Symmetry aspects of structural phase transitions

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Thermodynamic order of the phase transition (Ehrenfest's classification):

smallest order of the derivatives of the Gibbs free energy G (with respect to the relevant variable, T or p) which are discontinuous across the transition

First-order transitions:

the first-order derivatives (entropy S and volume V) are discontinuous, leading to enthalpy (latent heat) ΔH and volume ΔV jumps

$$dG = -SdT + Vdp \quad (1)$$

Second-order transitions:

the second-order derivatives (heat capacity C_p and compressibility β) are discontinuous, whereas the first-order ones are continuous (no heat or volume effects): $\Delta S = 0$, $\Delta H = 0$, $\Delta V = 0$

$$d^2G = - (C_p/T)dT^2 - V\beta dp^2 - V\alpha dTdp \quad (2)$$

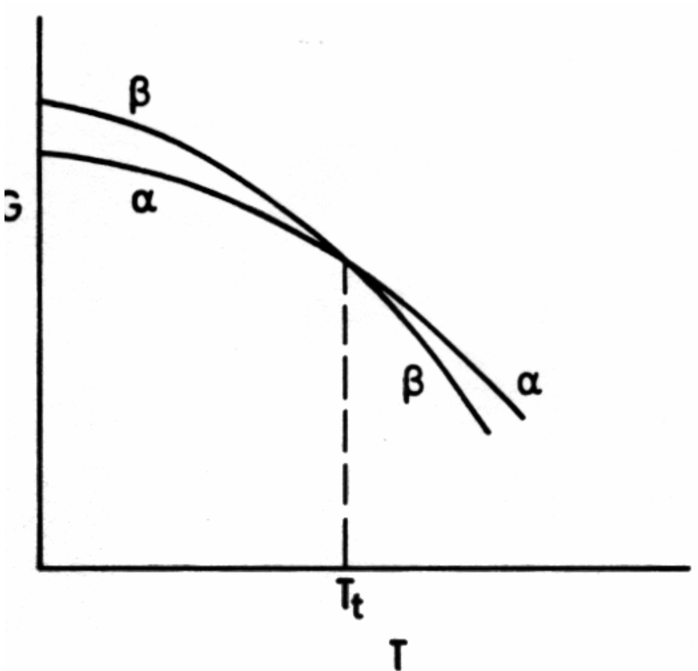
Phase α stable for $T < T_c$, phase β stable for $T > T_c$ $\rightarrow$

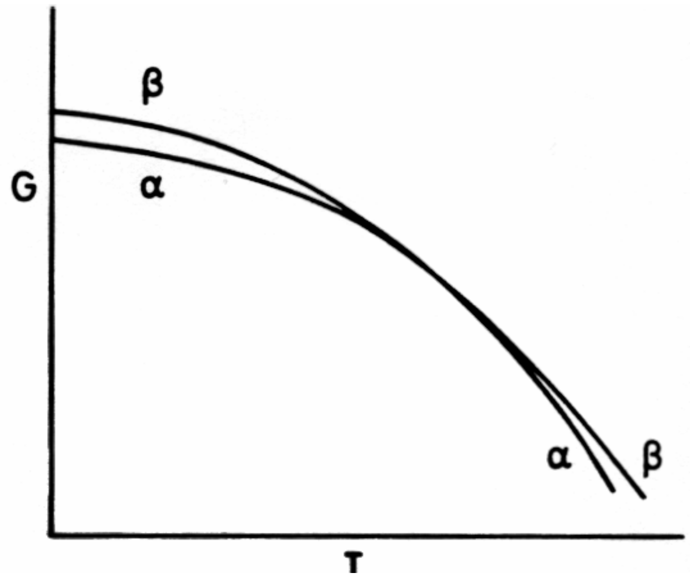
$\Delta G = G_\beta - G_\alpha > 0$ for $T < T_c$, $\Delta G = G_\beta - G_\alpha < 0$ for $T > T_c$?

But .... Taylor expansion about T_c of the Gibbs free energy of each phase:

$$G = G(T_c) - S(T-T_c) - \frac{C_{p,c}}{2T_c}(T-T_c)^2 + ... \qquad (3)$$

$$\Delta G = G_\beta - G_\alpha = -\frac{\Delta C_{p,c}}{2T_c}(T-T_c)^2 + ... \qquad \text{same sign for } T < T_c \text{ and for } T > T_c\,! \qquad (4)$$





Buerger's classification of structural phase transitions

<u>reconstructive</u>: 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)

<u>displacive</u>: 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

<u>order/disorder</u>: 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 η measures the 'distance' of the low-symmetry to the high-symmetry (η=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:

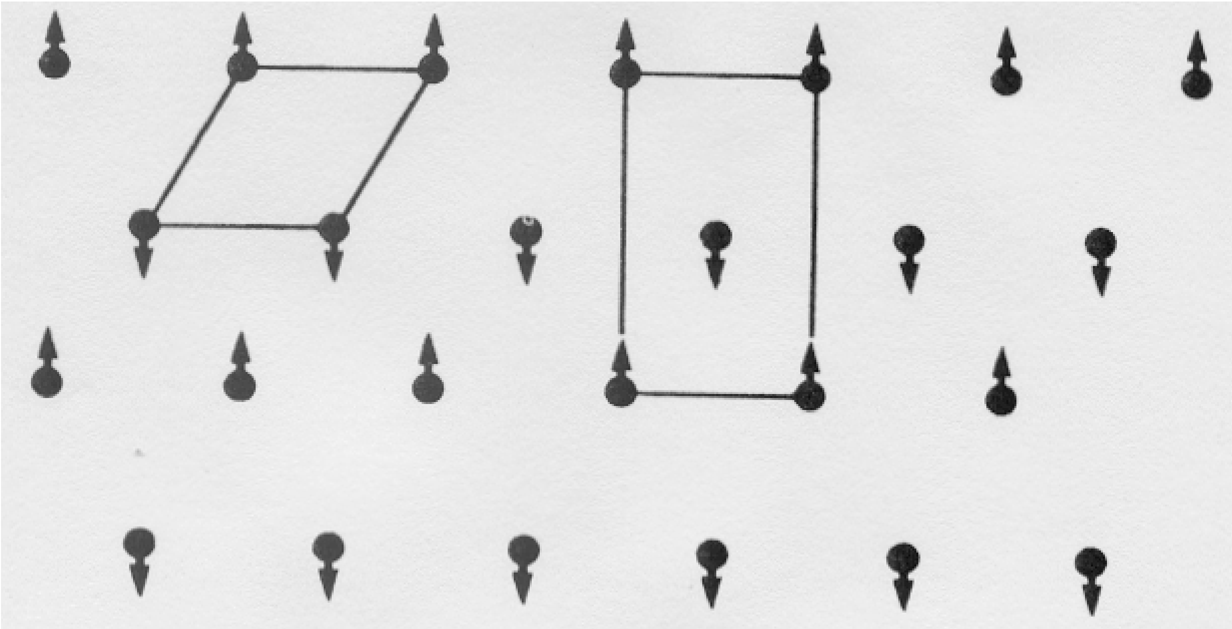
HCP to BCC, FCC to HCP and BCC to FCC in metals and alloys

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

Examples of displacive phase transitions:

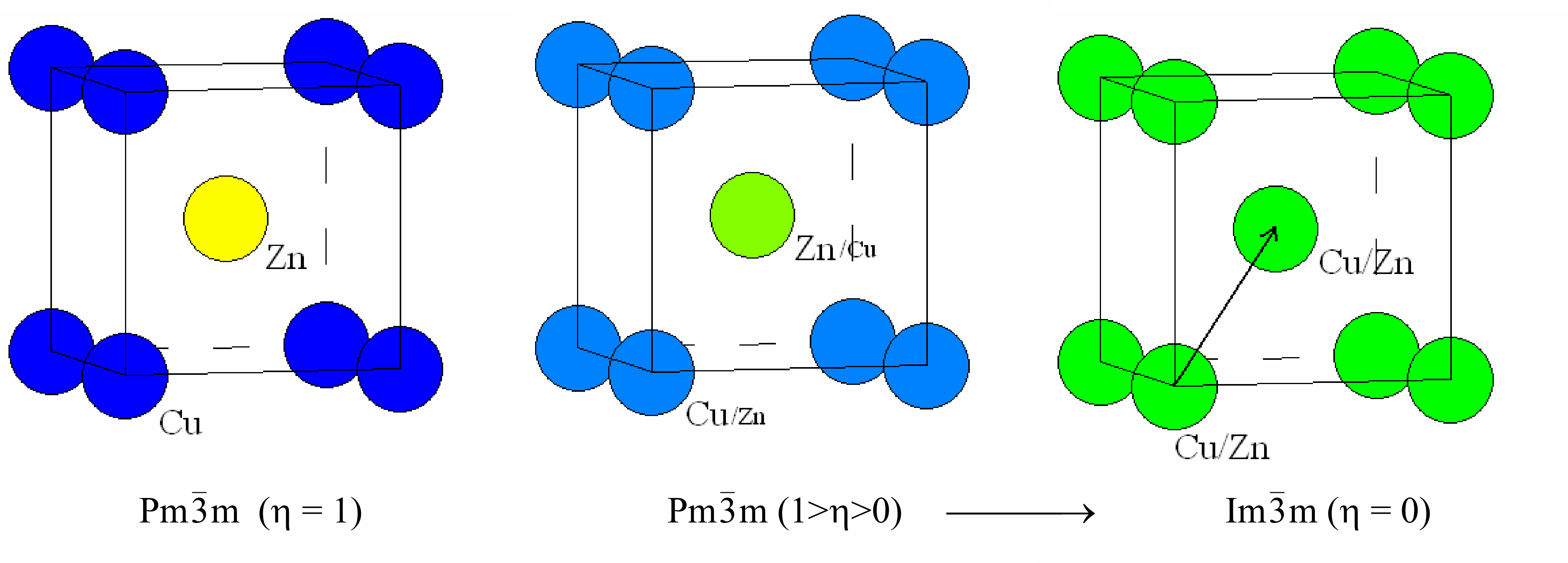
NiAs-type ($P6_3/mmc$) to MnP-type ($Pcmn$) of CoAs and VS



Hexagonal (NiAs-type) and orthorhombic (MnP-type) cells outlined

Order parameter η: length of the vector describing the structural distortion

Examples of order/disorder phase transitions: β - β' brass transition in CuZn: $Pm\bar{3}m$ to $Im\bar{3}m$



Order parameter: $\eta = 2f_{Cu} - 1$

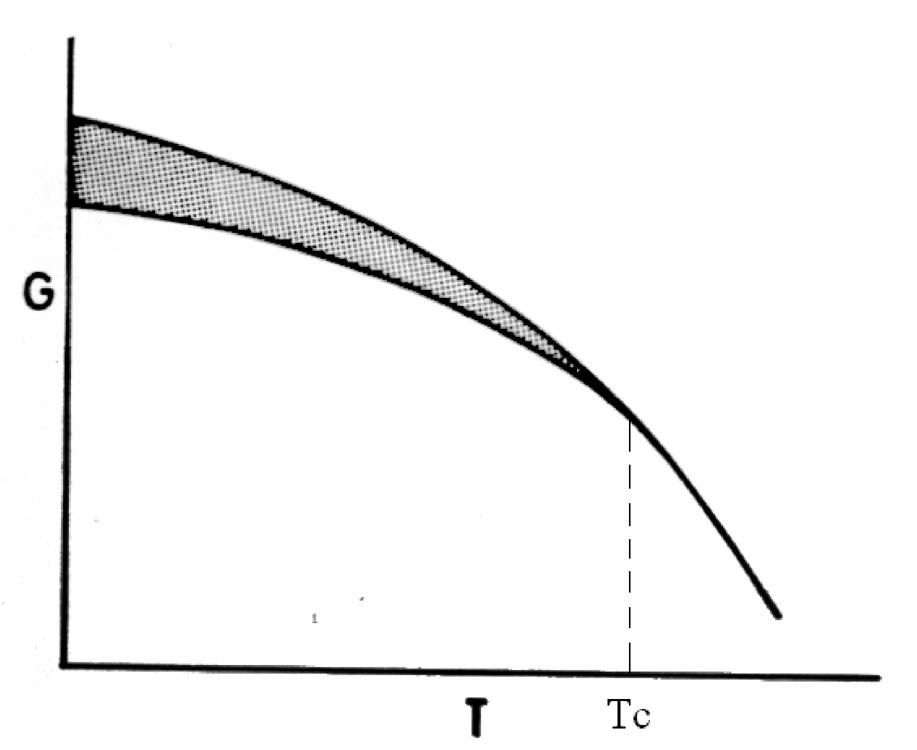
f_{Cu}: fraction of Cu atoms occupying the site at 0,0,0 → f_{Cu} changes from 1 (full ordered $Pm\bar{3}m$ structure) to 1/2 (full disordered $Im\bar{3}m$ structure)

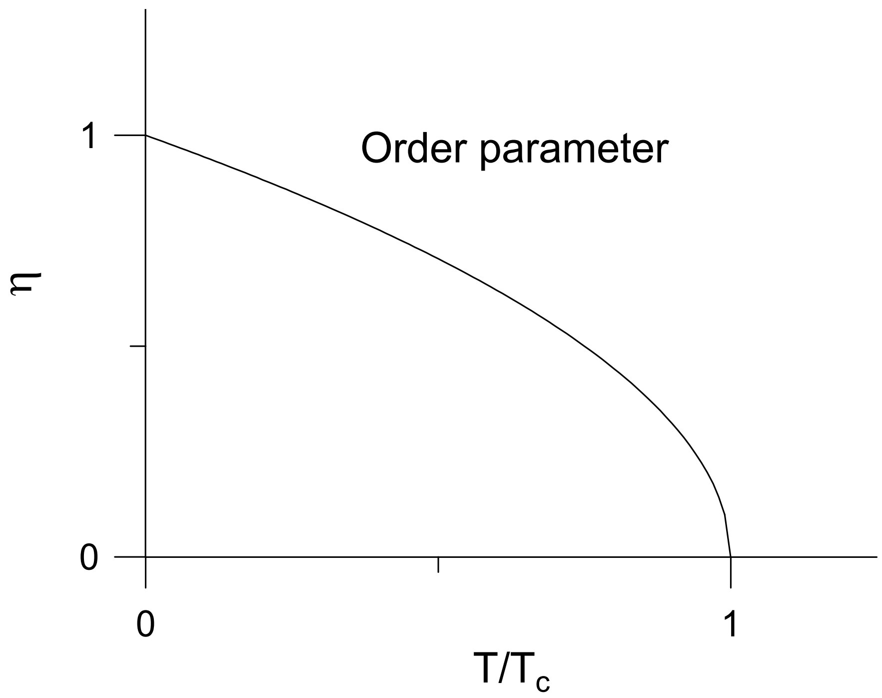
Continuous transformation with symmetry group/subgroup relation:

the low-symmetry phase approaches gradually the point where new symmetry elements are acquired

- the low-symmetry phase can not survive, even in a metastable form, above T_c $\longrightarrow$

  the Taylor expansion (3) is not allowed above T_c !





Elements of Landau's theory of continuous (displacive and order-disorder) phase transitions

Taylor expansion of $G(\eta)$ around its stationary point $\eta=0$:

$G = G(p,T,\eta) = G_0 + A\eta^2 + B\eta^3 + C\eta^4 + \ .... \ \rightarrow$ fourth-order truncation $\rightarrow$

$G - G_0 \cong A(p,T)\eta^2 + B(p,T)\eta^3 + C(p,T)\eta^4 \qquad (C > 0)$

$\partial G/\partial\eta = \eta(2A + 3B\eta + 4C\eta^2)$

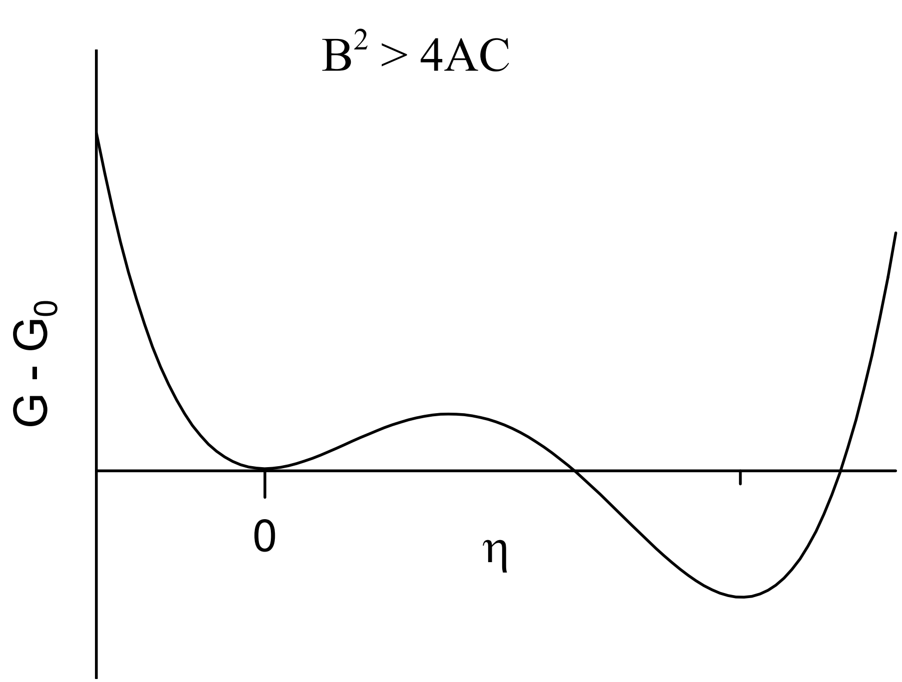
$$(\partial^2 G/\partial\eta^2)_{\eta=0} = 2A \rightarrow \begin{cases} A > 0 & \eta=0 \text{ is a minimum} \\ A < 0 & \eta=0 \text{ is a maximum} \end{cases}$$

1) $A > 0$

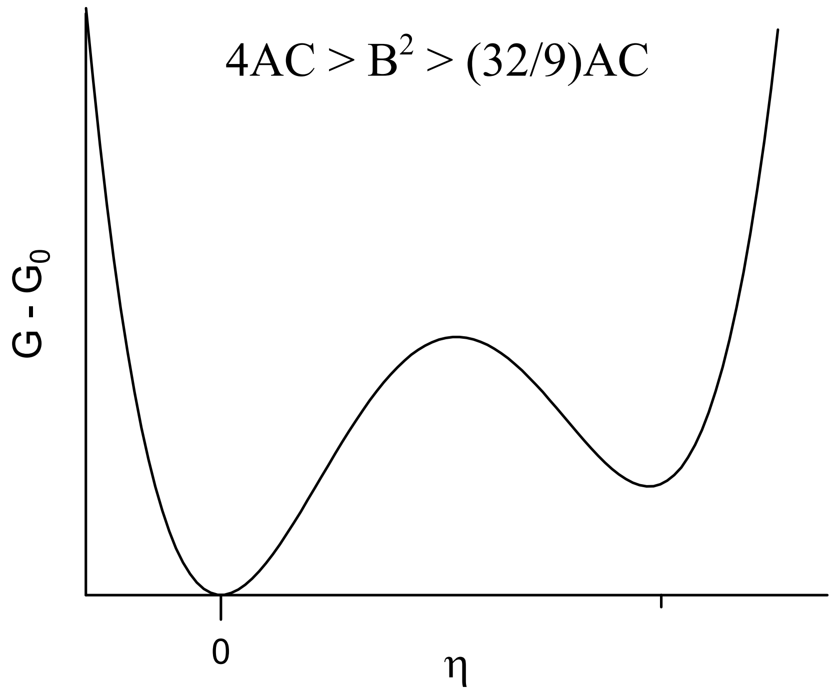
$G - G_0 = 0 \ \rightarrow$ either one, two or three roots, according to the sign of $B^2 - 4AC$

$\partial G/\partial\eta = 0 \ \rightarrow$ either one, two or three roots, according to the sign of $B^2 -(32/9)AC$

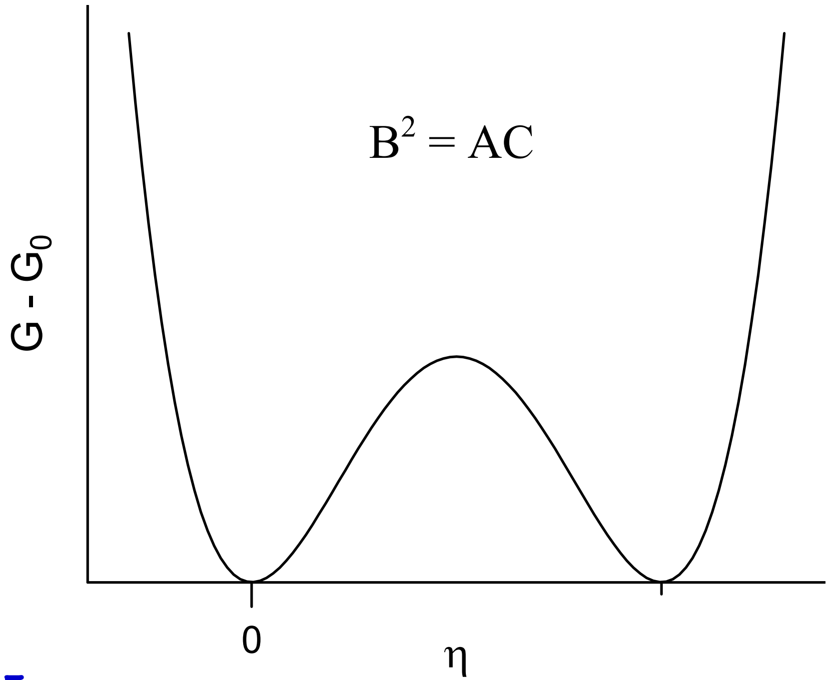
equilibrium of two phases at $T = T_c$, metastability at $T \neq T_c \ \rightarrow$ <u>first-order thermodynamics</u>



$B^2 > 4AC$
$G - G_0$
0
η

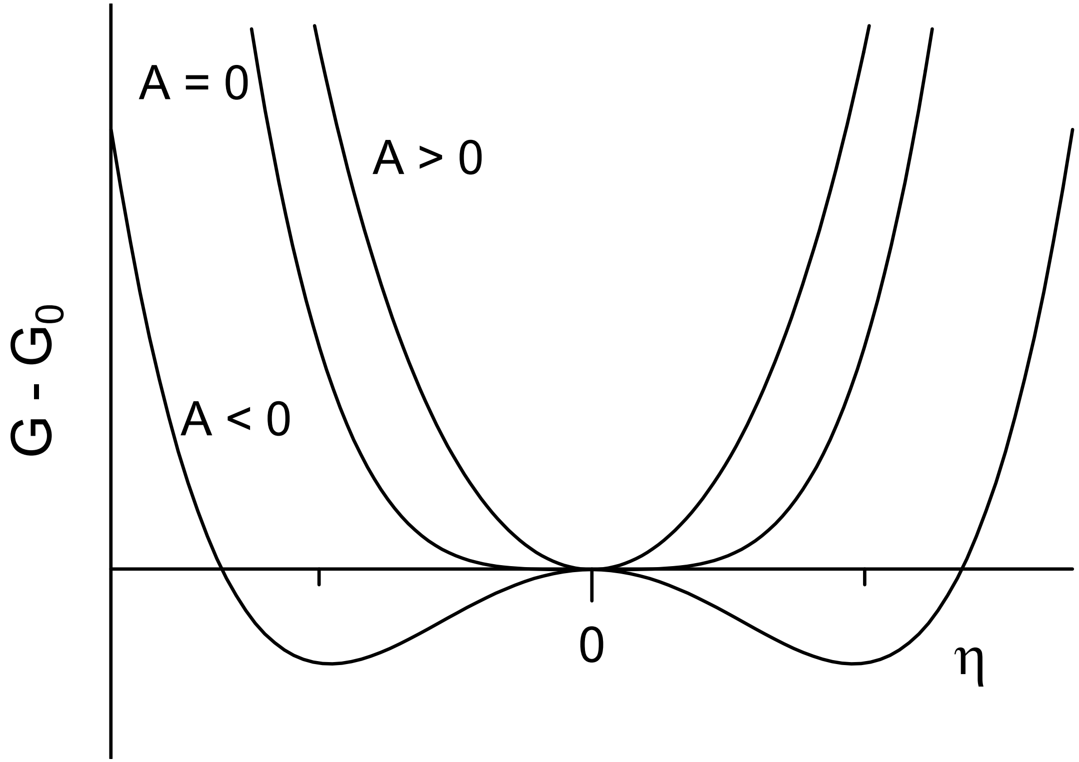


$4AC > B^2 > (32/9)AC$
$G - G_0$
0
η



$B^2 = AC$
$G - G_0$
0
η

2) $A > 0$, $A = 0$, $A < 0$ let $B = 0$ $\rightarrow$ $G - G_0 = A\eta^2 + C\eta^4$



$\partial G/\partial \eta = 2\eta(A + 2C\eta^2) = 0 \rightarrow$

$(A<0)$ $\eta = (-A/2C)^{1/2}$

order parameter of the low-symmetry phase as a function of p,T

No equilibrium of two phases at $T = T_c$, no metastability effects at $T \neq T_c$ $\rightarrow$

<u>second-order thermodynamics</u>

As $A(T_c) = 0$, and $A<0$ for $T<T_c$ and $A>0$ for $T>T_c$, in the neighbourhood of $T=T_c$:

$A(T) \approx a(T-T_c)$, $\eta = [a(T_c-T)/2C]^{1/2} \approx (T_c-T)^{1/2}$ consistent with experimental behaviour for second-order phase transitions

$S - S_0 = -\partial(G-G_0)/\partial T = a^2(T-T_c)/2C$ behaves continuously across the phase transition

$C_p - C_{p,0} = T\partial(S-S_0)/\partial T = a^2T/2C$

$\lim_{T\to Tc} (C_p-C_{p,0}) = a^2T_c/2C = \Delta C_p$ second-order discontinuity

Mechanisms of reconstructive phase transitions and symmetry of the intermediate states

G_1 (S.G. of phase 1) $\rightarrow$ G (S.G. of intermediate state) $\rightarrow$ G_2 (S.G. pf phase 2)

$$G \subset G_1, \quad G \subset G_2, \quad G_1 \not\subset G_2$$

Let T_1, T_2 and T be the translation groups of G_1, G_2 and G, respectively, and $T_1 \subseteq T_2$. Then:

$$T \subseteq T_1, \;\; T \subseteq T_2$$

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 G 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' of the superlattice).

The first step of a systematic search of the possible intermediate states (Stokes and Hatch, PRB 2002) involves the search for all common superlattices of phases 1 and 2.

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

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 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) !

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 $Q_1Q_2^{-1}$ 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 with the same geometry as T_1 and as 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 G must be a subgroup of P: $P' \subseteq P$.

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

Important constrain on the atomic displacements during the reconstructive phase transition:

<u>Atoms must remain in the same types of Wyckoff positions of G along the entire path $G_1 \rightarrow G_2$</u>.

Example: rocksalt (G_1= $Fm\bar{3}m$) to CsCl-type (G_2= $Pm\bar{3}m$) structure in NaCl under pressure
Na and Cl in Wyckoff positions (a) and (b), respectively, in both G_1 and G_2

Particular pair of Q_1 and Q_2 matrices:

Q_1 = [-1 1 1 / 0 -1 1 / 1 0 0] (for the conventional F cell: [1 0 0 / 0 ½ -½ / 0 ½ ½])
Q_2 = [1 0 1 / 1 0 -1 / 0 1 0]
$\det(Q_1) = \det(Q_2) = 2$ (index of the superlattice)

$Q_1Q_2^{-1}$ = [-½ 0 1 / 1 0 0 / -½ 1 0]   (for the conventional F cell: [½ ¼ -¼ / 0 ½ ½ / ½ -¼ ¼])

Notice that the $Q_1Q_2^{-1}$ matrix has not all integer components !

P_1 = 4/mmm P_2 = mmm $P' = P = P_1 \cap P_2$ = mmm

G may be either Pmmm or Pmmn

G = Pmmm: the Wyckoff position (a) in G_1 splits into positions (a) and (h) in G, and position (a) in G_2 splits into positions (a) and (d) in G.

There is no way that a structure with atoms at (a) and (h) can evolve continuously to a structure with atoms at (a) and (d) without losing the symmetry Pmmm of G   →   <u>Pmmm is rejected</u>

G = Pmmn: Na atoms are at position (a) and Cl are at (b) at both ends of the path:

the condition concerning Wyckoff positions is satisfied   →   <u>Pmmn is accepted</u>

Pmmn is a maximal common subgroup of $Fm\bar{3}m$ and $Pm\bar{3}m$, with a T translation group of index 2

Within the conditions that unit-cell vectors not longer than 6 Å can be chosen, and that the principal strain components are comprised within 0.66 and 1.5, the following 12 maximal common subgroups are derived (the superlattice index is shown below):

$R\bar{3}m$	Pmmn	$Cmc2_1$	C2(1)	C2(2)	Iba2	P2/c(1)	P2/c(2)	$P2_1/m$	C2/c	Pc	$P\bar{1}$
1	2	2	2	2	4	4	4	4	4	4	4

Transformation pathways can be based also on non-maximal common subgroups

Unstable normal vibrational mode at a special symmetry point of the Brillouin zone for a maximal subgroup (e.g., F point, three-dimensional irreducible representation F_2^- of $R\bar{3}m$) →

non-maximal common subgroups derived from the $R\bar{3}m$ maximal subgroup

$P2_1/m$	$C2/m$	$R3m$
2	4	4

$Fm\bar{3}m$ (B1) Z=4 M 0, 0, 0 ($m\bar{3}m$); X ½, ½, ½ ($m\bar{3}m$) a_I

$Pm\bar{3}m$ (B2) Z=1 M 0, 0, 0 ($m\bar{3}m$); X ½, ½, ½ ($m\bar{3}m$) a_{II}

Intermediate states:

I - Pmmn Z=2 M ¼, ¼, z (¼→ ½) (mm2); X ¼, ¾, z+ ½ (¾ → 0) (mm2)

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

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

$Fm\bar{3}m \rightarrow Pm\bar{3}m$ $$Q_1Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{1}{2} & \frac{1}{4} \end{bmatrix} \qquad (Q_1Q_2^{-1})^{-1} = \begin{bmatrix} 1 & 1 & -1 \\ 0 & 1 & 1 \\ 1 & -1 & 1 \end{bmatrix}$$

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

II1 - R$\bar{3}$m Z=1 M 0, 0, 0 ($\bar{3}$m); X ½, ½, ½ ($\bar{3}$m)

Fm$\bar{3}$m → R$\bar{3}$m $Q_1 = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix}$ $Q_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$

Pm$\bar{3}$m → R$\bar{3}$m $Q_2 = Q_2^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Fm$\bar{3}$m → Pm$\bar{3}$m $Q_1Q_2^{-1} = Q_1 = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix}$ $(Q_1Q_2^{-1})^{-1} = Q_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$

R$\bar{3}$m (B1): $a_R = a_I/\sqrt{2}$, $\alpha_R = 60°$; R$\bar{3}$m (B2): $a_R = a_{II}$, $\alpha_R = 90°$

II2 - $P2_1/m$ $Z=2$ M $x_1(\frac{1}{4}), \frac{1}{4}, z_1(0)$ (m); X $x_2(\frac{3}{4}), \frac{1}{4}, z_2(\frac{1}{2})$ (m)

$Fm\bar{3}m \rightarrow P2_1/m$ $$Q_1 = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \qquad Q_1^{-1} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & -1 & 0 \\ 1 & 1 & -1 \end{bmatrix}$$

$Pm\bar{3}m \rightarrow P2_1/m$, $R\bar{3}m \rightarrow P2_1/m$ $$Q_2 = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad Q_2^{-1} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$Fm\bar{3}m \rightarrow Pm\bar{3}m$ $$Q_1Q_2^{-1} = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix} \qquad (Q_1Q_2^{-1})^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

$P2_1/m$ (B1): $a = a_I\sqrt{(3/2)}$, $b = c = a_I/\sqrt{2}$, $\beta = \arccos(1/\sqrt{3}) = 54.74°$;

$P2_1/m$ (B2): $a = b = a_{II}\sqrt{2}$, $c = a_{II}$, $\beta = 90°$;

$P2_1/m$ ($R\bar{3}m$): $a = a_R[2(1+\cos\alpha_R)]^{1/2}$, $b = a_R[2(1-\cos\alpha_R)]^{1/2}$, $c = a_R$, $\beta = \arccos[\cos\alpha_R/\cos(\alpha_R/2)]$

II3 - R3m $Z=4$ M_1 0, 0, 0 (3m); M_2 $x_1(½), x_1(½), z_1(0)$ (3m)
X_1 $x_2(½), x_2(½), x_2(½)$ (3m); X_2 $x_3(0), x_3(0), z_2(½)$ (3m)

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

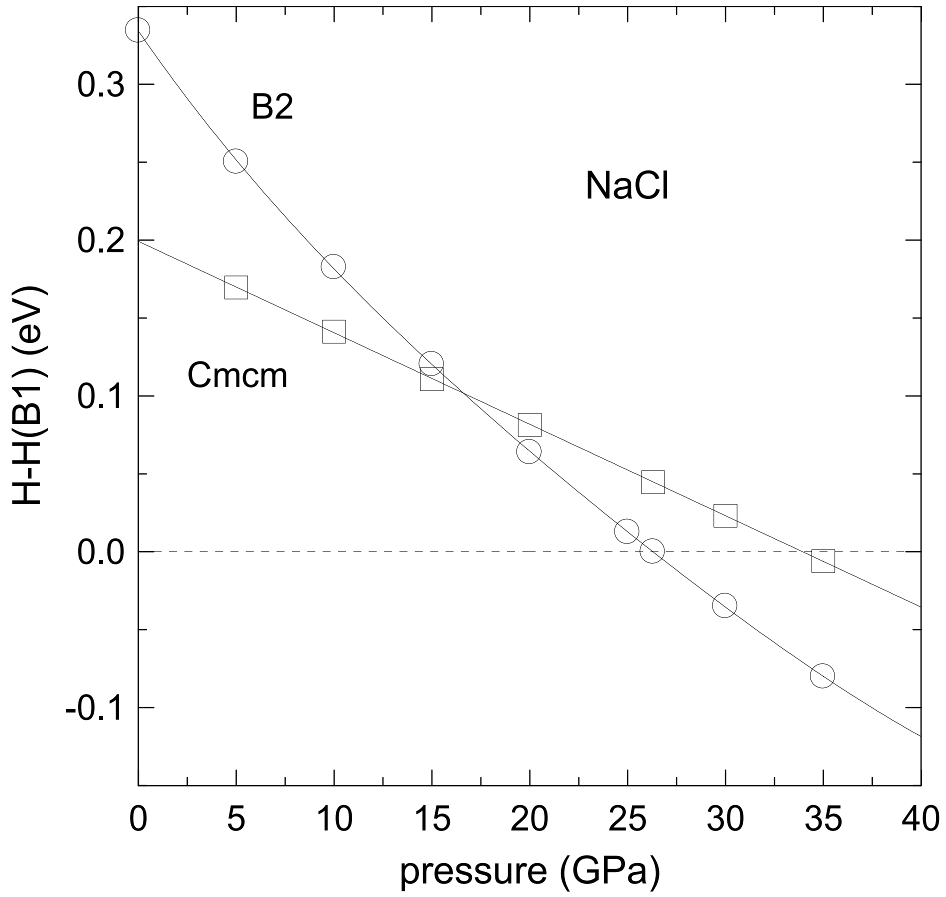
$Pm\bar{3}m \rightarrow R3m$, $R\bar{3}m \rightarrow R3m$ $$Q_2 = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix} \qquad Q_2^{-1} = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix}$$

$Fm\bar{3}m \rightarrow Pm\bar{3}m$ $$Q_1Q_2^{-1} = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix} \qquad (Q_1Q_2^{-1})^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

R3m (B1): $a_R' = a_I$, $\alpha_R = 90°$;

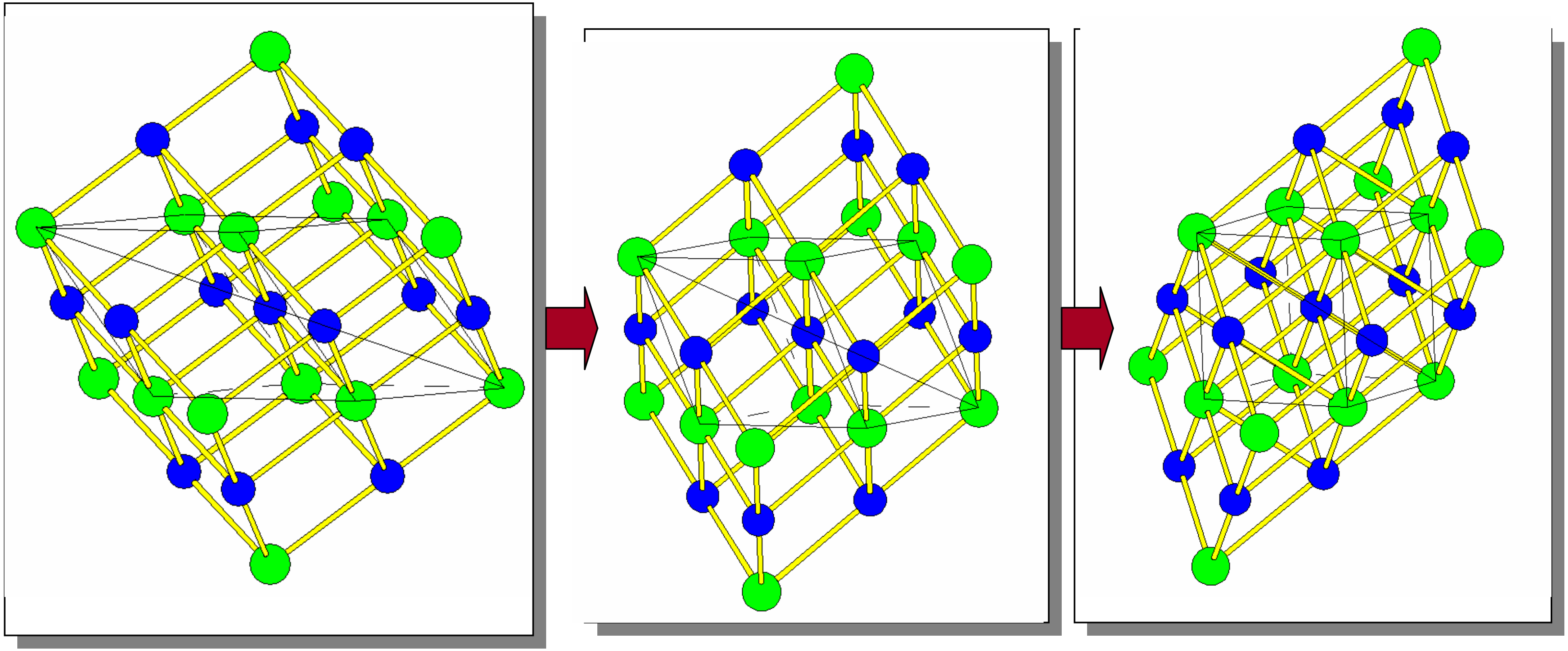
R3m (B2): $a_R' = a_{II}\sqrt{3}$, $\alpha_R = \arccos(-1/3)=109.47°$;

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



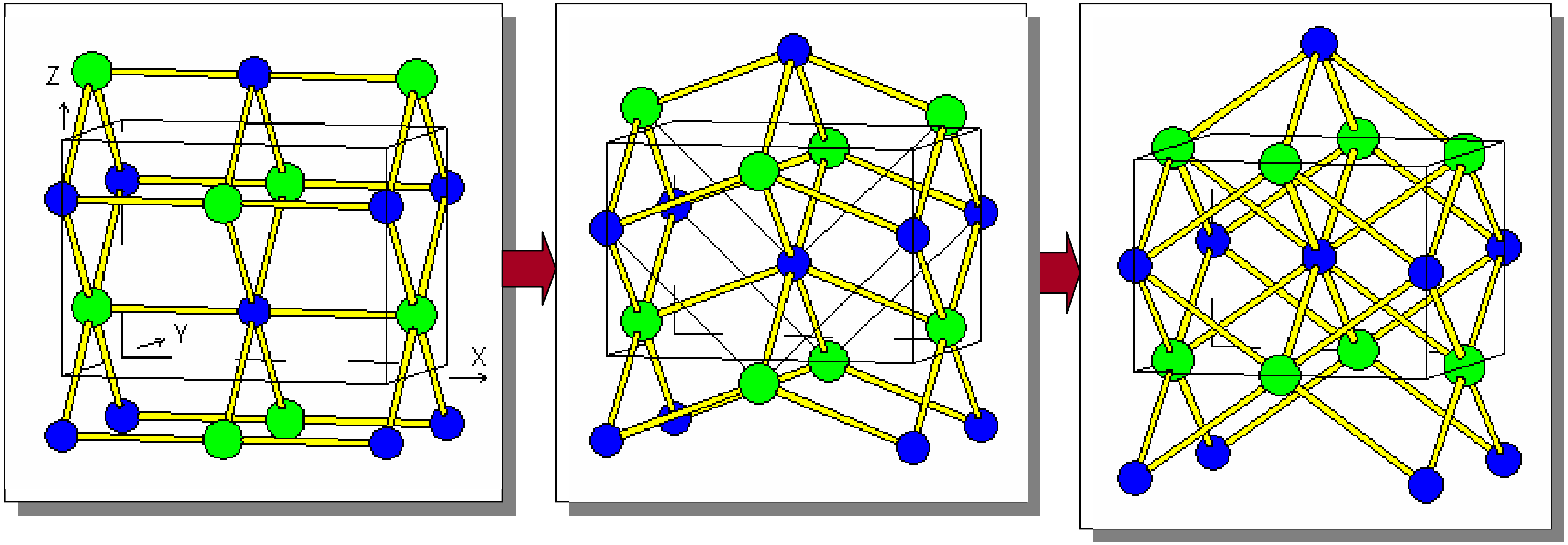
Theoretical phase diagram of NaCl (enthalpy vs. pressure). Enthalpy curves of the B2 ($Pm\bar{3}m$ CsCl-type) and of the metastable (Cmcm TlI-type) phases are referred to that of B1 ($Fm\bar{3}m$ rocksalt, dashed horizontal line) (cf. Catti, PRB 2003 and JPCM 2003)

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



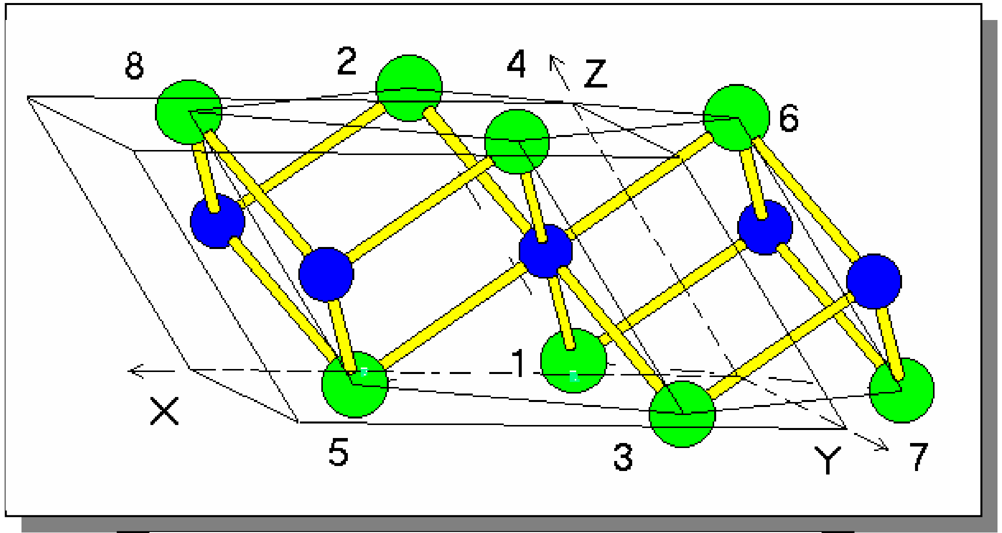
B1(Fm$\bar{3}$m) R$\bar{3}$m B2(Pm$\bar{3}$m)

Pmmn pathway of the B1/B2 phase transition



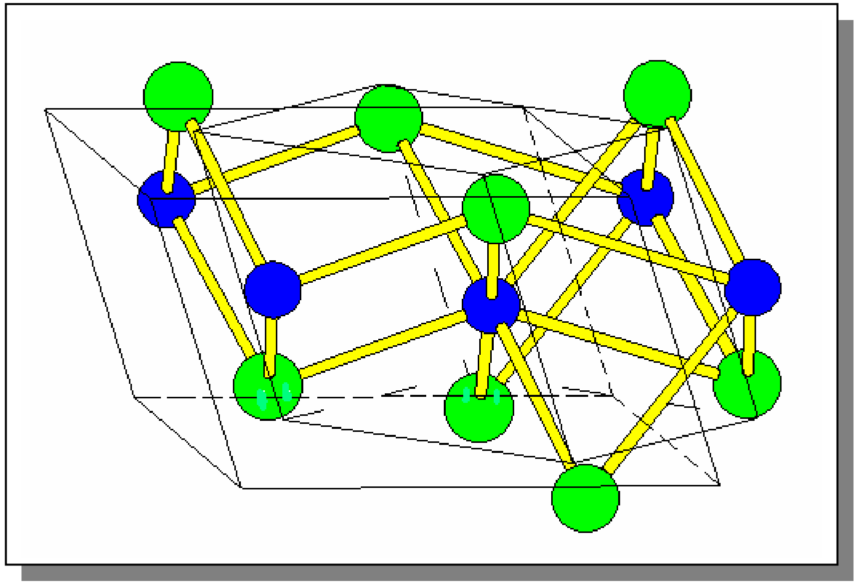
B1($Fm\bar{3}m$) Pmmn B2($Pm\bar{3}m$)

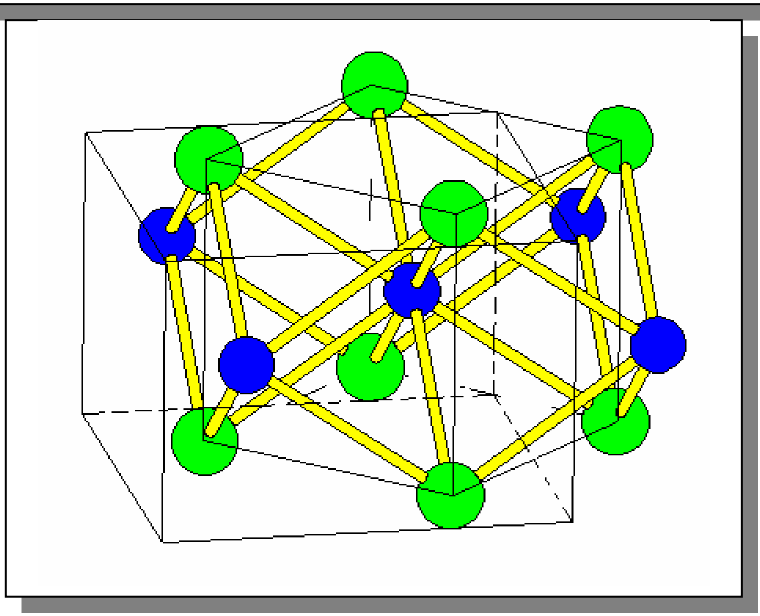
$P2_1/m$ pathway of the B1/B2 phase transition



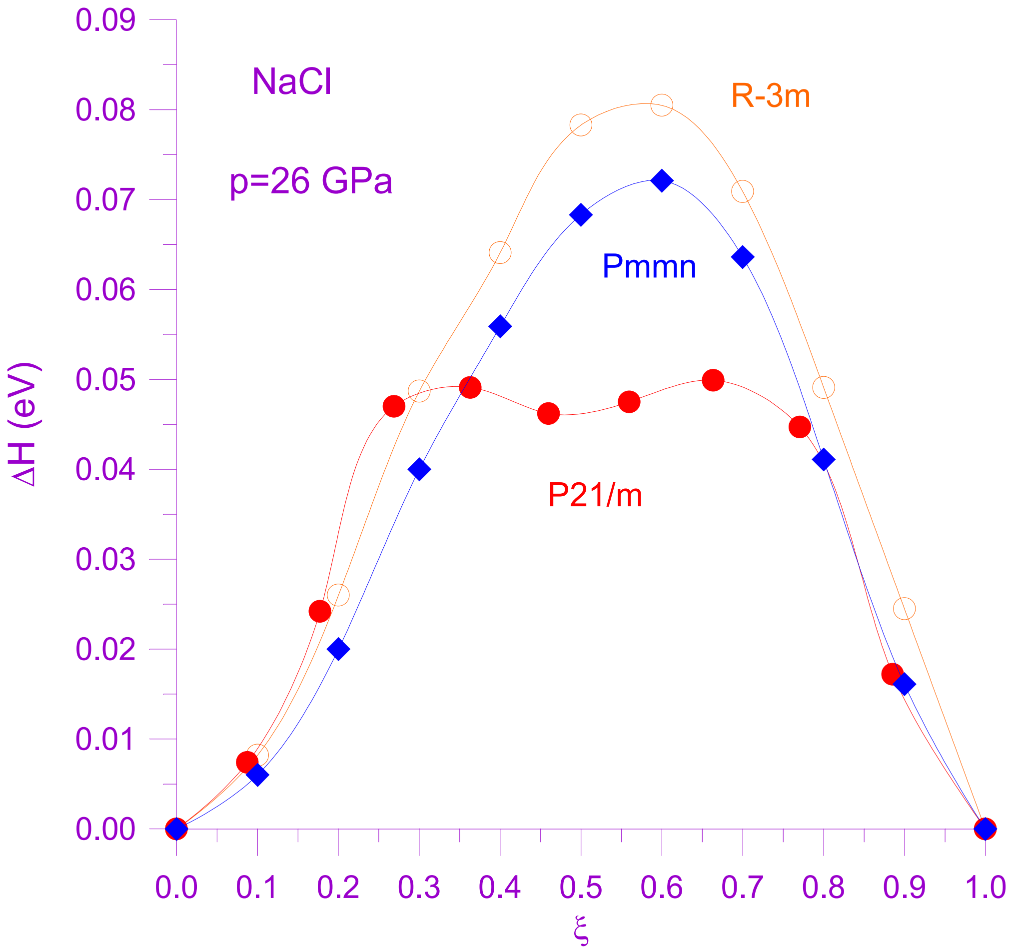
B1

$P2_1/m$





B2

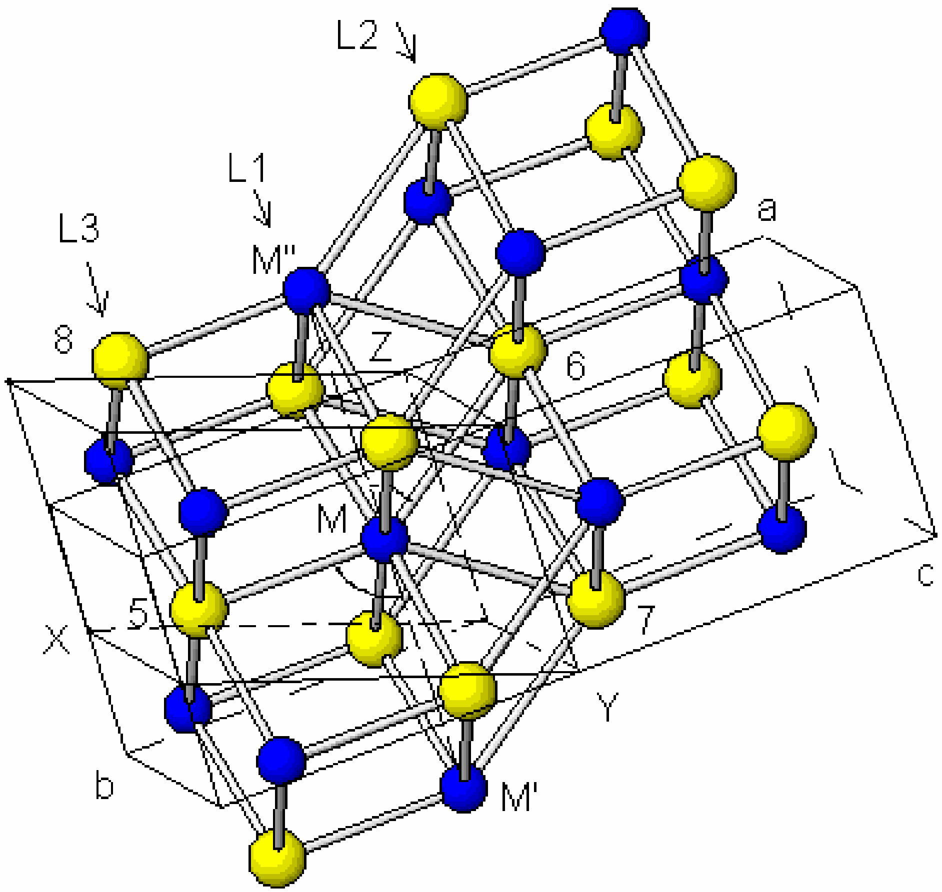


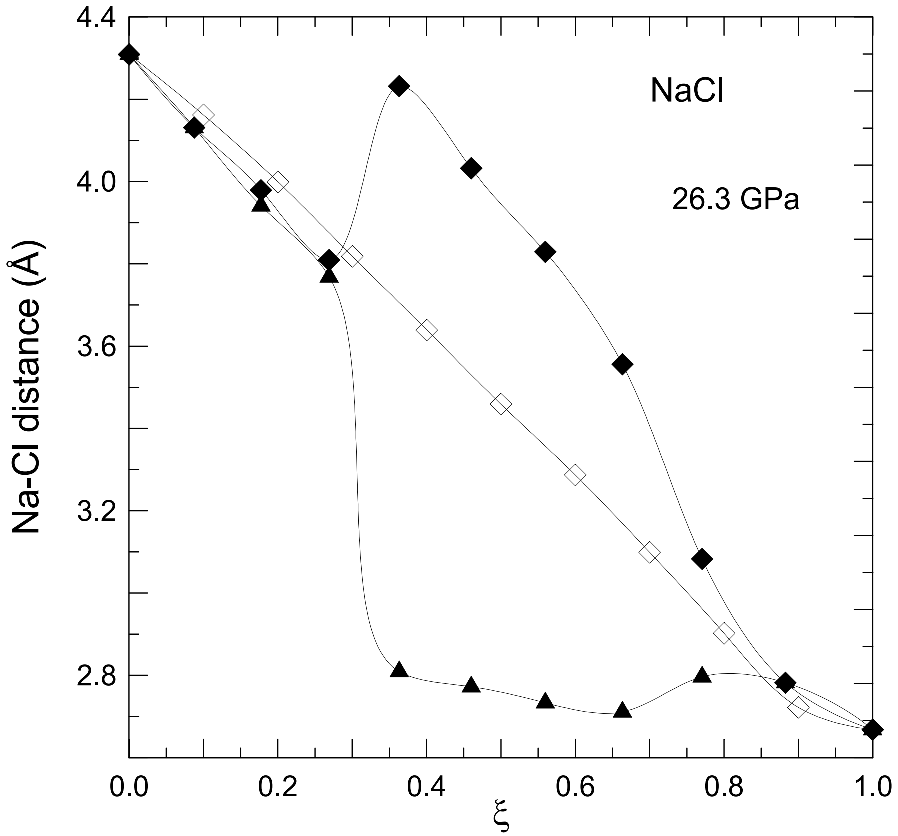
Enthalpy of the intermediate state of NaCl along the B1-B2 transformation path vs. order parameter

ξ for three different pathways: rhombohedral $R\bar{3}m$, monoclinic $P2_1/m$ orthorhombic Pmmn

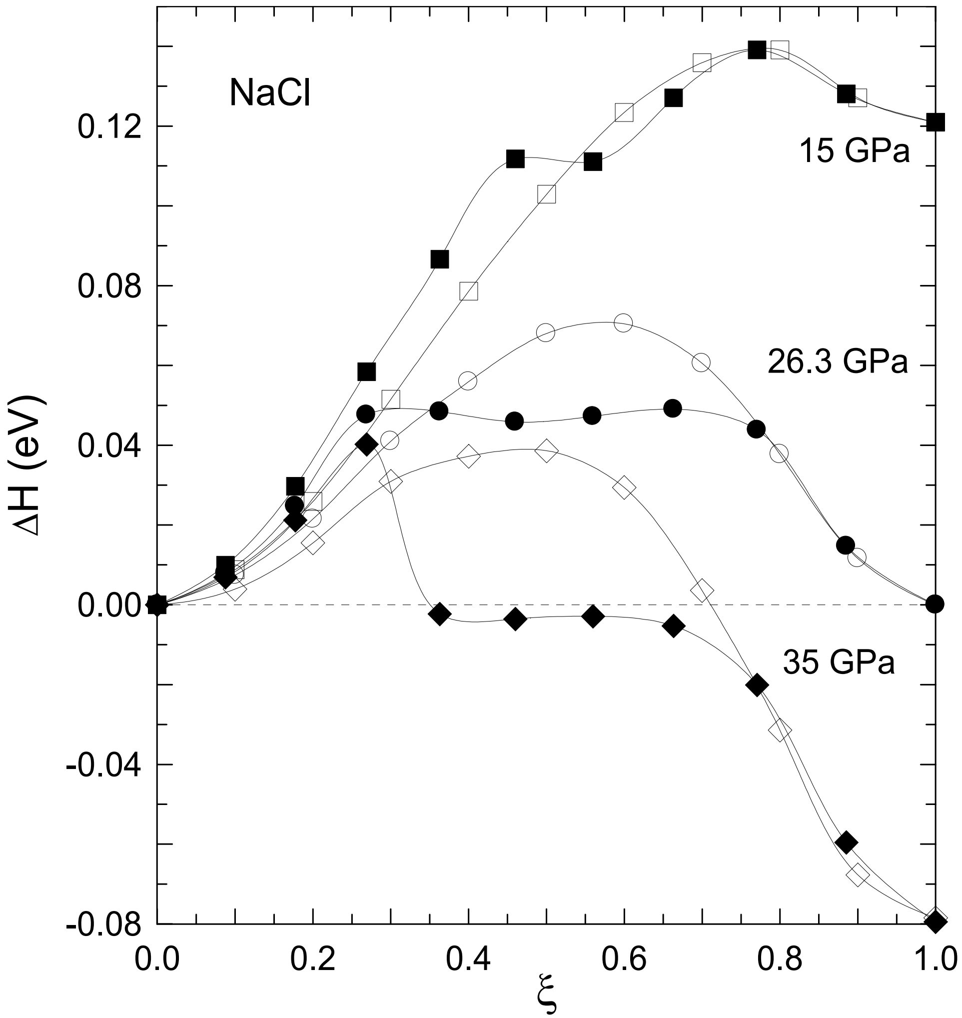
Intermediate metastable Cmcm phase along the $P2_1/m$ pathway:

TlI-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 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)

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:
R3m, Imm2

F$\bar{4}$3m	(B3)	Z=4	M	¼, ¼, ¼ ($\bar{4}$3m);	X 0, 0, 0 ($\bar{4}$3m)	a_I
Fm$\bar{3}$m	(B1)	Z=4	M	½, ½, ½ (m$\bar{3}$m);	X 0, 0, 0 (m$\bar{3}$m)	a_{II}

Intermediate states:

I - R3m Z=1 M x (¼→ ½), x (¼→ ½), x (¼→ ½) (3m); X 0, 0, 0 (3m)

order parameter: x(M)

$\underline{F\bar{4}3m} \rightarrow R3m$ $\qquad Q_1 = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix}$ $\qquad Q_1^{-1} = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$

$Fm\bar{3}m \rightarrow R3m$ $\qquad Q_2 = Q_1 = \begin{bmatrix} 0 & ½ & ½ \\ ½ & 0 & ½ \\ ½ & ½ & 0 \end{bmatrix}$

$\underline{F\bar{4}3m} \rightarrow Fm\bar{3}m$ $\qquad Q_1Q_2^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

R3m (B3): $a_R = a_I/\sqrt{2}$, $\alpha_R = 60°$; $\qquad$ R3m (B1): $a_R = a_{II}/\sqrt{2}$, $\alpha_R = 60°$

II - Imm2 $\quad$ Z=2 $\quad$ M $\quad$ 0, ½, z (¼→ ½) (mm2); $\quad$ X $\quad$ 0, 0, 0 (mm2)

Order parameter: $\quad$ z(M)

$\underline{F\bar{4}3m} \rightarrow Imm2$ $\qquad Q_1 = \begin{bmatrix} ½ & -½ & 0 \\ ½ & ½ & 0 \\ 0 & 0 & 1 \end{bmatrix}$ $\qquad Q_1^{-1} = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

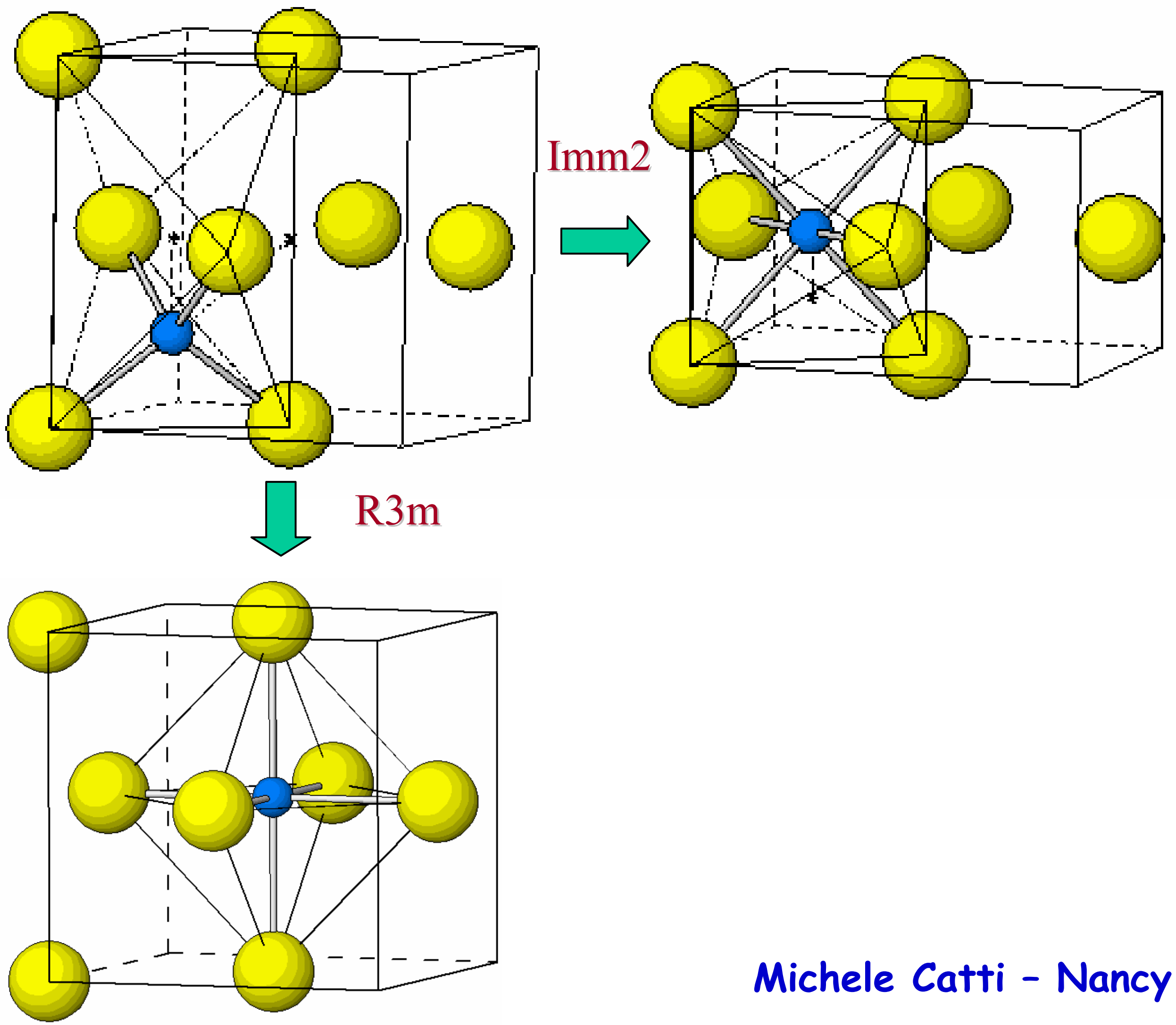
$Fm\bar{3}m \rightarrow Imm2$ $\qquad Q_2 = \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \qquad Q_2^{-1} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & -1 & 0 \\ 1 & 1 & 0 \end{bmatrix}$

$\underline{F\bar{4}3m} \rightarrow Fm\bar{3}m$ $\qquad Q_1 Q_2^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 1 & 1 & 0 \end{bmatrix}$

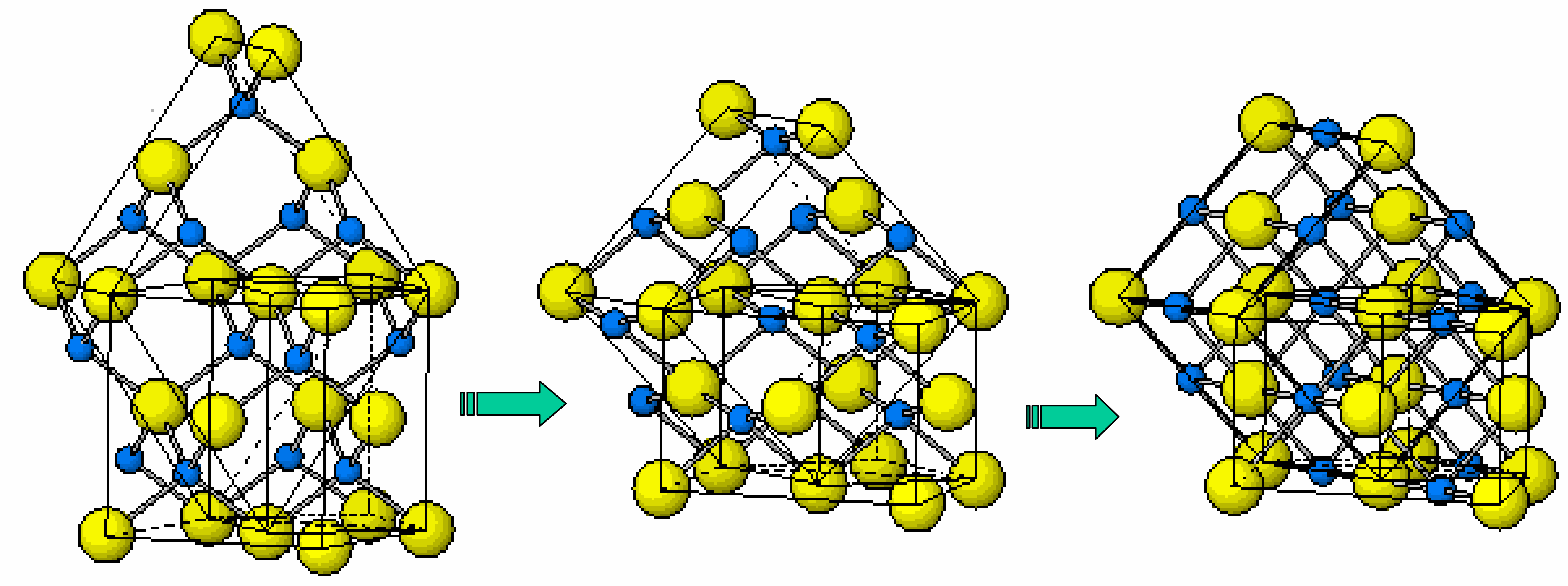
Imm2 (B3): $a = b = a_I/\sqrt{2}$, $c = a_I$;

Imm2 (B1): $b = c = a_{II}/\sqrt{2}$, $a = a_{II}$

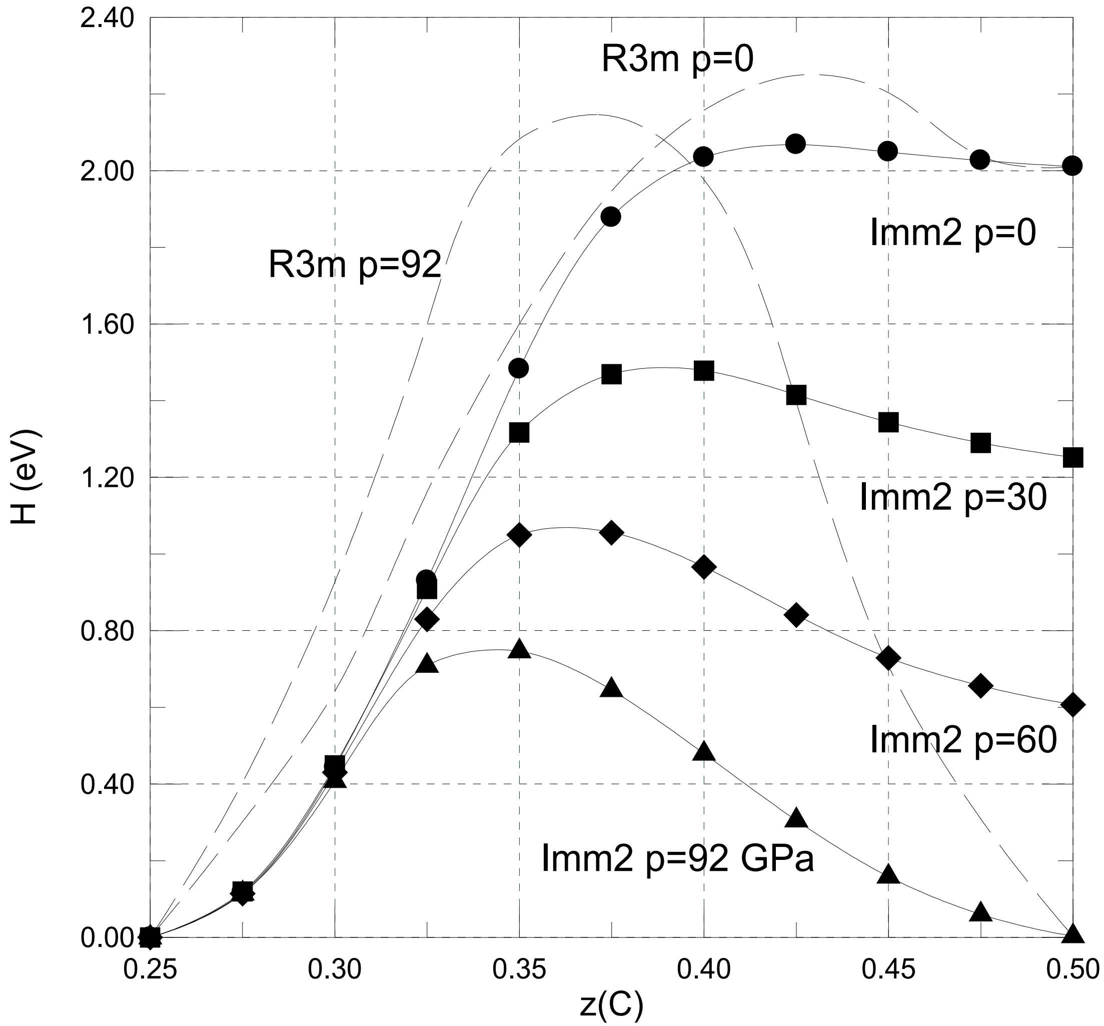
Imm2 and R3m mechanisms of the B3/B1 high-pressure phase transition



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



B3($F\bar{4}3m$) Imm2 B1($Fm\bar{3}m$)



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)

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

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 ¼, ¼, ¼;	I 0, 0, 0		a_I
P4/nmm	Z=2	Ag 0,0,0;	I 0, ½, z;		a_{III}, c_{III}
$Fm\bar{3}m$	Z=4	Ag ½, ½, ½;	I 0, 0, 0		a_{II}

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

Intermediate state:

Pm Z=2 Ag1 0,0,0; Ag2 x(Ag2), ½, z(Ag2) (½→ 0); I1 x(I1), ½, z(I1); I2 x(I2), 0, z(I2)

Order parameter : z(Ag2)

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

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

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

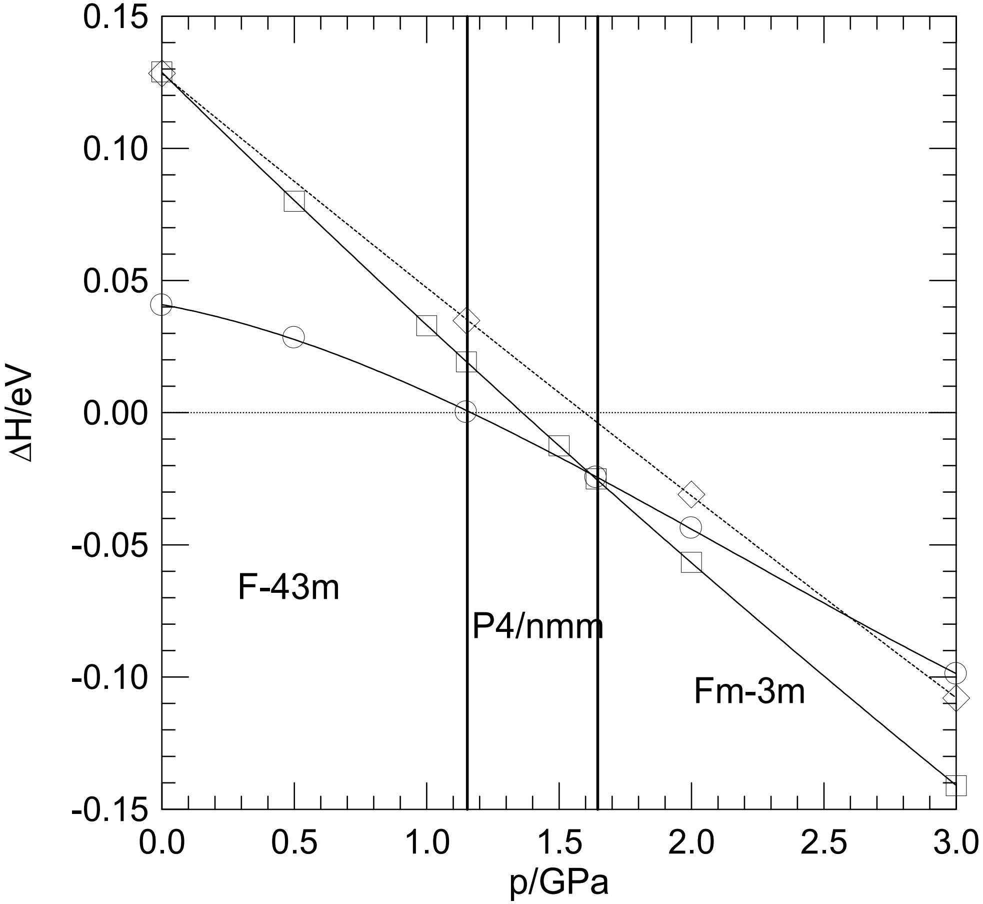
$Fm\bar{3}m \rightarrow Pm$ $\qquad Q_3 = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}$

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

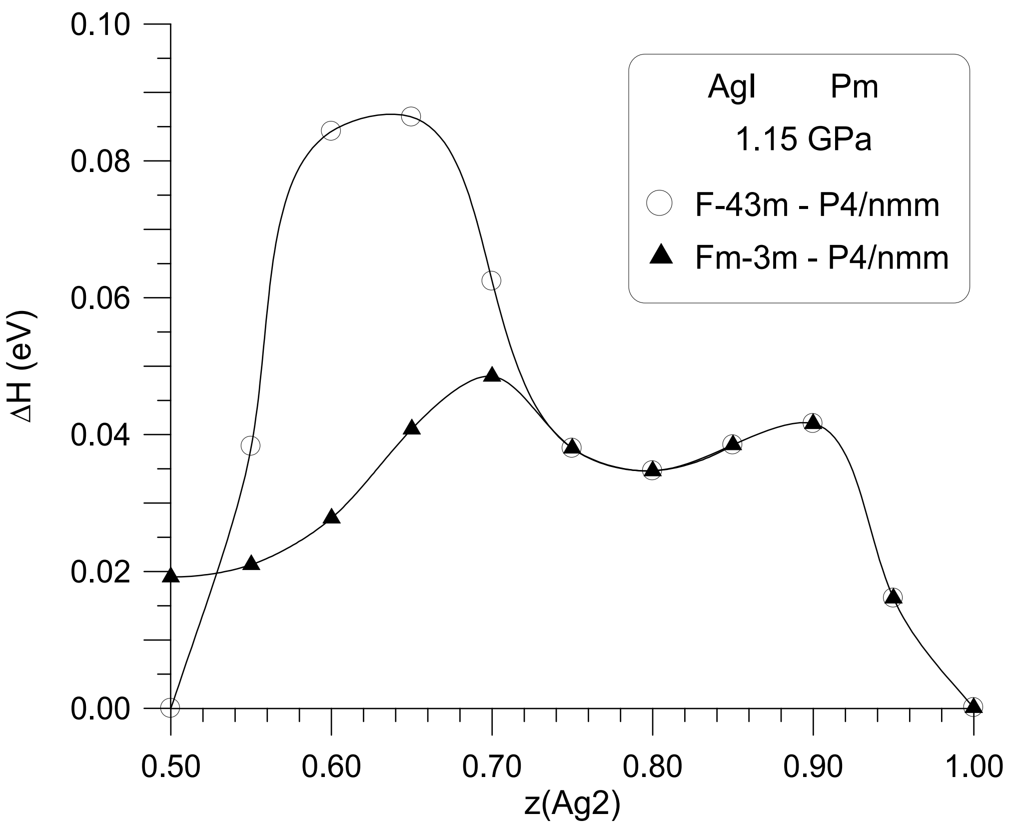
Pm (zincblende): $a = b = a_I/\sqrt{2}, \quad c = a_I;$

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

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



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(Ag2)) - H(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, at the zincblende/anti-litharge equilibrium pressure. The minimum corresponds to the metastable Bmm2 phase.

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