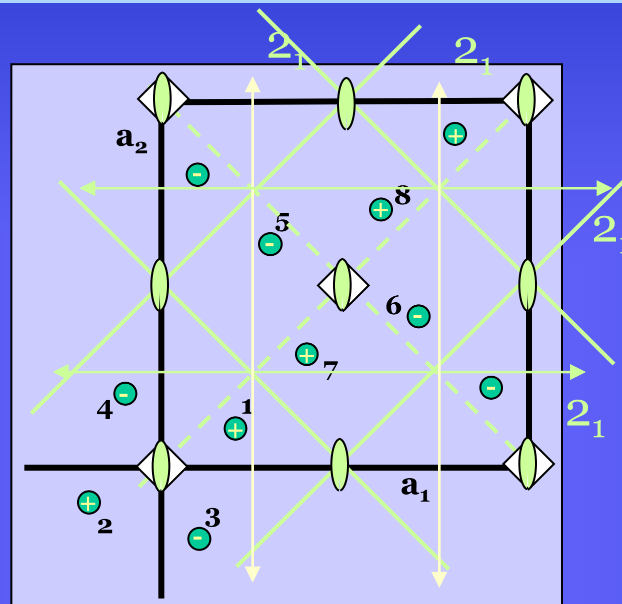
→ τ_4

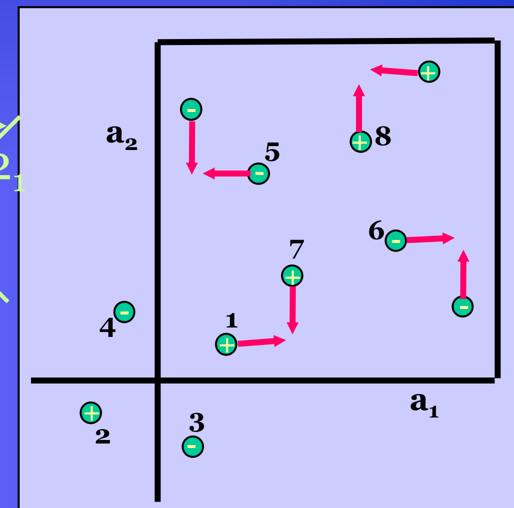
Kovalev: Irreducible representations of space groups

	1	m_x	2_x	m_y
τ_1	1	1	1	1
τ_2	1	- 1	1	- 1
τ_3	1	1	- 1	- 1
τ_4	1	- 1	- 1	1

Example: $P\bar{4}2_1m$







Maximal non-isomorphic subgroups

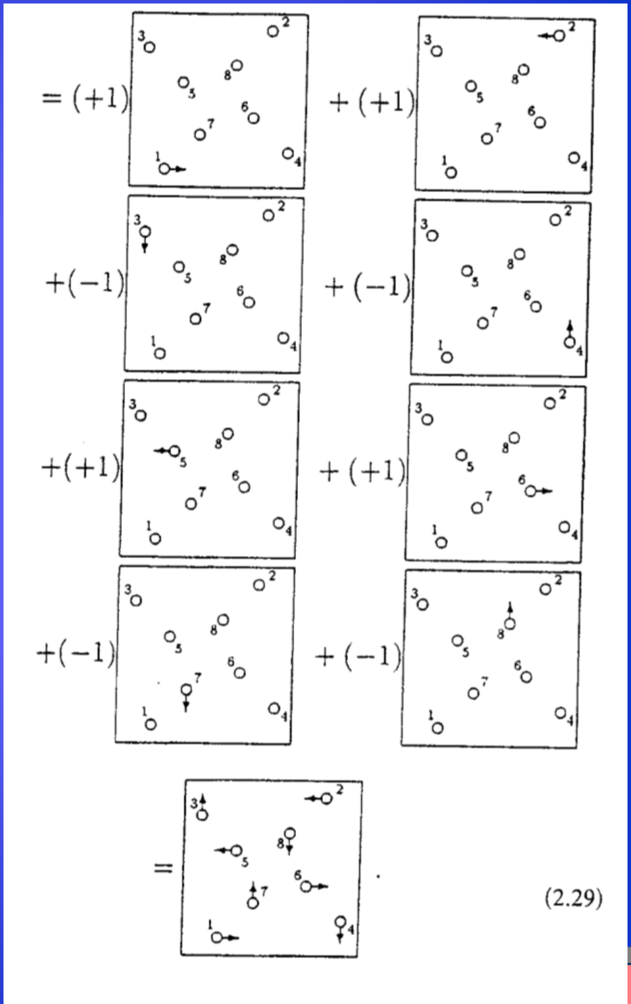
I	$[2]P\bar{4}11\,(P\bar{4})$	1; 2; 3; 4
	$[2]P22_11\,(P2_12_12)$	1; 2; 5; 6
	$[2]P21m\,(Cmm2)$	1; 2; 7; 8
IIa	none	
IIb	$[2]P\bar{4}2_1c\,(\mathbf{c}'=2\mathbf{c})$	

Example: $P\bar{4}2_1m$

Wave vector be $\boldsymbol{k}$= (0, 0, 0)

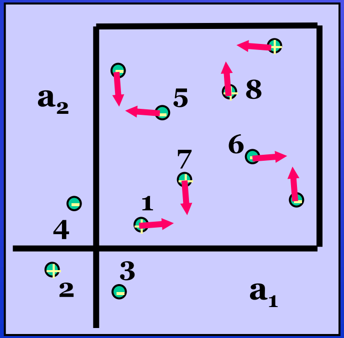
TABLE I. Irreducible representations of space group $P\bar{4}2_1m$, wave vector $\mathbf{k}=(0,0,0)$, respectively, of the assigned point group $\bar{4}2m$.

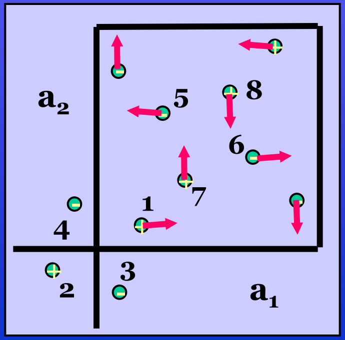
	1	2	3	4	5	6	7	8	
	$\Gamma^\alpha(1)$	$\Gamma^\alpha(2_z)$	$\Gamma^\alpha(\bar{4}_z)$	$\Gamma^\alpha(\bar{4}_z^3)$	$\Gamma^\alpha(2_{1,y})$	$\Gamma^\alpha(2_{1,x})$	$\Gamma^\alpha(m_{s,xy})$	$\Gamma^\alpha(n_{x\bar{y}})$	$G^\alpha(\bar{\eta})$
Γ^1	1	1	1	1	1	1	1	1	$P\bar{4}2_1m$
Γ^2	1	1	−1	−1	1	1	−1	−1	$P2_12_12$
Γ^3	1	1	−1	−1	−1	−1	1	1	$Cmm2$
Γ^4	1	1	1	1	−1	−1	−1	−1	$P\bar{4}$
Γ^5	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$P2_1$[a] Cm[b] $P1$[c]



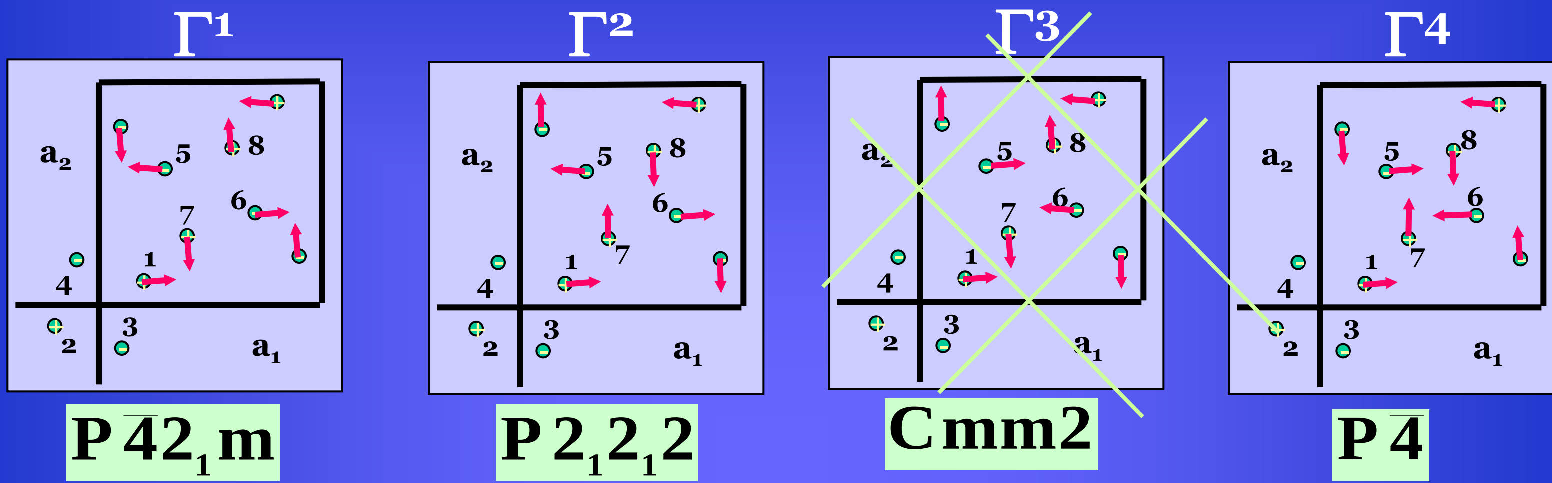
Projection operator:

$$\mathcal{P}^2 v(\underline{x}) = \sum_g \Gamma^2(g) v(g\underline{x})$$

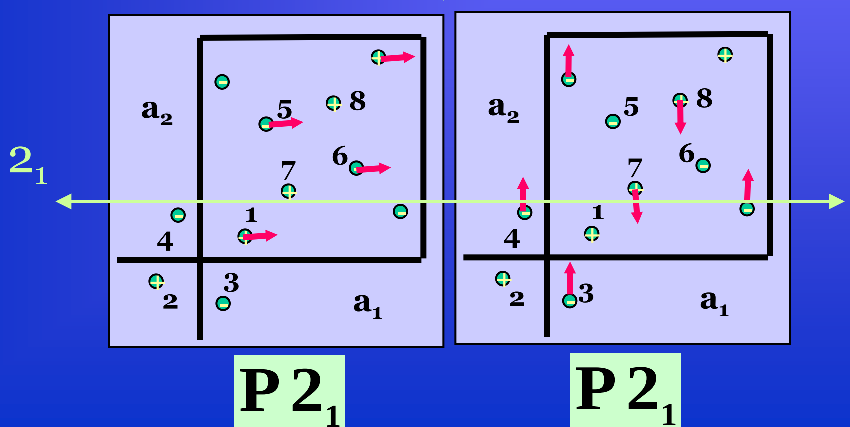


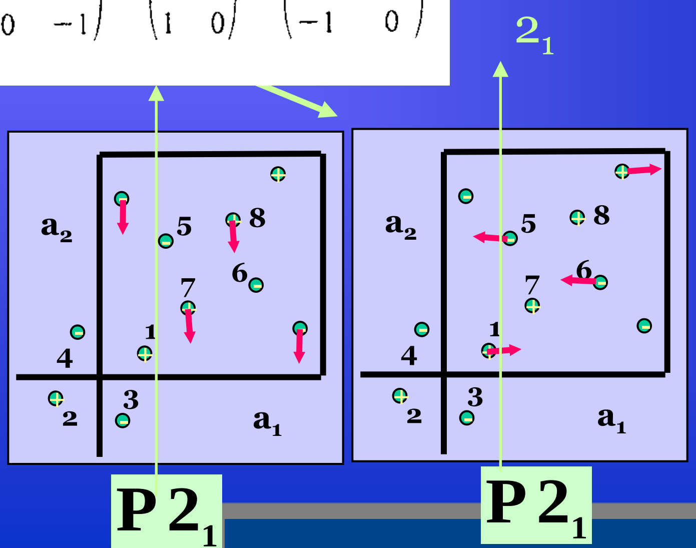


Example: $P\bar{4}2_1m$



$$\Gamma^5 \quad \begin{pmatrix}1&0\\0&1\end{pmatrix} \begin{pmatrix}-1&0\\0&-1\end{pmatrix} \begin{pmatrix}0&-1\\1&0\end{pmatrix} \begin{pmatrix}0&1\\-1&0\end{pmatrix} \begin{pmatrix}-1&0\\0&1\end{pmatrix} \begin{pmatrix}1&0\\0&-1\end{pmatrix} \begin{pmatrix}0&1\\1&0\end{pmatrix} \begin{pmatrix}0&-1\\-1&0\end{pmatrix}$$





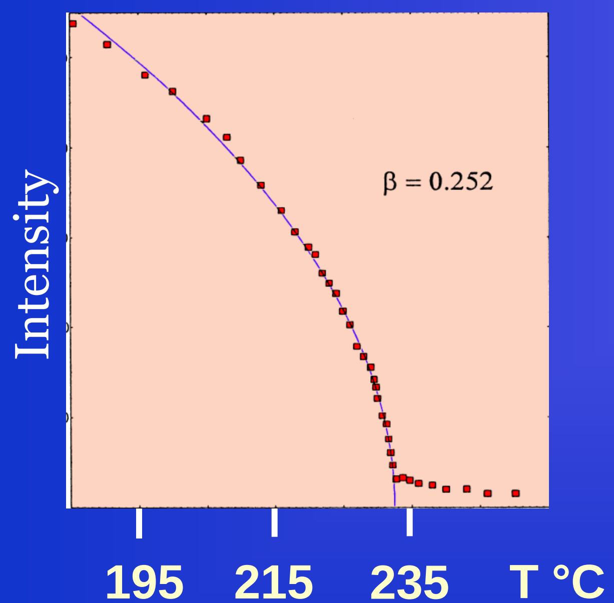
Example $Bi_2Ti_4O_{11}$

Sequence of phases

α - phase C2/c	$c_0(\alpha) = 2\, c_0(\beta)$ Tc = 233 °C ← →	β - phase C2/m

Maximal non-isomorphic subgroups $\mathcal{G}^0$ = C2/m

I	[2]A 1 1 2 (C 2)	(1; 2)+
	[2]A $\bar{1}$ (P $\bar{1}$)	(1; 3)+
	[2]A 1 1 m (C m)	(1; 4)+
IIa	[2]P 1 1 2/m (P 2/m)	1; 2; 3; 4
	[2]P 1 1 2/b (P 2/c)	1; 2; (3; 4)+(0,½,½)
	[2]P 1 1 2_1/b (P 2_1/c)	1; 3; (2; 4)+(0,½,½)
	[2]P 1 1 2_1/m (P 2_1/m)	1; 4; (2; 3)+(0,½,½)
IIb	[2]A 1 1 2/a (a′ = 2a)(C 2/c); [2]I 1 1 2/a (a′ = 2a)(C 2/c)	



Superstructure reflection

Temperature dependence of η:

$$\eta = \mu\,(T_c - T)^{\beta}$$

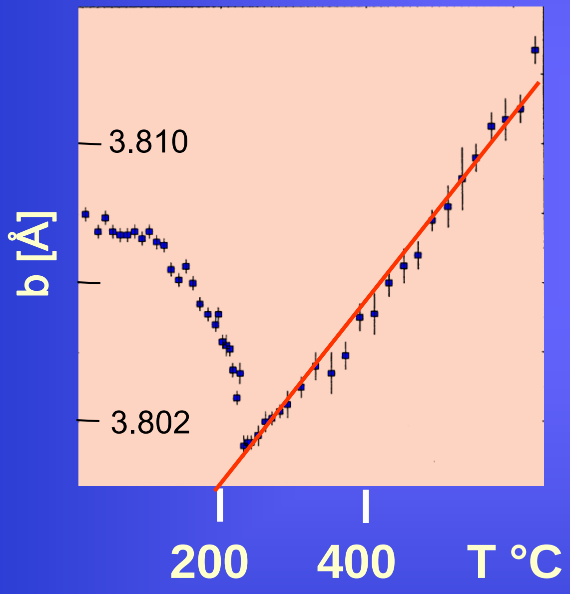
$$I \sim \eta^2 \sim (T_c - T)^{2\beta}$$

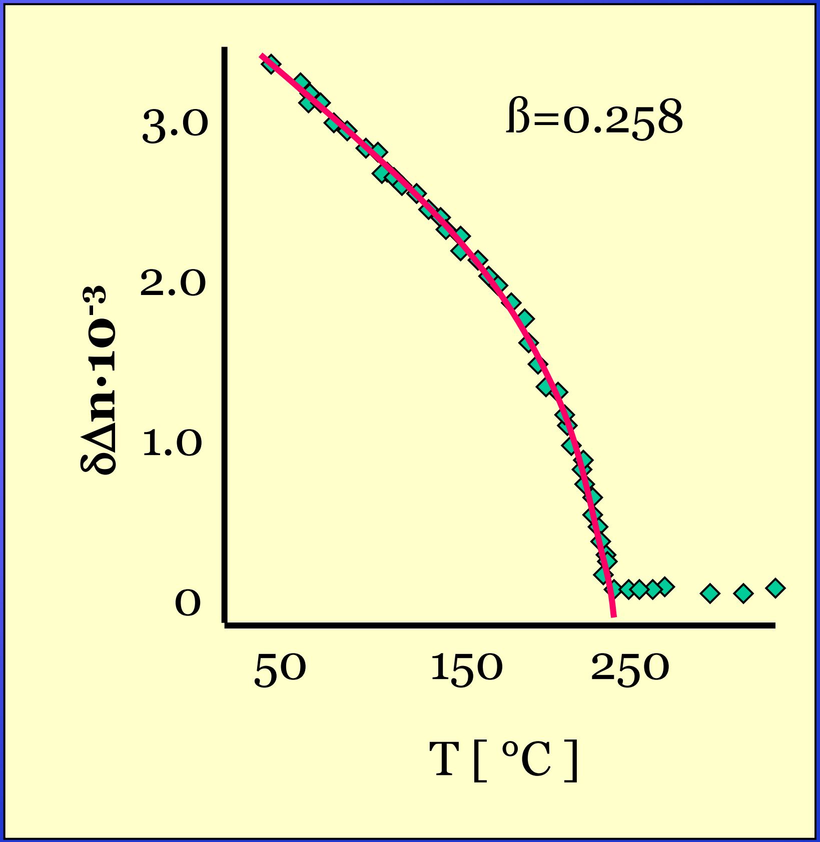
We find: β=0.25

Example $Bi_2Ti_4O_{11}$

Latticeparameter **b**

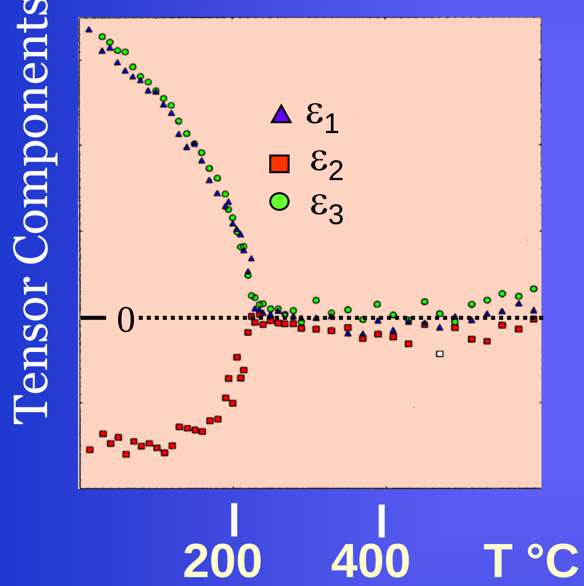
Excess birefringence $\delta\Delta n \sim \eta^2 \sim (T_c - T)^{2\beta}$



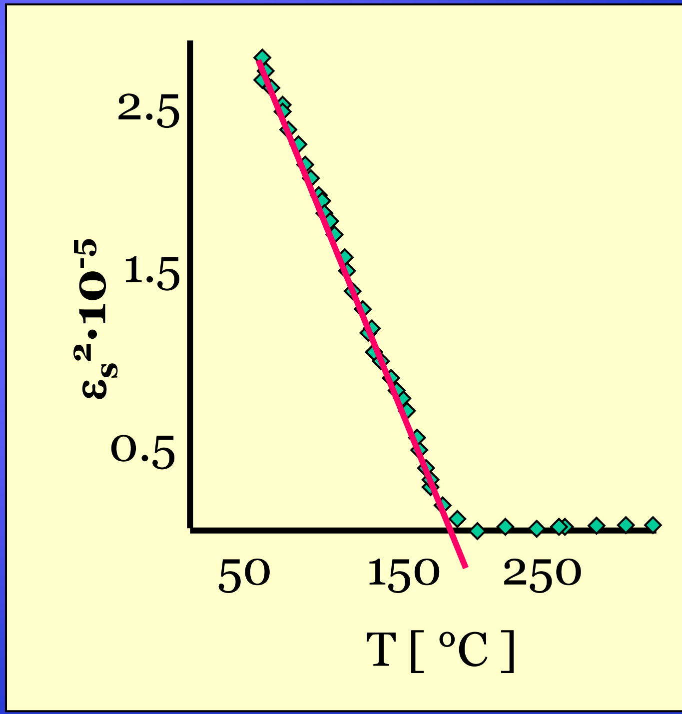


Example $Bi_2Ti_4O_{11}$

Spontaneous strain



For ß=0.25
$\varepsilon_s^2 \sim (T_c - T)$



$$\varepsilon_s = \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2}$$

$$\varepsilon_s \sim \eta^2 \sim (T_c - T)^{2\beta}$$

Example $Bi_2Ti_4O_{11}$

We observe:
$\Delta V = 0$ at the transition
No thermal hysteresis:
$\Rightarrow$ Phase transition of 2. order

Gibbs potential :

$$\Delta G = (T_c - T)\eta^2 + B\,\eta^4$$

$E\varepsilon^2$: term for the elastic energy
$D\varepsilon\eta^2$: term for the coupling between η and ε
B=0, if ß=0.25, therefore a term with η^6 is needed.

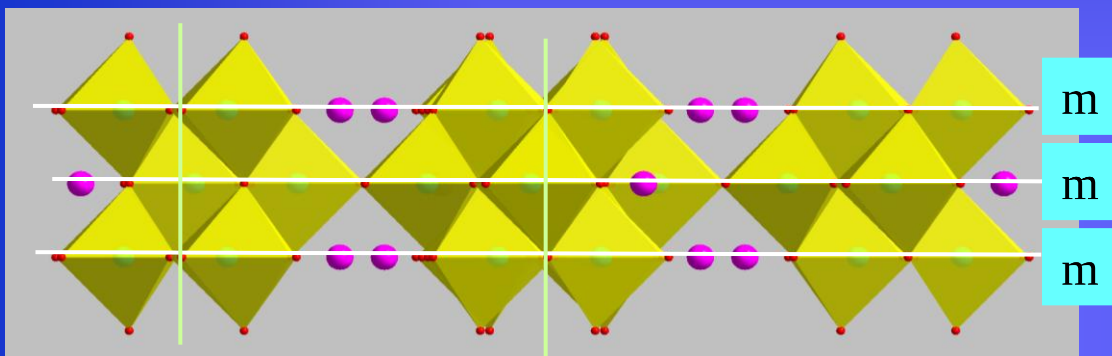
$$\Delta G = (T_c - T)\eta^2 + C\,\eta^6 + D\varepsilon\eta^2 + E\,\varepsilon^2$$

η: primary order parameter $\Rightarrow$ **shift of the Bi-atoms**
ε : secondary order parameter $\Rightarrow$ **spontaneous strain**

Example $Bi_2Ti_4O_{11}$

Structure : β-Phase C2/m

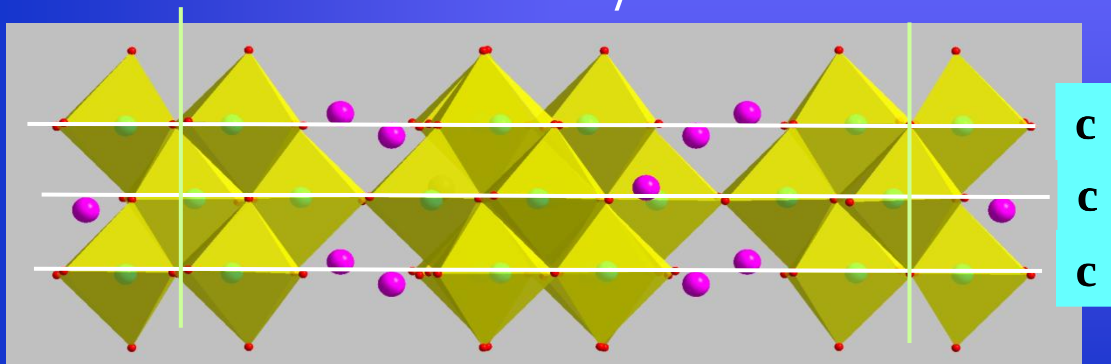
Bi - Atoms



Mechanism:

Continuous shift of the Bi- atoms off the mirror plane

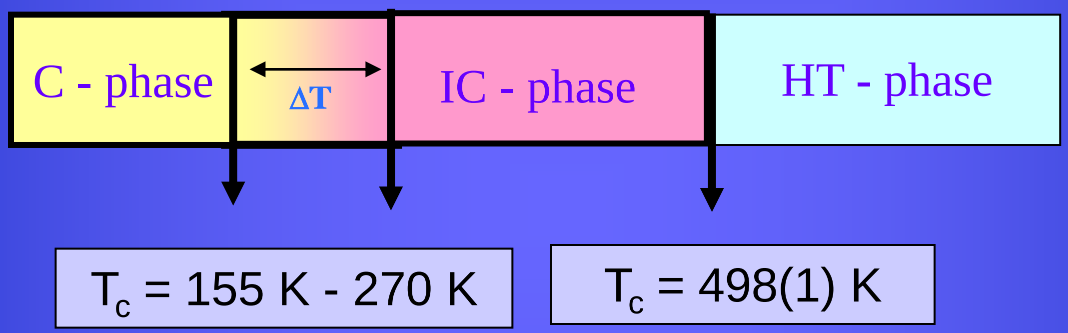
Structure : α-Phase C2/c



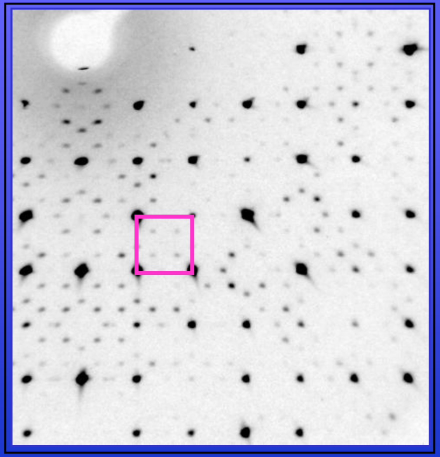
The phase transition is triggered by the „lone electron pair“ of Bi.

Example $Ca_2CoSi_2O_7$

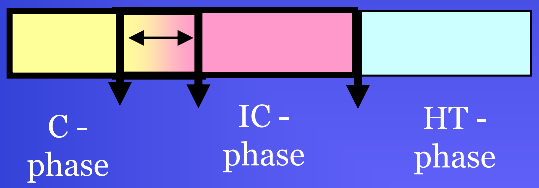
Sequence of phases:

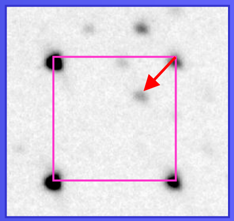


Diffraction pattern at RT:

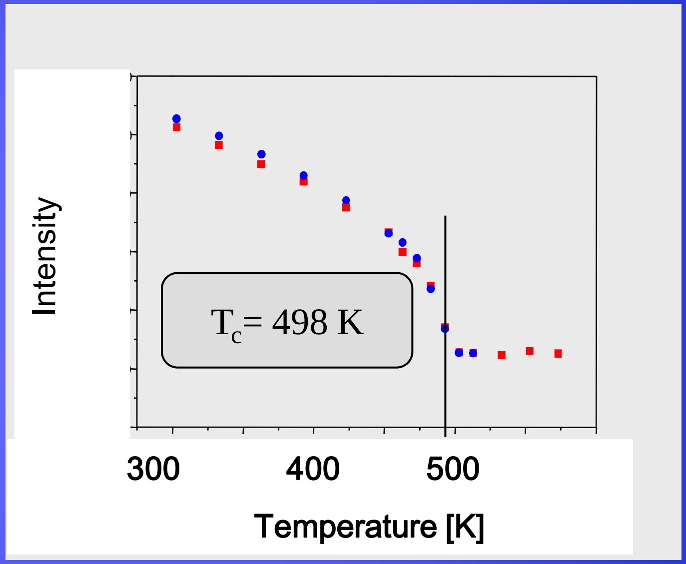


Example $Ca_2CoSi_2O_7$





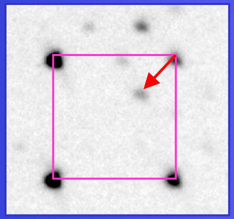
Satellite intensity

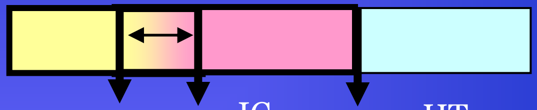


Phase transition at ~500 K

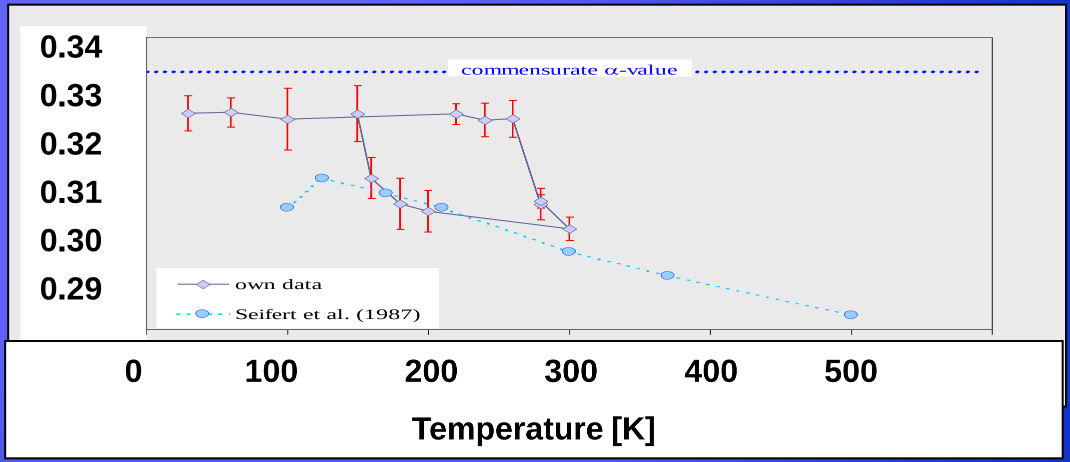
No thermal hysteresis:
⇒ 2. order phase transition

Example $Ca_2CoSi_2O_7$





Variation of the q-Vector

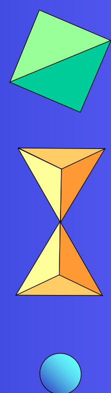


Phase transition
between 155 K and 270 K

Thermal hysteresis:
⇒ 1. order phase transition

Example $Ca_2CoSi_2O_7$

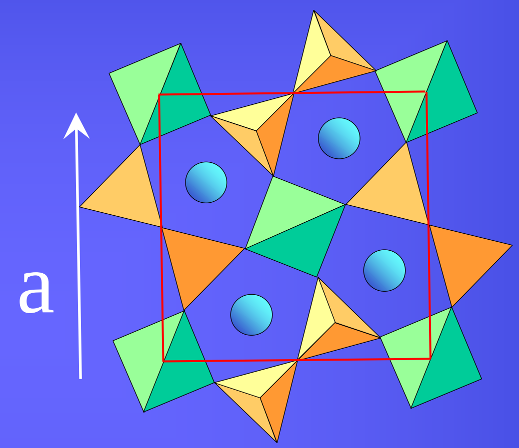
HT - Phase

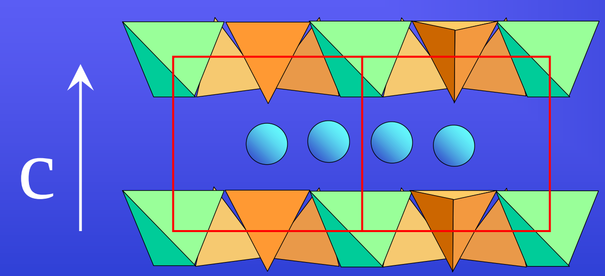


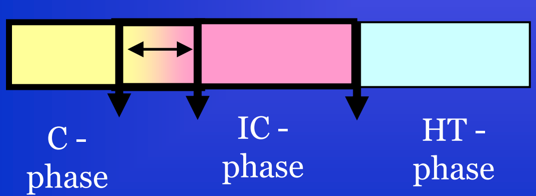
$= CoO_4$

$= Si_2O_7$

= Ca

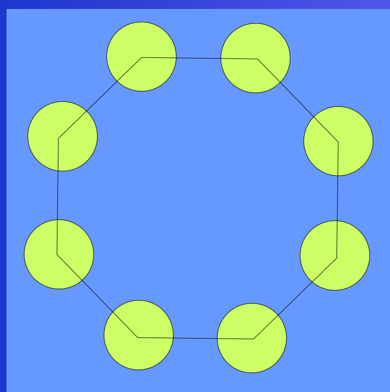


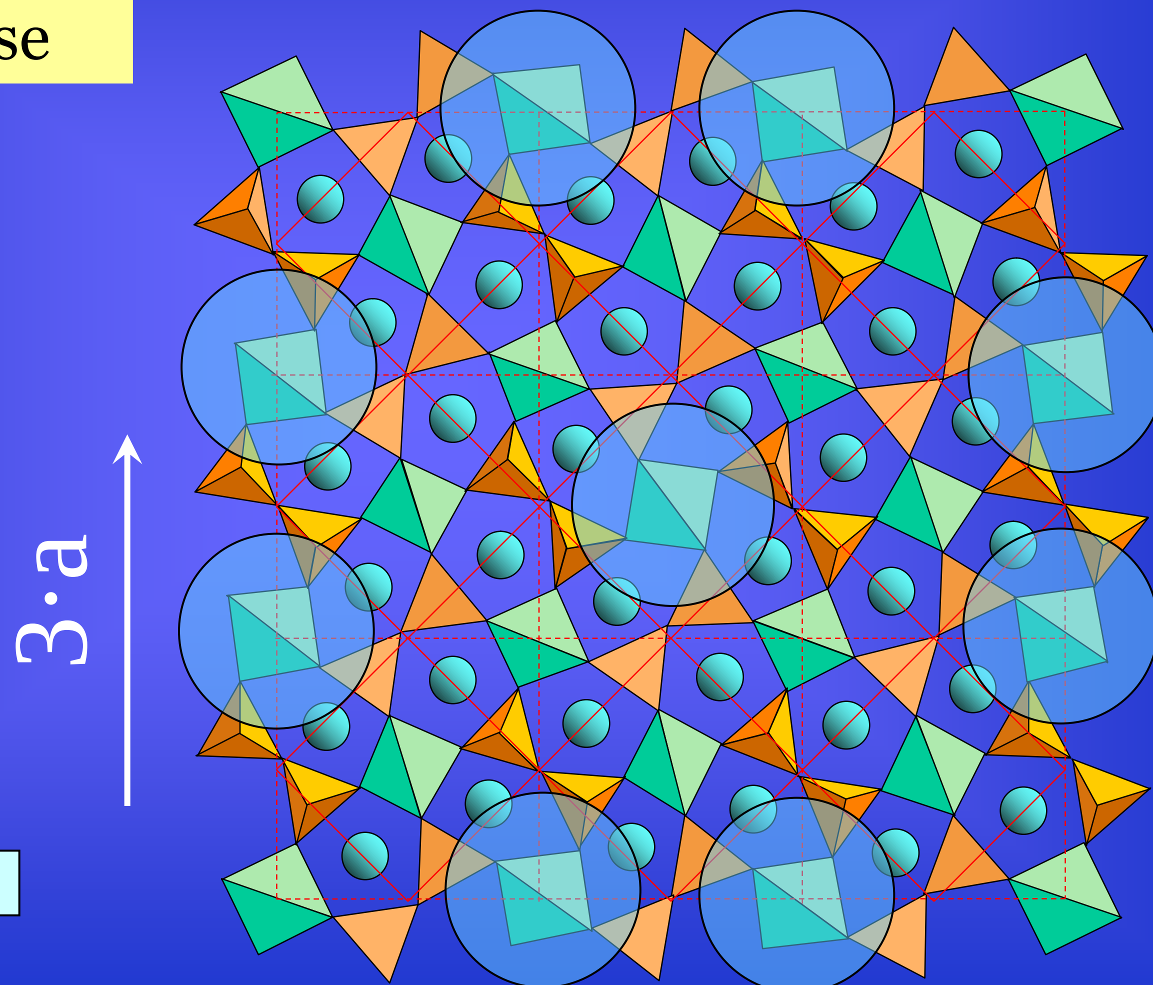


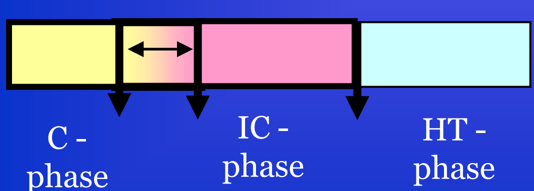


Example $Ca_2CoSi_2O_7$

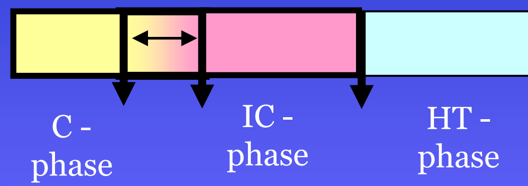
C - phase





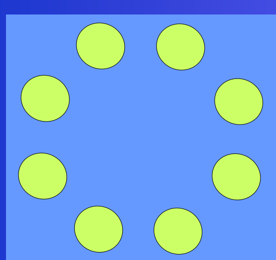


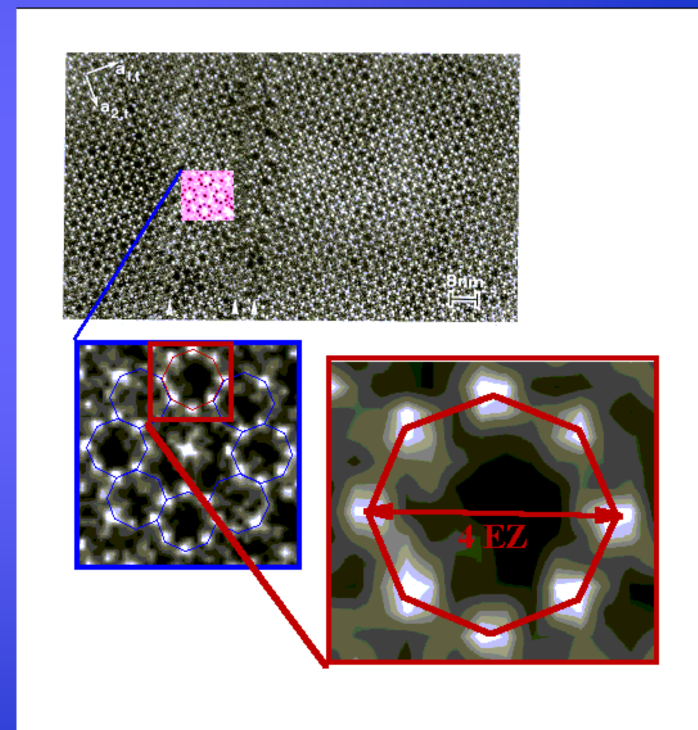
Example $Ca_2CoSi_2O_7$



IC - phase

TEM studies at RT:
pictures show octagonal rings.

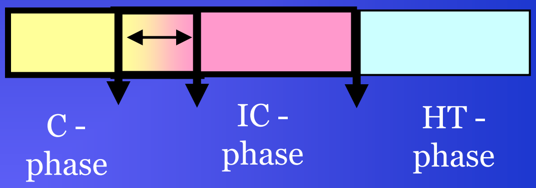


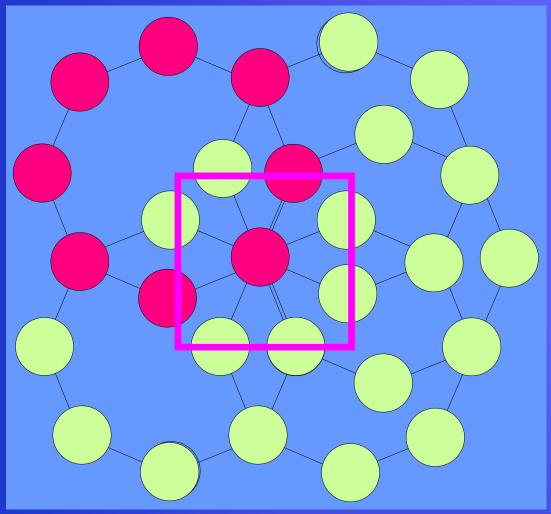


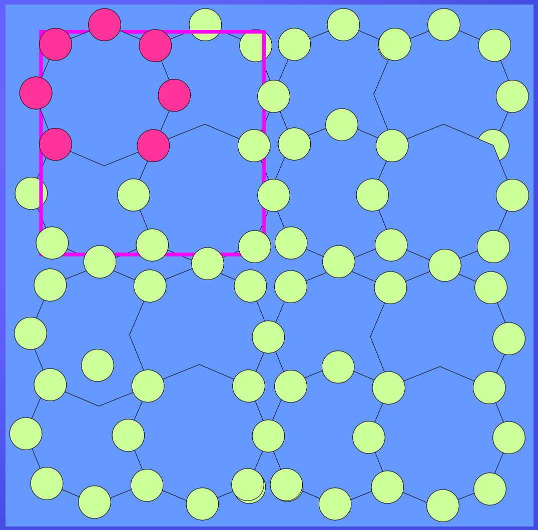
Van Heurk et al., 1992

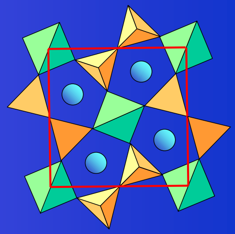
Example $Ca_2CoSi_2O_7$

Relations between the structures









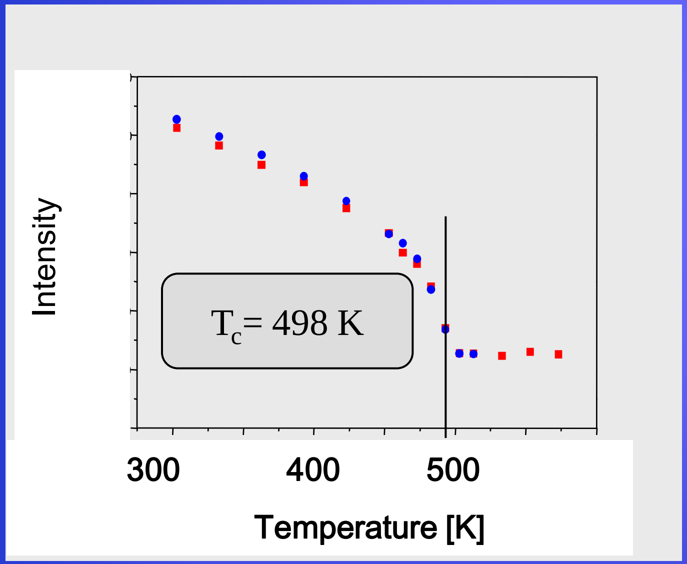
C-phase: An ordered superposition of octagonal rings.

IC-phase: An arbitrary superposition of octagonal rings

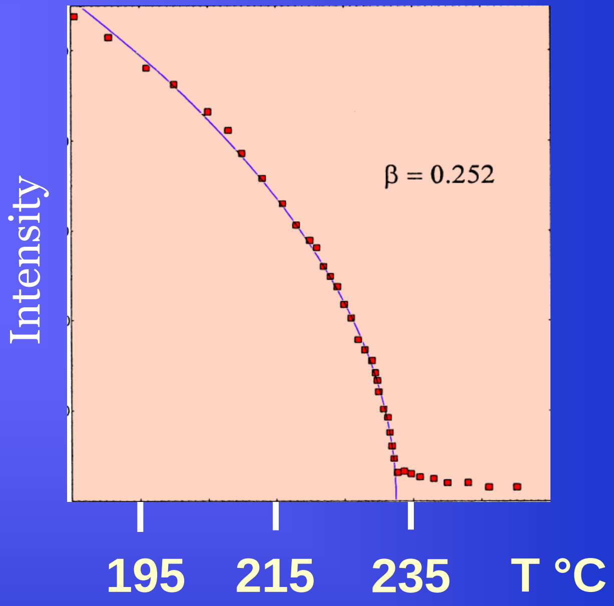
Mechanisms

$Ca_2CoSi_2O_7$

$Bi_2Ti_4O_{11}$



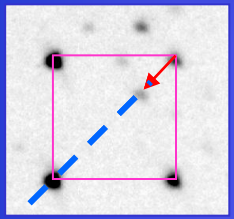
Satellite reflection

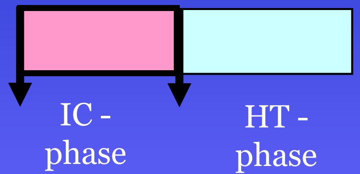


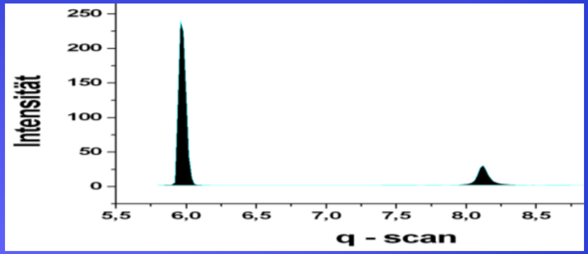
Superstructure reflection

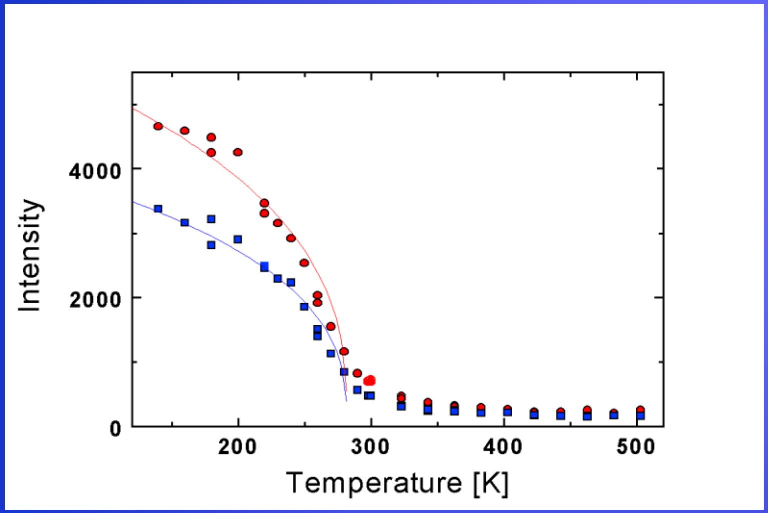
Mechanisms

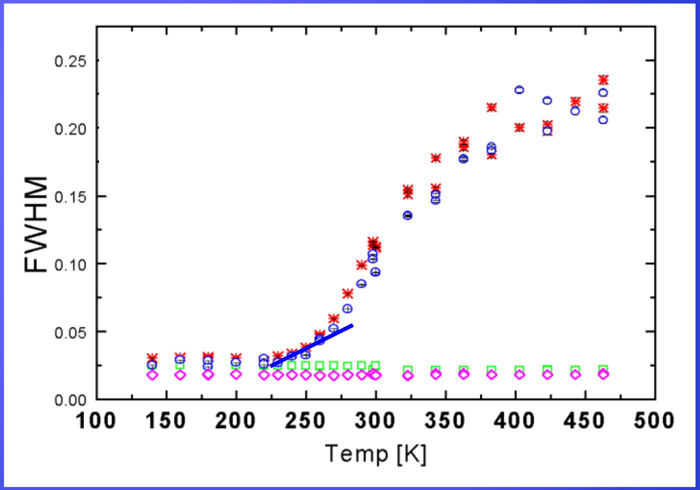
$(Ca_{1-x}Sr_x)_2MgSi_2O_7$; $x = 0.16$









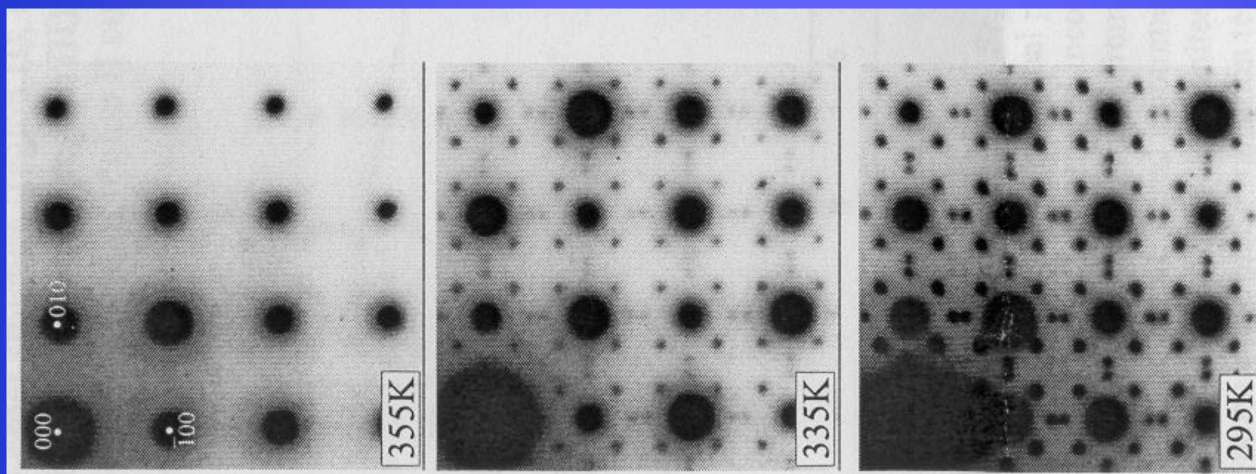


Tc = 277 K ? ⇔ ? Tc = 250 K

Transformation temperature

Mechanisms

TEM, IC- and HT-phase: Electron diffraction on $(Ca_{1-x}Sr_x)_2MgSi_2O_7$.



T = 355 K
No satellites

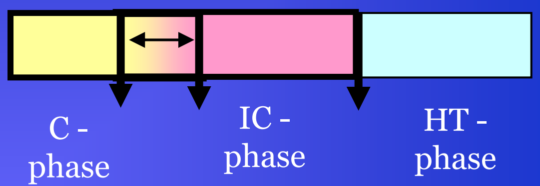
T = 335 K
satellites of
1. order

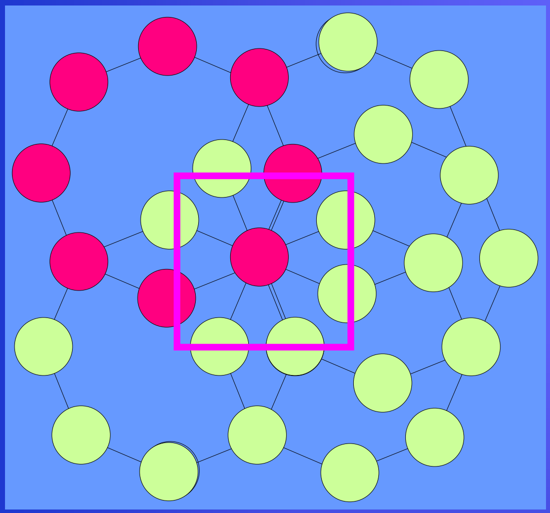
T = 295 K
satellites of
1. and 2. order

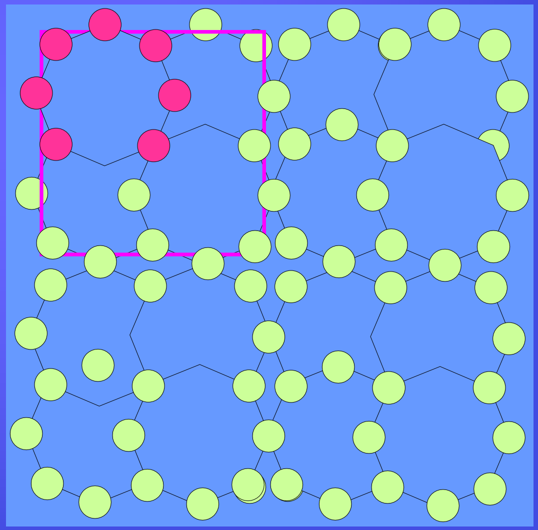
M. Schosnig et al., 2000

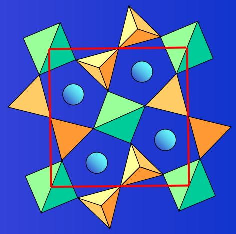
Example $Ca_2CoSi_2O_7$

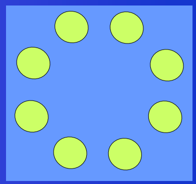
Relations between the structures











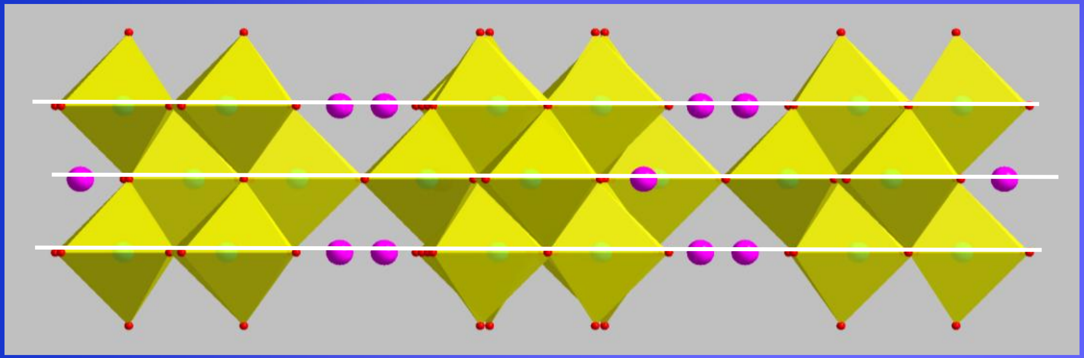
C-phase: An ordered superposition of octagonal rings.

IC-phase: An arbitrary superposition of octagonal rings

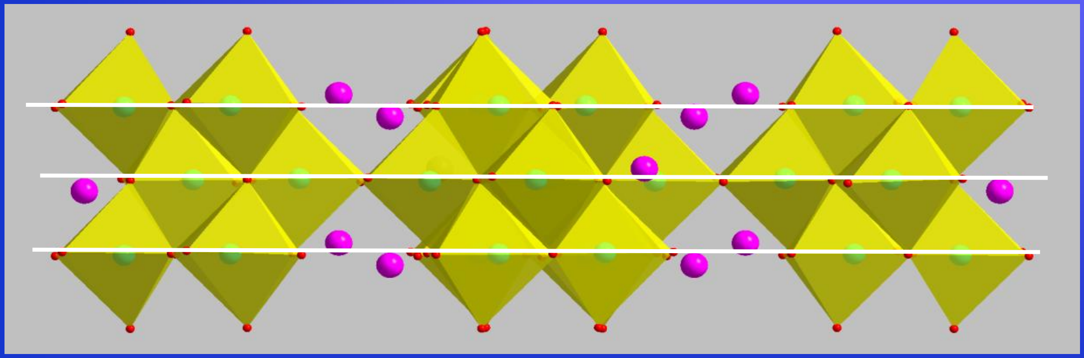
Example $Bi_2Ti_4O_{11}$

Bi - Atoms

structure : β-phase



structure : α-phase



<u>Mechanism:</u>
Continuous shift of the
Bi- atoms off the mirror plane

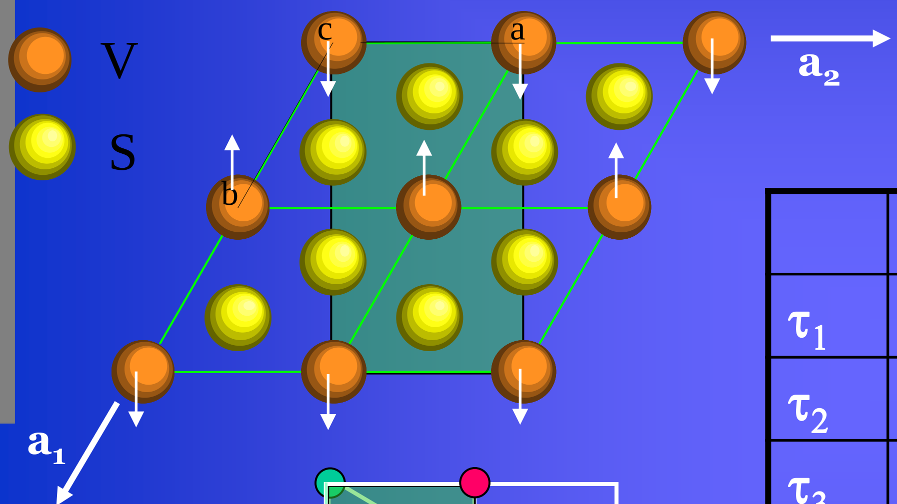
The phase transition is
triggered by the
„lone electron pair“ of Bi.

MnP-Type	NiAs-Type
Pcmn	P63/mmc

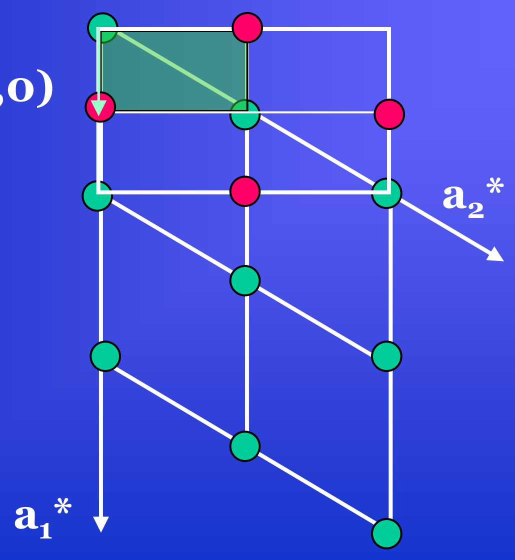
580 °C

The transition of VS.

Order parameter = shift of Vanadium

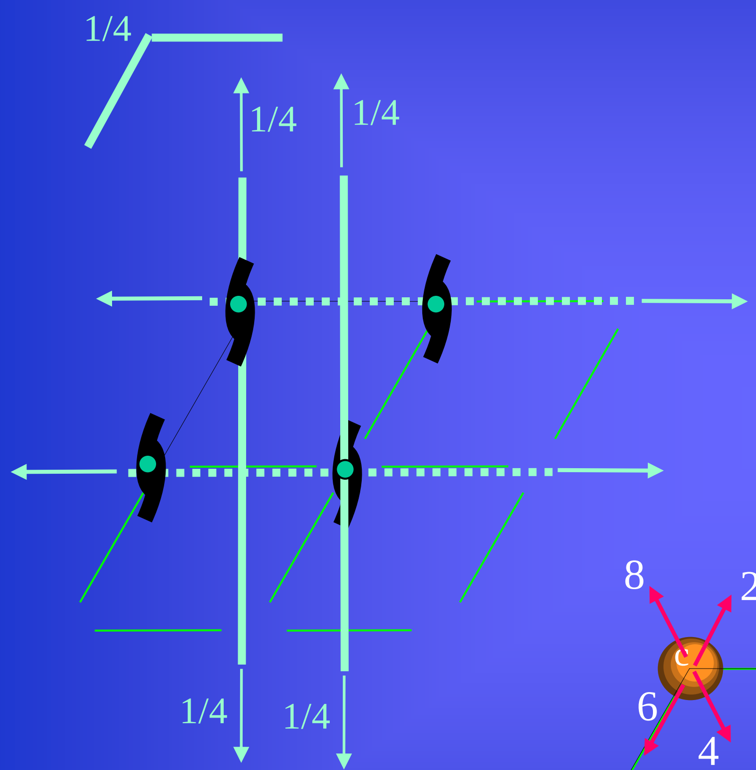


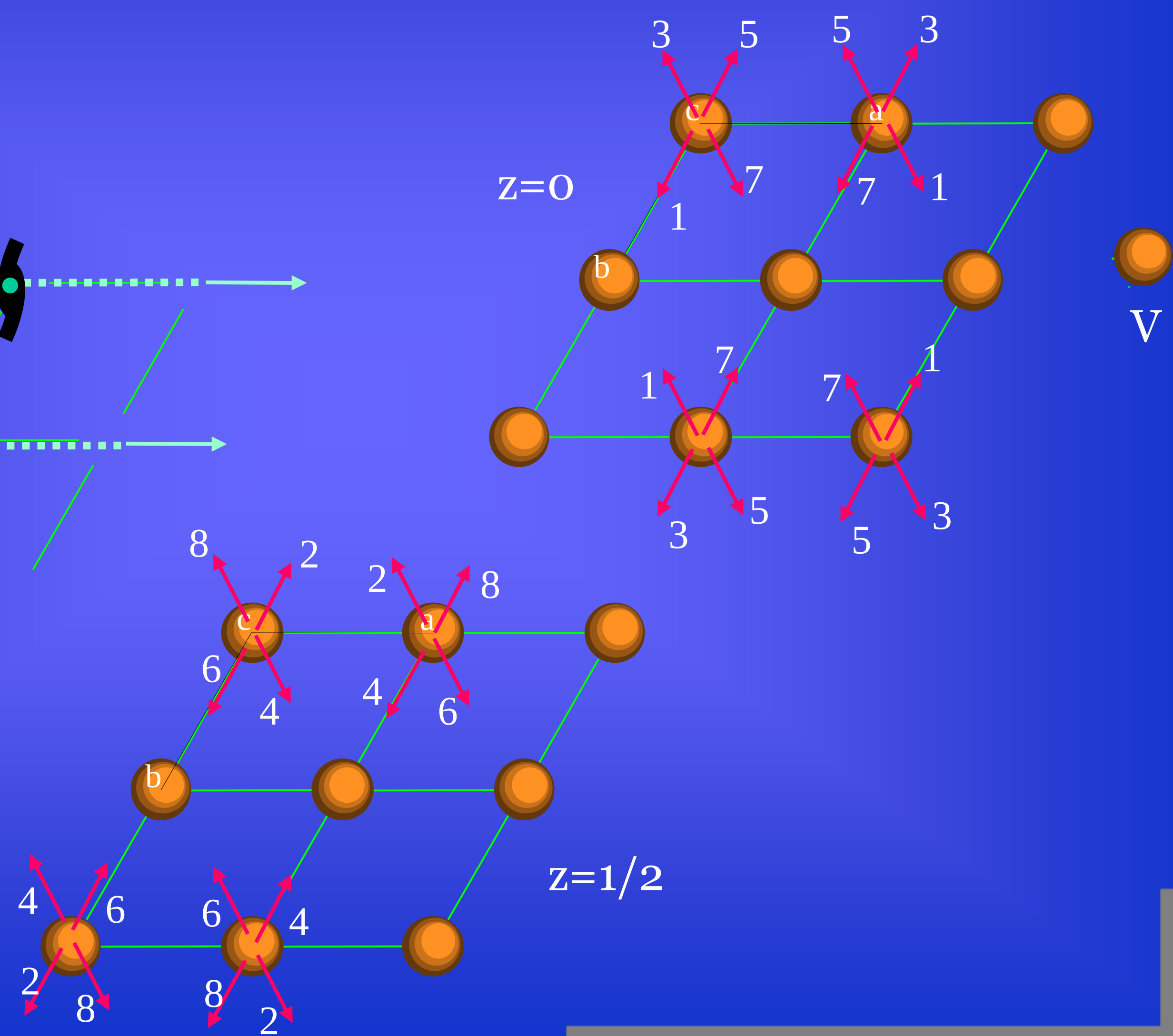
K=1/2(1,0,0)



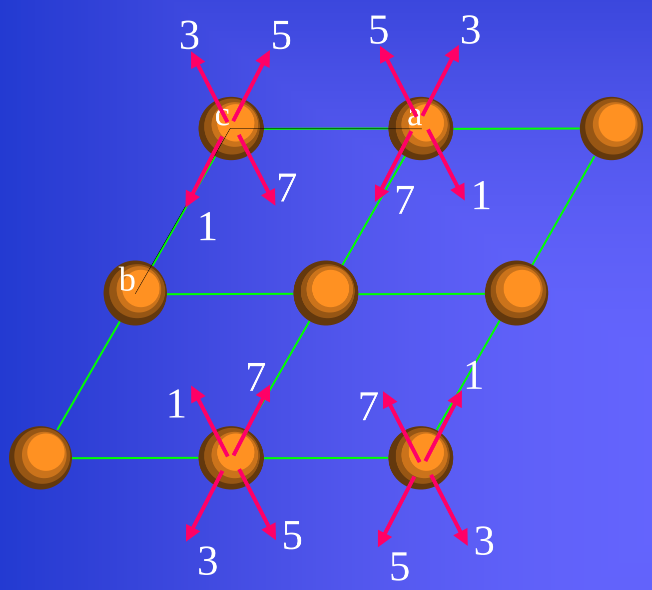
	1	$2_{1,z}$	2_y	2_{2xy}	-1	m_z	m_y	c_{2xy}
τ_1	1	1	1	1	1	1	1	1
τ_2	1	1	1	1	-1	-1	-1	-1
τ_3	1	1	-1	-1	1	1	-1	-1
τ_4	1	1	-1	-1	-1	-1	1	1
τ_5	1	-1	1	-1	1	-1	1	-1
τ_6	1	-1	1	-1	-1	1	-1	1
τ_7	1	-1	-1	1	1	-1	-1	1
τ_8	1	-1	-1	1	-1	1	1	-1

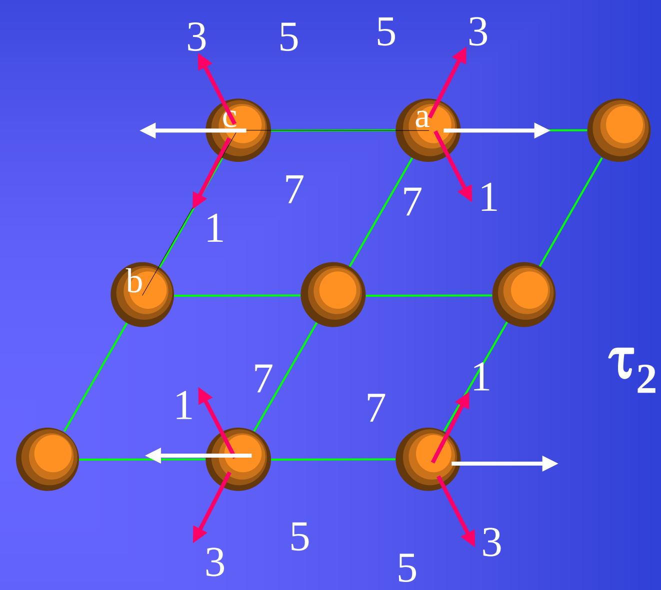
1	$2_{1,z}$	2_y	$2_{2xy,1/4}$	-1	$m_{z,1/4}$	m_y	c_{2xy}





τ_1

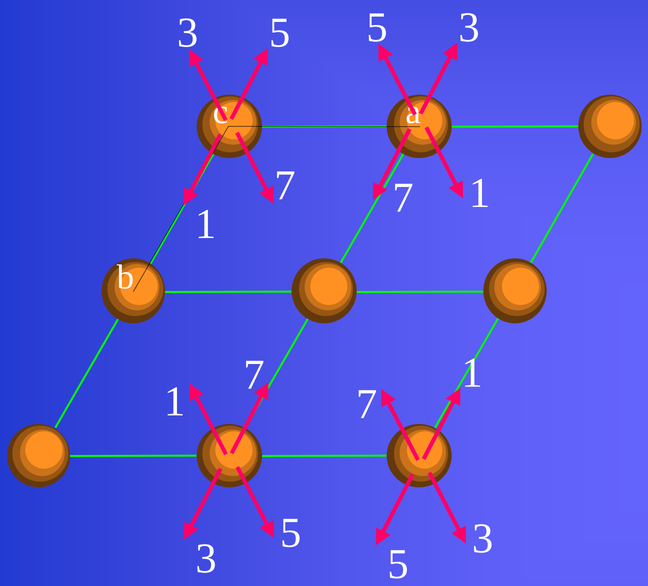




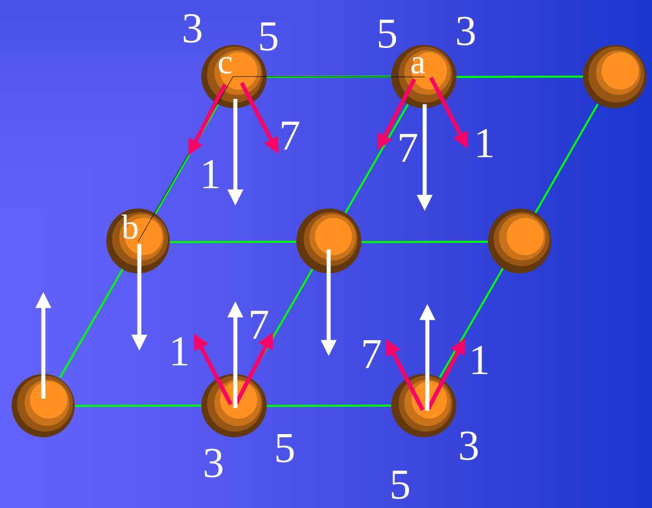
τ_2

τ_1	1	1	1	1	1	1	1	1
τ_2	1	1	1	1	-1	-1	-1	-1

τ_3

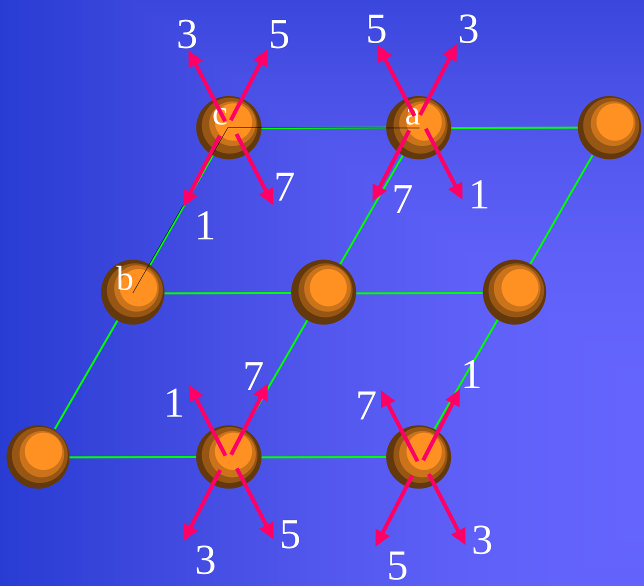


τ_4

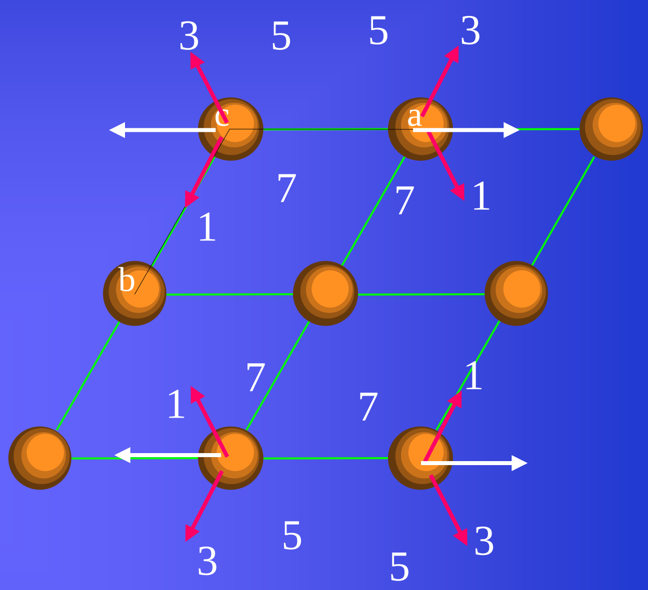


τ_3	1	1	-1	-1	1	1	-1	-1
τ_4	1	1	-1	-1	-1	-1	1	1

τ_5

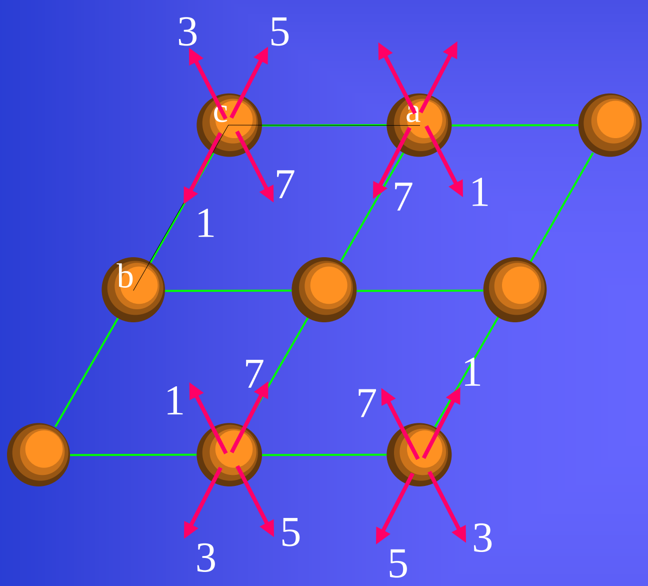


τ_6

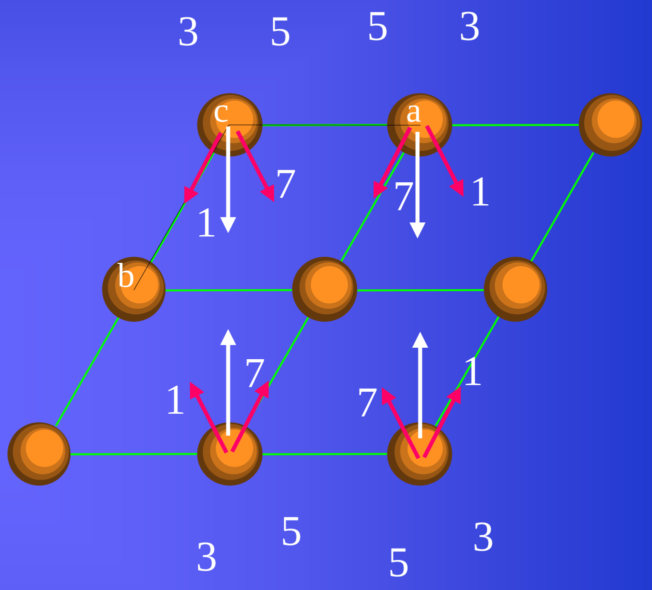


τ_5	1	-1	1	-1	1	-1	1	-1
τ_6	1	-1	1	-1	-1	1	-1	1

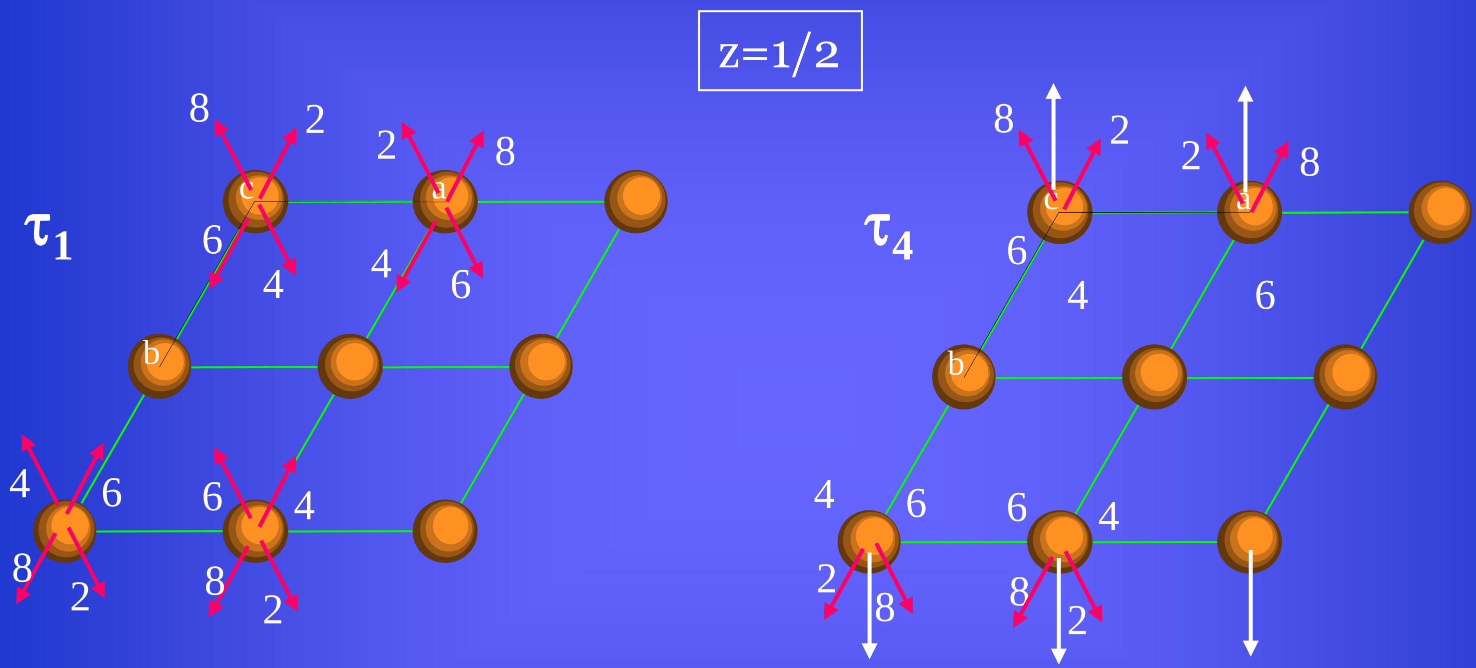
τ_7



τ_8



τ_7	1	-1	-1	1	1	-1	-1	1
τ_8	1	-1	-1	1	-1	1	1	-1



τ_4	1	1	-1	-1	-1	-1	1	1