

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 → discontinuous enthalpy and volume changes → 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 → small or vanishing enthalpy and volume changes → 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 → vanishing enthalpy and volume changes → 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 η 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 ($Fm\bar{3}m$) to CsCl-type ($Pm\bar{3}m$) structure in binary AB systems: C.N. changes from 6 to 8

zincblende ($F\bar{4}3m$) to rocksalt ($Fm\bar{3}m$) 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 (S.G. of phase 1) \rightarrow H (S.G. of intermediate state) \rightarrow G_2 (S.G. of phase 2)

$$H \subset G_1, \quad H \subset G_2, \quad G_1 \not\subset G_2 \quad (1)$$

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:

$$T \subseteq T_1, \quad T \subseteq T_2 \quad (2)$$

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 ΔV 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 ($T \subset T_1$, 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 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:

$$i_{k,1} = |T_1| / |T| = V/V_1, \quad i_{k,2} = |T_2| / |T| = V/V_2; \quad \text{hence: } i_{k,1}/i_{k,2} = V_2/V_1.$$

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:

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

$$i_{k,1}/i_{k,2} = V_2/V_1 = Z(G_2)/Z(G_1). \quad (3)$$

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 .

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.

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

1) Method of Stokes and Hatch (Phys. Rev. B **65** 144114 (2002))

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

$$\{\mathbf{a}_1\} \xrightarrow{Q_1} \{\mathbf{a}\}, \quad \{\mathbf{a}_2\} \xrightarrow{Q_2} \{\mathbf{a}\}, \quad \{\mathbf{a}_1\} \xrightarrow{Q_1 Q_2^{-1}} \{\mathbf{a}_2\}$$

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. $Q_1 Q_2^{-1}$ 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) !

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.

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: $i_{k,1} \leq i_k$, $i_{k,2} \leq i_k$.

For a given common subgroup type H , the lists of all subgroups H_1^p ($p=1,\dots,m$) $\subset G_1$ of the first branch, and of all subgroups H_2^q ($q=1,\dots,n$) $\subset G_2$ 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 $G_1 \rightarrow H_1^p$ and $G_2 \rightarrow H_2^q$ 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 $G_1 \rightarrow G_2$ 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.

B3/B1 reconstructive phase transition (cf. Catti, PRL 2001 and PRB 2002)

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, Imm2

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) ($\frac{1}{4} \rightarrow \frac{1}{2}$)

$$\underline{\text{F}\bar{4}3\text{m}} \rightarrow \text{R}3\text{m} \quad \text{Q}_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \quad \text{Q}_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

$$\text{Fm}\bar{3}\text{m} \rightarrow \text{R}3\text{m} \quad \text{Q}_2 = \text{Q}_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix}$$

$$\underline{\text{F}\bar{4}3\text{m}} \rightarrow \text{Fm}\bar{3}\text{m} \quad \text{Q}_1\text{Q}_2^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{R}3\text{m (B3):} \quad a_{\text{R}} = a_{\text{I}}/\sqrt{2}, \quad \alpha_{\text{R}} = 60^\circ;$$

$$\text{R}3\text{m (B1):} \quad a_{\text{R}} = a_{\text{II}}/\sqrt{2}, \quad \alpha_{\text{R}} = 60^\circ$$

$$\text{II - H} = \text{Imm}2 \quad Z=2 \quad \text{M} \quad 0, \frac{1}{2}, z \left(\frac{1}{4} \rightarrow \frac{1}{2}\right) \quad (2b, \text{mm}2); \quad \text{X} \quad 0, 0, 0 \quad (2a, \text{mm}2)$$

Order parameter: $z(\text{M})$

$$\underline{\text{F}\bar{4}3\text{m}} \rightarrow \text{Imm}2 \quad \text{Q}_1 = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{Q}_1^{-1} = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

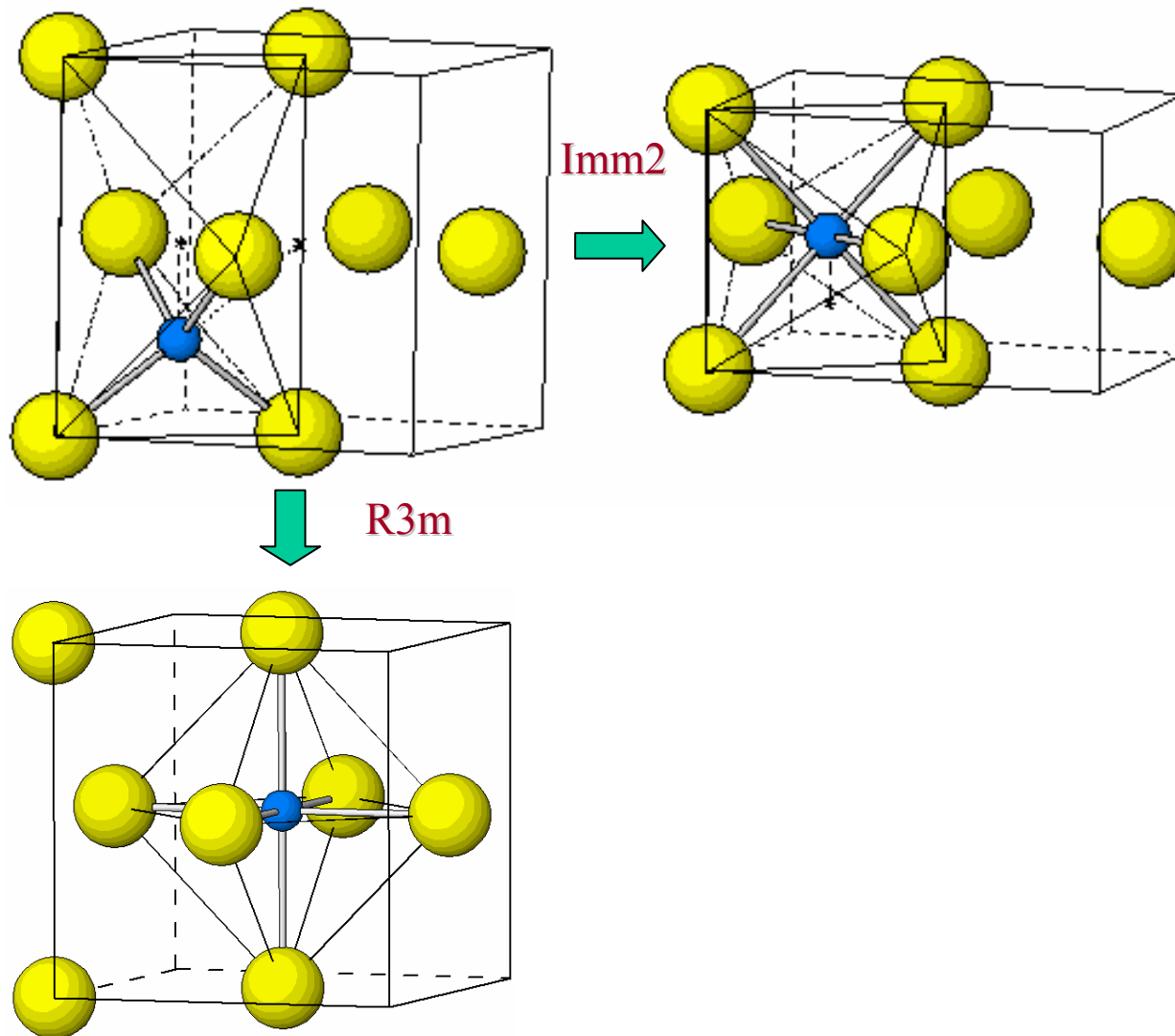
$$\text{Fm}\bar{3}\text{m} \rightarrow \text{Imm}2 \quad \text{Q}_2 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \quad \text{Q}_2^{-1} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & -1 & 0 \\ 1 & 1 & 0 \end{bmatrix}$$

$$\underline{\text{F}\bar{4}\underline{3}\text{m}} \rightarrow \text{Fm}\bar{3}\text{m} \quad \text{Q}_1\text{Q}_2^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 1 & 1 & 0 \end{bmatrix}$$

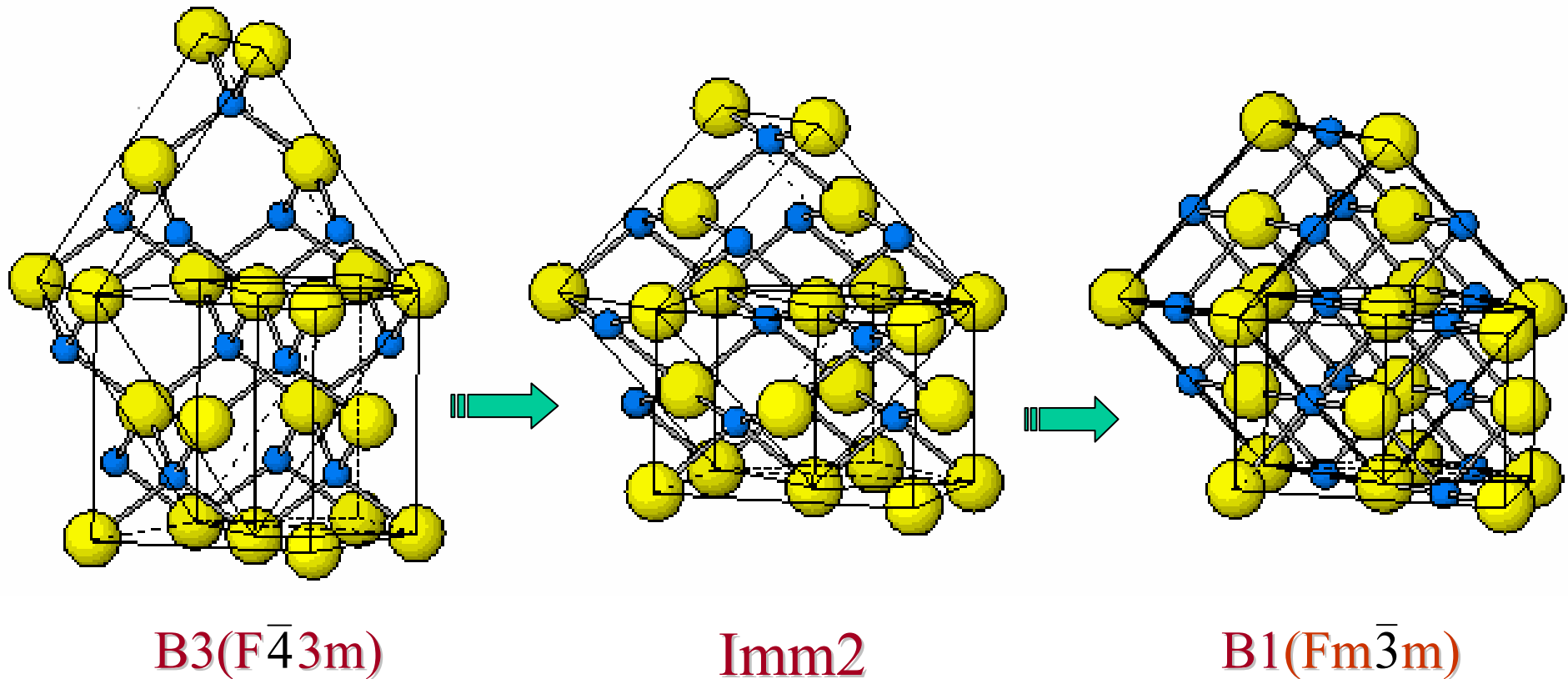
$$\text{Imm}2 \text{ (B3): } a = b = a_{\text{I}}/\sqrt{2}, \quad c = a_{\text{I}}$$

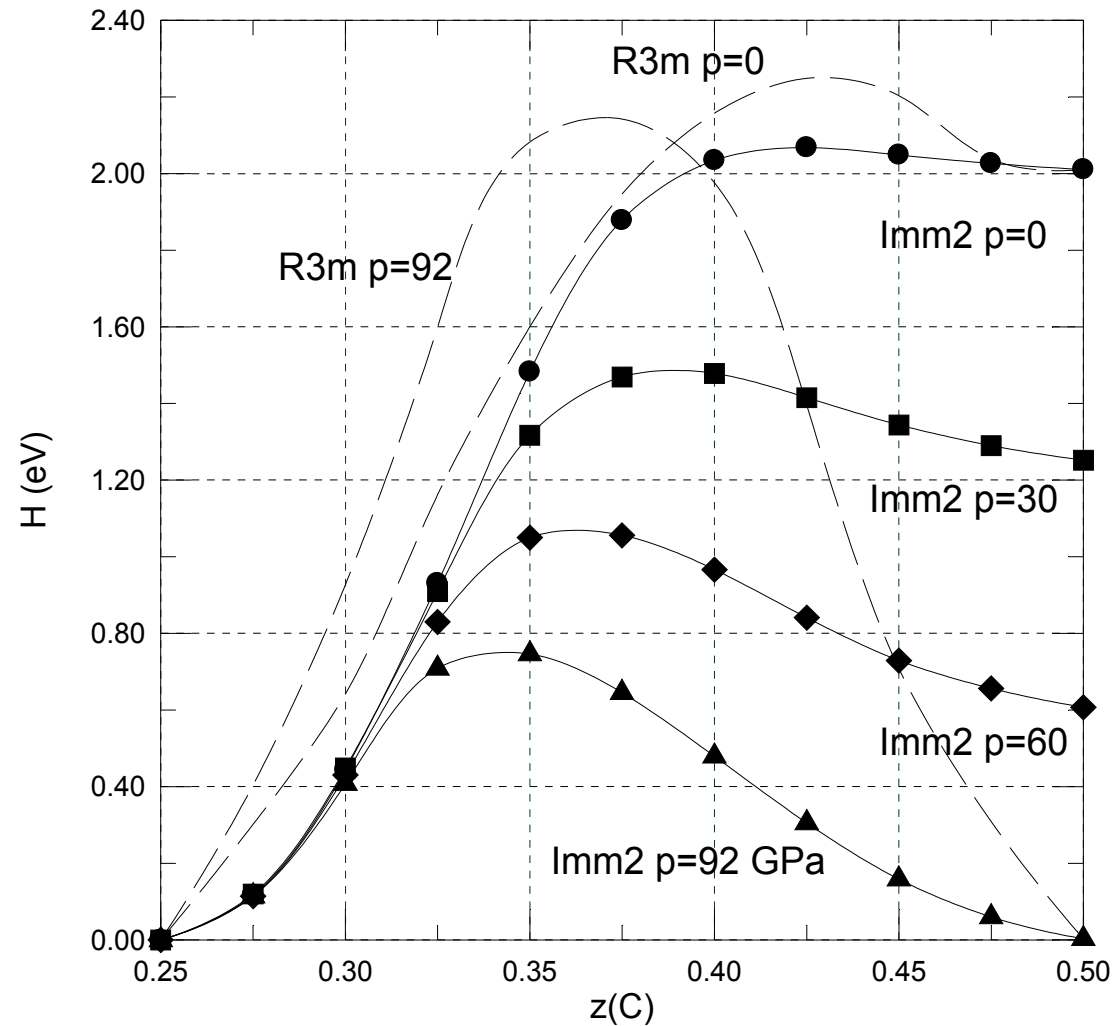
$$\text{Imm}2 \text{ (B1): } b = c = a_{\text{II}}/\sqrt{2}, \quad a = a_{\text{II}}$$

Imm2 and R3m mechanisms of the B3/B1 high-pressure phase transition



Imm2 pathway of the B3/B1 phase transition of ZnS and SiC





Enthalpy of the intermediate state of SiC along the B3-B1 transformation path vs. order parameter ξ 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

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

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

Intermediate states:

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

$$Fm\bar{3}m \rightarrow Pmmn \quad Q_1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \end{bmatrix} \quad Q_1^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{bmatrix}$$

$$Pm\bar{3}m \rightarrow Pmmn \quad Q_2 = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & -1 & 0 \end{bmatrix} \quad Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \end{bmatrix}$$

$$Fm\bar{3}m \rightarrow Pm\bar{3}m \quad Q_1 Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{1}{2} & \frac{1}{4} \end{bmatrix} \quad (Q_1 Q_2^{-1})^{-1} = \begin{bmatrix} 1 & 1 & -1 \\ 0 & 1 & 1 \\ 1 & -1 & 1 \end{bmatrix}$$

$$\text{Pmmn (B1): } a = a_I, \quad b = c = a_I/\sqrt{2};$$

$$\text{Pmmn (B2): } a = b = a_{II}\sqrt{2}, \quad c = a_{II}$$

$$\text{III - H = R}\bar{3}\text{m} \quad Z=1 \quad \text{M } 0, 0, 0 (3a, \bar{3}m); \quad \text{X } \frac{1}{2}, \frac{1}{2}, \frac{1}{2} (3b, \bar{3}m)$$

$$\text{Fm}\bar{3}\text{m} \rightarrow \text{R}\bar{3}\text{m} \quad \text{Q}_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \quad \text{Q}_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

$$\text{Pm}\bar{3}\text{m} \rightarrow \text{R}\bar{3}\text{m} \quad \text{Q}_2 = \text{Q}_2^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{Fm}\bar{3}\text{m} \rightarrow \text{Pm}\bar{3}\text{m} \quad \text{Q}_1\text{Q}_2^{-1} = \text{Q}_1 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \quad (\text{Q}_1\text{Q}_2^{-1})^{-1} = \text{Q}_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

$$\text{R}\bar{3}\text{m (B1): } a_R = a_I/\sqrt{2}, \quad \alpha_R = 60^\circ;$$

$$\text{R}\bar{3}\text{m (B2): } a_R = a_{II}, \quad \alpha_R = 90^\circ$$

II2 - H = P2₁/m Z=2 M x₁(1/4), 1/4, z₁(0) (2e, m); X x₂(3/4), 1/4, z₂(1/2) (2e, m)

$$\text{Fm}\bar{3}\text{m} \rightarrow \text{P2}_1/\text{m} \quad \text{Q}_1 = \begin{bmatrix} 1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \\ 1 & 0 & 0 \end{bmatrix} \quad \text{Q}_1^{-1} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & -1 & 0 \\ 1 & 1 & -1 \end{bmatrix}$$

$$\text{Pm}\bar{3}\text{m} \rightarrow \text{P2}_1/\text{m}, \quad \text{R}\bar{3}\text{m} \rightarrow \text{P2}_1/\text{m} \quad \text{Q}_2 = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{Q}_2^{-1} = \begin{bmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{Fm}\bar{3}\text{m} \rightarrow \text{Pm}\bar{3}\text{m} \quad \text{Q}_1\text{Q}_2^{-1} = \begin{bmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{bmatrix} \quad (\text{Q}_1\text{Q}_2^{-1})^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

P2₁/m (B1): a = a_I√(3/2), b = c = a_I/√2, β = arcos(1/√3) = 54.74°;

P2₁/m (B2): a = b = a_{II}√2, c = a_{II}, β = 90°;

P2₁/m (R $\bar{3}$ m): a = a_R[2(1+cosα_R)]^{1/2}, b = a_R[2(1-cosα_R)]^{1/2}, c = a_R, β = arcos[cosα_R/cos(α_R/2)]

$$\text{II3 - R3m} \quad Z=4 \quad \begin{array}{l} M_1 \quad 0, 0, 0 \quad (3m); \\ X_1 \quad x_2(1/2), x_2(1/2), x_2(1/2) \quad (3m); \end{array} \quad \begin{array}{l} M_2 \quad x_1(1/2), x_1(1/2), z_1(0) \quad (3m) \\ X_2 \quad x_3(0), x_3(0), z_2(1/2) \quad (3m) \end{array}$$

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

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

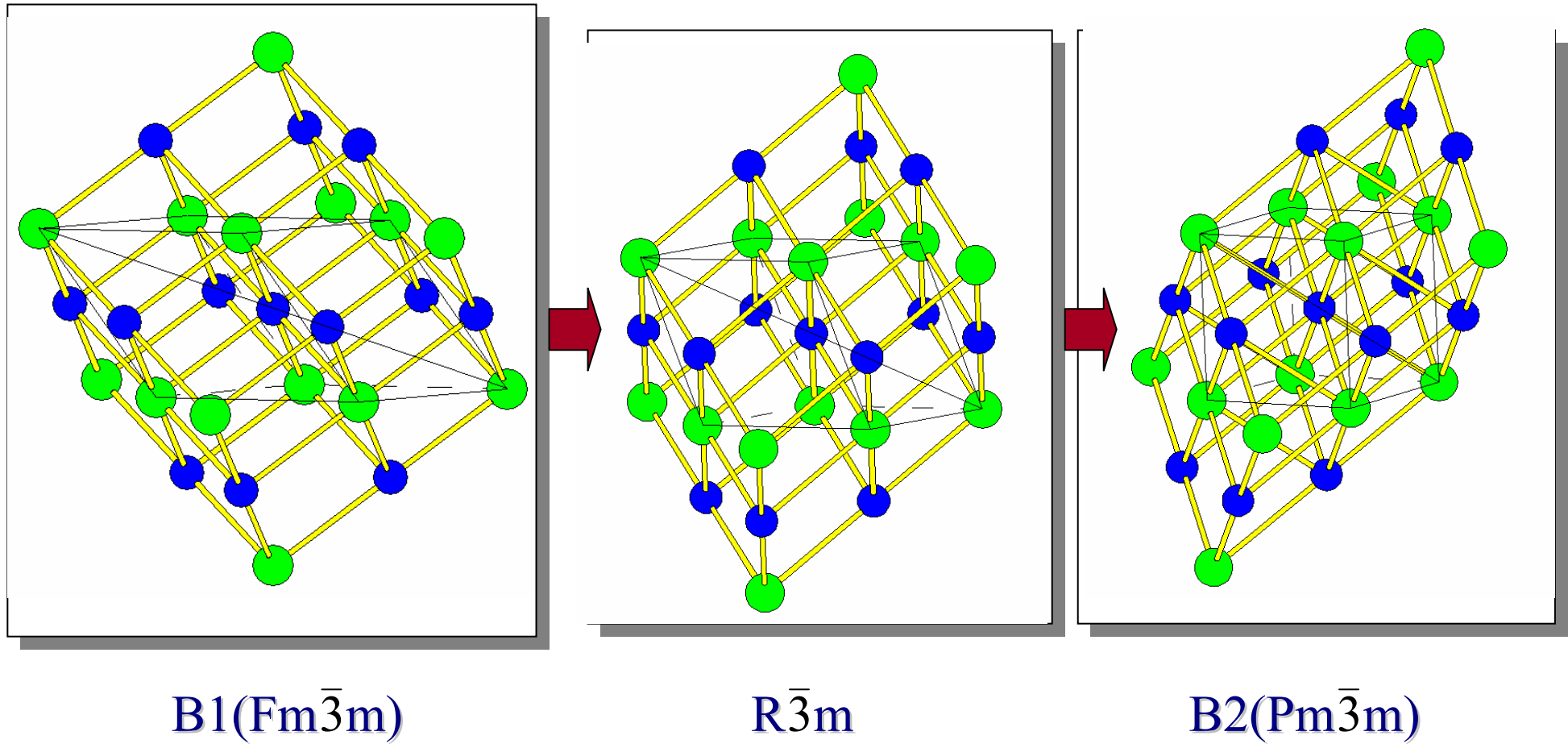
$$\text{Fm}\bar{3}\text{m} \rightarrow \text{Pm}\bar{3}\text{m} \quad Q_1 Q_2^{-1} = \begin{bmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{bmatrix} \quad (Q_1 Q_2^{-1})^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

$$\text{R3m (B1):} \quad a_R' = a_I, \quad \alpha_R = 90^\circ;$$

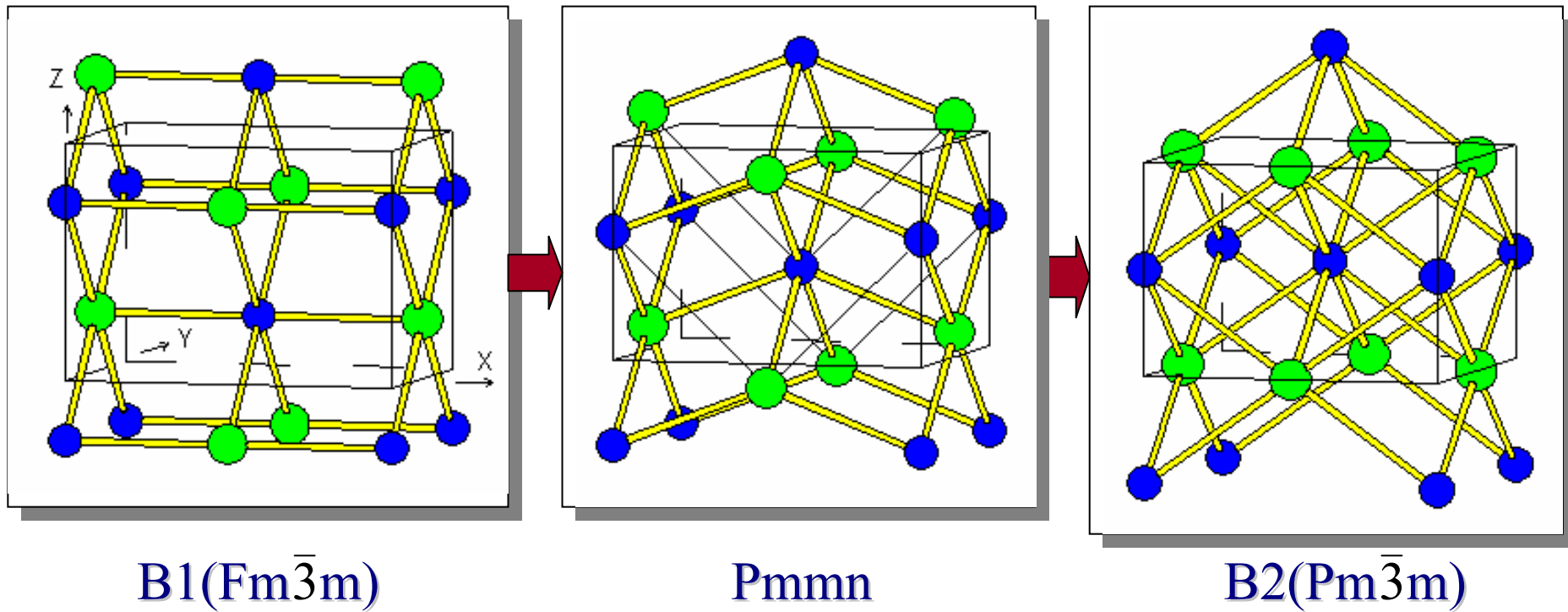
$$\text{R3m (B2):} \quad a_R' = a_{II}\sqrt{3}, \quad \alpha_R = \arccos(-1/3)=109.47^\circ;$$

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

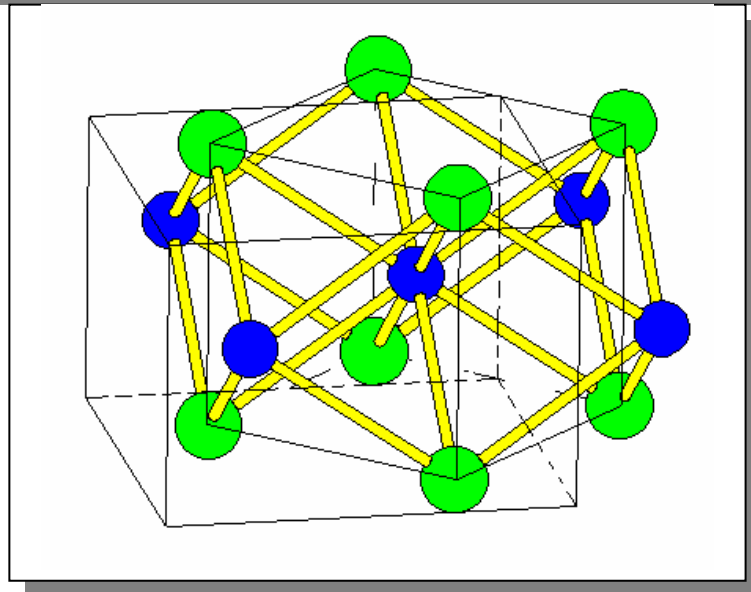
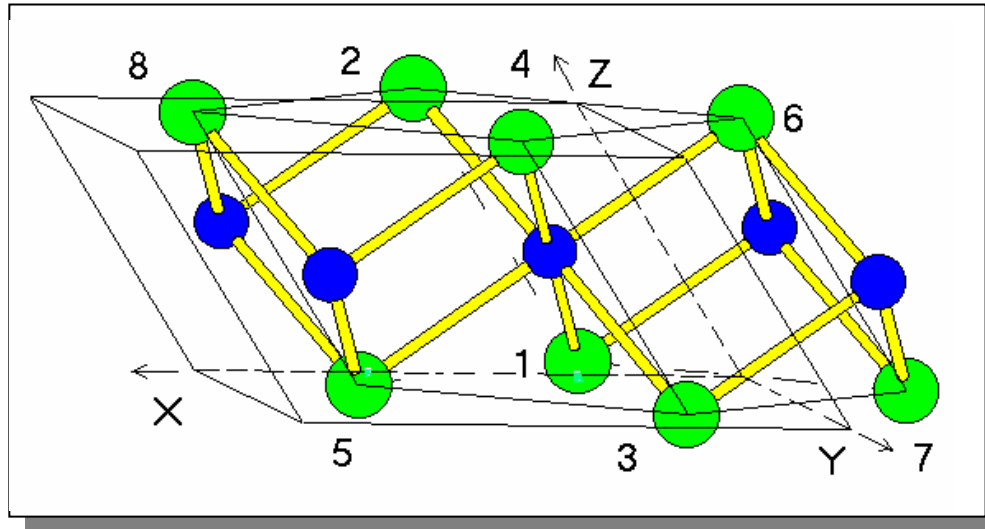
$R\bar{3}m$ pathway of the B1/B2 phase transition



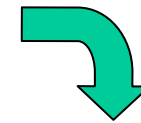
Pmmn pathway of the B1/B2 phase transition



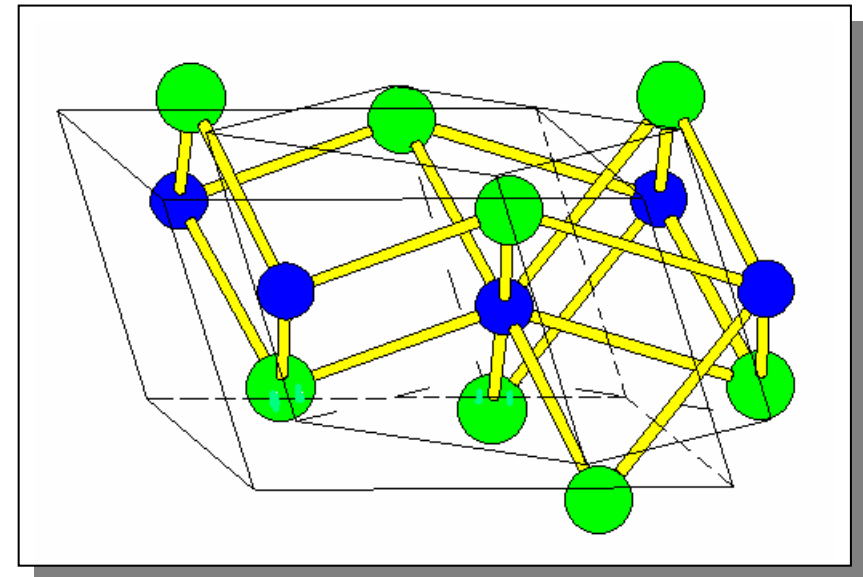
$P2_1/m$ pathway of the B1/B2 phase transition



B1

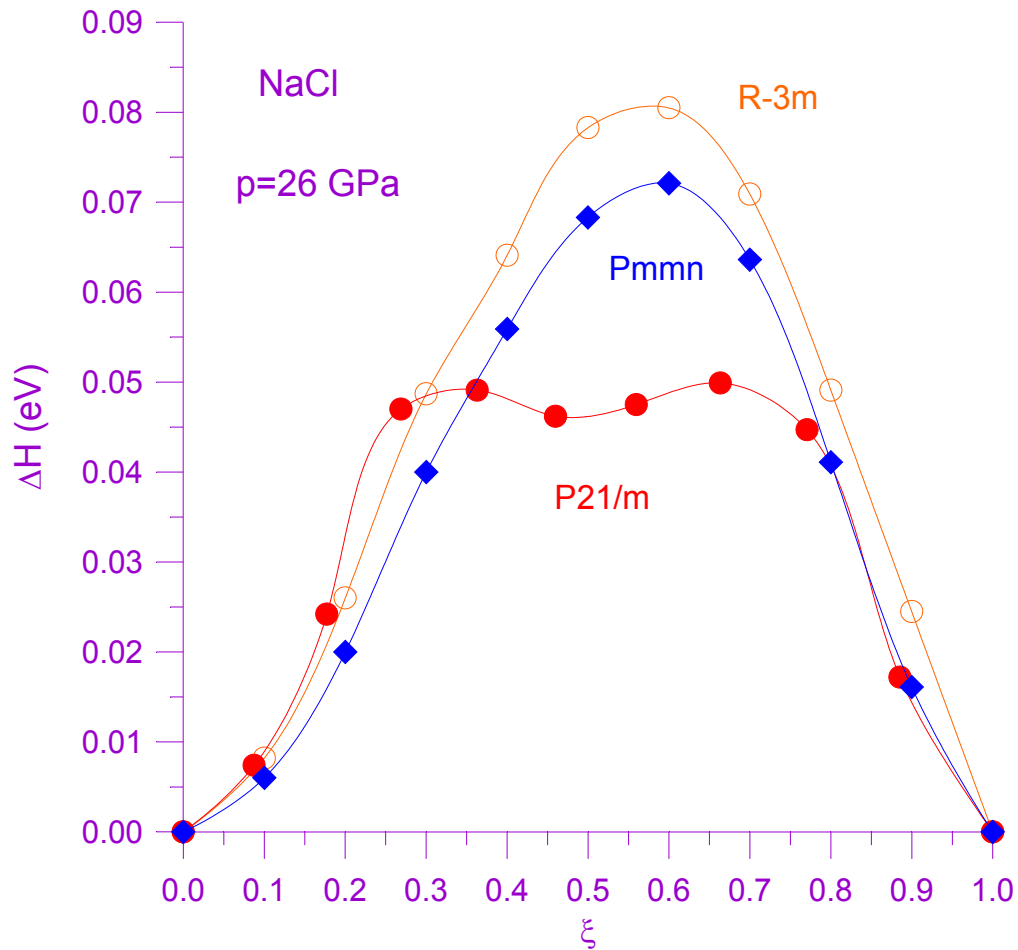


$P2_1/m$



B2

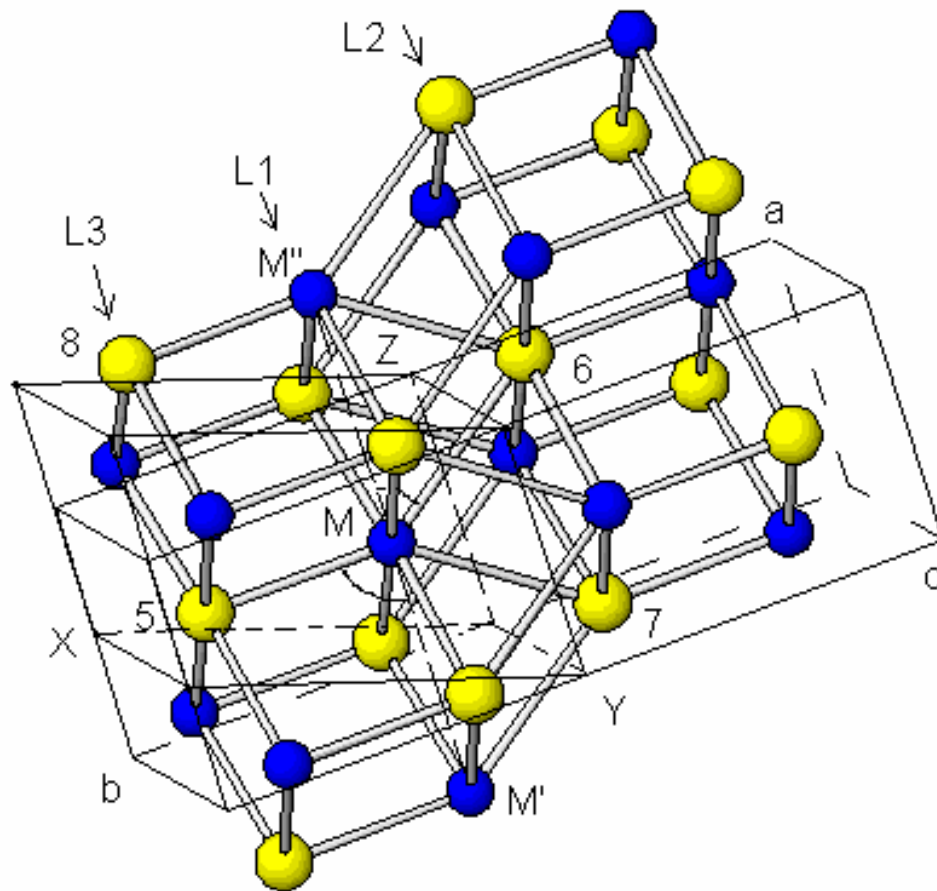


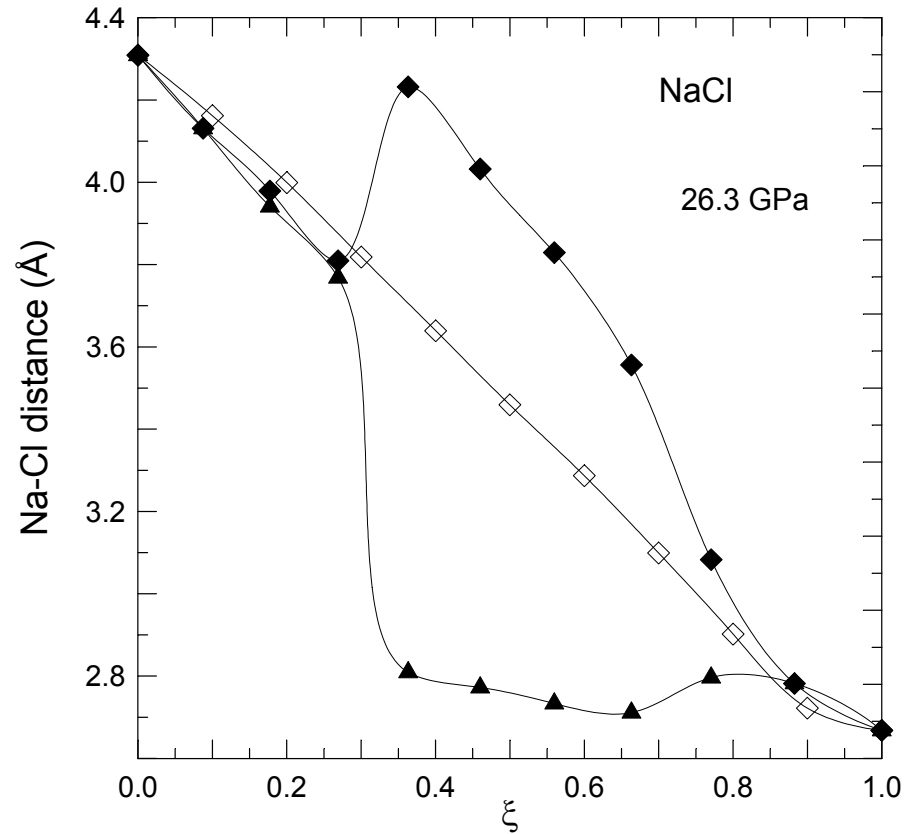


Enthalpy of the intermediate state of NaCl along the B1-B2 transformation path vs. order parameter ξ for three different pathways: rhombohedral $R\bar{3}m$, monoclinic $P2_1/m$ orthorhombic Pmmn

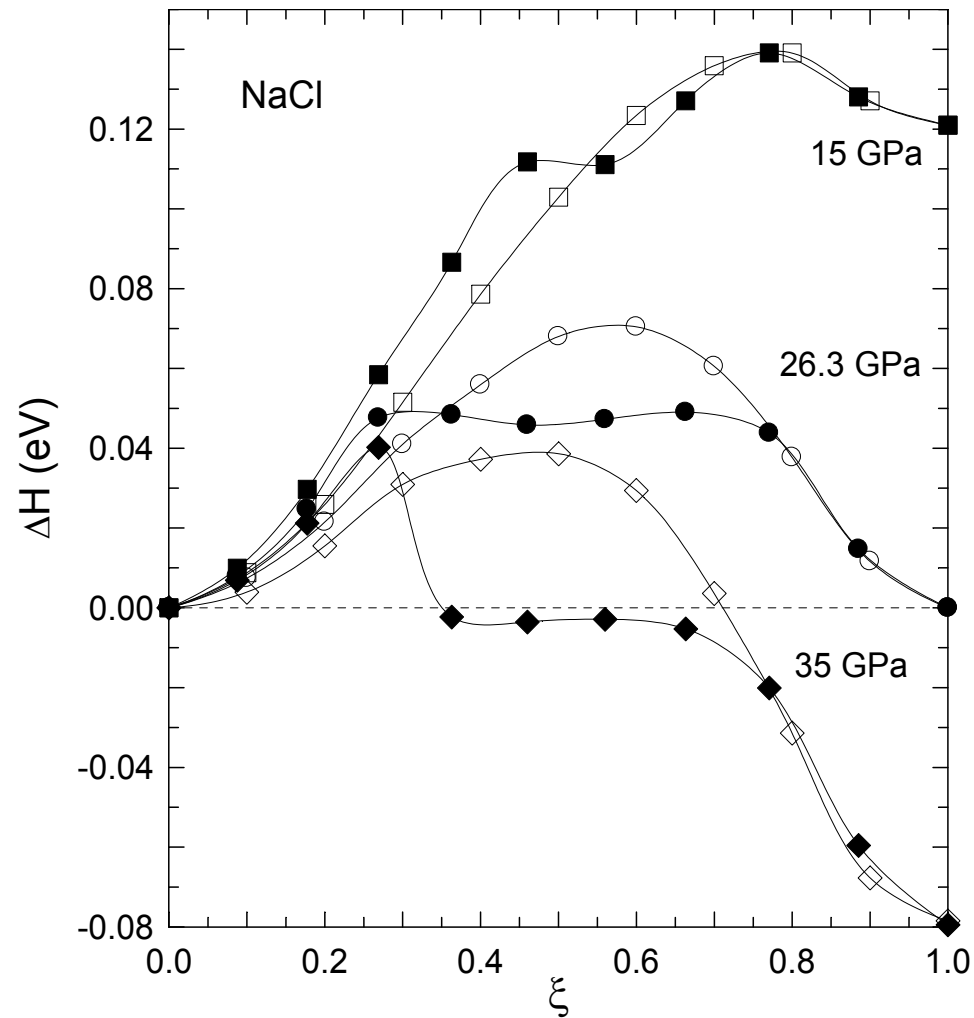
Intermediate metastable $Cmcm$ phase along the $P2_1/m$ pathway:

TII-like structure with both Na and Cl in seven-fold coordination





Na-Cl8 (full diamonds) and Na-Cl17 (full triangles) interatomic distances versus the order parameter ξ 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 ξ at three p values for two different pathways: $P2_1/m$ (closed symbols) and $Pmmn$ (open symbols)

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

$F\bar{4}3m$	$Z=4$	Ag (4a) 0, 0, 0;	I (4c) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4};$	a_I
P4/nmm	$Z=2$	Ag (2a) 0,0,0;	I (2c) 0, $\frac{1}{2}$, z; origin 1	a_{III}, c_{III}
		Ag (2a) $\frac{1}{4}, -\frac{1}{4}, z;$	I (2c) $\frac{1}{4}, \frac{1}{4}, z;$ origin 2	
$Fm\bar{3}m$	$Z=4$	Ag (4a) 0, 0, 0;	I (4b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	a_{II}

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

Intermediate state:

Pm	$Z=2$	Ag1 (1a) 0,0,0;	Ag2 (1b) $x(\text{Ag2}), \frac{1}{2}, z(\text{Ag2});$
		I1 (1b) $x(\text{I1}), \frac{1}{2}, z(\text{I1});$	I2 (1a) $x(\text{I2}), 0, z(\text{I2})$

Order parameter : $z(\text{Ag2}) (\frac{1}{2} \rightarrow 0)$

$$\underline{F\bar{4}3m} \rightarrow \text{Pm} \quad Q_1 = \begin{bmatrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$Q_1^{-1} = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{P4/nmm} \rightarrow \text{Pm} \quad Q_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\underline{F\bar{4}3m} \rightarrow \text{P4/nmm} \quad Q_1 Q_2^{-1} = Q_1 = \begin{bmatrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{Fm}\bar{3}m \rightarrow \text{Pm} \quad Q_3 = \begin{bmatrix} 1/2 & 0 & -1/2 \\ 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \end{bmatrix}$$

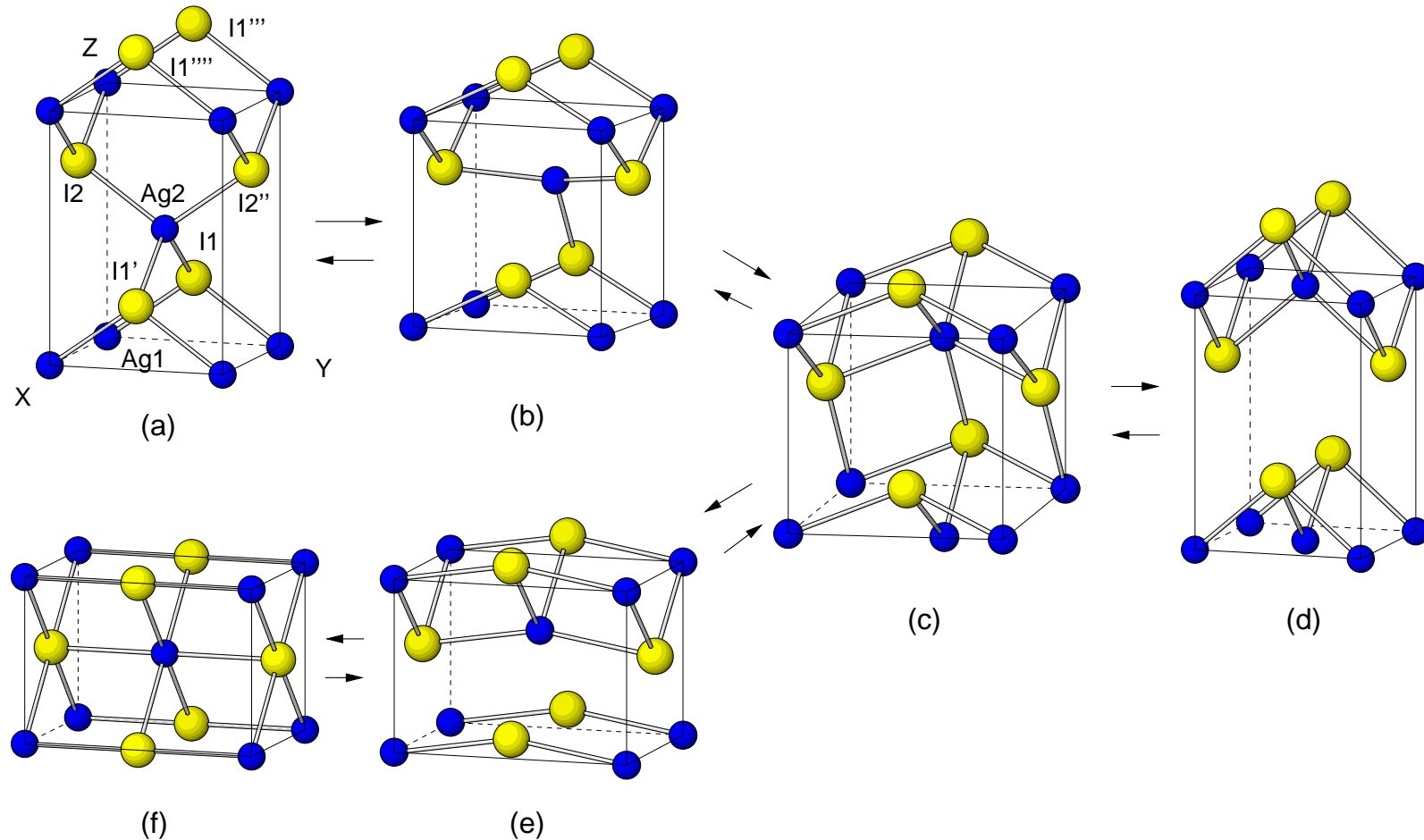
$$Q_3^{-1} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix}$$

$$\underline{\text{P4/nmm}} \rightarrow \text{Fm}\bar{3}m \quad Q_2 Q_3^{-1} = Q_3^{-1} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix}$$

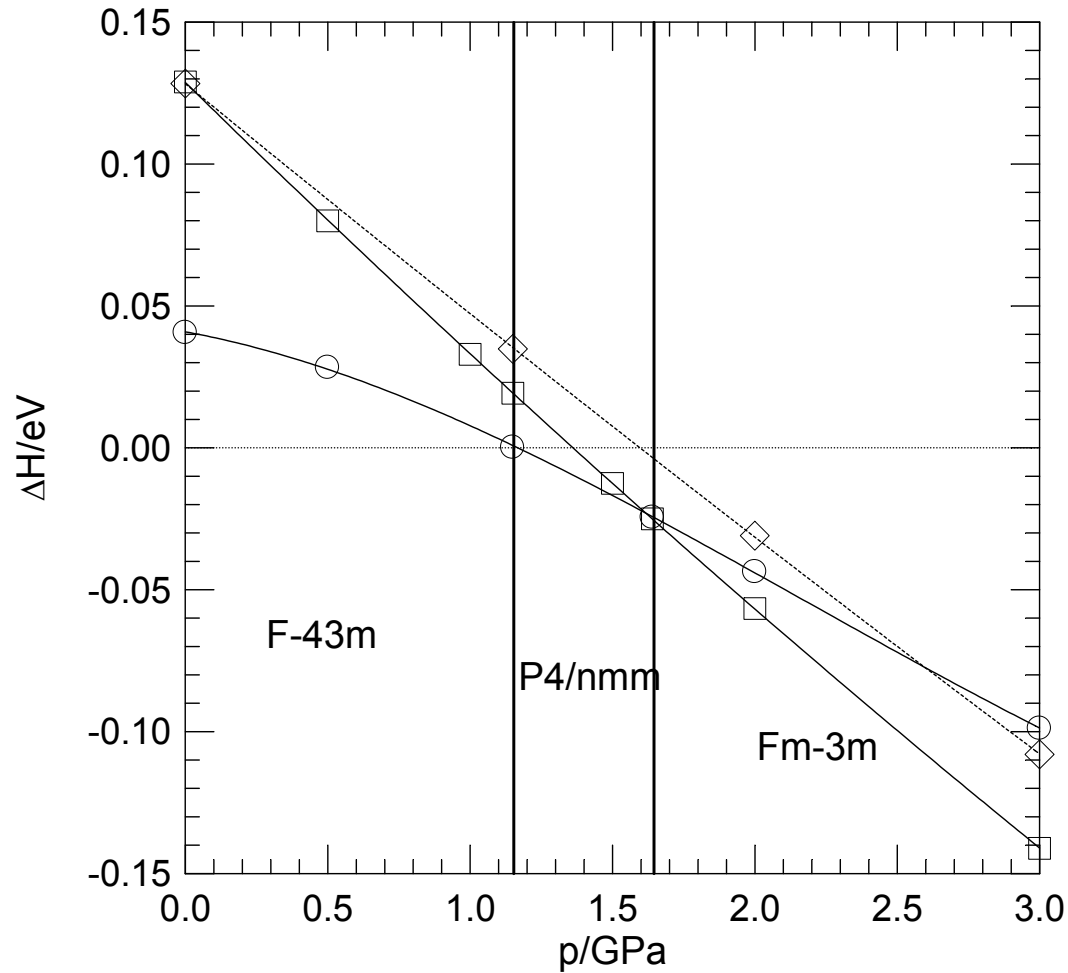
Pm (zincblende): $a = b = a_{\text{I}}/\sqrt{2}$, $c = a_{\text{I}}$;

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

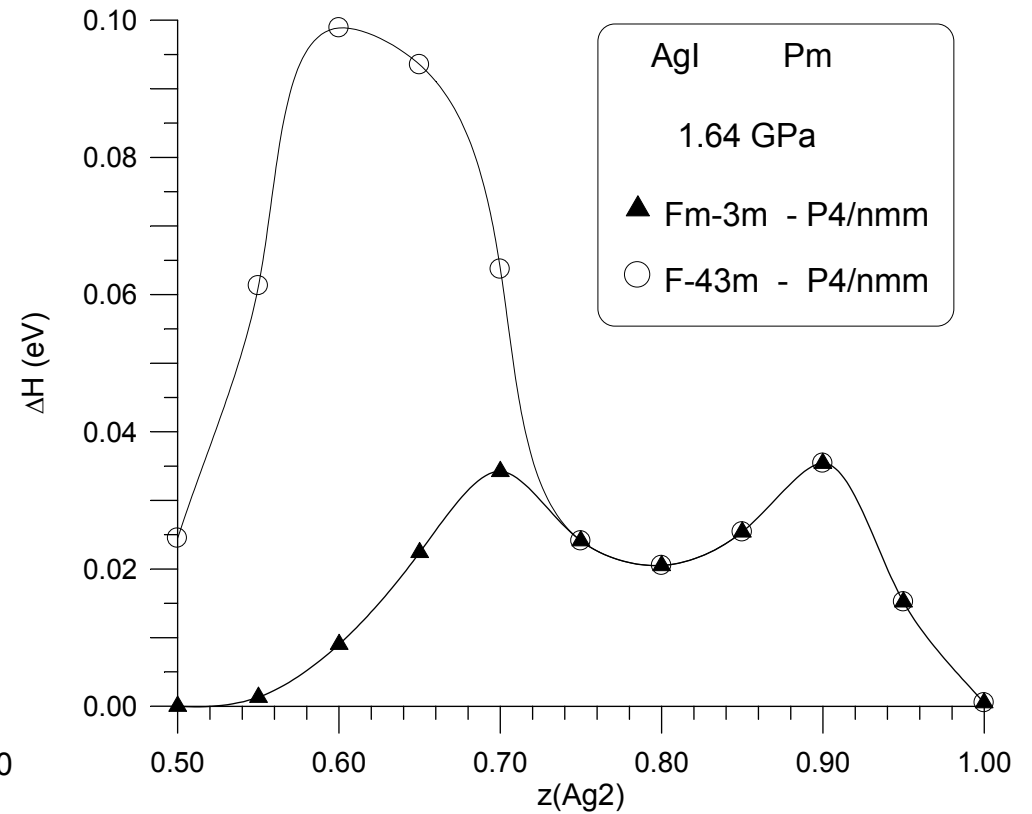
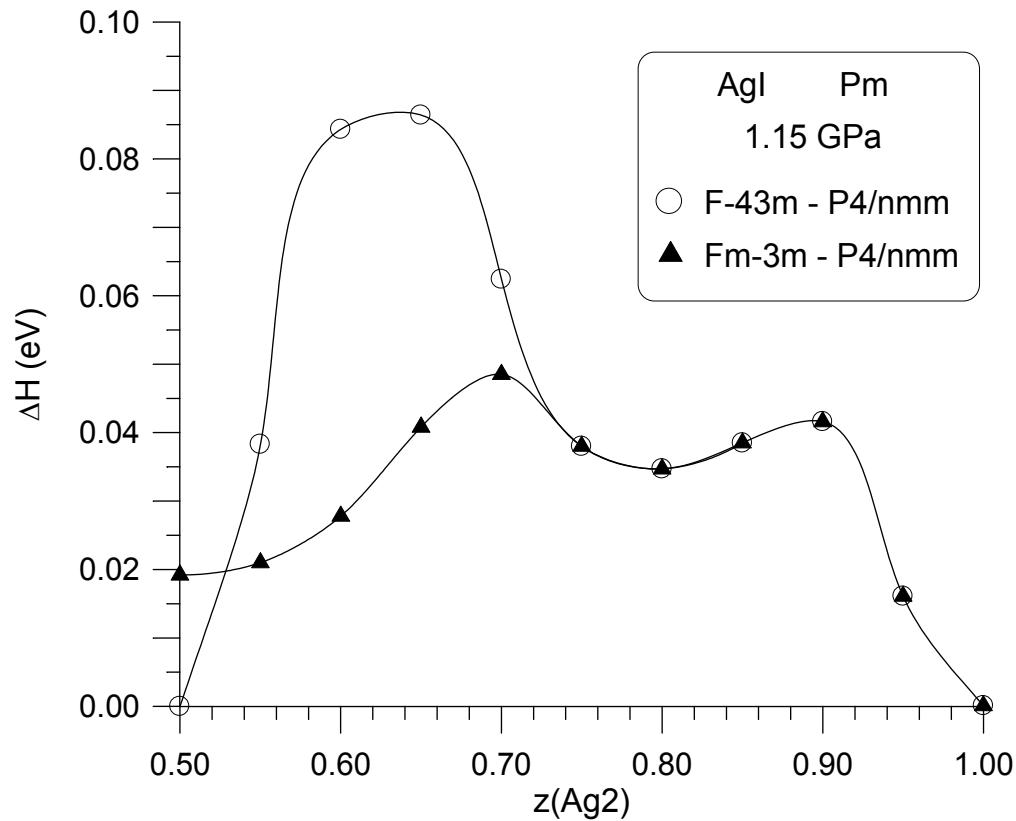
Pm (rocksalt): $a = c = a_{\text{II}}/\sqrt{2}$, $b = a_{\text{II}}$



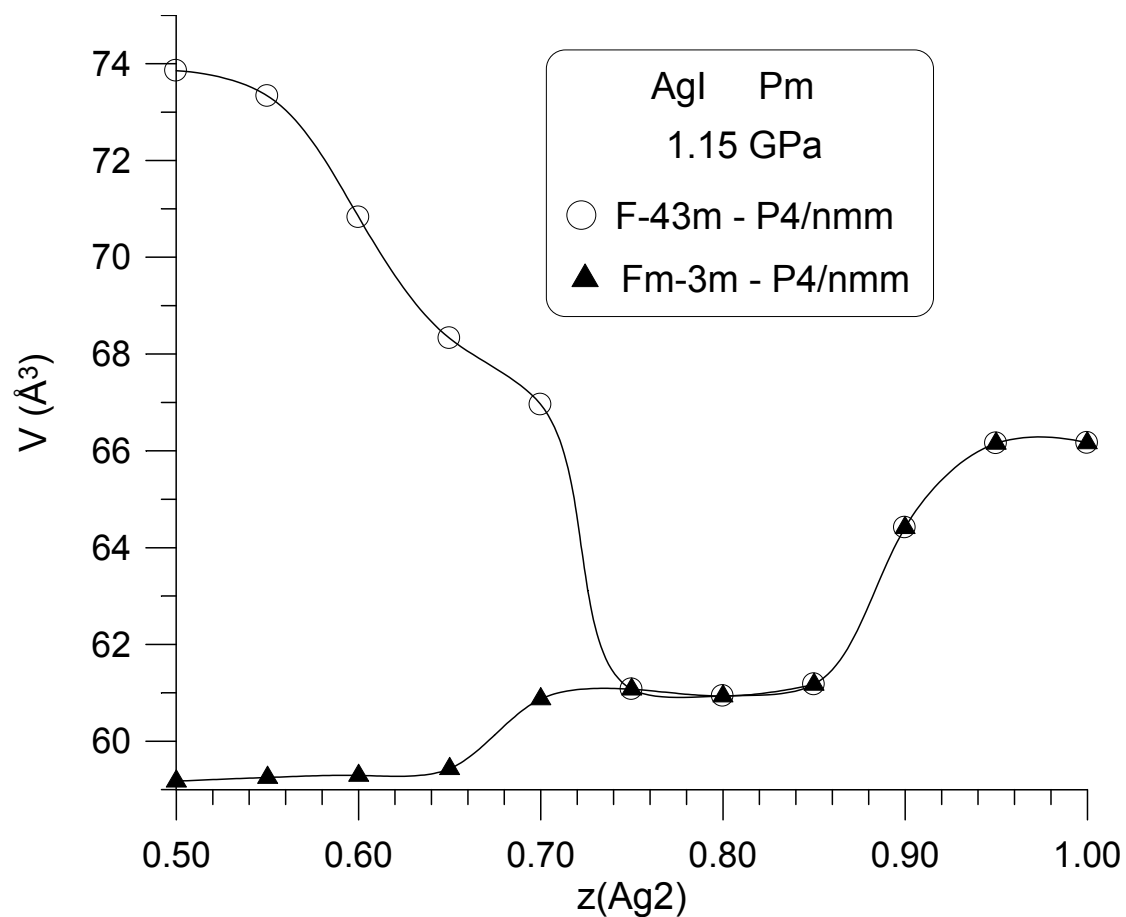
Pm monoclinic mechanisms for the zincblende (a) to anti-litharge (d), and anti-litharge (d) to rocksalt (f) phase transformations of AgI. The pseudo-orthorhombic Bmm2 intermediate state (c) is present in both pathways.



Theoretical enthalpy differences $H - H(F\bar{4}3m)$ plotted vs. pressure for the AgI phases P4/nmm (anti-litharge, circles), $Fm\bar{3}m$ (rocksalt, squares), and Bmm2 (metastable phase, diamonds). Vertical lines bound the predicted pressure stability fields



Theoretical enthalpy difference $H(z(\text{Ag}_2)) - H(\text{zincblende})$ 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 $z(\text{Ag}2)$ order parameter at the equilibrium pressure 1.15 GPa. Coordinates constrained by symmetry: $x(\text{Ag}1)=y(\text{Ag}1)=z(\text{Ag}1)=y(\text{I}2)=0$; $y(\text{Ag}2)=y(\text{I}1)=1/2$. The enthalpy values per formula unit, referred to that of the $F\bar{4}3m$ phase, are also given.

$z(\text{Ag}2)$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	β/deg	$x(\text{Ag}2)$	$x(\text{I}1)$	$z(\text{I}1)$	$x(\text{I}2)$	$z(\text{I}2)$	$\Delta H/\text{eV}$
0.5	4.709	4.709	6.660	90	0.5	0	0.25	0.5	0.75	0
0.55	4.858	4.852	6.228	87.39	0.4171	0.9585	0.2706	0.5114	0.7673	0.0383
0.60	5.005	4.931	5.754	85.88	0.3049	0.9206	0.2631	0.5147	0.7523	0.0843
0.65	5.058	5.055	5.350	87.51	0.2325	0.9013	0.2367	0.4989	0.7163	0.0864
0.70	5.004	5.065	5.283	89.95	0.1892	0.8947	0.2355	0.4853	0.6991	0.0624
0.75	4.745	5.452	4.796	100.12	0.1934	0.8049	0.1634	0.3901	0.5891	0.0380
0.80	4.801	5.390	4.787	100.39	0.2207	0.8194	0.1931	0.4013	0.6074	0.0347
0.85	4.864	5.313	4.808	99.99	0.2536	0.8385	0.2213	0.4149	0.6286	0.0385
0.90	4.750	5.035	5.418	96.12	0.3120	0.8680	0.2399	0.4436	0.6603	0.0416
0.95	4.389	4.662	6.467	91.14	0.4614	0.9730	0.2643	0.4884	0.6856	0.0161
1.00	4.474	4.474	6.610	90	0.5	0	0.2885	0.5	0.7115	0

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 $z(\text{Ag}2)$ 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.

$z(\text{Ag}2)$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	β/deg	$x(\text{Ag}2)$	$x(\text{I}1)$	$z(\text{I}1)$	$x(\text{I}2)$	$z(\text{I}2)$	$\Delta H/\text{eV}$
1.00	4.450	4.450	6.500	90	0.5	1	0.2938	0.5	0.7062	0
0.95	4.349	4.628	6.411	91.08	0.4631	0.9727	0.2684	0.4887	0.6816	0.0152
0.90	4.821	5.102	5.085	97.11	0.3087	0.8688	0.2467	0.4427	0.6534	0.0354
0.85	4.844	5.314	4.751	100.18	0.2536	0.8377	0.2233	0.4157	0.6266	0.0254
0.80	4.773	5.377	4.754	100.43	0.2209	0.8183	0.1945	0.4026	0.6058	0.0205
0.75	4.707	5.439	4.770	100.06	0.1945	0.8028	0.1641	0.3921	0.5876	0.0241
0.70	4.558	5.817	4.559	97.25	0.2994	0.8684	0.1315	0.4316	0.5684	0.0342
0.65	4.430	6.081	4.354	90.60	0.4776	0.9834	0.1121	0.4932	0.5380	0.0224
0.60	4.389	6.127	4.356	90.26	0.4856	0.9092	0.0749	0.4958	0.5262	0.0090
0.55	4.364	6.156	4.356	90.09	0.4890	0.9905	0.0407	0.4965	0.5145	0.0013
0.50	4.356	6.161	4.356	90	0.5	1	0	0.5	0.5	0

References

Capillas C, PhD Thesis, Bilbao (2006)

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

Catti M, *Phys. Rev. B* **65** 224115 (2002)

Catti M, *Phys. Rev. B* **68** 100101(R) (2003)

Catti M, *J. Phys.: Condens. Matter* **16** 3909 (2004)

Catti M, *Phys. Rev. B* **72** 64105 (2005)

Stokes H T and Hatch D M, *Phys. Rev. B* **65** 144114 (2002)

Toledano P and Dmitriev V, '*Reconstructive Phase Transitions*' Singapore: World Scientific (1996)

Toledano J C and Toledano P, '*The Landau Theory of Phase Transitions*' Singapore: World Scientific (1987)