Group-theoretical Applications in the Study of Reconstructive Phase Transitions

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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, Ti, Am...
How to describe this transformation?

Wurtzite (Z=2, Zp=2)  
\[ G_1 = P6_3mc \]

Rocksalt (Z=4, Zp=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

Structure 1
space group $G_1$

transient state

space group $H$

Structure 2
space group $G_2$

displacive distortion

Only a single symmetry break and symmetry gain for the whole transition path
Transformation Mechanism: Group-theoretical Model

- Group-subgroup transformation
- Symmetry break
- Affine transformation
- Group-subgroup transformation
- Symmetry gain

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Buerger Mechanism: Group-theoretical Scheme

Cesium Chloride
Z = 1
Na 1a 0 0 0
Cl 1b 1/2 1/2 1/2

Rocksalt
Z = 4
Na 4a 0 0 0
Cl 4b 1/2 1/2 1/2

\[ \alpha = 90 \rightarrow 60 \]

\[ \mathbf{Pm3m} \rightarrow \mathbf{R3m} \]

\[ 1/2(b+c),1/2(a+c),1/2(a+b) \]
Watanabe Mechanism: Group-theoretical Scheme

Cesium Chloride
Z = 1

Rocksalt
Z = 4

Na 4a 0 0 0
Cl 4b 1/2 1/2 1/2

Pm\bar{3}m

Na 1a 0 0 0
Cl 1b 1/2 1/2 1/2

-a+c, a+c, b+1/2

1/2(a+b)+1/4, c, 1/2(a-b)+1/4

Pm\bar{3}m

Na 2a 1/4 1/4 z1
Cl 2b 1/4 3/4 z2

Z = 2

Pmmn

z1 : 1/2 → 1/4
z2 : 1 → 3/4

Pmmn
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

Bilbao Crystallographic Server

www.cryst.ehu.es
Transformation Mechanism: Group-theoretical Model

- **Group-theoretical Model**

  - **Satellite Meeting AsCA’06/CrSJ**
  - **November 18-19, Tsukuba, Japan**
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

Phase 1

index \([i]\)

Phase 2

symmetry break

Group-subgroup transformation

transformation matrix \((P,p)\)

index \([i]\)

affine transformation

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Hermann, 1929:

For each pair $G > H$, there exists a uniquely defined intermediate subgroup $M$, $G \supseteq M \supseteq H$, 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
the set of common subgroup types is finite if a maximum k-index is defined

\[ Z_{\mathcal{H}_1} = Z_{\mathcal{H}_2} \]

\[ i_1 = \frac{|\mathcal{P}_{\mathcal{G}_1}|}{|\mathcal{P}_{\mathcal{H}_1}|} \cdot \frac{Z_{\mathcal{H}_1}^p}{Z_{\mathcal{G}_1}^p} \]

\[ i_2 = \frac{|\mathcal{P}_{\mathcal{G}_2}|}{|\mathcal{P}_{\mathcal{H}_2}|} \cdot \frac{Z_{\mathcal{H}_2}^p}{Z_{\mathcal{G}_2}^p} \]

index condition

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

Branch 1

F-43m

Imm2

Class 1
3 subgroups

Branch 2

Fm-3m

Imm2

Class 1
3 subgroups

Imm2

Class 2
9 subgroups
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 fullfilled by H, fullfilled 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
Minimum deformation strain in the transformation

Minimum distance between the corresponding atoms in the initial structures described in the subgroup reference frame
Strain Calculation

\[ X_1 = R_1 \cdot x_1 \quad X_2 = R_2 \cdot x_2 \]

\[ R_i = \begin{pmatrix} a_i \sin(\beta_i) \sin(\gamma^*_i) & 0 & 0 \\ -a_i \sin(\beta_i) \cos(\gamma^*_i) & b_i \sin(\alpha_i) & 0 \\ a_i \cos(\beta_i) & b_i \cos(\alpha_i) & c_i \end{pmatrix} \]

Strain definition:

\[ X_2 - X_1 = e \cdot X_1 \quad \text{with} \quad e = R_2^{-1} R_1 - I \]

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

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

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)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinates in $S_1$</th>
<th>Atom</th>
<th>Coordinates in $S_2$</th>
<th>Atomic Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1[1]</td>
<td>(0,0,0)</td>
<td>Si1[1]</td>
<td>(0,0,0)</td>
<td>$d_x$ $d_y$ $d_z$ $</td>
</tr>
<tr>
<td>Si1[2]</td>
<td>(1/2,1/2,1/2)</td>
<td>Si1[2]</td>
<td>(1/2,1/2,1/2)</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>C2[1]</td>
<td>(0,1/2,1/4)</td>
<td>C2[1]</td>
<td>(0,1/2,0)</td>
<td>0 0 +1/4 0.99350</td>
</tr>
<tr>
<td>C2[2]</td>
<td>(1/2,0,3/4)</td>
<td>C2[2]</td>
<td>(1/2,0,1/2)</td>
<td>0 0 +1/4 0.99350</td>
</tr>
</tbody>
</table>

Structural condition (maximum atomic distance in the transformation):

$$\Delta_{max} < \Delta_{tol}$$
Example: Wurtzite to rocksalt in GaN

Wurtzite (Z=2, Zp=2)

\[ G_1 = P6_3mc \]

Rocksalt (Z=4, Zp=1)

\[ G_2 = Fm\bar{3}m \]
Example: Wurtzite to rocksalt in GaN

Wurtzite (Z=2, Zp=2)
\[ G_1 = P6_3mc \]

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

Rocksalt (Z=4, Zp=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?
Cmc$_2\uparrow$ TP: Displacements

Wurtzite (Z=2, Zp=2)

\[ G_1 = P6_3mc \]

<table>
<thead>
<tr>
<th></th>
<th>2b</th>
<th>1/3</th>
<th>2/3</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2b</td>
<td>1/3</td>
<td>2/3</td>
<td>z \sim 3/8</td>
</tr>
</tbody>
</table>

- \(-a-b, a+b, c\)

\[ A \quad 2a \quad 0 \quad \gamma_1 \quad \gamma_1=0 \]

\[ B \quad 2a \quad 0 \quad \gamma_2 \quad \gamma_2 \]

Rocksalt (Z=4, Zp=1)

\[ G_2 = Fm-3m \]

<table>
<thead>
<tr>
<th></th>
<th>4a</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4c</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
</tbody>
</table>

\(-a-b, a+b, c\)

\[ A \quad 2a \quad 0 \quad \gamma_1 \quad \gamma_1=0 \]

\[ B \quad 2a \quad 0 \quad \gamma_2 \quad \gamma_2 \]

\[ y_1 = 1/3 \quad \longleftrightarrow \quad 1/4 \]

\[ y_2 = 1/3 \quad \longleftrightarrow \quad 1/4 \]

\[ z_2 \approx 3/8 \quad \longleftrightarrow \quad 1/2 \]

\[ y_1(A), y_2(B) \text{ and } z_2(B) \text{ coordinates are the internal degrees of freedom} \]
Cmc$_2$$_1$ TP: Cell parameters

Wurtzite (Z=2, Zp=2)

G$_1$ = P6$_3$mc

<table>
<thead>
<tr>
<th>A</th>
<th>2b</th>
<th>1/3</th>
<th>2/3</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2b</td>
<td>1/3</td>
<td>2/3</td>
<td>z ~3/8</td>
</tr>
</tbody>
</table>

Zp=2
H = Cmc$_2$$_1$

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

Rocksalt (Z=4, Zp=1)

G$_2$ = Fm-3m

<table>
<thead>
<tr>
<th>A</th>
<th>4a</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4c</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
</tbody>
</table>

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

Wurtzite (Z=2, Zp=2)
\[ G_1 = P6_3mc \]

Rocksalt (Z=4, Zp=1)
\[ G_2 = Fm-3m \]

Cmc\(_{21}\)
- Zp = 2
- cell mult = 1

P3\(_1\)
- Zp = 6
- cell mult = 3

P3\(_{2}\)
- Zp = 6
- cell mult = 3

Pna\(_{21}\)

\{ \{ Sowa 2001
- Lambrecht et al. 2001 \} \}

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Maximal Transition Paths

Class 1
Class 2
Class 3
Class 4

P63mc
Fm3m

Cmc2
solution
Cmc2

Pna2
Pna2
Pna2
Pna2

i=6
i=48

3 new Pna2 transition paths

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

<table>
<thead>
<tr>
<th>TP</th>
<th>$\mathcal{H}$</th>
<th>$S$</th>
<th>Lattice parameters in $(\mathcal{H}_1, \mathcal{H}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(036) Cmc2$_1$</td>
<td>0.1977</td>
<td>3.1900 5.5252 5.1890 90 90 90</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>4.0060 4.0060 4.0060 90 90 90</td>
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<tr>
<td>2</td>
<td>(033) Pna2$_1$</td>
<td>0.1218</td>
<td>5.5252 3.1900 5.1890 90 90 90</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>5.6653 2.8327 4.0060 90 90 90</td>
</tr>
<tr>
<td>3</td>
<td>(031) Pmn2$_1$</td>
<td>0.1218</td>
<td>3.1900 5.5252 5.1890 90 90 90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.8327 5.6653 4.0060 90 90 90</td>
</tr>
<tr>
<td>4</td>
<td>(026) Pmc2$_1$</td>
<td>0.1592</td>
<td>3.1900 5.5252 5.1890 90 90 90</td>
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<tr>
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<td>2.8327 4.0060 5.6653 90 90 90</td>
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<tr>
<td>5</td>
<td>(007) Pc</td>
<td>0.1576</td>
<td>7.5798 3.1900 5.5252 90 136.80 90</td>
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<td>4.9067 2.8327 5.6653 90 125.27 90</td>
</tr>
<tr>
<td>6</td>
<td>(007) Pc</td>
<td>0.1562</td>
<td>7.5798 3.1900 5.5252 90 136.80 90</td>
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<td>6.9386 2.8327 5.6653 90 144.74 90</td>
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