Application and Examples of Phase Transitions in Chemistry

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Literature

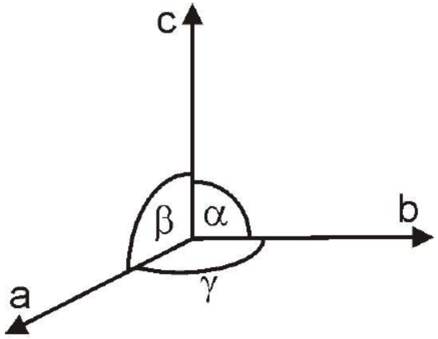
- H. Bärnighausen, Group-Subgroup Relations Between Space Groups: A Useful Tool in Crystal Chemistry, *MATCH* **1980**, *9*, 139-175
- U. Müller, Symmetriebeziehungen zwischen verwandten Kristallstrukturen, Teubner Verlag
- U. Müller, Symmetry Relationships between Crystal Structures, Oxford University Press
- International Tables for Crystallography, Vol. A, Kluwer Acedemic Publishers
- International Tables for Crystallography, Vol. A1, Kluwer Acedemic Publishers

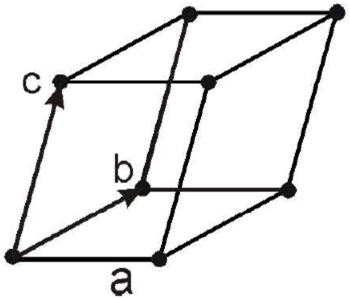
1 From point groups to space groups

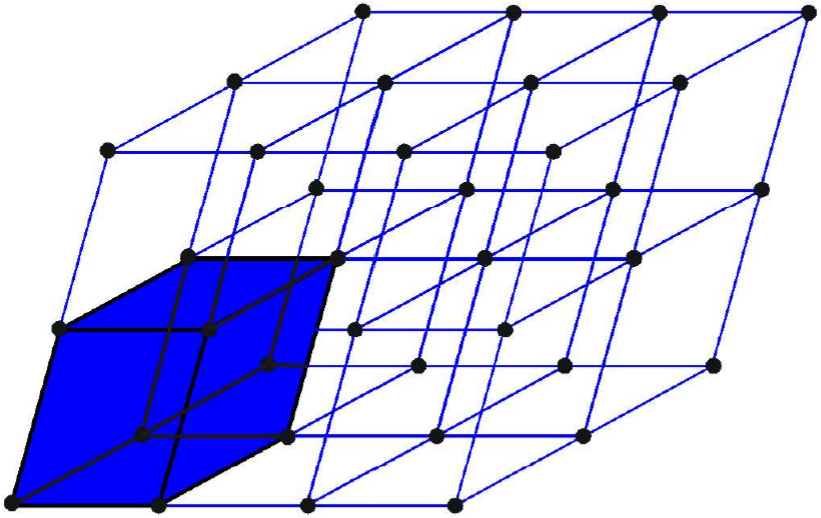
Classical definition of a crystal:

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)







1 From point groups to space groups

The seven crystal systems

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:

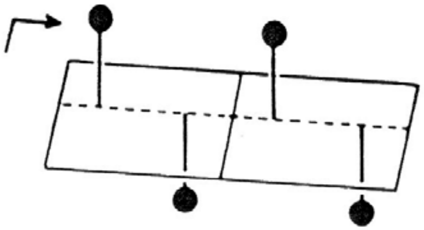
Two perpendicular mirror planes create a twofold axis in the intersetion line.

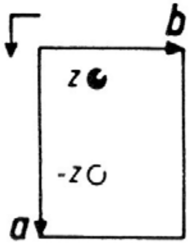
32 crystal classes: 11 with + **21 without center of symmetry**

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

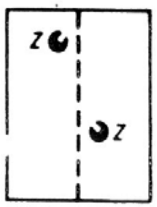
Coupling symmetry operations with translation – glide planes

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

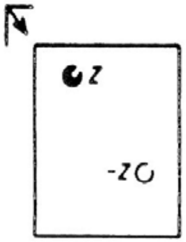




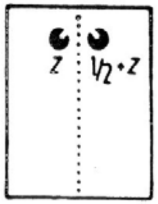
a (⊥ *c*)



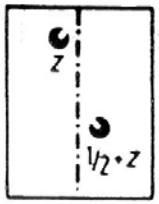
a (⊥ *b*)



n (⊥ *c*)



c (⊥ *b*)

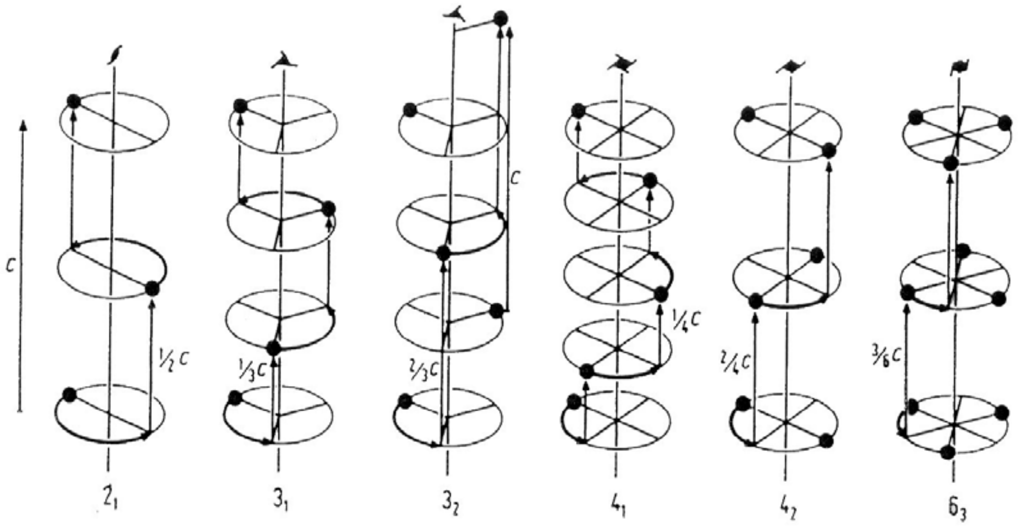


n (⊥ *b*)

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*

Coupling symmetry operations with translation – screw axes

Example: coupling of 6 und translation +(0, 0, ½) yileds 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).

Die 230 space group types: An overview

Crystal system	point group	viewing direction			space group type
triclinic	1				$P1$
	$\bar{1}$				$P\bar{1}$
monoclinic	2	[010]			$P2$, $P2_1$, $C2$
	m				Pm, Pc, Cm, Cc
	$2/m$				$P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$
orthorhombic	222	[100]	[010]	[001]	$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$
	*mm*2				$C222_1$, $C222$, $F222$, $I222$, $I2_12_12_1$, $Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2_1$, $Pca2_1$, $Pnc2_1$; $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Cmm2$, $Cmc2_1$; $Ccc2$, $Amm2$, $Abma$, $Ama2$, $Aba2$, $Fmm2$, $Fdd2$, $Imm2$, $Iba2$, $Ima2$
	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*

Die 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				$P422$, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_3212$, $I422$, $I4_122$
	$4mm$				$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
	$\bar{4}m$				$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
	$4/mmm$				$P4/mmm$, $P4/mcc$, $P4/nbm$, $P4/nnc$, $P4/mbm$, $P4/mnc$, $P4/nmm$, $P4/ncc$, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$, $P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$, $I4/mmm$, $I4/mcm$, $I4_1/amd$, $I4_1/acd$

Die 230 space group types: An overview

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

Die 230 space group types: An overview

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

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

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.

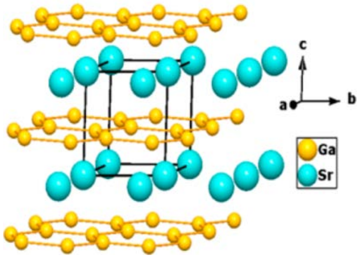
1) Transformation of a cubic lattice with lattice parameter a to a cubic lattice with lattice parameter a‘ = 2a (doubling of the lattice parameter)

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

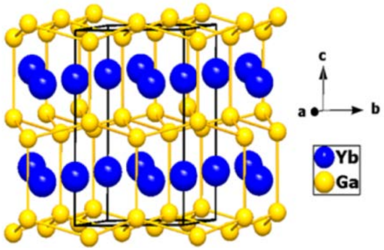
3) Transformation of a crystal structure with a = 323 pm, b = 513 pm, c = 1099 pm, α = 90°, β = 97°, γ = 90° and one atom in 0.22 0.08 0.00 to a‘ = 323 pm, b‘ = 1026 pm, c‘ = 1099 pm, α‘ = 90°, β‘ = 97°, γ‘ = 90° and one atom in 0.22 0.04 0.50.

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

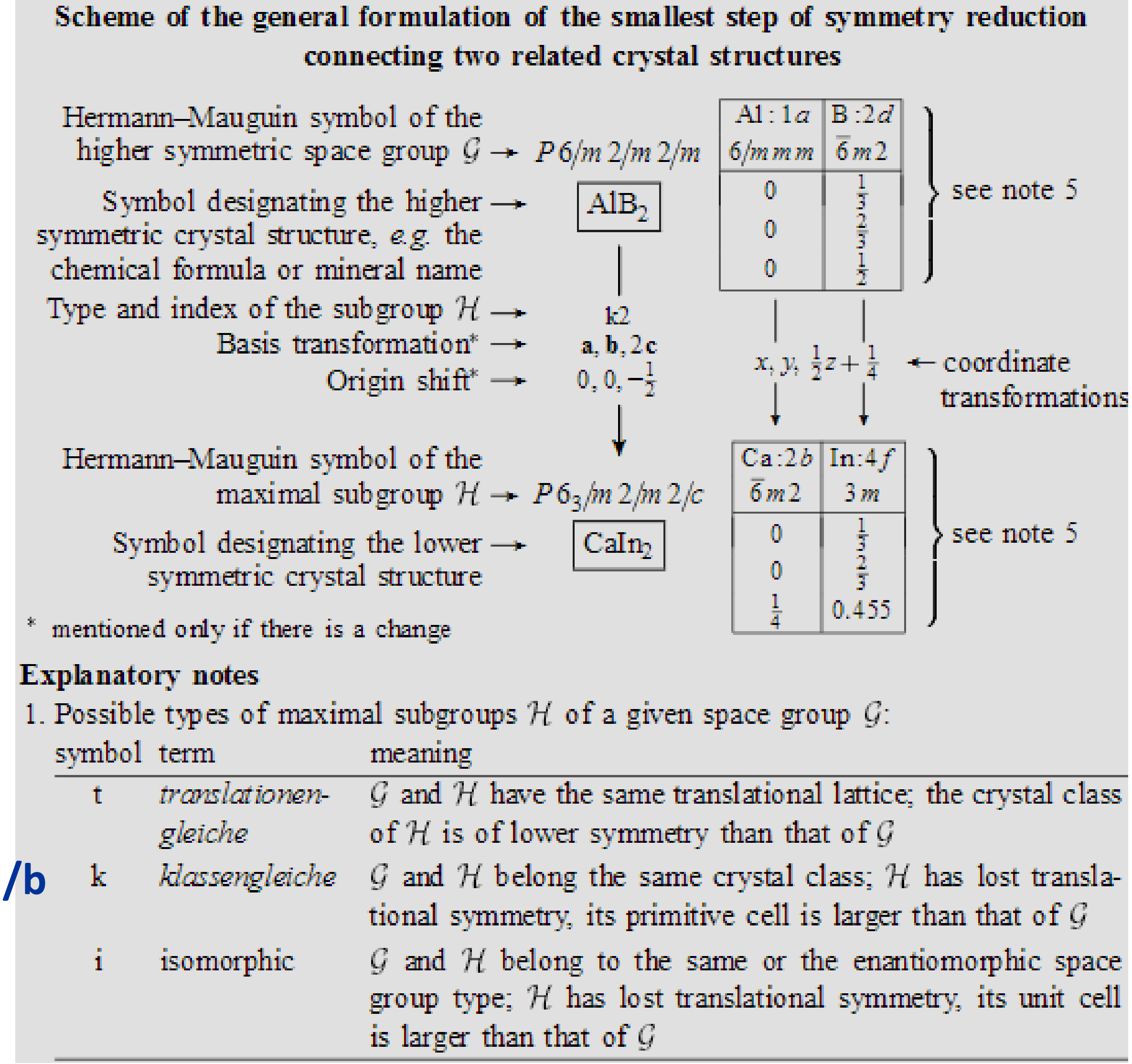
- crystallographic proof of structural relationships
- important for the classification of phase transitions (reconstructive or displacive)
- from a high symmetry **aristotype** to the low symmetry **hettotype**
- symmetry reduction in the smalles possible steps ➔ maximal subgroups
- often non-standard 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)



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

Hermann–Mauguin symbol of the higher symmetric space group $\mathcal{G}$ → $P6/m\,2/m\,2/m$

Symbol designating the higher symmetric crystal structure, e.g. the chemical formula or mineral name → AlB_2

Type and index of the subgroup $\mathcal{H}$ → k2

Basis transformation* → **a**, **b**, 2**c**

Origin shift* → $0, 0, -\frac{1}{2}$

Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ → $P6_3/m\,2/m\,2/c$

Symbol designating the lower symmetric crystal structure → $CaIn_2$

Al : 1*a*	B : 2*d*
$6/mmm$	$\bar{6}m2$
0	$\frac{1}{3}$
0	$\frac{2}{3}$
0	$\frac{1}{2}$

see note 5

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

Ca : 2*b*	In : 4*f*
$\bar{6}m2$	$3m$
0	$\frac{1}{3}$
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	*translationengleiche*	$\mathcal{G}$ 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 $\mathcal{G}$

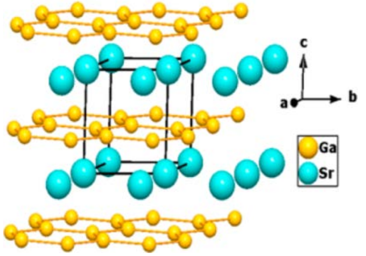
IT:

t = I

k = IIa/b

i = IIc

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



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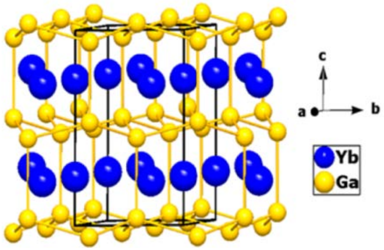
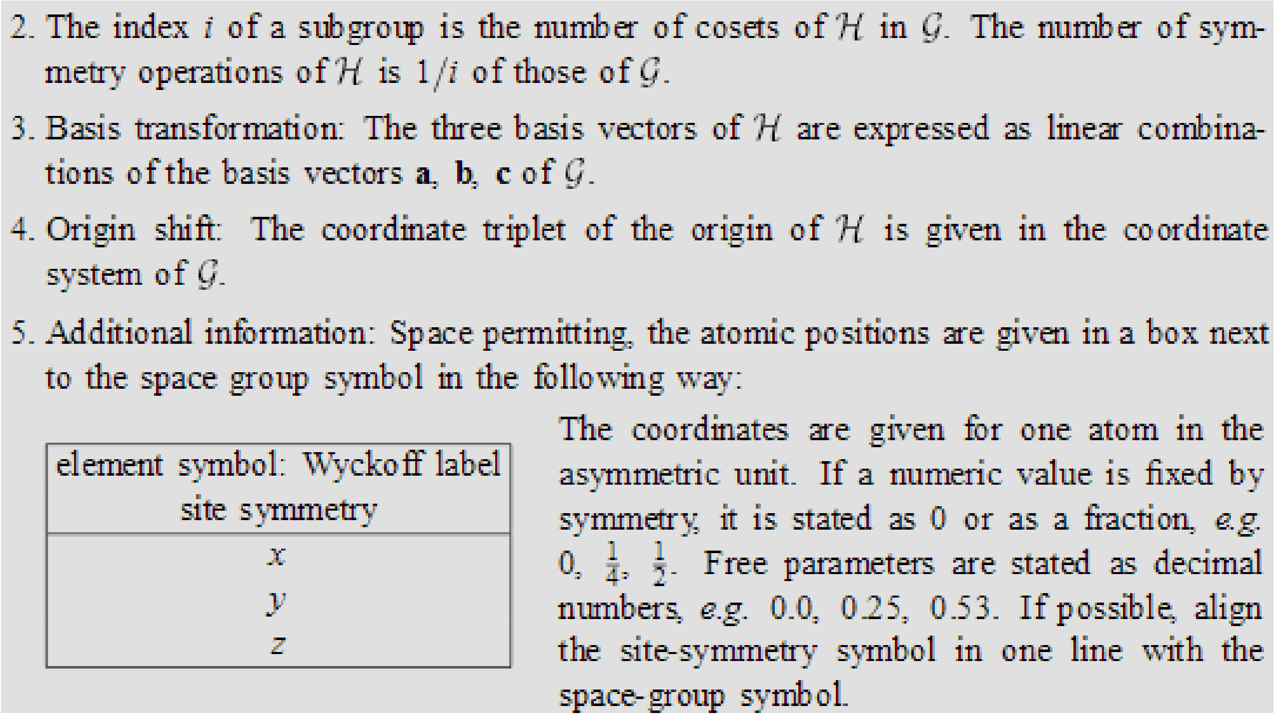


$YbGa_2$ ($CaIn_2$ type)



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 **a**, **b**, **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.

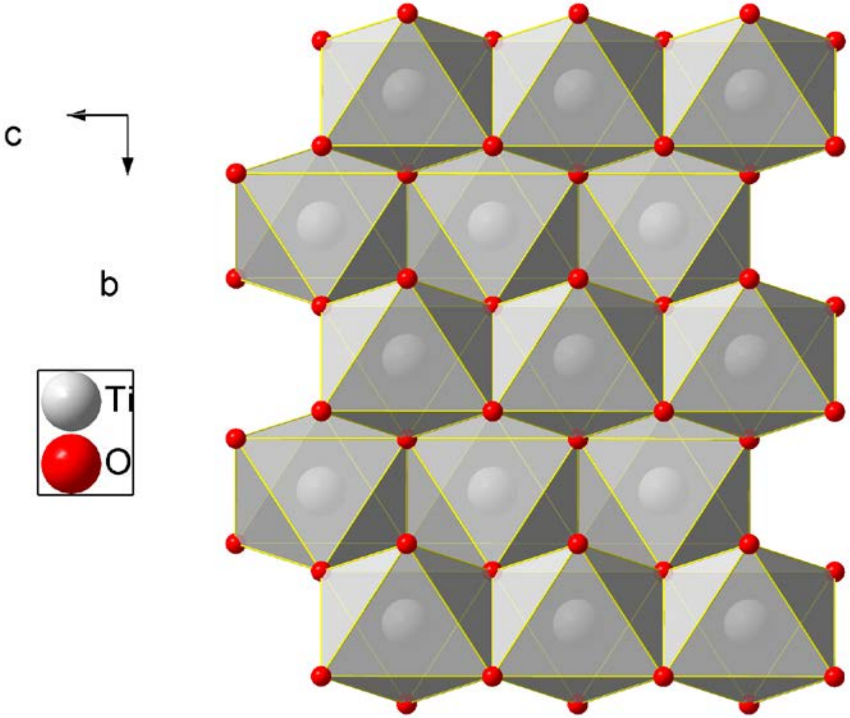
U. Müller, Symmetry Relationships between Crystal Structures, Oxford University Press

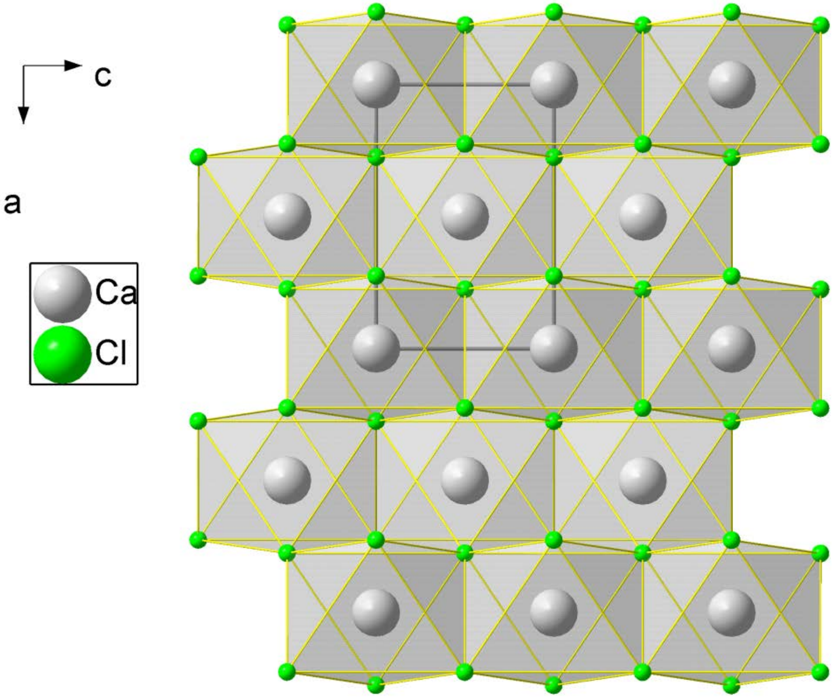
3 Examples of phase transitions in chemistry

From rutile type **to** **$CaCl_2$ type**

$P4_2/mnm$

$Pnnm$





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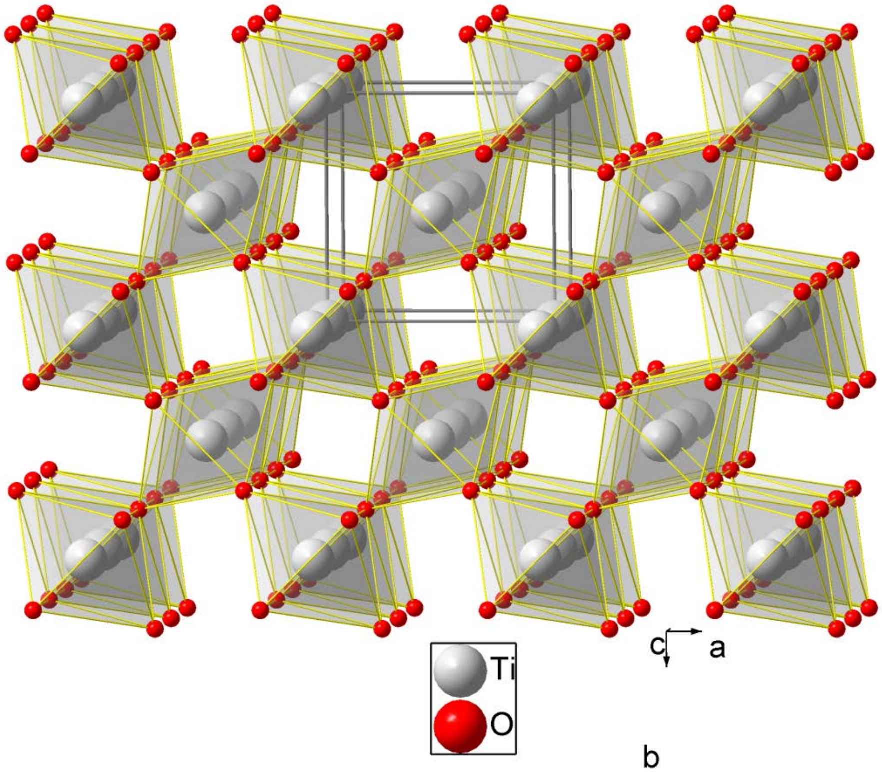
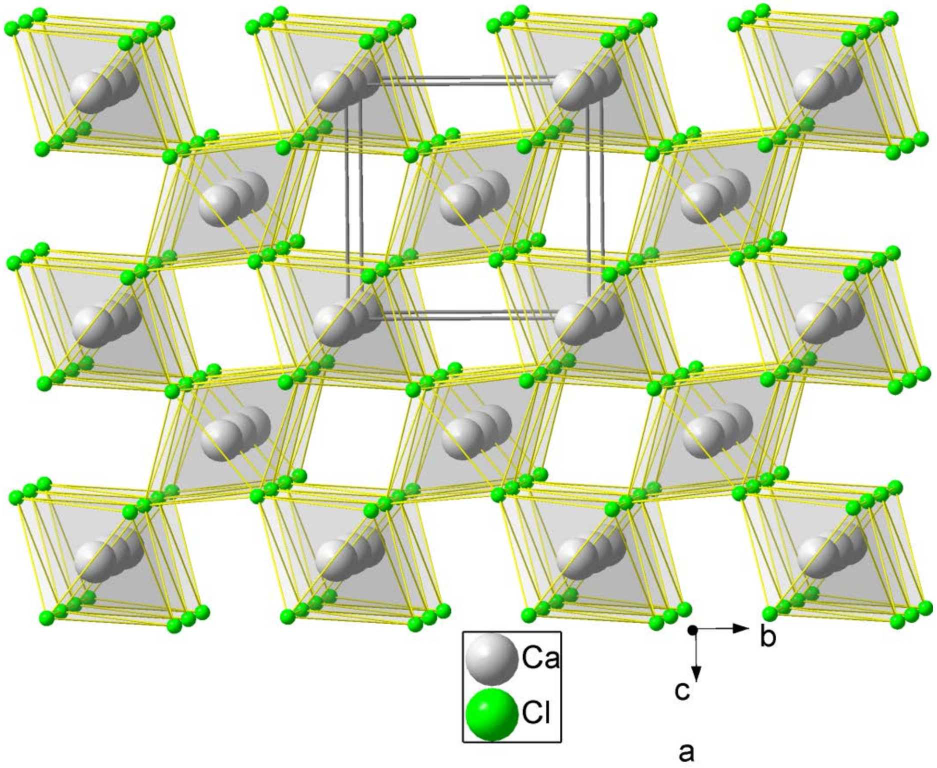




The relationship between rutile and $CaCl_2$ type: polymorphism in SnO_2

SnO_2: rutile type (ambient)

$P4_2/mnm$, a = 473.67 pm, c = 318.55 pm

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

SnO_2: $CaCl_2$ type (high pressure modification at 12.6 GPa)

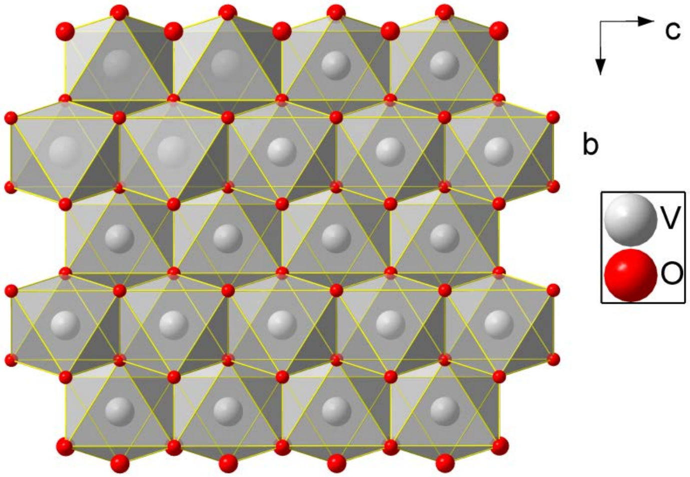
Pnnm, a = 465.33 pm, b = 463.13 pm, c = 315.50 pm

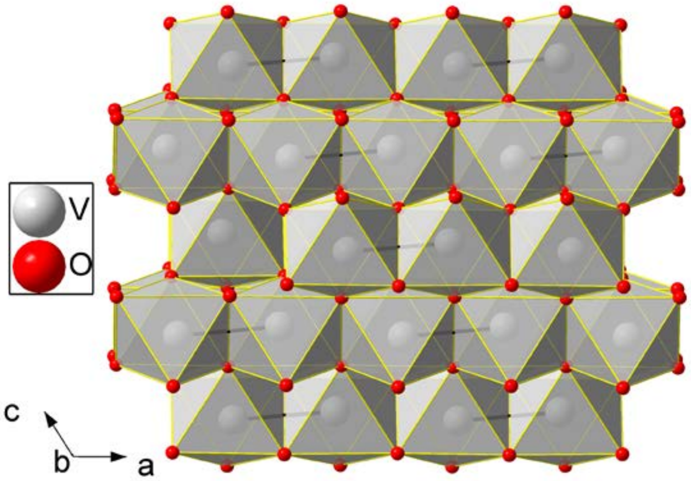
Sn in 2*a*	..2/*m*	0	0	0
O in 4*g*	..*m*	0.330	0.282	0

Exercise 4: Work out a *Bärnighausen* tree for the polymorphism of SnO_2.

Bärnighausen tree for the polymorphism of SnO_2

Polymorphism in VO_2





d(V-V) = 285.1 pm

d(V-V) = 261.9 pm, 316.9 pm

tetragonal rutile type structure
at 360 K

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

VO_2: VO_2 type (*M*1 type)

$P2_1/a$, a = 538.3 pm, b = 453.8 pm, c = 575.2 pm, β = 122.7°

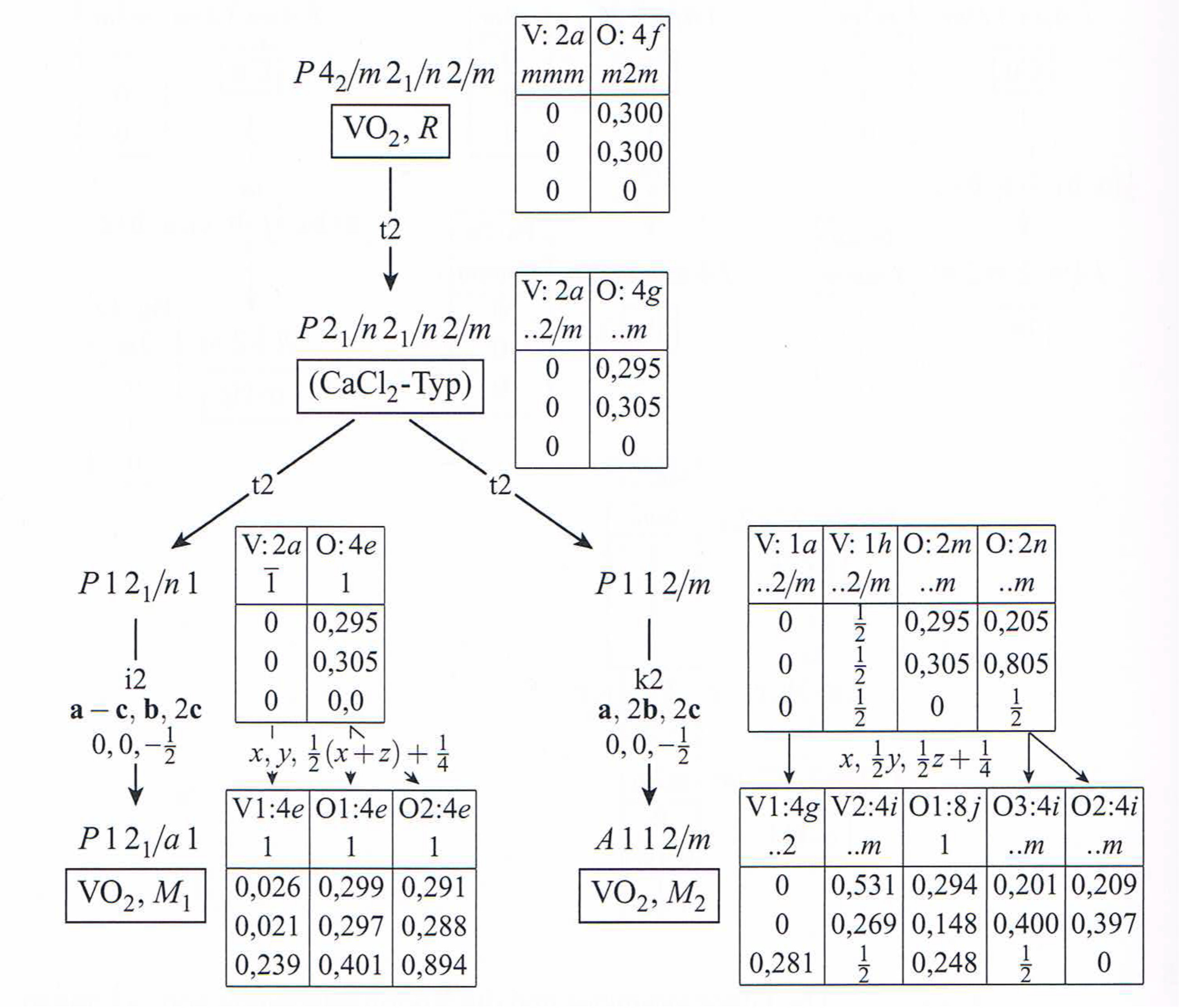
V in 4*e*	1	0.026	0.021	0.239
O1 in 4*e*	1	0.299	0.297	0.401
O2 in 4*e*	1	0.291	0.288	0.894

$V_{0.8}Cr_{0.2}O_2$: $V_{0.8}Cr_{0.2}O_2$ type (*M*2 type)

$A112/m$, a = 452.6 pm, b = 906.6 pm, c = 579.7 pm, γ = 91.9°

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

Polymorphism in VO_2



$P4_2/m\,2_1/n\,2/m$ (VO_2, R)

V: 2*a*	O: 4*f*
mmm	*m*2*m*
0	0,300
0	0,300
0	0

$P2_1/n\,2_1/n\,2/m$ ($CaCl_2$-Typ)

V: 2*a*	O: 4*g*
..2/*m*	..*m*
0	0,295
0	0,305
0	0

$P1\,2_1/n\,1$

V: 2*a*	O: 4*e*
$\bar{1}$	1
0	0,295
0	0,305
0	0,0

$P1\,2_1/a\,1$ (VO_2, M_1)

V1: 4*e*	O1: 4*e*	O2: 4*e*
1	1	1
0,026	0,299	0,291
0,021	0,297	0,288
0,239	0,401	0,894

$P1\,1\,2/m$

V: 1*a*	V: 1*h*	O: 2*m*	O: 2*n*
..2/*m*	..2/*m*	..*m*	..*m*
0	$\frac{1}{2}$	0,295	0,205
0	$\frac{1}{2}$	0,305	0,805
0	$\frac{1}{2}$	0	$\frac{1}{2}$

$A1\,1\,2/m$ (VO_2, M_2)

V1: 4*g*	V2: 4*i*	O1: 8*j*	O3: 4*i*	O2: 4*i*
..2	..*m*	1	..*m*	..*m*
0	0,531	0,294	0,201	0,209
0	0,269	0,148	0,400	0,397
0,281	$\frac{1}{2}$	0,248	$\frac{1}{2}$	0

U. Müller, Symmetriebeziehungen zwischen verwandten Kristallstrukturen,
Teubner Verlag

Classification of phase transitions

According to **Ehrenfest** a phase transition is of n^{th} order if the n^{th} 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).

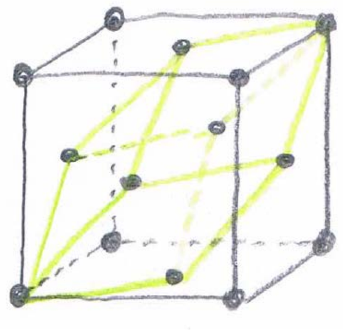
For continuos phase transitions the phenomenological theory of **Landau and Lifshitz** applies:

- free enthalpy $G = G_0 + 1/2a_2\eta^2 + 1/4a_4\eta^4 + 1/6a_6\eta^6$ ...
- 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

Exercise 5



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

Exercise 6

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

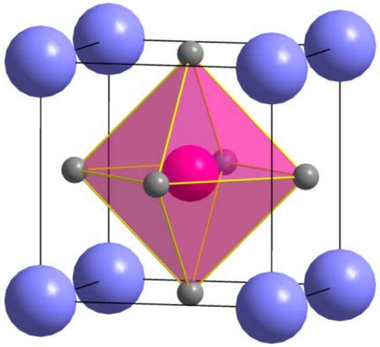
a = 441 pm, b = 441 pm, c = 441 pm, α = 90°, β = 90°, γ = 90°

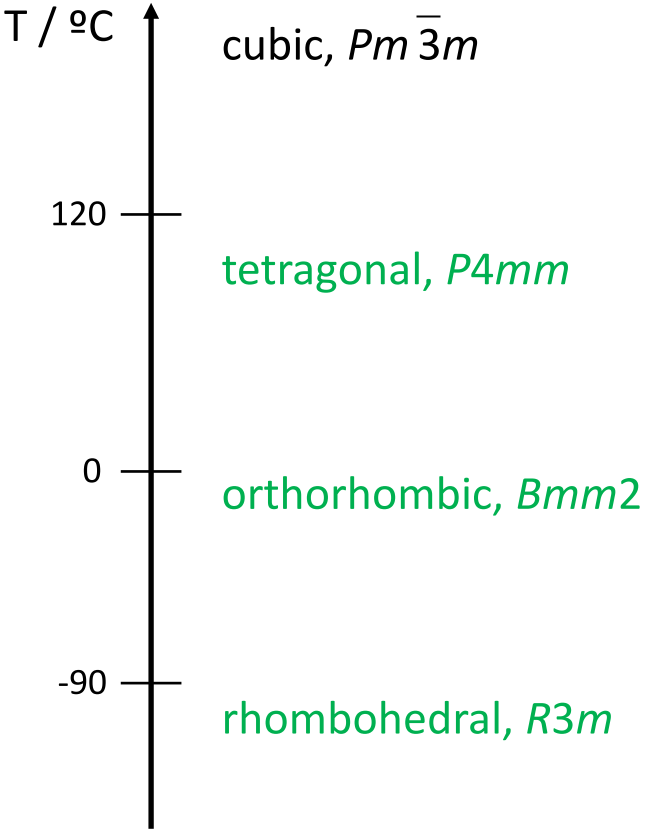
with one atom in 0, 0, 0 and one atom in ½, ½, ½ ➔

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, $Bmm2$

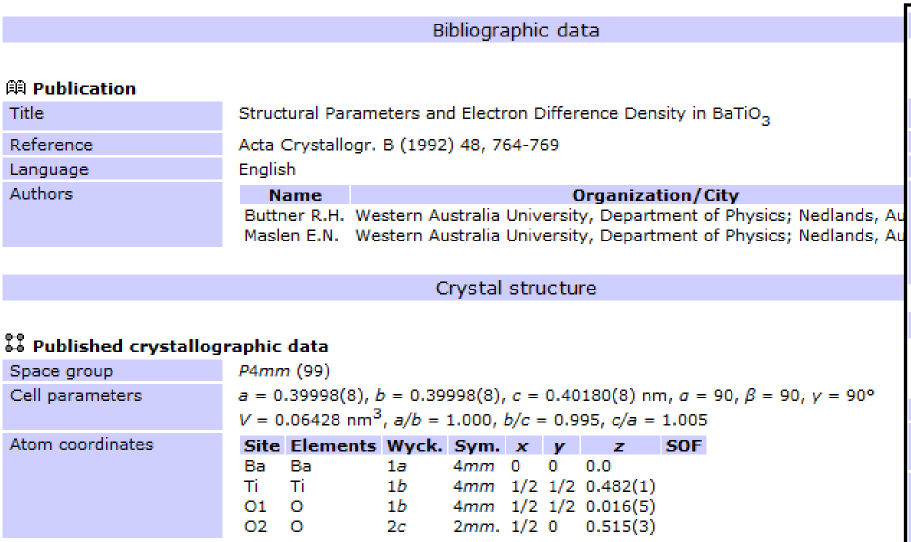
-90

rhombohedral, $R3m$

ferroelectric modifications

Exercise 7: 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

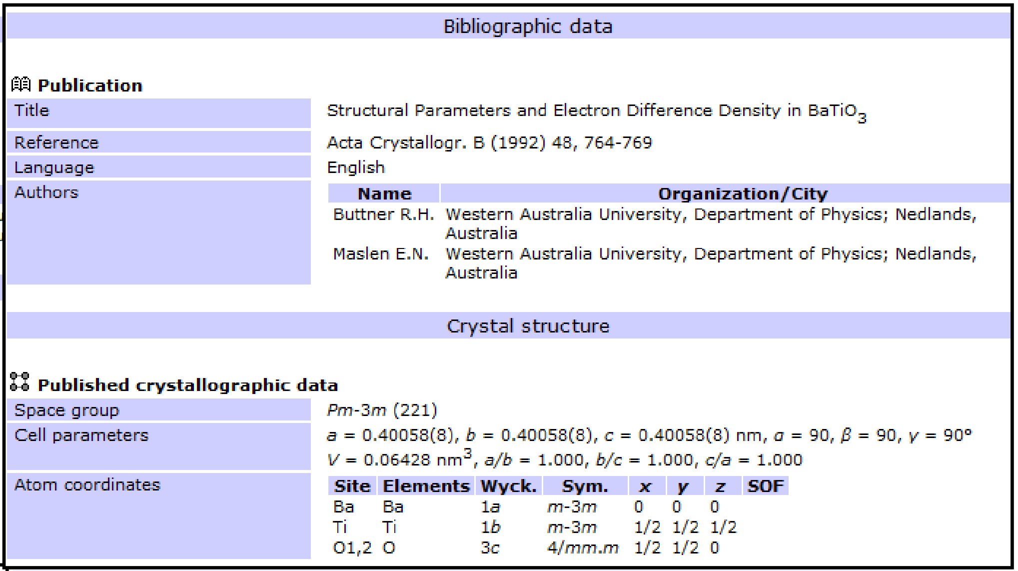
Crystal structure

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	1*a*	*4mm*	0	0	0.0	
Ti	Ti	1*b*	*4mm*	1/2	1/2	0.482(1)	
O1	O	1*b*	*4mm*	1/2	1/2	0.016(5)	
O2	O	2*c*	*2mm.*	1/2	0	0.515(3)	



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, Australia
Maslen E.N.	Western Australia University, Department of Physics; Nedlands, Australia

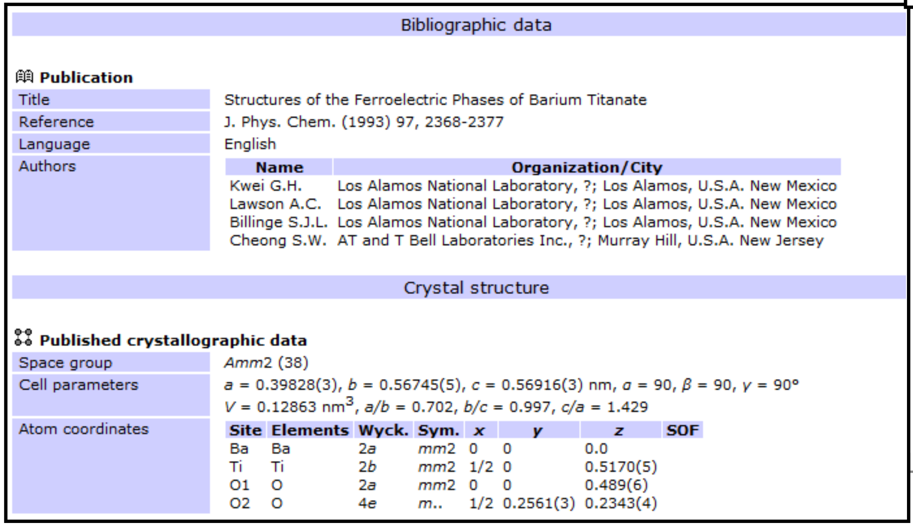
Crystal structure

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	1*a*	*m-3m*	0	0	0	
Ti	Ti	1*b*	*m-3m*	1/2	1/2	1/2	
O1,2	O	3*c*	*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

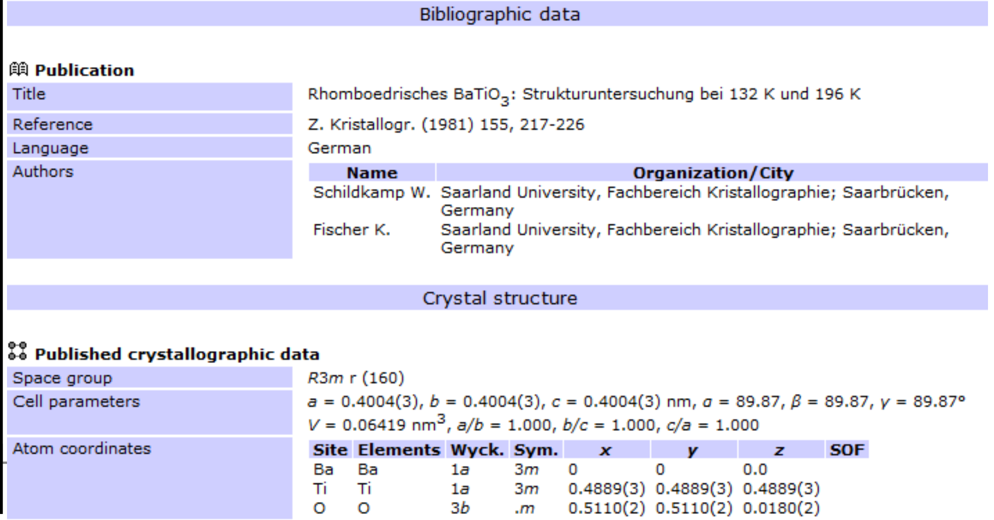
Crystal structure

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	2*a*	*mm2*	0	0	0.0	
Ti	Ti	2*b*	*mm2*	1/2	0	0.5170(5)	
O1	O	2*a*	*mm2*	0	0	0.489(6)	
O2	O	4*e*	*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

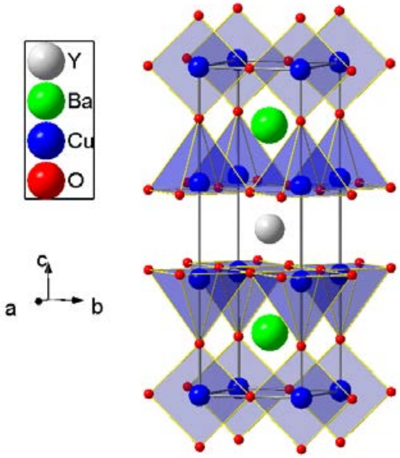
Atom coordinates

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

4 Do it yourself – apply crystallographic group theory to a phase transition

$YBa_2Cu_3O_{7-\delta}$

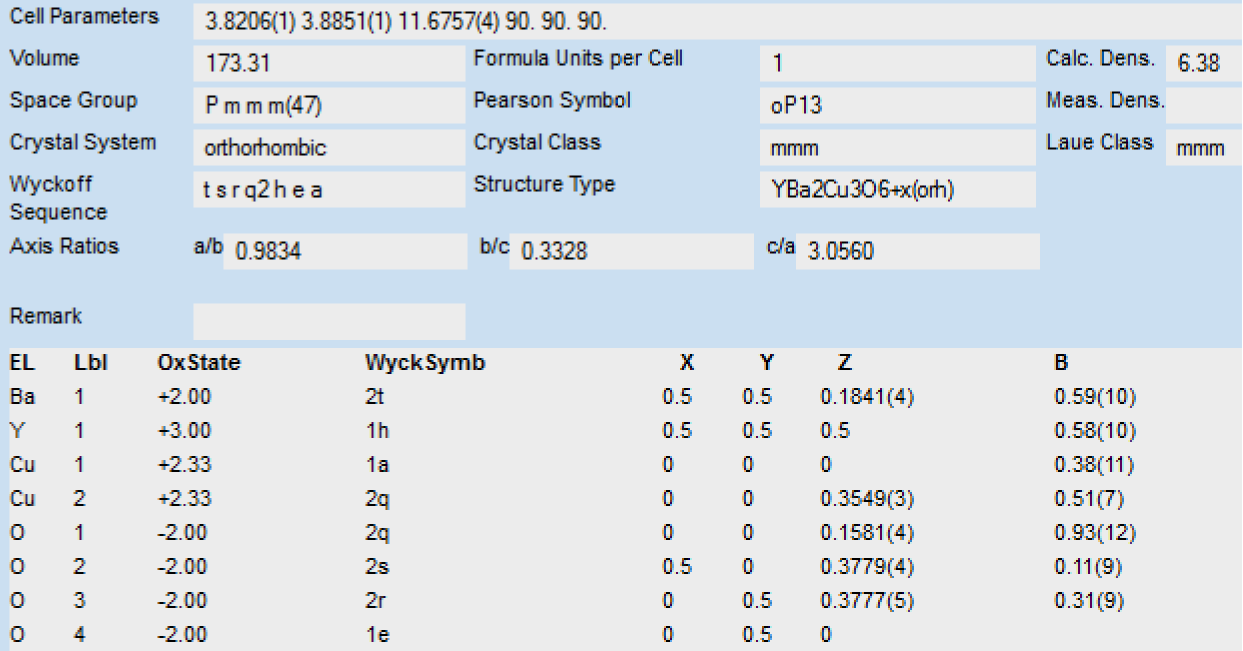
- a threefold superstructure of the cubic perovskite type
- T_c = 90 K
- nobel prize in physics for high temperature superconductivity (Bednorz and Müller, 1987)



Exercise 8

Describe the crystal structure of $YBa_2Cu_3O_{7-\delta}$ as a defect variant of the cubic perovskite type using a *Bärnighausen* tree.

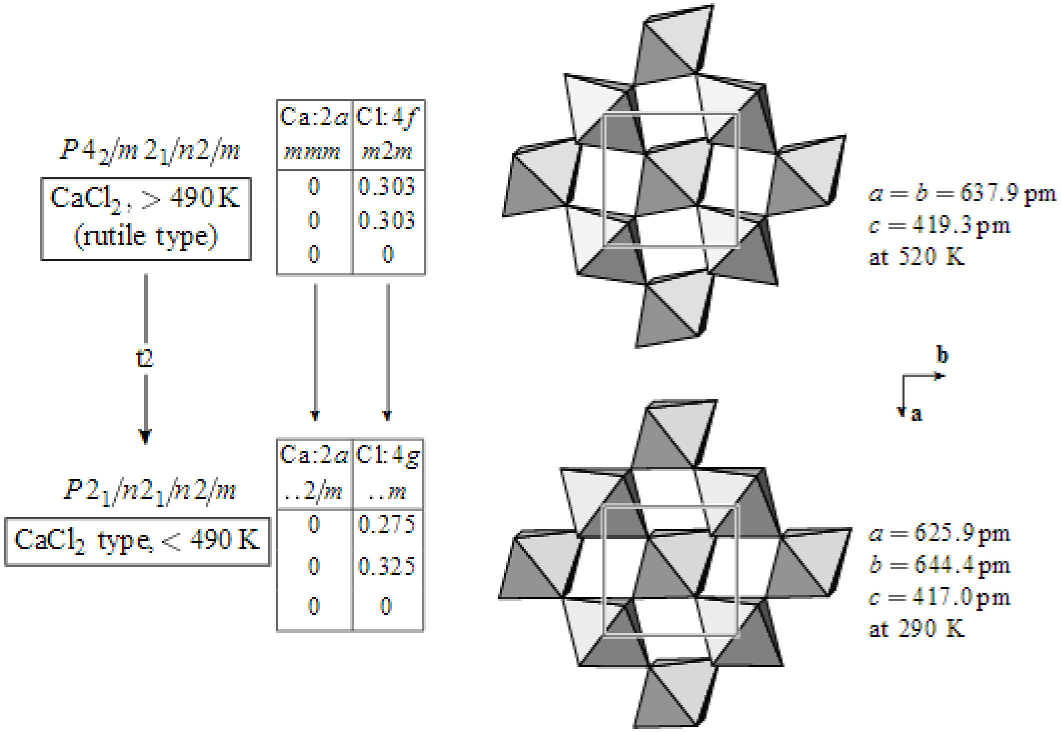
Capponi, J.J.; Chaillout, C.; Hewat, A.W.; Lejay, P.; Marezio, M.; Nguyen, N.; Raveau, B.; Soubeyroux, J.L.; Tholence, J.L.; Tournier, R., Europhysics Letters (1987) 3, p1301-p1307



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 q2 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	

Bärnighausen tree for the polymorphism of $CaCl_2$



$P4_2/m\,2_1/n\,2/m$

$CaCl_2$, > 490 K (rutile type)

Ca:2*a*	Cl:4*f*
mmm	*m*2*m*
0	0.303
0	0.303
0	0

t2

$P2_1/n\,2_1/n\,2/m$

$CaCl_2$ type, < 490 K

Ca:2*a*	Cl:4*g*
..2/*m*	..*m*
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

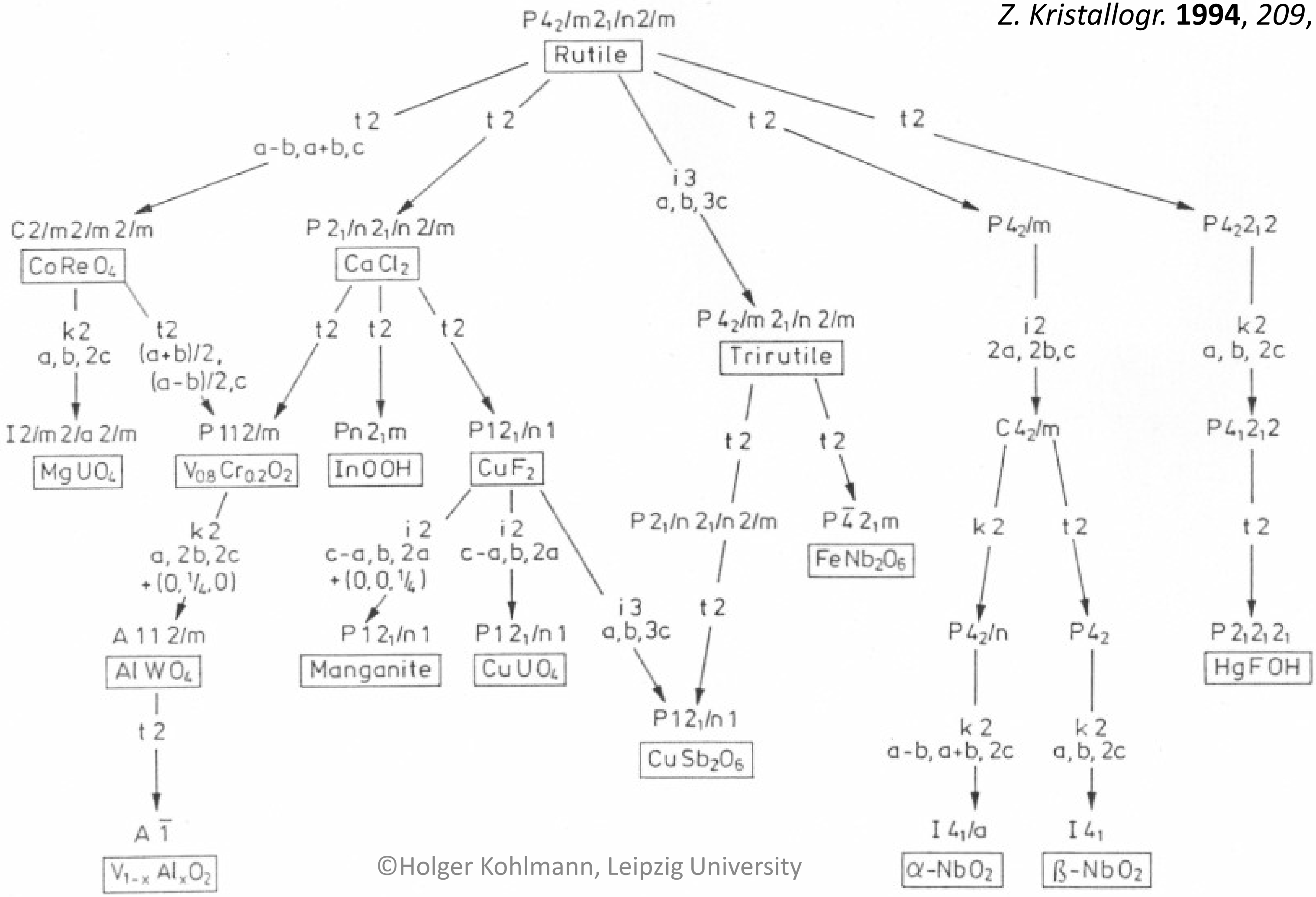
Figure 9: Group–subgroup relation between two modifications of calcium chloride and the mutual rotation of the coordination octahedra.

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

More examples in the expanded appendix of the online version free for download!
➔ pages 37-41

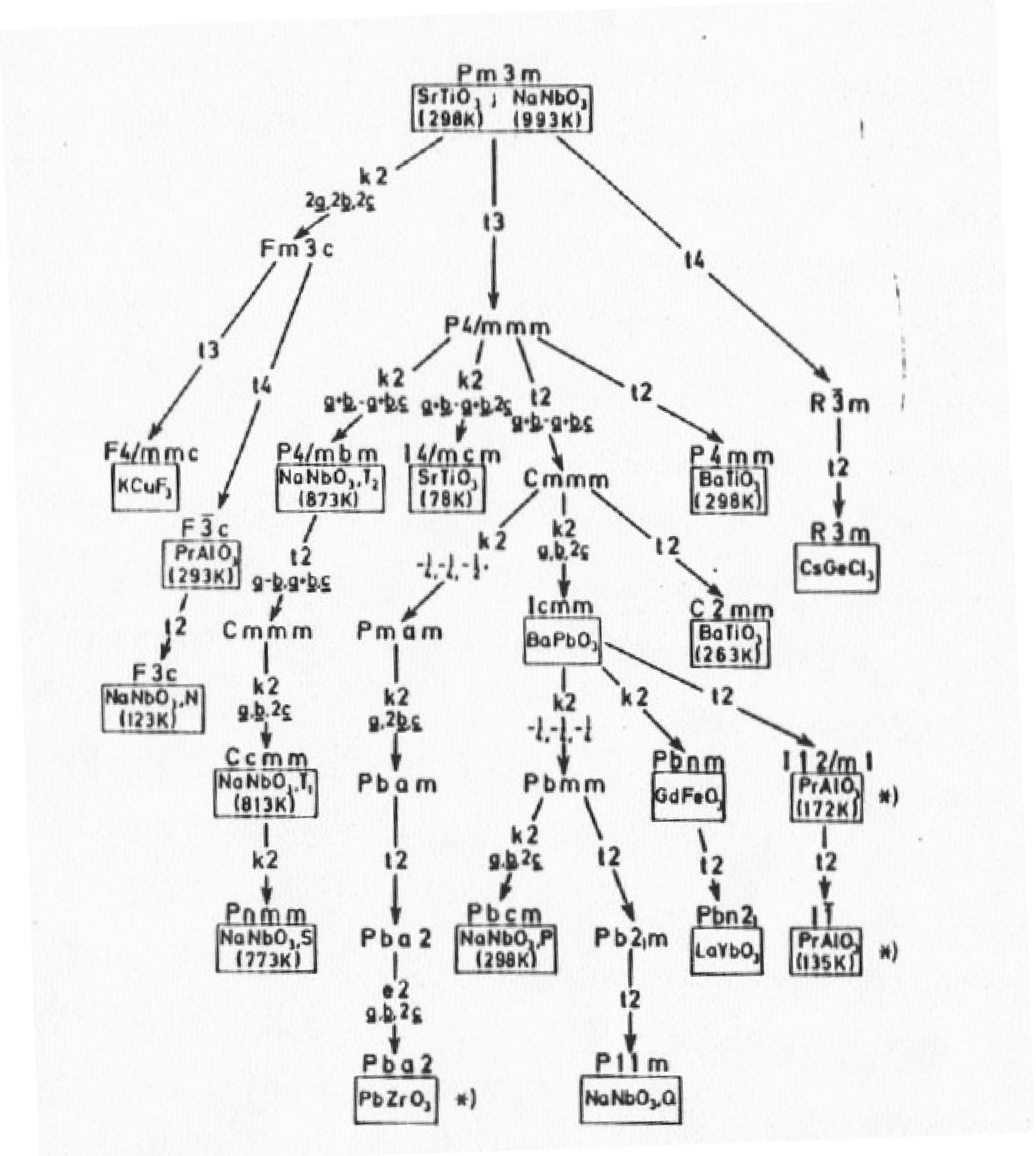
The structure family of the rutile type

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



Appendix

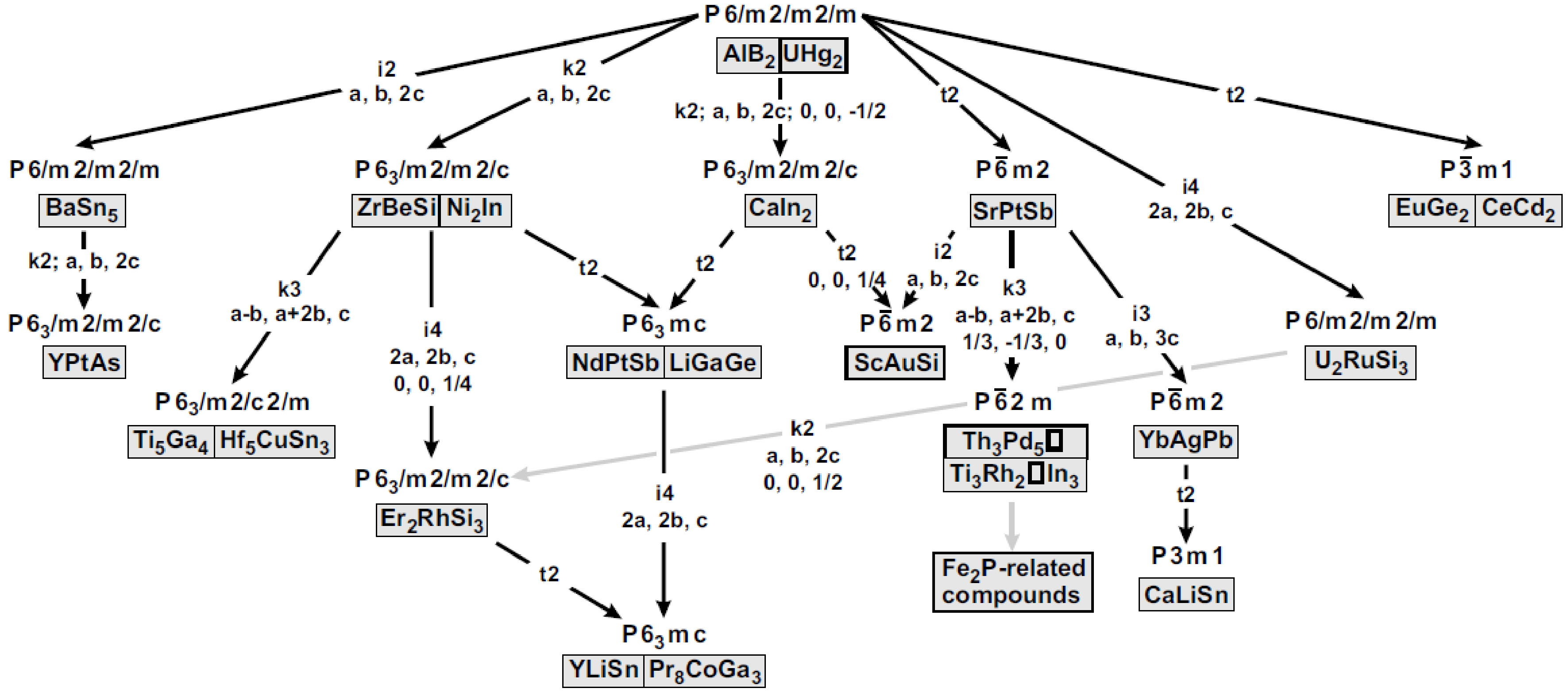
The structure family of the cubic perovskite type



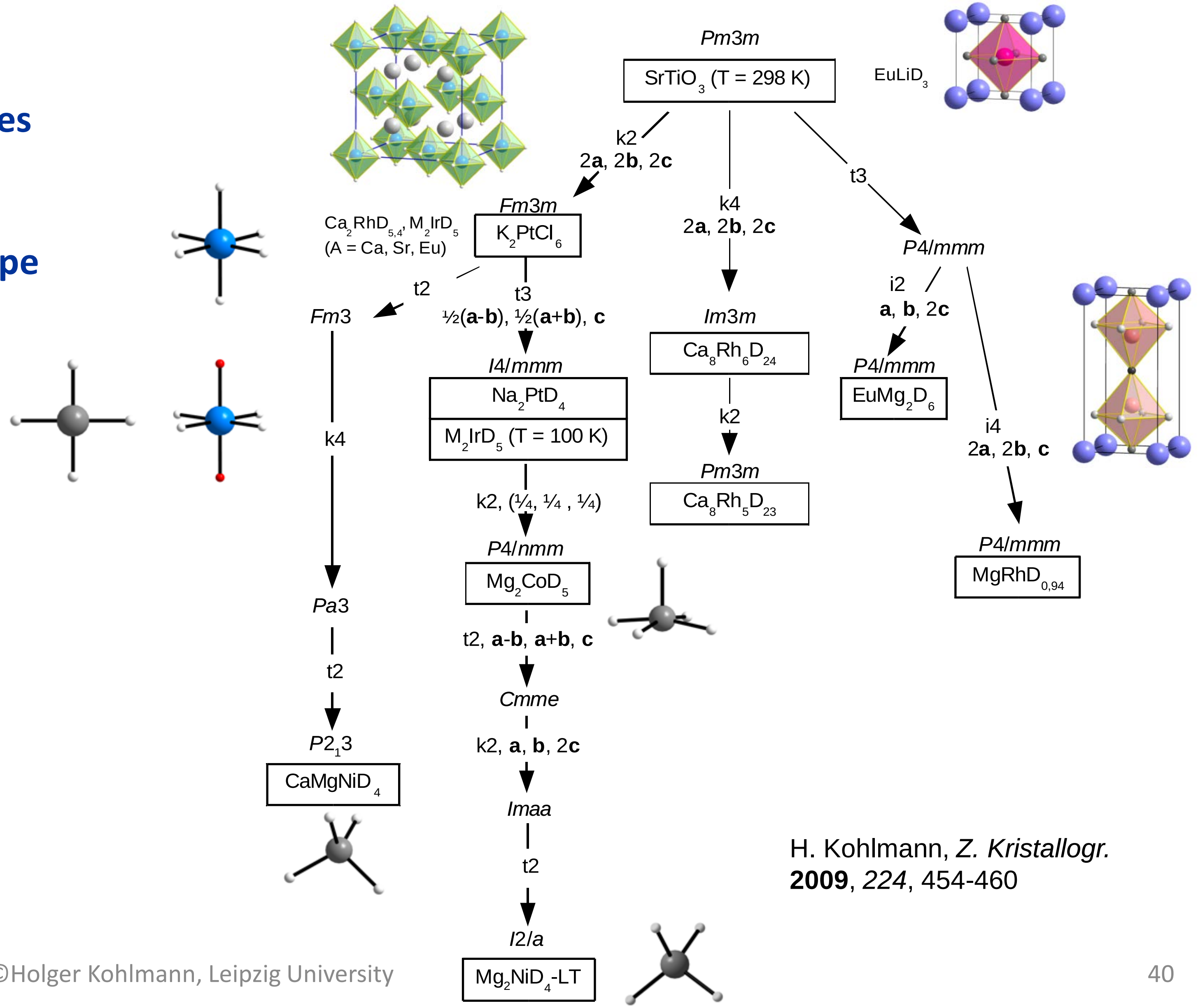
H. Bärnighausen, Group-Subgroup Relations Between Space Groups: A Useful Tool in Crystal Chemistry, *MATCH* **1980**, *9*, 139-175

The structure family of the AlB_2 type

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



Metal hydrides with relation to the cubic perovskite type



*Pm*3*m*
$SrTiO_3$ (T = 298 K)
$EuLiD_3$

k2, 2**a**, 2**b**, 2**c**
*Fm*3*m*
K_2PtCl_6
$Ca_2RhD_{5,4}$, M_2IrD_5 (A = Ca, Sr, Eu)

t2
*Fm*3
k4
*Pa*3
t2
$P2_13$
$CaMgNiD_4$

t3, ½(**a**-**b**), ½(**a**+**b**), **c**
*I*4/*mmm*
Na_2PtD_4
M_2IrD_5 (T = 100 K)
k2, (¼, ¼ , ¼)
*P*4/*nmm*
Mg_2CoD_5
t2, **a**-**b**, **a**+**b**, **c**
Cmme
k2, **a**, **b**, 2**c**
Imaa
t2
*I*2/*a*
Mg_2NiD_4-LT

k4, 2**a**, 2**b**, 2**c**
*Im*3*m*
$Ca_8Rh_6D_{24}$
k2
*Pm*3*m*
$Ca_8Rh_5D_{23}$

t3
*P*4/*mmm*
i2, **a**, **b**, 2**c**
*P*4/*mmm*
$EuMg_2D_6$
i4, 2**a**, 2**b**, **c**
*P*4/*mmm*
$MgRhD_{0,94}$

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

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 International Tables for Crystallography: **I**
- possibility of twins(t2), triplets (t3), ...

klassengleich

- group G and subgroup H belong to the same crystal class
- formed by loss of translational symmetry (loss of centering or enlargement of primitive cell)
- in International Tables for Crystallography: **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 International Tables for Crystallography: **IIc**