Topological and Symmetry-Broken Phases in Physics and Chemistry – Theoretical Basics and Phenomena Ranging from Crystals and Molecules to Majorana Fermions, Neutrinos and Cosmic Phase Transitions

International Summer School 2017

UNIVERSITÄT LEIPZIG

Group Theory 1 – Basic Principles

Group Theory 2 & 3 – Group Theory in Crystallography

TUTORIAL: Apply Crystallographic Group Theory to a Phase Transition

Group Theory 4 – Applications in Crystallography and Solid State Chemistry

Prof. Dr. Holger Kohlmann
Inorganic Chemistry – Functional Materials
University Leipzig, Germany
holger.kohlmann@uni-leipzig.de

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1.2 Classification of the group elements and subgroups

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2 From point groups to space groups – a brief introduction to crystallography

3.1 Crystallographic group-subgroup relationships

3.2 Examples of phase transitions in chemistry

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4.1 The relation between crystal structures and family trees

4.2 Complex cases of phase transitions and topotactic reactions

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Ressources

- T. Hahn, H. Wondratschek, Symmetry of Crystals, Heron Press, Sofia, Bulgaria, 1994

- International Tables for Crystallography, Vol. A, Kluwer Acedemic Publishers (= ITA)

- International Tables for Crystallography, Vol. A1, Kluwer Acedemic Publishers (= ITA1)

- H. Bärnighausen, Group-Subgroup Relations Between Space Groups: A Useful Tool in Crystal Chemistry, *MATCH* **1980**, *9*, 139-175

- U. Müller, Symmetry Relationships between Crystal Structures, Oxford University Press [in German: Symmetriebeziehungen zwischen verwandten Kristallstrukturen, Teubner Verlag]

- bilbao crystallographic server, http://cryst.ehu.es/

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Group (Oxford dictionary):

A number of people or things that are located, gathered, or classed together.

**Group in Mathematics**: An algebraic object which

- consists of a set of elements where any two elements combine to form a third element,
- satisfies four conditions called the group axioms (next slide).

Examples:

• integers: Z = {…, -3, -2, -1, 0, 1, 2, 3, …} with addition operation

• symmetry groups with symmetry operations

    - points groups in molecular chemistry, e. g. *mm*2 also called C_{2v}

    - line groups

    - planar groups for patterns and tilinigs, e. g. *p4mm*

    - space groups in crystals, e. g. *Fm* $\bar{3}m$

    - Lie groups in particle physics
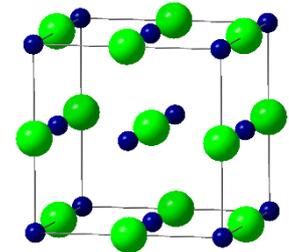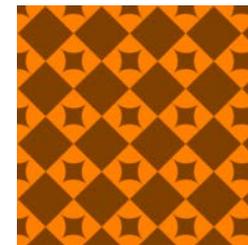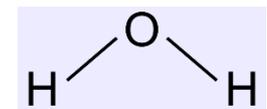
Symbols

G, H, …	group (note: in many ressources fancy fonts are used, e. g. ITA)
e, g, g_1, g_2, h, h_1', h_2'	group element
$G = \{g_1, g_2, …, g_n\}$	group G consists of a set of elements g_1, g_2, …, g_n
x, y, z	point coordinates
a, **b**, **c**	basis vectors
a, b, c	lattice parameters (lengths of basis vectors)

• Overline ˜ denotes an item after mapping (e. g. symmetry transformation)
• prime ' denotes an item after a change of the coordinate system

Group Axioms

1) Closure:

   The composition of any two elements g_1 and g_2 of the group G results in a uniquely determined element g_3 of group G.

   (This is called product of g_1 and g_2, and hence $g_1 g_2 = g_3$).

2) Associativity:

   If g_1, g_2 and g_3 are all elements of the group G, then $(g_1 g_2) g_3 = g_1 (g_2 g_3)$, which can thus be denoted $g_1 g_2 g_3$.

3) Identity:

   Amongst the group elements there exists a unit element (identity operation, neutral element) such that $g e = e g = g$ holds for all $g \in G$. (In crystallography e is called 1.)

4) Invertibility:

   For each $g_1 \in G$ there exists an element $g_2 \in G$ such that $g_1 g_2 = g_2 g_1 = e$. This is called the inverse of g_1: $g_2 = g_1^{-1}$.

Exercise 1: Check the four group axioms for the group of integers.

Further definitions

- group order $|G|$ / element order:

  the number of different elements $g \in G$ / the power which gives e (e. g. $m^2 = mm = e$)

- Abelian or commutative group:

  a group where $g_i \, g_j = g_j \, g_i$ holds for all pairs $g_i, g_j \in G$.

- set of generators of G:

  a set $g_1, g_2, g_3, \ldots \in G$ from which the complete group G can be otained by composition

- multiplication table:

  a square array, where the product $g_1 \, g_2$ is listed at the intersection of row g_1 and column g_2 ($\rightarrow$ symmetric with respect to the main diagonal for Abelian groups)

- isomorphic groups:

 groups with the same multiplication table (apart from names of element symbols)

Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)

Which symmetry operations do you see in this pattern?
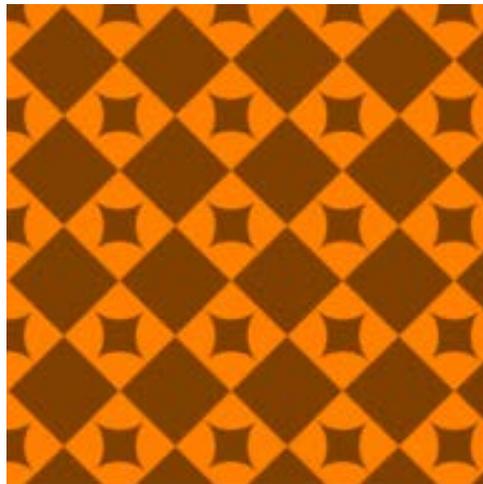
Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)

Which symmetry operations do you see in this pattern?
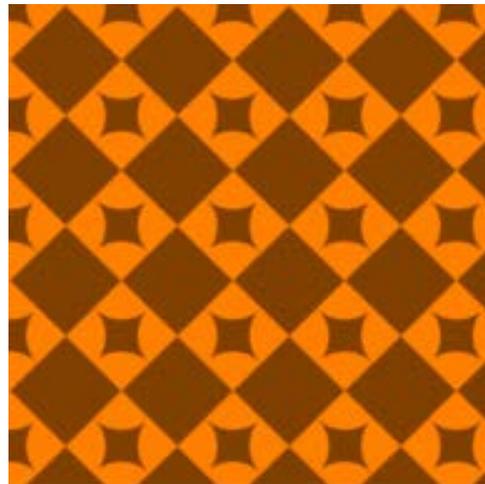
What is symmetry?

Geometric mappings leaving all distances invariant are called isometries or rigid motions. The set of isometries is called symmetry (, i. e. the symmetry of an object is the set of all isometries mapping it onto itself). This set is the symmetry group *G* of the object.

**Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)**

Which symmetry operations do you see in this pattern?

Example: *p4mm*, a planar group (symmetry operations in two dimensions)

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Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)

Which symmetry operations do you see in this pattern?

Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)

Which symmetry operations do you see in this pattern?

- mirror planes *m*: m_x, m_y, m_{xx}, m_{-xx}

- 4-fold rotation point, rotating by 90° (n-fold axis rotates by 360°/n),

  4⁺ (counterclockwise), **4⁻** (clockwise)

- 2-fold rotation point, rotating by 180° (n-fold axis rotates by 360°/n), **2**

- unity element **1**   - translation ***p***

Example: *p*4*mm*, a planar group (symmetry operations in two dimensions)

Which symmetry operations do you see in this pattern?

- mirror planes *m*: $\boldsymbol{m_x}$, $\boldsymbol{m_y}$, $\boldsymbol{m_{xx}}$, $\boldsymbol{m_{-xx}}$

- 4-fold rotation point, rotating by 90° (n-fold axis rotates by 360°/n),

 $\boldsymbol{4^+}$ (counterclockwise), $\boldsymbol{4^-}$ (clockwise)

- 2-fold rotation point, rotating by 180° (n-fold axis rotates by 360°/n), **2**

- unity element **1**   - translation ***p***

Example: *p4mm*, a planar group (symmetry operations in two dimensions)

Multiplication table for the group *4mm*

	1	m_x	m_y	m_{xx}	m_{x-x}	2	4^+	4^-
1								
m_x								
m_y								
m_{xx}								
m_{x-x}								
2								
4^+								
4^-								

Example: *p4mm*, a planar group (symmetry operations in two dimensions)

Multiplication table for the group 4mm

	1	m_x	m_y	m_{xx}	m_{x-x}	**2**	**4⁺**	**4⁻**
1	1	m_x	m_y	m_{xx}	m_{x-x}	2	4⁺	4⁻
m_x	m_x	1	2	4⁻	4⁺	m_y	m_{x-x}	m_{xx}
m_y	m_y	2	1	4⁺	4⁻	m_x	m_{xx}	m_{x-x}
m_{xx}	m_{xx}	4⁺	4⁻	1	2	m_{x-x}	m_x	m_y
m_{x-x}	m_{x-x}	4⁻	4⁺	2	1	m_{xx}	m_y	m_x
2	2	m_y	m_x	m_{x-x}	m_{xx}	1	4⁻	4⁺
4⁺	4⁺	m_{xx}	m_{x-x}	m_y	m_x	4⁻	2	1
4⁻	4⁻	m_{x-x}	m_{xx}	m_x	m_y	4⁺	1	2

Group Theory 1
Basic Principles

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Example: *p4mm*, a planar group (symmetry operations in two dimensions)

Multiplication table for the group 4mm

	1	m_x	m_y	m_{xx}	m_{x-x}	**2**	**4$^+$**	**4$^-$**
1	1	m_x	m_y	m_{xx}	m_{x-x}	2	4$^+$	4$^-$
m_x	m_x	1	2	4$^-$	4$^+$	m_y	m_{x-x}	m_{xx}
m_y	m_y	2	1	4$^+$	4$^-$	m_x	m_{xx}	m_{x-x}
m_{xx}	m_{xx}	4$^+$	4$^-$	1	2	m_{x-x}	m_x	m_y
m_{x-x}	m_{x-x}	4$^-$	4$^+$	2	1	m_{xx}	m_y	m_x
2	2	m_y	m_x	m_{x-x}	m_{xx}	1	4$^-$	4$^+$
4$^+$	4$^+$	m_{xx}	m_{x-x}	m_y	m_x	4$^-$	2	1
4$^-$	4$^-$	m_{x-x}	m_{xx}	m_x	m_y	4$^+$	1	2

- non-Abelian

- order of 4*mm*: 8

- generators of 4*mm*: 1, m_y, 2, 4$^+$

- order of elements: 1 (1), m_x, m_y, m_{xx}, m_{x-x}, 2 (2), 4$^+$, 4$^-$ (4)

- combination of translational symmetry *p* with point group 4*mm* ➜ plane group *p4mm*

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Classification of group elements

= distribution of elements of a set into subsets such that each element belongs to exactly one subset

- coset decomposition
- conjugacy classes

complex C of G

- any set of elements of a group
- gC or Cg denotes all products gc_i, $c_i \in C$

Subgroup H of group G

- a subset H of a group G which obey the group axioms; G and $I = \{e\}$ are called trivial subgroups, all other subgroups are called proper subgroups ($H < G$)

Coset decomposition

Group G is decomposed into cosets relative to its subgroup H (< G) in the following way:

- subgroup H as first coset

- g_2H as second (left) coset, if $g_2 \in G$ and $g_2 \notin H$

- g_3H as second (left) coset, if $g_3 \in G$ and $g_3 \notin H$

- continued until no elements of G left ➜ group G decomposed into left cosets

➔ Each $g_i \in G$ belongs to exactly one coset.

➔ Number of cosets = $|H|$.

➔ Number of left cosets = number of right coset = index [i] of H in G

➔ H is the only group amomgst cosets.

➔ Theorem of Lagrange:

If G is a finite group and $H < G$, then $|H|*[i] = |G|$.

For infinite groups G either $|H|$ or [i] or both are infinite.

Exercise 2: Decompose group $4mm$ into left and right cosets relative to the subgroups H_1 = {1, m_x}, H_2 = {1, m_y}, H_3 = {1, m_{xx}}, H_4 = {1, 2}, H_5 = {1, 2, 4^+, 4^-}, ... and evaluate the results.

Conjugacy relations in groups

- group-theoretical analogue to symmetry equivalent

  ➔ importance for twinning and domain formation

- $g_j \in G$ conjugate to $g_i \in G$ if an element $r \in G$ exists for which $r^{-1} g_i r = g_j$

- set of all elements of of G which are conjugate to g_i is called conjugacy class of g_j

➔ Each $g_i \in G$ belongs to exactly one conjugacy class.

➔ Elements of the same conjugacy class have the same order.

➔ e always forms a conjugacy class for itself.

➔ Number of elements $g_i \in G$ in a conjugacy class of G is called its length L.

Example: group of equilateral triangle ➔ conjugacy classes {1}, {3⁻, 3⁺}, {m_1, m_2, m_3}

of length 1, 2, 3 with order of elements 1, 3, 2

Exercise 3: Determine the 5 conjugacy classes of *4mm*, their lengths and order of elements.

Subgroup *H* of group *G*

- a subset *H* of a group *G* which obey the group axioms; *G* and *I* = {*e*} are called trivial subgroups, all other subgroups are called proper subgroups (*H* < *G*)
- order of *H* is a divisor of the order of *G*
- normal subgroup *N* satisfies $gNg^{-1} = N$ for all $g \in G$
- elements of *N* form complete conjugacy class + *e*

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Classical definition of a crystal:
A crystal is a solid with a three-dimensionally periodic arrangement of atoms.

➔ description of periodicity with three basis vectors defining a unit cell (right-handed)
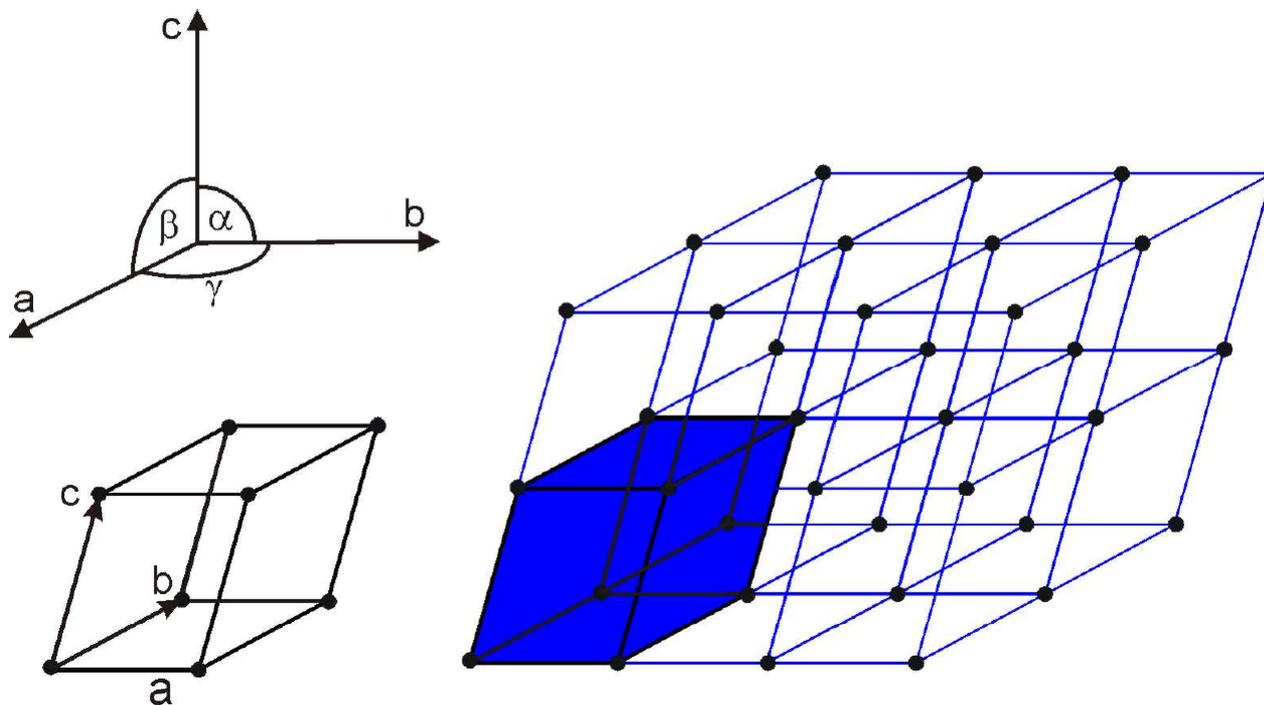
The seven crystal systems

2   From point groups to space groups

The fourteen Bravais lattices (translational lattices)

Symmetry = Invariance to possible tranformations

Symmetry operations	**Symmetry elements**
Translation	Translational lattices (14)
Unity: 1	
Inversion: $\bar{1}$	Inversion center or inversion point
Rotation: 2, 3, 4, 5, 6, 7, …	Rotational axes
reflection: *m*	mirror plane
rotoinversion	rotoinversion axes
glide reflection	glide plane

Remark: $\bar{1}$ reads „one bar", $\bar{3}$ „three bar" …

Combination of symmetry operations: symmetry rules

Symmetry rule 1:

A even-folded rotational axis (such as 2, 4, 6) perpendicular to a mirror plane (e. g. 2/*m*, 4/*m*, 6/*m*) creates a center of symmetry in the intercept.

Symmetry rule 2:

Two perpendicular mirror planes create a twofold axis in the intersetion line.

The development of point groups

It has been shown that *mm* =

Combine 1, m_{xy}, m_{yz} in a multiplication table and complete:

The set of symmetry operations {1,   ,   ,   } form a group which is called   .

**32 crystal classes:** 11 with + **21 without center of symmetry**

triclinic:	**1**	$\overline{1}$				
monoclinic:	**2**	*m*	2/*m*			
orthorhombic:	**222**	*mm*2	*mmm*			
			(2/*m* 2/*m* 2/*m*)			
tetragonal	**4**	$\overline{4}$	4/*m*	**422**	**4*mm***	$\overline{4}2m$	4/*mmm*
							(4/*m* 2/*m* 2/*m*)
trigonal	**3**	$\overline{3}$	**32**	**3*m***	$\overline{3}m$	
					($\overline{3}$ 2/*m*)	
hexagonal	**6**	$\overline{6}$	6/*m*	**622**	**6*mm***	$\overline{6}m2$	6/*mmm*
							(6/*m* 2/*m* 2/*m*)
cubic	**23**	$m\overline{3}$	**432**	$\overline{4}3m$	$m\overline{3}m$	
		(2/*m*$\overline{3}$)			(4/*m* $\overline{3}$ 2/*m*)	

Coupling symmetry operations with translation – glide planes

Example: Coupling of *m* perpendicular to **c** and translations +(½, 0, 0) yields glide plane *a*
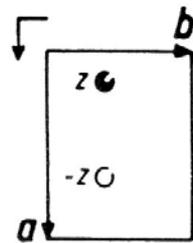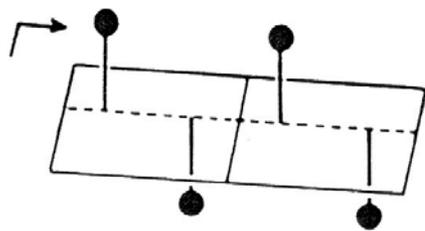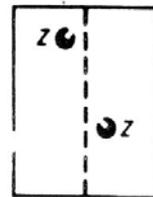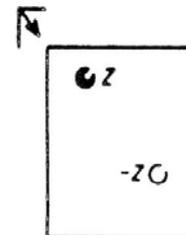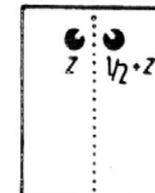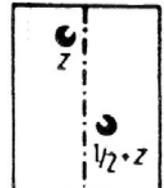
a (⊥ *c*)	*a* (⊥ *b*)	*n* (⊥ *c*)	*c* (⊥ *b*)	*n* (⊥ *b*)

Glide plane *d*:   • like *n* but translation halved, i. e. ¼ of the face diagonal
                                • only in combination with centering (why?)

Glide plane *e*:   • combination of two glide planes, e. g. *a* and *b*

2   From point groups to space groups

Coupling symmetry operations with translation – screw axes

Example: coupling of 6 und translation +(0, 0, ½) yields screw axis 6_3
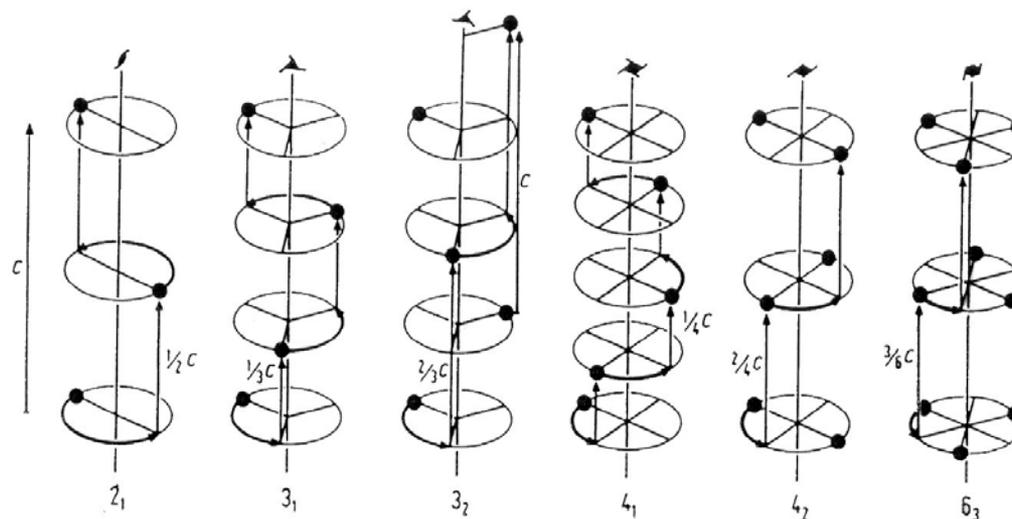
Space group types (space groups)

The combination of the known symmetry operations with the known translational lattices yields **230 space group types**. They enable a compact representation and complete description of the symmetry of crystals (classical definition).

2   From point groups to space groups

The 230 space group types: An overview

Crystal system	point group	viewing direction			space group type
triclinic	1				$P1$
	$\overline{1}$				$P\overline{1}$
monoclinic	2				$P2$, $P2_1$, $C2$
	m	[010]			Pm, Pc, Cm, Cc
	$2/m$				$P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$
orthorhombic	222				$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$
	$mm2$	[100]	[010]	[001]	$C222_1$, $C222$, $F222$, $I222$, $I2_12_12_1$, $Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2_1$, $Pca2_1$, $Pnc2_1$; $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Cmm2$, $Cmc2_1$; $Ccc2$, $Amm2$, $Abma$, $Ama2$, $Aba2$, $Fmm2$, $Fdd2$, $Imm2$, $Iba2$, $Ima2$
	mmm				$Pmmm$, $Pnnm$, $Pccm$, $Pban$, $Pmma$, $Pnna$, $Pmna$, $Pcca$, $Pbam$, $Pccn$, $Pbcm$, $Pnnm$, $Pmmn$, $Pbcn$, $Pbca$, $Pnma$, $Cmcm$, $Cmca$, $Cmmm$, $Cccm$, $Cmma$, $Ccca$, $Fmmm$, $Fddd$, $Immm$, $Ibam$, $Ibca$, $Imma$

2   From point groups to space groups

The 230 space group types: An overview

Crystal system	point group	viewing direction			space group type
tetragonal	4	[001]	[010]	[110]	$P4$, $P4_1$, $P4_2$, $P4_3$, $I4$, $I4_1$
	$\bar{4}$				$P\bar{4}$, $I\bar{4}$
	$4/m$				$P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$, $I4/m$, $I4_1/a$
	422				$P422$, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_3212$, $I422$, $I4_122$
	$4mm$				$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
	$\bar{4}m$				$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
	$4/mmm$				$P4/mmm$, $P4/mcc$, $P4/nbm$, $P4/nnc$, $P4/mbm$, $P4/mnc$, $P4/nmm$, $P4/ncc$, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$, $P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$, $I4/mmm$, $I4/mcm$, $I4_1/amd$, $I4_1/acd$

2 From point groups to space groups

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Crystal system	point group	viewing direction			space group type
trigonal	3				$P3$, $P3_1$, $P3_2$, $R3$
	$\bar{3}$				$P\bar{3}$, $R\bar{3}$
	32	[001]	[100]	[210]	$P312$, $P321$, $P3_112$, $P3_121$, $P3_212$, $P3_221$, $R32$
	$3m$				$P3m1$, $P31m$, $P3c1$, $P31c$, $R3m$, $R3c$
	$\bar{3}m$				$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
hexagonal	6				$P6$, $P6_1$, $P6_5$, $P6_3$, $P6_2$, $P6_4$
	$\bar{6}$				$P\bar{6}$
	$6/m$				$P6/m$, $P6_3/m$
	622	[001]	[100]	[210]	$P622$, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
	$6mm$				$P6mm$, $P6cc$, $P6_3cm$, $P6_3mc$
	$\bar{6}m$				$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
	$6/mmm$				$P6/mmm$, $P6/mcc$, $P6_3/mcm$, $P6_3/mmc$

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The 230 space group types: An overview

Crystal system	point group	viewing direction			space group type
cubic	23	[100]	[111]	[110]	$P23$, $F23$, $I23$, $P2_13$, $I2_13$
	$m\overline{3}$				$Pm\overline{3}$, $Pn\overline{3}$, $Fm\overline{3}$, $Fd\overline{3}$, $Im\overline{3}$, $Pa\overline{3}$, $Ia\overline{3}$
	432				$P432$, $P4_232$, $F432$, $F4_132$, $I432$, $P4_332$, $P4_132$, $I4_132$
	$\overline{4}3m$				$P\overline{4}3m$, $F\overline{4}3m$, $I\overline{4}3m$, $P\overline{4}3n$, $F\overline{4}3c$, $I\overline{4}3d$
	$m\overline{3}m$				$Pm\overline{3}m$, $Pn\overline{3}n$, $Pm\overline{3}n$, $Pn\overline{3}m$, $Fm\overline{3}m$, $Fm\overline{3}c$, $Fd\overline{3}m$, $Fd\overline{3}c$, $Im\overline{3}m$, $Ia\overline{3}d$

The *International Tables for Crystallography* (IT): A short history

1935   Internationale Tabellen zur Bestimmung von Kristallstrukturen

1952   International Tables for X-ray Crystallogaphy

1983   International Tables for Crystallography

2010   International Tables for Crystallography, Vols. A, A1, B, C, D, E, F, G

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4.2 Complex cases of phase transitions and topotactic reactions

Conventions for transformations in crystallography

Basis vectors before transformation **a**, **b**, **c**

Coordinates before transformation x, y, z

Basis vectors after transformation **a'**, **b'**, **c'**

Coordinates after transformation x', y', z'

(**a'**, **b'**, **c'**) =

x'

y' =

z'

Exercises: Work out matrices for the following crystallographic transformations.

4) Transformation of a cubic lattice with lattice parameter a to a cubic lattice with lattice parameter a' = 2a (doubling of the lattice parameter)

5) Transformation of a cubic F-centered lattice to a tetragonal I-centered lattice

6) Transformation of a crystal structure with a = 323 pm, b = 513 pm, c = 1099 pm, α = 90°, β = 97°, γ = 90° and one atom in 0.22 0.08 0.00 to a' = 323 pm, b' = 1026 pm, c' = 1099 pm, α' = 90°, β' = 97°, γ' = 90° and one atom in 0.22 0.04 0.50.

Representation of symmetry relationships between crystal structures (*Bärnighausen* tree)

• crystallographic proof of structural relationships

• important for the classification of phase transitions (reconstructive or displacive)

• from a high symmetry **aristotype** to the low symmetry **hettotype**

• symmetry reduction in the smalles possible steps ➜ maximal subgroups

• often non-standard representations of space groups (in order to minimize

   transformations and zero-point shifts)

• full space group symbols useful (e. g. $P\,6_3/m\;2/c\;2/m$ instead of $P6_3/mcm$)

SrGa$_2$ (AlB$_2$ type)

YbGa$_2$ (CaIn$_2$ type)

IT:

t = I

U. Müller, Symmetry Relationships between Crystal Structures, Oxford University Press

k = IIa/b

i = IIc
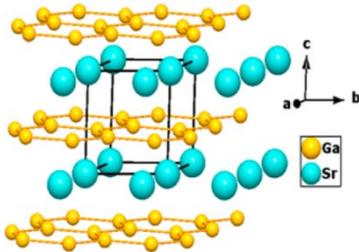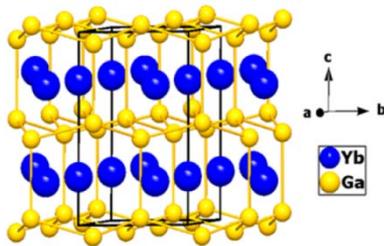
Scheme of the general formulation of the smallest step of symmetry reduction connecting two related crystal structures

		Al : 1a	B : 2d
Hermann–Mauguin symbol of the higher symmetric space group $\mathcal{G}$ → $P\,6/m\,2/m\,2/m$		$6/mmm$	$\bar{6}m2$
		0	$\frac{1}{3}$
Symbol designating the higher symmetric crystal structure, *e.g.* the chemical formula or mineral name → AlB$_2$		0	$\frac{2}{3}$
		0	$\frac{1}{2}$

} see note 5

Type and index of the subgroup $\mathcal{H}$ → $k2$
Basis transformation* → $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$
Origin shift* → $0, 0, -\frac{1}{2}$

$x, y, \frac{1}{2}z + \frac{1}{4}$ ← coordinate transformations

		Ca : 2b	In : 4f
Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ → $P\,6_3/m\,2/m\,2/c$		$\bar{6}m2$	$3m$
		0	$\frac{1}{3}$
Symbol designating the lower symmetric crystal structure → CaIn$_2$		0	$\frac{2}{3}$
		$\frac{1}{4}$	0.455

} see note 5

* mentioned only if there is a change

Explanatory notes

1. Possible types of maximal subgroups $\mathcal{H}$ of a given space group $\mathcal{G}$:

symbol	term	meaning
t	*translationen-gleiche*	$\mathcal{G}$ and $\mathcal{H}$ have the same translational lattice; the crystal class of $\mathcal{H}$ is of lower symmetry than that of $\mathcal{G}$
k	*klassengleiche*	$\mathcal{G}$ and $\mathcal{H}$ belong the same crystal class; $\mathcal{H}$ has lost translational symmetry, its primitive cell is larger than that of $\mathcal{G}$
i	isomorphic	$\mathcal{G}$ and $\mathcal{H}$ belong to the same or the enantiomorphic space group type; $\mathcal{H}$ has lost translational symmetry, its unit cell is larger than that of $\mathcal{G}$
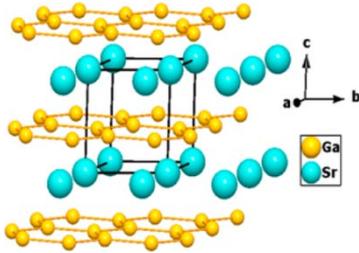
SrGa$_2$ (AlB$_2$ type)
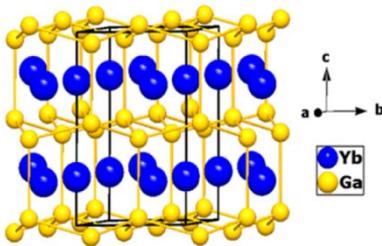
YbGa$_2$ (CaIn$_2$ type)

U. Müller, Symmetry
Relationships between
Crystal Structures,
Oxford University Press

2. The index i of a subgroup is the number of cosets of $\mathcal{H}$ in $\mathcal{G}$. The number of symmetry operations of $\mathcal{H}$ is $1/i$ of those of $\mathcal{G}$.

3. Basis transformation: The three basis vectors of $\mathcal{H}$ are expressed as linear combinations of the basis vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ of $\mathcal{G}$.

4. Origin shift: The coordinate triplet of the origin of $\mathcal{H}$ is given in the coordinate system of $\mathcal{G}$.

5. Additional information: Space permitting, the atomic positions are given in a box next to the space group symbol in the following way:

element symbol: Wyckoff label site symmetry
x
y
z

The coordinates are given for one atom in the asymmetric unit. If a numeric value is fixed by symmetry, it is stated as 0 or as a fraction, e.g. 0, $\frac{1}{4}$, $\frac{1}{2}$. Free parameters are stated as decimal numbers, e.g. 0.0, 0.25, 0.53. If possible, align the site-symmetry symbol in one line with the space-group symbol.

Types of maximal subgroups

translationengleich

- group G and subgroup H have got the same translational lattice
- the crystal class of H has got lower symmetry than that of G
- in IT: **I**
- possibility of twins(t2), triplets (t3), …

klassengleich

- group G and subgroup H belong to the same crystal class
- formed by loss of transl. symmetry (loss of centering or enlargement of primitive cell)
- in IT: **IIa** (loss of centering) or **IIb** (enlargement of primitive cell)
- possibility of anti-phase domains

isomorphic

- special case *klassengleich*, where G and H have got the same or an enantiomorphic space group type
- in IT: **IIc**

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3.2 Examples of phase transitions in chemistry
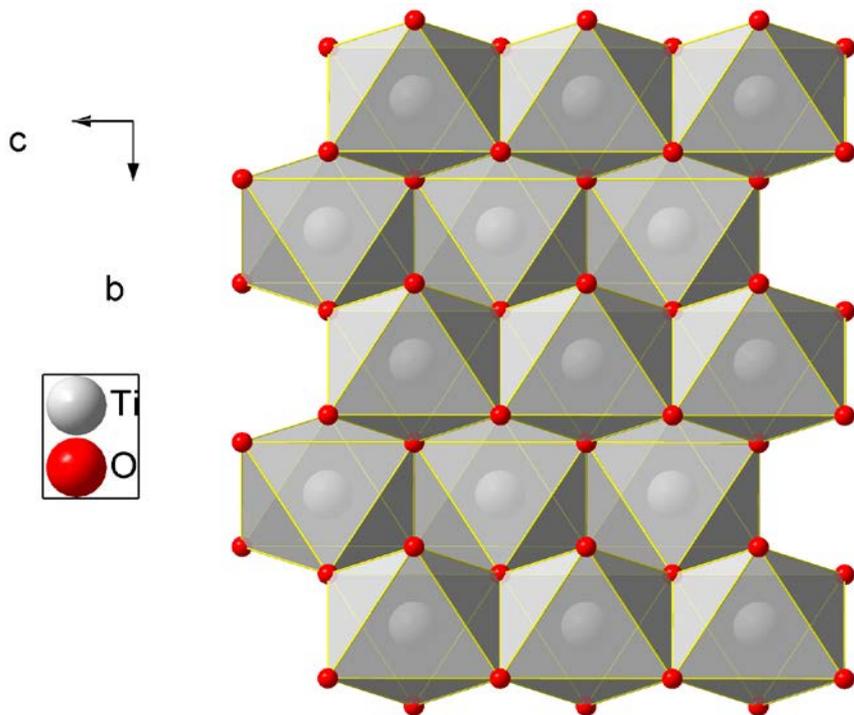
From rutile type   **to**   **CaCl$_2$ type**

P4$_2$/mnm   *Pnnm*

3.2 Examples of phase transitions in chemistry

From rutile type   **to**   **CaCl$_2$ type**

P4$_2$/mnm   *Pnnm*

Ti
O

Ca
Cl
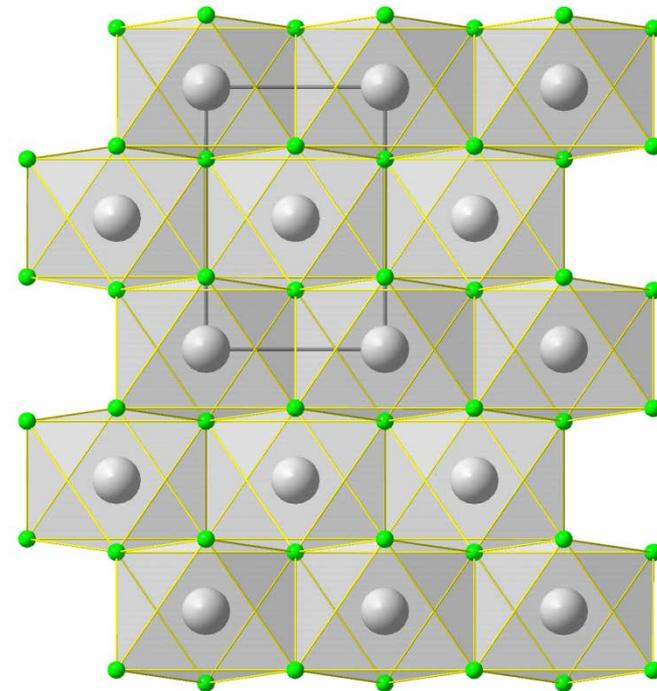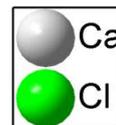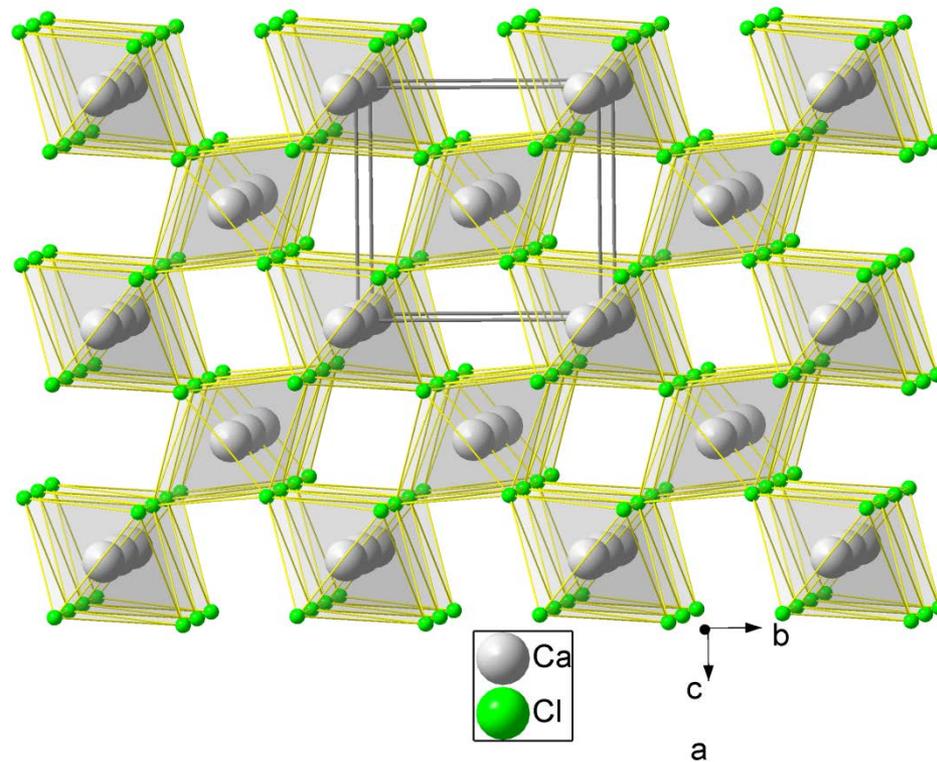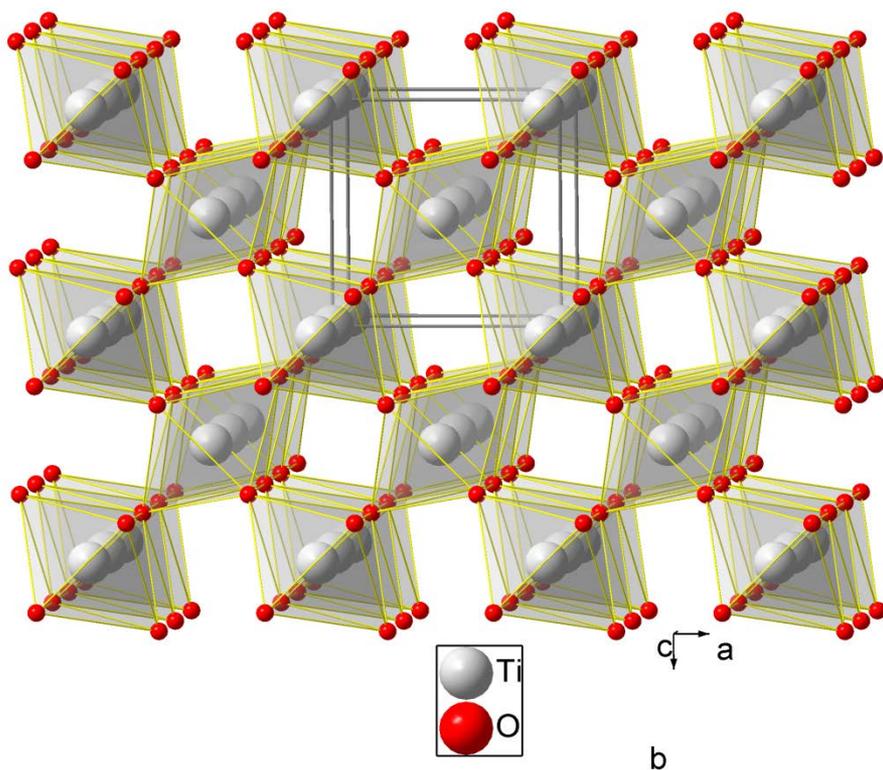
The relationship between rutile and CaCl$_2$ type: polymorphism in SnO$_2$

SnO$_2$: rutile type (ambient)
$P4_2/mnm$, a = 473.67 pm, c = 318.55 pm

Sn in 2a	$m.mm$	0	0	0
O in 4f	$m2.m$	0.307	x	0

SnO$_2$: CaCl$_2$ type (high pressure modification at 12.6 GPa)
$Pnnm$, a = 465.33 pm, b = 463.13 pm, c = 315.50 pm

Sn in 2a	..2/m	0	0	0
O in 4g	..m	0.330	0.282	0

Exercise 7: Work out a *Bärnighausen* tree for the polymorphism of SnO$_2$.

$Bärnighausen$ tree for the polymorphism of SnO_2

Classification of phase transitions

According to **Ehrenfest** a phase transition is of nth order if the nth derivative of the free enthalpy G goes through a sudden change at the phase transition, e. g. volume or entropy for first order or heat capacity or compressibility for second order.

First order phase transitions exhibit **hysteresis** with a coexistence of both phases and are **discontinuous**. They produce **latent heat** and proceed through migration of an interface between both phases (nucleation and growth). In second order phase transitions there is no latent heat, no coexistence of both phases and no hysteresis. Structural changes are **continuous** and a crystallographic group-subgroup relationship is mandatory.

In **displacive** phase transitions (usually second order) minute position changes of atoms mark the transition, whereas in **reconstructive** phase transitions chemical bonds are broken and reformed (always first order).

For continuos phase transitions the phenomenological theory of **Landau and Lifshitz** applies:
• free enthalpy $G = G_0 + 1/2a_2\eta^2 + 1/4a_4\eta^4 + 1/6a_6\eta^6 \ldots$
• order parameter changes continuously following an exponential law $\boldsymbol{\eta = A*[(T_c - T)/T_c]^\beta}$

The use of crystallographic group theory and *Bärnighausen* trees for phase transitions

• classification of phase transitions (n^{th} order, important for physical properties)

• understanding polymorphism (temperature, pressure)

• understanding piezo-, pyro- and ferroelectric phases

• understanding magnetic order phenomena (ferro-, ferri-, antiferro-)

• understanding structural changes during metal-seminconductor transitions

• understanding of order-disorder transitions (e. g. in intermetallic phases)

• understanding the occurrence of twins and antiphase domains

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Exercise 8

Work out the matrix for the transformation of a cubic F-centered
cell (black unit cell) to a primitive cell (yellow unit cell).
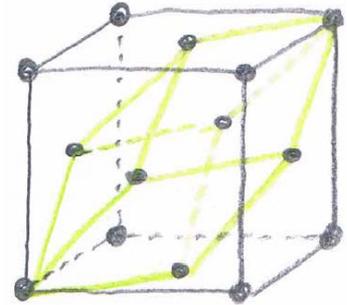
Exercise 9

Work out the matrix for the transformation of a crystal structure with

a = 441 pm, b = 441 pm, c = 441 pm, α = 90°, β = 90°, γ = 90°

with one atom in 0, 0, 0 and one atom in ½, ½, ½ ➔

a = 624 pm, b = 624 pm, c = 882 pm, α = 90°, β = 90°, γ = 90°

and give the transformed coordinates x', y', z' for both atoms.

Phase transitions and symmetry reduction: BaTiO$_3$ as technologically relevant example

T / ºC

cubic, $Pm\bar{3}m$

120

tetragonal, $P4mm$

0

orthorhombic, $Bmm2$

-90

rhombohedral, $R3m$ ferroelectric modifications
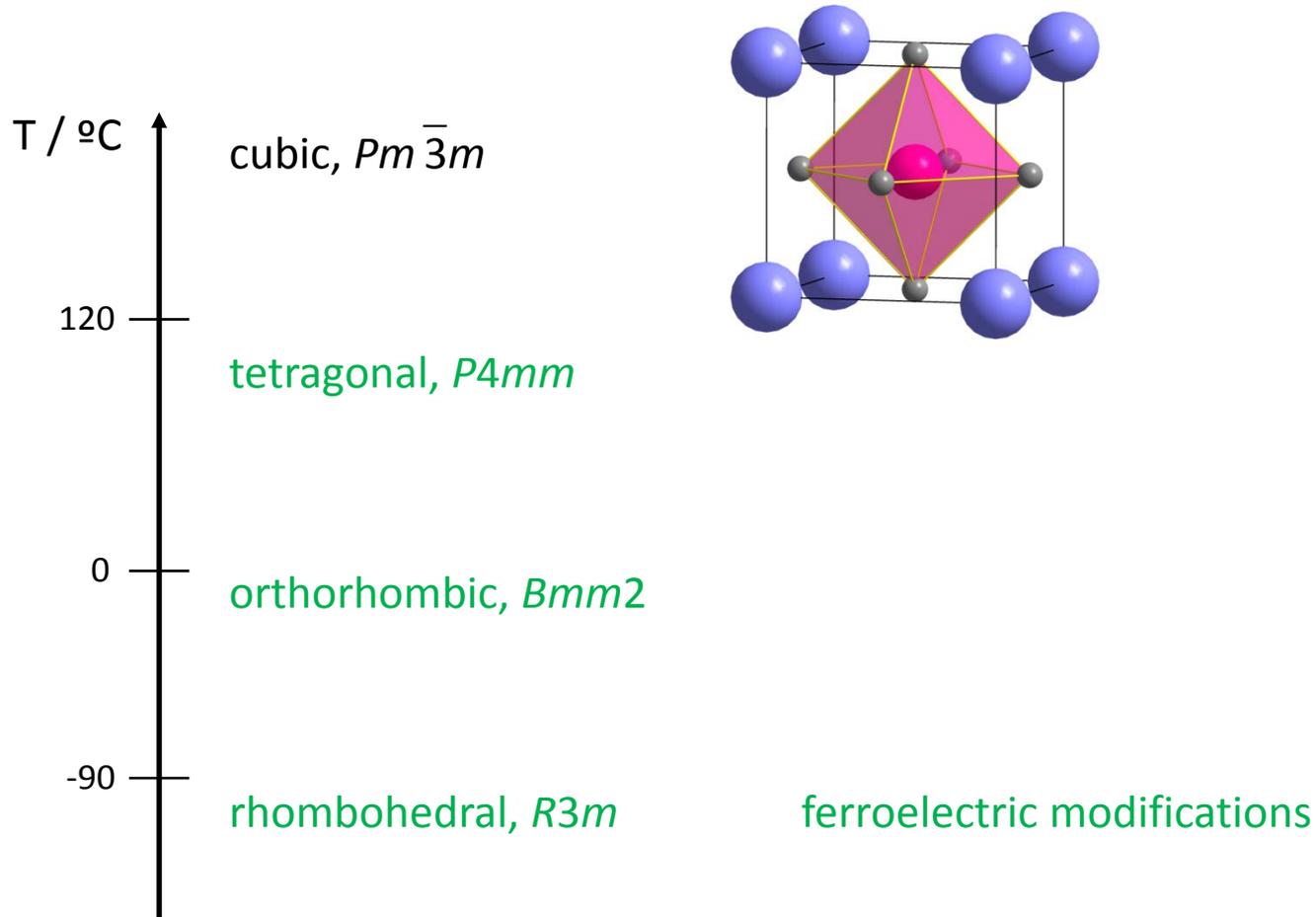
Exercise 10: Work out a *Bärnighausen* tree for the polymorphism of BaTiO$_3$.

(Analyze the result with respect to the formation of twins and antiphase domains.)

Bibliographic data

Publication

Title	Structural Parameters and Electron Difference Density in BaTiO$_3$
Reference	Acta Crystallogr. B (1992) 48, 764-769
Language	English

Authors	Name	Organization/City
	Buttner R.H.	Western Australia University, Department of Physics; Nedlands, Au
	Maslen E.N.	Western Australia University, Department of Physics; Nedlands, Au

Crystal structure

Published crystallographic data

Space group	P4mm (99)
Cell parameters	a = 0.39998(8), b = 0.39998(8), c = 0.40180(8) nm, α = 90, β = 90, γ = 90°
	V = 0.06428 nm^3, a/b = 1.000, b/c = 0.995, c/a = 1.005

Atom coordinates	Site	Elements	Wyck.	Sym.	x	y	z	SOF
	Ba	Ba	1a	4mm	0	0	0.0	
	Ti	Ti	1b	4mm	1/2	1/2	0.482(1)	
	O1	O	1b	4mm	1/2	1/2	0.016(5)	
	O2	O	2c	2mm.	1/2	0	0.515(3)	

Bibliographic data

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Title	Structural Parameters and Electron Difference Density in BaTiO$_3$
Reference	Acta Crystallogr. B (1992) 48, 764-769
Language	English

Authors	Name	Organization/City
	Buttner R.H.	Western Australia University, Department of Physics; Nedlands, Australia
	Maslen E.N.	Western Australia University, Department of Physics; Nedlands, Australia

Crystal structure

Published crystallographic data

Space group	Pm-3m (221)
Cell parameters	a = 0.40058(8), b = 0.40058(8), c = 0.40058(8) nm, α = 90, β = 90, γ = 90°
	V = 0.06428 nm^3, a/b = 1.000, b/c = 1.000, c/a = 1.000

Atom coordinates	Site	Elements	Wyck.	Sym.	x	y	z	SOF
	Ba	Ba	1a	m-3m	0	0	0	
	Ti	Ti	1b	m-3m	1/2	1/2	1/2	
	O1,2	O	3c	4/mm.m	1/2	1/2	0	

Bibliographic data

Publication

Title	Structures of the Ferroelectric Phases of Barium Titanate
Reference	J. Phys. Chem. (1993) 97, 2368-2377
Language	English

Authors	Name	Organization/City
	Kwei G.H.	Los Alamos National Laboratory, ?; Los Alamos, U.S.A. New Mexico
	Lawson A.C.	Los Alamos National Laboratory, ?; Los Alamos, U.S.A. New Mexico
	Billinge S.J.L.	Los Alamos National Laboratory, ?; Los Alamos, U.S.A. New Mexico
	Cheong S.W.	AT and T Bell Laboratories Inc., ?; Murray Hill, U.S.A. New Jersey

Crystal structure

Published crystallographic data

Space group	Amm2 (38)
Cell parameters	a = 0.39828(3), b = 0.56745(5), c = 0.56916(3) nm, α = 90, β = 90, γ = 90°
	V = 0.12863 nm^3, a/b = 0.702, b/c = 0.997, c/a = 1.429

Atom coordinates	Site	Elements	Wyck.	Sym.	x	y	z	SOF
	Ba	Ba	2a	mm2	0	0	0.0	
	Ti	Ti	2b	mm2	1/2	0	0.5170(5)	
	O1	O	2a	mm2	0	0	0.489(6)	
	O2	O	4e	m..	1/2	0.2561(3)	0.2343(4)	

Bibliographic data

Publication

Title	Rhomboedrisches BaTiO$_3$: Strukturuntersuchung bei 132 K und 196 K
Reference	Z. Kristallogr. (1981) 155, 217-226
Language	German

Authors	Name	Organization/City
	Schildkamp W.	Saarland University, Fachbereich Kristallographie; Saarbrücken, Germany
	Fischer K.	Saarland University, Fachbereich Kristallographie; Saarbrücken, Germany

Crystal structure

Published crystallographic data

Space group	R3m r (160)
Cell parameters	a = 0.4004(3), b = 0.4004(3), c = 0.4004(3) nm, α = 89.87, β = 89.87, γ = 89.87°
	V = 0.06419 nm^3, a/b = 1.000, b/c = 1.000, c/a = 1.000

Atom coordinates	Site	Elements	Wyck.	Sym.	x	y	z	SOF
	Ba	Ba	1a	3m	0	0	0.0	
	Ti	Ti	1a	3m	0.4889(3)	0.4889(3)	0.4889(3)	
	O	O	3b	.m	0.5110(3)	0	0.0180(2)	

YBa$_2$Cu$_3$O$_{7-\delta}$

• a threefold superstructure of the cubic perovskite type

• T_c = 90 K

• nobel prize in physics for high temperature superconductivity (Bednorz and Müller, 1987)
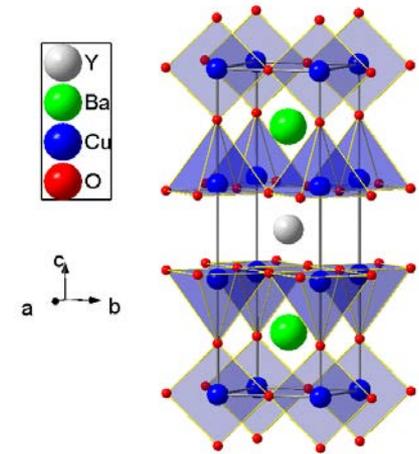
Exercise 11

Describe the crystal structure of YBa$_2$Cu$_3$O$_{7-\delta}$ as a defect variant of the cubic perovskite type using a *Bärnighausen* tree.

Capponi, J.J.; Chaillout, C.; Hewat, A.W.; Lejay, P.; Marezio, M.; Nguyen, N.; Raveau, B.; Soubeyroux, J.L.; Tholence, J.L.; Tournier, R., Europhysics Letters (1987) 3, p1301-p1307

Cell Parameters	3.8206(1) 3.8851(1) 11.6757(4) 90. 90. 90.				
Volume	173.31	Formula Units per Cell	1	Calc. Dens.	6.38
Space Group	P m m m(47)	Pearson Symbol	oP13	Meas. Dens.	
Crystal System	orthorhombic	Crystal Class	mmm	Laue Class	mmm
Wyckoff Sequence	t s r q 2 h e a	Structure Type	YBa2Cu3O6+x(orh)		
Axis Ratios	a/b 0.9834	b/c 0.3328	c/a 3.0560		
Remark					

EL	Lbl	OxState	WyckSymb	X	Y	Z	B
Ba	1	+2.00	2t	0.5	0.5	0.1841(4)	0.59(10)
Y	1	+3.00	1h	0.5	0.5	0.5	0.58(10)
Cu	1	+2.33	1a	0	0	0	0.38(11)
Cu	2	+2.33	2q	0	0	0.3549(3)	0.51(7)
O	1	-2.00	2q	0	0	0.1581(4)	0.93(12)
O	2	-2.00	2s	0.5	0	0.3779(4)	0.11(9)
O	3	-2.00	2r	0	0.5	0.3777(5)	0.31(9)
O	4	-2.00	1e	0	0.5	0	

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4.1 The relation between crystal structures and family trees

	Ca:2a	C1:4f
$P4_2/m\,2_1/n\,2/m$	mmm	$m2m$
$CaCl_2$, > 490 K (rutile type)	0	0.303
	0	0.303
	0	0

t2

	Ca:2a	C1:4g
$P2_1/n\,2_1/n\,2/m$	$..2/m$	$..m$
$CaCl_2$ type, < 490 K	0	0.275
	0	0.325
	0	0

$a = b = 637.9$ pm
$c = 419.3$ pm
at 520 K

$a = 625.9$ pm
$b = 644.4$ pm
$c = 417.0$ pm
at 290 K

Figure 9: Group–subgroup relation between two modifications of calcium chloride and the mutual rotation of the coordination octahedra.
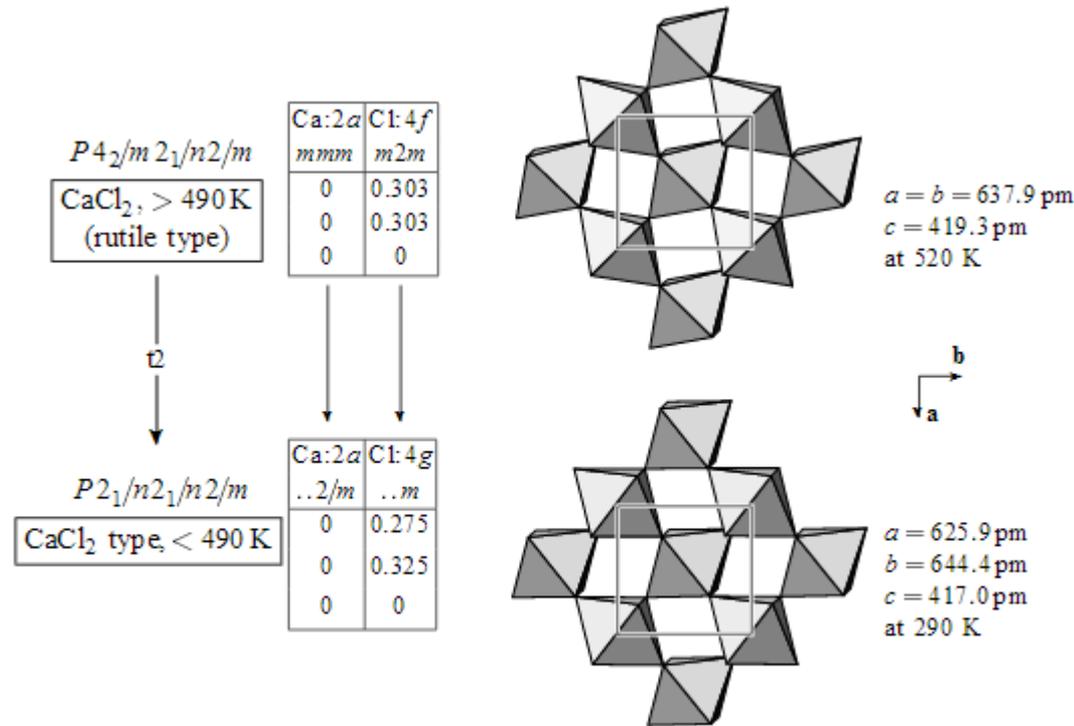
Bärnighausen tree for the polymorphism of $CaCl_2$ (equivalent to the one worked out earlier for SnO_2)

U. Müller, Symmetry Relationships between Crystal Structures, Oxford University Press

W. H. Baur, Rutile type derivatives,
Z. Kristallogr. **1994**, *209*, 143-150

Structure family of the rutile type

4.1 The relation between crystal structures and family trees

Structure family of the cubic perovskite type

H. Bärnighausen, Group-Subgroup Relations Between Space Groups: A Useful Tool in Crystal Chemistry, *MATCH* **1980**, *9*, 139-175
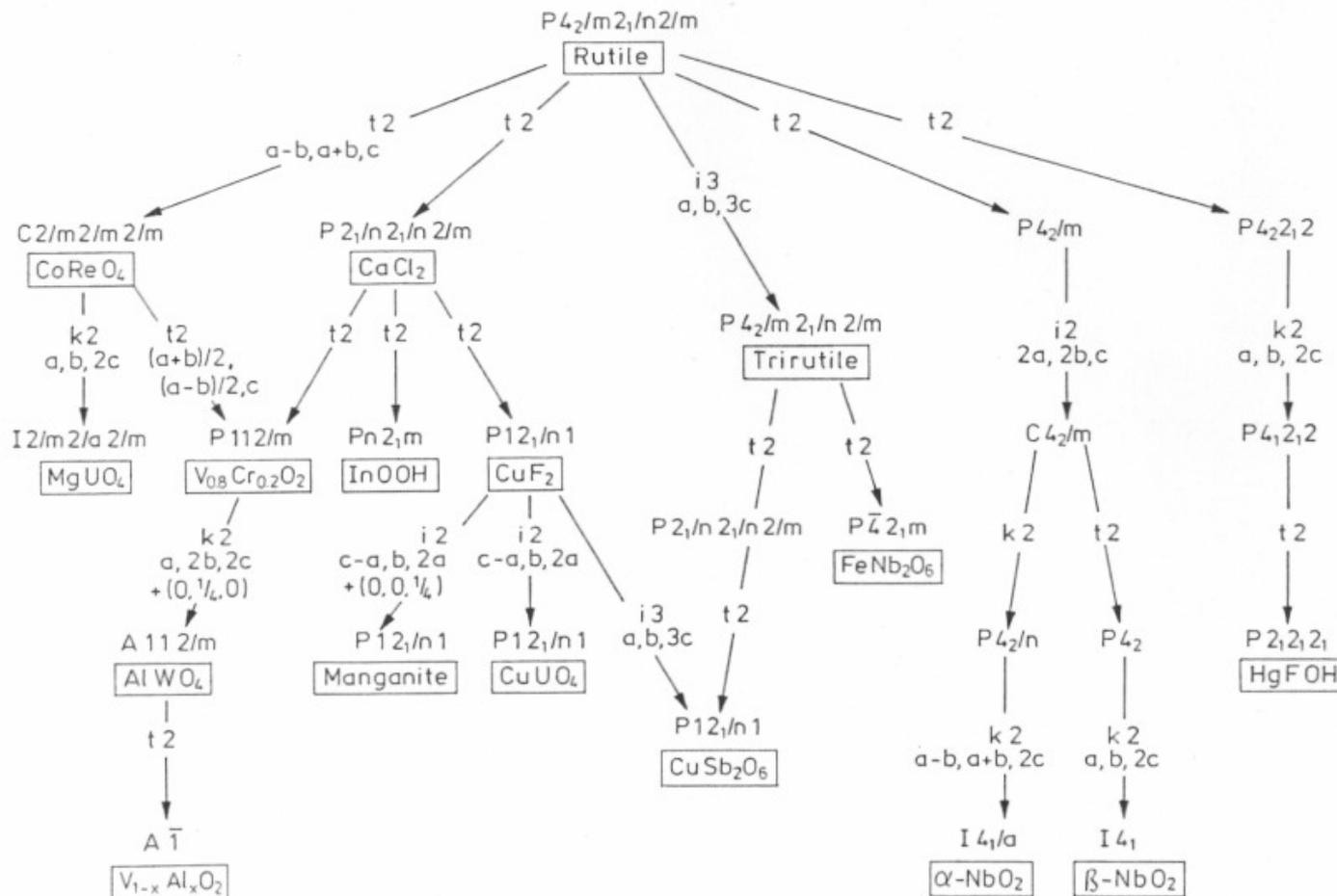
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Structure family of the AlB$_2$ type

R.-D. Hoffmann, R. Pöttgen, *Z. Kristallogr.* **2001**, *216*, 127-145

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Two (of many) modifications von SiO$_2$
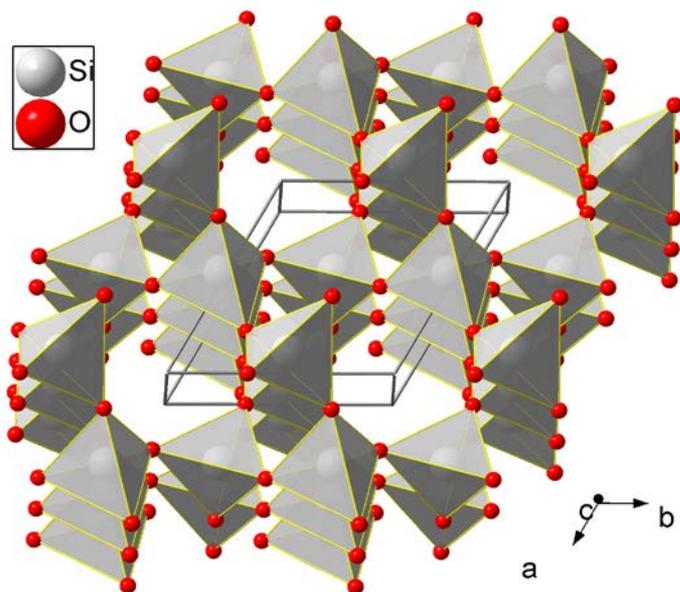
α-Quarz ($P3_221$)
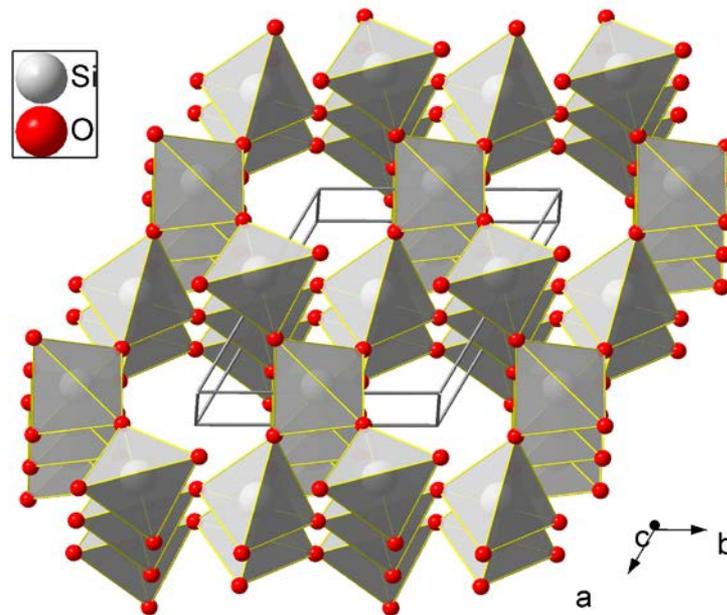
β-Quarz ($P6_222$)

4.2 Complex cases of phase transitions and topotactic reactions

The origin of twinning in quartz: phase transition between high and low quartz at 846 K
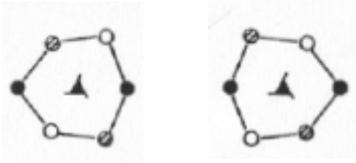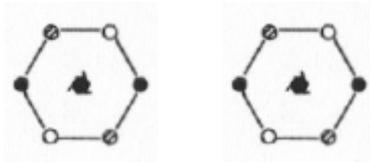
Silicon atoms at $z=0$: O, $z=\frac{1}{3}$: ⊘, and $z=\frac{2}{3}$: ●.
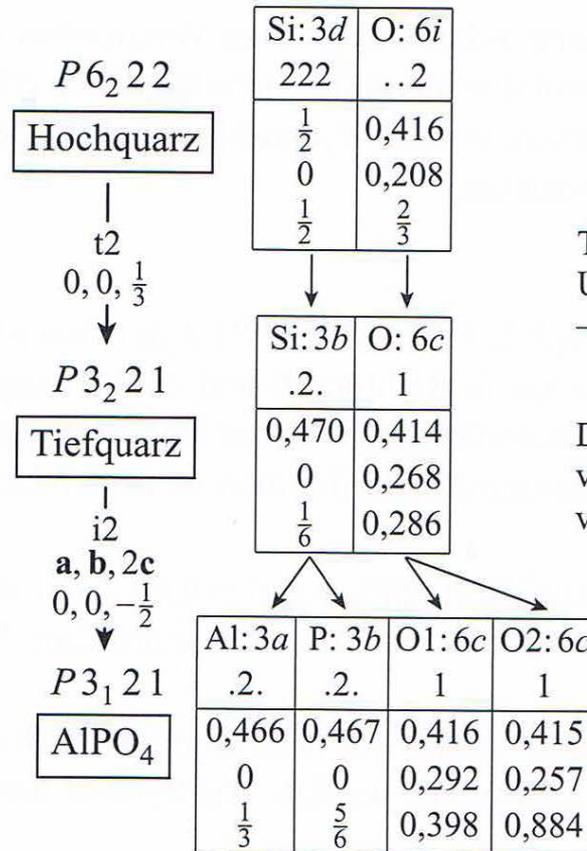
$P6_222$

Hochquarz

	Si: $3d$	O: $6i$
	222	. . 2
	$\frac{1}{2}$	0,416
	0	0,208
	$\frac{1}{2}$	$\frac{2}{3}$

$t2$
$0, 0, \frac{1}{3}$

$P3_221$

Tiefquarz

	Si: $3b$	O: $6c$
	.2.	1
	0,470	0,414
	0	0,268
	$\frac{1}{6}$	0,286

$i2$
$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$
$0, 0, -\frac{1}{2}$

$P3_121$

$AlPO_4$

	Al: $3a$	P: $3b$	O1: $6c$	O2: $6c$
	.2.	.2.	1	1
	0,466	0,467	0,416	0,415
	0	0	0,292	0,257
	$\frac{1}{3}$	$\frac{5}{6}$	0,398	0,884

U. Müller, Symmetriebeziehungen zwischen verwandten Kristallstrukturen, Teubner Verlag

Translationengleiche Untergruppe; Ursprungsverschiebung beachten: $-\frac{1}{3}$ zu den z-Koordinaten addieren

Die x-Koordinate von Si und die z-Koordinate von O werden frei, die x- und y-Koordinaten von O werden voneinander unabhängig

Wegen der Verdoppelung von c z-Koordinaten halbieren, dann wegen der Ursprungsverschiebung $\frac{1}{4}$ und $\frac{3}{4}$ zu den z-Koordinaten addieren

## 4.2 Complex cases of phase transitions and topotactic reactions

$Pm3m$

SrTiO$_3$ (T = 298 K)

EuLiD$_3$

k2
2**a**, 2**b**, 2**c**

k4
2**a**, 2**b**, 2**c**

t3

Ca$_2$RhD$_{5,4}$, M$_2$IrD$_5$
(A = Ca, Sr, Eu)

$Fm3m$
K$_2$PtCl$_6$

$P4/mmm$

t2

t3
½(**a-b**), ½(**a+b**), **c**

i2
a, **b**, 2**c**

$Fm3$

$I4/mmm$
Na$_2$PtD$_4$

$Im3m$
Ca$_8$Rh$_6$D$_{24}$

$P4/mmm$
EuMg$_2$D$_6$

M$_2$IrD$_5$ (T = 100 K)

i4
2**a**, 2**b**, **c**

k4

k2

k2, (¼, ¼ , ¼)

$Pm3m$
Ca$_8$Rh$_5$D$_{23}$

$Pa3$

$P4/nmm$
Mg$_2$CoD$_5$

$P4/mmm$
MgRhD$_{0,94}$

t2

t2, **a-b**, **a+b**, **c**

$P2_13$
CaMgNiD$_4$

$Cmme$

k2, **a**, **b**, 2**c**

$Imaa$
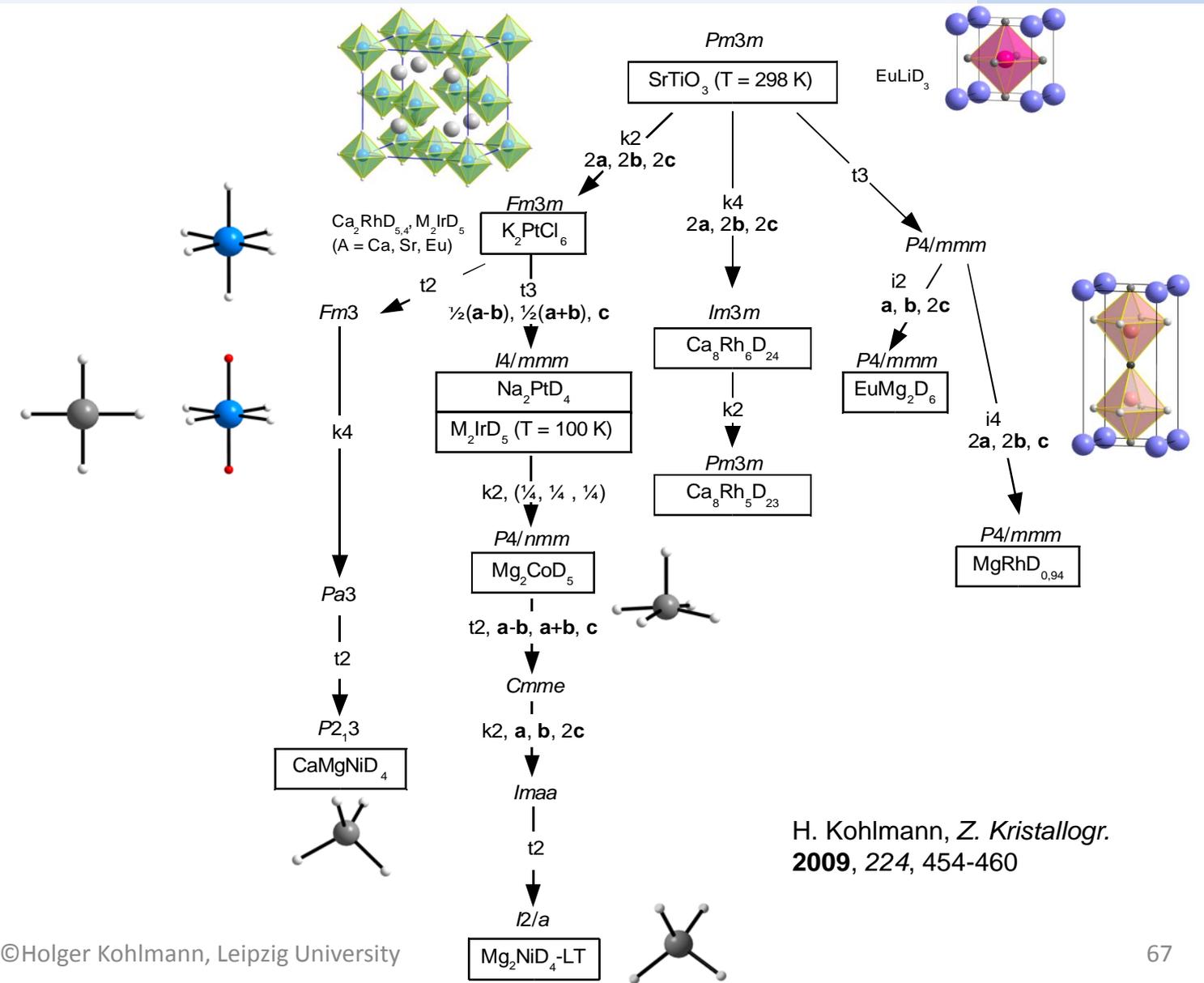
H. Kohlmann, *Z. Kristallogr.*
2009, *224*, 454-460

t2

$I2/a$
Mg$_2$NiD$_4$-LT

Polymorphism and Peirls distortion in VO_2
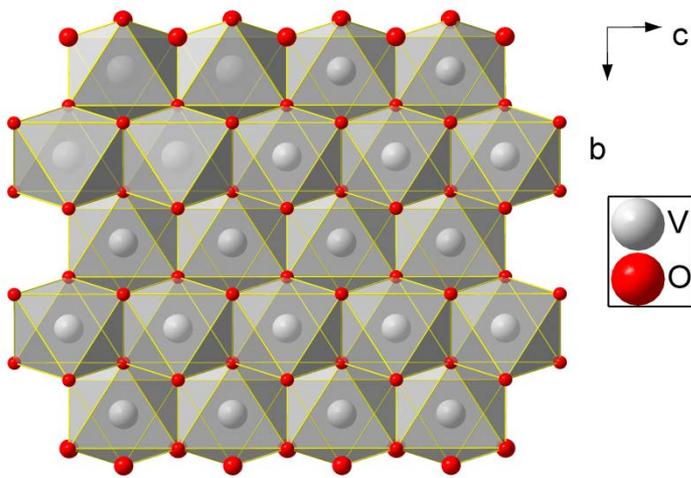
d(V-V) = 285.1 pm

tetragonal rutile type structure
at 360 K
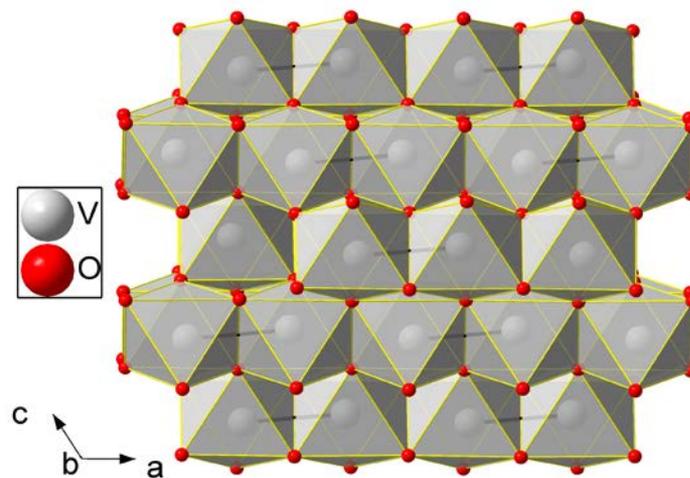
d(V-V) = 261.9 pm, 316.9 pm

monoclinic structure at ambient
(distorted rutile structure)

phase transition accompanied by ➔ metal – insulator transition
➔ Peierls distortion

Polymorphism in VO_2

VO_2:   rutile type (high temperature modification at 373 K)
           $P4_2/nmm$, a = 455.46 pm, c = 285.28 pm

V in 2a	$m.mm$	0	0	0
O in 4f	m2.m	0.3001	x	0

VO_2: VO_2 type (M1 type)
           $P2_1/a$, a = 538.3 pm, b = 453.8 pm, c = 575.2 pm, β = 122.7°

V in 4e	1	0.026	0.021	0.239
O1 in 4e	1	0.299	0.297	0.401
O2 in 4e	1	0.291	0.288	0.894

$V_{0.8}Cr_{0.2}O_2$: $V_{0.8}Cr_{0.2}O_2$ type (M2 type)
           $A112/m$, a = 452.6 pm, b = 906.6 pm, c = 579.7 pm, γ = 91.9°

V in 4e	1	0.026	0.021	0.239
O1 in 4e	1	0.299	0.297	0.401
O2 in 4e	1	0.291	0.288	0.894

4.2 Complex cases of phase transitions and topotactic reactions

**Symmetry analysis
of a Peierls distortion
in VO$_2$**

U. Müller,
Symmetrie-
beziehungen
zwischen
verwandten Kristall-
strukturen,
Teubner Verlag
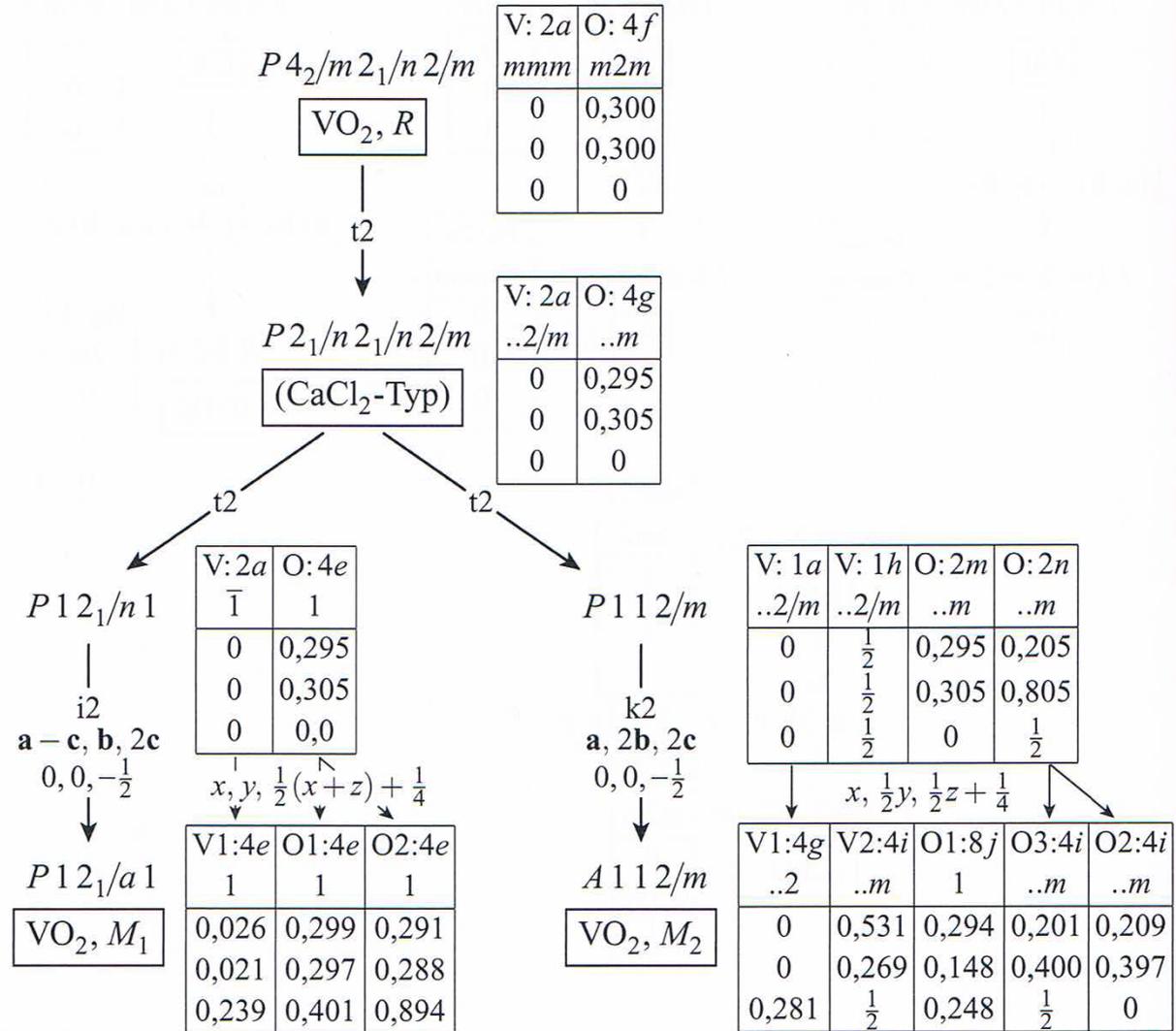
4.2 Complex cases of phase transitions and topotactic reactions

**Order-disorder phase transitions
in ccp-related structures
(ccp = cubic close packing)**

AuCu₃
type
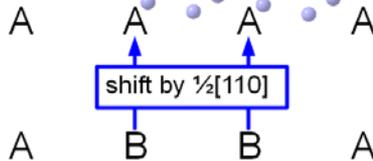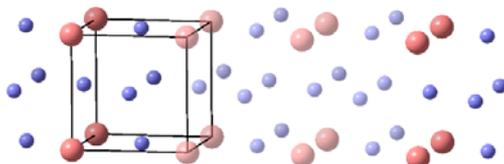
ZrAl₃
type
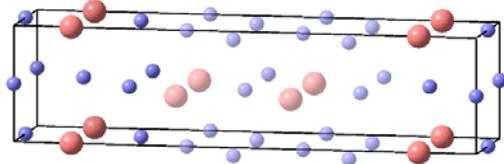
H. Kohlmann, C. Ritter, Reaction Pathways
in the Formation of Intermetallic $InPd_3$
Polymorphs, *Z. Anorg. Allg. Chem.* **2009**,
635, 1573-1579
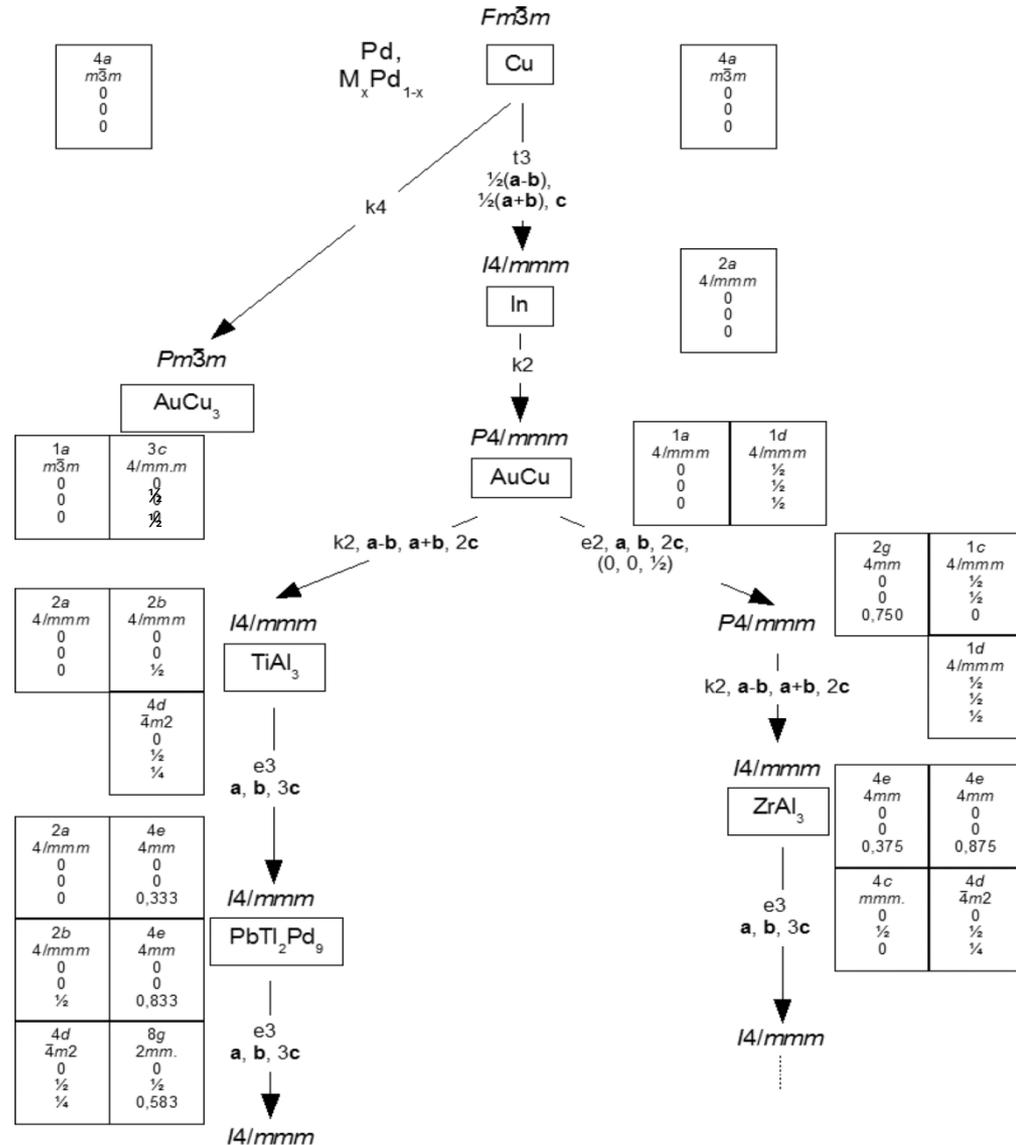
Topotactic Reactions - Definitions
Bonev (I. Bonev, On the Terminology of the Phenomena of Mutual Crystal Orientation, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1972**, *28*, 508-512):
epitaxy - for oriented growth of a phase on the crystal surface of another phase
syntaxy - for simultaneous growth of the mutually oriented crystals of two or more phases
topotaxy - for oriented transformation in an open system with a partial alteration in chemical composition of the primary crystal
endotaxy - for oriented transformation in a closed system, without exchange of components between the system (primary crystal) and its environment

Günther and Oswald (J. R. Günter, H. R. Oswald, Attempt to a Systematic Classification of Topotactic Reactions, *Bull. Inst. Chem. Res., Kyoto Univ.* **1975**, *53*, 249-255):

A chemical reaction of a solid is called topotactic, if the product is formed in one or several crystallographically equivalent orientations relative to the parent crystal, if there has been an exchange of components with the surroundings, and if the reaction can proceed throughout the entire volume of the parent crystal.

If the product is formed in a small number of defined, but not equivalent orientations, the reaction is treated as a case of several different topotactic reactions occurring simultaneously.

4.2 Complex cases of phase transitions and topotactic reactions

In operando diffraction on a lithium ion battery
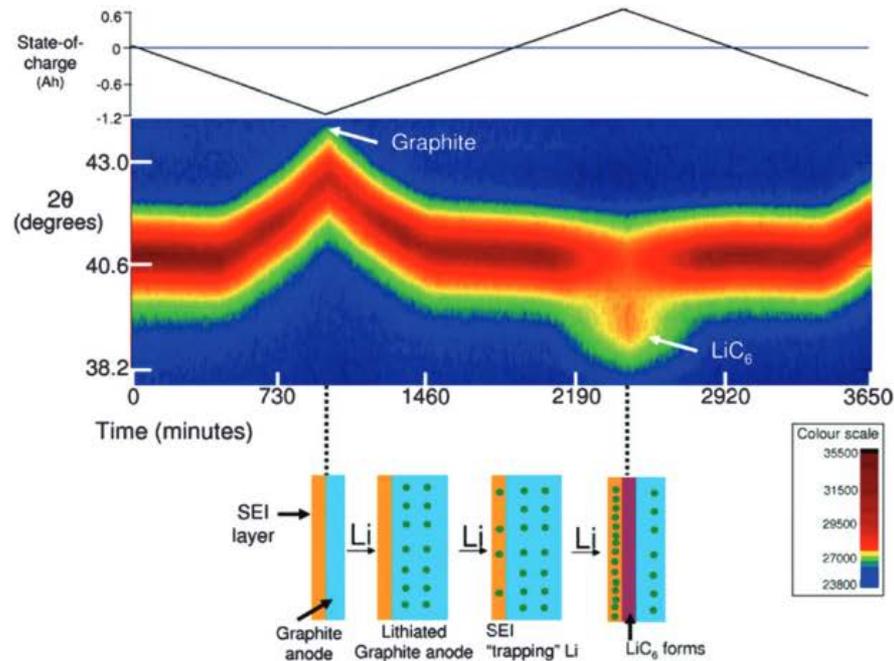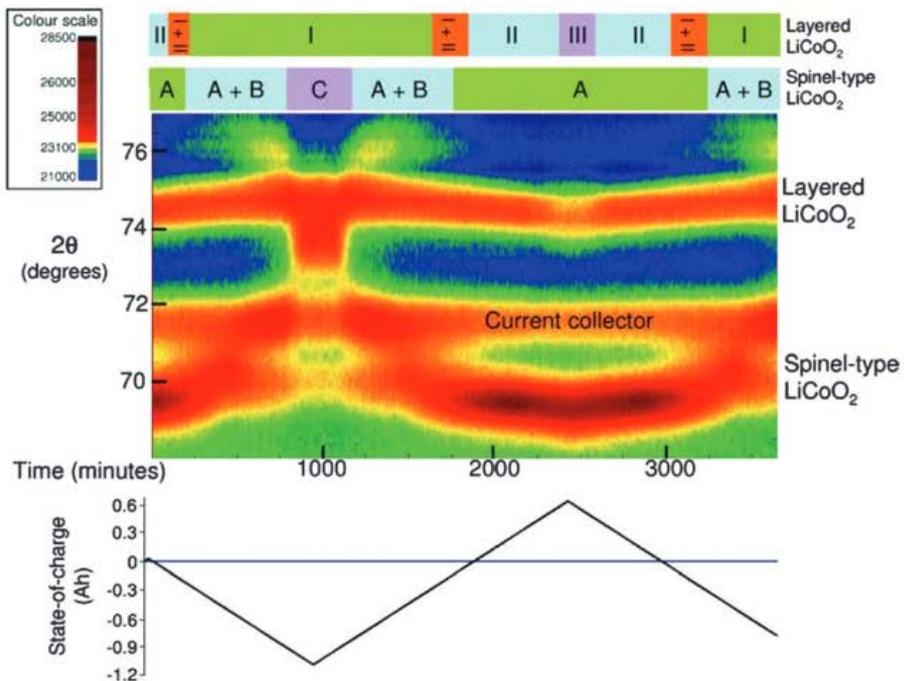
J. Yang, S. Muhammad, M. R. Jo, H. Kim, K. Song, D. A, Agyeman, Y.-I. Kim, W.-S. Yoon, Y.-M. Kang, *Chem. Soc. Rev.* **2016**, *45*, 5717-5770

Application of crystallographic group theory

• describe symmetry and understand symmetry dependent phenomena
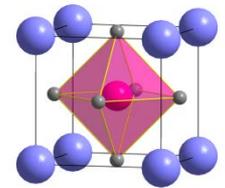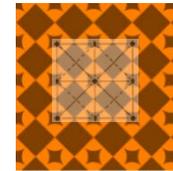
Application of crystallographic group-subgroup relationships

• bring order to the huge number of crystal structures ➜ family trees

• understand substititutional, defect and stuffed variants
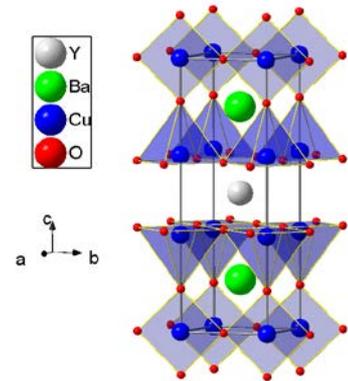
  (splitting of Wyck. pos.)

• classify phase transitions (huge implications for properties!)

• understand and predict formation of twins and anti-phase domains

• understand orientational relations in topotactic reactions

  (e. g. intercalation in lithium ion batteries and

   ion exchange in minerals)

$P4_2/m\,2_1/n\,2/m$	Ca:2a mmm	Cl:4f m2m
CaCl$_2$, > 490 K (rutile type)	0	0.303
	0	0.303
	0	0

t2

$P2_1/n\,2_1/n\,2/m$	Ca:2a ..2/m	Cl:4g ...m
CaCl$_2$ type, < 490 K	0	0.275
	0	0.325
	0	0