

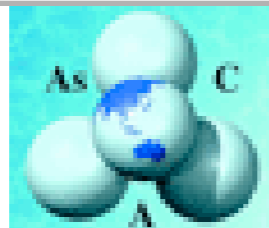
Group-theoretical Applications in the Study of Reconstructive Phase Transitions

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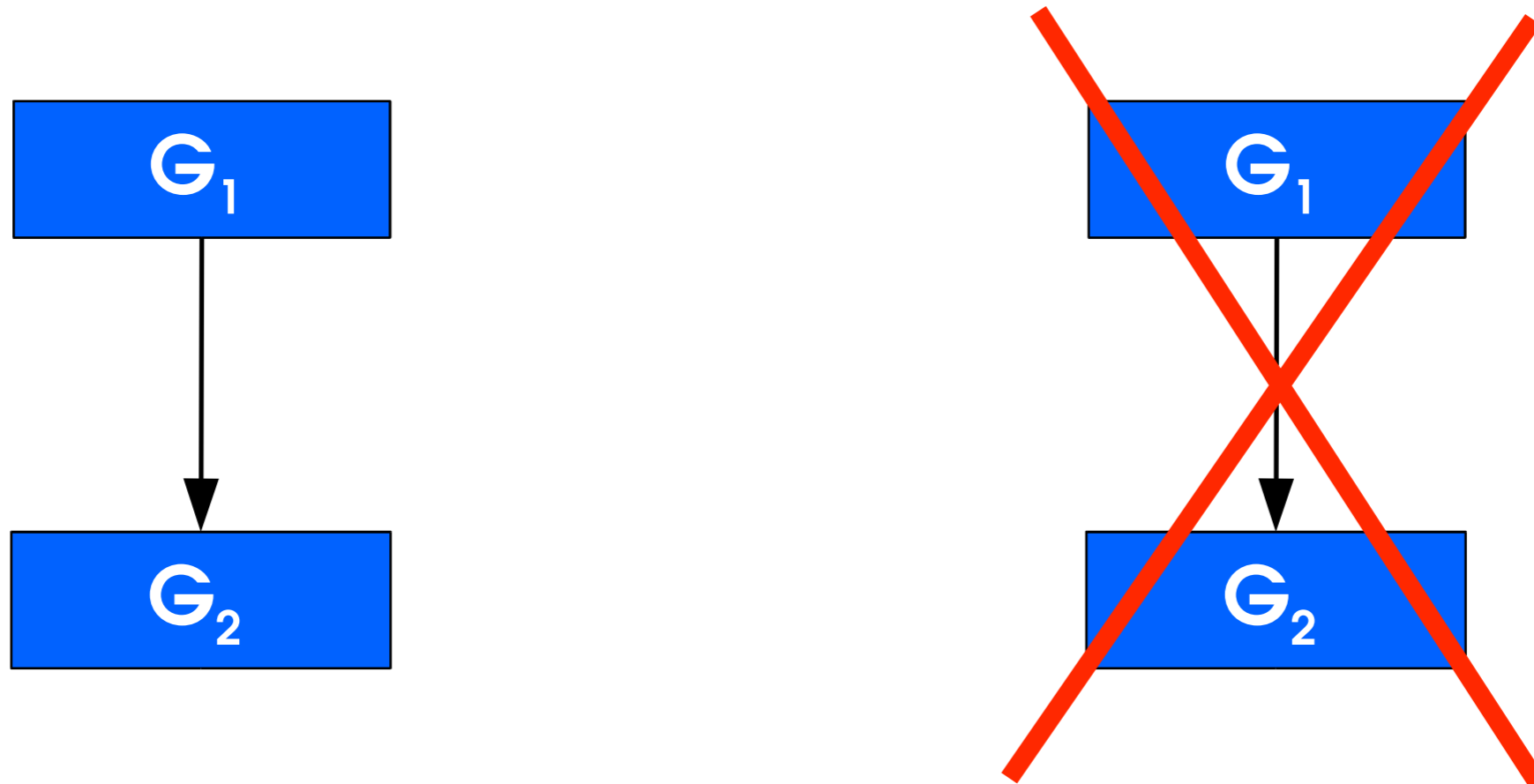


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Symmetry and Phase Transitions



Can symmetry relations be useful in the description of phase transitions with no group-subgroup relations between the phases ?

Examples of

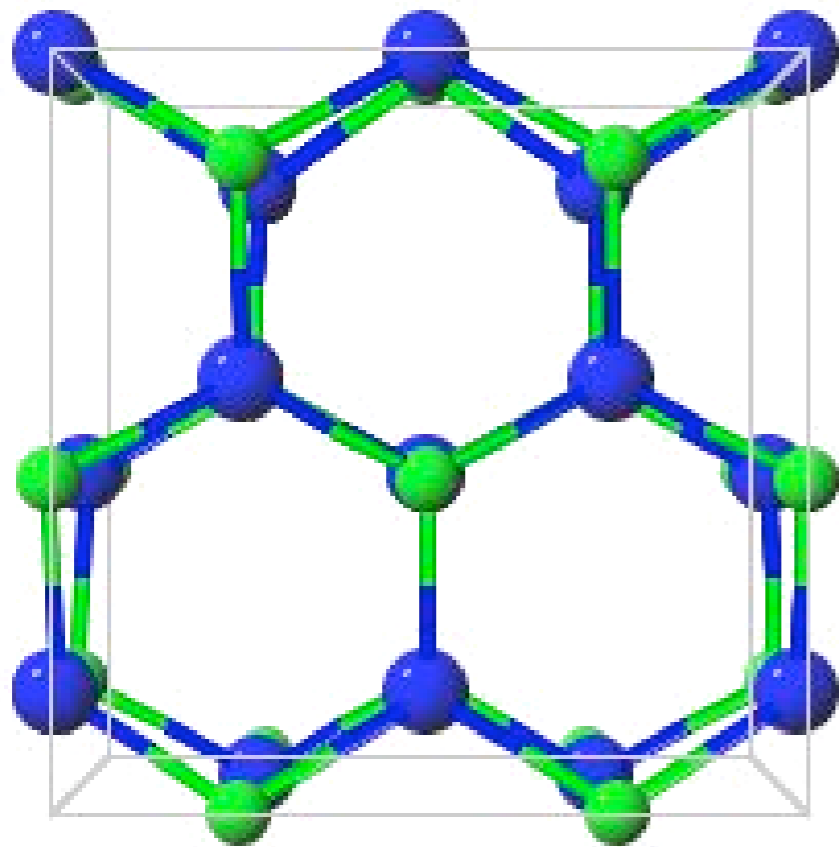
RECONSTRUCTIVE phase transitions

- ◆ NaCl (rocksalt) to CsCl type in alkali halides
- ◆ fcc to bcc in alkali metals as Cs
- ◆ Zincblende to rocksalt in SiC
- ◆ Wurtzite to NaCl (rocksalt) in binary semiconductors III-V and II-VI as GaN, InN, AlN, ZnO, MgO, CdS, CdSe...
- ◆ Wurtzite to Zincblende
- ◆ hcp to bcc phase in transition metals as Ti, Zr.
- ◆ hcp to bcc in Co, Fe, Tl, Am...

How to describe this transformation?

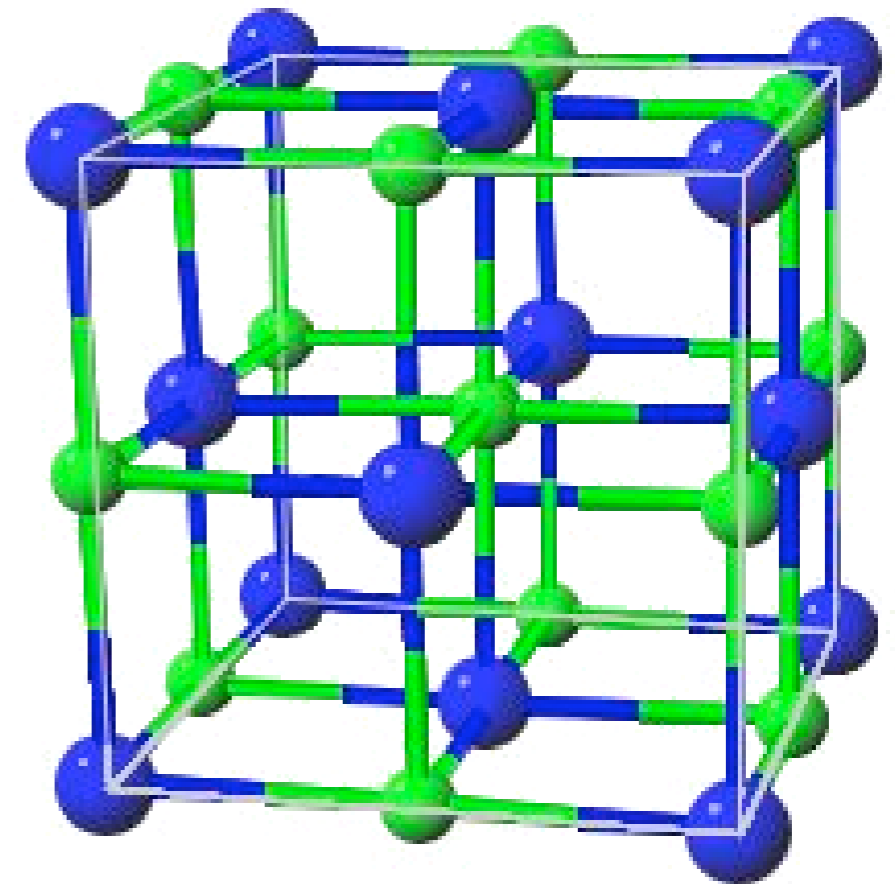
Wurtzite ($Z=2$, $Z_p=2$)

$$G_1 = P6_3mc$$



Rocksalt ($Z=4$, $Z_p=1$)

$$G_2 = Fm-3m$$



No group-subgroup relation between the phases

Example:

FERROELECTRIC phases in the system $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$

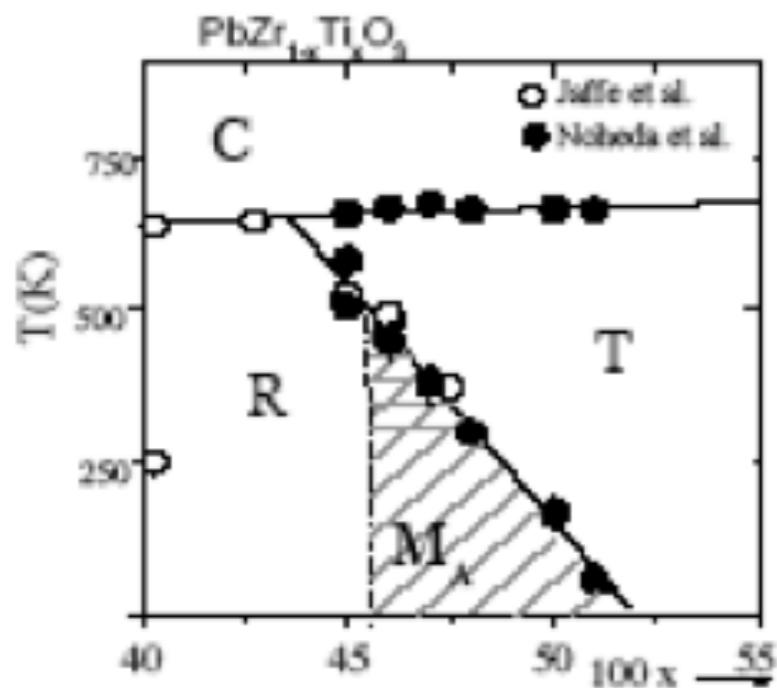
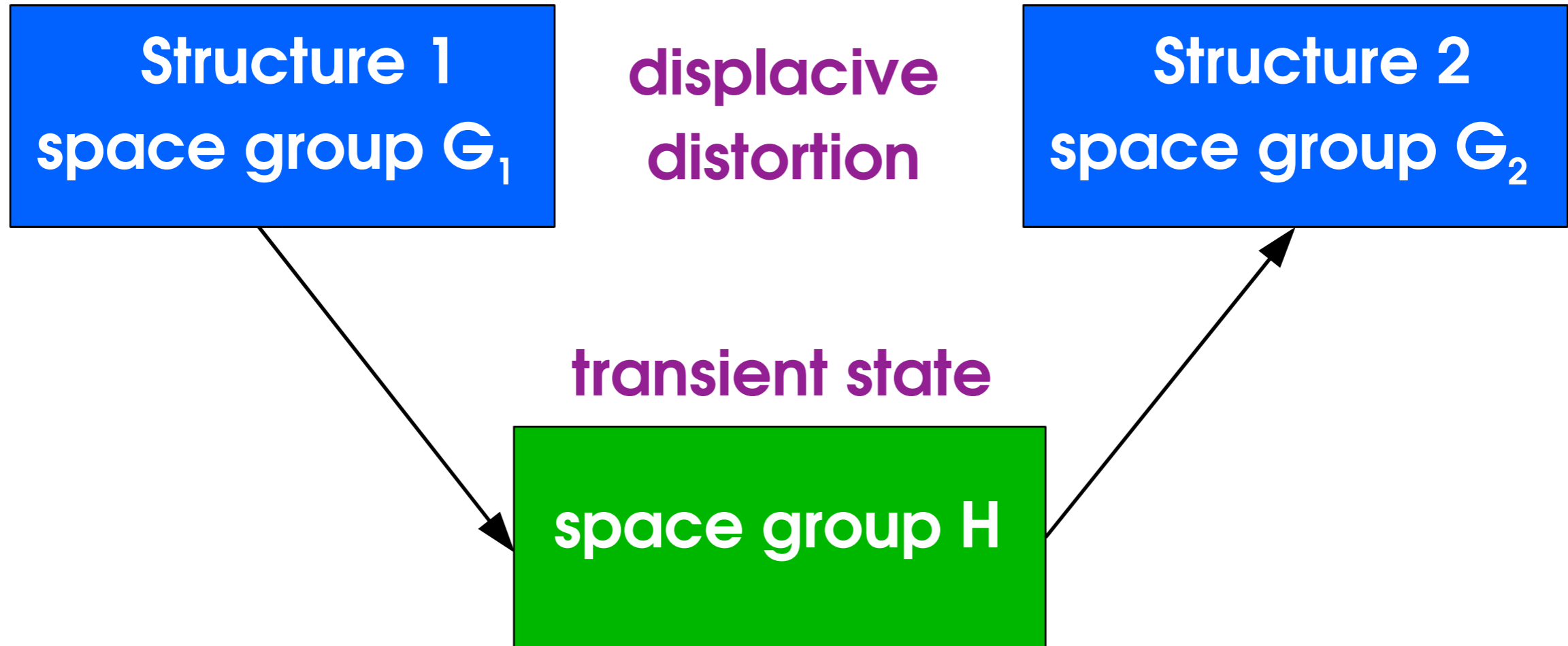


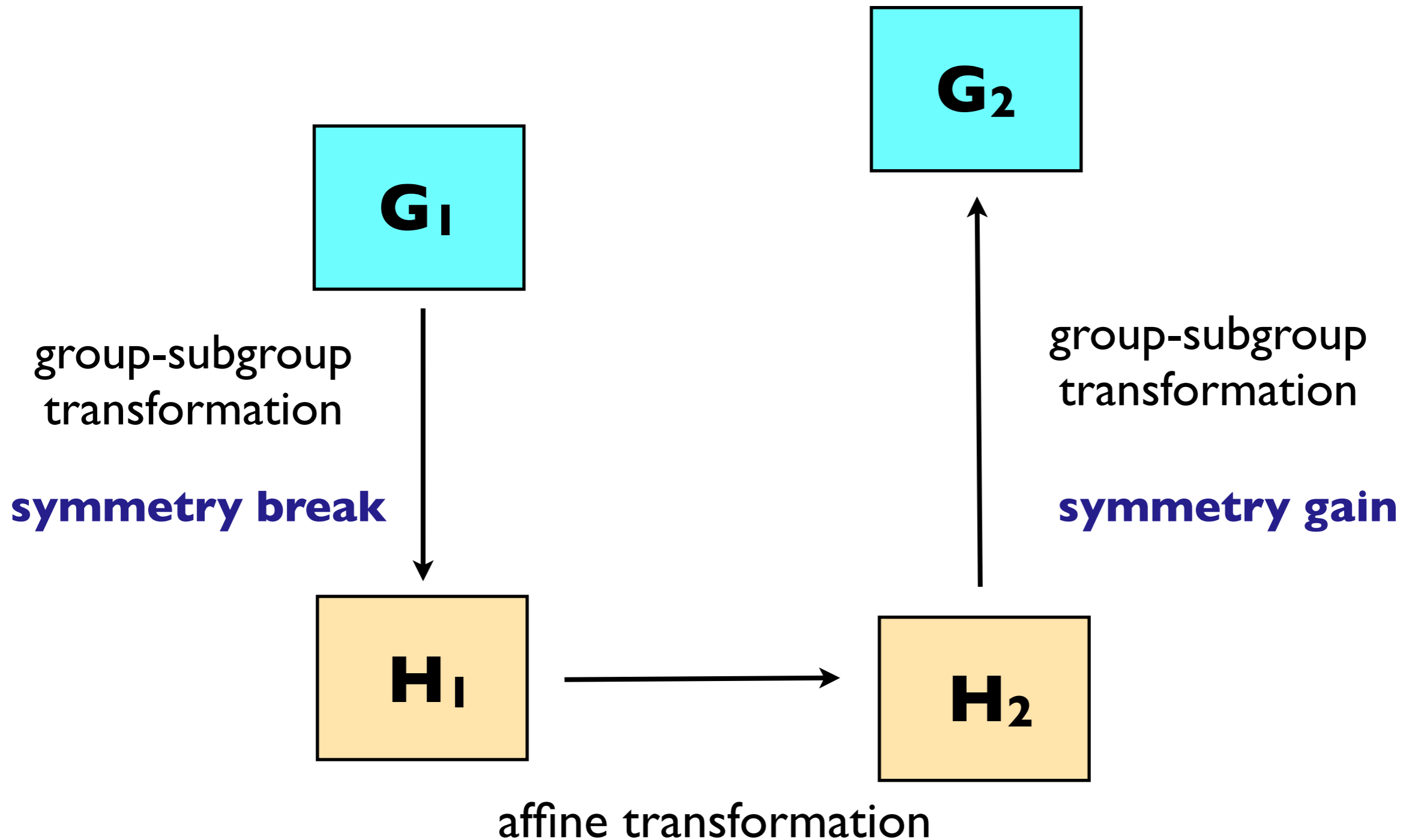
Fig.3. Phase diagram of PZT in the vicinity of its morphotropic phase boundary. C, R, and T represent cubic, rhombohedral and tetragonal regions. The diagonally-shaded M_A area represents the stability region of monoclinic phase. (D.E. Cox et al. Condensed Matter, cond-mat/0102457, 2001.)

Transition Paths

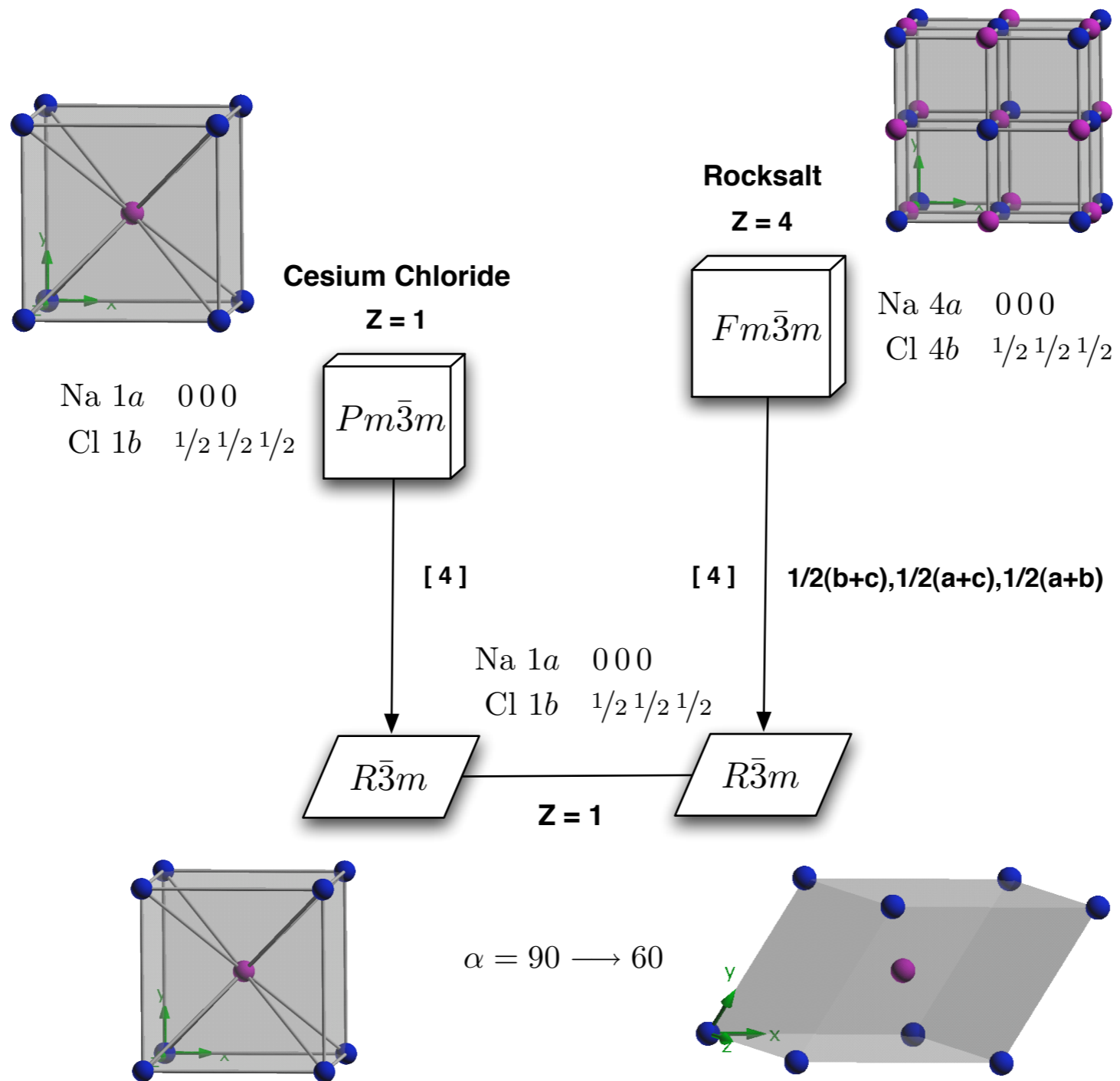


Only a single symmetry break and symmetry *gain*
for the whole transition path

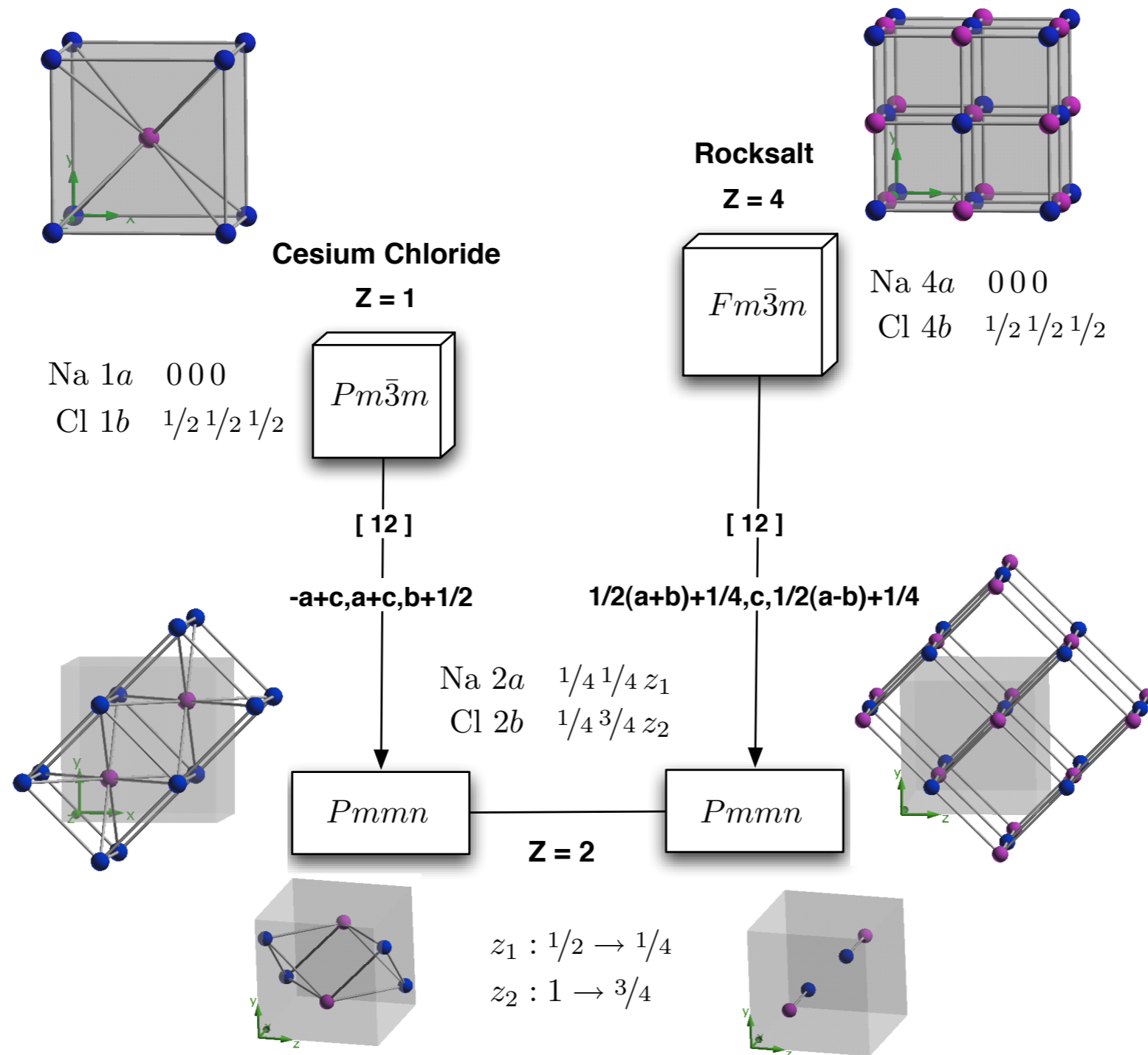
Transformation Mechanism: Group-theoretical Model



Buerger Mechanism: Group-theoretical Scheme



Watanabe Mechanism: Group-theoretical Scheme



The general problem:
**to find and analyze the most (energetically)
favourable transition paths**

Previous work:

phenomenology:

- **P. Tolédano, V. Dimtriev**

on symmetry aspects:

- **Sowa**
- **Hatch & Stokes**

Our problem:

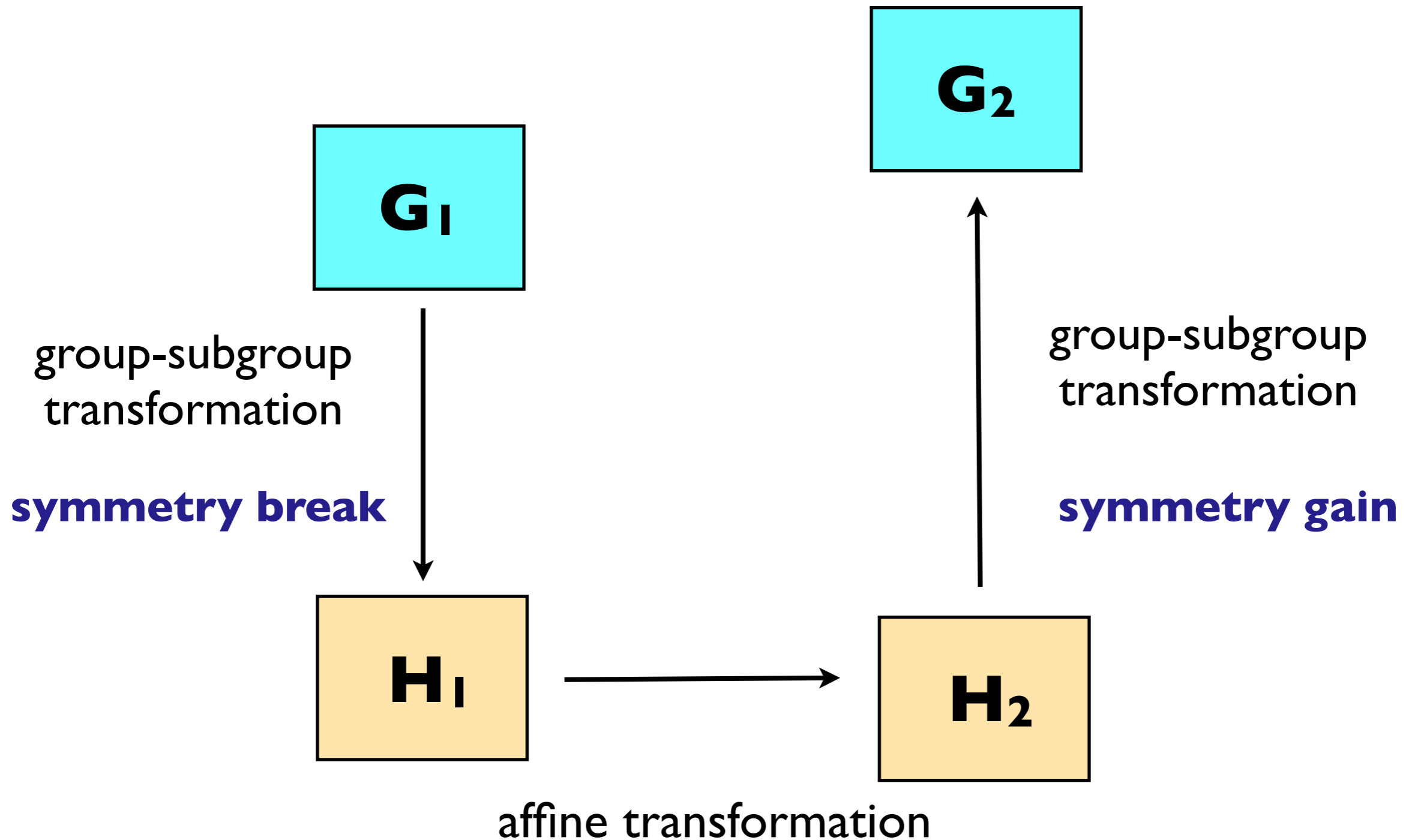
What can be derived only from symmetry arguments?

AIMs

- Description and classification of possible transition paths based on:
 - SYMMETRY conditions
 - STRUCTURAL conditions
- Development of the corresponding computer tools

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www.cryst.ehu.es

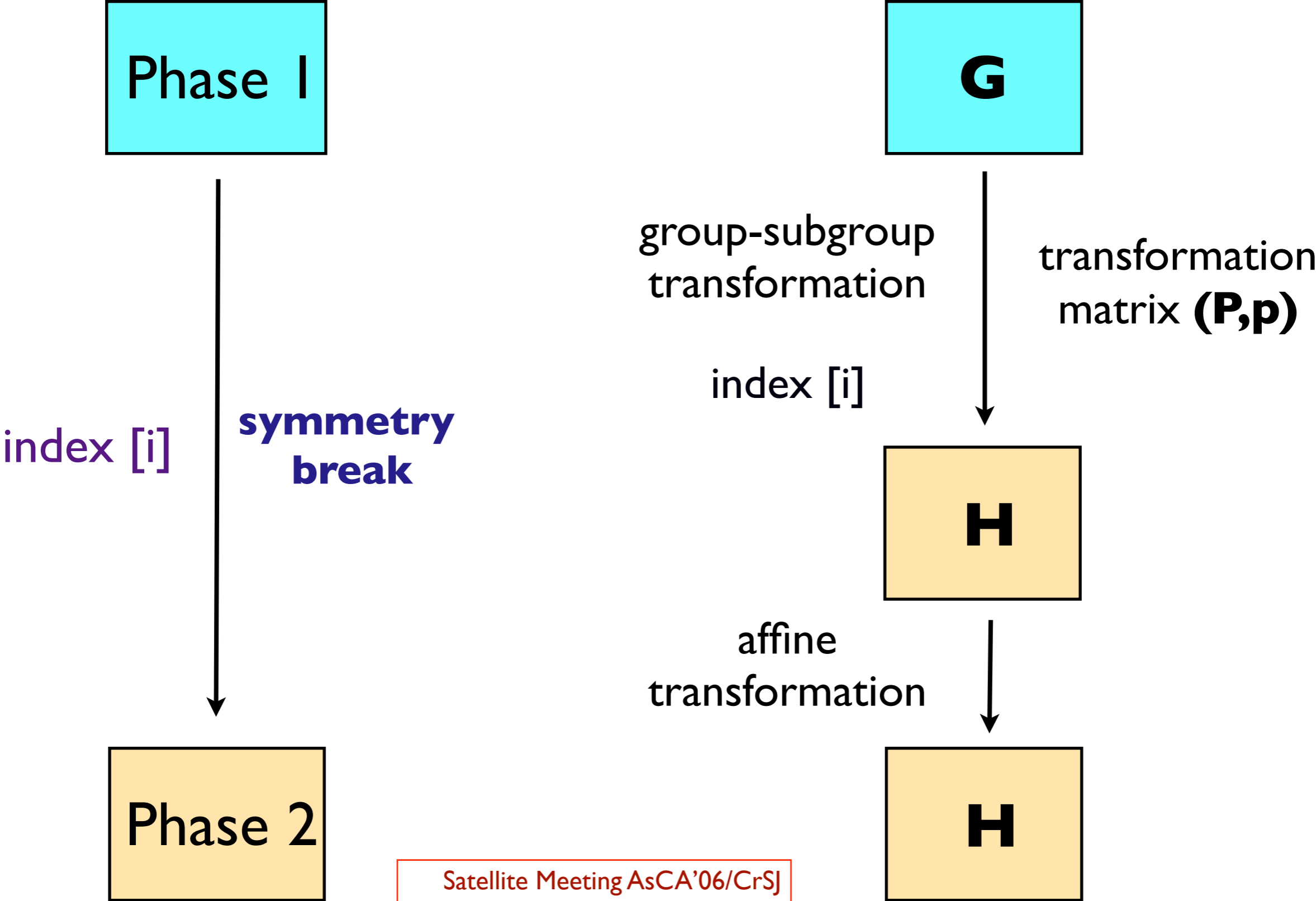
Transformation Mechanism: Group-theoretical Model



Symmetry Conditions

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

Group-subgroup related transformations



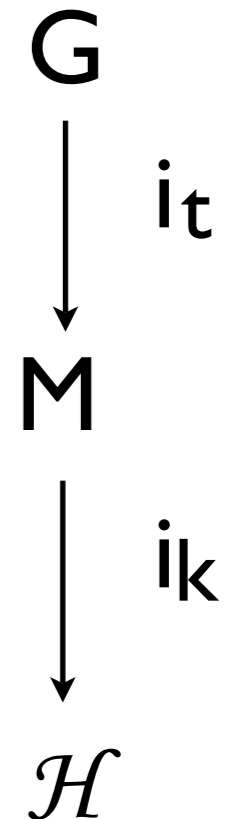
GROUP-SUBGROUP RELATIONS

Hermann, 1929:

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

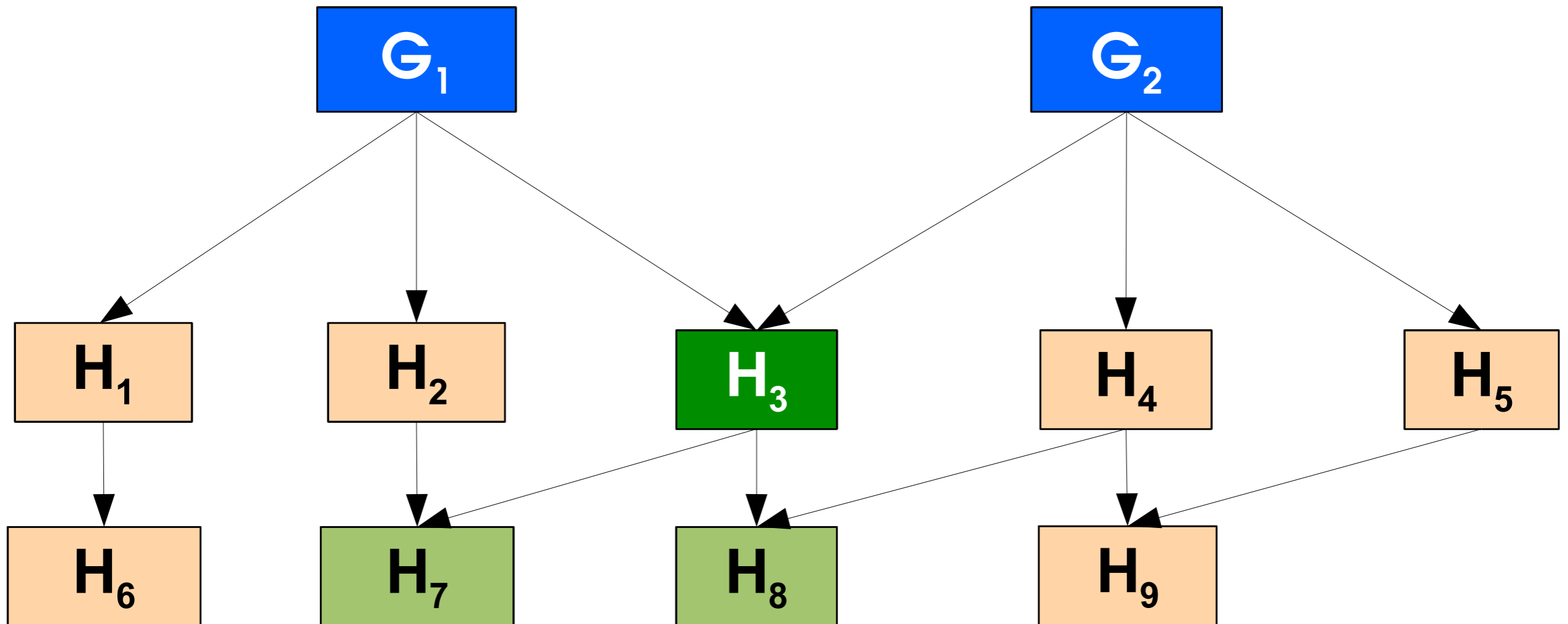
M is a t -subgroup of G

H is a k -subgroup of M

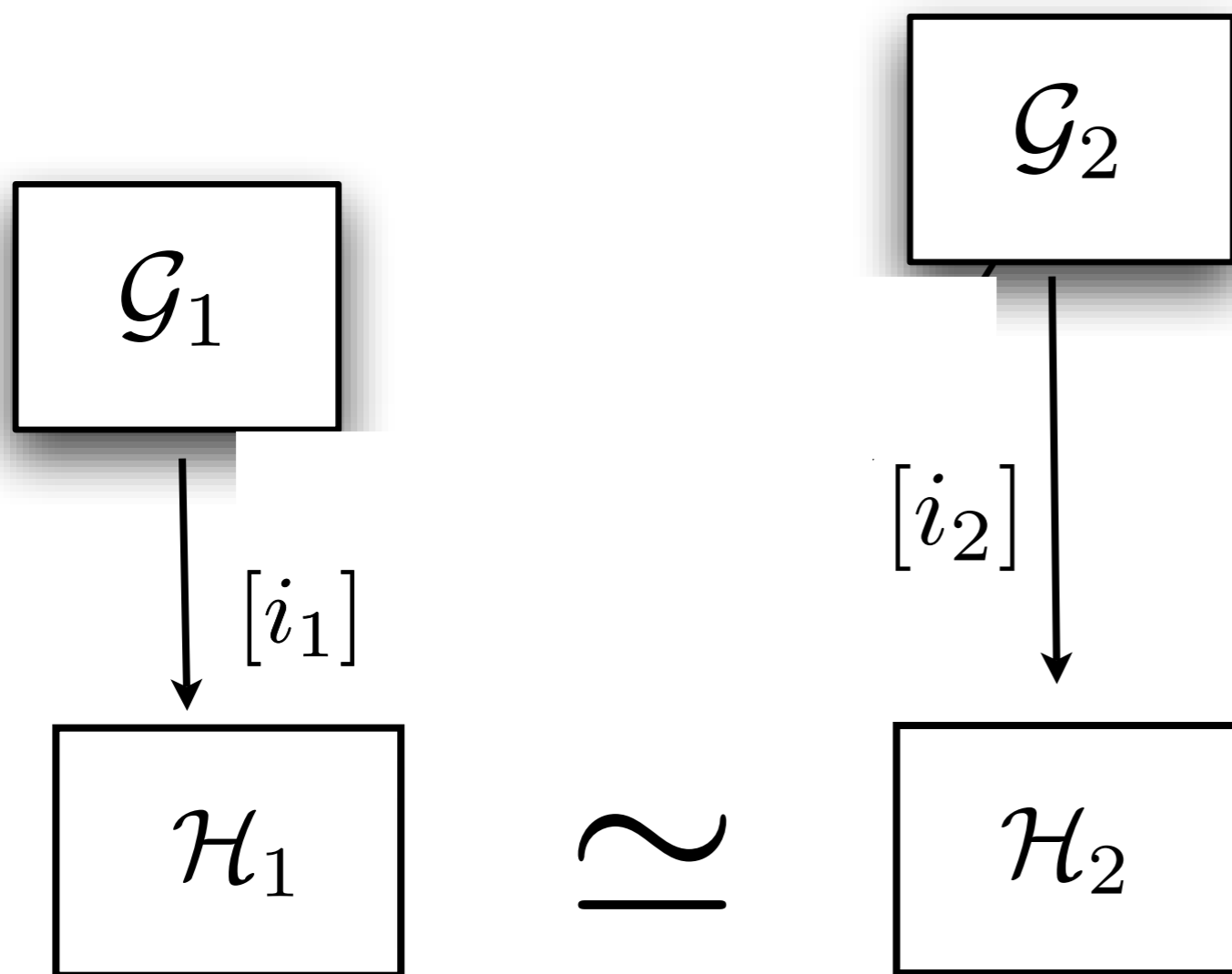


Symmetry conditions for TP

- ◆ **H is a common subgroup**



COMMON SUBGROUPS



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

$$i_1 = \frac{|\mathcal{P}_{G_1}|}{|\mathcal{P}_{\mathcal{H}_1}|} \cdot \frac{Z_{\mathcal{H}_1}^p}{Z_{G_1}^p}$$

$$i_2 = \frac{|\mathcal{P}_{G_2}|}{|\mathcal{P}_{\mathcal{H}_2}|} \cdot \frac{Z_{\mathcal{H}_2}^p}{Z_{G_2}^p}$$

index condition

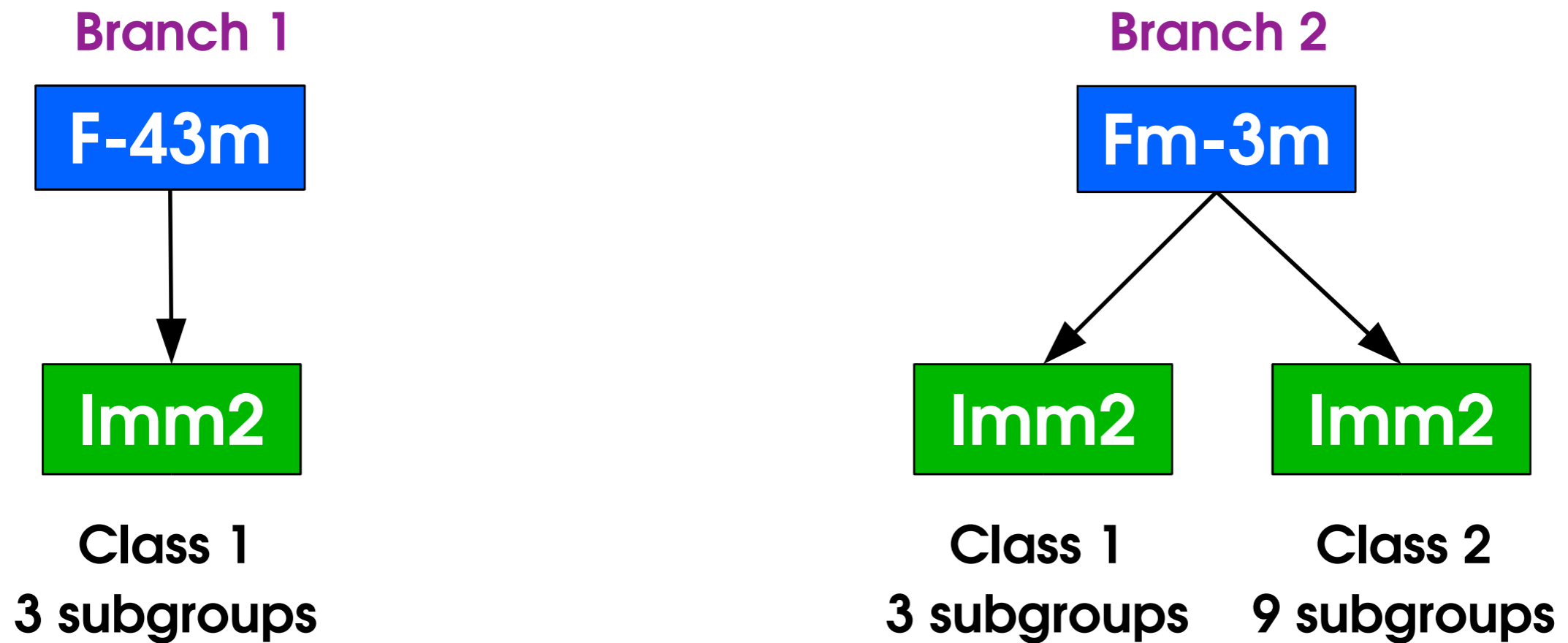
$$i_2 = i_1 \cdot \frac{Z_1}{Z_2} \cdot \frac{|\mathcal{P}_{G_2}|}{|\mathcal{P}_{G_1}|} \cdot \frac{f_{G_2}}{f_{G_1}}$$

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

COMMON SUBGROUPS

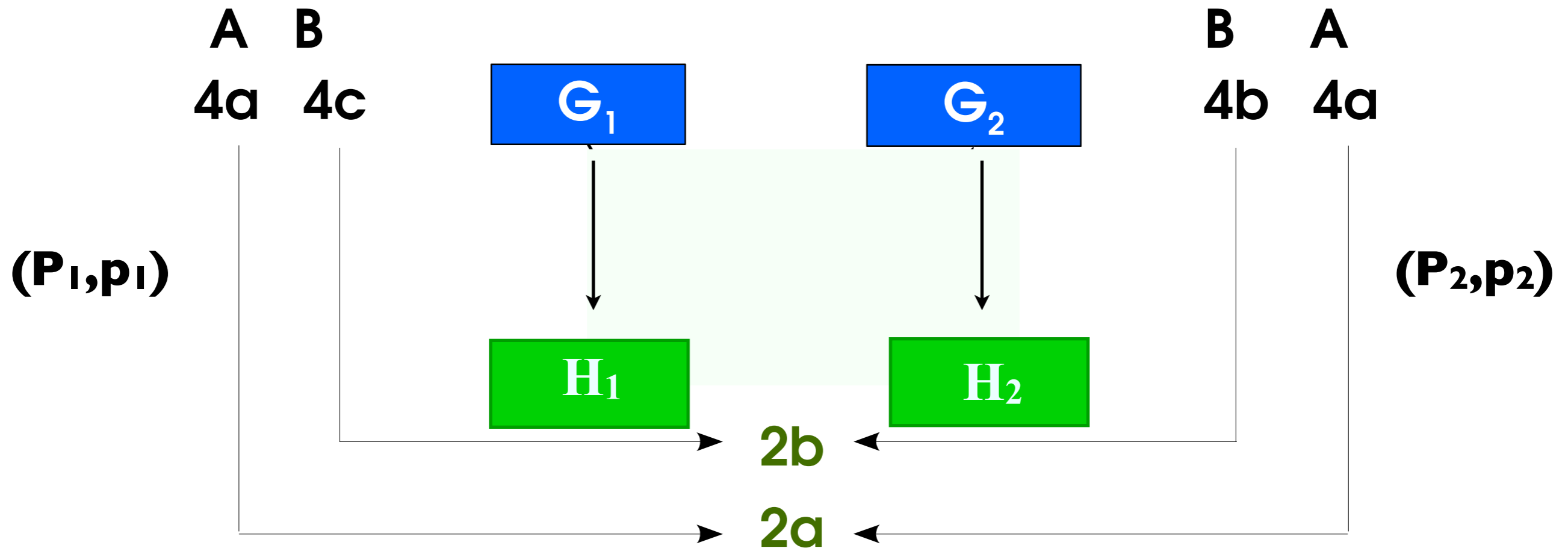
For each common subgroup (with determined indices)

- i. Lattice of maximal subgroups of the two lattices
- ii. Classification in conjugate subgroups
- iii. Only a representative for each class



Symmetry conditions for TP

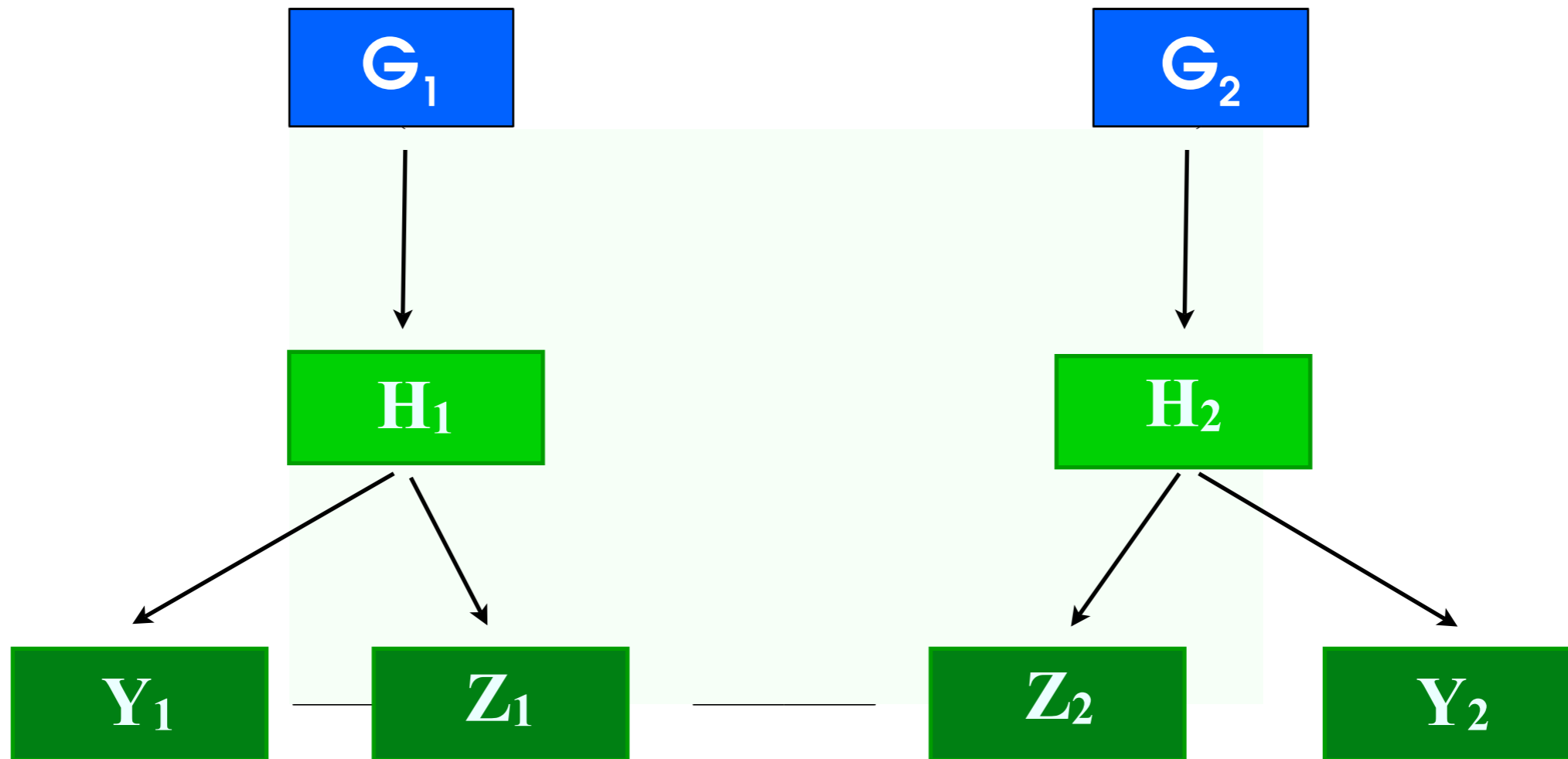
- ◆ H is a common subgroup
- ◆ Compatibility of the splittings of the occupied WP of the two structures in the common subgroup H.



Order – disorder mechanisms not included!

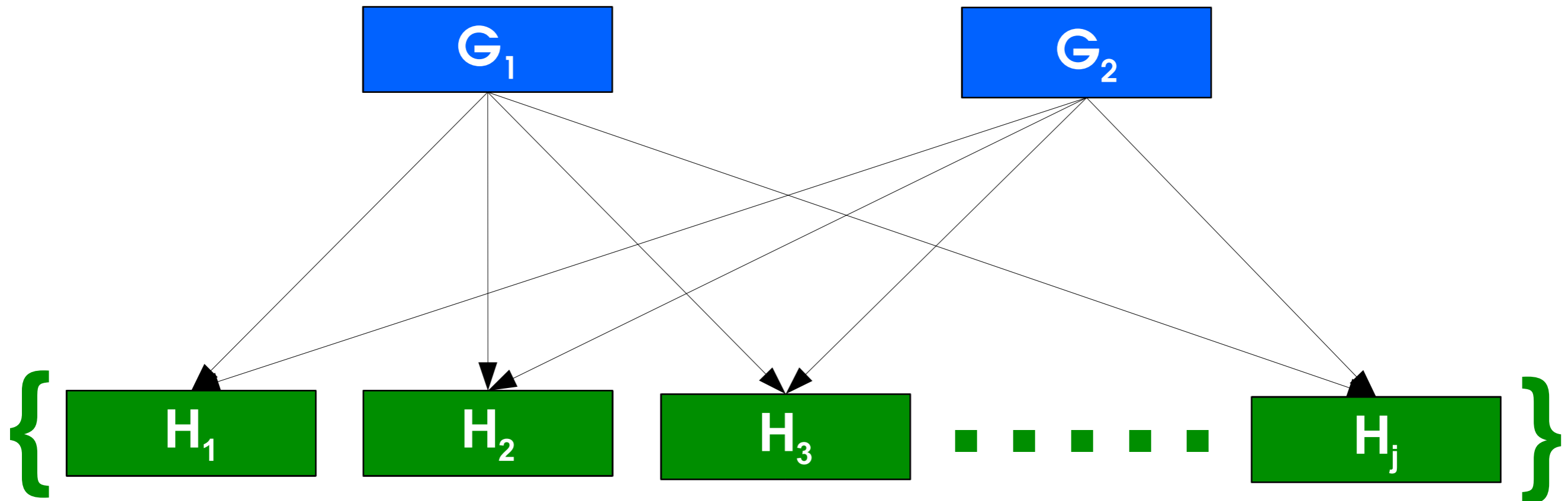
Symmetry conditions for TP

If symmetry conditions are fulfilled by H,
fulfilled by all its subgroups



Maximal-symmetry transition paths are candidates for energetically favourable transient states!

Maximal symmetry transition paths



Set of paths fulfilling the two symmetry conditions and having maximal symmetry

Finite if the cell multiplication in H is limited

Structural Conditions

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

Strain Calculation

$$\mathbf{X}_1 = R_1 \cdot \mathbf{x}_1 \quad \mathbf{X}_2 = R_2 \cdot \mathbf{x}_2 \quad R_i = \begin{pmatrix} a_i \sin(\beta_i) \sin(\gamma_i^*) & 0 & 0 \\ -a_i \sin(\beta_i) \cos(\gamma_i^*) & b_i \sin(\alpha_i) & 0 \\ a_i \cos(\beta_i) & b_i \cos(\alpha_i) & c_i \end{pmatrix}$$

Strain definition:

$$\mathbf{X}_2 - \mathbf{X}_1 = e \cdot \mathbf{X}_1 \quad \text{with} \quad e = R_2^{-1} R_1 - I$$

$$M_i = \begin{pmatrix} \vec{a}_i \cdot \vec{a}_i & \vec{a}_i \cdot \vec{b}_i & \vec{a}_i \cdot \vec{c}_i \\ \vec{b}_i \cdot \vec{a}_i & \vec{b}_i \cdot \vec{b}_i & \vec{b}_i \cdot \vec{c}_i \\ \vec{c}_i \cdot \vec{a}_i & \vec{c}_i \cdot \vec{b}_i & \vec{c}_i \cdot \vec{c}_i \end{pmatrix}$$

← metric tensor

← standard root tensor

$$\eta = \frac{1}{2}(e + e^T + e^T e) = \frac{1}{2} R_1^{-T} (M_1 - M_2) R_1^{-1}$$

Degree of lattice distortion:

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

Valid for linear and non-linear strains!

Mappings of the Atoms

Establishes the connection between the two end phases
in the subgroup reference frame
(defines the transition path)

Atom	Coordinates in S_1	Atom	Coordinates in S_2	Atomic Distances			
				d_x	d_y	d_z	$ d $
Si1[1]	(0,0,0)	Si1[1]	(0,0,0)	0	0	0	0
Si1[2]	(1/2,1/2,1/2)	Si1[2]	(1/2,1/2,1/2)	0	0	0	0
C2[1]	(0,1/2,1/4)	C2[1]	(0,1/2,0)	0	0	+1/4	0.99350
C2[2]	(1/2,0,3/4)	C2[2]	(1/2,0,1/2)	0	0	+1/4	0.99350

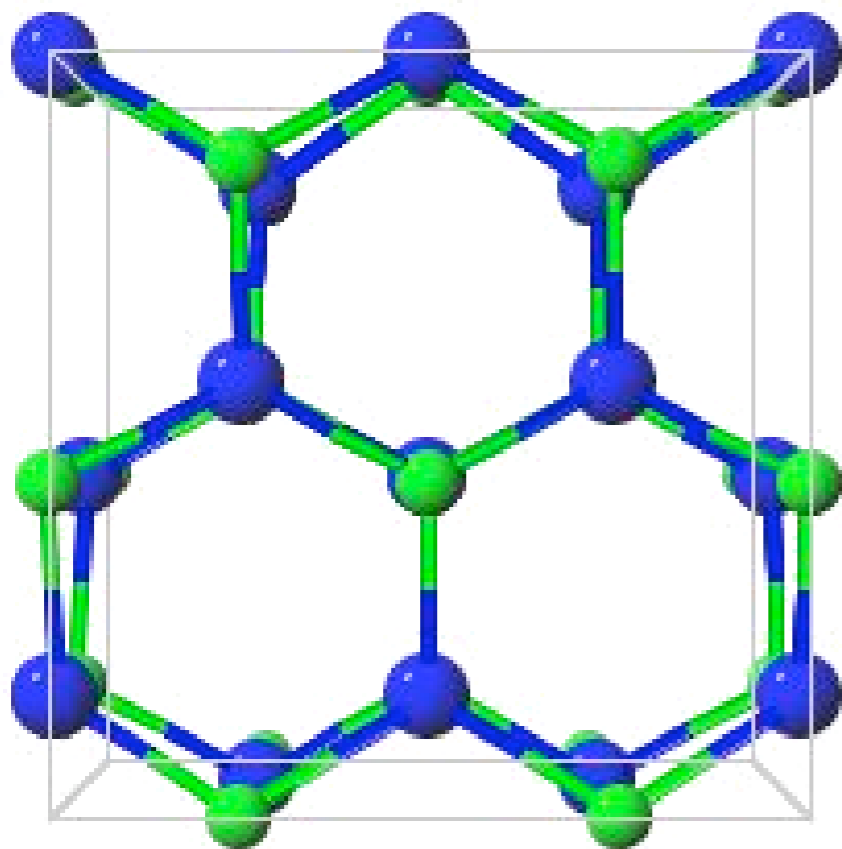
Structural condition (maximum atomic distance in the transformation):

$$\Delta_{max} < \Delta_{tol}$$

Example: Wurtzite to rocksalt in GaN

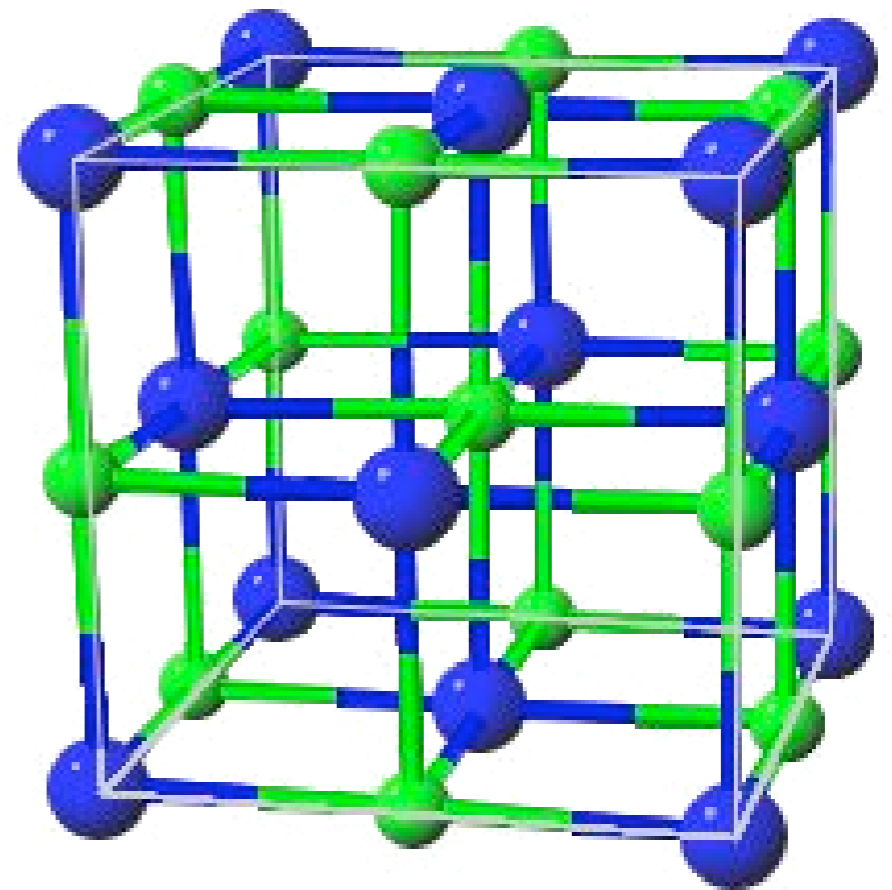
Wurtzite ($Z=2$, $Z_p=2$)

$G_1 = P6_3mc$



Rocksalt ($Z=4$, $Z_p=1$)

$G_2 = Fm-3m$



Example: Wurtzite to rocksalt in GaN

Wurtzite ($Z=2$, $Z_p=2$)

$$G_1 = P6_3mc$$

A	$2b$	$1/3$	$2/3$	0
B	$2b$	$1/3$	$2/3$	$z \sim 3/8$

Rocksalt ($Z=4$, $Z_p=1$)

$$G_2 = Fm-3m$$

A	$4a$	0	0	0
B	$4c$	$1/2$	$1/2$	$1/2$



What is the full set of symmetries, candidates for energetically favorable intermediate transient states?

Cmc2₁ TP: Displacements

Wurtzite (Z=2, Z_p=2)

$$G_1 = P6_3mc$$

A	2b	1/3	2/3	0
B	2b	1/3	2/3	z ~ 3/8

-a-b, a+b, c

A	2a	0	y ₁	z ₁ =0
B	2a	0	y ₂	z ₂

Rocksalt (Z=4, Z_p=1)

$$G_2 = Fm-3m$$

A	4a	0	0	0
B	4c	1/2	1/2	1/2

a, b-1/4, c

A	2a	0	y ₁	z ₁ =0
B	2a	0	y ₂	z ₂

Z_p=2
H = Cmc2₁

$$\begin{array}{ccc}
 y_1 = 1/3 & \longleftrightarrow & 1/4 \\
 y_2 = 1/3 & \longleftrightarrow & 1/4 \\
 z_2 \approx 3/8 & \longleftrightarrow & 1/2
 \end{array}$$

y₁(A), y₂(B) and z₂(B)
coordinates are
the internal degrees
of freedom

Cmc2₁ TP: Cell parameters

Wurtzite (Z=2, Z_p=2)

$$G_1 = P6_3mc$$

A	2b	1/3	2/3	0
B	2b	1/3	2/3	z ~ 3/8

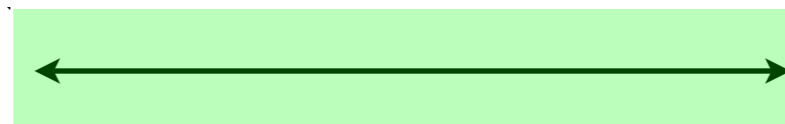
Rocksalt (Z=4, Z_p=1)

$$G_2 = Fm-3m$$

A	4a	0	0	0
B	4c	1/2	1/2	1/2

Z_p=2
H = Cmc2₁

$$a_w, \sqrt{3}a_w, c_w$$



$$a_r, a_r, a_r$$

$$\begin{array}{l} \mathbf{a:} \quad a_w \text{ --- } a_r \\ \mathbf{b:} \quad \sqrt{3}a_w \text{ --- } a_r \\ \mathbf{c:} \quad c_w \text{ --- } a_r \end{array}$$

Cell parameters
a,b,c are the
external degrees
of freedom

Maximal Transition Paths

Wurtzite ($Z=2$, $Z_p=2$)

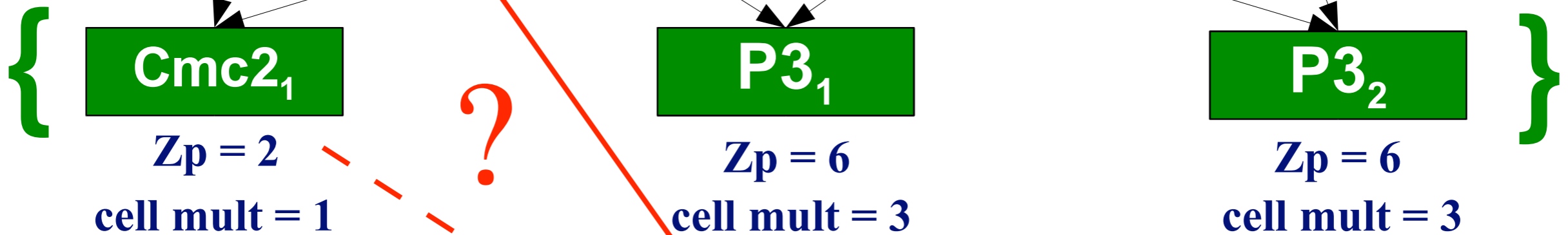
$$G_1 = P6_3mc$$

G_1

Rocksalt ($Z=4$, $Z_p=1$)

$$G_2 = Fm-3m$$

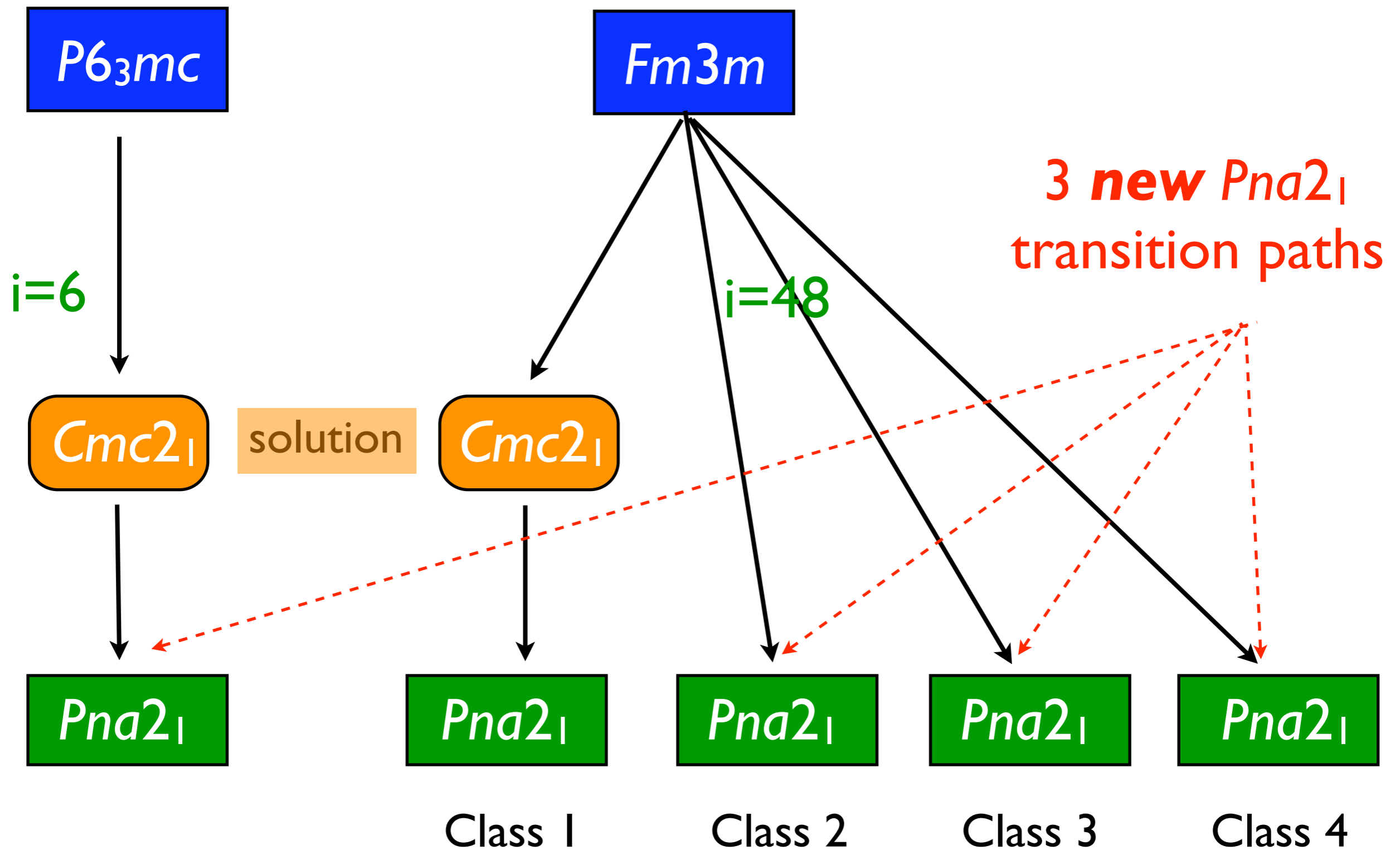
G_2



- Sowa 2001
- Lambrecht et al. 2001

$Pna2_1$

Maximal Transition Paths



Example: Wurtzite to Rocksalt

Maximal symmetry transition paths: $\mathcal{S} < 0.25$ $\Delta_{tol} < 2\text{\AA}$

TP	\mathcal{H}	\mathcal{S}	Lattice parameters in $(\mathcal{H}_1, \mathcal{H}_2)$					
1	(036) $Cmc2_1$	0.1977	3.1900	5.5252	5.1890	90	90	90
			4.0060	4.0060	4.0060	90	90	90
2	(033) $Pna2_1$	0.1218	5.5252	3.1900	5.1890	90	90	90
			5.6653	2.8327	4.0060	90	90	90
3	(031) $Pmn2_1$	0.1218	3.1900	5.5252	5.1890	90	90	90
			2.8327	5.6653	4.0060	90	90	90
4	(026) $Pmc2_1$	0.1592	3.1900	5.5252	5.1890	90	90	90
			2.8327	4.0060	5.6653	90	90	90
5	(007) Pc	0.1576	7.5798	3.1900	5.5252	90	136.80	90
			4.9067	2.8327	5.6653	90	125.27	90
6	(007) Pc	0.1562	7.5798	3.1900	5.5252	90	136.80	90
			6.9386	2.8327	5.6653	90	144.74	90

