MS21

SIAM Conference on Mathematical Aspects of Materials Science

17-28 MAY 2021

Organizers:

siam Society for Industrial and Applied Mathematics

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ONLINE MATERIALS STUDIES BY THE BILBAO CRYSTALLOGRAPHIC SERVER

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FCT/ZTF

bilbao crystallographic server

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ews:

- **New Article in Nature**
  07/2017: Bradlyn *et al.* "Topological quantum chemistry" *Nature* (2017). **547**, 298-305.
- **New program: BANDREP**
  04/2017: Band representations and Elementary Band representations of Double Space Groups.
- **New section: Double point and space groups**
  - **New program: DGENPOS**
    04/2017: General positions of Double Space Groups
  - **New program: REPRESENTATIONS DPG**
    04/2017: Irreducible representations of the Double Point Groups
  - **New program: REPRESENTATIONS DSG**
    04/2017: Irreducible representations of the Double Space Groups
  - **New program: DSITESYM**
    04/2017: Site-symmetry induced representations of Double Space Groups
  - **New program: DCOMPREL**
    04/2017: Compatibility relations between the irreducible representations of Double Space Groups

tutorials

aterial used in workshops and schools

rchive

Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

Representations and Applications

Solid State Theory Applications

Structure Utilities

Subperiodic Groups: Layer, Rod and Frieze Groups

Structure Databases

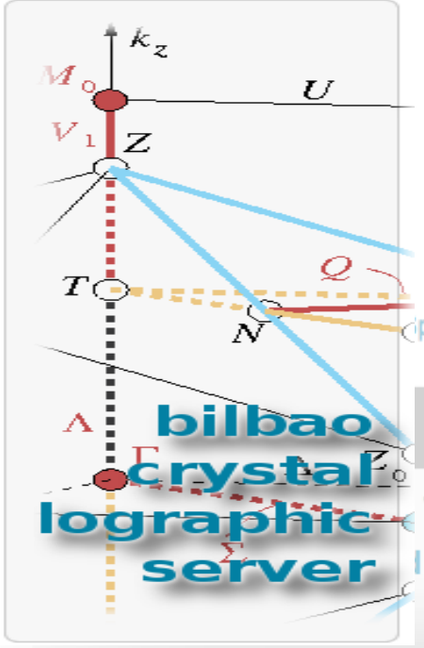
Raman and Hyper-Raman scattering

Point-group symmetry

Plane-group symmetry

Double point and space groups

www.cryst.ehu.es



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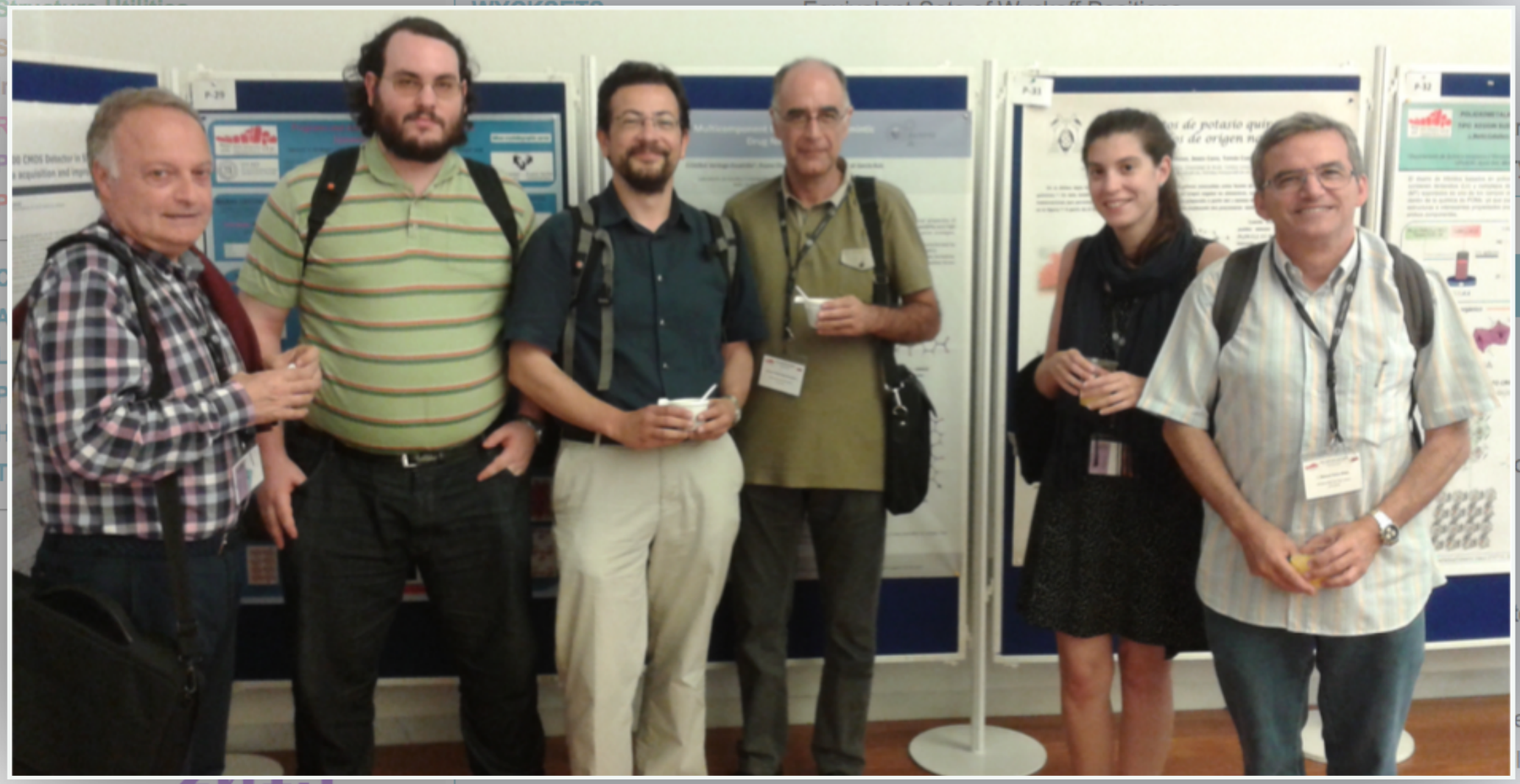
UPV EHU

present team

Gemma de la Flor **Gotzon Madariaga**
Emre Tasci **J. Manuel Perez-Mato**
Luis Elcoro **Mois. I. Aroyo**



http://www.cryst.ehu.es

Crystallographic Databases

International Tables for Crystallography

Bilbao Crystallographic Server

Working Environment

Crystallographic databases

Symmetry relations between crystallographic groups

Structure utilities

Representations of crystallographic groups

Solid-state applications

STRUCTURE UTILITIES

FCT/ZTF

bilbao crystallographic server

News:

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Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

Structure Utilities

CELLTRAN	Transform Unit Cells
STRAIN	Strain Tensor Calculation
WPASSIGN	Assignment of Wyckoff Positions
TRANSTRU	Transform structures.
SETSTRU	Alternative Settings for a given Crystal Structure
EQUIVSTRU	Equivalent Descriptions for a given Crystal Structure
VISUALIZE	Visualize structures using Jmol
COMPSTRU	Comparison of Similar Structures with the same Symmetry
STRUCTURE RELATIONS	Finds the transformation matrix that relates the two given group-subgroup related structures within a tolerance.

Tutorials

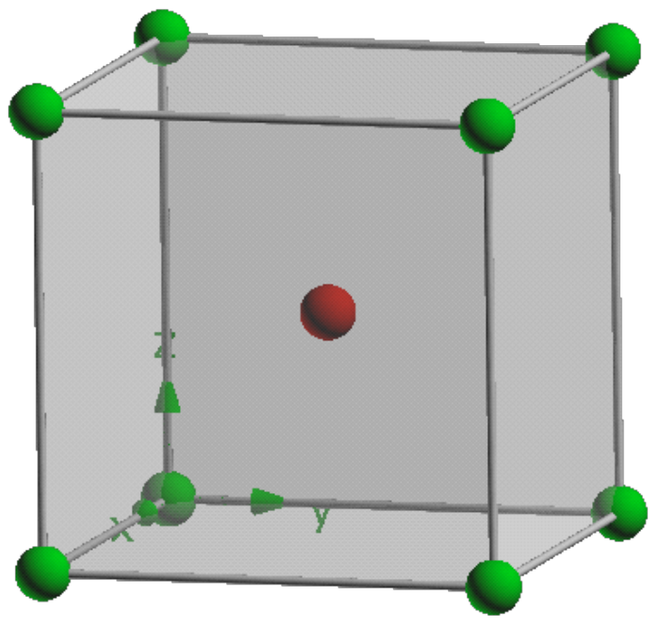
Material used in workshops and schools

Archive

Plane-group symmetry

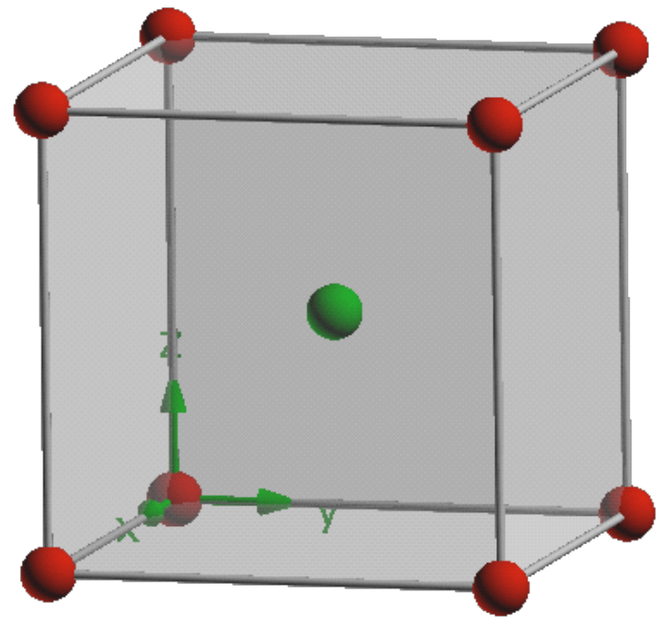
Double point and space groups

Problem: EQUIVALENT DESCRIPTIONS **EQUIVSTRU**



CsCl

Pm-3*m* (221)



1a (0,0,0) ⟶ 1b (1/2,1/2,1/2)

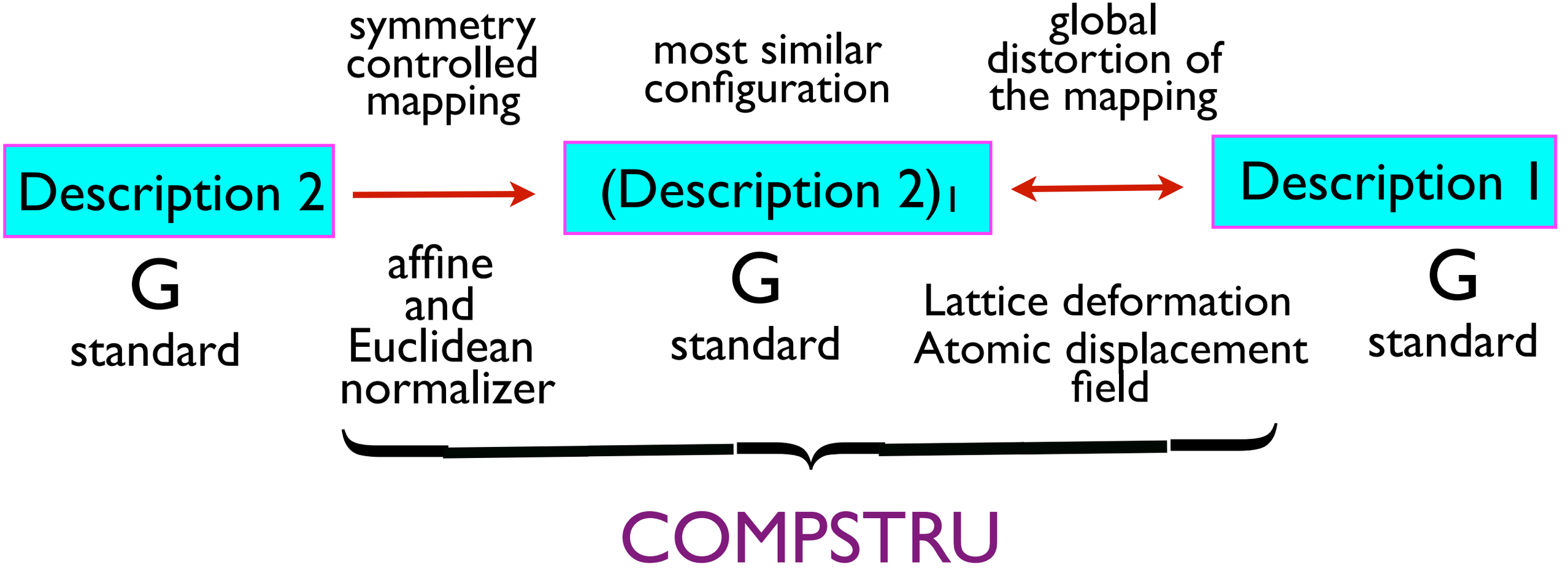
1b (1/2,1/2,1/2) ⟶ 1a (0,0,0)

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

Problem: COMPARISON OF STRUCTURES **COMPSTRU**

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 structures such that the global distortion accompanying the mapping is tolerably small.



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

$$d_{av} = \frac{1}{n}\sqrt{\sum_i m_i u_i^2}$$

u_i-atomic displacements

maximal atomic displacements

maximal displacements of the paired atoms

structural descriptor

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

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

Example COMPSTRU: $Pb_3(PO_4)_2$

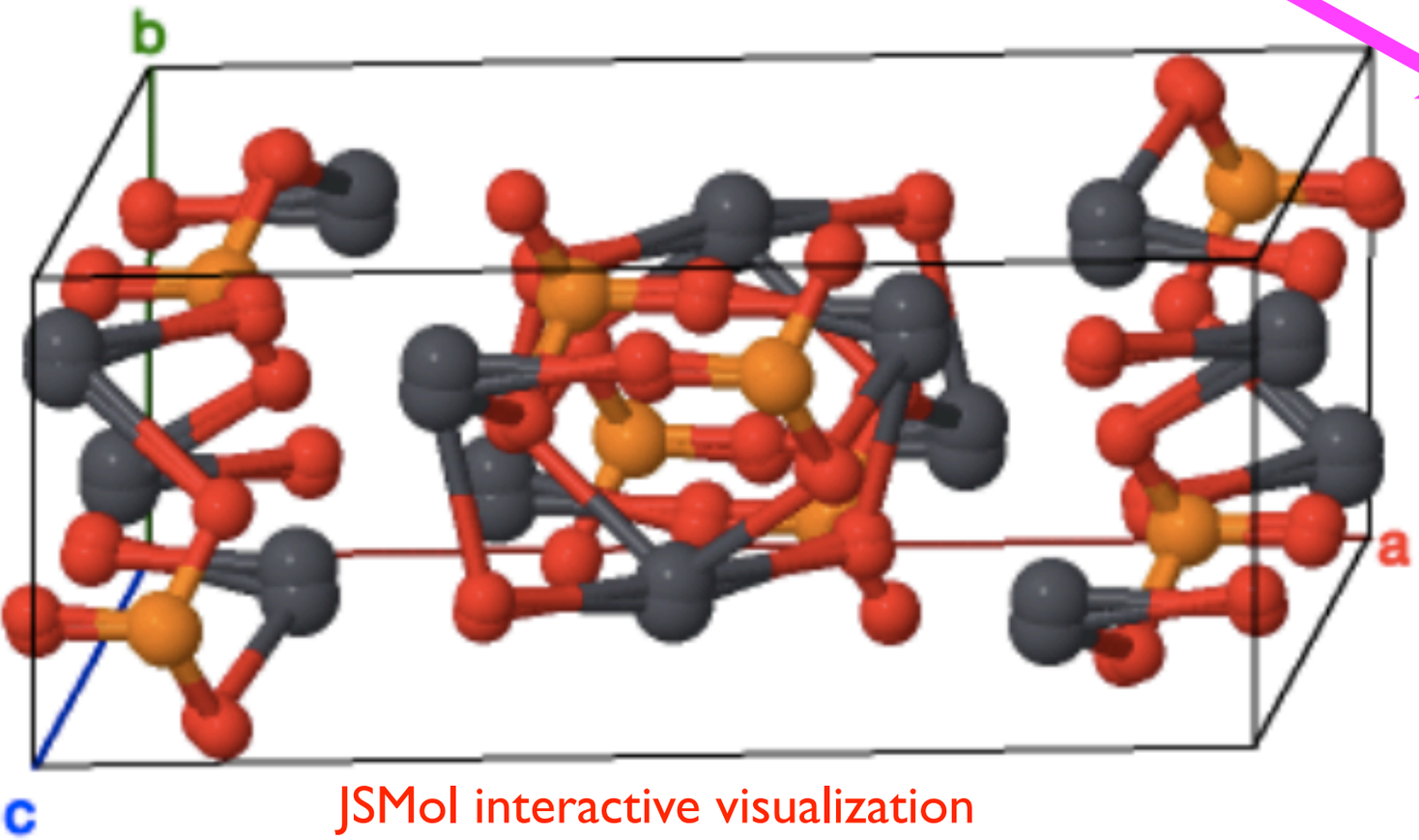
Structure #1

```
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 + Euclidean normalizers



JSMol interactive visualization

(**Robert M. Hanson**, Northfield, MN)

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
```

Evaluation of the structure similarity

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

structural descriptor $\Delta = 0.066$

Problem: Isoconfigurational Structure Types **COMPSTRU**

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

Isopointal structure types

Space group

Wyckoff position sequence

Pearson symbol

(crystal system, centring type, total number of atoms in the unit cell)

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

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

isoconfigurational structure types?

Isoconfigurational structure types

Isopointal

similar

Crystallographic orbits

Geometrical interrelationships

Composition type (ANX formula)

Range of c/a ratio

β-range

Atomic coordinates

Chemical properties

Example: STRUCTURE TYPES **COMPSTRU**

STUDY OF THE FAMILY **ABF6**

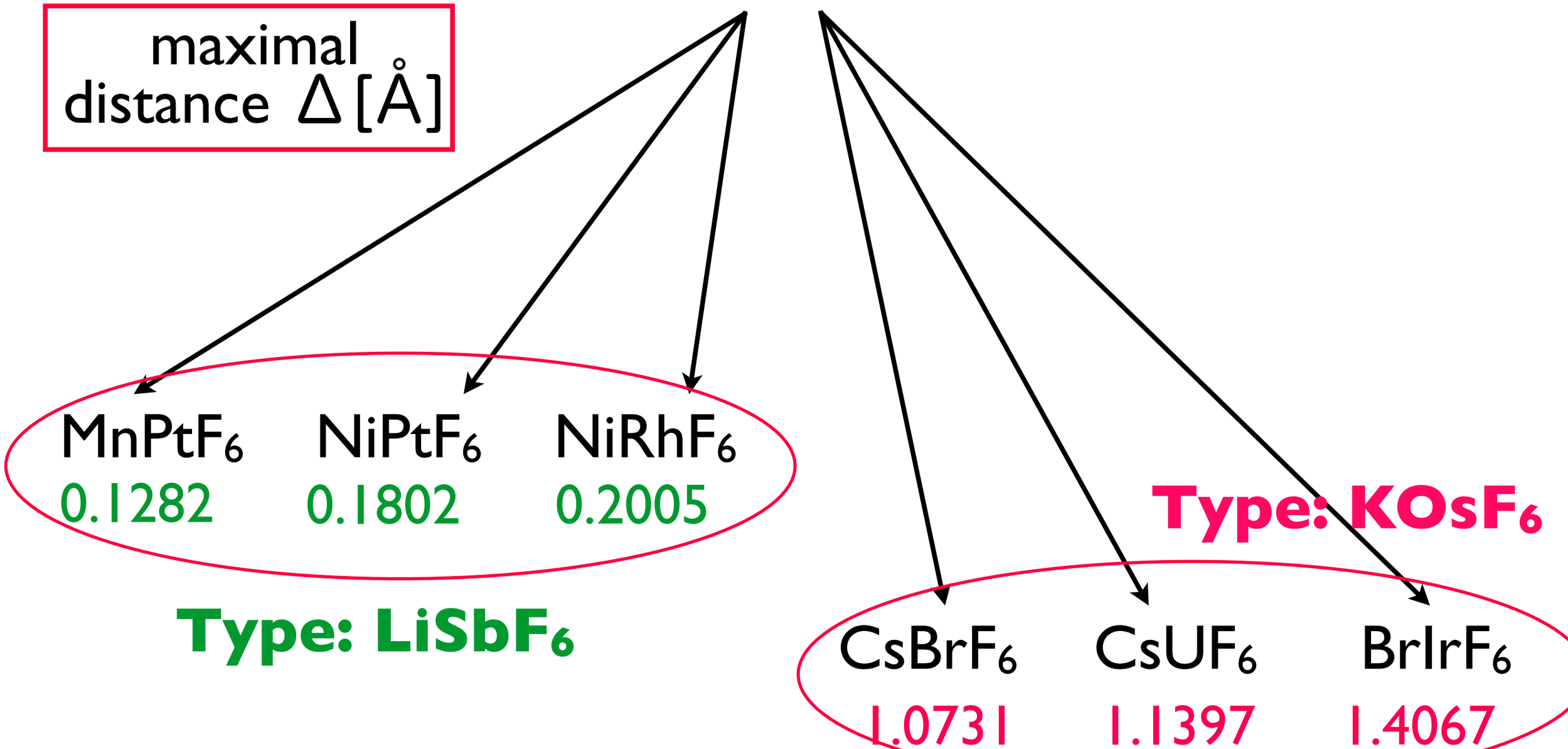
KCrF6	LiNbF6	VNbF6	HgRhF6	MgPbF6	InAsF6
RbCrF6	LiRuF6	CoZrF6	NiRhF6	ZnPbF6	CsNbF6
KAsF6	LiRhF6	PdPtF6	CaCrF6	NiPbF6	HgCrF6
RuAsF6	LiTaF6	FeNbF6	MgCrF6	MgPdF6	CoSnF6
CsAsF6	LiOsF6	CaSnF6	CdCrF6	CaPdF6	CsNbF6
RbSbF6	LiIrF6	FeZrF6	MnSnF6	ZnPdF6	MnPtF6
BaSnF6	LiPtF6	CuZrF6	FeSnF6	CdPdF6	CdRhF6
CsBrF6	LiAuF6	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]



Problem: Structural Phase transitions **STRUCTURE RELATIONS**

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.

Fd-3m High-symmetry phase

Symmetry-controlled mapping

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

(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

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

Evaluation of the Global Distortion

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

Low-symmetry structure

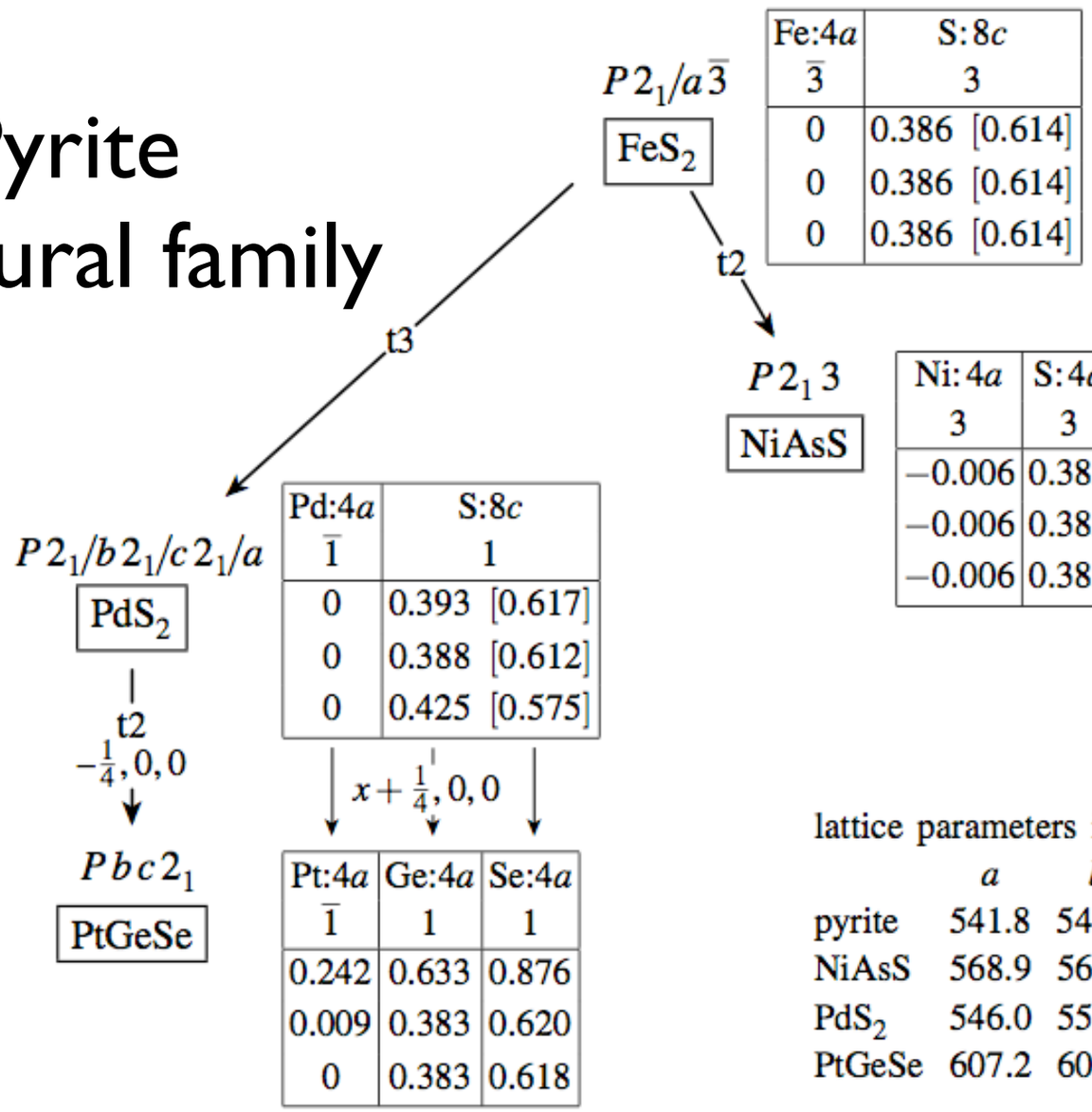
```
92
4.9586 4.9586 6.9074 90 90 90
1
Si     1    4a     0.302800 0.302800 0.000000
```

Problem:

Symmetry Relations between Homeotypic Crystal Structures Baernighausen Trees

STRUCTURE RELATIONS

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

Problem: PSEUDOSYMMETRY SEARCH

PSEUDO

Initial Structure $\mathcal{H}$ low symmetry	**Structural Pseudosymmetry** $\Leftrightarrow$ *Distortion*	Prototype Structure $\mathcal{G}$ high symmetry

Search for a structure of space-group symmetry G, supergroup of H, such that:

Structure H	=	**Structure G**	+	**small (symmetry-breaking) distortion**

If the distortion is small enough, it can indicate a symmetry change at high temperature.

phase transition

search for ferroics

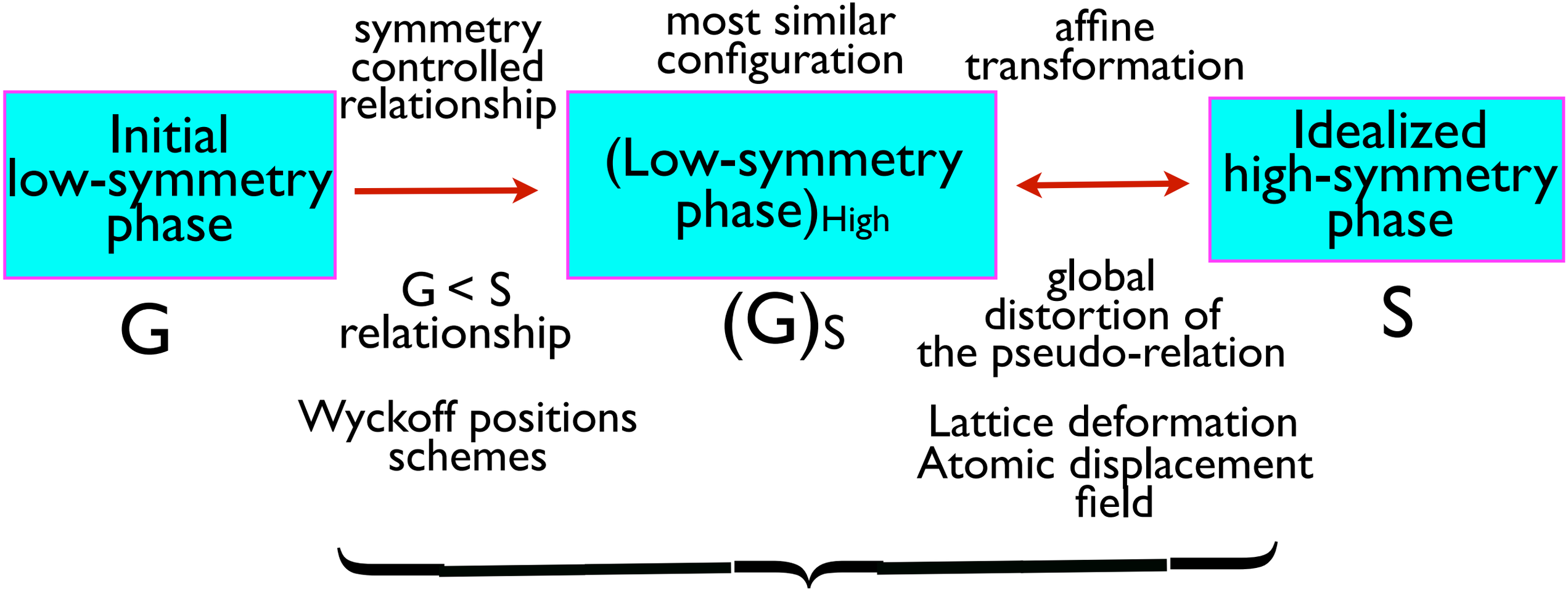
false symmetry assignments

Problem: Structural Pseudosymmetry PSEUDO

PROBLEM:

Given the initial structure specified by space-group symmetry G its unit-cell parameters and atomic coordinates

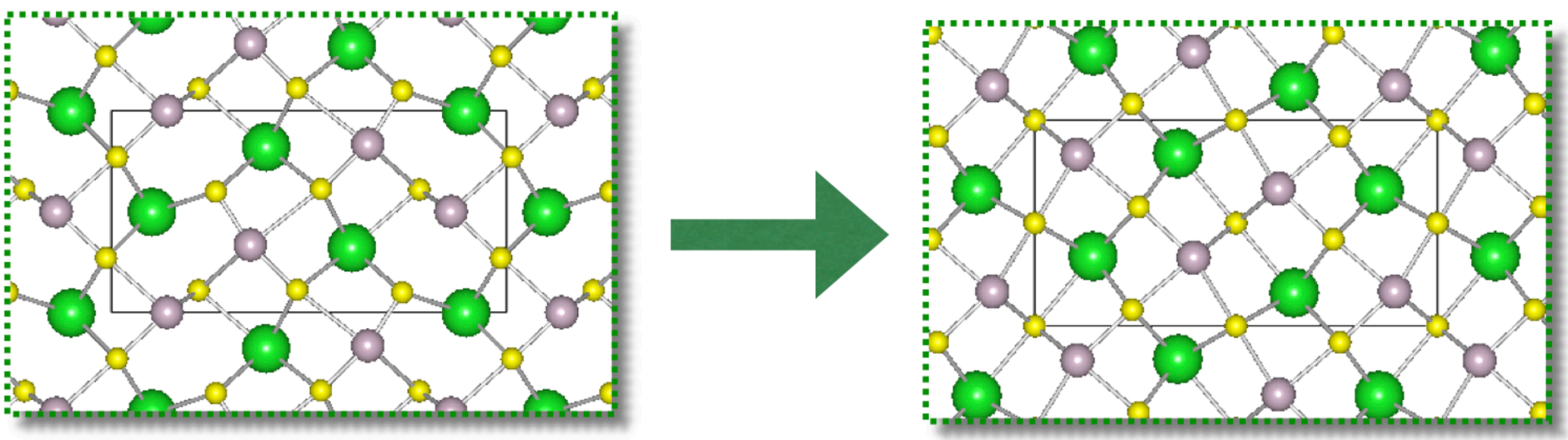
Search for a structure of space-group symmetry S>G such that the initial structure can be described by the high-symmetry structure with tolerably small distortion



Problem: Search for ferroelectrics as pseudosymmetric structures **PSEUDO**

Two necessary conditions for a structure to be ferroelectric:

- Polar symmetry group (it should allow non-zero polarization)
- Pseudosymmetry with respect to a non-polar symmetry group (the polar distortion should be small and “multistable”)



$Pna2_1$ $BaHgS_2$ Pbam

(max. displacement 0.49 A)

Problem: Prediction of *Pna2₁* ferroelectrics **PSEUDO**

	Binary	Ternary	Quaternary	Total
Entries	39	202	223	464
Compounds	26	125	161	312
Pseudo. Entries	20	100	40	160
Pseudo. Compounds	12	66	36	114
Overlooked Sym.	7	30	9	46
Known Ferro.	1	14	4	19
Candidates?	1	13	4	18

REPRESENTATIONS OF CRYSTALLOGRAPHIC GROUPS

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Space-group symmetry

Representations and Applications

REPRES	Space Groups Representations
Representations PG	Irreducible representations of the crystallographic Point Groups
Representations SG	Irreducible representations of the Space Groups
Get_irreps	Irreps and order parameters in a space group-subgroup phase transition
Get_mirreps	Irreps and order parameters in a paramagnetic space group- magnetic subgroup phase transition
DIRPRO	Direct Products of Space Group Irreducible Representations
CORREL	Correlations relations between the irreducible representations of a group-subgroup pair
POINT	Point Group Tables
SITESYM	Site-symmetry induced representations of Space Groups
COMPATIBILITY RELATIONS	Compatibility relations between the irreducible representations of a space group
MECHANICAL REP. ⚠	Decomposition of the mechanical representation into irreps
MAGNETIC REP. ⚠	Decomposition of the magnetic representation into irreps
BANDREP ⚠	Band representations and Elementary Band representations of Double Space Groups

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20-21 August 20

News:

- New Article in Nature
  07/2017: Bradlyn *et al.* "Topolo
  chemistry" *Nature* (2017). **547**,
- New program: BANDRE
  04/2017: Band representations
  Band representations of Doubl
- New section: Double po
  groups
  - New program: DG
    04/2017: General positi
    Space Groups
  - New program:
    REPRESENTATIONS DPG

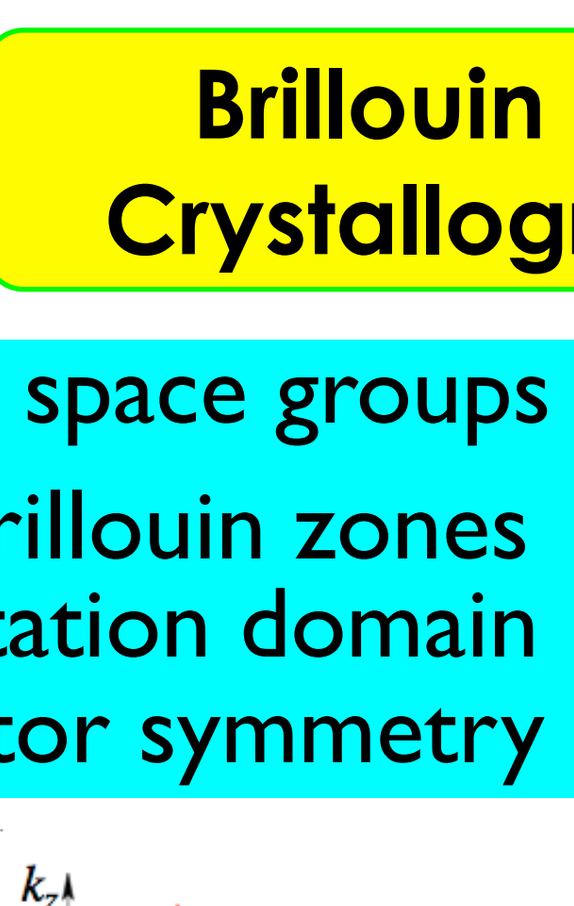
Brillouin Zone Database
Crystallographic Approach

Reciprocal space groups

Brillouin zones

Representation domain

Wave-vector symmetry

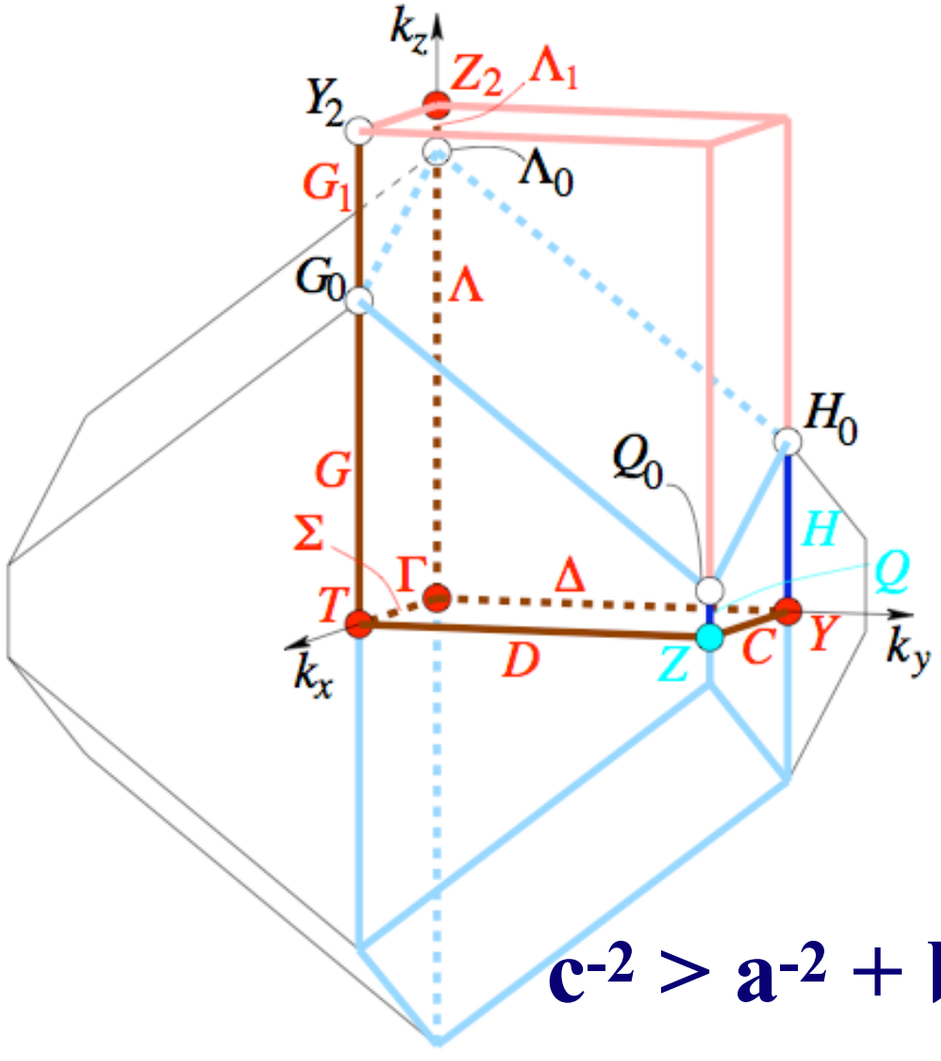


Symmorphic space groups

IT unit cells

Asymmetric unit

Wyckoff positions



The k-vector Types of Group 22 [*F*222]

k-vector description			Wyckoff Position			ITA description
CDML*		Conventional-ITA	ITA			
Label	Primitive					Coordinates
GM	0,0,0	0,0,0	a	2	222	0,0,0
T	1,1/2,1/2	0,1,1	b	2	222	0,1/2,1/2
T~T_2			b	2	222	1/2,0,0
Z	1/2,1/2,0	0,0,1	c	2	222	0,0,1/2
Y	1/2,0,1/2	0,1,0	d	2	222	0,1/2,0
Y~Y_2			d	2	222	1/2,0,1/2
SM	0,u,u ex	2u,0,0	e	4	2..	x,0,0 : 0 < x <= sm_0
U	1,1/2+u,1/2+u ex	2u,1,1	e	4	2..	x,1/2,1/2 : 0 < x < u_0
U~SM_1=[SM_0 T_2]			e	4	2..	x,0,0 : 1/2-u_0=sm_0 < x < 1/2
SM+SM_1=[GM T_2]			e	4	2..	x,0,0 : 0 < x < 1/2
A	1/2,1/2+u,u ex	2u,0,1	f	4	2..	x,0,1/2 : 0 < x <= a_0
C	1/2,u,1/2+u ex	2u,1,0	f	4	2..	x,1/2,0 : 0 < x < c_0

$$c^{-2} > a^{-2} + b^{-2}$$

Problem:

Compatibility relations between little-group representations **COMPREL**

Group-subgroup little-group pair

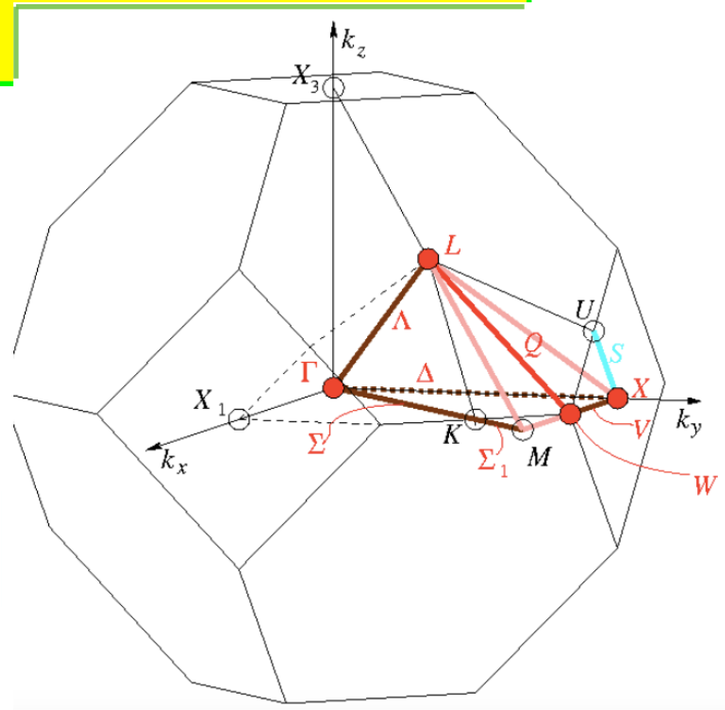
$$k' = k + \delta \begin{cases} k, G^k, D^{k,i} \\ k', G^{k'}, D^{k',j} \end{cases}$$

$G^k > G^{k'}$

Subduction of little group irreps

in the limit $\delta \longrightarrow 0$

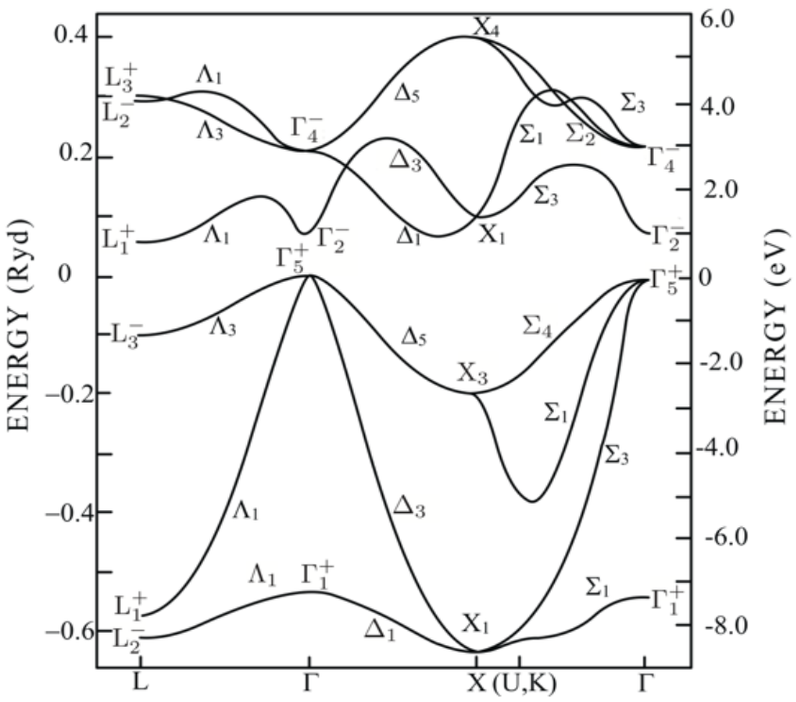
$$D^{k,i}(G^k)\downarrow G^{k'} \sim \bigoplus m_j D^{k'j}(G^{k'})$$

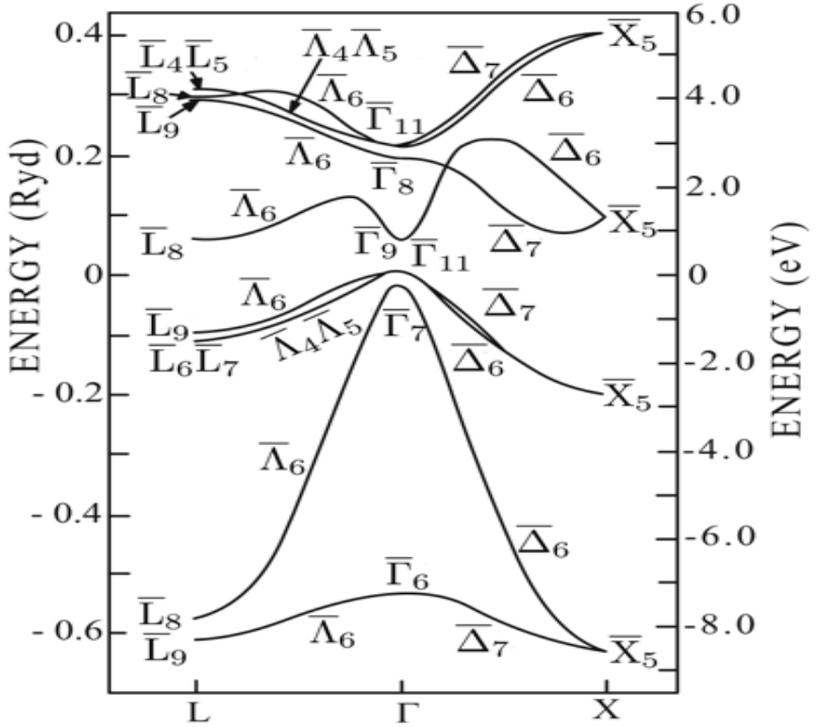


Electronic energy bands of Ge, Fd-3m (227)

Compatibility Relations
$GM_1^+(1) \rightarrow DT_1(1)$
$GM_1^-(1) \rightarrow DT_4(1)$
$GM_2^+(1) \rightarrow DT_2(1)$
$GM_2^-(1) \rightarrow DT_3(1)$
$GM_3^+(2) \rightarrow DT_1(1) \oplus DT_2(1)$
$GM_3^-(2) \rightarrow DT_3(1) \oplus DT_4(1)$
$GM_4^+(3) \rightarrow DT_4(1) \oplus DT_5(2)$
$GM_4^-(3) \rightarrow DT_1(1) \oplus DT_5(2)$
$GM_5^+(3) \rightarrow DT_3(1) \oplus DT_5(2)$
$GM_5^-(3) \rightarrow DT_2(1) \oplus DT_5(2)$
$\overline{GM}_6(2) \rightarrow \overline{DT}_7(2)$
$\overline{GM}_7(2) \rightarrow \overline{DT}_6(2)$
$\overline{GM}_8(2) \rightarrow \overline{DT}_7(2)$
$\overline{GM}_9(2) \rightarrow \overline{DT}_6(2)$
$\overline{GM}_{10}(4) \rightarrow \overline{DT}_6(2) \oplus \overline{DT}_7(2)$
$\overline{GM}_{11}(4) \rightarrow \overline{DT}_6(2) \oplus \overline{DT}_7(2)$

$X_1(2) \rightarrow DT_1(1) \oplus DT_3(1)$
$X_2(2) \rightarrow DT_2(1) \oplus DT_4(1)$
$X_3(2) \rightarrow DT_5(2)$
$X_4(2) \rightarrow DT_5(2)$

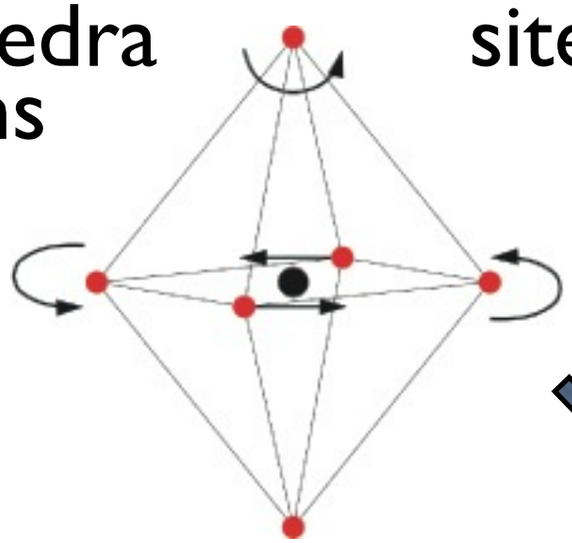




Problem: LOCALIZED and EXTENDED STATES **SITESYM**

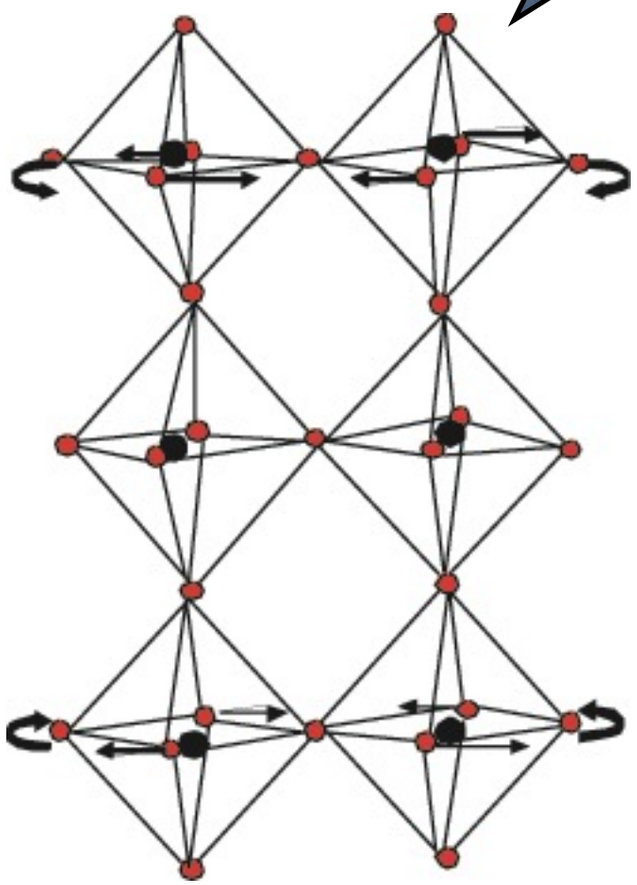
BO_6 octahedra rotations

site symmetry 4mm irrep A_2

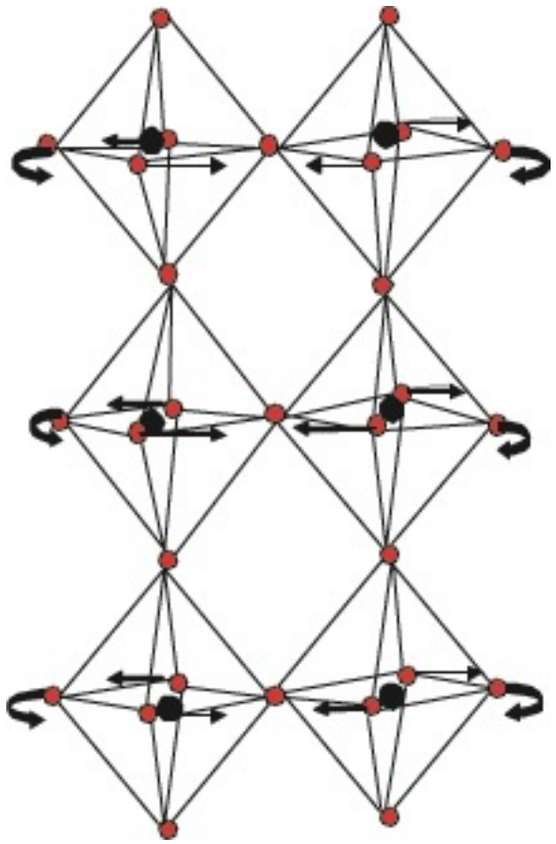


X_1^-

X_2^+



Crystal-extended modes in Aurivillius compounds



THANK YOU FOR YOUR ATTENTION!