Phase transitions with no group-subgroup relations between the phases

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Buerger's classification of structural phase transitions

**reconstructive:** primary (first-coordination) chemical bonds are broken and reconstructed $\rightarrow$ discontinuous enthalpy and volume changes $\rightarrow$ first-order thermodynamic character (coexistence of phases at equilibrium, hysteresis and metastability)

**displacive:** secondary (second-coordination) chemical bonds are broken and reconstructed, primary bonds are not $\rightarrow$ small or vanishing enthalpy and volume changes $\rightarrow$ second-order or weak first-order thermodynamic character

**order/disorder:** the structural difference is related to different chemical occupation of the same crystallographic sites, leading to different sets of symmetry operators in the two phases $\rightarrow$ vanishing enthalpy and volume changes $\rightarrow$ second-order thermodynamic character
Symmetry aspects of Buerger’s phase transitions

♦ Displacive and second-order phase transitions:
  - the space group symmetries of the two phases show a group/subgroup relationship
  - the low-symmetry phase approaches the transition to higher symmetry continuously;
  - the order parameter $\eta$ measures the 'distance' of the low-symmetry to the high-symmetry
    ($\eta=0$) structure

T-driven transition: usually the symmetry of the l.t. phase is a subgroup of that of the h.t. phase
p-driven transition: it is hard to predict which one of the two phases (l.p. and h.p.) is more
symmetric
Reconstructive phase transitions:
- the space group symmetries of the two phases are unrelated
- the transition is quite abrupt (no order parameter)

but:
- any kinetic mechanism of the transformation must be based on an intermediate structure whose space group is subgroup of both space groups of the two end phases
- the intermediate state transforms continuously from one to the other end phase, according to the change of the 'reaction coordinate', or kinetic order parameter

Examples of simple reconstructive phase transitions:

HCP to BCC, FCC to HCP and BCC to FCC in metals and alloys
rocksalt (Fm$\overline{3}$m) to CsCl-type (Pm$\overline{3}$m) structure in binary AB systems: C.N. changes from 6 to 8
zincblende (F$\overline{4}$3m) to rocksalt (Fm$\overline{3}$m) structure in binary AB systems: C.N. changes from 4 to 6
**Mechanisms of reconstructive phase transitions and symmetry of the intermediate states**

\[ G_1 \text{ (S.G. of phase 1)} \rightarrow H \text{ (S.G. of intermediate state)} \rightarrow G_2 \text{ (S.G. pf phase 2)} \]

\[ H \subset G_1, \; H \subset G_2, \; G_1 \not\subset G_2 \quad (1) \]

Let \( T_1, T_2 \) and \( T \) be the translation groups of \( G_1, G_2 \) and \( H \), respectively, and \( T_1 \subseteq T_2 \). Then:

\[ T \subseteq T_1, \; T \subseteq T_2 \quad (2) \]

In the simplest case \( T_1=T_2 \), so that \( G_1 \) and \( G_2 \) have the same translation group (i.e., the primitive unit-cells of phases 1 and 2 have the same volume, except for a minor difference due to the \( \Delta V \) jump of first-order transitions).

The translation group of \( H \) may coincide with that of \( G_1 \) and \( G_2 \) \((T=T_1)\), but it may also be a subgroup of it \((T \subset T_1, \text{i.e., the volume of the primitive cell of the intermediate state is an integer multiple of that of the end phases, called the index } i_k \text{ of the superlattice})\).
The index of the superlattice $T$ of $T_1$ is equal to the klassen-gleich index of the subgroup $H$ of $G_1$. In the general case, we have then that:

\[
\frac{i_{k,1}}{i_{k,2}} = V_2/V_1.
\]

$V$, $V_1$ and $V_2$ are the volumes of the primitive unit-cells associated to subgroup $H$ and groups $G_1$ and $G_2$, respectively.

As the volume per formula-unit should be the same in all cases, it turns out that:

\[
\frac{V}{Z(H)} = \frac{V_1}{Z(G_1)} = \frac{V_2}{Z(G_2)}; \quad \text{it follows that:} \quad i_{k,1} = \frac{Z(H)}{Z(G_1)}, \quad i_{k,2} = \frac{Z(H)}{Z(G_2)},
\]

\[
\frac{i_{k,1}}{i_{k,2}} = \frac{V_2}{V_1} = \frac{Z(G_2)}{Z(G_1)}.
\]

In other words, the ratio of the two k-indexes of the subgroup $H$ is inversely proportional to the ratio of the corresponding numbers of f.u. in the primitive unit-cell volumes of $G_1$ and $G_2$. 

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If a conventional centred (non-primitive) unit-cell is used, then the relations $V^c = f^c V$, $Z^c = f^c Z$ should be used, where $f^c$ is the number of lattice points contained in the conventional cell.

The relation (3) gives the first general constraint on the determination of the common subgroups $H$.

The second important constraint concerns the atomic displacements during the reconstructive phase transition:

Atoms must remain in the same types of Wyckoff positions of $H$ along the entire path $G_1 \rightarrow G_2$.

If that were not true, then the $H$ symmetry would be broken to allow atoms to change their Wyckoff positions.

As a consequence, the Wyckoff positions of corresponding atoms in $G_1$ and $G_2$ must transform into the same Wyckoff position of the common subgroup $H$. 

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Systematic search for the common subgroups $H$ of the symmetry groups $G_1$ and $G_2$:


The first step of a systematic search of the possible intermediate states involves the search for all common superlattices of phases 1 and 2.

$$
\{a_1\} \xrightarrow{Q_1} \{a\}, \quad \{a_2\} \xrightarrow{Q_2} \{a\}, \quad \{a_1\} \xrightarrow{Q_1Q_2^{-1}} \{a_2\}
$$

$Q_1$ and $Q_2$ are the transformation matrices from the primitive unit-cells of phases 1 and 2 to the primitive cell of the intermediate structure. Their components must be integer numbers.

$\det(Q_1)$ and $\det(Q_2)$ are the indexes $i_{k,1}$ and $i_{k,2}$ of the intermediate superlattice with respect to the lattices of phase 1 and 2, respectively. $Q_1Q_2^{-1}$ is the transformation matrix relating the lattices of the two end phases, for the transition mechanism considered - Important for a comparison with the experimental relative crystallographic orientation of the end phases (if available)!

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Search for common superlattices: all possible combinations of two sets of nine integers, corresponding to the components of the $Q_1$ and $Q_2$ matrices, are considered.

Two limiting conditions:
- a reasonable limit on the maximum length of the primitive lattice basis vectors of $T$
- a reasonable limit on the total strain involved in the $T_1 \rightarrow T_2$ transformation, which can be calculated from the $Q_1 Q_2^{-1}$ matrix.

Once the superlattice $T$ is defined, its symmetry point group $P$ has to be found; Let $P_1$ and $P_2$ be the point groups of $T_1$ and $T_2$, respectively: then $P = P_1 \cap P_2$.

$P$ is found simply by selecting the point group operators of $G_1$ and $G_2$ which, in the reference frame of $T$, are represented by matrices with integer components.

The point group $P'$ of $H$ must be a subgroup of $P$: $P' \subseteq P$.

$P'$ and $H$ are found by selecting, within the symmetry operators of $G_1$ and $G_2$, only those which are compatible with $P$ and $T$.

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2) Program TRANPATH of the Bilbao Crystallographic Package

- A separate search is performed for the subgroups of $G_1$ and $G_2$, and the common subgroup types shared by both symmetry groups are determined (COMMONSUBS module), within the constraint of a maximum value of the $i_k$ index: $i_{k,1} \leq i_k \leq i_{k,2}$. For a given common subgroup type $H$, the lists of all subgroups $H_1^p$ ($p=1,\ldots,m$) $\subset G_1$ of the first branch, and of all subgroups $H_2^q$ ($q=1,\ldots,n$) $\subset G_2$ of the second branch are obtained. The indexes $p$ and $q$ label different classes of conjugated subgroups; conjugated subgroups of the same class are completely equivalent and then they are represented by a single member of the class.

- Every $H_1^p$ or $H_2^q$ subgroup is associated to a transformation matrix $Q$ relating the basis vectors of $G_1$ to those of the subgroup, according to $(a,b,c)_H = (a,b,c)_G Q$. This matrix is by no means unique, of course, because different basis can be chosen to represent the same lattice.
• Each pair \((H_1^p, H_2^q)\) defines an independent possible transformation path relating \(G_1\) and \(G_2\) with common subgroup type \(H\). Every path is checked for compatibility of the Wyckoff position splittings in the two \(G_1 \to H_1^p\) and \(G_2 \to H_2^q\) branches (WYCKSPLIT module). The WP's occupied by a given atom in \(G_1\) and \(G_2\) must give rise to the same WP for that atom in \(H\).

• The lattice strain in the \(H\) reference frame is computed for the \(G_1 \to G_2\) transformation, and its value is compared to a threshold given in input to TRANPATH.

• The coordinates of all independent atoms are computed in the \(H\) reference frame for the two \(G_1\) and \(G_2\) end structures. The corresponding atomic shifts are compared to a threshold value given in input to TRANPATH.

zincblende ($G_1 = F\bar{4}3m$) to rocksalt ($G_2 = Fm\bar{3}m$) structure in ZnS and SiC under pressure

Two examples of maximal common subgroups, giving rise to well-studied transition mechanisms:

$H = R3m, \text{Imm}_2$

$F\bar{4}3m$ (B3) $Z=4$ $M \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ (4c, $\bar{4}3m$); $X 0, 0, 0$ (4a, $\bar{4}3m$) $a_I$

$Fm\bar{3}m$ (B1) $Z=4$ $M \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (4b, $m\bar{3}m$); $X 0, 0, 0$ (4a, $m\bar{3}m$) $a_{II}$

Intermediate states:

$I - H = R3m$ $Z=1$ $M x, x, x$ (3a, 3m); $X 0, 0, 0$ (3a, 3m)

order parameter: $x(M) (\frac{1}{4} \rightarrow \frac{1}{2})
\[
\begin{align*}
\mathbf{F}_{\bar{4}3m} \rightarrow \mathbf{R}_{3m} & \quad Q_1 = \begin{bmatrix}
0 & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & 0 & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & 0
\end{bmatrix} \quad Q_1^{-1} = \begin{bmatrix}
-1 & 1 & 1 \\
1 & -1 & 1 \\
1 & 1 & -1
\end{bmatrix} \\
\mathbf{Fm\bar{3}m} \rightarrow \mathbf{R}_{3m} & \quad Q_2 = Q_1 = \begin{bmatrix}
\frac{1}{2} & 0 & \frac{1}{2} \\
\frac{1}{2} & 0 & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & 0
\end{bmatrix} \\
\mathbf{F}_{\bar{4}3m} \rightarrow \mathbf{Fm\bar{3}m} & \quad Q_1 Q_2^{-1} = \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\end{align*}
\]

\(\mathbf{R}_{3m} (B3): \quad a_R = a_l/\sqrt{2}, \quad \alpha_R = 60^\circ; \quad \mathbf{R}_{3m} (B1): \quad a_R = a_{II}/\sqrt{2}, \quad \alpha_R = 60^\circ\)

\(\mathbf{I} - \mathbf{H} = \mathbf{Imm2} \quad Z=2 \quad \mathbf{M} \quad 0, \frac{1}{2}, z \left(\frac{1}{4} \rightarrow \frac{1}{2}\right) \quad (2b, \text{mm2}); \quad \mathbf{X} \quad 0, 0, 0 \quad (2a, \text{mm2})\)

Order parameter: \(z(M)\)

\[
\begin{align*}
\mathbf{F}_{\bar{4}3m} \rightarrow \mathbf{Imm2} & \quad Q_1 = \begin{bmatrix}
\frac{1}{2} & -\frac{1}{2} & 0 \\
\frac{1}{2} & \frac{1}{2} & 0 \\
0 & 0 & 1
\end{bmatrix} \quad Q_1^{-1} = \begin{bmatrix}
1 & 1 & 0 \\
-1 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\end{align*}
\]
$$\begin{align*}
\text{Fm}\bar{3}m \rightarrow \text{Imm2} & \quad Q_2 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \\
\text{F}\bar{4}3m \rightarrow \text{Fm}\bar{3}m & \quad Q_1Q_2^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 1 & 1 & 0 \end{bmatrix}
\end{align*}$$

\text{Imm2 (B3): } a = b = a_l/\sqrt{2}, \quad c = a_l; \quad \text{Imm2 (B1): } b = c = a_{II}/\sqrt{2}, \quad a = a_{II} \quad \text{M. Catti - Lekeitio 2009}
Imm2 and R3m mechanisms of the B3/B1 high-pressure phase transition
Imm2 pathway of the B3/B1 phase transition of ZnS and SiC

B3(\overline{F}43m) → Imm2 → B1(Fm\overline{3}m)
Enthalpy of the intermediate state of SiC along the B3-B1 transformation path vs. order parameter $\xi$ at several p values for two different pathways: Imm2 (closed symbols) and R3m (dashed lines)
Example: rocksalt ($G_1 = Fm\bar{3}m$) to CsCl-type ($G_2 = Pm\bar{3}m$) structure in NaCl under pressure

$Fm\bar{3}m$ (B1)  $Z = 4$  $M$  $0, 0, 0$ (4a, $m\bar{3}m$);  $X$  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (4b, $m\bar{3}m$)  $a_I$

$Pm\bar{3}m$ (B2)  $Z = 1$  $M$  $0, 0, 0$ (1a, $m\bar{3}m$);  $X$  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (1b, $m\bar{3}m$)  $a_{II}$

Intermediate states:

$I - H = Pmnn$  $Z = 2$  $M$  $\frac{1}{4}, \frac{1}{4}, z$ ($\frac{1}{4} \rightarrow \frac{1}{2}$) (2a, mm2);  $X$  $\frac{1}{4}, \frac{3}{4}, z + \frac{1}{2}$ ($\frac{3}{4} \rightarrow 0$) (2b, mm2)

\[ Q_1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \end{bmatrix}, \quad Q_1^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{bmatrix} \]

\[ Q_2 = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & -1 & 0 \end{bmatrix}, \quad Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \end{bmatrix} \]

\[ Q_1 Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{1}{2} & \frac{1}{4} \end{bmatrix}, \quad (Q_1 Q_2^{-1})^{-1} = \begin{bmatrix} 1 & 1 & -1 \\ 0 & 1 & 1 \\ 1 & -1 & 1 \end{bmatrix} \]

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Pmmn (B1): \( a = a_I, \quad b = c = a_I/\sqrt{2}; \quad Pmmn (B2): \quad a = b = a_{II}/\sqrt{2}, \quad c = a_{II}\)

**II1 - H = R\overline{3}m** \( Z = 1 \) \( M \quad 0, 0, 0 \) (3a, \( \overline{3}m \)); \( X \quad \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) (3b, \( \overline{3}m \))

\[
\text{Fm}\overline{3}m \rightarrow R\overline{3}m \quad Q_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \quad Q_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}
\]

\[
\text{Pm}\overline{3}m \rightarrow R\overline{3}m \quad Q_2 = Q_2^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]

\[
\text{Fm}\overline{3}m \rightarrow \text{Pm}\overline{3}m \quad Q_1 Q_2^{-1} = Q_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \quad (Q_1 Q_2^{-1})^{-1} = Q_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}
\]

\( R\overline{3}m \) (B1): \( a_R = a_I/\sqrt{2}, \quad \alpha_R = 60^\circ; \quad R\overline{3}m \) (B2): \( a_R = a_{II}, \quad \alpha_R = 90^\circ \)

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II2 - H = P2₁/m  

Z=2  

M  \times 1(\frac{1}{4}), \frac{1}{4}, z₁(0)  \quad (2e, m);  

X  \times 2(\frac{3}{4}), \frac{1}{4}, z₂(\frac{1}{2})  \quad (2e, m)

\[
Fm\bar{3}m \rightarrow P2₁/m  
Q₁ = \begin{bmatrix}
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\
1 & 0 & 0
\end{bmatrix}  
Q₁^{-1} = \begin{bmatrix}
0 & 0 & 1 \\
1 & -1 & 0 \\
1 & 1 & -1
\end{bmatrix}
\]

\[
Pm\bar{3}m \rightarrow P2₁/m  
Q₂ = \begin{bmatrix}
1 & -1 & 0 \\
1 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}  
Q₂^{-1} = \begin{bmatrix}
\frac{1}{2} & \frac{1}{2} & 0 \\
-\frac{1}{2} & \frac{1}{2} & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

\[
Fm\bar{3}m \rightarrow Pm\bar{3}m  
Q₁Q₂^{-1} = \begin{bmatrix}
\frac{1}{2} & 0 & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & 0
\end{bmatrix}  
(Q₁Q₂^{-1})^{-1} = \begin{bmatrix}
1 & -1 & 1 \\
1 & 1 & -1
\end{bmatrix}
\]

P₂₁/m (B₁):  \quad a = a₁\sqrt{3/2},  \quad b = c = a₁/\sqrt{2},  \quad \beta = \arccos(1/\sqrt{3}) = 54.74°;

P₂₁/m (B₂):  \quad a = b = a₁\sqrt{2},  \quad c = a₁,  \quad \beta = 90°;

P₂₁/m (R\bar{3}m):  \quad a = a₁[2(1+\cos\alpha₉)]^{1/2},  \quad b = a₁[2(1-\cos\alpha₉)]^{1/2},  \quad c = a₁,  \quad \beta = \arccos[\cos\alpha₉/\cos(\alpha₉/2)]
II\textsuperscript{3} - R\textsuperscript{3m}  
\( Z=4 \)  
\( M_1 \) 0, 0, 0 (3m);  
\( M_2 \)  \( x_1(1/2), x_1(1/2), z_1(0) \) (3m)  
\( X_1 \)  \( x_2(1/2), x_2(1/2), x_2(1/2) \) (3m);  
\( X_2 \)  \( x_3(0), x_3(0), z_2(1/2) \) (3m)

\[
\text{Fm}\overline{3}\text{m} \rightarrow \text{R3m} \quad Q_1 = Q_1^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]

\[
\text{Pm}\overline{3}\text{m} \rightarrow \text{R3m}, \text{ R}\overline{3}\text{m} \rightarrow \text{R3m} \quad Q_2 = \begin{bmatrix} -1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & -1 \end{bmatrix} \quad Q_2^{-1} = \begin{bmatrix} 1 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{bmatrix}
\]

\[
\text{Fm}\overline{3}\text{m} \rightarrow \text{Pm}\overline{3}\text{m} \quad Q_1Q_2^{-1} = \begin{bmatrix} 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{bmatrix} \quad (Q_1Q_2^{-1})^{-1} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \end{bmatrix}
\]

R3m (B1): \( a_{R'} = a_I, \ \alpha_R = 90^\circ; \)

R3m (B2): \( a_{R'} = a_{II}\sqrt{3}, \ \alpha_R = \arccos(-1/3)=109.47^\circ; \)

R3m (R\overline{3}m): \( a_{R'} = a_R(3-2\cos\alpha_R)^{1/2}, \ \alpha_R = \arccos[(2\cos\alpha_R-1)/(3-2\cos\alpha_R)] \)

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R$\bar{3}$m pathway of the B1/B2 phase transition
Pmmn pathway of the B1/B2 phase transition

B1(Fm$\bar{3}$m) → Pmmn → B2(Pm$\bar{3}$m)
P2₁/m pathway of the B1/B2 phase transition

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Enthalpy of the intermediate state of NaCl along the B1-B2 transformation path vs. order parameter $\xi$ for three different pathways: rhombohedral $R\bar{3}m$, monoclinic $P2_1/m$ orthorhombic $Pmnn$. 

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Intermediate metastable Cmcm phase along the P2₁/m pathway:

TII-like structure with both Na and Cl in seven-fold coordination
Na-Cl8 (full diamonds) and Na-Cl7 (full triangles) interatomic distances versus the order parameter $\xi$ along the P2$_1$/m pathway; open diamonds indicate the corresponding Na-Cl distance along the Pmmn path.
Enthalpy of the intermediate state of NaCl along the B1-B2 transformation path vs. order parameter \( \xi \) at three \( p \) values for two different pathways: \( P2_1/m \) (closed symbols) and \( Pmmn \) (open symbols).

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Multiple reconstructive phase transition of AgI under pressure (cf. Catti, PRB 2005)

zincblende \((G_1 = F\bar{4}3m)\) to anti-litharge \((G_2 = P4/nmm)\) to rocksalt \((G_3 = Fm\bar{3}m)\) structure

\[
\begin{align*}
F\bar{4}3m & \quad Z=4 \quad Ag \ (4a) \ 0, 0, 0; \quad I \ (4c) \ \frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \quad a_I \\
P4/nmm & \quad Z=2 \quad Ag \ (2a) \ 0,0,0; \quad I \ (2c) \ 0, \frac{1}{2}, z; \quad origin \ 1 \quad a_{III}, c_{III} \\
& \quad Ag \ (2a) \ \frac{1}{4}, -\frac{1}{4}, z; \quad I \ (2c) \ \frac{1}{4}, \frac{1}{4}, z; \quad origin \ 2 \\
Fm\bar{3}m & \quad Z=4 \quad Ag \ (4a) \ 0, 0, 0; \quad I \ (4b) \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \quad a_{II}
\end{align*}
\]

Transformation pathway within the non-maximal common subgroup \(Pm\) (derived from maximal common subgroup \(Pmm2\)):

Intermediate state:

\[
\begin{align*}
Pm & \quad Z=2 \quad Ag_1 \ (1a) \ 0,0,0; \quad Ag_2 \ (1b) \ x(Ag2), \frac{1}{2}, z(Ag2); \\
& \quad I_1 \ (1b) \ x(I1), \frac{1}{2}, z(I1); \quad I_2 \ (1a) \ x(I2), 0, z(I2)
\end{align*}
\]

Order parameter : \(z(Ag2) \ \left( \frac{1}{2} \rightarrow 0 \right)\)
\[
\begin{align*}
F\bar{4}3m \rightarrow Pm & \quad Q_1 = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} & \quad Q_1^{-1} = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
P4/nmm \rightarrow Pm & \quad Q_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
F\bar{4}3m \rightarrow P4/nmm & \quad Q_1Q_2^{-1} = Q_1 = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
Fm\bar{3}m \rightarrow Pm & \quad Q_3 = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix} & \quad Q_3^{-1} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix} \\
P4/nmm \rightarrow Fm\bar{3}m & \quad Q_2Q_3^{-1} = Q_3^{-1} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix}
\end{align*}
\]

Pm (zincblende): \( a = b = a_I/\sqrt{2}, \quad c = a_I \);  

Pm (anti-litharge): \( a = b = a_{III}, \quad c = c_{III} \)

Pm (rocksalt): \( a = c = a_{II}/\sqrt{2}, \quad b = a_{II} \)

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Pm monoclinic mechanisms for the zincblende (a) to anti-litharge (d), and anti-litharge (d) to rocksalt (f) phase transformations of AgI. The pseudo-orthorhombic Bmm2 intermediate state (c) is present in both pathways.
Theoretical enthalpy differences $H - H(\text{F}43\text{m})$ plotted vs. pressure for the AgI phases $\text{P}4/\text{nmm}$ (anti-litharge, circles), $\text{Fm}3\text{m}$ (rocksalt, squares), and $\text{Bmm}2$ (metastable phase, diamonds). Vertical lines bound the predicted pressure stability fields.
Theoretical enthalpy difference $H(z(\text{Ag2})) - H(\text{zincblende})$ for the monoclinic Pm intermediate state of AgI along the zincblende to anti-litharge (open circles), and anti-litharge to rocksalt (full triangles) phase transitions. Zincblende/anti-litharge (left) and anti-litharge/rocksalt (right) equilibrium pressures.
Theoretical molecular volume for the monoclinic Pm intermediate state of AgI along the zincblende to anti-litharge (open circles), and anti-litharge to rocksalt (full triangles) phase transitions at $p = 1.15$ GPa.
Cell constants and atomic fractional coordinates of the Pm monoclinic intermediate state of AgI along the $F\bar{4}3m$ (zinc-blende) to $P4/nmm$ (anti-litharge) phase transformation, optimized for fixed $z(\text{Ag2})$ order parameter at the equilibrium pressure 1.15 GPa. Coordinates constrained by symmetry: $x(\text{Ag1})=y(\text{Ag1})=z(\text{Ag1})=y(\text{I2})=0$; $y(\text{Ag2})=y(\text{I1})=1/2$. The enthalpy values per formula unit, referred to that of the $F\bar{4}3m$ phase, are also given.

<table>
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<tr>
<th>$z(\text{Ag2})$</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>$\beta$/deg</th>
<th>x(\text{Ag2})</th>
<th>x(\text{I1})</th>
<th>z(\text{I1})</th>
<th>x(\text{I2})</th>
<th>z(\text{I2})</th>
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Cell constants and atomic fractional coordinates of the Pm monoclinic intermediate state of AgI along the P4/nmm (anti-litharge) to Fm$\bar{3}$m (rock-salt) phase transformation, optimized for fixed $z$(Ag2) order parameter at the equilibrium pressure 1.64 GPa. The enthalpy values per formula unit, referred to that of the P4/nmm phase, are also given.

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<th>c/Å</th>
<th>$\beta$/deg</th>
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<th>z(I1)</th>
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References


Catti, M  *Phys. Rev. Lett.* **87** 035504 (2001)


