Bilbao Crystallographic Server Group-Subgroup Relations of Space Groups

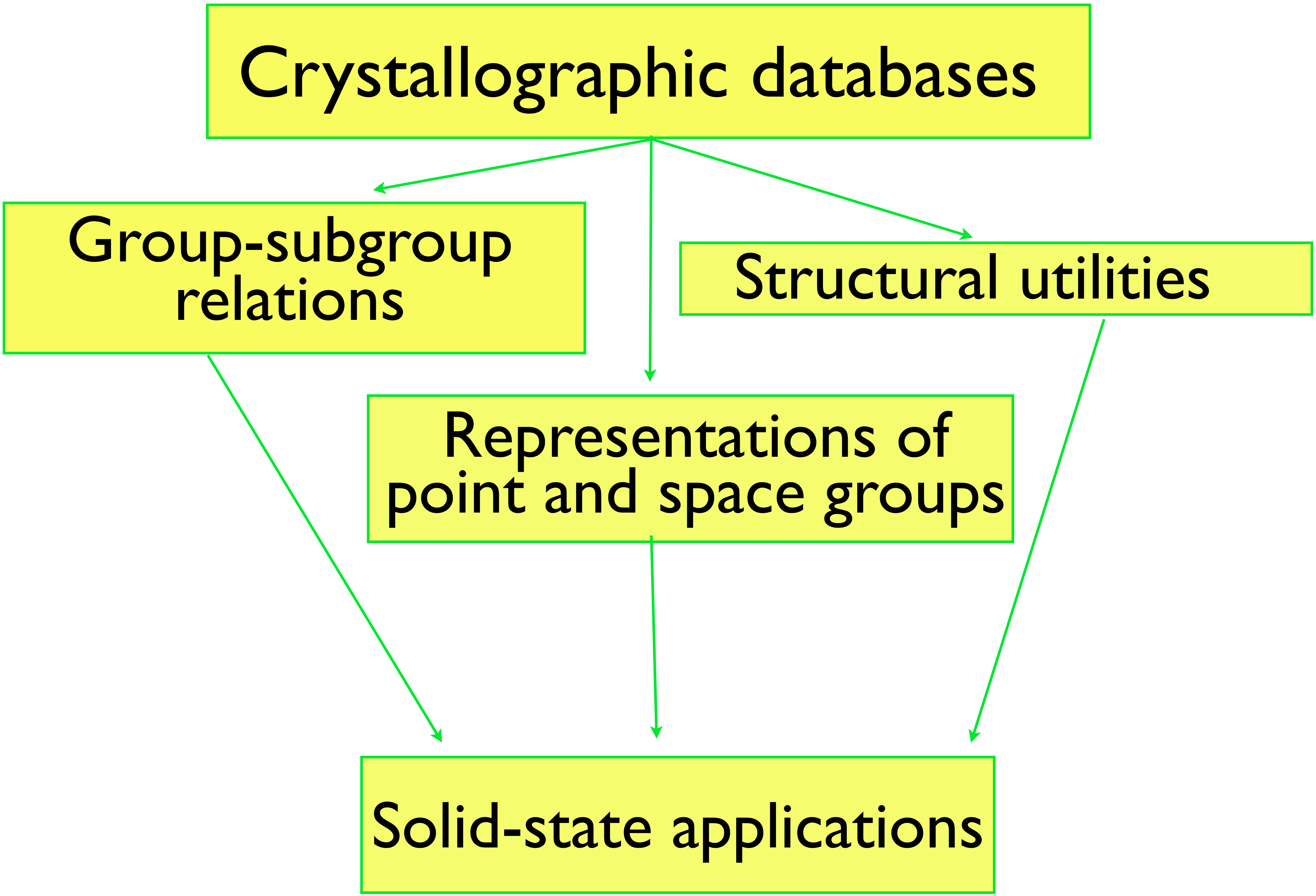
I. Maximal subgroup database

II. Group-subgroup suite

III. Structure utilities II

-equivalent descriptions

-descriptions compatible with symmetry reduction


Crystallographic databases
Group-subgroup relations
Structural utilities
Representations of point and space groups
Solid-state applications

Crystallographic Databases

International Tables for Crystallography

Space-group Data

International Tables for Crystallography

Volume A: Space-group symmetry

generators
Wyckoff positions
Wyckoff sets
normalizers

Volume A1: Symmetry Relations between space groups

maximal subgroups of index 2,3 and 4
series of isomorphic subgroups

Retrieval tools

Example ITA1: Space group I4/mmm

$I4/mmm$ No. 139 $I4/m2/m2/m$ D_{4h}^{17}

GENPOS

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5); (9)

General position

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
			$(0,0,0)+$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$			
32	o	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z

MAXSUB

I Maximal *translationengleiche* subgroups

[2] $I\bar{4}2m$ (121)	(1; 2; 5; 6; 11; 12; 15; 16)+		
[2] $I\bar{4}m2$ (119)	(1; 2; 7; 8; 11; 12; 13; 14)+		
[2] $I4mm$ (107)	(1; 2; 3; 4; 13; 14; 15; 16)+		
[2] $I422$ (97)	(1; 2; 3; 4; 5; 6; 7; 8)+		
[2] $I4/m11$ (87, $I4/m$)	(1; 2; 3; 4; 9; 10; 11; 12)+		
[2] $I2/m2/m1$ (71, $Immm$)	(1; 2; 5; 6; 9; 10; 13; 14)+		
[2] $I2/m12/m$ (69, $Fmmm$)	(1; 2; 7; 8; 9; 10; 15; 16)+	$\mathbf{a}-\mathbf{b},\mathbf{a}+\mathbf{b},\mathbf{c}$	

II Maximal *klassengleiche* subgroups

- **Loss of centring translations**

[2] $P4_2/nmc$ (137)	1; 2; 7; 8; 11; 12; 13; 14; (3; 4; 5; 6; 9; 10; 15; 16) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		1/4,3/4,1/4
[2] $P4_2/mnm$ (136)	1; 2; 7; 8; 9; 10; 15; 16; (3; 4; 5; 6; 11; 12; 13; 14) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		
[2] $P4_2/nnm$ (134)	1; 2; 5; 6; 11; 12; 15; 16; (3; 4; 7; 8; 9; 10; 13; 14) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		1/4,3/4,1/4
[2] $P4_2/mmc$ (131)	1; 2; 5; 6; 9; 10; 13; 14; (3; 4; 7; 8; 11; 12; 15; 16) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		0,1/2,0
[2] $P4/nmm$ (129)	1; 2; 3; 4; 13; 14; 15; 16; (5; 6; 7; 8; 9; 10; 11; 12) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		1/4,1/4,1/4
[2] $P4/mnc$ (128)	1; 2; 3; 4; 9; 10; 11; 12; (5; 6; 7; 8; 13; 14; 15; 16) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		
[2] $P4/nnc$ (126)	1; 2; 3; 4; 5; 6; 7; 8; (9; 10; 11; 12; 13; 14; 15; 16) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		1/4,1/4,1/4
[2] $P4/mmm$ (123)	1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16		

- **Enlarged unit cell**

[3] $\mathbf{c}'=3\mathbf{c}$

$I4/mmm$ (139)	$\langle 2; 3; 5; 9\rangle$	$\mathbf{a},\mathbf{b},3\mathbf{c}$	
$I4/mmm$ (139)	$\langle 2; 3; (5; 9)+(0,0,2)\rangle$	$\mathbf{a},\mathbf{b},3\mathbf{c}$	0,0,1
$I4/mmm$ (139)	$\langle 2; 3; (5; 9)+(0,0,4)\rangle$	$\mathbf{a},\mathbf{b},3\mathbf{c}$	0,0,2

- **Series of maximal isomorphic subgroups**

SERIES

[p] $\mathbf{c}'=p\mathbf{c}$

$I4/mmm$ (139) $\langle 2; 3; (5; 9)+(0,0,2u)\rangle$ $\mathbf{a},\mathbf{b},p\mathbf{c}$ $0,0,u$

$p>2$; $0\le u<p$

p conjugate subgroups for the prime p

[p^2] $\mathbf{a}'=p\mathbf{a}$, $\mathbf{b}'=p\mathbf{b}$

$I4/mmm$ (139) $\langle (2; 9)+(2u,2v,0); 3+(u+v,-u+v,0);$ $5+(2u,0,0)\rangle$ $p\mathbf{a},p\mathbf{b},\mathbf{c}$ $u,v,0$

$p>2$; $0\le u<p$; $0\le v<p$

p^2 conjugate subgroups for the prime p

MINSUP

I Minimal *translationengleiche* supergroups

[3] $Fm\bar{3}m$ (225); [3] $Im\bar{3}m$ (229)

II Minimal non-isomorphic *klassengleiche* supergroups

- **Additional centring translations** none
- **Decreased unit cell**

[2] $\mathbf{c}'=\frac{1}{2}\mathbf{c}$ $C4/mmm$ (123, $P4/mmm$)

DATA-BASE: MAXIMAL ISOMORPHIC SUBGROUPS **MAXSUB**

Maximal subgroups of group 139 (*I4/mmm*)

Note: The program uses the default choice for the group settings.

table the list of maximal subgroups is given. Click over "setting..." to see the possible setting(s) for t

N	IT number	HM symbol	Index	Transformations
1	69	*Fmmm*	2	show..
2	71	*Immm*	2	show..
3	87	*I4/m*	2	show..
4	97	*I422*	2	show..
5	107	*I4mm*	2	show..
6	119	*I-4m2*	2	show..
7	121	*I-42m*	2	show..
8	123	*P4/mmm*	2	show..
9	126	*P4/nnc*	2	show..
10	128	*P4/mnc*	2	show..
11	129	*P4/nmm*	2	show..
12	131	$P4_2/mmc$	2	show..
13	134	$P4_2/nnm$	2	show..
14	136	$P4_2/mnm$	2	show..
15	137	$P4_2/nmc$	2	show..
16	139	*I4/mmm*	3	show..

DATA-BASE: MAXIMAL ISOMORPHIC SUBGROUPS **MAXSUB**

Maximal subgroup(s) of type 69 (*Fmmm*) of index 2

for Space Group 139 (*I4/mmm*)

Click over **[ChBasis]** to view the general positions of the subgroup in the basis of the supergroup.

Conjugacy class a

Subgroup(s)	Transformation Matrix	More...
group No 1	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	ChBasis

(P,p)

[Click here for the Maximal Subgroups of group 69]

group G $\{e, g_2, g_3, \ldots, g_i, \ldots, g_{n-1}, g_n\}$

subgroup H<G non-conventional $\{e, \ldots\ldots, g_3, \ldots, g_i, \ldots\ldots\ldots, g_n\}$

(P,p)

subgroup H<G $\{e, h_2, h_3, \ldots, h_m\}$

Problem: MAXIMAL ISOMORPHIC SUBGROUPS **SERIES**

International Tables, Volume A1, space group I4/m (No. 87)

- **Series of maximal isomorphic subgroups**

$[p]$ $\mathbf{c}' = p\mathbf{c}$			
$I4/m$ (87)	$\langle 2;\ 3;\ 5 + (0,0,2u)\rangle$ $p > 2;\ 0 \le u < p$ p conjugate subgroups for the prime p	$\mathbf{a}, \mathbf{b}, p\mathbf{c}$	0
$[p^2]$ $\mathbf{a}' = p\mathbf{a},\ \mathbf{b}' = p\mathbf{b}$			
$I4/m$ (87)	$\langle (2;\ 5) + (2u, 2v, 0);\ 3 + (u+v, -u+v, 0)\rangle$ $p > 2;\ 0 \le u < p;\ 0 \le v < p$ p^2 conjugate subgroups for prime $p \equiv 3 \pmod 4$	$p\mathbf{a}, p\mathbf{b}, \mathbf{c}$	u
$[p = q^2 + r^2]$ $\mathbf{a}' = q\mathbf{a} - r\mathbf{b},\ \mathbf{b}' = r\mathbf{a} + q\mathbf{b}$			
$I4/m$ (87)	$\langle (2;\ 5) + (2u, 0, 0);\ 3 + (u, -u, 0)\rangle$ $q > 0;\ r > 0;\ p > 4;\ 0 \le u < p$ p conjugate subgroups for prime $p \equiv 1 \pmod 4$	$q\mathbf{a} - r\mathbf{b}, r\mathbf{a} + q\mathbf{b}, \mathbf{c}$	u

INFINITE number of maximal isomorphic subgroups

Maximal isomorphic subgroups

Bilbao Crystallographic Server → Series of Maximal Isomorphic Subgroups

Series of Maximal Isomorphic Subgroups

Series of maximal isomorphic subgroups

For each space group you can obtain the list with its maximal isomorphic subgroups. The list contains the numbers and the symbols of the maximal subgroups as well as, the corresponding index and the transformation matrix that relates the basis of the group with that of the subgroup.

If you are using this program in the preparation of a paper, please cite it in the following form:

Aroyo, *et. al. Zeitschrift fuer Kristallographie* (2006), **221**, 1, 15-27.

If you are interested in other publications related to Bilbao Crystallographic Server, click here

Please, enter the sequential number of group as given in *International Tables for Crystallography*, Vol. A or

Maximum index:

Optional: only subgroups with the chosen index

NOTE: the program uses the default choice for the group setting.

NOTE: the maximum index available is 131.

Show series

Static databases

[Bilbao Crystallographic Server Main Menu]

Bilbao Crystallographic Server
http://www.cryst.ehu.es

Data generated online
(max. index 131)

Maximal isomorphic subgroups

Static Databases

Series of maximal isomorphic subgroups of group 87 (*I4/m*)

Note: Only series with an index less or equal to 27 are displayed

Series 1

Parametric form of the series 1 of maximal isomorphic subgroups of space group 87 (*I4/m*)

Subgroup	Index	Transformation	Conditions
I4/m (87)	p	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & p & u \end{bmatrix}$	p > 2 0 <= u < p

Number of conjugate subgroups: p conjugate subgroups for the prime p

Click over **[show..]** to view a specific transformation for a given index

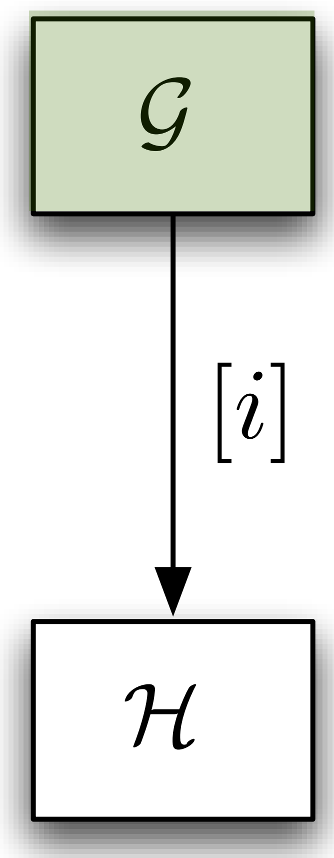
N	IT number	HM symbol	Index	Transformations
1	87	*I4/m*	3	show..
2	87	*I4/m*	5	show..
3	87	*I4/m*	7	show..
4	87	*I4/m*	11	show..
5	87	*I4/m*	13	show..
6	87	*I4/m*	17	show..
7	87	*I4/m*	19	show..
8	87	*I4/m*	23	show..

Crystallographic computing programs

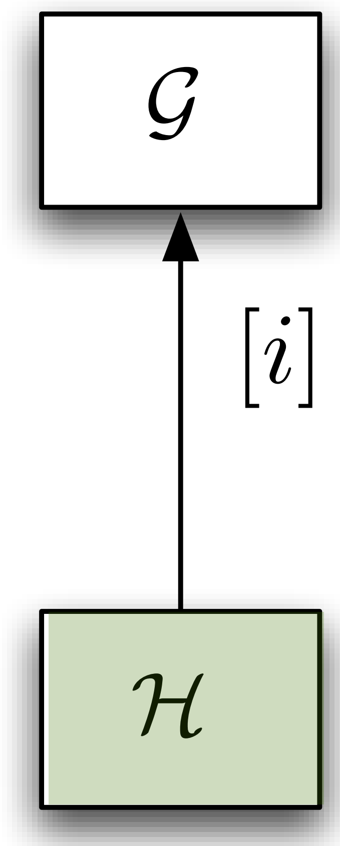
THE GROUP-SUBGROUPS SUITE

Group - Subgroup Relations of Space Groups	
SUBGROUPGRAPH	Lattice of Maximal Subgroups
HERMANN	More group-subgroup relations
COSETS	Coset decomposition for a group-subgroup pair
WYCKSPLIT	The splitting of the Wyckoff Positions
MINSUP	Minimal Supergroups of Space Groups
SUPERGROUPS	Supergroups of Space Groups
CELLSUB	List of subgroups for a given k-index.
CELLSUPER	List of supergroups for a given k-index.
COMMONSUBS	Common Subgroups of Two Space Groups
COMMONSUPER	Common Supergroups of Two Space Groups

GROUP-SUBGROUP RELATIONS



SUBGROUPGRAPH



SUPERGROUPS

APPLICATIONS

- Possible low symmetry structures
- Domain structure analysis
- Prediction of new structures

- Possible high symmetry structures
- Prediction of phase transitions
- Determination of prototype structures

Subgroups calculation: SUBGROUPGRAPH

Chains of maximal subgroups

$$(\mathrm{P}, \mathbf{p})_m \Rightarrow \mathcal{H}_m$$

$\downarrow$

Direct comparison of the $\mathcal{H}_m$

$$\mathcal{H}_k \overset{[i]}{\sim} \mathcal{H}$$

$\downarrow$

$$\boldsymbol{\mathcal{G} = \mathcal{H} + \sum_{l=2}^{[i]} g_l \mathcal{H}}$$

Conjugation $\boldsymbol{\mathcal{H}_k}$ with $\boldsymbol{g_l}$

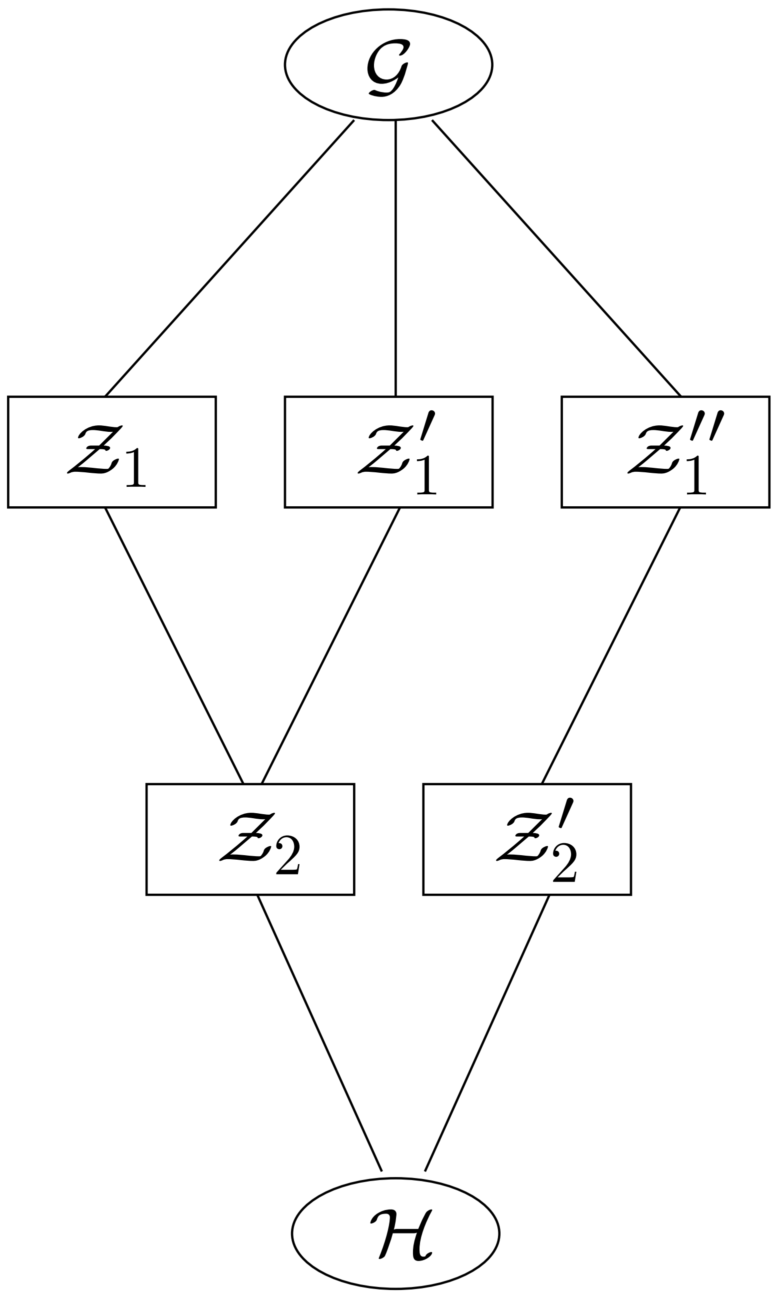
Comparison of the subgroup elements

$\mathcal{G} > \mathcal{H},\ [i]$

Classes of $\mathcal{H}_k \overset{[i]}{\sim} \mathcal{H}$

http://www.cryst.ehu.es/subgroupgraph.html

Chains of maximal subgroups



Group-subgroup pair

$$\mathcal{G} > \mathcal{H} \;:\; \mathcal{G},\ \mathcal{H},\ [i],\ (\mathrm{P},\mathbf{p})$$

Pairs: group - maximal subgroup

$$\mathcal{Z}_k > \mathcal{Z}_{k+1},\ (\mathrm{P},\mathbf{p})_k$$

$$(\mathrm{P},\mathbf{p}) = \prod_{k=1}^{n} (\mathrm{P},\mathbf{p})_k$$

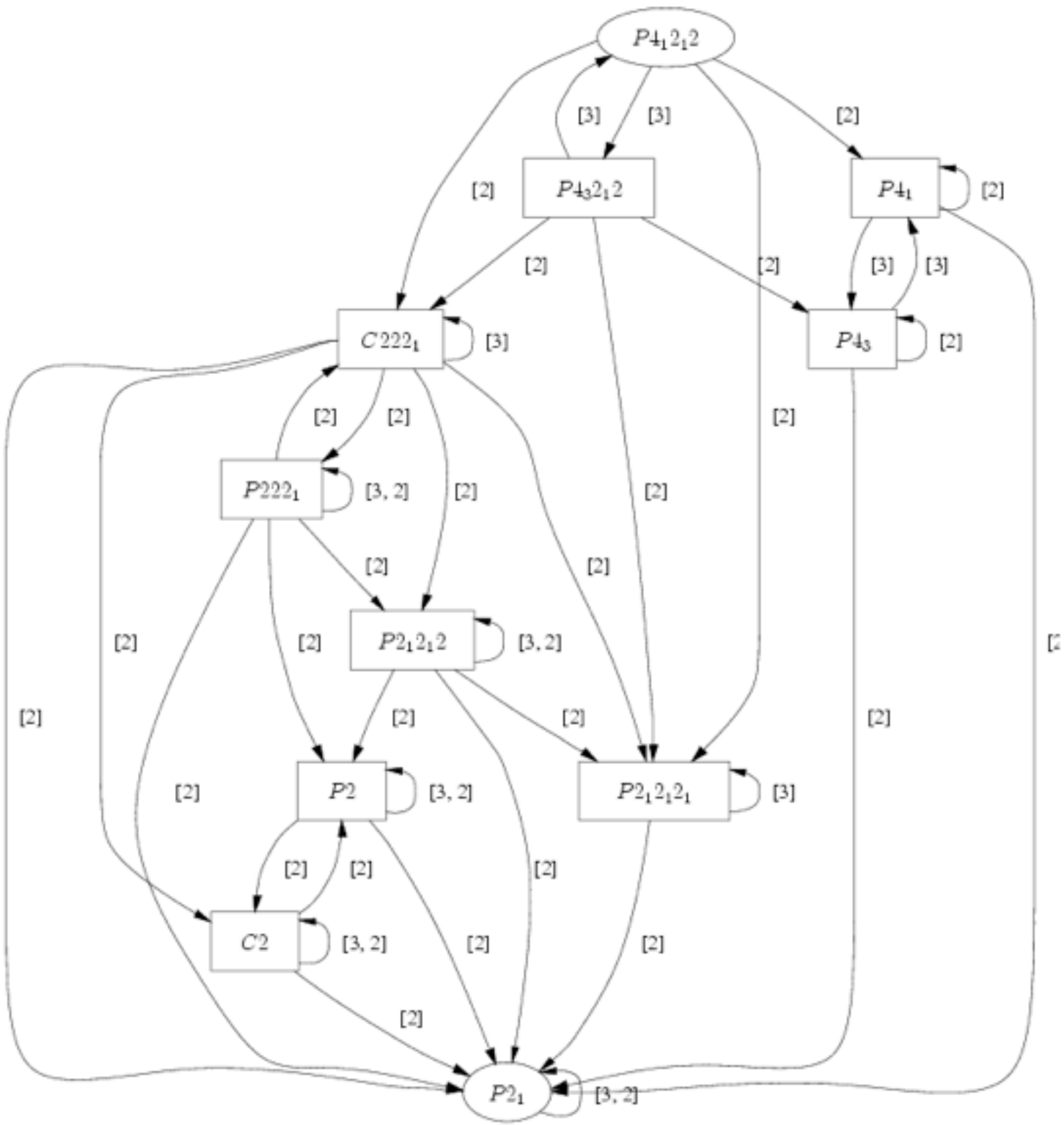
Problem 7.1

Study the group--subgroup relations between the groups G=$P4_12_12$, No.92, and H=$P2_1$ No.~4 using the program SUBGROUPGRAPH. Consider the cases with specified index e.g. [i]=4, and not specified index of the group-subgroup pair.

Problem 7.1

SOLUTION

SUBGROUPGRAPH: $P4_12_12 > P2_1$

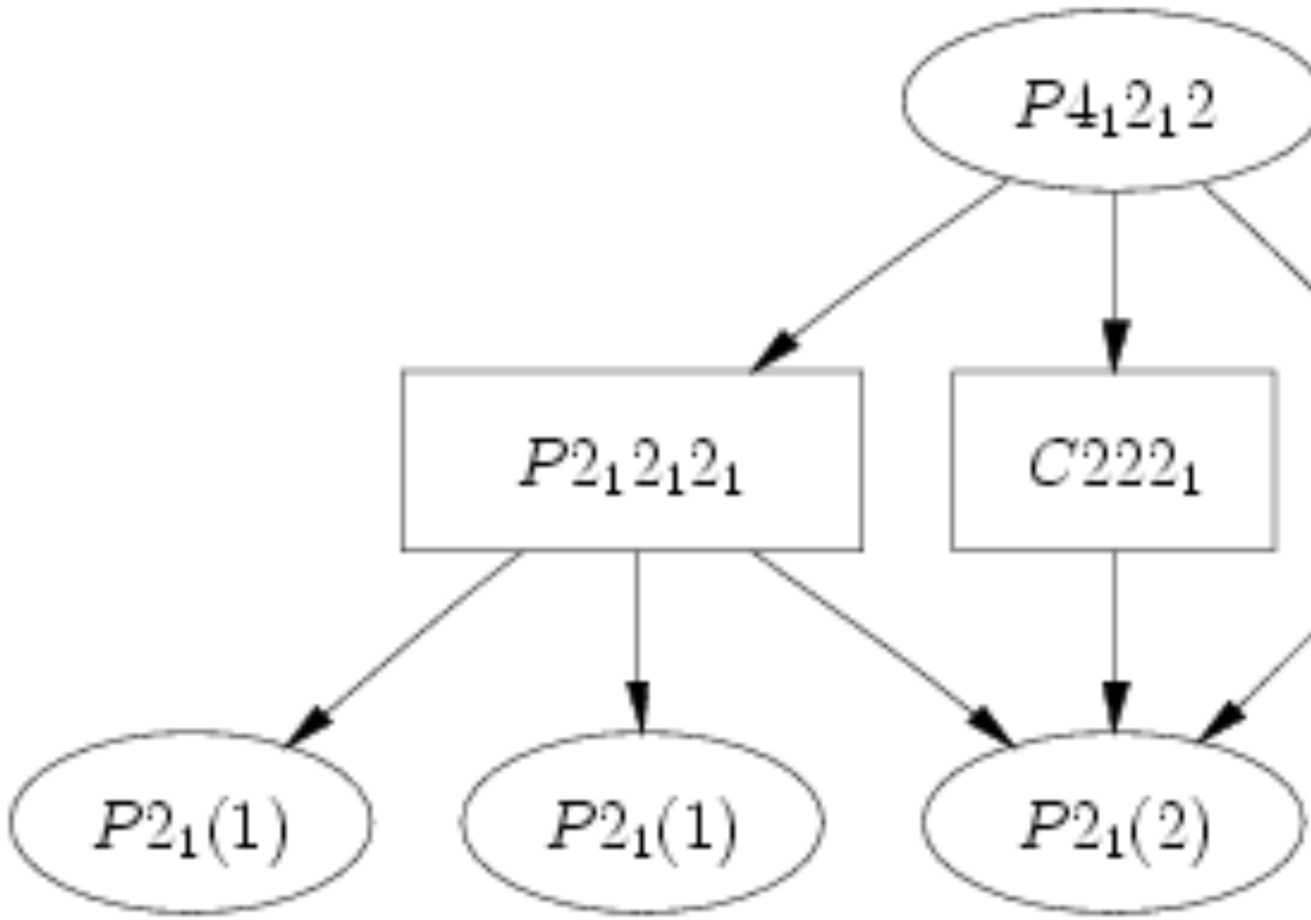


General contracted graph for $P4_12_12 > P2_1$

Problem 7.1

SOLUTION

SUBGROUPGRAPH: $P4_12_12 > P2_1$, index 4



Complete graph for $P4_12_12 > P2_1$, index 4.

Three $P2_1$ subgroups in two conjugacy classes

Problem 7.2

Explain the difference between the contracted and complete graphs of the t-subgroups of P4mm (No. 99) obtained by the program SUBGROUPGRAPH. Compare the complete graph with the results of Problems 3.2 and 4.1. Explain why the t-subgroup graphs of all 8 space groups from No. 99 P4mm to No. 106 $P4_2bc$ have the same `topology' (i.e. the same type of `family tree'), only the corresponding subgroup entries differ.

Problem 7.2

SOLUTION

Bilbao Crystallographic Server → SUBGROUPGRAPH | Help

Group-Subgroup Lattice and Chains of Maximal Subgroups

Lattice and chains ...

For a given group and supergroup the program SUBGROUPGRAPH will give the lattice of maximal subgroups that relates these two groups and, in the case that the index is specified, all of the possible chains of maximal subgroup that relate the two groups. In the latter case, also there is a possibility to obtain all of the different subgroups of the same type.

Please, enter the sequential numbers of group and subgroup as given in International Tables for Crystallography, Vol. A:	
Enter supergroup number (G) or choose it:	
Enter subgroup number (H) or choose it:	
Enter the index [G:H] (optional):	

Construct the lattice

What INPUT data should be introduced?

SUBGROUPS CALCULATIONS: HERMANN

PROBLEMS:

- No tools for space groups involving series of isomorphic subgroups
- High indices: Hermann group method

Hermann, 1929:

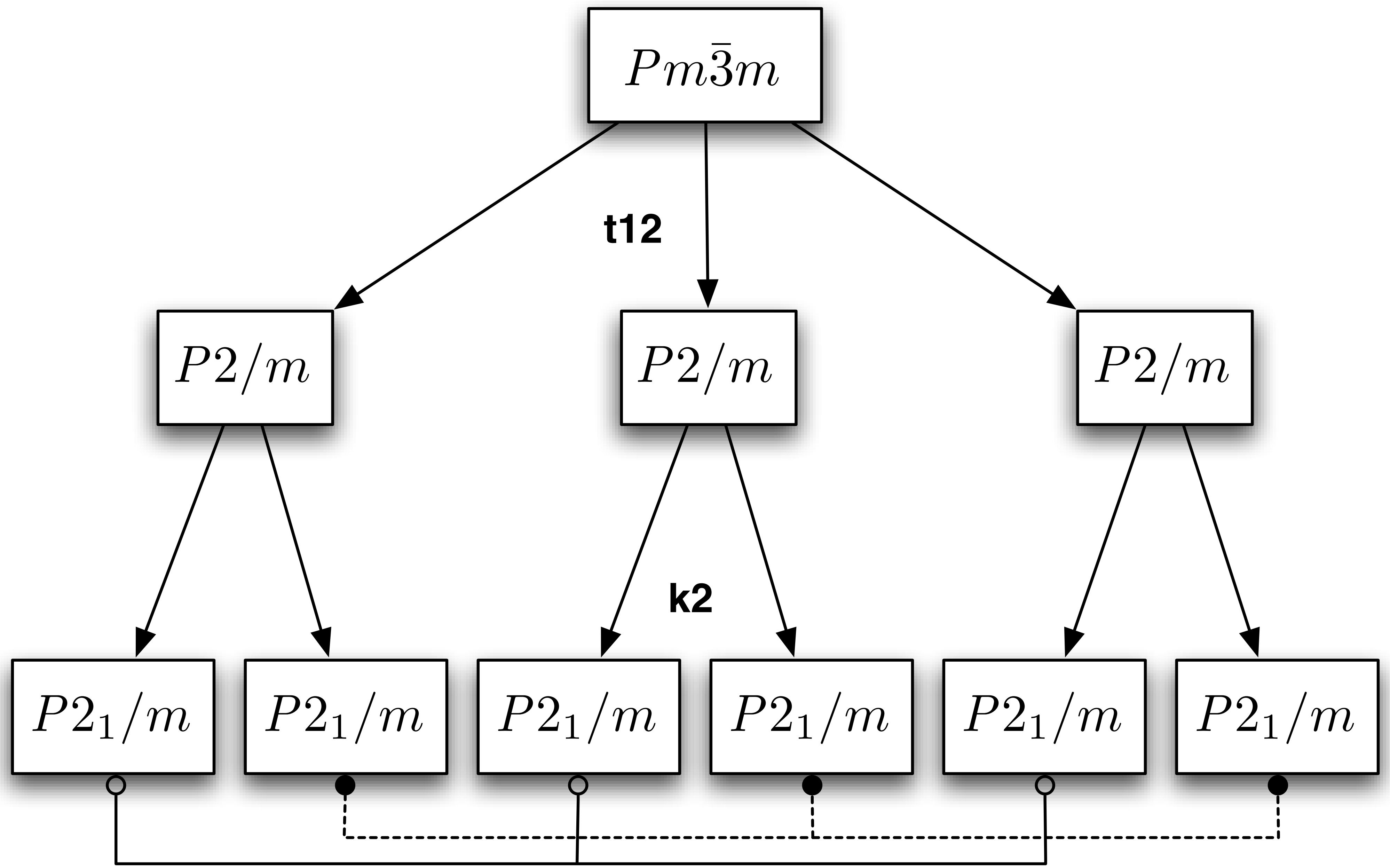
For each pair $\mathcal{G}>\mathcal{H}$, there exists a uniquely defined intermediate subgroup $\mathcal{M}$, $\mathcal{G} \geqq \mathcal{M} \geqq \mathcal{H}$, such that:

$\mathcal{M}$ is a *t-subgroup* of $\mathcal{G}$

$\mathcal{H}$ is a *k-subgroup* of $\mathcal{M}$

$$\begin{tikzcd} \mathcal{G} \arrow[d, "i_t"] \\ \mathcal{M} \arrow[d, "i_k"] \\ \mathcal{H} \end{tikzcd}$$

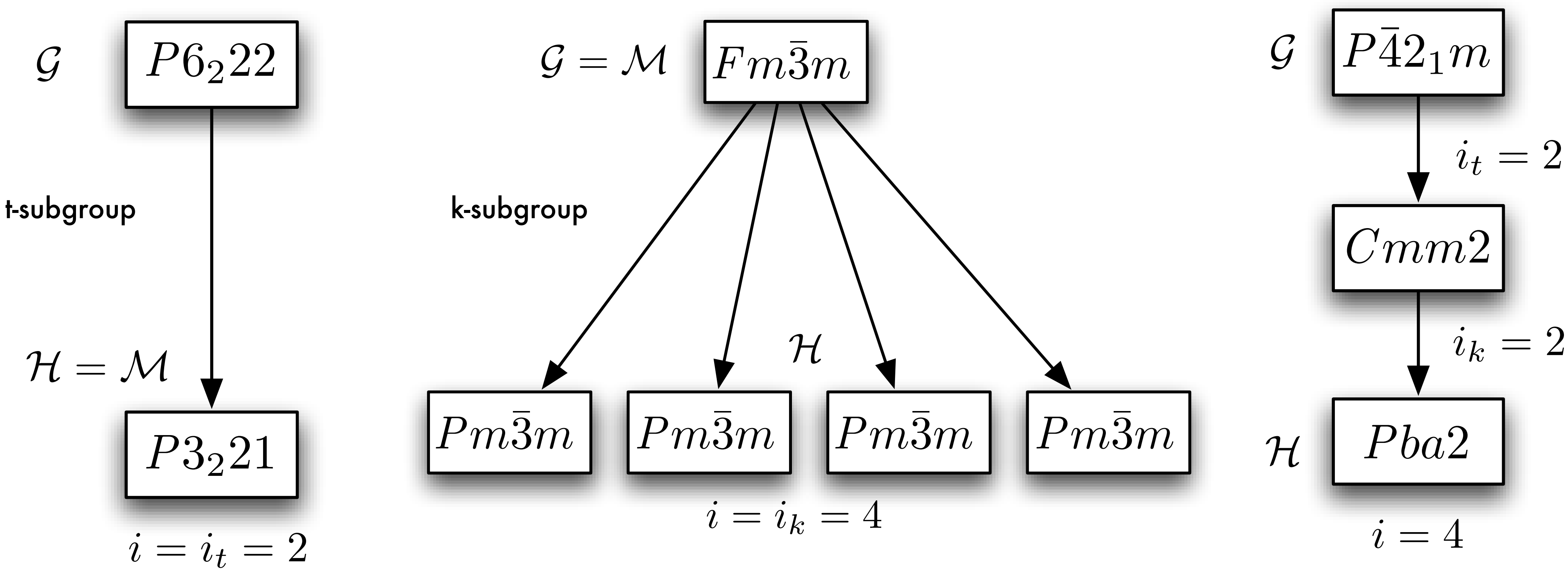
Example: $Pm\text{-}3m > P2_1/m$ with index 24



Hermann Group M= $P2/m$

Problem: CLASSIFICATION OF DOMAINS HERMANN

Quartz | Cu_3Au | $Gd_2(MoO_4)_3$



twin domains

antiphase domains

twin and antiphase domains

Problem 7.3

The retrieval tool MAXSUB gives an access to the database on maximal subgroups of space groups as listed in ITA1. Consider the maximal subgroups of the group Pmna (No.53). Compare its k-subgroups obtained by doubling the b lattice parameter, i.e. a',b',c' = a,2b,c and compare with the list of subgroups derived in Problem 4.2.

Problem 7.5

At high temperatures, $BiTiO_3$ has the cubic perovskite structure, space group Pm-3m. Upon cooling, it distorts to three slightly deformed structures, all three being ferroelectric, with space groups P4mm, Amm2 and R3m. Can we expect twinned crystals of the low symmetry forms? If so, how many kinds of domains?

What program can be used?

What INPUT data should be introduced?

Index [i] for a group-subgroup pair G>H

Hermann, 1929:

$[i]=[i_P].[i_L]$

$$\begin{array}{l} \mathcal{G} \\ \big\downarrow \quad i_P = P_G/P_H \\ \mathcal{M} \\ \big\downarrow \quad i_L = Z_H/Z_G \\ \mathcal{H} \end{array}$$

Example: $Pb_3(VO_4)_2$

$[i]=3.2=6$

$$\begin{array}{l} R\text{-}3m \\ \big\downarrow \quad i_P = P_G/P_H = 3 \\ C2/m \\ \big\downarrow \quad i_L = Z_H/Z_G = 2 \\ P2_1/c \end{array}$$

$\mathcal{M}$ is a *t*-subgroup of $\mathcal{G}$

$\mathcal{H}$ is a *k*-subgroup of $\mathcal{M}$

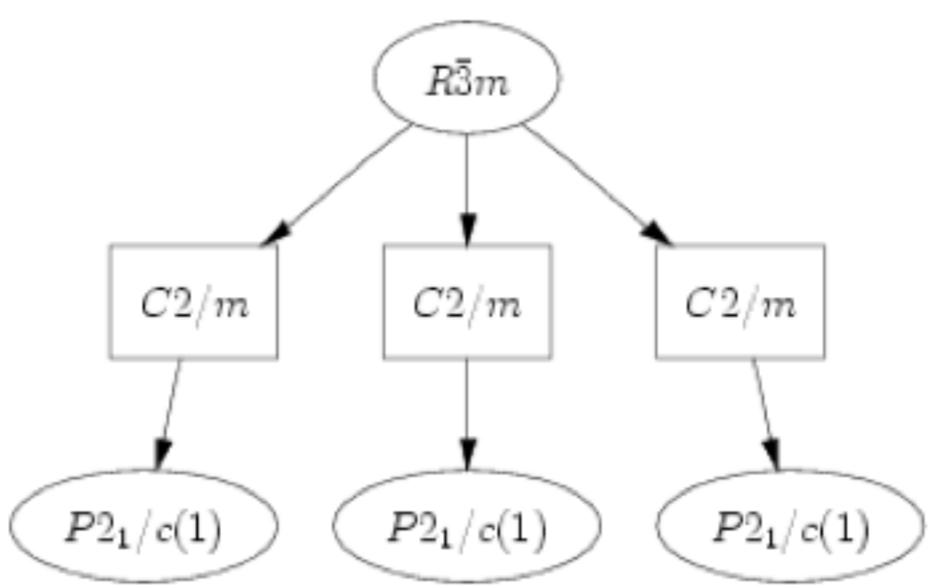
Transformation matrix (P,p) for G>H
Group-subgroup graph

Input for SUBGROUPGRAPH

Please, enter the sequential numbers of group and subgroup as given in International Tables for Crystallography, Vol. A:	
Enter supergroup number (G) or choose it:	166
Enter subgroup number (H) or choose it:	14
Enter the index [G:H] (optional):	6

Construct the lattice

Group-subgroup graph for $Pb_3(VO_4)_2$



Ferroelastic phase transition $Pb_3(VO_4)_2$

R-3m High-symmetry phase

5.67 5.67 20.38

symmetry reduction

$$(P,p) \quad \left|\begin{array}{ccc:c} 2/3 & 0 & -2 & 0 \\ 1/3 & 1 & -1 & 0 \\ 1/3 & 0 & 0 & 0 \end{array}\right|$$

$P2_1/c$

7.54 5.67 9.82 β=115.75

affine transformation

$P2_1/c$ Low-symmetry phase

7.51 5.67 9.51 β=115.18

Transformation matrix (P,p) for G>H

Subgroups $P2_1/c$ of R-3m of index 6 (data ITA1)

Check		Chain [indices]	Chain with HM symbols	Transformation	Identical
◉	1	166 012 014 [3 2]	*R-3m > C2/m > P2₁/c*	$\begin{pmatrix} 0 & -1 & 1/3 & 0 \\ 0 & -1 & -1/3 & 0 \\ 1 & 0 & 2/3 & 0 \end{pmatrix}$	--
○	2	166 012 014 [3 2]	*R-3m > C2/m > P2₁/c*	$\begin{pmatrix} 0 & 1 & 1/3 & 0 \\ 0 & 0 & 2/3 & 0 \\ 1 & 0 & 2/3 & 0 \end{pmatrix}$	--
○	3	166 012 014 [3 2]	*R-3m > C2/m > P2₁/c*	$\begin{pmatrix} 0 & 0 & -2/3 & 0 \\ 0 & 1 & -1/3 & 0 \\ 1 & 0 & 2/3 & 0 \end{pmatrix}$	--

Show graph

$(P,p)_{ITA1}$

Arbitrariness of (P,p)

$$[(P,p)_{exp}]^{-1}(P,p)_{ITA1} = N(P2_1/c)$$

$$(P,p)_{exp} = \left|\begin{array}{ccc:c} 2/3 & 0 & -2 & 0 \\ 1/3 & 1 & -1 & 0 \\ 1/3 & 0 & 0 & 0 \end{array}\right|$$

Problem: LATTICE DISTORTION — CELLTRAN STRAIN

Example: Ferroelastic phase transition $Pb_3(VO_4)_2$

High-symmetry phase

R-3m

5.67 5.67 20.38

90 90 120

CELLTRAN

1/3(2a+b+c),b,-2a-b

Low-symmetry phase

$P2_1/c$

7.51 5.67 9.51

β=115.18

STRAIN

7.54 5.67 9.82

β=115.75

Degree of lattice distortion

Δ=0.0279

Problem 7.6

$SrTiO_3$ has the cubic perovskite structure, space group Pm-3m. Upon cooling below 105K, the coordination octahedra are mutually rotated and the space group is reduced to I4/mcm; c is doubled and the unit cell is increased by the factor of four. Can we expect twinned crystals of the low symmetry form? If so, how many kinds of domains?

Problem: COSET DECOMPOSITION

COSET

Please, enter the sequential numbers of group and subgroup as given in International Tables for Crystallography, Vol. A:

Enter supergroup number (G) or choose it:

Enter subgroup number (H) or choose it:

Please, define the transformation that relates the group and the subgroup bases.

Enter transformation matrix :

Rotational part			Origin Shift
1	0	0	0
0	1	0	0
0	0	1	0

Decomposition: left ◉ right ○

right: $G>H,\ G=H+H(W_2,w_2) + \ldots + H(W_n,w_n)$

$\Delta = t_H$

left: $G>H,\ G=H+(V_2,v_2)H + \ldots + (V_n,v_n)H$

$\Delta = V_2 t_H$

Problem 7.7

Consider the group--subgroup pair G=R-3m, No.~166, and H=$P2_1/c$, No.14, of index [i]=6. The relations between the conventional basis (a,b,c) of R-3m (hexagonal axes) and that of $P2_1/c$, (a',b',c') (unique axis b, cell choice 1) are as follows: a'=1/3(2a+b+c), b'=b, c'=-2a-b. Compare the right and left coset decompositions of R-3m with respect to H=$P2_1/c$ obtained by the program COSETS. Explain the differences between the two decompositions, if any.

SUPERGROUPS OF SPACE GROUPS

Group-supergroup relations

Applications

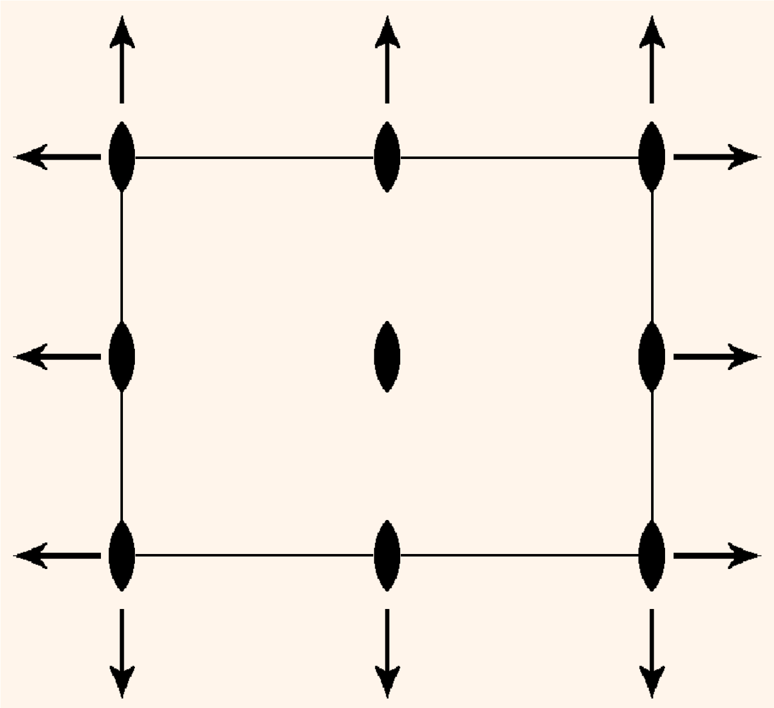
- Possible high-symmetry structures
- Prediction of phase transitions
- Prototype structures

AIM

$$\mathcal{G} > \mathcal{H}, \ [i]$$

to obtain the $\mathcal{G}_k \overset{[i]}{\sim} \mathcal{G}$

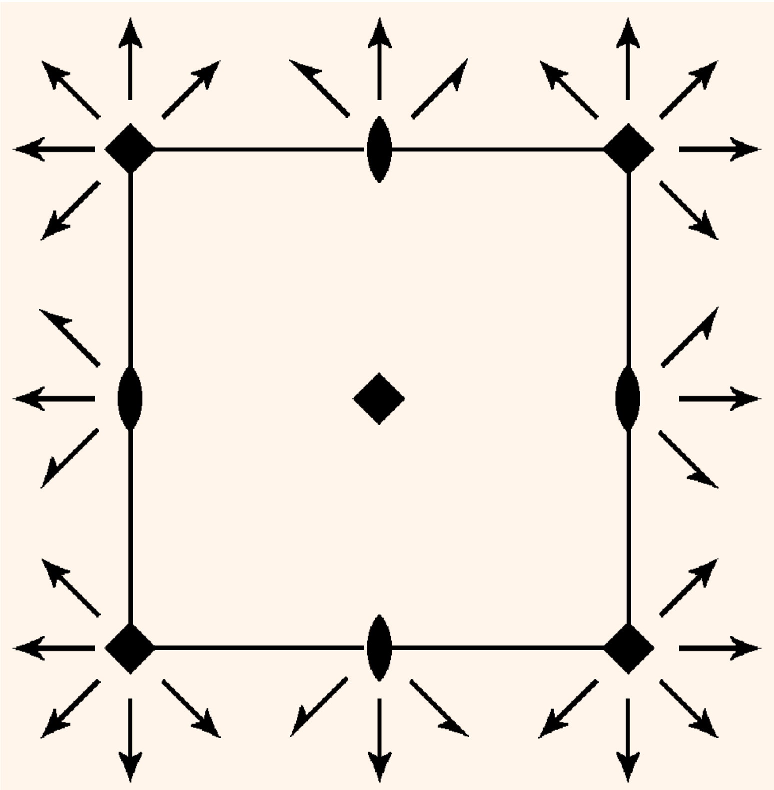
Supergroups of the same type



$$\mathcal{H} = \mathrm{P}\mathbf{222}$$

$$\mathcal{G} = \mathrm{P}\mathbf{422}$$

$$\mathrm{P}\mathbf{422} = \mathrm{P}\mathbf{222} + (\mathbf{4}|\omega)\mathrm{P}\mathbf{222}$$



	4 en	ω	$\mathcal{G}$
4_z	$(0,0,0)$	$(0,0,0)$	$(P422)_1$
4_y	$(0,0,0)$	$(0,0,0)$	$(P422)_2$
4_x	$(0,0,0)$	$(0,0,0)$	$(P422)_3$
4_z	$(\frac{1}{2},0,0)$	$(\frac{1}{2},\frac{1}{2},0)$	$(P422)'_1$
4_y	$(\frac{1}{2},0,0)$	$(\frac{1}{2},0,\bar{\frac{1}{2}})$	$(P422)'_2$
4_x	$(0,\frac{1}{2},0)$	$(0,\bar{\frac{1}{2}},\frac{1}{2})$	$(P422)'_3$

Supergroups calculation: SUPERGROUPS

$$\mathcal{G},\ \mathcal{H},\ (\mathrm{P},\mathbf{p})$$
$$\downarrow$$
Normalizer method
$$\downarrow$$
Different supergroups $\mathcal{G}_k \overset{[i]}{\sim} \mathcal{G} > \mathcal{H}$

http://www.cryst.ehu.es/supergroups.html

Special cases

Polar groups:

Infinite number of super-groups $\mathcal{G}_k \overset{[i]}{\sim} \mathcal{G}$

Monoclinic groups and triclinic:

normalizers ''enhanced''

THE SUPERGROUPS SUITE

MINSUP, SUPERGROUPS, COSETS CELLSUPER & COMMONSUPER

Group - Subgroup Relations of Space Groups	
SUBGROUPGRAPH	Lattice of Maximal Subgroups
HERMANN	More group-subgroup relations
COSETS	Coset decomposition for a group-subgroup pair
WYCKSPLIT	The splitting of the Wyckoff Positions
MINSUP	Minimal Supergroups of Space Groups
SUPERGROUPS	Supergroups of Space Groups
CELLSUB	List of subgroups for a given k-index.
CELLSUPER	List of supergroups for a given k-index.
COMMONSUBS	Common Subgroups of Two Space Groups
COMMONSUPER	Common Supergroups of Two Space Groups

Problem 8.1

Consider the group--supergroup pair H< G with H = P222, No. 16, and the supergroup G= P422, No. 89, of index [i]=2. Using the program MINSUP determine all supergroups P422 of P222 of index [i]=2. How does the result depend on the normalizer of the supergroup and/or that of the subgroup.

Problem 8.1 SOLUTION

Subgroup Normalizer: Euclidean

tetragonal axis: along c

No	Transformation matrix	Coset representatives	Wyckoff Splitting	More...
1	[1 0 0] [0] [0 1 0] [0] [0 0 1] [0]	(x, y, z) (-y, x, z)	[WP splitting]	Full cosets
2	[1 0 0] [1/2] [0 1 0] [0] [0 0 1] [0]	(x, y, z) (-y-1/2, x+1/2, z)	[WP splitting]	Full cosets

Problem 8.1

SOLUTION

Subgroup Normalizer: Affine

supergroup tetragonal axis

No	Transformation matrix	Coset representatives	Wyckoff Splitting	More...
1	[1 0 0] [0] [0 1 0] [0] [0 0 1] [0]	(x, y, z) (-y, x, z)	[WP splitting]	Full cosets
2	[1 0 0] [1/2] [0 1 0] [0] [0 0 1] [0]	(x, y, z) (-y-1/2, x+1/2, z)	[WP splitting]	Full cosets
3	[0 0 1] [0] [1 0 0] [0] [0 1 0] [0]	(x, y, z) (z, y, -x)	[WP splitting]	Full cosets
4	[0 0 1] [0] [1 0 0] [1/2] [0 1 0] [0]	(x, y, z) (z-1/2, y, -x-1/2)	[WP splitting]	Full cosets
5	[0 1 0] [0] [0 0 1] [0] [1 0 0] [0]	(x, y, z) (x, -z, y)	[WP splitting]	Full cosets
6	[0 1 0] [1/2] [0 0 1] [0] [1 0 0] [0]	(x, y, z) (x, -z-1/2, y+1/2)	[WP splitting]	Full cosets

along c

along a

along b

Problem 8.2

Consider the minimal supergroups of $Pna2_1$ obtained by the program MINSUP. Explain the differences between the relations between the conventional bases for the group-subgroup pair $Pnma>Pna2_1$, [i]=2 (e.g. accessed by the program MAXSUB), and the corresponding relations for the supergroup-group pair $Pnma>Pna2_1$, [i]=2 (e.g. the program MINSUP).

RELATIONS BETWEEN WYCKOFF POSITIONS

Splitting of Wyckoff positions

Applications

- ◇ Phase transitions
- ◇ Derivative structures
- ◇ Symmetry modes

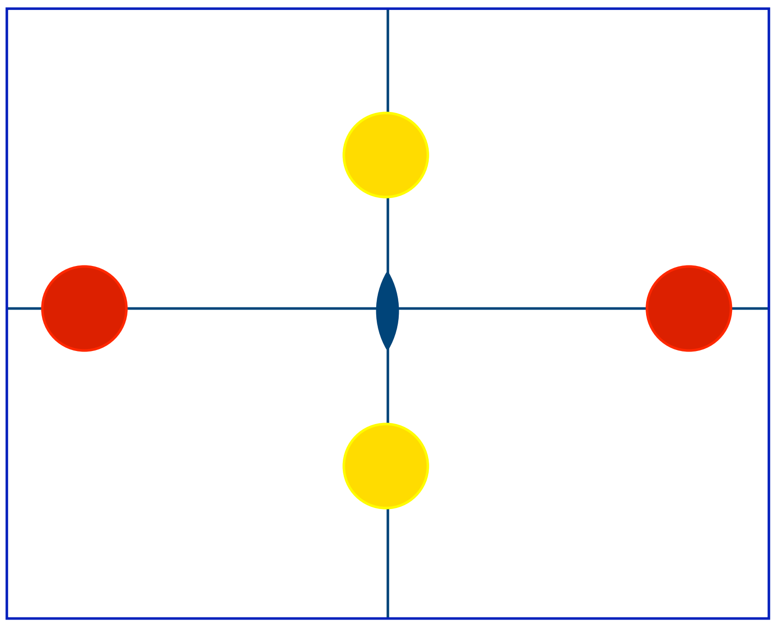
AIM

$$\mathcal{G} > \mathcal{H},\ (\mathrm{P}, \mathbf{p}),\ \mathcal{W}^{\mathcal{G}}$$

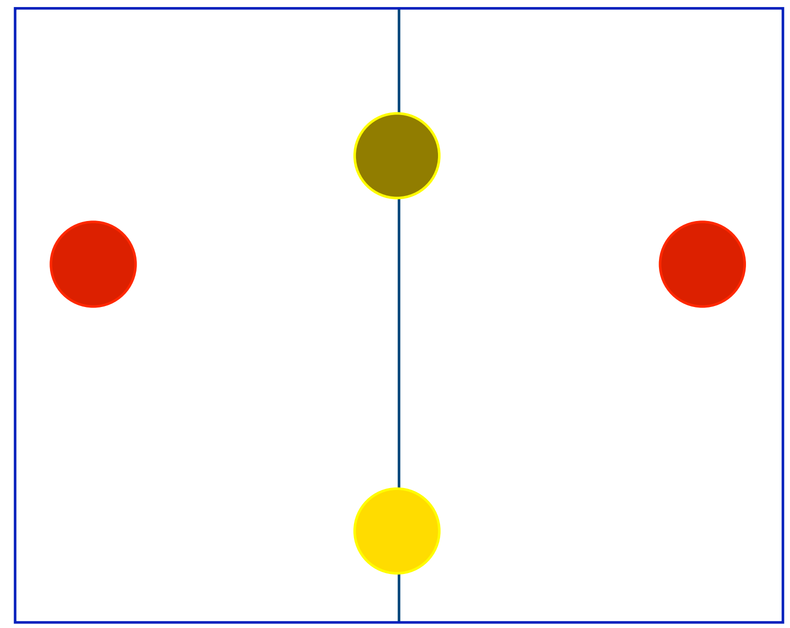
- ◇ splitting of $\mathcal{W}^{\mathcal{G}}$ in suborbits
- ◇ relation between the suborbits and $\mathcal{W}_i^{\mathcal{H}}$

SYMMETRY REDUCTION

$$\mathcal{G} = \mathrm{P}mm2 > \mathcal{H} = \mathrm{P}m,\ \ [i] = 2$$



$S_0,\ \mathcal{G} = \mathrm{P}mm2$



$S_1,\ \mathcal{H} = \mathrm{P}m$

2*h* m.. (1/2,y,z) $\longrightarrow$ 2*c* 1 (x,y,z)

2*f* .m. (x,1/2,z) $\longrightarrow$ 1*b* m (x_2,1/2,z_2)

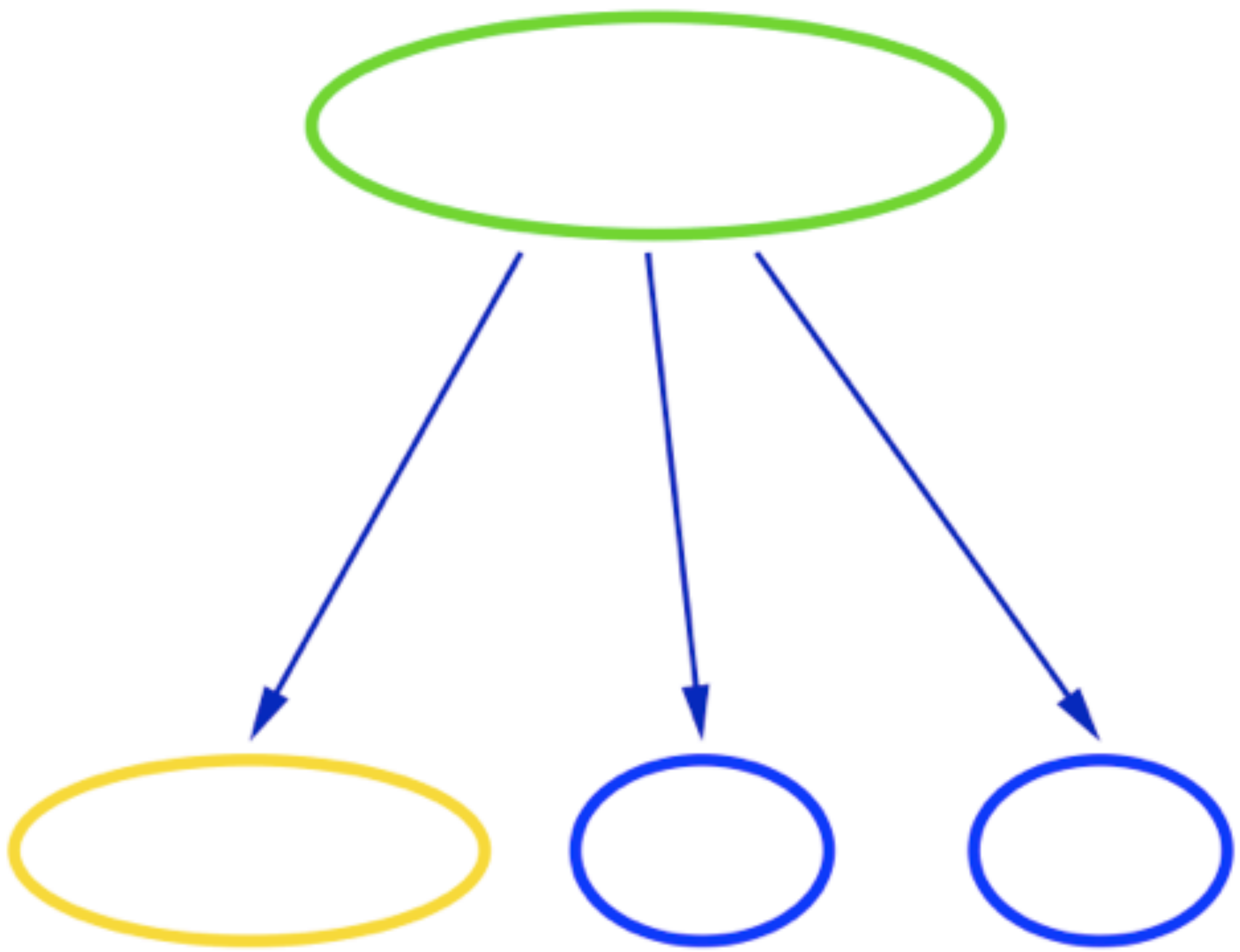
2*f* .m. (x,1/2,z) $\longrightarrow$ 1*b* m (x_1,1/2,z_1)

Splitting of Wyckoff positions

General splitting rules

(Wondratschek 1993,1995)

$\mathcal{W}^{\mathcal{G}}$



$\mathcal{W}_i^{\mathcal{H}}$

$$\mathcal{G} > \mathcal{H}, \ (\mathrm{P}, \mathbf{p})$$

$$R_i = \frac{|\mathcal{S}_{\mathcal{G}}(X)|}{|\mathcal{S}_{\mathcal{H}}(X_i)|}$$

$$[i] = \sum_{i=1}^{q} R_i$$

*ITA*1 Space group $P4_2/mnm$ (selection)

D_{4h}^{14} $\quad P4_2/m2_1/n2/m$ $\quad$ No. 136 $\quad P4_2/mnm$

Axes	Coordinates	Wyckoff positions					
		$2a$	$2b$ $4g$	$4c$ $8h$	$4d$ $8i$	$4e$ $8j$	$4f$ $16k$
I Maximal *translationengleiche* subgroups							
[2] $P\bar{4}n2$ (118)	$x+\frac{1}{2},y,z+\frac{1}{4}$	$2d$	$2c$ $4f$	$4e$ $2\times4e$	$2a;2b$ $8i$	$4h$ $8i$	$4g$ $2\times8i$
[2] $P\bar{4}2_1m$ (113)	$x+\frac{1}{2},y,z+\frac{1}{4}$	$2c$	$2c$ $4e$	$4d$ $2\times4d$	$2a;2b$ $8f$	$2\times2c$ $2\times4e$	$4e$ $2\times8f$
[2] $P4_2nm$ (102)		$2a$	$2a$ $4c$	$4b$ $2\times4b$	$4b$ $8d$	$2\times2a$ $2\times4c$	$4c$ $2\times8d$
[2] $P4_22_12$ (94)		$2a$	$2b$ $4f$	$4d$ $2\times4d$	$4d$ $8g$	$4c$ $8g$	$4e$ $2\times8g$
[2] $P4_2/m$ (84)	$x+\frac{1}{2},y,z$	$2d$	$2c$ $4j$	$2a;2b$ $4g;4h$	$2e;2f$ $2\times4j$	$4i$ $8k$	$4j$ $2\times8k$
[2] $Pnnm$ (58)		$2a$	$2b$ $4g$	$2c;2d$ $2\times4f$	$4f$ $2\times4g$	$4e$ $8h$	$4g$ $2\times8h$
[2] $Cmmm$ (65) **a−b, a+b, c**	$\frac{1}{2}(x-y)$, $\frac{1}{2}(x+y),z$; $+(\frac{1}{2},\frac{1}{2},0)$	$2a;2c$	$2b;2d$ $4g;4j$	$4e;4f$ $2\times8m$	$8m$ $8p;8q$	$4k;4l$ $8n;8o$	$4h;4i$ $2\times16r$

Example

Example: WYCKSPLIT: $P4_2/mnm$>$Cmmm$, index 2

Wyckoff Positions Splitting

136 ($P4_2/mnm$) > 65 ($Cmmm$)

Splitting of Wyckoff position 4g

Representative			Subgroup Wyckoff position	
No	**group basis**	**subgroup basis**	**name[n]**	**representative**
1	(x, -x, 0)	(x, 0, 0)	**$4g_1$**	(x_1, 0, 0)
2	(-x, x, 0)	(-x, 0, 0)		($-x_1$, 0, 0)
3	(x+1, -x, 0)	(x+1/2, 1/2, 0)		(x_1+1/2, 1/2, 0)
4	(-x+1, x, 0)	(-x+1/2, 1/2, 0)		($-x_1$+1/2, 1/2, 0)
5	(x+1/2, x+1/2, 1/2)	(0, x+1/2, 1/2)	**$4j_1$**	(0, y_2, 1/2)
6	(-x+1/2, -x+1/2, 1/2)	(0, -x+1/2, 1/2)		(0, $-y_2$, 1/2)
7	(x+1/2, x-1/2, 1/2)	(1/2, x, 1/2)		(1/2, y_2+1/2, 1/2)
8	(-x+1/2, -x-1/2, 1/2)	(1/2, -x, 1/2)		(1/2, $-y_2$+1/2, 1/2)

Problem 9.2

Study the splittings of the Wyckoff positions for the group-subgroup pair P4mm (No.99) > Cm (No.4) of index 4 by the program WYCKSPLIT. Compare the results with the data obtained in Problem 5.1.

Symmetry Relations between Crystal Structures

Problem: Symmetry Relations between Crystal Structures

Baernighausen Trees

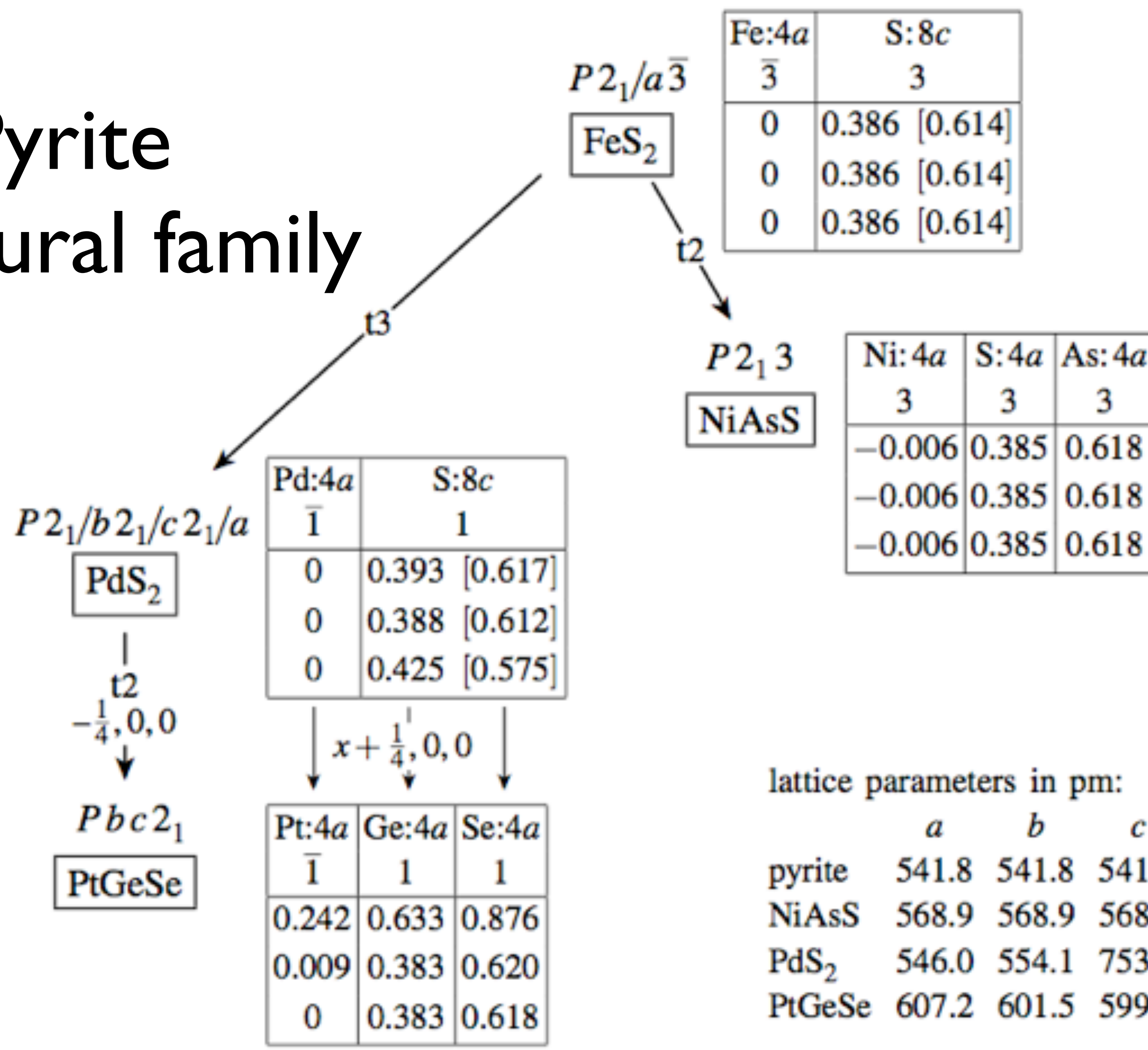
Pyrite
Structural family

Aristotype

Basic structure

Hettotypes

Derivative structures



lattice parameters in pm:

	a	*b*	*c*	references
pyrite	541.8	541.8	541.8	[32]
NiAsS	568.9	568.9	568.9	[33]
PdS_2	546.0	554.1	753.1	[34]
PtGeSe	607.2	601.5	599.2	[35]

U. Mueller, Gargnano 2008

Baernighausen Trees

Modul design of crystal symmetry relations

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 $\mathcal{G}$ → $P6/m2/m2/m$

Symbol designating the higher symmetric crystal structure, *e.g.* the chemical formula or mineral name → $\boxed{AlB_2}$

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

Element symbol
Wyckoff posit.
cite symmetry
coordinates

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

Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ → $P6_3/m2/m2/c$

Symbol designating the lower symmetric crystal structure → $\boxed{CaIn_2}$

Ca : 2*b*	In : 4*f*
$\bar{6}m2$	$3m$
0	$\frac{1}{3}$
0	$\frac{2}{3}$
$\frac{1}{4}$	0.455

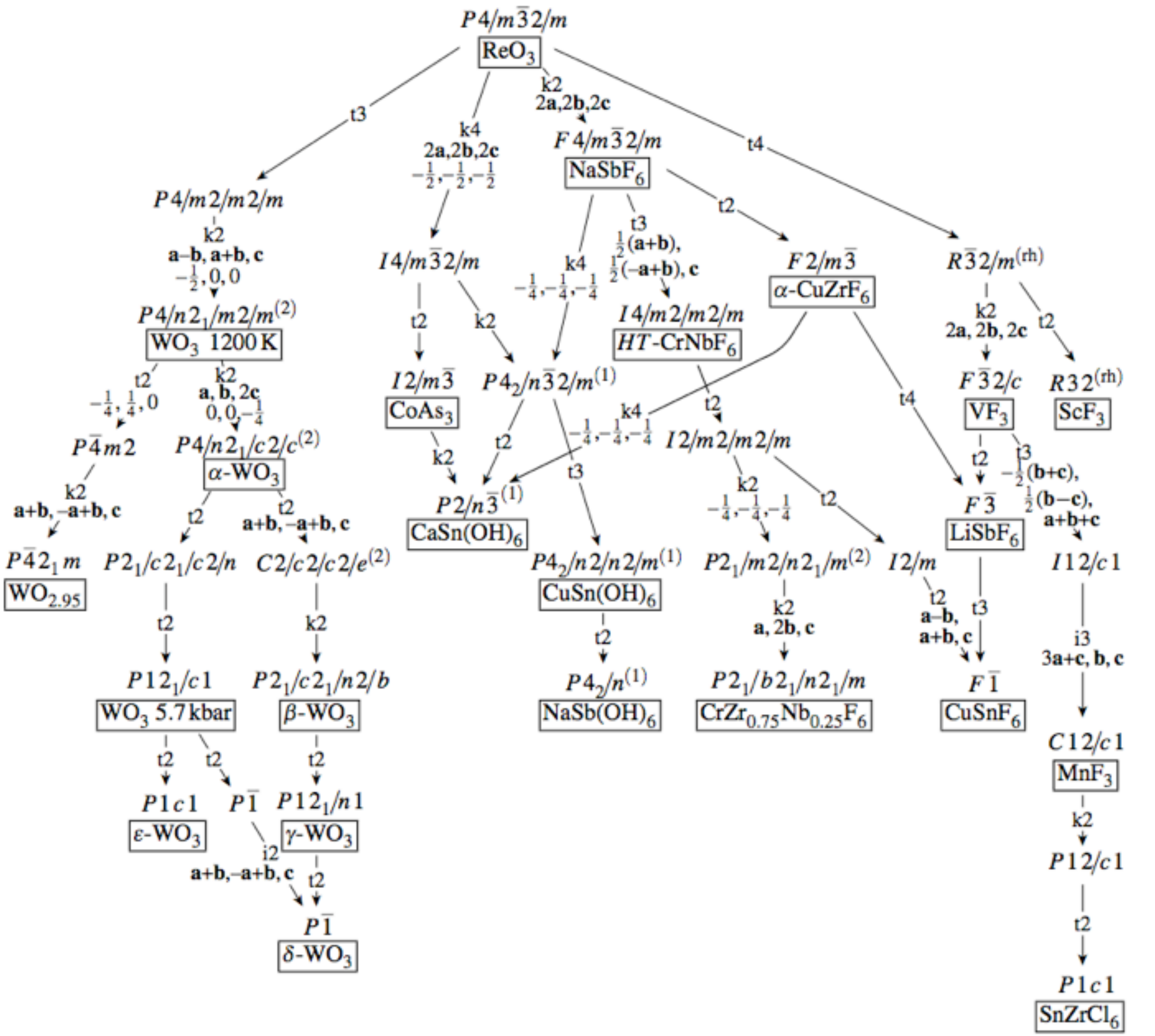
Element symbol
Wyckoff posit.
cite symmetry
coordinates

* mentioned only if there is a change

U. Mueller, Gargnano 2008

Family tree of hettotypes of ReO3

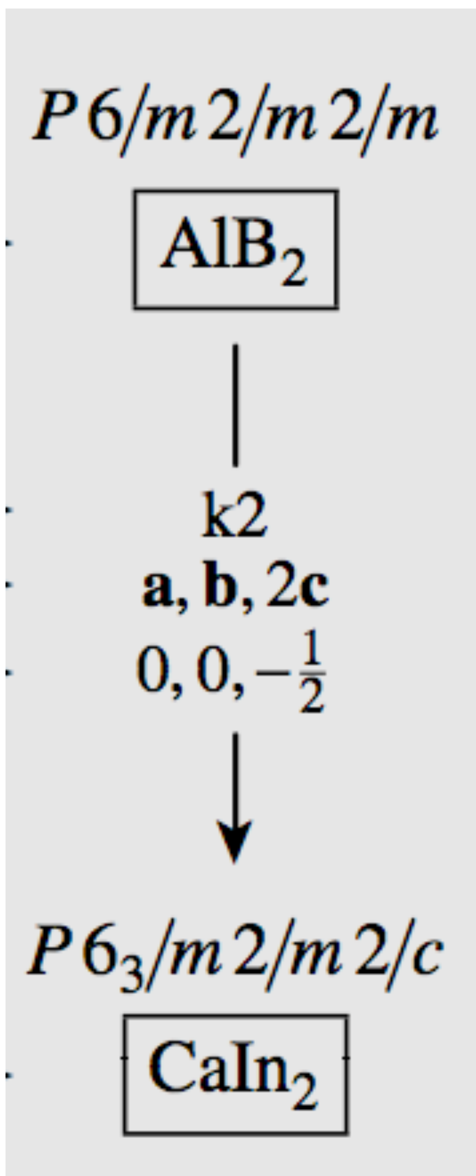
Baernighausen Trees



Baernighausen Trees

Basic tools for structure symmetry relations

Group-Subgroup relations

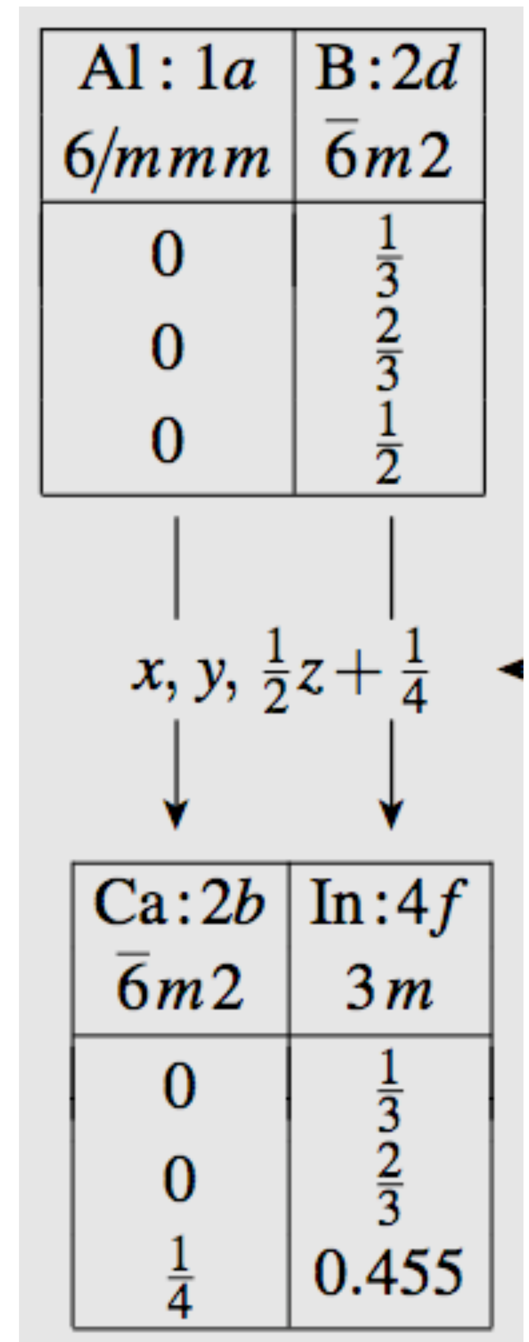


MAXSUB

SUBGROUPGRAPH

HERMANN

Wyckoff-splitting schemes



WYCKSPLIT

Family tree of hettotypes of ReO_3

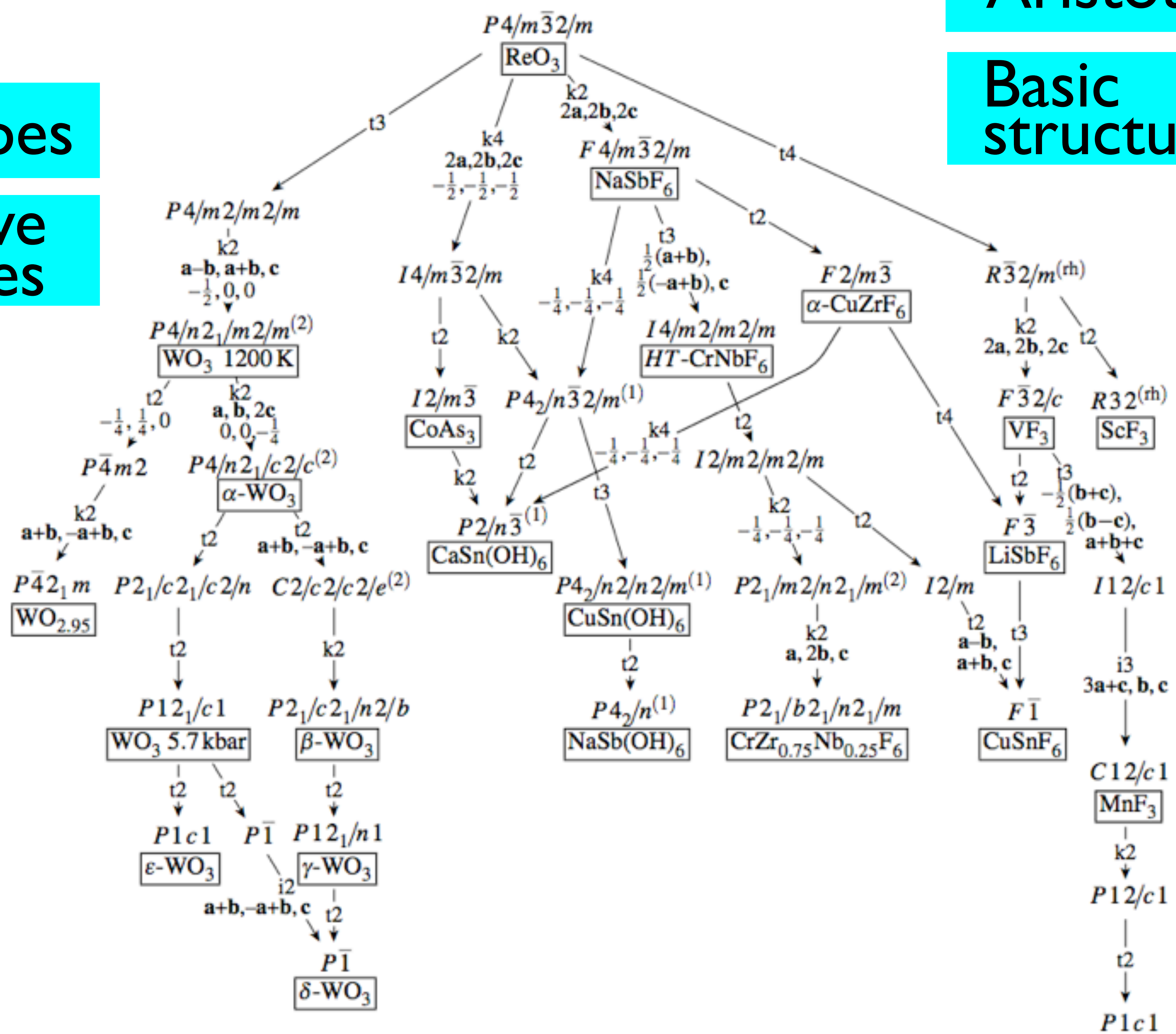
Baernighausen Trees

Aristotype

Basic structure

Hettotypes

Derivative structures



Problem 10.1 Cristobalite phase transitions

At low temperatures, the space-group symmetry of cristobalite is given by the space group is $P4_12_12$ (92) with lattice parameters a=4.9586A, c=6.9074A. The four silicon atoms are located in Wyckoff position 4(a) ..2 with the coordinates x, x, 0; -x, -x, 1/2; 1/2-x,1/2+x, 1/4; 1/2+x,1/2-x,3/4, x = 0.3028.

During the phase transition, the tetragonal structure is transformed into a cubic one with space group Fd-3m (227), a=7.147A. It is listed in the space-group tables with two different origins. If 'Origin choice 2' setting is used (with point symmetry -3m at the origin), then the silicon atoms occupy the position 8(a) -43m with the coordinates 1/8, 1/8, 1/8; 7/8, 3/8, 3/8 and those related by the face-centring translations.

Describe the structural distortion from the cubic to the tetragonal phase by the determination of (i) the displacements if the Si atoms in relative and absolute units, and (ii) the changes on the lattice parameters during the transition.

Which programs can be used for the analysis of the cristobalite problem?

SUBGROUPGRAPH

Symmetry break Fd-3m(227) → $P4_12_12$(92)

Index?

Transformation matrix?

TRANSTRU

Problem 10.1

SOLUTION

Symmetry break: Fd-3m→$P4_12_12$

$a_t=1/2(a_c-b_c)$, $b_t=1/2(a_c+b_c)$, $c_t=c_c$

origin shift: (5/8,3/8,3/8)

Experiment:

Cubic phase:

a=7.147 Å

Si 8a 1/8 1/8 1/8

7/8 3/8 3/8

$\xrightarrow{(P,p)}$

Tetragonal phase:

a=4.9586 Å, c=6.9074

Si 4a 0.3028 0.3028 0

Calculated:

a=5.053 Å, c=7.147 Å

Si 8a 0.25 0.25 0

affine deformation

atomic displacements

Problem 10.2

CaF_2 - structure data

(*fcc*, *a*=*b*=*c*, α=β=γ)

Ca	$4a$	$m\bar{3}m$	$0,0,0$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	
F	$8c$	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{3}{4},\frac{3}{4}$	$\frac{3}{4},\frac{1}{4},\frac{3}{4}$	$\frac{3}{4},\frac{3}{4},\frac{1}{4}$	
			$\frac{3}{4},\frac{3}{4},\frac{3}{4}$	$\frac{3}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{3}{4},\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$	

Coordinate transformation

$$\mathbf{a}' = \tfrac{1}{2}(\mathbf{a}-\mathbf{b}),\ \mathbf{b}' = \tfrac{1}{2}(\mathbf{a}+\mathbf{b}),\ \mathbf{c}' = \mathbf{c}$$

p=1/4,0,1/4

Problem 10.2

Questions:

(i) Display the relation between the new and the old basis.

(ii) Which is the crystal system of the new unit cell?

(iii) Construct the transformation matrix $\boldsymbol{P}$ and the corresponding 4x4 augmented matrix.

(iv) Determine the ratio of the new and old unit cell volumes.

(v) New coordinate-system description of the structure.

(iv) New description: program TRANSTRU

Transform Structure

Structure

```
225
5.0 5.0 5.0 90 90 90
2
Ca    1   4a    0.0 0.0 0
F     2   8c    0.25 0.25 0.25
```

Low symmetry Space Group: 129

Transformation Matrix:

In matrix form:	Rotational part			Origin Shift
	1/2	1/2	0	1/4
	-1/2	1/2	0	0
	0	0	1	1/4

Transform structure

Transformation matrix: 1/2a-1/2b+1/4,1/2a+1/2b,c+1/4

High symmetry structure

```
225
5.0 5.0 5.0 90 90 90
2
Ca     1    4a     0.0 0.0 0
F      2    8c     0.25 0.25 0.25
```

Low symmetry structure

```
129
3.535534 3.535534 5.000000 90.000000 90.000000 90.000000
3
Ca       1       2c       0.750000         0.750000         0.750000
F        2       2a       0.750000         0.250000         0.000000
F        2_2     2b       0.250000         0.750000         0.500000
```

Space Group: 129
Lattice Parameters: 3.535534 3.535534 5 90 90 90

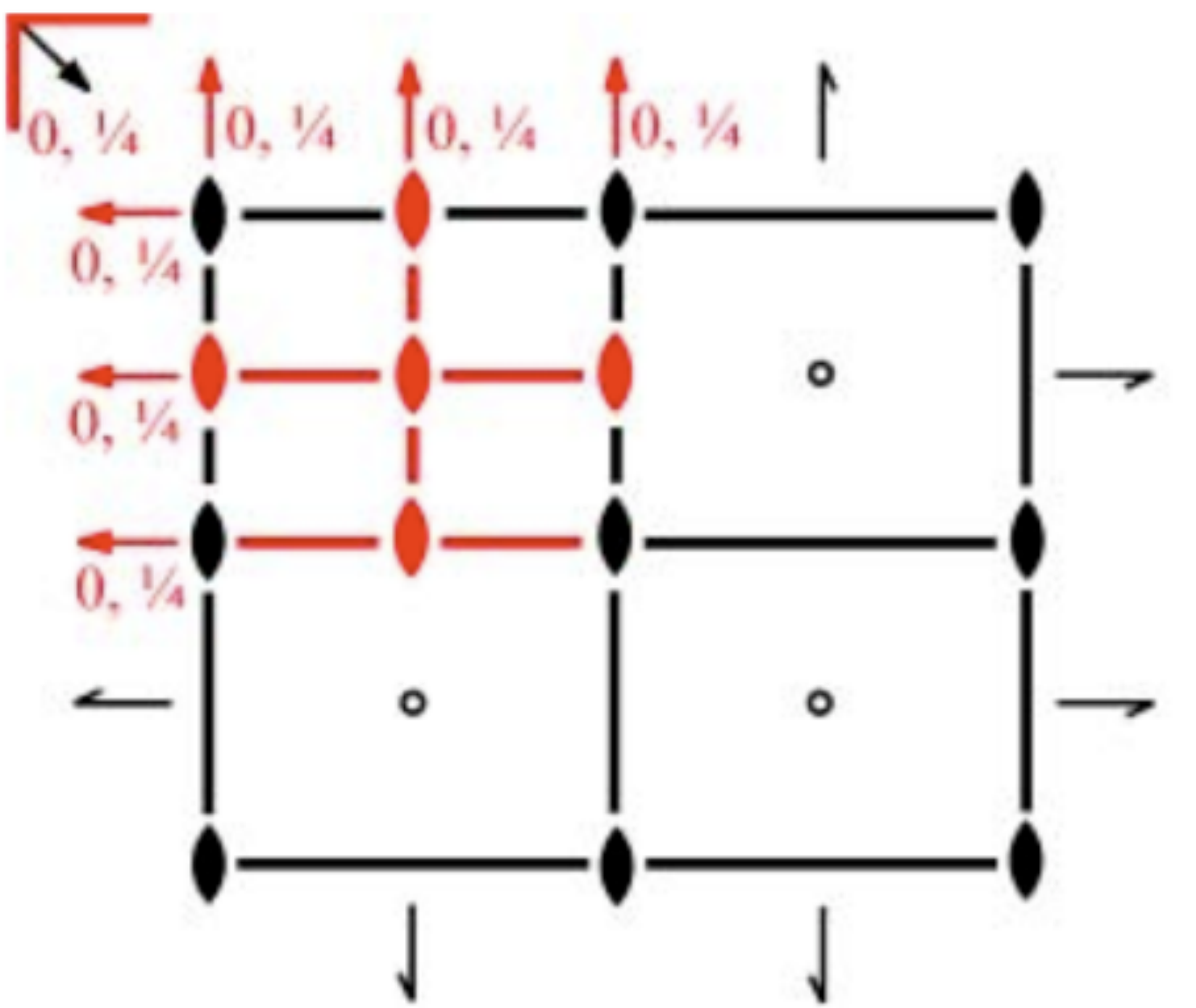
AT	#	WP	Coordinates		
Ca	1	2c	3/4	3/4	3/4
F	2	2a	3/4	1/4	0
F	2_2	2b	1/4	3/4	1/2

Note: You can save the CIF file and visualize it with an application as Jmol

Normalizers of space groups

Normalizers N(G) : $g^{-1}\{G\}g = \{G\}$ $\begin{cases} \text{Euclidean} \\ \text{Affine} \end{cases}$

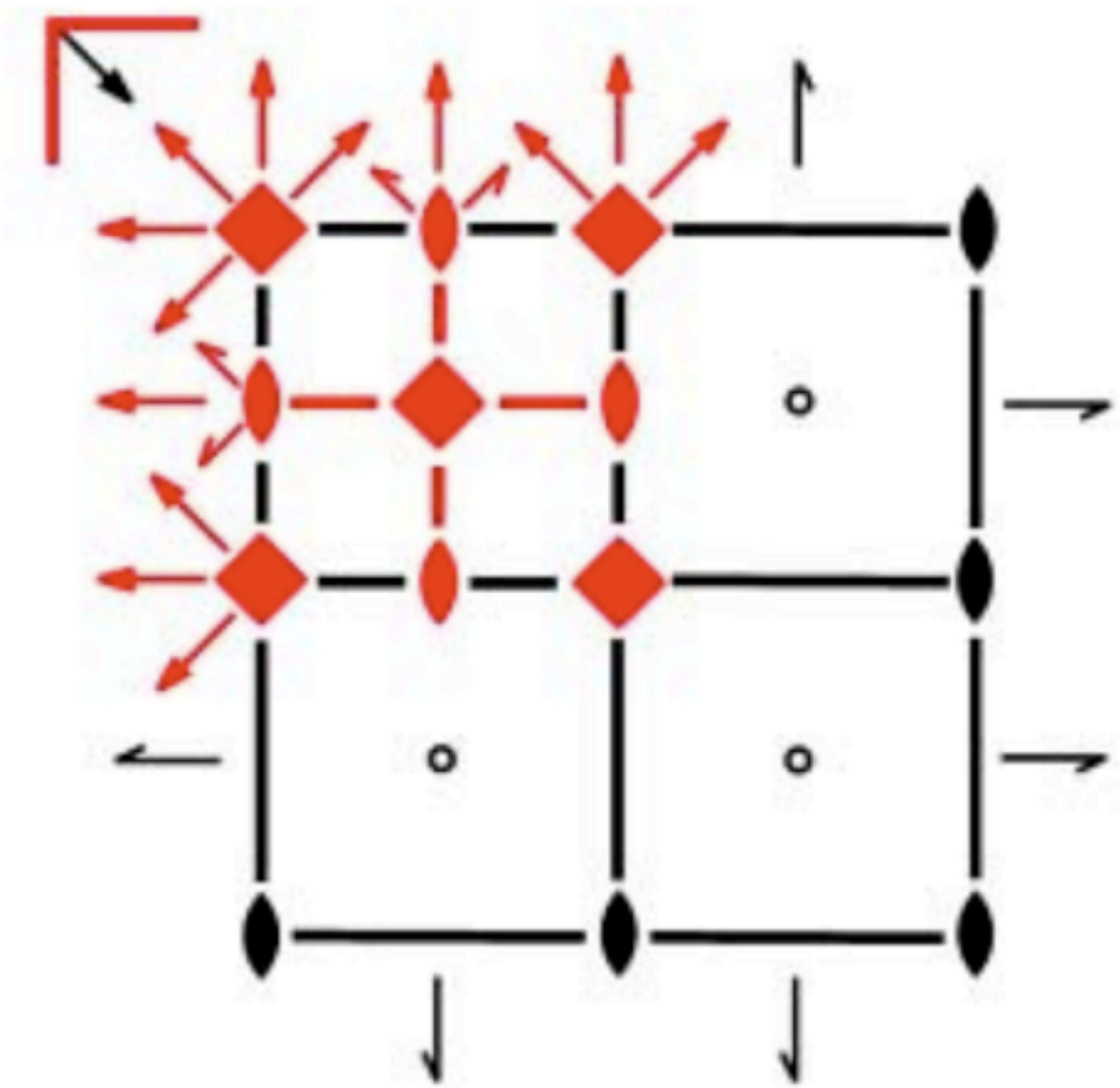
the symmetry
of symmetry



Space group: Pmmn (a,b,c)

Euclidean normalizer:
Pmmm (1/2a,1/2b,1/2c)

Normalizers for specialized metrics



Space group:
Pmmn (a,b,c), **a=b**

Euclidean normalizer for specialized metrics:
P4/mmm (1/2a,1/2b,1/2c)

Applications: Equivalent point configurations
Wyckoff sets
Equivalent structure descriptions

Normalizers of space groups

NORMALIZER

Cosets representatives of the Affine Normalizer with respect to the Space Group 99 (*P4mm*)

The Affine normalizer coincides with the *Euclidean* one.

Transformation of the Wyckoff Positions of Space Group 99 (*P4mm*) under Affine Normalizer N(G):

Index: 4*(infinite)

Coset Representative		Transformed WP
x,y,z	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$	a b c d e f g
x+1/2,y+1/2,z	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 \\ 1/2 \\ 0 \end{bmatrix}$	b a c d f e g
-x,-y,-z	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$	a b c d e f g
-x+1/2,-y+1/2,-z	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1/2 \\ 1/2 \\ 0 \end{bmatrix}$	b a c d f e g
x,y,z+t	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ t \end{bmatrix}$	a b c d e f g

Symmetry-equivalent Wyckoff positions

WYCKOFF SETS

Additional Generators for the Normalizer of the Group 221 (*Pm*-3*m*)

Additional generators of Euclidean normalizer (*Im*-3*m*) **a,b,c**

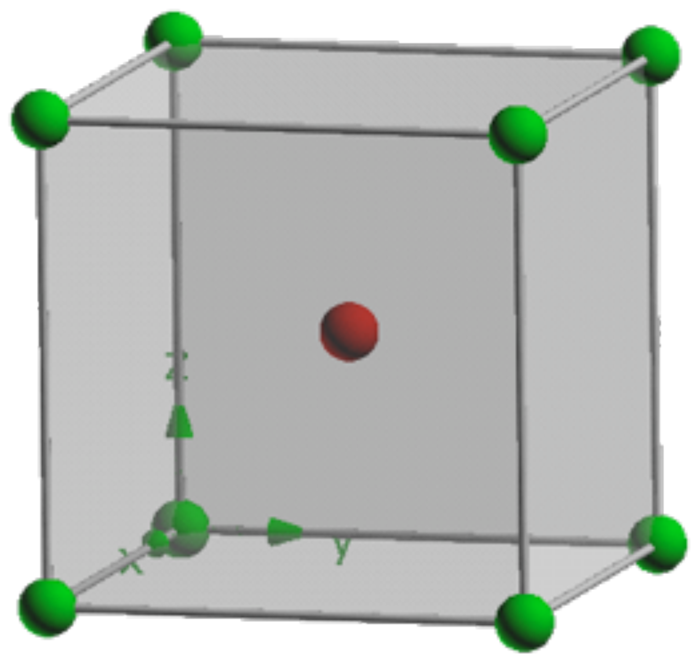
x+1/2,y+1/2,z+1/2	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix}$

Wyckoff Sets of Space Group 221 (*Pm*-3*m*)

NOTE: The program uses the default choice for the group settings.

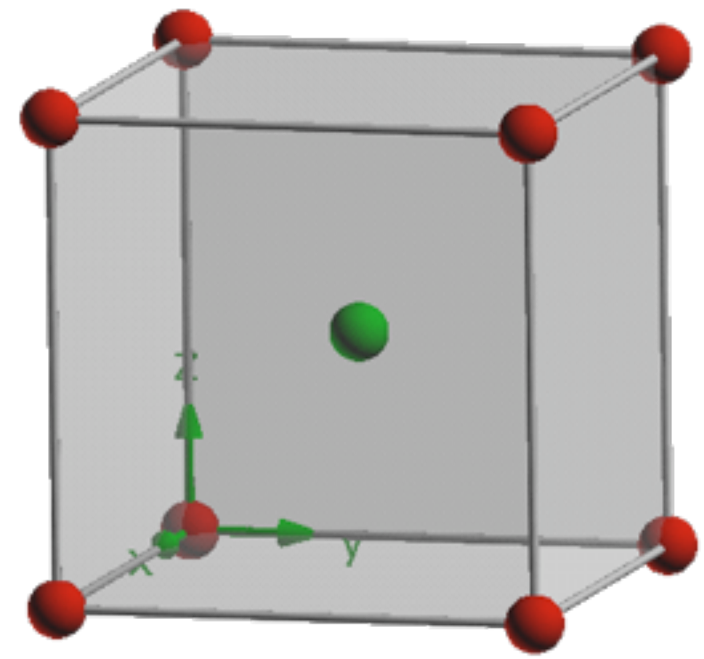
Letter	Mult	SS	Rep.	Equivalent Positions
n	48	1	(x, y, z)	n
m	24	..m	(x, x, z)	m
f	6	4m. m	(x, 1/2 , 1/2)	ef
e	6	4m. m	(x, 0, 0)	ef
d	3	4/mm. m	(1/2 , 0, 0)	cd
c	3	4/mm. m	(0, 1/2 , 1/2)	cd
b	1	m-3m	(1/2 , 1/2 , 1/2)	ab
a	1	m-3m	(0, 0, 0)	ab

Equivalent descriptions of crystal structures



CsCl

Pm-3*m* (221)



Normalizer operation: x+1/2, y+1/2, z+1/2

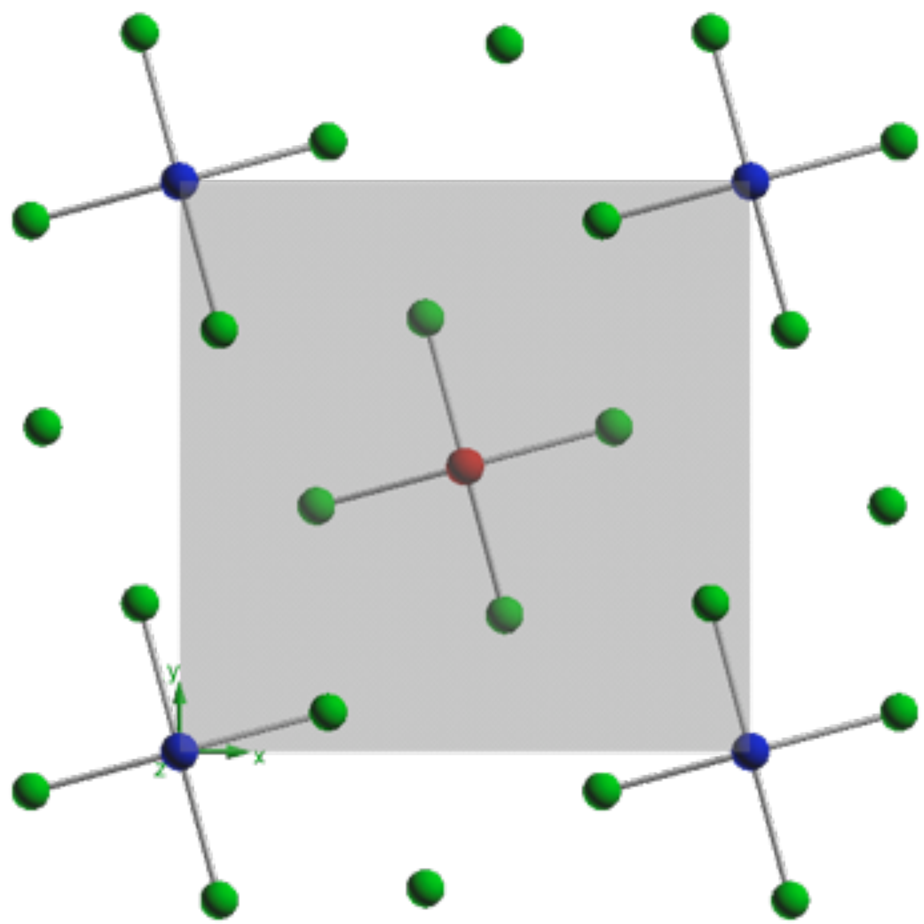
1*a* (0,0,0) $\longrightarrow$ 1*b* (1/2,1/2,1/2)

1*b* (1/2,1/2,1/2) $\longrightarrow$ 1a (0,0,0)

Problem: EQUIVALENT DESCRIPTIONS

EQUIVSTRU

Example: $WOBr_4$



Space Group: $I4$

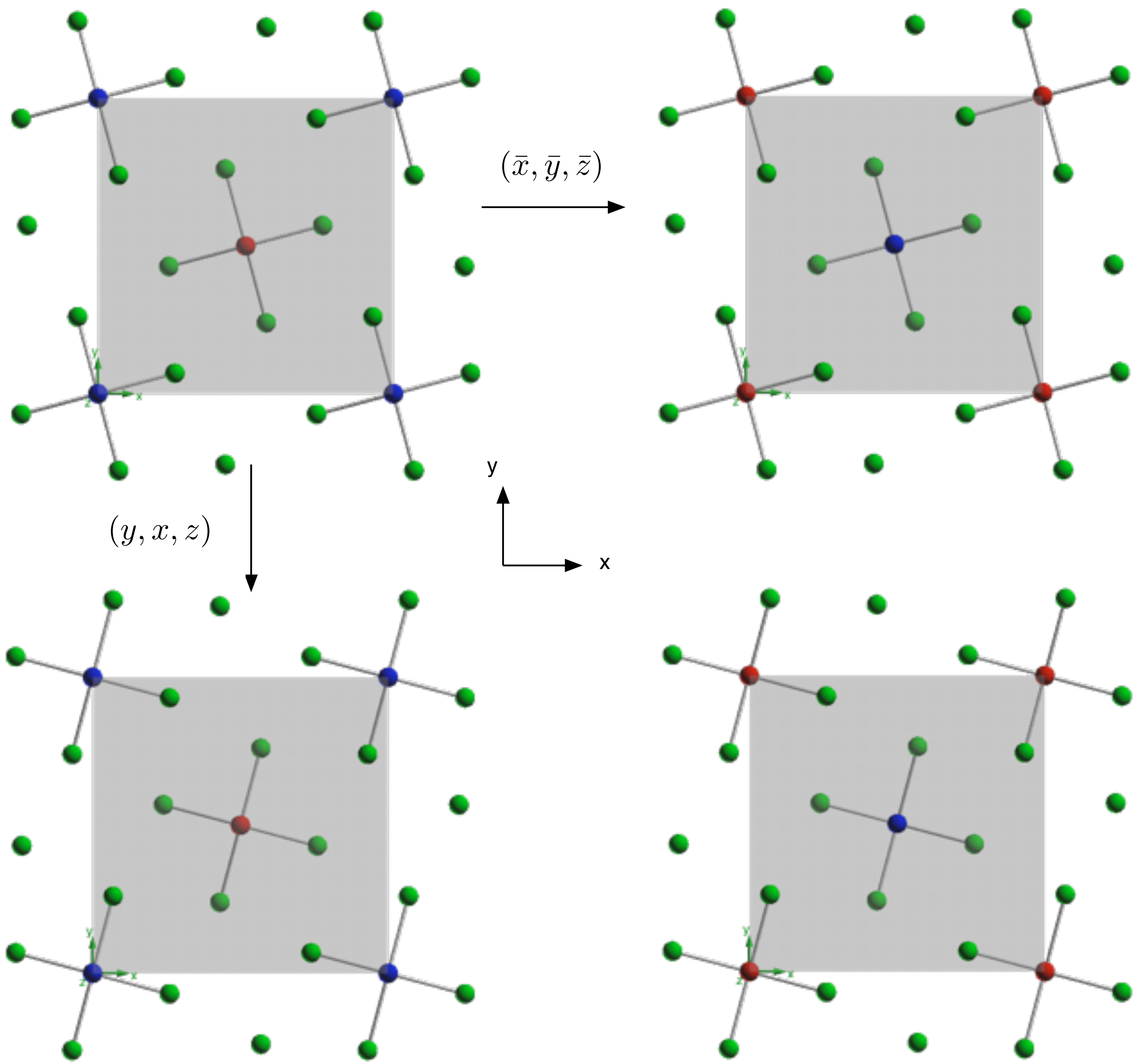
Euclidean Normalizer: P^14/mmm

Index: 4

$$P4/mmm = I4 + (\bar{x}, \bar{y}, \bar{z})I4 + (y, x, z)I4 + (\bar{y}, \bar{x}, \bar{z})I4$$

EQUIVALENT DESCRIPTIONS

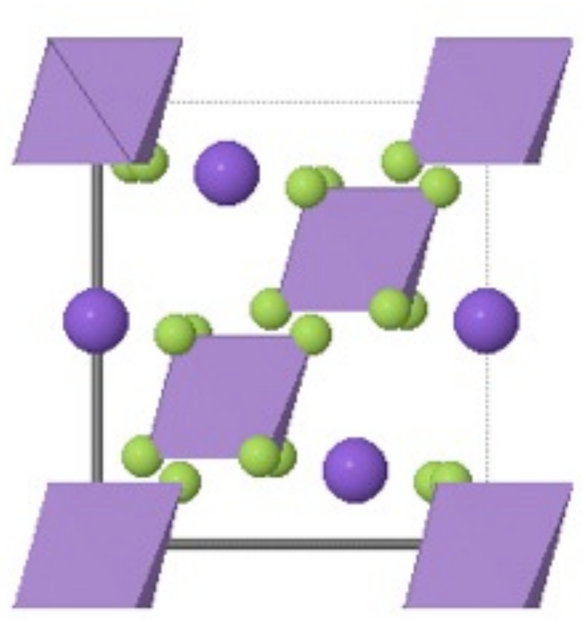
Example: $WOBr_4$



EXERCISES

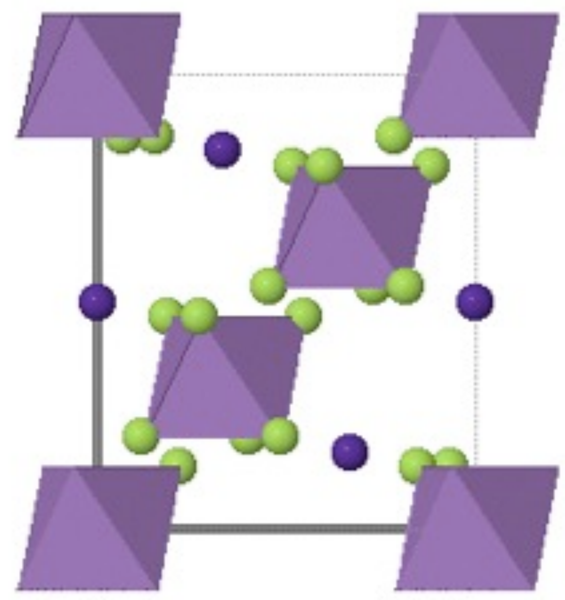
Problem 10.3

$KAsF_6$



```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1   3b    0.3333 0.66666 0.16667
As     1   3a    0  0  0
F      1   18f   0.1292 0.2165 0.1381
```

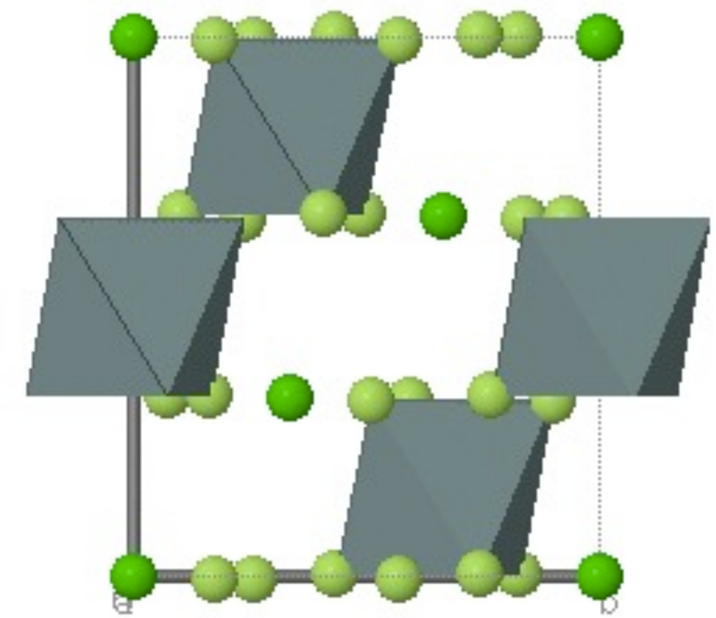
$CsSbF_6$



```
148
7.9040 7.9040 8.2610 90.00 90.00 120.00
3
Cs     1   3b    0. 0. 0.5
SB     1   3a    0  0  0
F      1   18f   0.06562 0.2158 0.1337
```

Maximum distance Δ: 0.4657

$BaSnF_6$



```
148
7.4279 7.4279 7.4180 90.00 90.00 120.00
3
Ba     1   3a    0. 0. 0.0
Sn     1   3b    0  0  0.5
F      1   18f   0.2586 0.8262 0.0047
```

No pairing found for tolerance: 2

Space-group symmetry: R-3

Euclidean normalizer: R-3m(-a,-b, 1/2c)

Coset representatives: x,y,z; x,y,z+1/2;
-y,-x,z; -y,-x,z+1/2;

Problem: EQUIVALENT STRUCTURE DESCRIPTION **EQUISTRU**

Equivalent Descriptions of Crystal Structures

Equivalent Structures

Given a space group IT*A* number, the cell parameters (separated with spaces) and the atom positions, the program EQUIVSTRU transforms the corresponding structure with the elements of the euclidean normalizer of the space group. All the transformed structures are equivalent symmetry descriptions of the given initial structure. The atom positions are identified generating the Wyckoff sets.

Structure Data [in CIF format] Examinar...

HINT: [The option for a given filename is preferential]

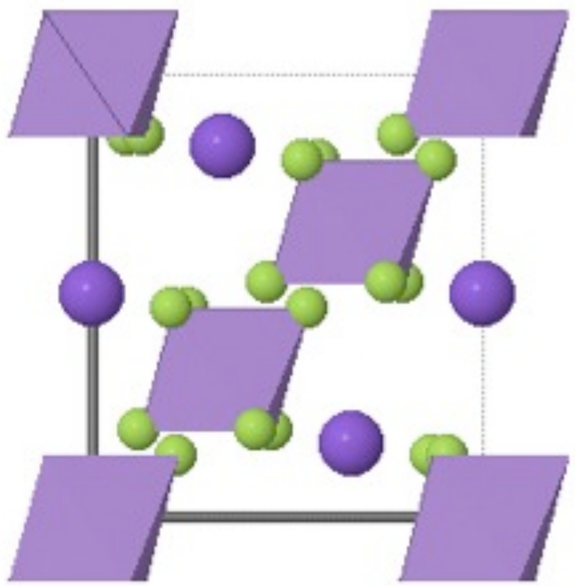
Structure

```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1    3b    0.33333 0.66666 0.16667
As     1    3a    0 0 0
F      1    18f   0.1292 0.2165 0.1381
```

Show

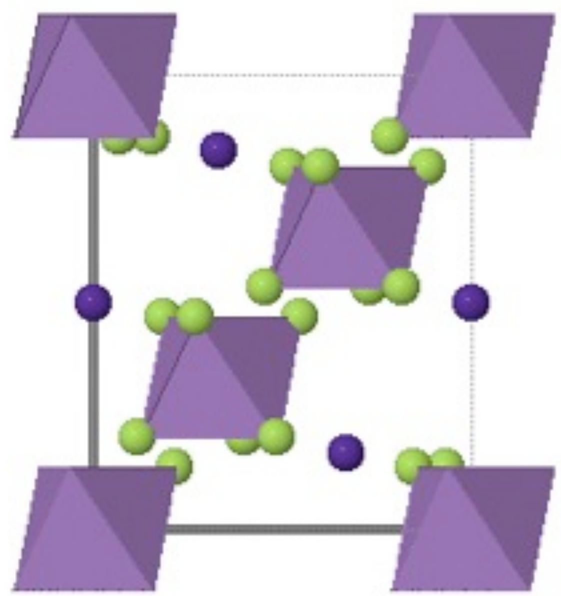
SOLUTION

KAsF$_6$



```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1    3b    0.3333 0.66666 0.16667
As     1    3a    0 0 0
F      1    18f   0.1292 0.2165 0.1381
```

CsSbF$_6$



```
148
7.9040 7.9040 8.2610 90.00 90.00 120.00
3
Cs     1    3b    0. 0. 0.5
SB     1    3a    0 0 0
F      1    18f   0.06562 0.2158 0.1337
```

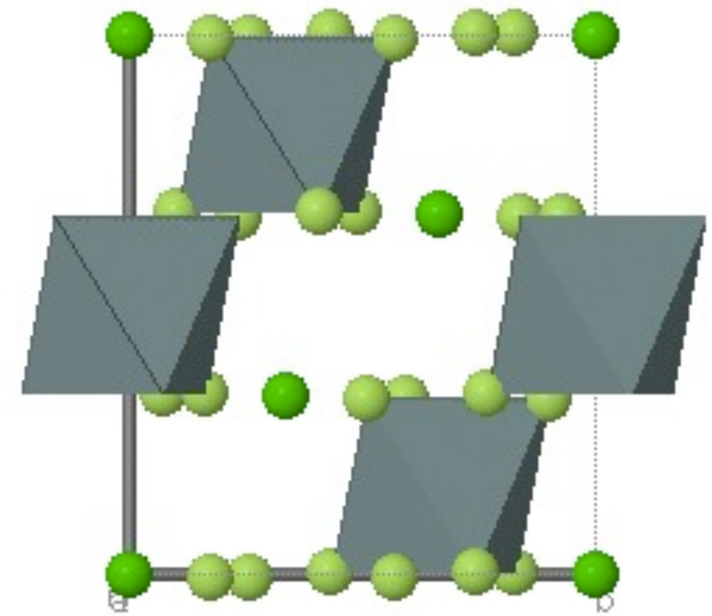
Maximum distance Δ: 0.4657

-y,-x,z

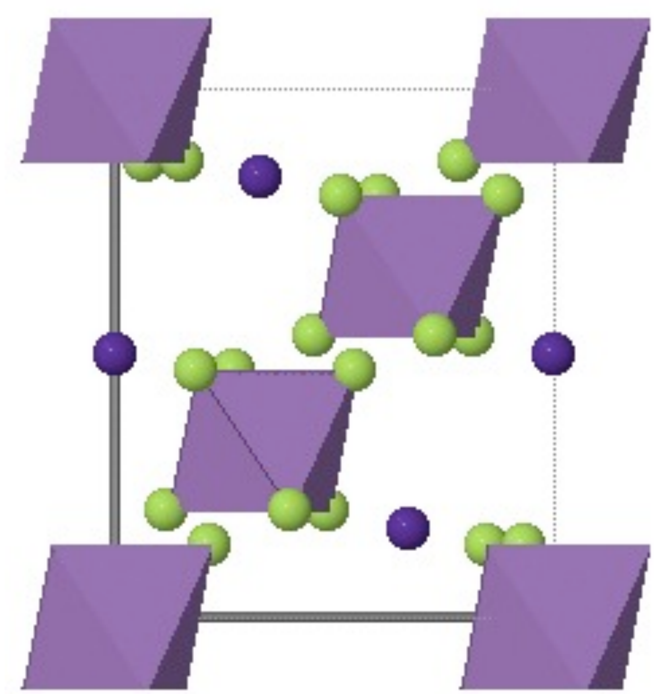
```
148
7.9040 7.9040 8.2610 90.00 90.00 120.00
3
Cs     1    3b    0. 0. 0.5
SB     1    3a    0 0 0
F      1    18f   0.150180 0.215800 0.133700
```

Maximum distance Δ: 0.1600

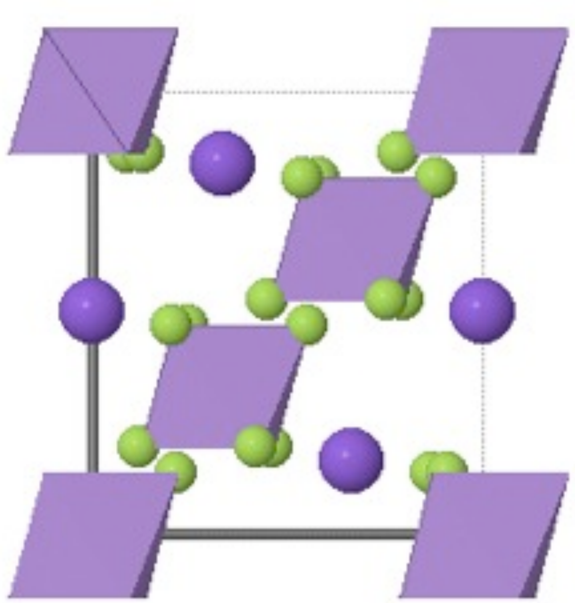
BaSnF$_6$

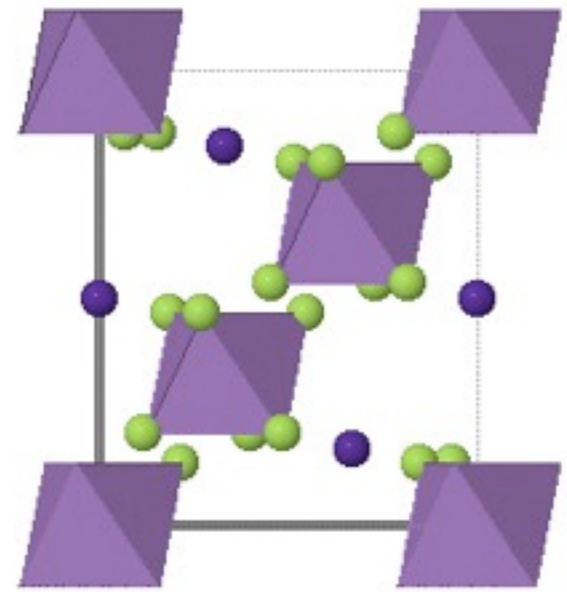


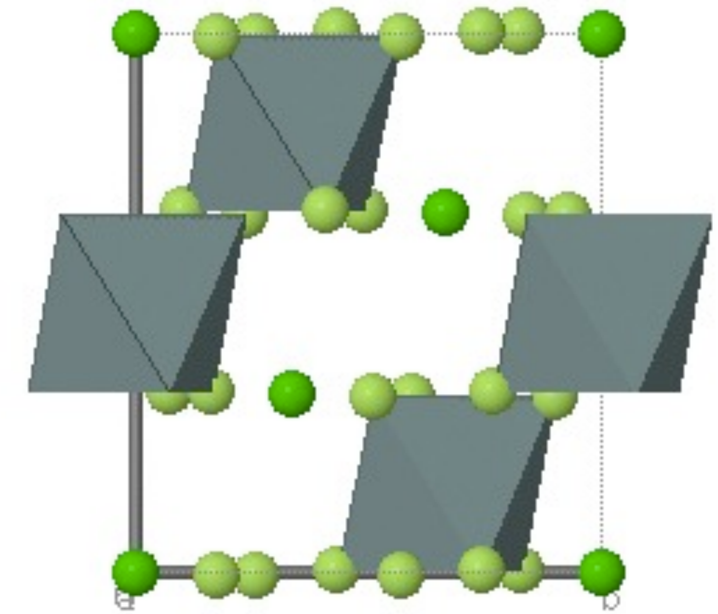
```
148
7.4279 7.4279 7.4180 90.00 90.00 120.00
3
Ba     1    3a    0. 0. 0.0
Sn     1    3b    0 0 0.5
F      1    18f   0.2586 0.8262 0.0047
```



$KAsF_6$ $CsSbF_6$ $BaSnF_6$







```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1    3b    0.3333 0.66666 0.16667
As     1    3a    0 0 0
F      1    18f   0.1292 0.2165 0.1381
```

```
148
7.9040 7.9040 8.2610 90.00 90.00 120.00
3
Cs     1    3b    0. 0. 0.5
SB     1    3a    0 0 0
F      1    18f   0.06562 0.2158 0.1337
```

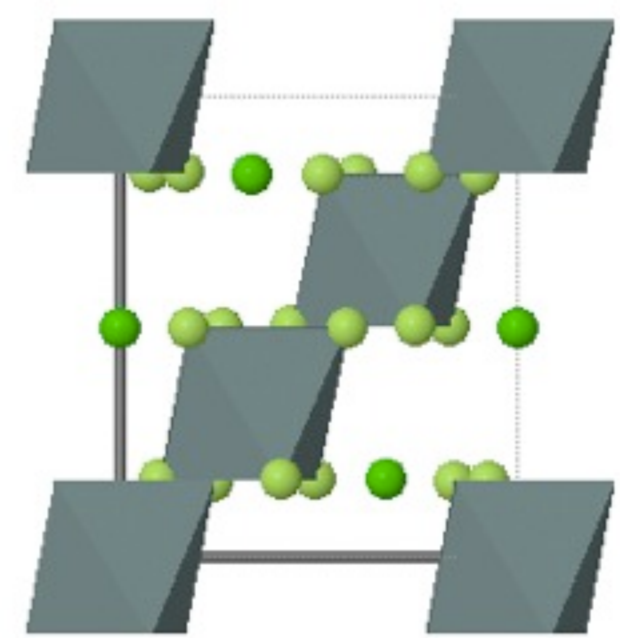
```
148
7.4279 7.4279 7.4180 90.00 90.00 120.00
3
Ba     1    3a    0. 0. 0.0
Sn     1    3b    0 0 0.5
F      1    18f   0.2586 0.8262 0.0047
```

No pairing found for tolerance: 2

x,y,z+1/2

```
148
7.4279 7.4279 7.4180 90.00 90.00 120.00
3
Ba     1    3b    0. 0. 0.5
Sn     1    3a    0 0 0
F      1    18f   0.159533 0.234267 0.161967
```

Maximum distance Δ: 0.2603



EXERCISES

Problem 10.4

Equivalent structure descriptions

Space group: P4/n

Exercise 6.4. $P(C_6C_5)_4[MoNCl_4]$ is tetragonal, spac

Atom	Wyckoff position	Coordinate x	triplets y	z
P	$2b$	0.25	0.75	0
Mo	$2c$	0.25	0.25	0.121
N	$2c$	0.25	0.25	−0.093
C1	$8g$	0.362	0.760	0.141
C2	$8g$	0.437	0.836	0.117
Cl	$8g$	0.400	0.347	0.191

N(P4/n) = P4/mmm (a’,b’,1/2c)

a’=1/2(a-b), b’=1/2(a+b)

Problem: LOW-SYMMETRY STRUCTURES FOR A GIVEN CELL MULTIPLICATION

CELLSUB

Example: $CsMgInF_6$

aristotype — Fd-3m

structure data: P lattice, orthorhombic

$[i_k=2]$

unknown — ?

List of P-centred orthorhombic subgroups of Fd-3m(227) i_k=2

N	HM Symbol	ITA	index	t-index	k-index	More info
1	*Pnma*	062	12	6	2	show...
2	*Pmna*	053	12	6	2	show...
3	*Pnna*	052	12	6	2	show...
4	*Pmma*	051	12	6	2	show...
5	*Pnn2*	034	24	12	2	show...
6	$Pna2_1$	033	24	12	2	show...
7	$Pmn2_1$	031	24	12	2	show...
8	*Pnc2*	030	24	12	2	show...
9	*Pma2*	028	24	12	2	show...
10	$Pmc2_1$	026	24	12	2	show...
11	*Pmm2*	025	24	12	2	show...
12	$P2_12_12_1$	019	24	12	2	show...
13	$P222_1$	017	24	12	2	show...

Problem: PHASES WITH NO GROUP-SUBGROUP RELATIONS **COMMON SUBGROUPS**

$$
\begin{tikzcd}
 & \mathcal{G}_2 \arrow[d, "{[i_2]}"] \\
\mathcal{G}_1 \arrow[d, "{[i_1]}"] & \\
\mathcal{H}_1 \arrow[r, phantom, "\simeq"] & \mathcal{H}_2
\end{tikzcd}
$$

$$Z_{\mathcal{H}_1} = Z_{\mathcal{H}_2}$$

$$i_1 = \frac{|\mathcal{P}_{\mathcal{G}_1}|}{|\mathcal{P}_{\mathcal{H}_1}|} \cdot \frac{Z^p_{\mathcal{H}_1}}{Z^p_{\mathcal{G}_1}}$$

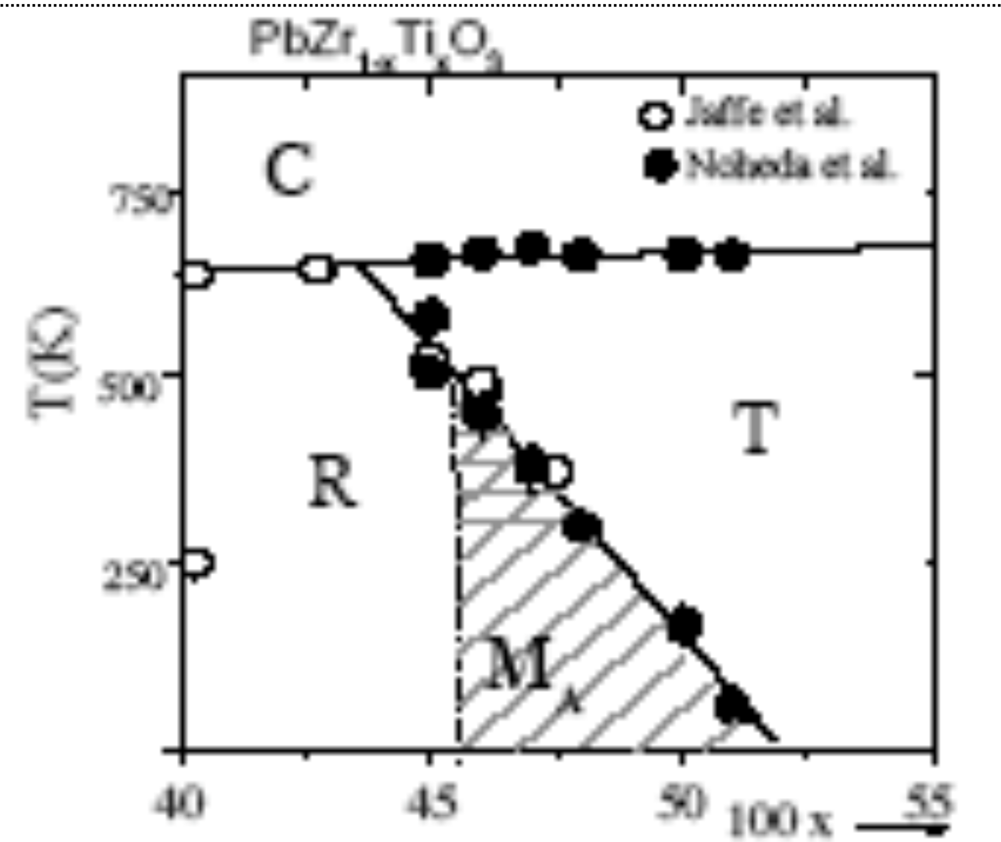
$$i_2 = \frac{|\mathcal{P}_{\mathcal{G}_2}|}{|\mathcal{P}_{\mathcal{H}_2}|} \cdot \frac{Z^p_{\mathcal{H}_2}}{Z^p_{\mathcal{G}_2}}$$

index condition

$$i_2 = i_1 \cdot \frac{Z_1}{Z_2} \cdot \frac{|\mathcal{P}_{\mathcal{G}_2}|}{|\mathcal{P}_{\mathcal{G}_1}|} \cdot \frac{f_{\mathcal{G}_2}}{f_{\mathcal{G}_1}}$$

the set of common subgroup types is finite if a maximum k-index is defined

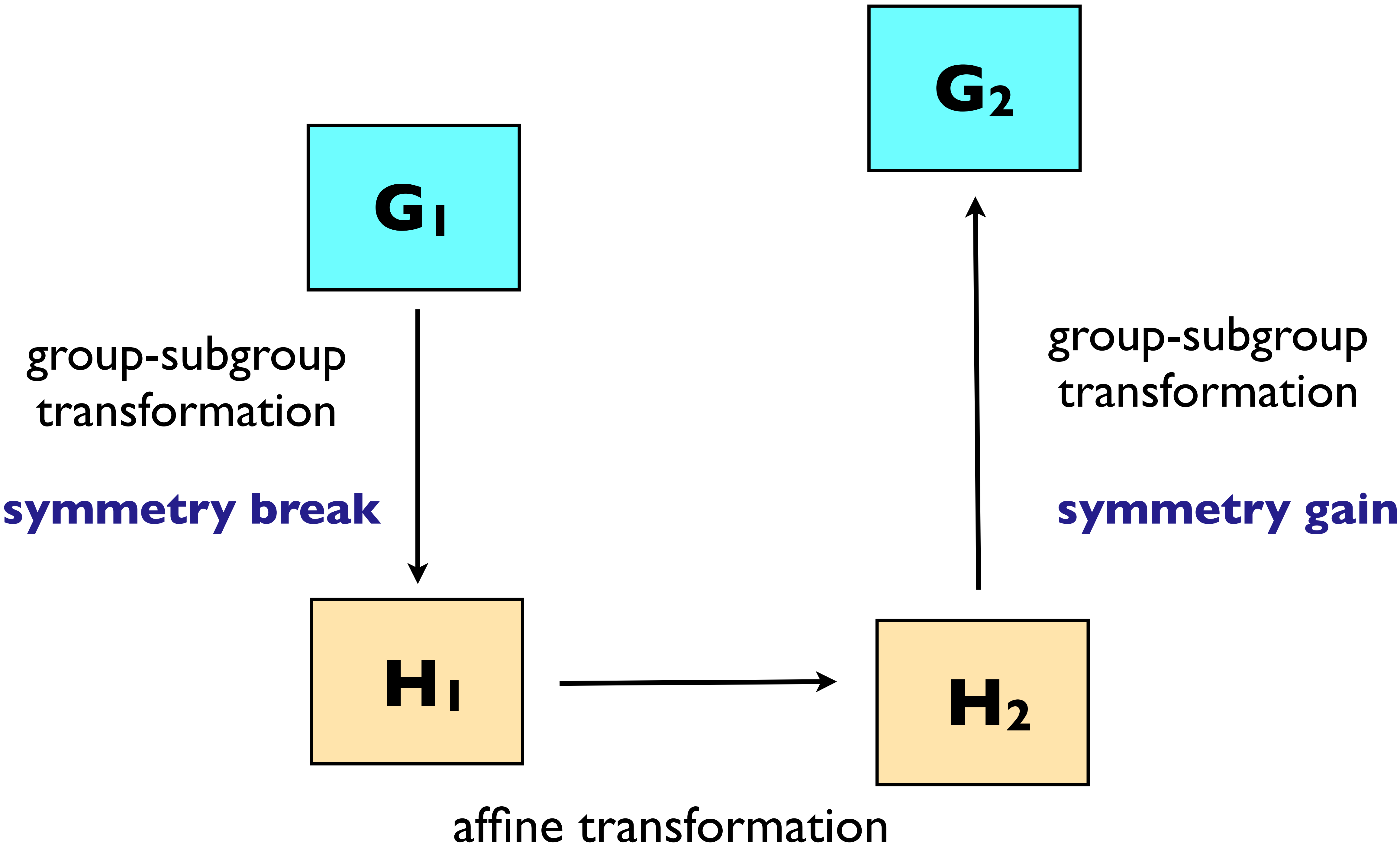
Example: Monoclinic phase of the system $PbZr_{1-x}Ti_xO_3$



Phase diagram of PZT in the vicinity of its morphotropic phase boundary. C, R, and T represent cubic, rhombohedral and tetragonal regions. The diagonally-shaded M_A area represents the stability region of monoclinic phase.
(D.E. Cox et al. Condensed Matter, cond-mat/0102457, 2001.)

Symmetry arguments for the determination of the monoclinic phase ?

Problem: STRUCTURAL RELATIONSHIP — GROUP-THEORETICAL MODEL



Symmetry Conditions

- The description of the intermediate state involves a common subgroup pair (H_1, H_2) of the symmetry groups of the two phases such $G_1 > H_1$ and $G_2 > H_2$.
- The compatibility between the occupied Wyckoff orbits in the intermediate state.

Example PZT:COMMON SUBGROUPS

Branch 1

$$P4mm \xrightarrow[i_1=4]{Z_1=1} Cm$$

Branch 2

$$R3m \xrightarrow[i_2=3]{Z_2=3} Cm$$

index condition: $i_2 = i_1 \dfrac{Z_1 \; f_2 \; |P_2|}{f_1 \; Z_2 \; |P_1|}$

Example PZT: Wyckoff positions compatibility

Branch 1				Branch 2
P4mm		*Cm*		*R3m*
Pb1 1a 4mm $(00z_1)$	→	2a m (x0z)	←	3a 3m $(00z_1)$ Pb1
Ti/Zr 1b 4mm $(1/2\ 1/2\ z_2)$	→	2a m (x0z)	←	3a 3m $(00z_2)$ Ti/Zr
O1 1b 4mm $(1/2\ 1/2\ z_3)$	→	2a m (x0z)	←	9b .m $(x\text{-}xz_3)$ O1
O2 2c 2mm. $(1/2\ 0\ z_4)$	→	4b 1 (xyz)	↙	

Structural Conditions

- Minimum deformation strain in the transformation
- Minimum distance between the corresponding atoms in the initial structures described in the subgroup reference frame

FURTHER APPLICATIONS OF

GROUP-NOT-SUBGROUP RELATIONS:

-PHASE TRANSITIONS WITH NO GROUP-SUBGROUP RELATIONS

-FERROELECTRIC PHASES WITH DIFFERENT ORIENTATIONS OF POLARIZATIONS

Problem: PHASES WITH NO GROUP-SUBGROUP RELATIONS

COMMON SUPERGROUPS

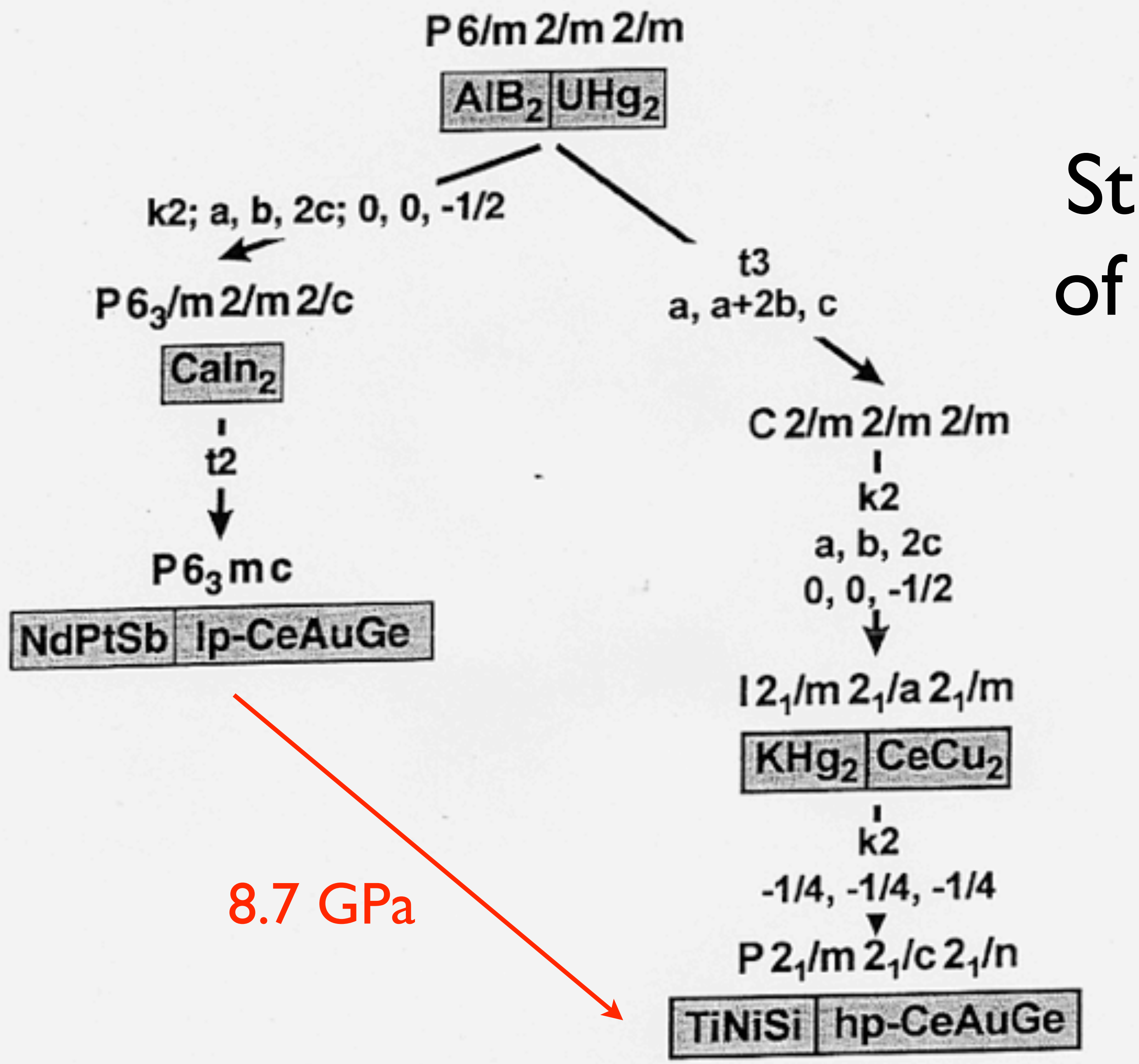


Fig. 7. *Bärnighausen* tree of the group-subgroup relationship [17] of the AlB_2-type and the distorted low-pressure (lp) and high-pressure (hp) modifications of CeAuGe (excerpt of Fig. 3. in Ref. [1]). The indices of the *klassengleiche* (*k*) and *translationengleiche* (*t*) transitions, as well as the unit cell transformations and origin shifts are given.

Structural phase transitions of CeAuGe at high pressure

Brouskov *et al.*

Z. Kristallogr. 220(2005) 122

Common subgroup candidates

Common Subgroup H					Branch $G_1 > H$			Branch $G_2 > H$		
N	HM Symbol	P_H	Z_H	ITA	i_1	it_1	ik_1	i_2	it_2	ik_2
1	$Pna2_1$	mm2	4	033	6	3	2	2	2	1
2	$Pmn2_1$	mm2	4	031	6	3	2	2	2	1
3	$Pmc2_1$	mm2	4	026	6	3	2	2	2	1
4	Pc	m	4	007	12	6	2	4	4	1
5	Pm	m	4	006	12	6	2	4	4	1
6	$P2_1$	2	4	004	12	6	2	4	4	1
7	$P1$	1	4	001	24	12	2	8	8	1

ADDITIONAL

Problem 10.2

SOLUTION

Comparison: CaF_2 structure $\longleftrightarrow$ α-XOF structures

lattice parameters

c'/a'=1.414

	LaOF	YOF	PuOF
c'/a'	1.427	1.389	1.413

atomic coordinates

CaF_2

$Ca:$	$1/2,0,1/4$	$0,1/2,3/4$		
$F:$	$\boxed{1/2,1/2,1/2}$	$0,0,0$	$1/2,1/2,0$	$\boxed{0,0,1/2}$

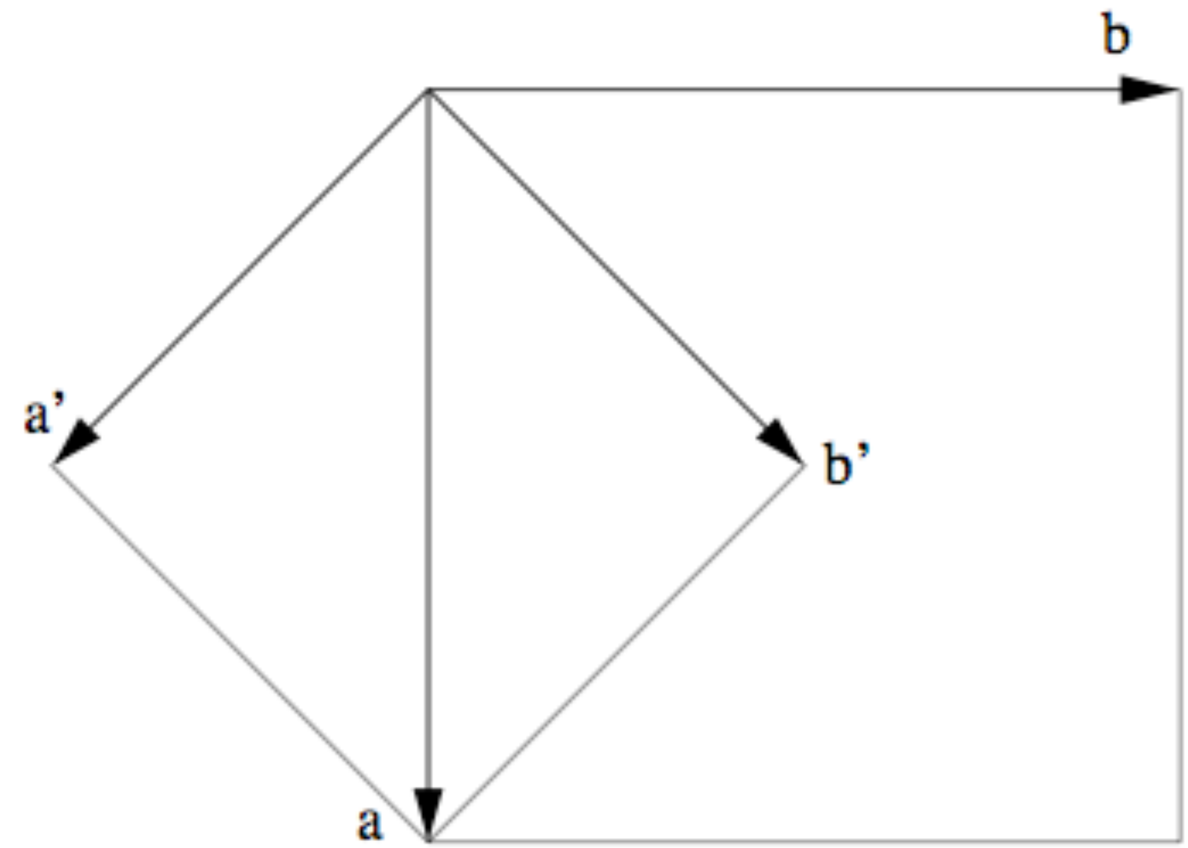
α-XOF

$X:$	2	c	$4mm$	$1/2,0,u$	$0,1/2,\bar{u}$	$u=0.222$
$O:$	2	b	$\bar{4}2m$	$\boxed{0,0,1/2}$	$\boxed{1/2,1/2,1/2}$	
$F:$	2	a	$\bar{4}2m$	$0,0,0$	$1/2,1/2,0$	

Problem 10.2

SOLUTION

(i) Relations between the old (***a***,***b***,***c***) and the new basis (***a'***,***b'***,***c'***)



(ii) The new unit cell is tetragonal I

(iv) Volume 'new cell' to Volume 'old cell':

$$V_{new}/V_{old} = 1/2$$

Problem 10.2

SOLUTION

(iii) Transformation matrix and the corresponding augmented one

$$\boldsymbol{P} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbb{P} = \left(\begin{array}{ccc|c} \frac{1}{2} & \frac{1}{2} & 0 & -\frac{1}{4} \\ -\frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{4} \\ 0 & 0 & 1 & -\frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right), \quad \mathbb{P}^{-1} = \left(\begin{array}{ccc|c} 1 & -1 & 0 & \frac{1}{2} \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right)$$

(iv) New description

$$\begin{array}{lllllll}
Ca: & 0,0,0 & \longrightarrow & 1/2,0,1/4 & 1/2,1/2,0 & \longrightarrow & 1/2,1,1/4 \\
 & 1/2,0,1/2 & \longrightarrow & 1,1/2,3/4 & 0,1/2,1/2 & \longrightarrow & 0,1/2,3/4 \\
 & & & & & & \\
F: & 1/4,1/4,1/4 & \longrightarrow & 1/2,1/2,1/2 & 1/4,3/4,3/4 & \longrightarrow & 0,1,1 \\
 & 3/4,1/4,3/4 & \longrightarrow & 1,1,1 & 3/4,3/4,1/4 & \longrightarrow & 1/2,3/2,1/2 \\
 & 3/4,3/4,3/4 & \longrightarrow & 1/2,3/2,1 & 3/4,1/4,1/4 & \longrightarrow & 1,1,1/2 \\
 & 1/4,3/4,1/4 & \longrightarrow & 0,1,1/2 & 1/4,1/4,3/4 & \longrightarrow & 1/2,1/2,1
\end{array}$$

Subgroups of space groups

General subgroups H<G:

$$\begin{cases} T_H < T_G \\ P_H < P_G \end{cases}$$

Theorem Hermann, 1929:

For each pair G>H, there exists a uniquely defined intermediate subgroup M, G ≧ M ≧ H, such that:

$$\begin{tikzcd} G \arrow[d, "i_t"] \\ M \arrow[d, "i_k"] \\ H \end{tikzcd}$$

M is a *t*-subgroup of G

H is a *k*-subgroup of M

Corollary

A maximal subgroup is either a *t*- or *k*-subgroup

Baernighausen Trees

Modul design of crystal symmetry relations

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 $\mathcal{G}$ → $P6/m2/m2/m$

Symbol designating the higher symmetric crystal structure, *e.g.* the chemical formula or mineral name → $\boxed{AlB_2}$

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

Element symbol
Wyckoff posit.
cite symmetry
coordinates

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

Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ → $P6_3/m2/m2/c$

Symbol designating the lower symmetric crystal structure → $\boxed{CaIn_2}$

Ca : $2b$	In : $4f$
$\bar{6}m2$	$3m$
0	$\frac{1}{3}$
0	$\frac{2}{3}$
$\frac{1}{4}$	0.455

Element symbol
Wyckoff posit.
cite symmetry
coordinates

* mentioned only if there is a change

U. Mueller, Gargnano 2008

Problem: Symmetry Relations between Crystal Structures

Baernighausen Trees

Pyrite

Structural family

Aristotype

Basic structure

Hettotypes

Derivative structures

$P\,2_1/a\,\bar{3}$

FeS_2

Fe:4a	S:8c	
$\bar{3}$	3	
0	0.386	[0.614]
0	0.386	[0.614]
0	0.386	[0.614]

t3 ↙ ; t2 ↘

$P\,2_1\,3$

NiAsS

Ni: 4a	S: 4a	As: 4a
3	3	3
−0.006	0.385	0.618
−0.006	0.385	0.618
−0.006	0.385	0.618

$P\,2_1/b\,2_1/c\,2_1/a$

PdS_2

Pd:4a	S:8c	
$\bar{1}$	1	
0	0.393	[0.617]
0	0.388	[0.612]
0	0.425	[0.575]

t2

$-\frac{1}{4},0,0$

$x+\frac{1}{4},0,0$

$P\,b\,c\,2_1$

PtGeSe

Pt:4a	Ge:4a	Se:4a
$\bar{1}$	1	1
0.242	0.633	0.876
0.009	0.383	0.620
0	0.383	0.618

lattice parameters in pm:

	a	b	c	references
pyrite	541.8	541.8	541.8	[32]
NiAsS	568.9	568.9	568.9	[33]
PdS_2	546.0	554.1	753.1	[34]
PtGeSe	607.2	601.5	599.2	[35]

U. Mueller, Gargnano 2008