राष्ट्रीय प्रौद्योगिकी संस्थान राउरकेला

National Institute of Technology Rourkela

INTERNATIONAL SCHOOL ON FUNDAMENTAL CRYSTALLOGRAPHY AND WORKSHOP ON STRUCTURAL PHASE TRANSITIONS

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The Abdus Salam International Centre for Theoretical Physics

Indian National Science Academy

ROURKELA INTERNATIONAL CRYSTALLOGRAPHY SCHOOL

BILBAO CRYSTALLOGRAPHIC SERVER PRACTICAL EXERCISES I

CRYSTAL-STRUCTURE TOOLS

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eman ta zabal zazu

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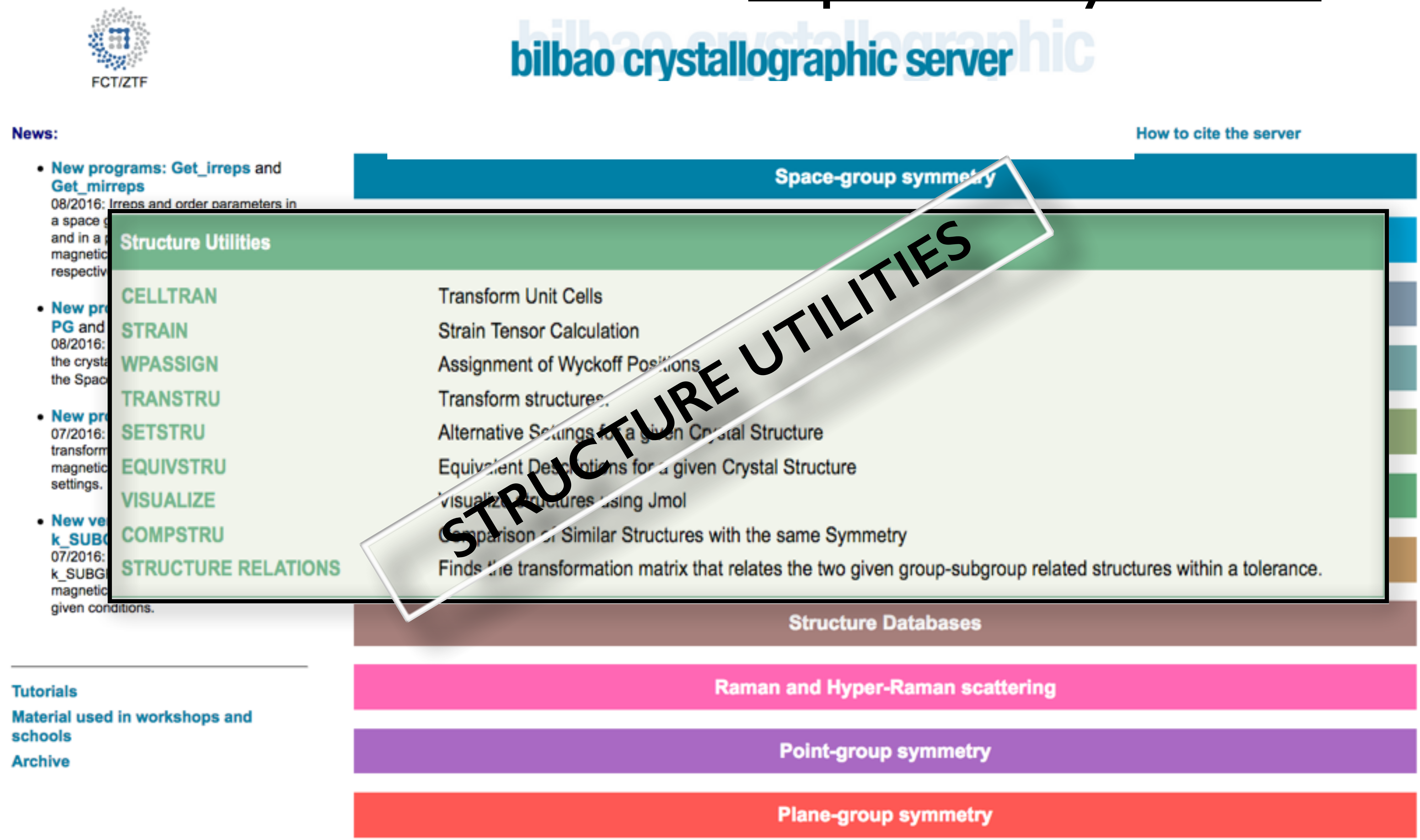
Bilbao Crystallographic Server

http://www.cryst.ehu.es



CRYSTAL-STRUCTURE DESCRIPTIONS

Conventional and ITA settings of space groups

Non-conventional settings of space groups

Equivalent structure descriptions

Crystal Structure Descriptions

Inorganic Crystal Structure Database

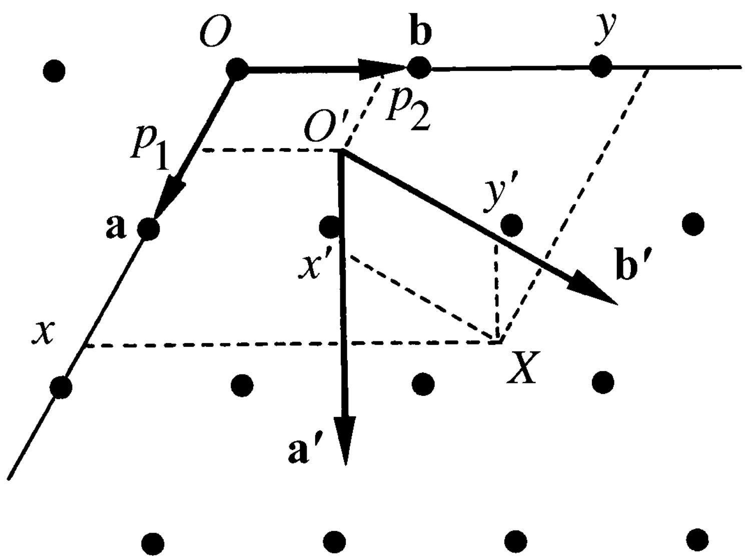
CC=45520	Details Bonds Pattern Structure Jmol
Title	Redetermination of the oxygen parameters in zircon (Zr Si O4).
Authors	Krstanovic, I.R.
Reference	Acta Crystallographica (1958) **11**, 896-897 **Link XRef SCOPUS SCIRUS Google**
Compound	**Zr (Si O4) - [Zircon]** Zirconium silicate **[ABX4] [tI24] [h b a] [ZrSiO4]**
Cell	6.6164(5), 6.6164, 6.0150(5), 90., 90., 90. **I41/AMDZ (141)** V=263.32
Remarks	R=0.070000 : PDC =01-073-6646 : PDF =6-266 : TYP =ZrSiO4 : XDS MIN =Zircon : At least one temperature factor missing in the paper. hk0- and 0kl-data, crystals not metamict

Atom (site) Oxid.			**x, y, z, B, Occupancy**				
Zr1	(4a)	4	0	0.75	0.125	0	1
Si1	(4b)	4	0	0.75	0.625	0	1
O1	(16h)	-2	0	0.067(3)	0.198(3)	0	1

Bilbao Crystallographic Server

```
# Space Group ITA number
141
# Lattice parameters
6.6164 6.6164 6.0150 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Zr 1 4a   0 0.75 0.125
Si 1 4b   0 0.75 0.625
O  1 16h  0 0.067 0.198
```

Problem: BASIS TRANSFORMATION



$$(\mathbf{a},\mathbf{b},\mathbf{c}),\ \text{origin O: point X}(x,y,z)$$

$$\Big\downarrow (\boldsymbol{P},\boldsymbol{p})$$

$$(\mathbf{a}',\mathbf{b}',\mathbf{c}'),\ \text{origin O': point X}(x',y',z$$

(i) linear part: change of orientation or length

$$(\mathbf{a}',\mathbf{b}',\mathbf{c}') = (\mathbf{a},\mathbf{b},\mathbf{c})\boldsymbol{P}$$

$$= (\mathbf{a},\mathbf{b},\mathbf{c})\begin{pmatrix} P_{11} & P_{12} & P_{13} \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{pmatrix} = (P_{11}\mathbf{a} + P_{21}\mathbf{b} + P_{31}\mathbf{c},\ P_{12}\mathbf{a} + P_{22}\mathbf{b} + P_{32}\mathbf{c},\ P_{13}\mathbf{a} + P_{23}\mathbf{b} + P_{33}\mathbf{c}).$$

(ii) origin shift by a shift vector $\boldsymbol{p}(p_1,p_2,p_3)$:

$$\boldsymbol{O'} = \boldsymbol{O} + \boldsymbol{p}$$

the origin ***O'*** has coordinates (p_1,p_2,p_3) in the old coordinate system

Transformation of the coordinates of a point X(x,y,z):

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \boldsymbol{Q} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \boldsymbol{q}$$

with

$$\boldsymbol{Q} = \boldsymbol{P}^{-1}$$
$$\boldsymbol{q} = -\boldsymbol{P}^{-1}\boldsymbol{p}.$$

$$= \begin{pmatrix} Q_{11}x + Q_{12}y + Q_{13}z + q_1 \\ Q_{21}x + Q_{22}y + Q_{23}z + q_2 \\ Q_{31}x + Q_{32}y + Q_{33}z + q_3 \end{pmatrix}.$$

Transformation of symmetry operations (*W*,*w*):

$$(W',w')=(P,p)^{-1}(W,w)(P,p)$$

Transformation of the metric tensor *G*:

$$G'=P^{T}(G)P$$

Bilbao Crystallographic Server

Problem: *ITA* SETTINGS STRUCTURE DESCRIPTIONS

SETSTRU

ITA-settings for the space group C2/c (No.15)

initial setting structure description

$X_f=(P,p)^{-1}X_i$

final setting structure description

Choose the initial and final space groups symbols

n matrices must be read by columns. **P** is the transformation from standard to non-

$(a, b, c)_n = (a, b, c)_s\ P$

Initial	Final	Setting	P	P^{-1}
○	○	*C* 1 2/*c* 1	a,b,c	a,b,c
○	○	*A* 1 2/*n* 1	-a-c,b,a	c,b,-a-c
○	○	*I* 1 2/*a* 1	c,b,-a-c	-a-c,b,a
○	○	*A* 1 2/*a* 1	c,-b,a	c,-b,a
○	○	*C* 1 2/*n* 1	a,-b,-a-c	a,-b,a-c
○	○	*I* 1 2/*c* 1	-a-c,-b,c	-a-c,-b,c
○	○	*A* 1 1 2/*a*	c,a,b	b,c,a
○	○	*B* 1 1 2/*n*	a,-a-c,b	a,c,-a-b
○	○	*I* 1 1 2/*b*	-a-c,c,b	-a-b,c,b
○	○	*B* 1 1 2/*b*	a,c,-b	a,-c,b
○	○	*A* 1 1 2/*n*	-a-c,a,-b	b,-c,-a-b
○	○	*I* 1 1 2/*a*	c,-a-c,-b	-a-b,-c,a
○	○	*B* 2/*b* 1 1	b,c,a	c,a,b
○	○	[illegible]	[illegible]	[illegible]

EXERCISES

Problem 3.1

Compare the two structure descriptions and check if they belong to the same structure type.

Print **2** entries selected.

CC=Collection Code: [AB2X4]=ANX Form: [cF56]=Pearson: [e d a]=Wyckoff Symbol: [Al2MgO4]=Structure Type:

****Click the ANX, Pearson or Wyckoff Symbol to find structures with that symbol****

CC=45520 Details Bonds Pattern Structure Jmol

Title	Redetermination of the oxygen parameters in zircon (Zr Si O4).
Authors	Krstanovic, I.R.
Reference	Acta Crystallographica (1958) **11**, 896-897 **Link XRef SCOPUS SCIRUS Google**
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Cell	6.6164(5), 6.6164, 6.0150(5), 90., 90., 90. **I41/AMDZ (141)** V=263.32
Remarks	R=0.070000 : PDC =01-073-6646 : PDF =6-266 : TYP =ZrSiO4 : XDS MIN =Zircon : At least one temperature factor missing in the paper. hk0- and 0kl-data, crystals not metamict

Atom (site) Oxid.			**x, y, z, B, Occupancy**				
Zr1	(4a)	4	0	0.75	0.125	0	1
Si1	(4b)	4	0	0.75	0.625	0	1
O1	(16h)	-2	0	0.067(3)	0.198(3)	0	1

CC=31101 Details Bonds Pattern Structure Jmol

Title	Die Kristallstruktur von Zirkon und die Kriterien fuer spezielle Lagen in tetragonalen Raumgruppen..
Authors	Wyckoff, R.W.G.;Hendricks, S.B.
Reference	Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie (1927) **66**, 73-102 **Link XRef SCOPUS SCIRUS Google** **Also:** Philosophical Magazine, Serie (1926) **1**, 1151-1151
Compound	**Zr (Si O4) - [Zircon]** Zirconium silicate **[ABX4] [tI24] [h b a] [ZrSiO4]**
Cell	6.61, 6.61, 5.98, 90., 90., 90. **I41/AMDS (141)** V=261.28
Remarks	COR MIN =Zircon : PDF =6-266 : TYP =ZrSiO4 : XDS At least one temperature factor missing in the paper. No R value given in the paper. Revised data of 31084

Atom (site) Oxid.			**x, y, z, B, Occupancy**				
Zr1	(4a)	4	0	0	0	0	1
Si1	(4b)	4	0	0	0.5	0	1
O1	(16h)	-2	0	0.2(1)	0.34(2)	0	1

origin choice 2

origin choice 1

EXERCISES

Problem 3.1

Structure 1: Space group $I4_1/amd$ (141) a=6.60 $\mathring{A}$ c=5.88 $\mathring{A}$

origin choice 1 at $\bar{4}m2$

Structure 2: Space group $I4_1/amd$ (141) a=6.616 $\mathring{A}$ c=6.015 $\mathring{A}$

origin choice 2 at $2/m$ at 0,-1/4,1/8 from $\bar{4}m2$

Compare the two structure descriptions and check if they belong to the same structure type.

Use the tools of Bilbao Crystallographic server: **SETSTRU**

Hint: In order to compare the different data, the parameters of Structure 1 are to be transformed to 'origin at center 2/m', i. e. ORIGIN CHOICE 2.

Problem 3.1

SOLUTION

Structure tools: SETSTRU

Origin 2 description $x' = x - p$

(i) $Zr: \ (a) \ \ 0, \frac{1}{4}, \frac{\bar{1}}{8} \sim \frac{7}{8}; \ 0, \frac{3}{4}, \frac{1}{8}; \ \frac{1}{2}, \frac{1}{4}, \frac{5}{8}; \ \frac{1}{2}, \frac{3}{4}, \frac{3}{8};$

(ii) $Si: \ (b) \ \ 0, \frac{1}{4}, \frac{3}{8}; \ 0, \frac{3}{4}, \frac{5}{8}; \ \frac{1}{2}, \frac{1}{4}, \frac{1}{8}; \ \frac{1}{2}, \frac{3}{4}, \frac{\bar{1}}{8} \sim \frac{7}{8};$

(iii) $O: \ (h) \ \ 0, 0.20 + 0.25, 0.34 - 0.125 = 0, 0.45, 0.215.$

the rest of oxygen atoms

$\boxed{0, 0.05, 0.215}$ 0.20, 0.25, 0.535 0.80, 0.25, 0.535 0, 0.95, 0.785
0, 0.55, 0.785 0.80, 0.75, 0.465 0.20, 0.75, 0.465, all also with $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$.

0, 0.067, 0.198

Bilbao Crystallographic Server

Problem: UNIT CELL TRANSFORMATION **CELLTRAN**

lattice parameters hexagonal cell

$G' = P^T G P$

lattice parameters monoclinic cell

Transform Unit Cell

Cell Parameters: 5.6748 5.6748 20.3784 90 90 120 Centering R

Please, define the rotational part of the transformation matrix that relates the group and the subgroup bases

in abc form: Ex: c,a,b (read by columns)

or in matrix form:

Rotational part

2/3	0	-2
1/3	1	-1
1/3	0	0

(P,p) Transformation matrix

Bilbao Crystallographic Server

Problem: STRUCTURE TRANSFORMATION

TRANSTRU

Transform Structure

TRANSTRU can transform a structure in two ways:

- To a lower symmetry space group. The transformed structure is given in the low symmetry space group basis, taking care of all possible splittings of the Wyckoff positions.
- With an arbitrary matrix. The structure, including the cell parameters and the atoms in the unit cell, is transformed with an arbitrary matrix introduced by the user.

Only the default choice for the conventional setting of the space groups is used.

Structure Data [in CIF format] Examinar...

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

High Symmetry Structure

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb      1      3a      0.000000      0.000000      0.000000
Pb      2      6c      0.000000      0.000000      0.207100
PV      3      6c      0.000000      0.000000      0.388400
O       4      6c      0.000000      0.000000      0.324000
O       5      18i     0.842400      0.157600      0.430100
```

asymmetric unit

default settings

Transform structure to a subgroup basis

Transform structure with an arbitrary matrix

Show

subgroup basis

arbitrary transformation

Bilbao Crystallographic Server

Example **TRANSTRU**: $Pb_3(VO_4)_2$

Description
R-3m (166)

Validity (P,p)

WP
splittings

Description
$P2_1/c$ (14)

(P,p)

Structure

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb   1   3a    0.000000   0.000000   0.000000
Pb   2   6c    0.000000   0.000000   0.207100
PV   3   6c    0.000000   0.000000   0.388400
O    4   6c    0.000000   0.000000   0.324000
O    5   18h   0.842400   0.157600   0.430100
```

Low symmetry Space Group: 14

Transformation Matrix:

In matrix form:

Rotational part			Origin Shift
2/3	0	-2	0
1/3	1	-1	0
1/3	0	0	0

Example TRANSTRU: $Pb_3(VO_4)_2$

High symmetry structure

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb     1    3a     0.000000 0.000000 0.000000
Pb     2    6c     0.000000 0.000000 0.207100
PV     3    6c     0.000000 0.000000 0.388400
O      4    6c     0.000000 0.000000 0.324000
O      5    18h    0.842400 0.157600 0.430100
```

R-3m structure

$\Downarrow$ (P,p)

$P2_1/c$ structure

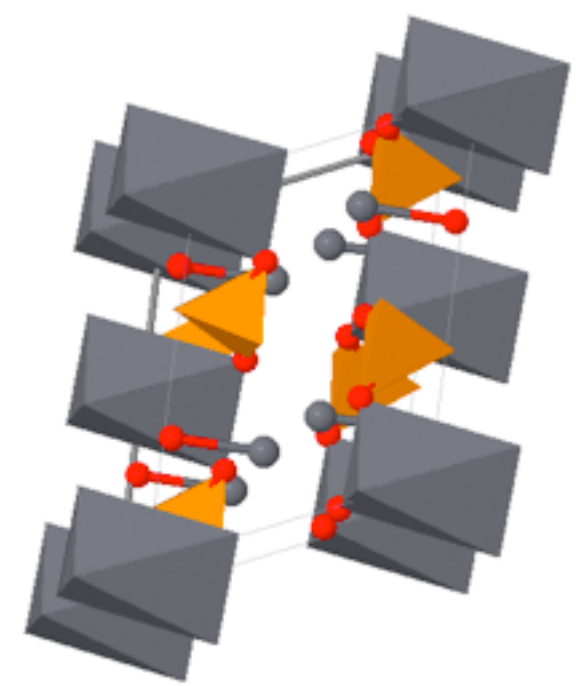
Pb1(3a) Pb2(6c) PV(6c) O1(6c) O2(18h)

Pb1(2a) Pb2(4e) PV(4e) O1(4e) O21(4e) O22(4e)

WP splitting

Low symmetry structure

```
014
7.541657 5.674800 9.829041 90.000000 115.749245 90.000000
7
Pb      1      2a      0.000000      0.000000      0.000000
Pb      2      4e      0.621300      0.000000      0.207100
PV      3      4e      0.165200      0.000000      0.388400
O       4      4e      0.972000      0.000000      0.324000
O       5      4e      0.290300      0.736400      0.008900
O       5_2    4e      0.290300      0.500000      0.772500
O       5_3    4e      0.709700      0.763600      0.491100
```



View Structure (with Jmol applet)

EXERCISES

Problem 3.1 (cont.)

Apply the program **TRANSTRU** in order to check if the two structure descriptions belong to the same structure type.

Structure 1: Space group *$I4_1/amd$* (141) a=6.60 $\AA$ c=5.88 $\AA$
origin choice 1 at $\bar{4}m2$

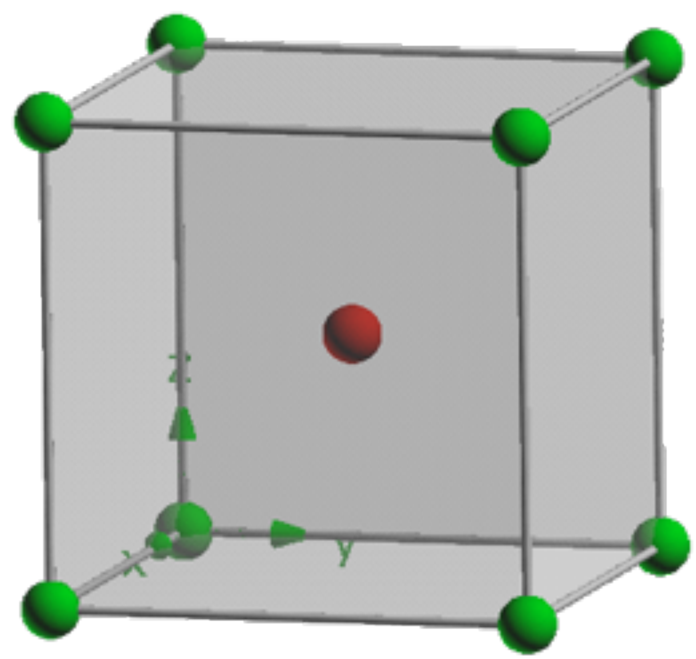
Structure 2: Space group *$I4_1/amd$* (141) a=6.616 $\AA$ c=6.015 $\AA$
origin choice 2 at $2/m$ at 0,-1/4,1/8 from $\bar{4}m2$

Coordinate transformation

Origin choice 2 $\longrightarrow$ Origin choice 1

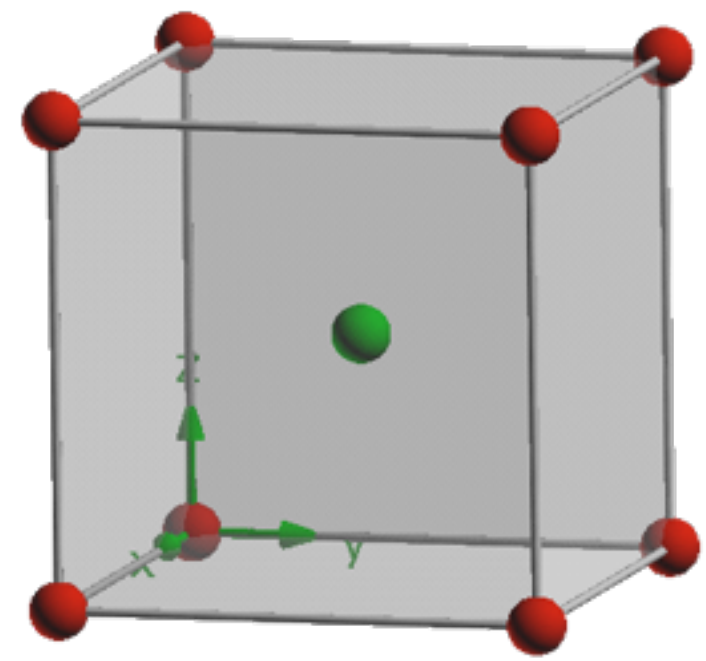
$\boldsymbol{p}$=0,1/4,-1/8

Problem: EQUIVALENT DESCRIPTIONS   EQUIVSTRU



CsCl

Pm-3*m* (221)



1*a* (0,0,0)	⟶	1*b* (1/2,1/2,1/2)
1*b* (1/2,1/2,1/2)	⟶	1a (0,0,0)

How to find all possible equivalent descriptions of a crystal structure?

Number of equivalent descriptions= |N(G)|/|G|

index of the group in its Euclidean normalizer

Problem 3.2a

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Equivalent descriptions: CsCl EQUIVSTRU

Equivalent Descriptions of Crystal Structures

Equivalent Structures

Given a space group ITA 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.

Only the default choice for the conventional setting of the space groups is used.

Structure Data [in CIF format] Examinar...

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

Structure

```
# Space Group ITA number
221
# Lattice parameters
5.3 5.3 5.3 90 90 90
# Number of independent atoms in the asymmetric unit
2
# [atom type] [number] [WP] [x] [y] [z]
Cs 1  1a  0   0   0
Cl 1  1b  0.5 0.5 0.5
```

space group in default setting

Example EQUIVSTRU: CsCl

Equivalent Descriptions of Crystal Structures

Equivalent Structures

Given a space group ITA 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.

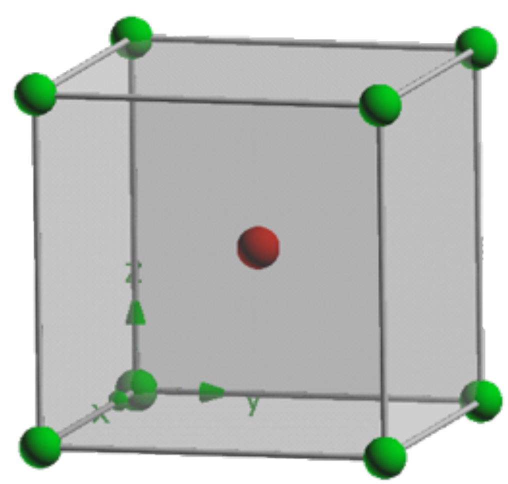
Structure Data
[in CIF format]

Examinar...

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

Structure

```
#Exercise 3.2a(CsCl)
# Space Group ITA number
221
# Lattice parameters
4.12599 4.12599 4.12599 90.0 90.0 90.0
# Number of independent atoms in the asymmetric unit
2
# [atom type] [number] [WP] [x] [y] [z]
Cl     1    1a    0.000000 0.000000 0.000000
Cs     1    1b    0.500000 0.500000 0.500000
```



Structure number 1

Normalizer coset representative: x,y,z

Transformed unit cell:

4.1260 4.1260 4.1260 90.00 90.00 90.00

Transformed structure:

AT.	WP	SS	Representative	Atomic orbit
Cl1	1a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000)
Cs1	1b (1/2,1/2,1/2)	m-3m	(0.500000,0.500000,0.500000)	(0.500000,0.500000,0.500000)

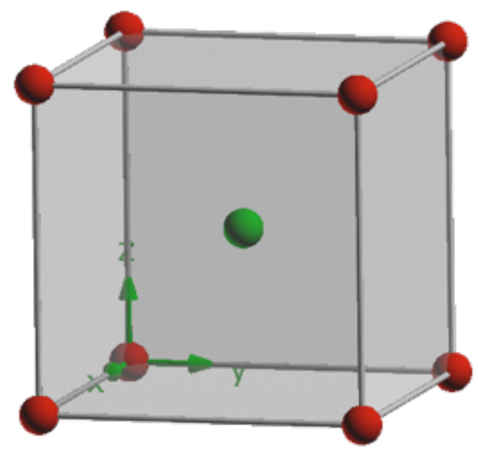
Structure number 2

Normalizer coset representative: x+1/2,y+1/2,z+1/2

Transformed unit cell:

4.1260 4.1260 4.1260 90.00 90.00 90.00

Transformed structure:



AT.	WP	SS	Representative	Atomic orbit
Cl1	1b (1/2,1/2,1/2)	m-3m	(0.500000,0.500000,0.500000)	(0.500000,0.500000,0.500000)
Cs1	1a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000)

EXERCISES

Problem 3.2b

Equivalent structure descriptions

Space group: P4/n

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

Atom	Wyckoff position	Coordinate triplets x	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)

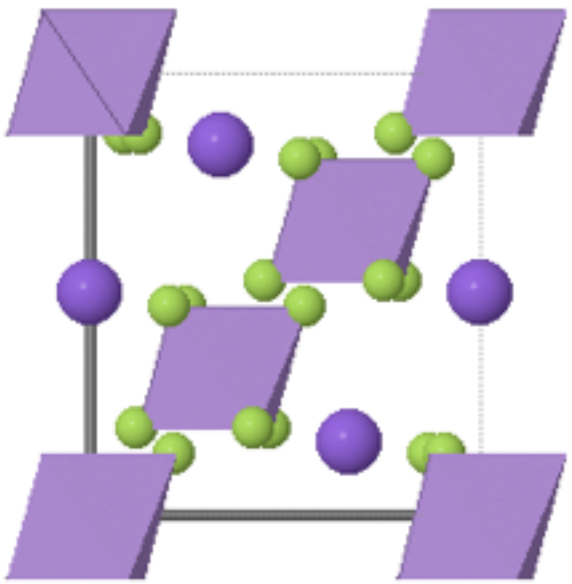
a’=1/2(a-b), b’=1/2(a+b)

EXERCISES

Problem 3.3

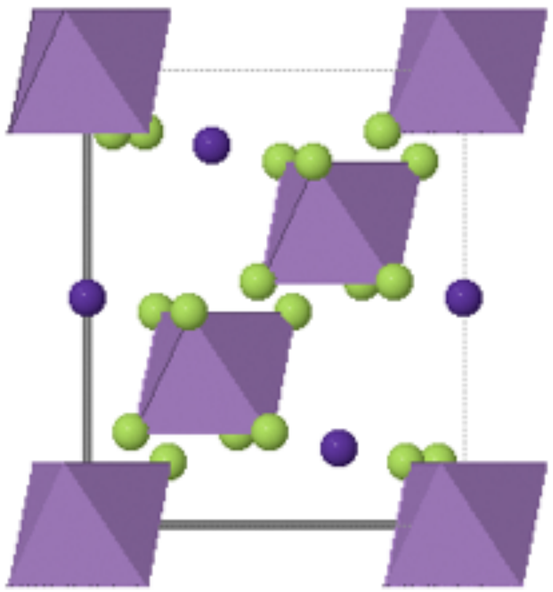
EQUIVSTRU

$KAsF_6$



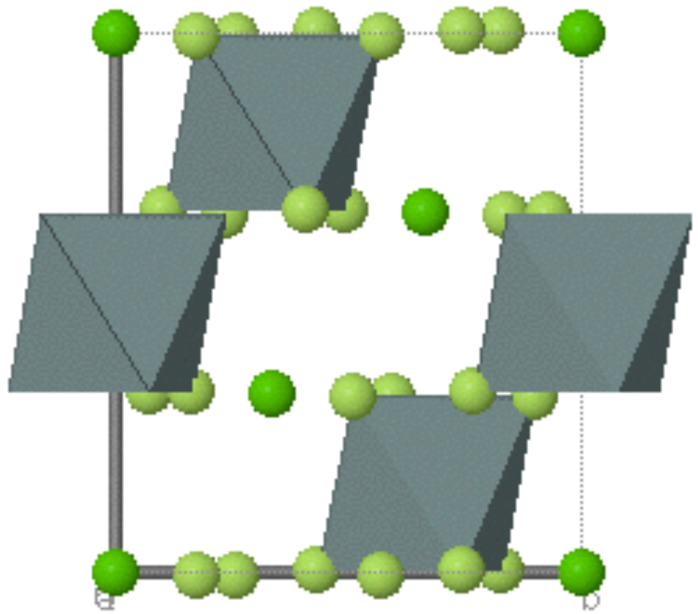
```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1    3b    0.333333 0.666666 0.166666
As     1    3a    0 0 0
F      1    18f   0.1292 0.2165 0.1381
```

$BaIrF_6$



```
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba     1    3b    0.333333 0.666666 0.166666
Ir     1    3a    0 0 0
F      1    18f   0.0729 0.2325 0.1640
```

$BaSnF_6$



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

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;

CRYSTAL-STRUCTURE RELATIONSHIPS

Comparison of crystal structures

Phase transitions

Symmetry relations between crystal structures

COMPARISON OF CRYSTAL STRUCTURES

Different descriptions of the same structure

PROBLEM:

Two descriptions of the same structure with respect to the same space group, specified by unit-cell parameters and atomic coordinates data.

Search for a mapping of the two descriptions such that the global distortion accompanying the mapping is tolerably small.

Description 2	$\xrightarrow{\text{symmetry controlled mapping}}$	(Description 2)$_1$	$\xleftrightarrow{\text{global distortion of the mapping}}$	Description 1
G standard	affine normalizer	most similar configuration G standard	Lattice deformation Atomic displacement field	G standard

$\underbrace{\text{affine normalizer} \quad \text{G standard} \quad \text{Lattice deformation, Atomic displacement field}}_{\text{COMPSTRU}}$

COMPSTRU

Problem: **Similarity of the descriptions**

Description 1
a_1, b_1, c_1
(x_1, y_1, z_1)

How to measure the ***similarity*** between two descriptions ?

Description 2
a_2, b_2, c_2
(x_2, y_2, z_2)

degree of lattice distortion

$$S = \frac{1}{3}\sqrt{\sum_i \eta_i^2}$$

η_i-eigenvalues of the Lagrangian strain tensor

average atomic displacements

$$d_{av} = \frac{1}{n}\sum_i m_i u_i$$

u_i-atomic displacements

maximal atomic displacements

maximal displacements of the paired atoms

Problem: **Similarity of the descriptions**

Description 1
a_1, b_1, c_1
(x_1, y_1, z_1)

How to measure the ***similarity*** between two descriptions ?

Description 2
a_2, b_2, c_2
(x_2, y_2, z_2)

Bergerhoff *et al.* *Acta Cryst.*(1999), **B**55, 147

structural descriptor

$$\Delta = [\sqrt{2}\Delta(c) + 1]\Delta(d) - 1$$

$$\sum_i m[(x_i - y_i)^2]^{\frac{1}{2}} / \sum m$$

weighted mean difference between atomic coordinates

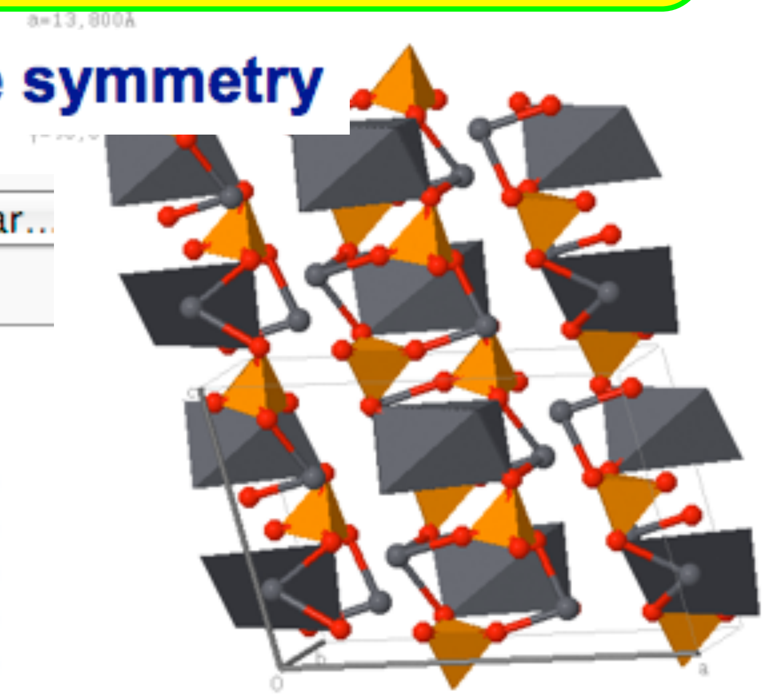
$$[(b_1/a_1)(c_1/a_1)]/[(b_2/a_2)(c_2/a_2)]$$

relation between axial ratios

Problem: COMPARISON OF STRUCTURES

COMPSTRU

Comparison of crystal structures of the same symmetry



structure 1

default settings

structure 2

Structure Data
[in CIF format]

Examinar...

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

Structure 1

```
15
13.800 5.691 9.420 90.0 102.3 90.0
7
Pb     1    4e     0.0000 0.2910 0.2500
Pb     2    8f     0.3170 0.3090 0.3520
P      1    8f     0.5990 0.2410 0.4470
O      1    8f     0.6430 0.0300 0.3920
O      2    8f     0.6340 0.4640 0.3740
O      3    8f     0.6420 0.2800 0.6120
O      4    8f     0.4910 0.2220 0.4200
```

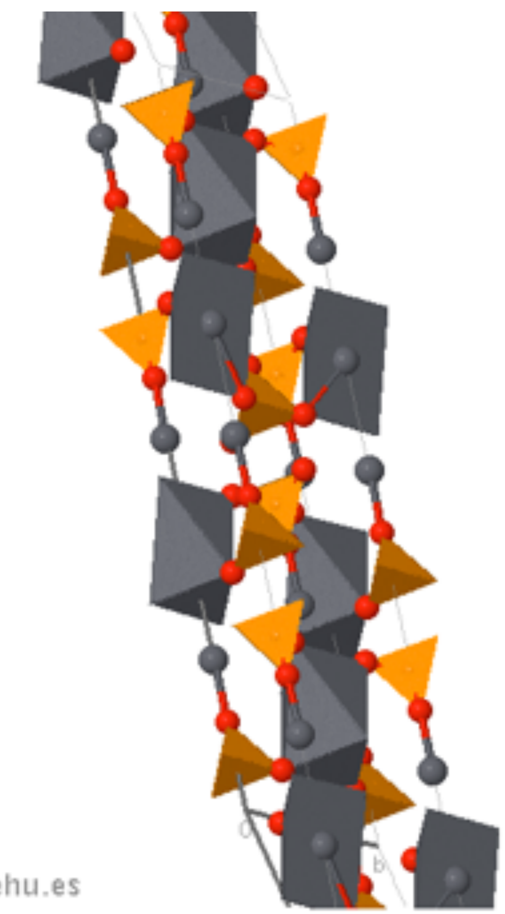
Structure Data
[in CIF format]

Examinar...

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

Structure 2

```
15
13.967 5.560 40.778 90.0 166.713 90.0
7
Pb   1   4e   0.0000   0.0000   0.7500
Pb   2   8f   0.0000   0.0000   0.8563
P    1   8f   0.0000   0.0000   0.9511
O    1   8f   0.0000   0.0000   0.9145
O    2   8f   0.2715   0.7285   0.8885
O    3   8f   0.9570   0.5000   0.1170
O    4   8f   0.7285   0.2715   0.6115
```



tolerances

Enter the maximum distance allowed between the paired atoms: 1 Å

Enter the allowed tolerance (a b c α β γ): .5 .5 .5 5 5 5

Example COMPSTRU: $Pb_3(PO_4)_2$

Structure #1

```
15
13.800 5.691 9.420 90.0 102.3 90.0
7
Pb     1    4e      0.0000 0.2910 0.2500
Pb     2    8f      0.3170 0.3090 0.3520
P      1    8f      0.5990 0.2410 0.4470
O      1    8f      0.6430 0.0300 0.3920
O      2    8f      0.6340 0.4640 0.3740
O      3    8f      0.6420 0.2800 0.6120
O      4    8f      0.4910 0.2220 0.4200
```

Structure #2

```
15
13.967 5.560 40.778 90.0 166.713 90.0
7
Pb   1   4e  0.0000   0.0000   0.7500
Pb   2   8f  0.0000   0.0000   0.8563
P    1   8f  0.0000   0.0000   0.9511
O    1   8f  0.0000   0.0000   0.9145
O    2   8f  0.2715   0.7285   0.8885
O    3   8f  0.9570   0.5000   0.1170
O    4   8f  0.7285   0.2715   0.6115
```

affine
normalizer

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0116	0.3386	0.1430	0.066

structural
descriptor

$$\Delta = 0.066$$

Most similar configuration to Structure #1

```
015
13.967000 5.560000 9.630055 90.000000 103.295059 90.000000
7
Pb     1     4e     0.000000     0.250000     0.250000
Pb     2     8f     0.318900     0.250000     0.356300
P      1     8f     0.603300     0.250000     0.451100
O      1     8f     0.493500     0.250000     0.414500
O      2     8f     0.644000     0.478500     0.388500
O      3     8f     0.644000     0.250000     0.617000
O      4     8f     0.644000     0.021500     0.388500
```

Atom pairings and distances

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
4e	(0,y,1/4)	Pb1	0.0000	-0.0410	0.0000	0.2333
8f	(x,y,z)	Pb2	0.0019	-0.0590	0.0043	0.3386
8f	(x,y,z)	P1	0.0043	0.0090	0.0041	0.0816
8f	(x,y,z)	O1	0.0010	-0.0085	-0.0035	0.0617
8f	(x,y,z)	O2	0.0100	0.0145	0.0145	0.1910
8f	(x,y,z)	O3	0.0020	-0.0300	0.0050	0.1777
8f	(x,y,z)	O4	0.0025	0.0280	-0.0055	0.1733

maximal
displacement

d_{max}=0.34 Å

Problem: COMPARISON OF STRUCTURE DESCRIPTIONS

COMPSTRU

Problem 3.4

In ICSD can be found several structure data sets of ε-Fe_2O_3, all of them of symmetry $Pna2_1$(No.33). Compare the following two descriptions and check if they belong to the same structure type.

Problem 3.4

ICSD data for ε-Fe_2O_3,

ICSD for WWW

Details of the selected entries

Print **2** entries selected.

CC=Collection Code: [AB2X4]=ANX Form: [cF56]=Pearson: [e d a]=Wyckoff Symbol: [Al2MgO4]=Structure Type:

****Click the ANX, Pearson or Wyckoff Symbol to find structures with that symbol***.*

CC=173024 Details Bonds Pattern Structure Jmol

Title	High- and low-temperature crystal and magnetic structure of epsilon-Fe2 O3 and their correlation to its magnetic properties.
Authors	Gich, M.;Frontera, C.;Roig, A.;Taboada, E.;Molins, E.;Rechenberg, H.R.;Ardisson, J.D.;Macedo, W.A.A.;Ritter, C.;Hardy, V.;Sort, J.;Skumryev, V.;Nogues, J.
Reference	Chemistry of Materials (2007) **18**, 3889-3897 **Link XRef SCOPUS SCIRUS Google**
Compound	**Fe2 O3** - Iron(III) oxide - epsilon **[A2X3] [oP40] [a10] [AlFeO3]**
Cell	5.0885(5), 8.7802(14), 9.4709(13), 90., 90., 90. **PNA21 (33)** V=423.14
Remarks	R=0.013300 : NDP RVP SNP TEM =200 : TYP =AlFeO3 : XDP MAG At least one temperature factor missing in the paper.

Atom	(site)	Oxid.	x	y	z	B	Occupancy
O1	(4a)	-2	0.978(2)	0.3282(15)	0.4314(11)	0	1
O2	(4a)	-2	0.515(2)	0.4907(17)	0.4187(16)	0	1
O3	(4a)	-2	0.650(3)	0.9979(13)	0.1883(9)	0	1
O4	(4a)	-2	0.160(3)	0.1637(15)	0.1956(7)	0	1
O5	(4a)	-2	0.841(3)	0.1680(15)	0.6669(7)	0	1
O6	(4a)	-2	0.527(2)	0.1637(19)	0.9362(9)	0	1
Fe1	(4a)	3	0.1928(11)	0.1506(6)	0.5807(3)	0	1
Fe2	(4a)	3	0.6826(6)	0.0291(3)	0.7897(5)	0	1
Fe3	(4a)	3	0.1858(10)	0.1519(6)	0	0	1
Fe4	(4a)	3	0.8104(7)	0.1580(4)	0.3071(3)	0	1

CC=415250 Details Bonds Pattern Structure Jm

Title	Synthesis and structural analysis of epsilon-(Fe2 O3).
Authors	Kelm, K.;Mader, W.
Reference	Zeitschrift fuer Anorganische und Allgemeine Chemie (2005) **631**, 2383-2389 **Link XRef SCOPUS SCIRUS Google**
Compound	**Fe2 O3** - Diiron(III) oxide - epsilon **[A2X3] [oP40] [a10] [AlFeO3]**
Cell	5.0715(2), 8.7359(4), 9.4178(4), 90, 90, 90 **PNA21 (33)** V=417.24
Remarks	R=0.039000 : TYP =AlFeO3 : XDP RVP

Atom	(site)	Oxid.	x	y	z	B	Occupancy
Fe1	(4a)	3	0.6768(9)	0.8427(5)	0.0000000	0.050(2)	1.00000
Fe2	(4a)	3	0.204(1)	0.3509(8)	0.7726(9)	0.063(3)	1.00000
Fe3	(4a)	3	0.807(1)	0.6605(8)	0.693(1)	0.069(2)	1.00000
Fe4	(4a)	3	0.6852(9)	0.4634(5)	0.983(2)	0.046(1)	1.00000
O1	(4a)	-2	0.337(2)	0.853(2)	0.887(1)	0.0063326	1.00000
O2	(4a)	-2	0.019(3)	0.474(2)	0.610(2)	0.0063326	1.00000
O3	(4a)	-2	0.453(3)	0.677(2)	0.651(2)	0.0063326	1.00000
O4	(4a)	-2	0.527(3)	0.669(2)	0.100(1)	0.0063326	1.00000
O5	(4a)	-2	0.868(3)	0.334(2)	0.863(1)	0.0063326	1.00000
O6	(4a)	-2	0.336(3)	0.513(1)	0.891(1)	0.0063326	1.00000

Problem: Isoconfigurational Structure Types **COMPSTRU**

Lima-de Faria *et al.* *Acta Cryst.*(1990), **A**46, 1

Isopointal structure types	**Isoconfigurational structure types**
Space group	Isopointal
Wyckoff position sequence	Crystallographic orbits
Pearson symbol	Geometrical interrelationships

similar

Allmann, Hinek. *Acta Cryst.*(2007), **A**63, 412

Inorganic Crystal Structure Database (2009)
http://icsdweb.fiz-karlsruhe.de

isoconfigurational structure types?

Composition type (ANX formula)

Range of c/a ratio

β-range

Atomic coordinates

Chemical properties

Isoconfigurational (configurationally isotypic) Structure Types

PROBLEM:

Consider two isopointal structures specified by their space-group symmetry, unit-cell parameters and atomic coordinates data.

We search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.

Structure 2	symmetry controlled mapping →	(Structure 2)$_1$	most similar configuration ↔ global distortion of the mapping	Structure 1
G standard	atomic species correspondence scheme	G standard	Lattice deformation Atomic displacement field	G standard

COMPSTRU

Problem: Isoconfigurational Structure Types COMPSTRU

Structure1
a_1, b_1, c_1
(x_1, x_2, x_3)

How to measure the ***similarity*** between two isopointal structures ?

isoconfigurational?

Structure2
a_2, b_2, c_2
(y_1, y_2, y_3)

degree of lattice distortion

$$S = \frac{1}{3}\sqrt{\sum_i \eta_i^2}$$

η_i-eigenvalues of the Lagrangian strain tensor

average atomic displacements

$$d_{av} = \frac{1}{n}\sum_i m_i u_i$$

u_i-atomic displacements

structural descriptor

$$\Delta = [\sqrt{2}\Delta(c) + 1]\Delta(d) - 1$$

Bergerhoff *et al.* *Acta Cryst.*(1999), **B**55, 147

Problem: Isoconfigurational Structure Types

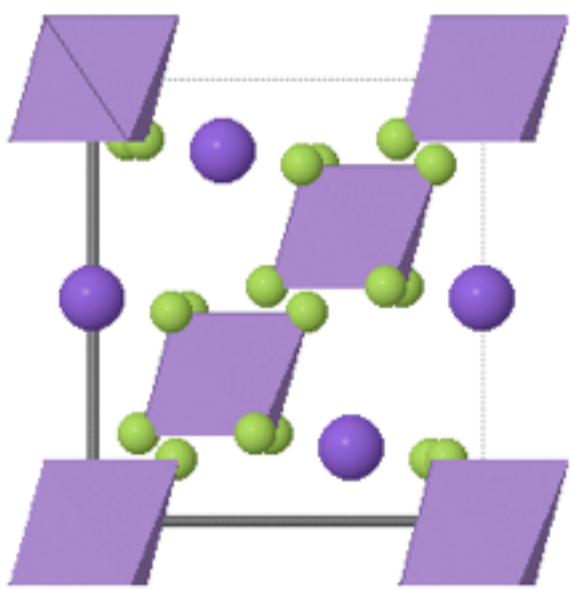
COMPSTRU

EXERCISES

Problem 3.3(cont.)

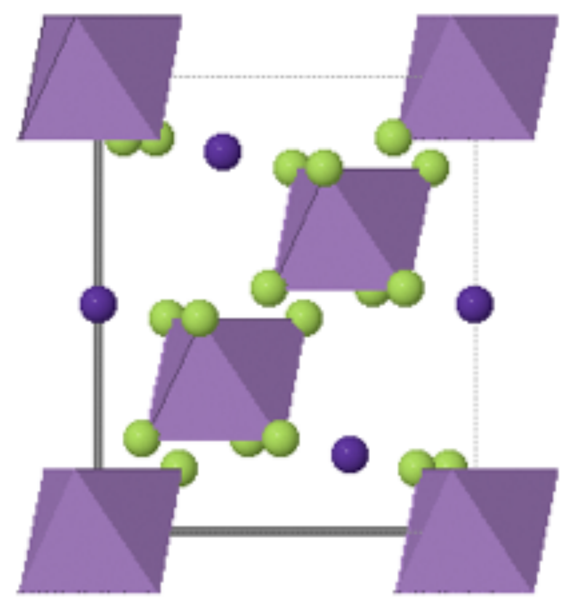
Do these compounds belong to the **same structure type ?**

$KAsF_6$



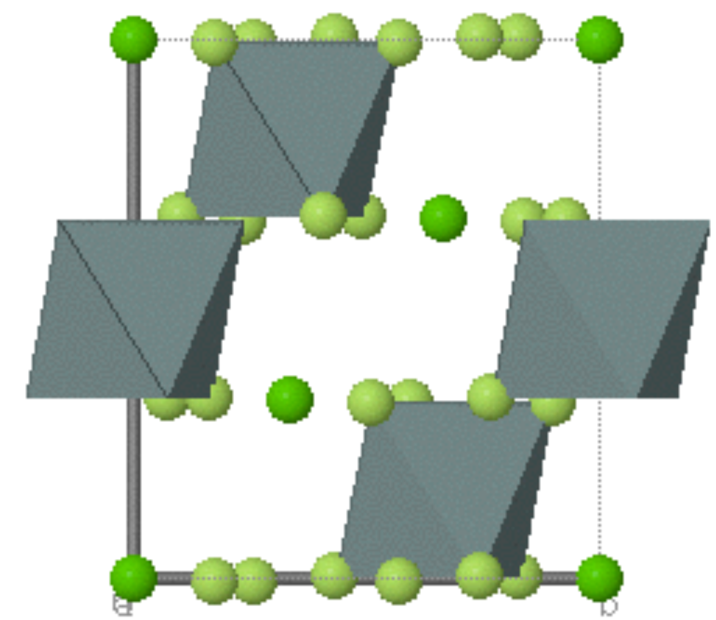
```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1   3b     0.333333 0.666666 0.166666
As     1   3a     0 0 0
F      1   18f    0.1292 0.2165 0.1381
```

$BaIrF_6$



```
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba     1   3b     0.333333 0.666666 0.166666
Ir     1   3a     0 0 0
F      1   18f    0.0729 0.2325 0.1640
```

$BaSnF_6$



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

Koch, Fischer. *MathCryst Satell.*, ECM22, Budapest 2004

COMPSTRU

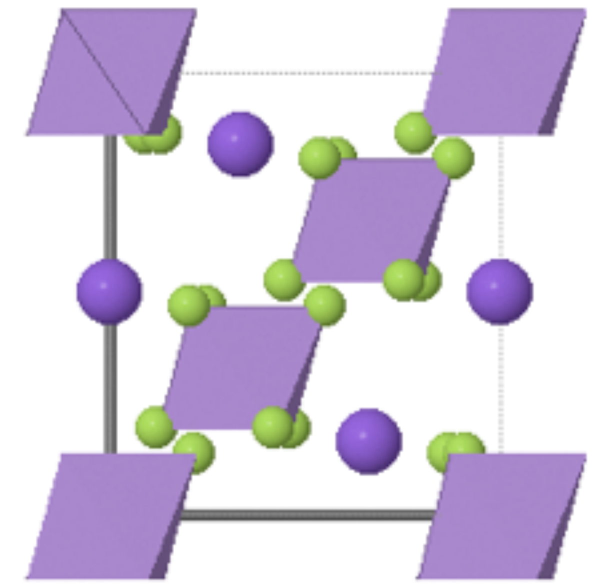
Problem 3.3

SOLUTION

structure 1

Structure 1

```
#KAsF6
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K       1    3b     0.333333 0.666666 0.166666
As      1    3a     0  0  0
F       1    18f    0.1292 0.2165 0.1381
```

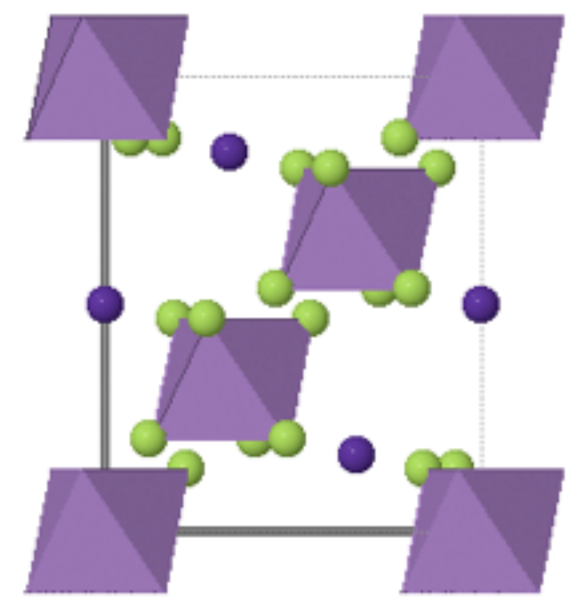


default settings

Structure 2

```
#BaIrF6
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba      1    3b     0.333333 0.666666
0.166666
Ir      1    3a     0  0  0
F       1    18f    0.0729 0.2325 0.1640
```

structure 2



tolerances

Enter the maximum distance allowed between the paired atoms: 1 Å

Enter the allowed tolerance (a b c α β γ): .5 .5 .5 5 5 5

Problem 3.3 SOLUTION COMPSTRU

Comparison of crystal structures of the same symmetry *R*-3 (No. 148)

Structure 1

```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K       1    3b     0.333333 0.666666 0.166666
As      1    3a     0.000000 0.000000 0.000000
F       1    18f    0.129200 0.216500 0.138100
```

Structure 2

```
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba      1    3b     0.333333 0.666666 0.166666
Ir      1    3a     0.000000 0.000000 0.000000
F       1    18f    0.072900 0.232500 0.164000
```

option 1

correspondence scheme proposed by the program

Structure #1	Structure #2
F	F
K	Ba
As	Ir

Do you agree with the proposed correspondence scheme?

Yes No

option 2

correspondence scheme based on Wyckoff sets

Structure 1	Structure 2
Wyckoff set (ab)	Wyckoff set (ab)
K 1 3b 0.333333 0.666666 0.166666	Ba 1 3b 0.333333 0.666666 0.166666
As 1 3a 0.000000 0.000000 0.000000	Ir 1 3a 0.000000 0.000000 0.000000
Wyckoff set (f)	Wyckoff set (f)
F 1 18f 0.129200 0.216500 0.138100	F 1 18f 0.072900 0.232500 0.164000

Problem 3.3

SOLUTION

COMPSTRU

$KAsF_6$

Structure 1

```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K      1    3b     0.333333 0.666666 0.166666
As     1    3a     0.000000 0.000000 0.000000
F      1    18f    0.129200 0.216500 0.138100
```

$BaIrF_6$

Structure 2

```
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba     1    3b     0.333333 0.666666 0.166666
Ir     1    3a     0.000000 0.000000 0.000000
F      1    18f    0.072900 0.232500 0.164000
```

affine normalizer

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0031	0.2701	0.2205	0.051

structural descriptor

$$\Delta = 0.051$$

Description of Structure #2 in the most similar configuration to Structure #1

```
148
7.396500 7.396500 7.282600 90.000000 90.000000 120.000000
3
Ba   1   3b   0.333334   0.666667   0.166666
Ir   1   3a   0.000000   0.000000   0.000000
F    1   18f  0.159600   0.232500   0.164000
```

Atom pairings and distances

WP		Atom Structure1	Atom Structure2	Atomic Displacements			
				u_x	u_y	u_z	|u|
3b	(0,0,1/2)	K1	Ba1	0.0000	0.0000	0.0000	0.0000
3a	(0,0,0)	As1	Ir1	0.0000	0.0000	0.0000	0.0000
18f	(x,y,z)	F1	F1	0.0304	0.0160	0.0259	0.2701

maximal displacement

d_{max}=0.27 Å

Example: STRUCTURE TYPES **COMPSTRU**

STUDY OF THE FAMILY **ABF6**

KCrF6	LiNbF6	VNbF6	HgRhF6	MgPbF6	InAsF6
RbCrF6	LiRuF6	CoZrF6	NiRhF6	ZnPbF6	CsNbF6
KAsF6	LiRhF6	PdPtF6	CaCrF6	NiPbF6	HgCrF6
RuAsF6	LiTaF6	FeNbF6	MgCrF6	MgPdF6	CoSnF6
CsAsF6	LiOsF6	CaSnF6	CdCrF6	CaPdF6	CsNbF6
RbSbF6	LiIrF6	FeZrF6	MnSnF6	ZnPdF6	MnPtF6
BaSnF6	LiPtF6	CuZrF6	FeSnF6	CdPdF6	CdRhF6
CsBrF6	LiAuF6	CaPtF6	ZnSnF6	LiSbF6	NaBiF6
CsSbF6	NiPtF6	ZnPtF6	NiSnF6	BaIrF6	TlAsF6
CsBiF6	CdPtF6	CoPtF6	CuSnF6	RbBiF6	
CsUF6	LiPF6	MgRhF6	CdSnF6	KRhF6	
KOsF6	LiAsF6	CaRhF6	CdTiF6	CsReF6	
NaCrF6	PdZrF6	ZnRhF6	LiBiF6	KPF6	

Example: STRUCTURE TYPES COMPSTRU

STUDY OF THE FAMILY **ABF6**

Reference structure:
$CaCrF_6$

maximal distance Δ [Å]

Type: $LiSbF_6$

$MnPtF_6$	$NiPtF_6$	$NiRhF_6$
0.1282	0.1802	0.2005

Type: $KOsF_6$

$CsBrF_6$	$CsUF_6$	$BrIrF_6$
1.0731	1.1397	1.4067

STUDY OF THE FAMILY **ABX3**

R-3 (148);WP sequence: fc^2; Pearson: hR10

	MgO3	CoO3	(FeSb	MnNi	NiO3	CoM	O3T	MnO	CdO	GeMg	MnO	GeO3	FeO3	CaO3	Cl3M	CuO	GeMn	MgO	CdGe	AsLi	NaO3	CrSi	(AlC	KO3	H4F3N
MgO3Ti	0	0,0	0,2	0,3	0,1	0,3	0,3	0,2	0,6	0,2	0,2	0,3	0,1	0,5	0,3	0,2	0,4	0,4	0,6	0,5	0,6	2,4	2,2	1,2	1,7
CoO3Ti	0,0	0	0,2	0,3	0,1	0,3	0,3	0,2	0,6	0,2	0,2	0,3	0,0	0,5	0,3	0,2	0,4	0,3	0,6	0,4	0,6	2,4	2,2	1,1	1,7
(FeSb0.5)MnO3	0,2	0,2	0	0,4	0,3	0,5	0,4	0,2	0,7	0,1	0,1	0,1	0,2	0,3	0,3	0,2	0,2	0,2	0,4	0,3	0,4	2,6	2,4	1,1	1,6
MnNiO3	0,3	0,3	0,4	0	0,2	0,1	0,2	0,3	0,5	0,4	0,4	0,5	0,3	0,7	0,5	0,4	0,6	0,5	0,8	0,6	0,8	2,3	2,2	1,2	1,7
NiO3Ti	0,1	0,1	0,3	0,2	0	0,2	0,3	0,3	0,6	0,3	0,3	0,4	0,2	0,6	0,4	0,3	0,5	0,4	0,7	0,5	0,6	2,3	2,1	1,2	1,7
CoMnO3	0,3	0,3	0,5	0,1	0,2	0	0,3	0,4	0,6	0,4	0,5	0,5	0,4	0,8	0,5	0,4	0,6	0,6	0,8	0,7	0,8	2,3	2,1	1,2	1,8
O3TiZn	0,3	0,3	0,4	0,2	0,3	0,3	0	0,3	0,5	0,3	0,4	0,4	0,3	0,6	0,5	0,4	0,5	0,5	0,7	0,6	0,7	2,4	2,3	1,2	1,6
MnO3Sn	0,2	0,2	0,2	0,3	0,3	0,4	0,3	0	0,6	0,2	0,2	0,3	0,2	0,4	0,3	0,3	0,3	0,3	0,5	0,4	0,5	2,6	2,4	1,2	1,6
CdO3Ti	0,6	0,6	0,7	0,5	0,6	0,6	0,5	0,6	0	0,7	0,7	0,8	0,7	1,0	0,8	0,8	0,9	0,8	1,0	0,9	1,0	4,9	2,5	1,6	1,8
GeMgO3	0,2	0,2	0,1	0,4	0,3	0,4	0,3	0,2	0,7	0	0,2	0,2	0,2	0,4	0,2	0,2	0,2	0,2	0,4	0,3	0,4	2,6	2,4	1,0	1,6
MnO3Ti	0,2	0,2	0,1	0,4	0,3	0,5	0,4	0,2	0,7	0,2	0,0	0,2	0,1	0,3	0,3	0,1	0,2	0,2	0,4	0,3	0,4	2,5	2,3	1,1	1,6
GeO3Zn	0,3	0,3	0,1	0,5	0,4	0,5	0,4	0,3	0,8	0,2	0,2	0	0,3	0,2	0,3	0,3	0,1	0,2	0,3	0,2	0,3	2,7	2,5	1,0	1,6
FeO3Ti	0,1	0,0	0,2	0,3	0,2	0,4	0,3	0,2	0,7	0,2	0,1	0,3	0	0,4	0,3	0,1	0,3	0,3	0,5	0,4	0,5	2,4	2,2	1,1	1,7
CaO3Sn	0,5	0,5	0,3	0,7	0,6	0,8	0,6	0,4	1,0	0,4	0,3	0,2	0,4	0	0,5	0,4	0,1	0,2	0,2	0,2	0,2	2,9	2,7	1,0	1,6
Cl3MnNa	0,3	0,3	0,3	0,5	0,4	0,5	0,5	0,3	0,8	0,2	0,3	0,3	0,3	0,5	0	0,3	0,3	0,2	0,5	0,3	0,4	3,1	2,8	1,2	2,0
CuO3V	0,2	0,2	0,2	0,4	0,3	0,4	0,4	0,3	0,8	0,2	0,1	0,3	0,1	0,4	0,3	0	0,3	0,3	0,5	0,4	0,5	2,4	2,2	1,1	1,7
GeMnO3	0,4	0,4	0,2	0,6	0,5	0,6	0,5	0,3	0,9	0,2	0,2	0,1	0,3	0,1	0,3	0,3	0	0,1	0,2	0,1	0,2	5,1	2,6	1,0	1,6
MgO3Si	0,4	0,3	0,2	0,5	0,4	0,6	0,5	0,3	0,8	0,2	0,2	0,2	0,3	0,2	0,2	0,3	0,1	0	0,2	0,1	0,2	5,0	2,5	1,0	1,6
CdGeO3	0,6	0,6	0,4	0,8	0,7	0,8	0,7	0,5	1,0	0,4	0,4	0,3	0,5	0,2	0,5	0,5	0,2	0,2	0	0,2	0,2	5,1	2,7	1,0	1,7
AsLiO3	0,5	0,4	0,3	0,6	0,5	0,7	0,6	0,4	0,9	0,3	0,3	0,2	0,4	0,2	0,3	0,4	0,1	0,1	0,2	0	0,1	2,9	4,8	0,9	1,7
NaO3Sb	0,6	0,6	0,4	0,8	0,6	0,8	0,7	0,5	1,0	0,4	0,4	0,3	0,5	0,2	0,4	0,5	0,2	0,2	0,2	0,1	0	5,2	2,8	1,0	1,7
CrSiTe3	2,4	2,4	2,6	2,3	2,3	2,3	2,4	2,6	4,9	2,6	2,5	2,7	2,4	2,9	3,1	2,4	5,1	5,0	5,1	2,9	5,2	0	0,4	5,4	3,1
(AlCu)PSe3	2,2	2,2	2,4	2,2	2,1	2,1	2,3	2,4	2,5	2,4	2,3	2,5	2,2	2,7	2,8	2,2	2,6	2,5	2,7	4,8	2,8	0,4	0	3,1	3,1
KO3Sb	1,2	1,1	1,1	1,2	1,2	1,2	1,2	1,2	1,6	1,0	1,1	1,0	1,1	1,0	1,2	1,1	1,0	1,0	1,0	0,9	1,0	5,4	3,1	0	1,4
H4F3NSn	1,7	1,7	1,6	1,7	1,7	1,8	1,6	1,6	1,8	1,6	1,6	1,6	1,7	1,6	2,0	1,7	1,6	1,6	1,7	1,7	1,7	3,1	3,1	1,4	0

ICSD (c/a)

$FeTiO_3$

$FePSe_3$

Bergerhoff (structure descriptor)

Bilbao Server (global distortion)

0.3 $FeTiO_3$ ($NaSbO_3$)

0.4 $FePSe_3$

STRUCTURAL PHASE TRANSITIONS

Structure Relationships

PROBLEM:

Consider two phases of the same compound (specified by their unit-cell parameters and atomic coordinates) with group-subgroup related symmetry groups G>H

Search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.

High-symmetry phase	symmetry controlled mapping →	(High-symmetry phase)$_{Low}$	↔ affine transformation	Low-symmetry phase
G	G > H relationship	(G)$_{H}$	global distortion of the mapping	H
	Wyckoff positions schemes	most similar configuration	Lattice deformation Atomic displacement field	

STRUCTURE RELATIONS

Given the high- and low-symmetry phases:

1. Characterize the symmetry reduction between the high- and low-symmetry phases
   - index of the group-subgroup pair: INDEX
   - group-subgroup graph, (P,p): SUBGROUPGRAPH

2. Domain-structure analysis

3. Determine the so-called *reference* structure, *i.e.* high-symmetry structure in the low-symmetry basis
   - lattice parameters: CELLTRANS
   - atomic coordinates: TRANSTRU or WYCKSPLIT

4. Evaluate the lattice strain and the atomic displacements accompanying the phase transitions: STRAIN, COMPSTRU

Problem 3.5 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=4.9586Å, c=6.9074Å. 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=7.147Å. 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.

Example: α-Cristobalite → β-Cristobalite

2 entries selected.
CC=Collection Code: [AB2X4]=ANX Form: [cF56]=Pearson: [e d a]=Wyckoff Symbol: [Al2MgO4]=Structure Type:
Click the ANX, Pearson or Wyckoff Symbol to find structures with that symbol.

CC=44094	Details Bonds Pattern Structure Jmol
Title	First-principles study of crystalline silica.
Authors	Feng Liu;Garofalini, H.;King-Smith, D.;Vanderbilt, D.
Reference	Physical Review, Serie 3. B - Condensed Matter (1994) **49**, 12528-12534 **Link XRef SCOPUS SCIRUS Google** **Also:** Phase Transition (1992) **38**, 127-220
Compound	**Si O2** - **[Cristobalite alpha]** Silicon oxide - HT **[AX2]** **[tP12]** **[b a]** **[TeO2(alpha)]**
Cell	4.9586, 4.9586, 6.9074, 90., 90., 90. **P41212 (92)** V=169.84
Remarks	MIN =Cristobalite alpha : PDC =01-089-3434 : PDF =39-1425 : THE TYP =TeO2(alpha) : XDS At least one temperature factor missing in the paper. No R value given in the paper. Metastable up to 500 K (2nd ref. , Tomaszewski), above Fd3-m

Atom	**(site)**	**Oxid.**	**x, y, z, B, Occupancy**				
Si1	(4a)	4	0.3028	0.3028	0	0	1
O1	(8b)	-2	0.2383	0.1093	0.1816	0	1

CC=44095	Details Bonds Pattern Structure Jmol
Title	First-principles study of crystalline silica.
Authors	Feng Liu;Garofalini, H.;King-Smith, D.;Vanderbilt, D.
Reference	Physical Review, Serie 3. B - Condensed Matter (1994) **49**, 12528-12534 **Link XRef SCOPUS SCIRUS Google** **Also:** Phase Transition (1992) **38**, 127-220
Compound	**Si O2** - **[Cristobalite beta]** Silicon oxide - HT **[AX2]** **[cF24]** **[h a]** **[]**
Cell	7.147, 7.147, 7.147, 90., 90., 90. **FD3-MS (227)** V=365.07
Remarks	MIN =Cristobalite beta : PDC =01-089-3435 : PDF =4-359 : THE XDS At least one temperature factor missing in the paper. The coordinates are those given in the paper but the atomic distances do not agree with those calculated during testing.The coordinates are probably correct. No R value given in the paper. Metastable above 500 K (2nd ref. , Tomaszewski), stable above 1743 K

Atom	**(site)**	**Oxid.**	**x, y, z, B, Occupancy**				
Si1	(8a)	4	0	0	0	0	1
O1	(96h)	-2	0.125	0.081	0.169	0	0.1667

Origin choice 2:

Si 8a 1/8,1/8,1/8 7/8,3/8,3/8

Problem 3.5

SOLUTION

1. Characterize the symmetry break between the high- and low-symmetry phases

- -index of the group-subgroup pair: INDEX
- -transformation matrix: SUBGROUPGRAPH

2. Calculate the lattice parameters of the low-symmetry phase: CELLTRANS

3. Calculate the atomic coordinates of the low-symmetry phase: TRANSFORM (or WYCKSPLIT)

4. Evaluate the lattice strain and the atomic displacements accompanying the phase transitions: STRAIN, COMPSTRU

Step 1. Determination of the index of the group-subgroup pair

INDEX

INDEX: Index of a group-subgroup pair

Please, enter the sequential number of group as given in *International Tables for Crystallography*, Vol. A : choose 227

Please, enter the sequential number of group as given in *International Tables for Crystallography*, Vol. A : choose 92

space-group identification

- **Option A: Introduce the formula units (conventional) of the high and low symmetry structure.**

The formula units (conventional) on the high symmetry structure:

The formula units (conventional) on the low symmetry structure:

formula units

- **Option B: Introduce the lattice parameters of the high and low symmetry structure.**

The lattice parameters on the high symmetry structure: 7.12637 7.12637 7.12637 90. 90. 90.

The lattice parameters on the low symmetry structure: 4.9501 4.9501 6.8760 90. 90. 90.

Show index

lattice parameters

Index of a group-subgroup pair

High symmetry Space Group:	227 (*Fd-3m*) [origin choice 2]
Low symmetry Space Group:	92 ($P4_12_12$)
i_L	2
i_P	6
Total index	12

The corresponding subgroup data can be found here.

$$\left.\begin{array}{l}[i_L]=2\\[i_P]=6\end{array}\right\}\ [i]=12$$

Step 2. Study of the group-subgroup symmetry break

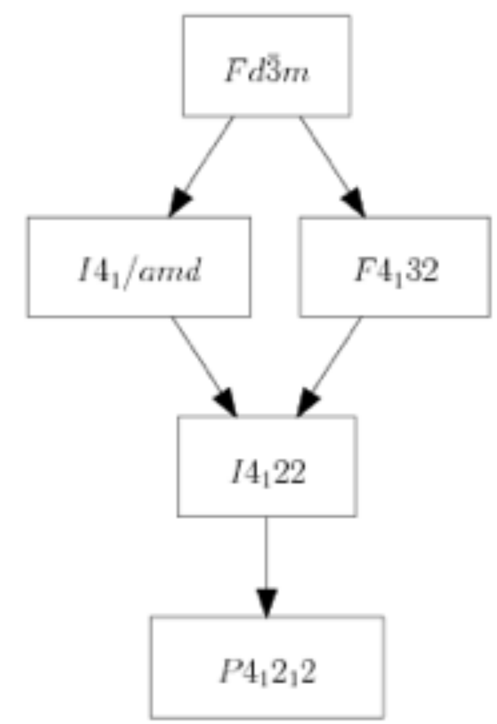
SUBGROUPGRAPH

Class 1

Check	Chain [indices]	Chain with HM symbols	Transformation	Identical
◉ 1	227 210 098 092 [2 3 2]	$Fd\text{-}3m > F4_132 > I4_122 > P4_12_12$	$\begin{pmatrix} -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \\ 1/2 & 1/2 & 0 & 5/8 \end{pmatrix}$	to group 1
○ 2	227 141 098 092 [3 2 2]	$Fd\text{-}3m > I4_1/amd > I4_122 > P4_12_12$	$\begin{pmatrix} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{pmatrix}$	to group 2
○ 3	227 141 098 092 [3 2 2]	$Fd\text{-}3m > I4_1/amd > I4_122 > P4_12_12$	$\begin{pmatrix} 0 & 0 & 1 & 3/8 \\ 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \end{pmatrix}$	to group 3

Show graph

Group-Subgroup Graph



Which of the three matrices corresponds to the cristobalite case?

Step 3. Lattice parameters of the reference structure

CELLTRANS

High-symmetry phase

G

$\xrightarrow{G > H}$ relationship

(High-symmetry phase)$_{Low}$

$(G)_H$

Transform Unit Cell

Cell Parameters: 7.147 7.147 7.147 90 90 90 Centering P

Please, define the rotational part of the transformation matrix that relates the group and the subgroup bases

in abc form: Ex: c,a,b (read by columns)

Rotational part

or in matrix form:

$$\begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Show

5.053 5.053 7.147 90 90 90

lattice parameters of the reference structure

Step 3. Atomic coordinates of the reference structure

High-symmetry phase $\xrightarrow[\text{relationship}]{G > H}$ (High-symmetry phase)$_{Low}$

G (G)$_H$

TRANSTRU

Transform Structure

Structure

```
227
7.147 7.147 7.147 90 90 90
1
Si        1        8a        0.125000        0.125000        0.125000
```

Low symmetry Space Group: 92

Transformation Matrix:

In matrix form: (P,p)

Rotational part			Origin Shift
1/2	1/2	0	5/8
-1/2	1/2	0	3/8
0	0	1	3/8

Space Group: 92
Lattice Parameters: 5.053692 5.053692 7.147000 90 90 90

AT	#	WP	Coordinates		
Si	1	4a	3/4	1/4	3/4

atomic coordinates of the reference structure

Step 4. Characterization of the global distortion

Symmetry break:
Fd-3m→$P4_12_12$, index 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

(P,p)

Calculated:

Reference description:
a=5.053 Å, c=7.147 Å

Si 4a 0.75 0.25 0.75
0.25 0.25 0

Tetragonal phase:
a=4.9586 Å, c=6.9074

Si 4a 0.3028 0.3028 0

affine deformation ?

atomic displacements ?

Step 4a. Determination of the affine deformation

Symmetry break:
$Fd\text{-}3m \rightarrow P4_12_12$, index 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

CELLTRANS

$$P = \begin{bmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Calculated:
Reference description:
a=5.053 Å, c=7.147 Å

Tetragonal phase:
a=4.9586 Å, c=6.9074

STRAIN

affine deformation

Step 4a. Determination of the affine deformation

(High-symmetry phase)$_{Low}$ ⟷ Low-symmetry phase

$(G)_H$ $\qquad$ H

Unit cell 1:	[a1] [b1] [c1] [α1] [β1] [γ1] 5.053 5.053 7.147 90 90 90
Unit cell 2:	[a2] [b2] [c2] [α2] [β2] [γ2] 4.9586 4.9586 6.9074 90 90 90

STRAIN

Finite Lagrangian Strain Tensor (finite deformation)

```
[ -0.018507  0.000000  0.000000 ]
[  0.000000 -0.018507  0.000000 ]
[  0.000000  0.000000 -0.032963 ]
```

Strain tensor

Eigenvalues

-0.01851 -0.01851 -0.03296

Degree of lattice distortion

0.01403

$$S=1/3(\sum \eta_i^2)^{1/2}$$

Step 4b. Atomic displacement field

Symmetry break:
Fd-3m→$P4_12_12$, index 12

Experiment:
Cubic phase:

a=7.147 Å

Si 8a 1/8 1/8 1/8
7/8 3/8 3/8

TRANSTRU

$$\left(\begin{array}{ccc|c} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{array}\right)$$

Calculated:
Reference description:

a=5.053 Å, c=7.147 Å

Si 4a 0.75 0.25 0.75
0.25 0.25 0

COMPSTRU

atomic displacement field

Tetragonal phase:

a=4.9586 Å, c=6.9074

Si 4a 0.3028 0.3028 0

Step 4b. Atomic displacement field

COMPSTRU

Reference structure

Structure #1

```
92
5.053692 5.053692 7.147000 90.000000 90.000000 90.000000
1
Si      1      4a      0.750000      0.250000      0.750000
```

Experimental data

Structure #2

```
92
4.9586 4.9586 6.9074 90 90 90
1
Si      1      4a      0.302800      0.302800      0.000000
```

affine normalizer

Most similar configuration

```
092
4.958600 4.958600 6.907400 90.000000 90.000000 90.000000
1
Si      1      4a      0.697200      0.302800      0.750000
```

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0149	0.3774	0.7548	0.122

structural descriptor $\Delta = 0.122$

Atom pairings and distances

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
4a	(x,x,0)	Si1	-0.0528	0.0528	0.0000	0.3774

maximal displacement

d_{max}=0.377 Å

PROBLEM:

Structural Relationship between two structures with group-subgroup related symmetry groups **G** → **H**

High-symmetry phase: G

symmetry reduction

Group-subgroup relation G>H

Wyckoff positions splittings

Reference description: $(G)_H$

affine transformation

lattice deformation

atomic displacement field

Low-symmetry phase: H

INDEX

SUBGROUPGRAPH

HERMANN

WYCKSPLIT

STRAIN

COMPSTRU

STRUCTURE RELATIONS

Problem 3.5

STRUCTURE RELATIONS

SOLUTION

Cristobalite phase transition

high-symmetry structure

High symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data [CIF format] Examinar...

BCS Format

```
227
7.147 7.147 7.147 90 90 90
1
Si 1 8a 0.125 0.125 0.125
```

low-symmetry structure

Low symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data [CIF format] Examinar...

BCS Format

```
92
4.9586 4.9586 6.9074 90 90 90
1
Si 1 4a 0.3028 0.3028 0
```

tolerances

Enter the allowed tolerance (a b c α β γ): .2 .2 .3 2 2 2

Enter the maximum distance allowed between the paired atoms: 1.5 Å

Problem 3.5

SOLUTION

STRUCTURE RELATIONS

Cristobalite phase transition

Fd-3m High-symmetry phase

$$(P,p)= \begin{pmatrix} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{pmatrix}$$

Symmetry-controlled mapping

(High-symmetry phase)$_{P4_12_12}$

Global distortion

Lattice deformation
Atomic displacement field

$P4_12_12$ Low-symmetry phase

High Symmetry Structure

```
227
7.147 7.147 7.147 90 90 90
1
Si     1    8a     0.125000 0.125000 0.125000
```

Description of the High Symmetry Structure in the most similar configuration to the Low Symmetry Structure

```
092
5.053692 5.053692 7.147000 90.000000 90.000000 90.000000
1
Si     1     4a     0.250000     0.250000     0.000000
```

Low Symmetry Structure

```
92
4.9586 4.9586 6.9074 90 90 90
1
Si     1    4a     0.302800 0.302800 0.000000
```

Problem 3.5

SOLUTION

STRUCTURE RELATIONS

Cristobalite phase transition

Fd-3m High-symmetry phase

$$(P,p)= \begin{pmatrix} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{pmatrix}$$

alternative transformation matrices

$$(P,p)_1= \begin{pmatrix} 0 & 0 & 1 & 3/8 \\ 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \end{pmatrix}$$

$$(P,p)_2= \begin{pmatrix} -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \\ 1/2 & 1/2 & 0 & 5/8 \end{pmatrix}$$

$P4_12_12$ low-symmetry phase

Global distortion

average distance

$$d_{av} = \frac{1}{n}\sum_i m_i u_i$$

structural descriptor Δ

$$[\sqrt{2}\Delta(c)+1]\Delta(d)-1$$

lattice deformation

$$S = \frac{1}{3}\sqrt{\sum_i \eta_i^2}$$

Evaluation of the Global Distorti

S	dmax. (Å)	dav. (Å)	Δ
0.0149	0.3774	0.7548	0.122

maximal distance

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
4a	(x,x,0)	Si1	0.0528	-0.0528	0.0000	0.3774

Problem 3.5

SOLUTION

STRUCTURE RELATIONS

NON-STANDARD settings

Cristobalite phase transition

high-symmetry structure

Origin choice 1

High symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data [CIF format] | Examina

BCS Format

```
#Exercise 3.5 (cristobalite):
# Space Group ITA number (high-symmetry phase)
227
7.147 7.147 7.147 90 90 90
1
Si 1 8a 0.0 0.0 0.0
```

low-symmetry structure

Low symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data [CIF format] | Examina

BCS Format

```
# Space Group ITA number (low-symmetry phase)
92
4.9586 4.9586 6.9074 90 90 90
1
Si 1 4a 0.3028 0.3028 0
```

tolerances

Enter the allowed tolerance (a b c α β γ): .2 .2 .3 2 2 2

Enter the maximum distance allowed between the paired atoms: 1.5 Å

NON-standard settings

One or both of the structures are given in a non-standard setting? ○ No | ⊙ Yes

Problem 3.5

SOLUTION

STRUCTURE RELATIONS

NON-STANDARD settings

high-symmetry structure

Origin choice 1

Please choose the setting in which the high symetry structure is given:

	Setting	P	P^{-1}
◉	*F d* -3 *m* [origin 2]	a,b,c	a,b,c
○	*F d* -3 *m* [origin 1]	a-1/8,b-1/8,c-1/8	a+1/8,b+1/8,c+1/8

Please choose the setting in which the low symetry structure is given:
(You can choose one of the ITA settings or define your own setting introducin
a label and the transformation matrix to the standard setting)

low-symmetry structure

	Setting	P	P^{-1}
○	$P\,4_1\,2_1\,2$	a,b,c	a,b,c

◉ User defined setting:

Label

	Rotational part			Origin shift
Transformation Matrix	1	0	0	0
	0	1	0	0
	0	0	1	0

Cristobalite phase transition

Problem 3.6(a)

Lead phosphate phase transition

Lead phosphate $Pb_3(PO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry *R-3m* (No. 166) to a ferroelastic phase of symmetry *C2/c* (No.15).

Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server:*

(i)characterize the symmetry reduction between the high- and low-symmetry phases (index, graph of maximal subgroups, etc.);

(ii)describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

Problem 3.6 (b) Lead vanadate phase transition

Lead phosphate $Pb_3(VO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry *R-3m* (No. 166) to a ferroelastic phase of symmetry *P2₁/c* (No.14).

Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server:*

(i)characterize the symmetry reduction between the high- and low-symmetry phases (index, graph of maximal subgroups, etc.);

(ii)describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

Problem 3.6(b)

STRUCTURE RELATIONS

SOLUTION

$Pb_3(VO_4)_2$
ferroelastic
phase transition

High symmetry structure

high-symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

formula units: 3

Structure Data [CIF format] Examinar...

BCS Format

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb    1    3a    0.000000    0.000000    0.000000
Pb    2    6c    0.000000    0.000000    0.207100
PV    3    6c    0.000000    0.000000    0.388400
O     4    6c    0.000000    0.000000    0.324000
O     5    18i   0.842400    0.157600    0.430100
```

Low symmetry structure:

low-symmetry structure

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

formula units: 2

Structure Data [CIF format] Examinar...

BCS Format

```
14
7.5075 6.0493 9.4814 90. 115.162 90.
7
Pb 1 2a 0 0 0
Pb 2 4e 0.3835 0.5815 0.2879
PV 1 4e 0.2071 0.0143 0.3999
O  1 4e 0.2872 0.2559 0.0159
O  2 4e 0.2598 0.7979 0.0216
O  3 4e 0.3194 0.9784 0.2823
O  4 4e 0.0335 0.5431 0.2091
```

Enter the allowed tolerance (a b c α β γ): .2 .5 .5 2 2 2

higher tolerances

Enter the maximum distance allowed between the paired atoms: 1.5 Å

Problem 3.6(b)

STRUCTURE RELATIONS

SOLUTION

Ferroelastic phase transition $Pb_3(VO_4)_2$

R-3m High-symmetry phase

P2₁/c low-symmetry phase

(P,p)= $\begin{pmatrix} -1/3 & -1 & 1 & 0 \\ 1/3 & -1 & -1 & 0 \\ 1/3 & 0 & 0 & 0 \end{pmatrix}$

Atom pairings and distances

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2a	(0,0,0)	Pb1	(0.000000,0.000000,0.000000)	Pb1	(0.000000,0.000000,0.000000)
4e	(x,y,z)	Pb2	(0.378700,0.500000,0.292900)	Pb2	(0.383500,0.581500,0.287900)
4e	(x,y,z)	PV3	(0.165200,0.000000,0.388400)	PV1	(0.207100,0.014300,0.399900)
4e	(x,y,z)	O53	(0.290300,0.263600,0.008900)	O1	(0.287200,0.255900,0.015900)
4e	(x,y,z)	O52	(0.290300,0.736400,0.008900)	O2	(0.259800,0.797900,0.021600)
4e	(x,y,z)	O5	(0.290300,0.000000,0.272500)	O3	(0.319400,0.978400,0.282300)
4e	(x,y,z)	O4	(0.028000,0.500000,0.176000)	O4	(0.033500,0.543100,0.209100)

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
2a	(0,0,0)	Pb1	0.0000	0.0000	0.0000	0.0000
4e	(x,y,z)	Pb2	-0.0048	-0.0815	0.0050	0.4981
4e	(x,y,z)	PV3	-0.0419	-0.0143	-0.0115	0.2986
4e	(x,y,z)	O53	0.0031	0.0077	-0.0070	0.0918
4e	(x,y,z)	O52	0.0305	-0.0615	-0.0127	0.4783
4e	(x,y,z)	O5	-0.0291	0.0216	-0.0098	0.2370
4e	(x,y,z)	O4	-0.0055	-0.0431	-0.0331	0.3964

Evaluation of the Global Distortion

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0236	0.4981	0.2536	0.105

SYMMETRY RELATIONS BETWEEN CRYSTAL STRUCTURES

Problem: **Symmetry Relations between Crystal Structures**

Baernighausen Trees

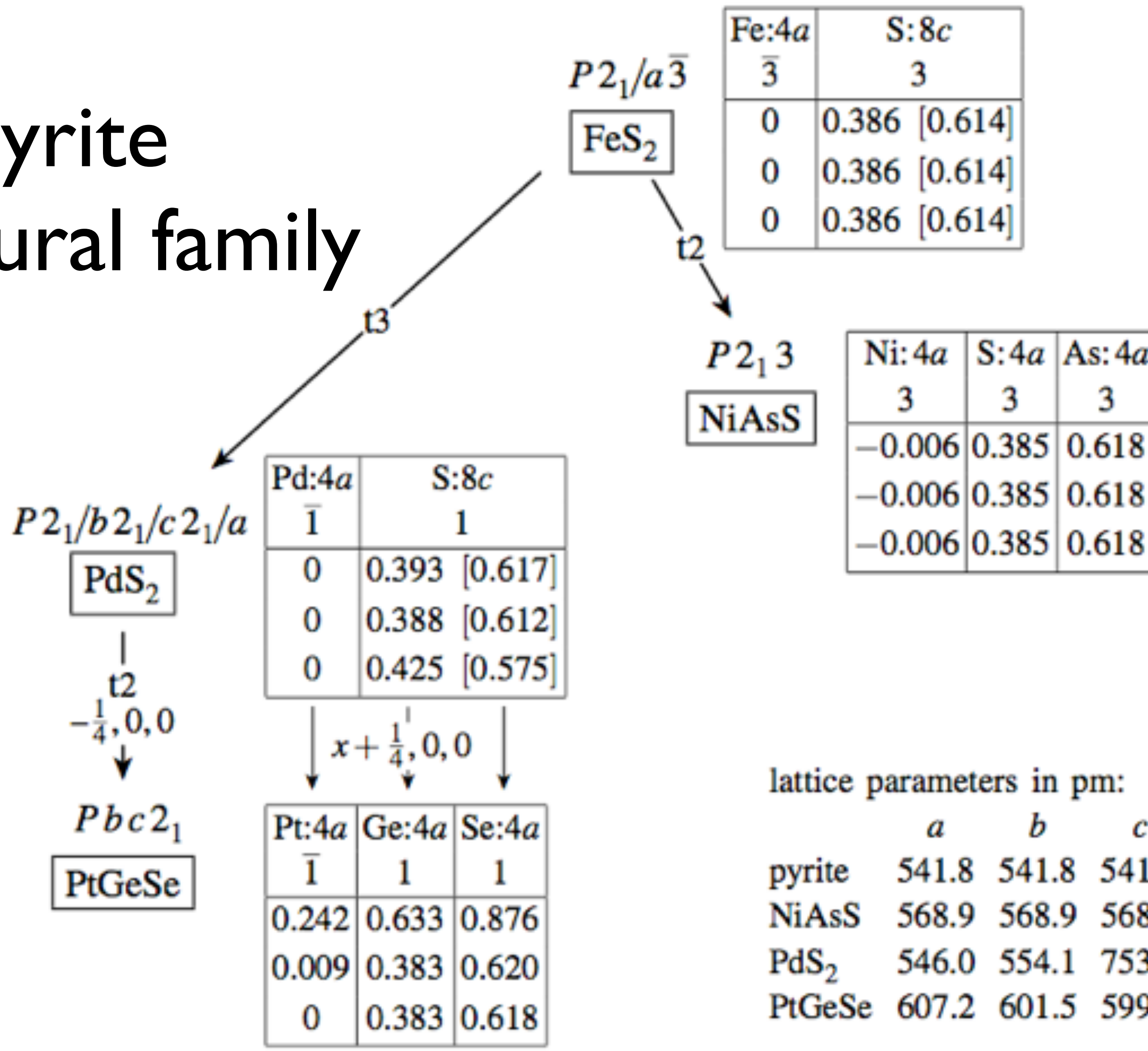
Pyrite
Structural family

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

Module 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 $\mathcal{G}$ → $P\,6/m\,2/m\,2/m$

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

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 $\mathcal{H}$ → $P\,6_3/m\,2/m\,2/c$

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

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

Element symbol
Wyckoff posit.
site symmetry
coordinates

$x, y, \frac{1}{2}z + \frac{1}{4}$ ← 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

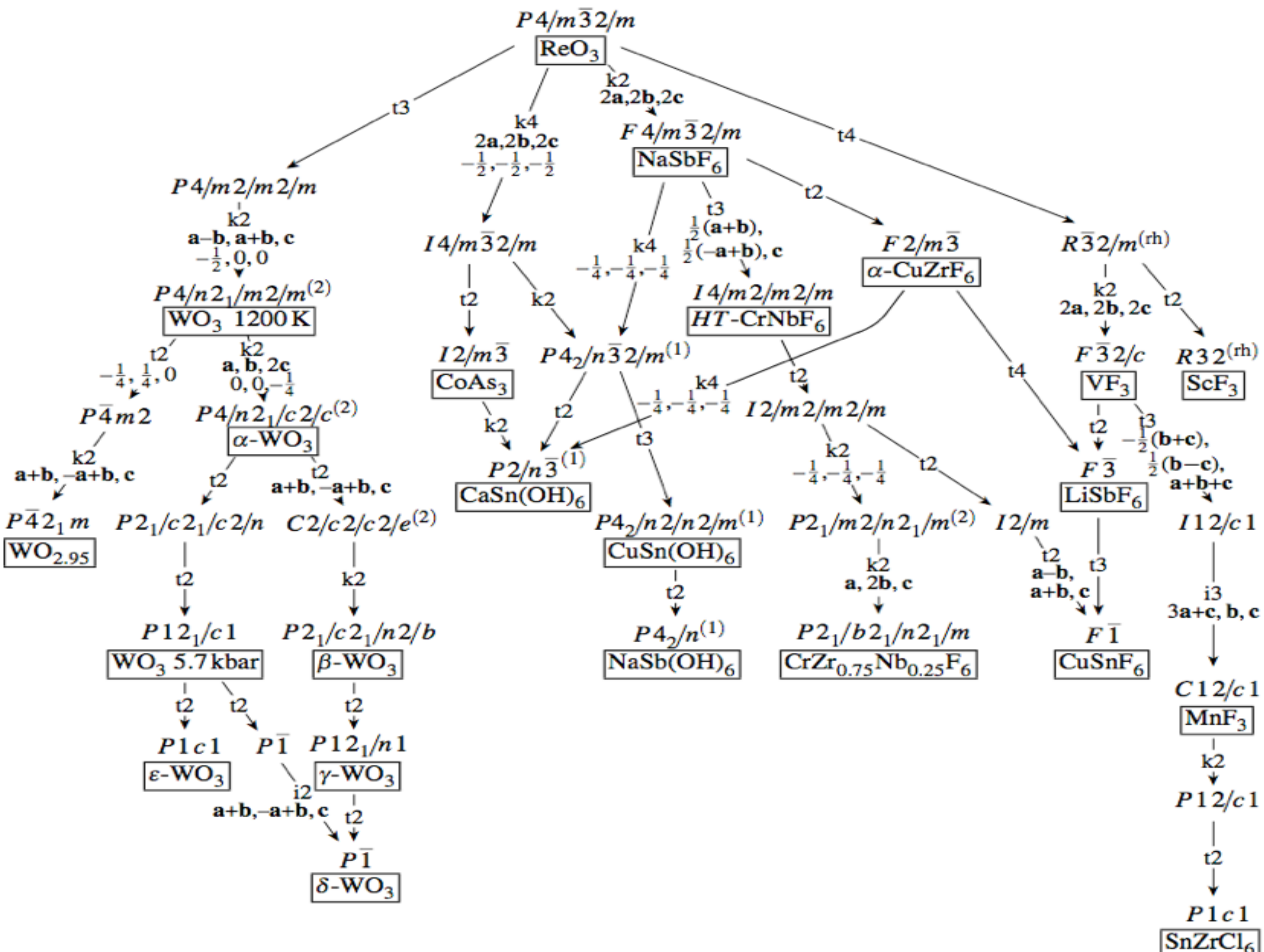
Element symbol
Wyckoff posit.
site symmetry
coordinates

* mentioned only if there is a change

U. Mueller, Gargnano 2008

Family tree of hettotypes of ReO_3

Baernighausen Trees



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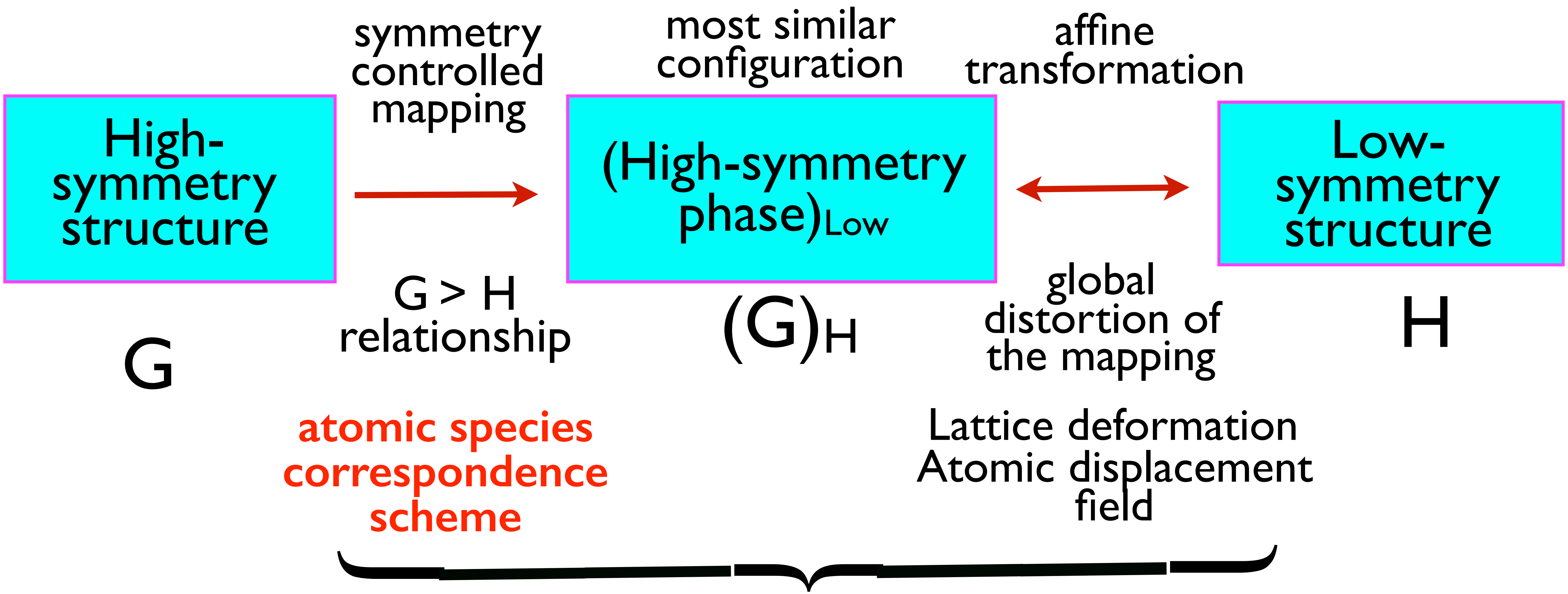
Structure Relationships

PROBLEM:

Consider two structures (specified by their unit-cell parameters and atomic coordinates) with group-subgroup related symmetry groups G>H

Search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.



STRUCTURE RELATIONS

Problem 3.8

Problem: Symmetry relations between crystal structures

Hettotype of CsCl structure

Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or β−brass, CuZn)-type structure. Using the structural data in the *Exercise Data* file, characterize the structural relationship between the CoU structure and CsCl structure.

Problem 3.8

STRUCTURE RELATIONS

SOLUTION

high-symmetry structure

High symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

1

formula units per unit cell

Structure Data
[CIF format]

Examinar...

BCS Format

```
#CuZn (CsCl type)
221
#V=25.67
2.959 2.959 2.959 90. 90. 90.
2
Cu 1 1a 0 0 0
Zn1 1 1b 0.5 0.5 0.5
```

low-symmetry structure

Low symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

8

Structure Data
[CIF format]

Examinar...

BCS Format

```
199 #I213
#V=256.74
6.3557 6.3557 6.3557 90. 90. 90.
2
Co 1 8a 0.294 0.294 0.294
U 1 8a 0.0347 0.0347 0.0347
```

atomic species correspondence scheme

Co ↔ Cu

U ↔ Zn

tolerances

Enter the allowed tolerance (a b c α β γ): 1 1 1 5 5 5

Enter the maximum distance allowed between the paired atoms: 1.5 Å

One or both of the structures are given in a non-standard setting? ⊙No | ○Yes

Problem 3.9

Problem: Symmetry relations between crystal structures

HT-quartz and *LT*-quartz

(i) Upon heating above 573 °C the *LT*-quartz transforms to its *HT* form. Set up the corresponding Baernighausen tree that describes the symmetry relations between the two quartz forms. Which additional degree of freedom are present in the lower symmetry form? (The crystal structures of *HT*-quartz and *LT*-quartz can be found in the *ExerciseData* file.)

(ii) Consider the structure data of $AlPO_4$ listed in the *ExerciseData* file. Describe its structural relationship to quartz and construct the corresponding Baernighausen tree.

Hint: In order to find the structural relationship between quartz and $AlPO_4$ consider the splitting of Si positions into two: one for Al and one for P.