

Summer School on Mathematical and Theoretical Crystallography

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Role of symmetry and energy in structural phase transitions

Michele Catti

*Dipartimento di Scienza dei Materiali, Università di
Milano Bicocca, Milano, Italy*

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 $T > T_c \rightarrow$

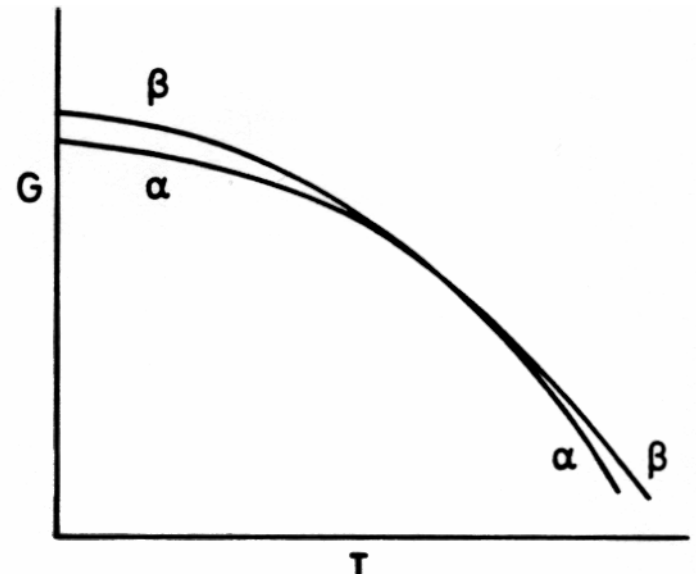
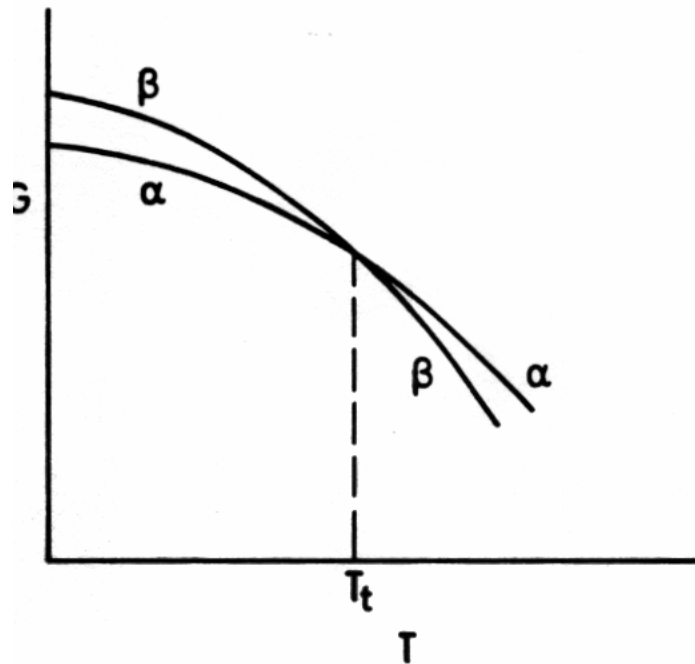
$$\Delta G = G_\beta - G_\alpha > 0 \text{ for } T < T_c, \quad \Delta G = G_\beta - G_\alpha < 0 \text{ for } T > T_c \quad ?$$

But

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

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

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



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 g_0 /subgroup g relationship ($g \subset g_0$)
- the g low-symmetry phase approaches the transition to g_0 higher symmetry continuously;
- the order parameter η measures the 'distance' of the low-symmetry to the high-symmetry ($\eta=0$) structure; it may have one or more components (η_1, η_2, \dots)

- T-driven transition:

usually the g symmetry of the l.t. phase is a subgroup of the g_0 group 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, although in most cases $g_0 \rightarrow g$ with increasing pressure

Reconstructive phase transitions:

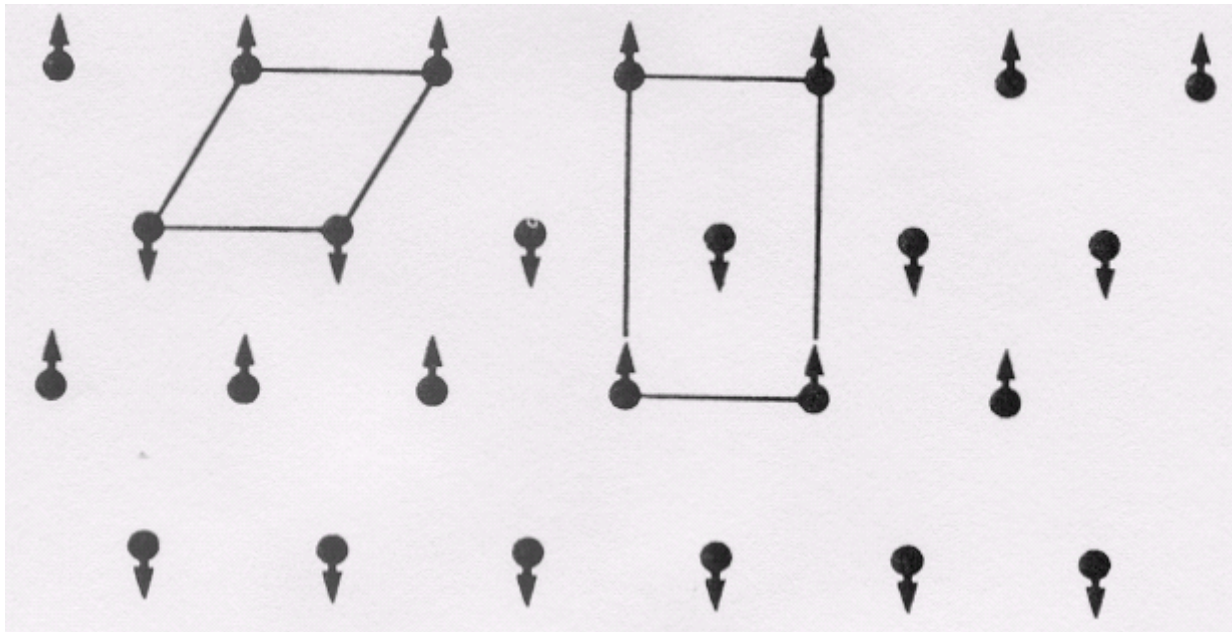
- the space group symmetries of the two phases are unrelated
- the transition is quite abrupt (no order parameter)

Examples of simple reconstructive phase transitions:

- HCP to BCC, FCC to HCP and BCC to FCC in metals and alloys
- rocksalt (Fm-3m) to CsCl-type (Pm-3m) structure in binary AB systems:
the C.N. changes from 6 to 8
- zinblende (F-43m) to rocksalt (Fm-3m) structure in binary AB systems:
the 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

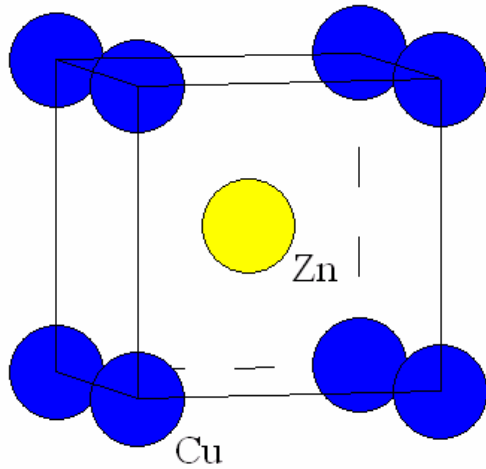


Hexagonal (NiAs-type) and orthorhombic (MnP-type) cells outlined

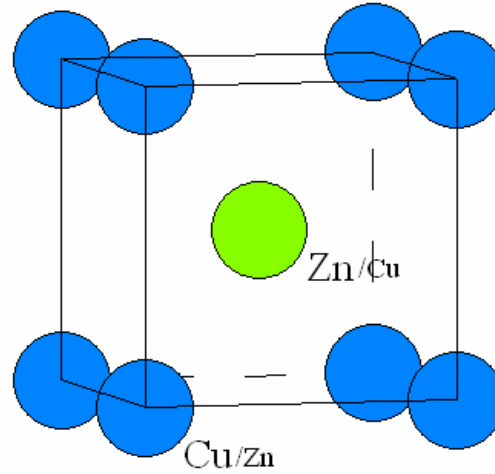
Order parameter η : length of the vector describing the structural distortion

Examples of order/disorder phase transitions:

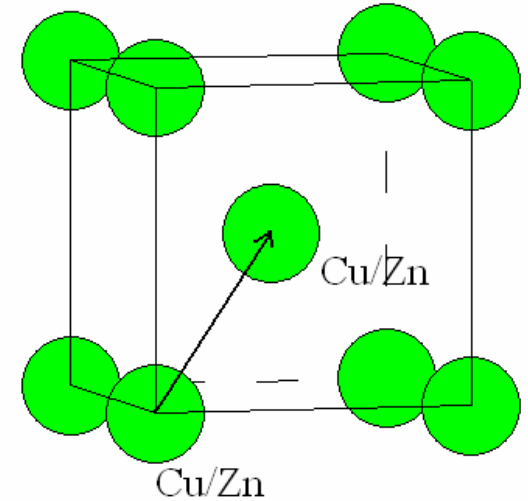
β - β' brass transition in CuZn (Pm-3m to Im-3m)



Pm-3m ($\eta = 1$)



Pm-3m ($1 > \eta > 0$)



Im-3m ($\eta = 0$)

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

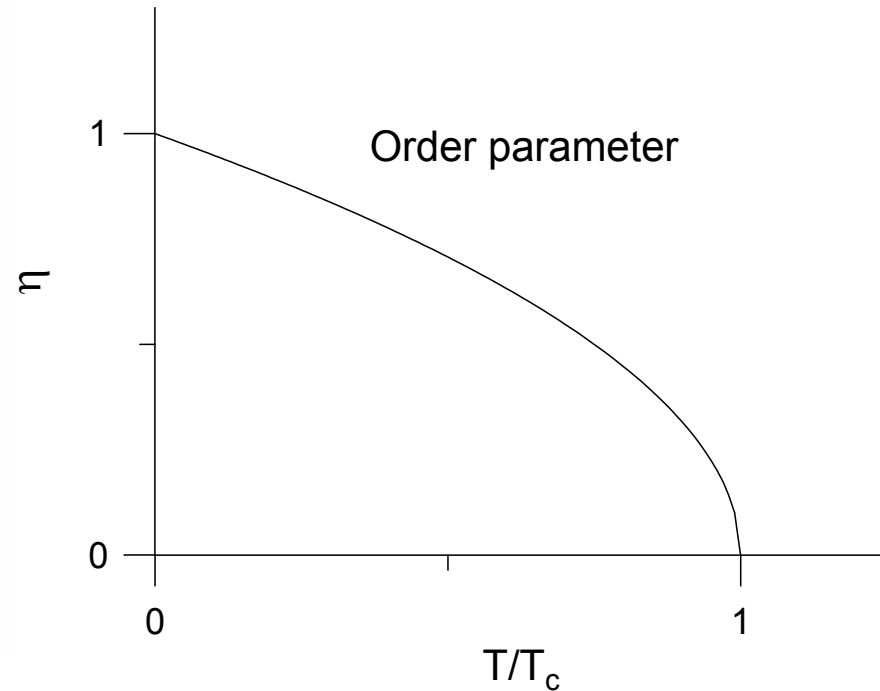
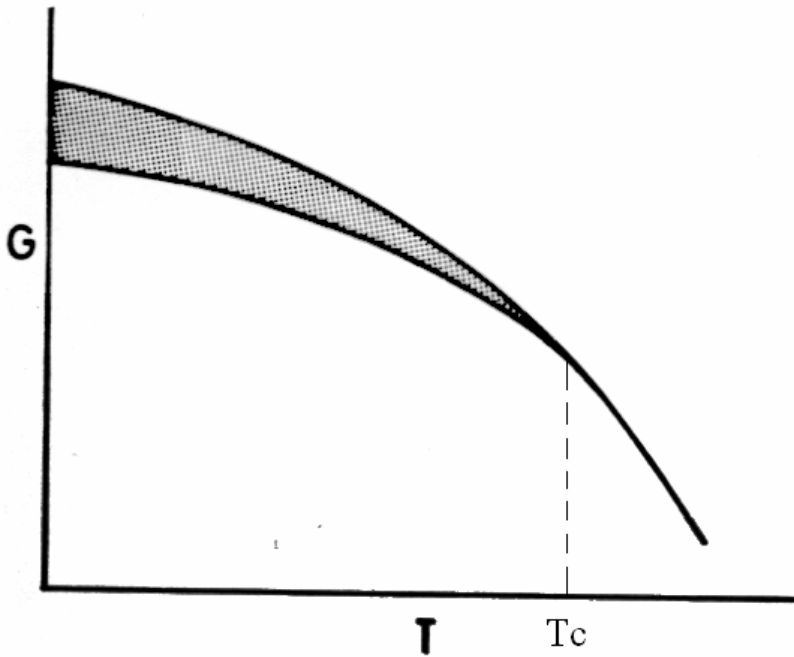
f_{Cu} : fraction of Cu atoms occupying the site at 0,0,0 \rightarrow
 f_{Cu} changes from 1 (full ordered Pm-3m structure) to 1/2 (full disordered Im-3m structure)

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 →

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 $\eta=0$
(simple case of one-component order parameter):

$$G = G(p, T, \eta) = G_0 + A\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + \dots$$

- truncation to the smallest order reproducing the physics of the transition (usually 4 or 6)

Only the powers of η which are invariant with respect to the symmetry operations of the G_0 group are allowed to be present in the $G(\eta)$ Landau polynomial:



even powers are always invariant, whereas odd powers may be invariant ('Landau condition') only when G_0 belongs to the trigonal, hexagonal or cubic symmetry systems

Three most important cases of Landau polynomials:

- $G - G_0 = A(p,T)\eta^2 + C(p,T)\eta^4$ ($C > 0$) 2-4 even powers, second-order transition
- $G - G_0 = A(p,T)\eta^2 + C(p,T)\eta^4 + E(p,T)\eta^6$ ($E > 0$) 2-4-6 even powers, first-order tr.
- $G - G_0 = A(p,T)\eta^2 + B(p,T)\eta^3 + C(p,T)\eta^4$ ($C > 0$) 2-3-4 even/odd powers, first-order tr

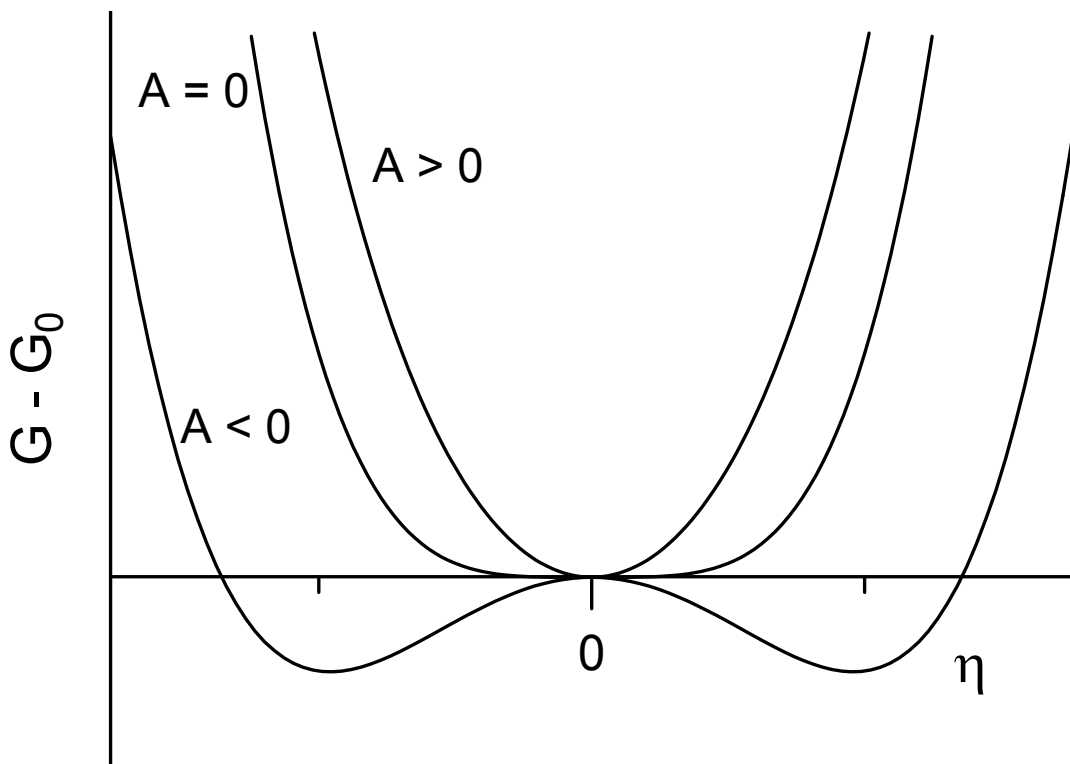
$$\partial G / \partial \eta = \eta(2A + 3B\eta + 4C\eta^2 + 6E\eta^4)$$

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

In the surrounding of T_c : B, C and E are approximately constant, only $A = A(T)$

$$1) \quad G - G_0 = A\eta^2 + C\eta^4$$

$$A > 0, A = 0, A < 0$$



$$\frac{\partial G}{\partial \eta} = 2\eta(A + 2C\eta^2) = 0 \rightarrow$$

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



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 $T \neq T_c \rightarrow$

second-order thermodynamics

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

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

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

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

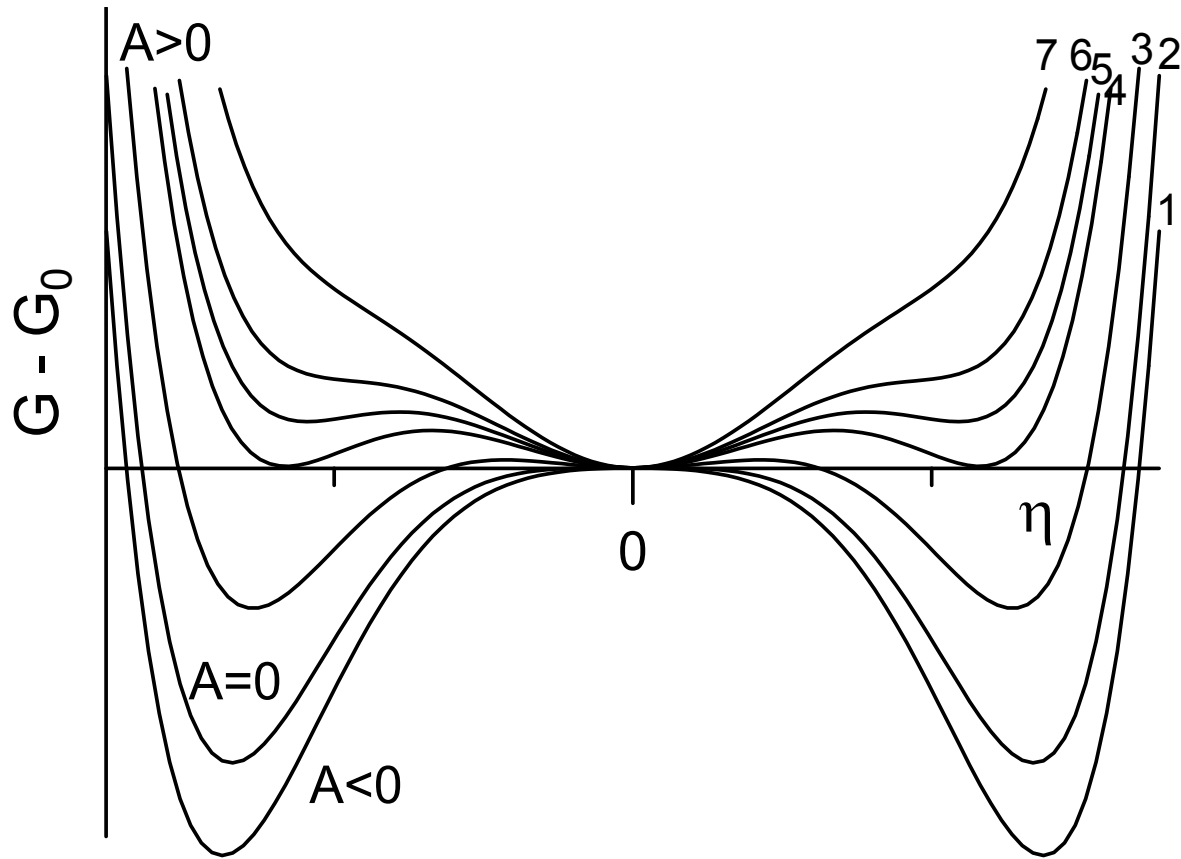
$\lim_{T \rightarrow T_c} (C_p - C_{p,0}) = a^2T_c/2C = \Delta C_p$ second-order discontinuity

$$2) \quad G - G_0 = A\eta^2 + C\eta^4 + E\eta^6$$

$$A = a(T - T_c)$$

$$A > 0, A = 0, A < 0$$

$$C \leq 0 \quad E > 0$$



- | | |
|---|-----------------|
| 1 | $T < T_c$ |
| 2 | $T = T_c$ |
| 3 | $T_c < T < T_0$ |
| 4 | $T = T_0$ |
| 5 | $T_0 < T < T_1$ |
| 6 | $T = T_1$ |
| 7 | $T > T_1$ |

equilibrium of two phases at $T = T_0$, metastability region for $T_c < T < T_1$

→ first-order thermodynamics

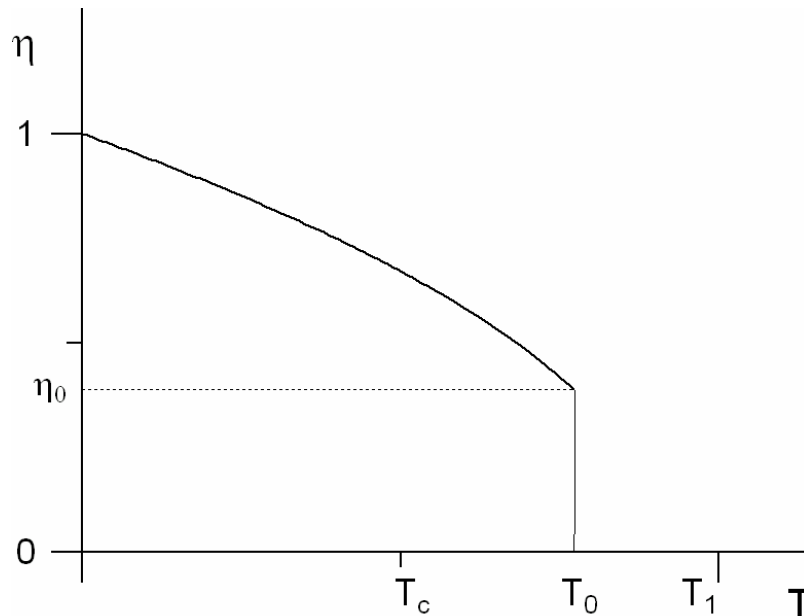
- Condition of two-phase equilibrium at $T=T_0$:

$$\partial G/\partial \eta = 2\eta(A + 2C\eta^2 + 3E\eta^4) = 0 \quad \text{for } \eta \neq 0$$

$$\rightarrow T_0 = T_c + C^2/4aE$$

$$G - G_0 = A\eta^2 + C\eta^4 + E\eta^6 = 0$$

- Discontinuous jump of the order parameter at $T=T_0$: $\eta(T_0) = (-C/2E)^{1/2}$



$$S - S_0 = -\partial(G-G_0)/\partial T = -a\eta^2 = aC/2E$$

behaves discontinuously across
the phase transition

latent heat $\Delta H = T_0\Delta S = (aC/2E)T_0 \rightarrow$ typical first-order effect

$C_p - C_{p,0} = T\partial(S-S_0)/\partial T = (a^2/2C)T$ for $T \leq T_c$, 0 for $T > T_c \rightarrow$ second-order
discontinuity, as in the 2-4 case

For $E=0$ (case 2-4), $C=0$ (case 2-6, ‘tricritical polynomial’) or $C>0$ the first-order discontinuity disappears, and the second-order behaviour is recovered: $T_0 = T_c$; $\eta(T_0)=0$

$$G - G_0 = A\eta^2 + E\eta^6$$

second-order tricritical thermodynamics



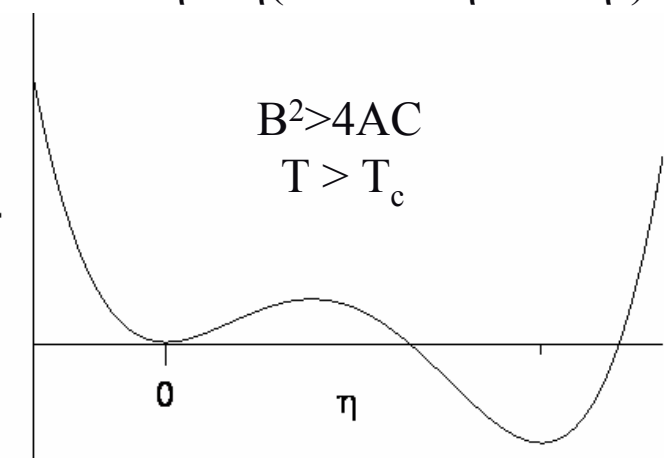
$$\eta = \pm[a(T_c-T)/3E]^{1/4} \approx (T_c-T)^{1/4}$$

$$3) G - G_0 = A\eta^2 + B\eta^3 + C\eta^4$$

$$A > 0, \quad B < 0, \quad C > 0$$

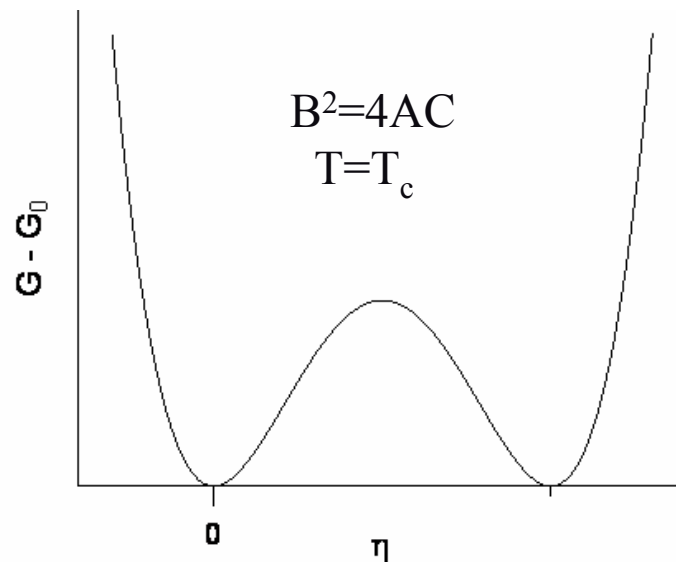
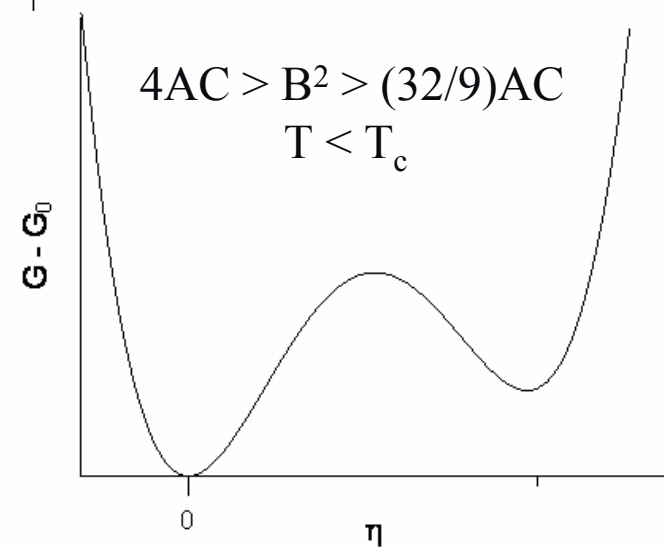
$G - G_0 = 0 \rightarrow$ either one, two or three roots, according to the sign of $B^2 - 4AC$

$\partial G / \partial \eta = \eta(2A + 3B\eta + 4C\eta^2) = 0 \rightarrow$ 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 first-order thermodynamics



Thermodynamics: effect of pressure

Static calculation at the athermal limit ($T = 0$ K)

- Static equation of state: $p = -dE_{st}/dV$

elastic bulk modulus $K = -Vdp/dV$; $K' = dK/dp$

Murnaghan equation of state ($K' = \text{constant}$):

$$E_{st}(V) = K_0 V_0 \left[\frac{1}{K'(K'-1)} \left(\frac{V_0}{V} \right)^{K'-1} + \frac{1}{K'} \frac{V}{V_0} - \frac{1}{K'-1} \right] + E_0$$

V_0 , E_0 , K_0 , and K' parameters:

obtained by fitting the numerical $E(V)$ results

(constant volume energy minimizations)

$$p(V) = \frac{K_0}{K'} \left[\left(\frac{V_0}{V} \right)^{K'} - 1 \right]; \quad V(p) = V_0 \left(\frac{K'}{K_0} p + 1 \right)^{-\frac{1}{K'}}$$

free energy ($T=0$ K) = enthalpy $H = E + pV$

$$H(p) = \frac{K_0 V_0}{K' - 1} \left[\left(\frac{K'}{K_0} p + 1 \right)^{1-1/K'} - 1 \right] + E_0$$

Phase equilibrium vs. pressure and pressure-driven transition between phase A and phase B:

$$\Delta H(p) = H_B(p) - H_A(p) = 0 \Rightarrow p = p_t \quad \text{equilibrium pressure}$$

$$\Delta H(p) > 0 \Rightarrow \text{phase A stable}; \quad \Delta H(p) < 0 \Rightarrow \text{phase B stable}$$

Thermodynamics: effect of temperature

Quasi-harmonic lattice-dynamical model



thermal vibrations only are taken into account
(correct for insulating diamagnetic ordered crystals)

Thermodynamic functions of phase assembly



$$\Delta_t G(p, T) = \sum_h n_h G_h(p, T) = 0$$



Thermodynamics of phase transitions / chemical reactions

Athermal limit case:

only pressure is considered, enthalpy replaces G function

$$\Delta_t H(p) = \sum_h n_h H_h(p) = 0$$

Reconstructive phase transitions: B1/B2 (NaCl and CaO); B3/B1 (ZnS and SiC)

No group-subgroup relation + large enthalpic (heat) effect \Rightarrow
strong first-order character

Rocksalt- (B1, *Fm-3m*, C.N.=6)



CsCl-type (B2, *Pm-3m*, C.N.=8)

Zincblende- (B3, *F-43m*, C.N.=4)



Rocksalt- (B1, *Fm-3m*, C.N.=6)

ρ_{exp}

$\rho_{\text{calc(PBE)}}$

ρ_{exp}

$\rho_{\text{calc(B3LYP)}}$

NaCl 27 26 GPa

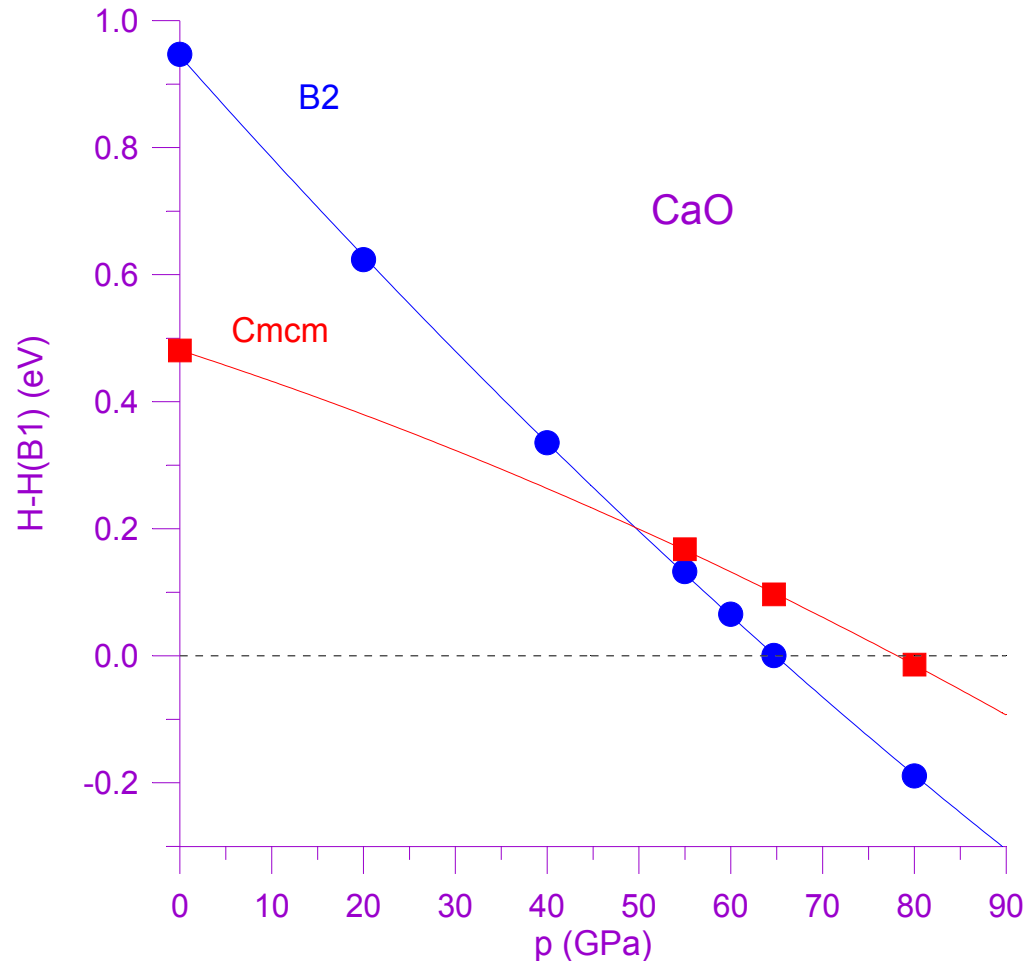
ZnS 15 19 GPa

CaO 60 65

SiC ~100 92

Enthalpy differences B2-B1 and *Cmcm*(TII-like)-B1 vs. pressure for CaO

$\Delta H(p) = 0$
Equilibrium condition
 \Downarrow
 $p = p_t$



Catti M (2003); Catti M (2004)

Displacive phase transitions: AgCl and AgI

Catti M, Di Piazza L (2006); Catti M (2006)

Group-subgroup relation + small/vanishing enthalpic effect \Rightarrow
second-order or weak first-order character

pressure \rightarrow

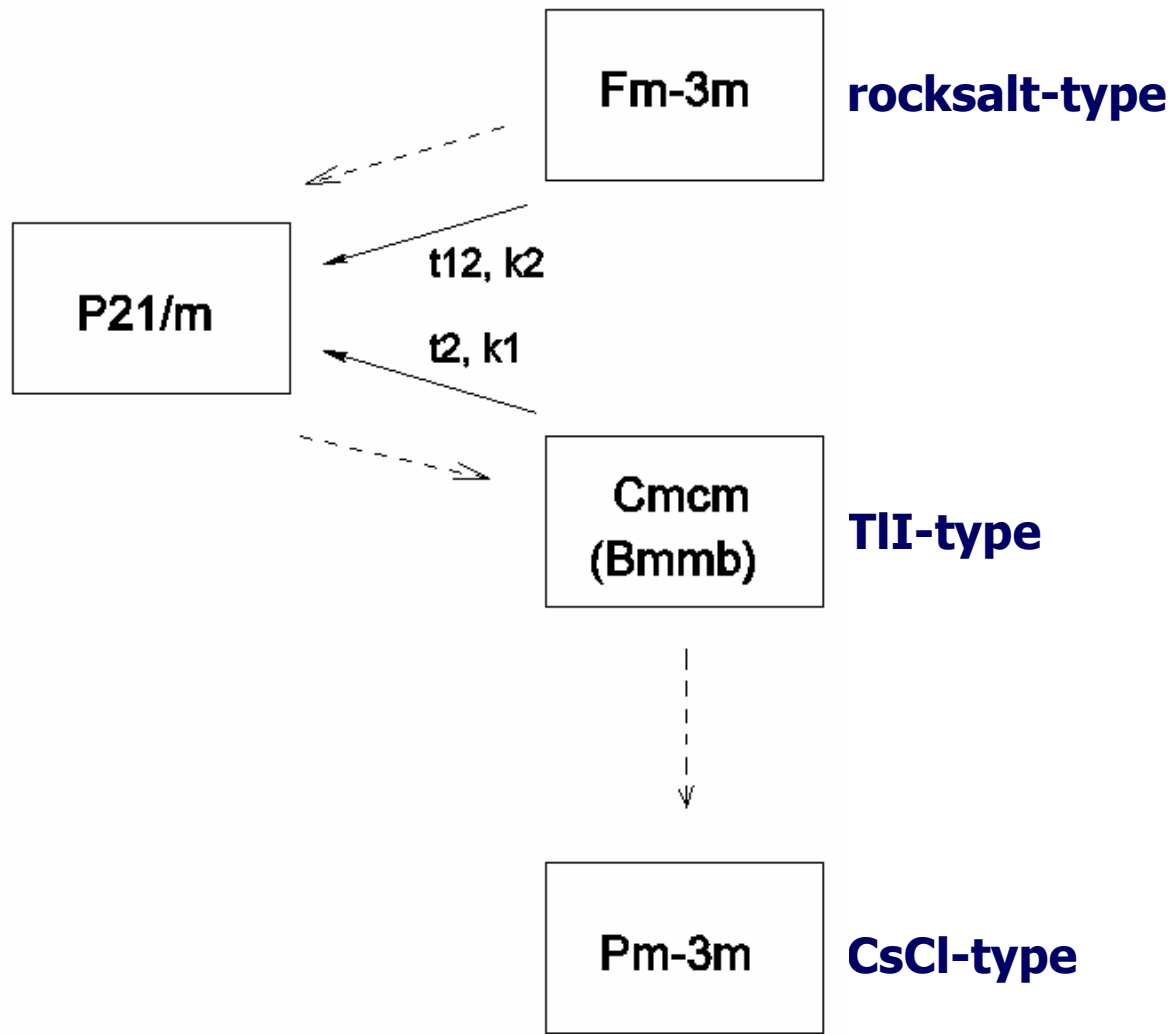
Rocksalt-(*Fm-3m*) \rightarrow KOH-(*P2₁/m*) \rightarrow TlI-(*Cmcm*) \rightarrow CsCl-type (*Pm-3m*)

AgCl	7	11	17 GPa
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AgI	11	?	?
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Hull and Keen, Phys. Rev. B (1999); Kusaba et al., J. Phys. Chem. Solids (1995)
Synchrotron X-ray diffraction with diamond-anvil-cell

KOH-type



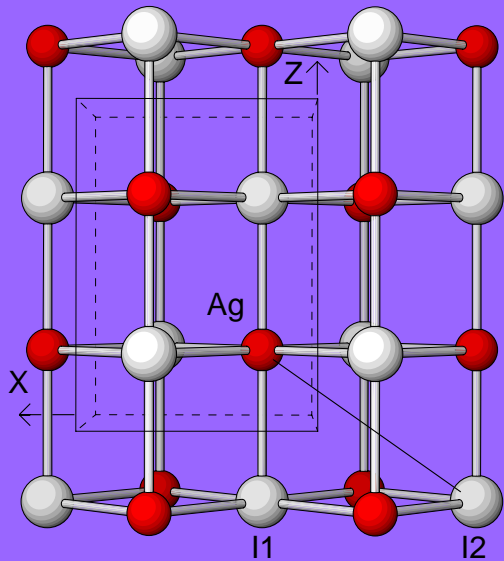
—————→
points towards
lower symmetry

- - - - -→
points towards
higher pressure

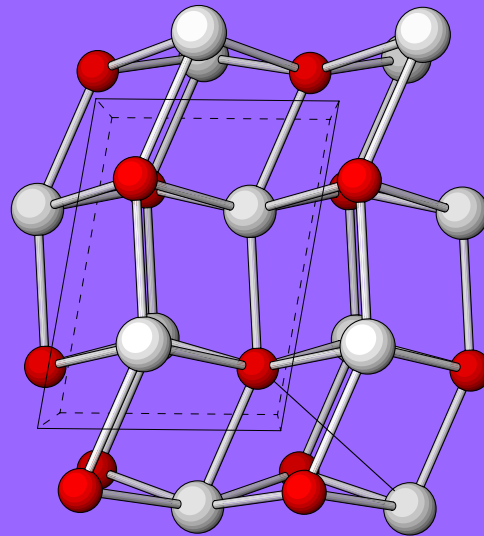
Structures of high-pressure polymorphs of silver halides

pressure →

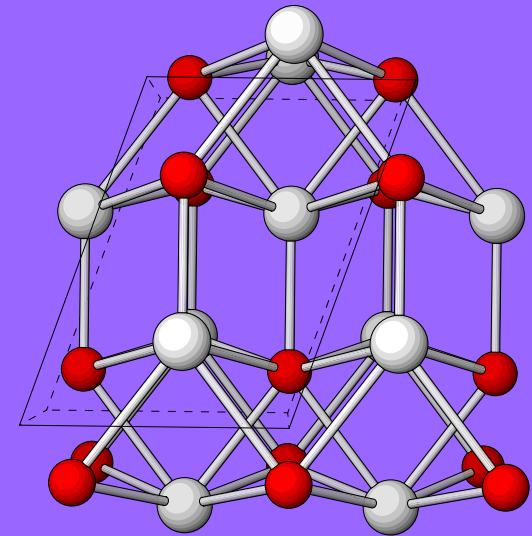
rocksalt
cubic



KOH-type
monoclinic



TII-type
orthorhombic



Two subsequent *displacive* (continuous) phase transitions

- ▶ symmetry group/subgroup relations in the first ($Fm-3m \mid P2_1/m$) and second ($Cmcm \mid P2_1/m$) pair of phases
- ▶ same order parameter (continuous lattice distortion) for both transformations
- ▶ a reconstructive (discontinuous) $Fm-3m$ to $Cmcm$ transition with intermediate $P2_1/m$ state is mimicked
- ▶ Landau potential at the athermal limit:
enthalpy $H = E + pV$

Two orientation states of the $P2_1/m$ structure, and orthorhombic $Bmmb$ ($Cmcm$) lattice in the middle

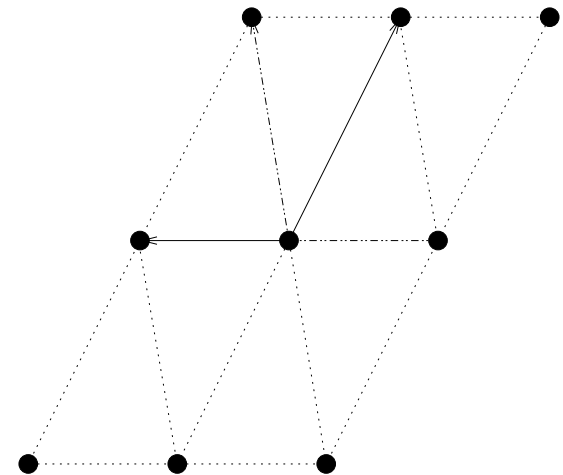
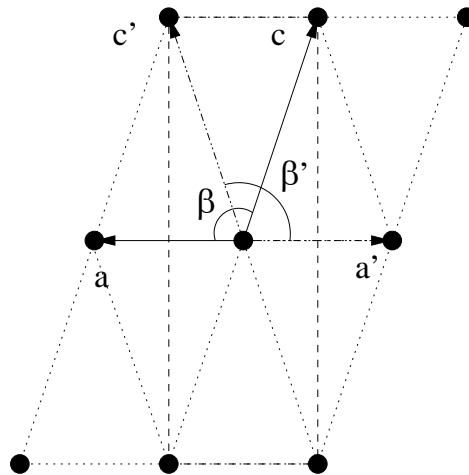
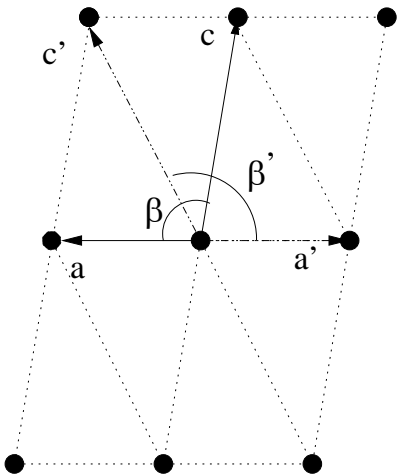
Rocksalt: $\beta=90^\circ$, $\eta=0$

TII-type: $\cos\beta= -a/2c$, $\eta=1$

$$\eta = -(2c \cos\beta)/a$$

$$\eta = 1$$

$$\eta' = 2 - \eta$$



Theoretical method

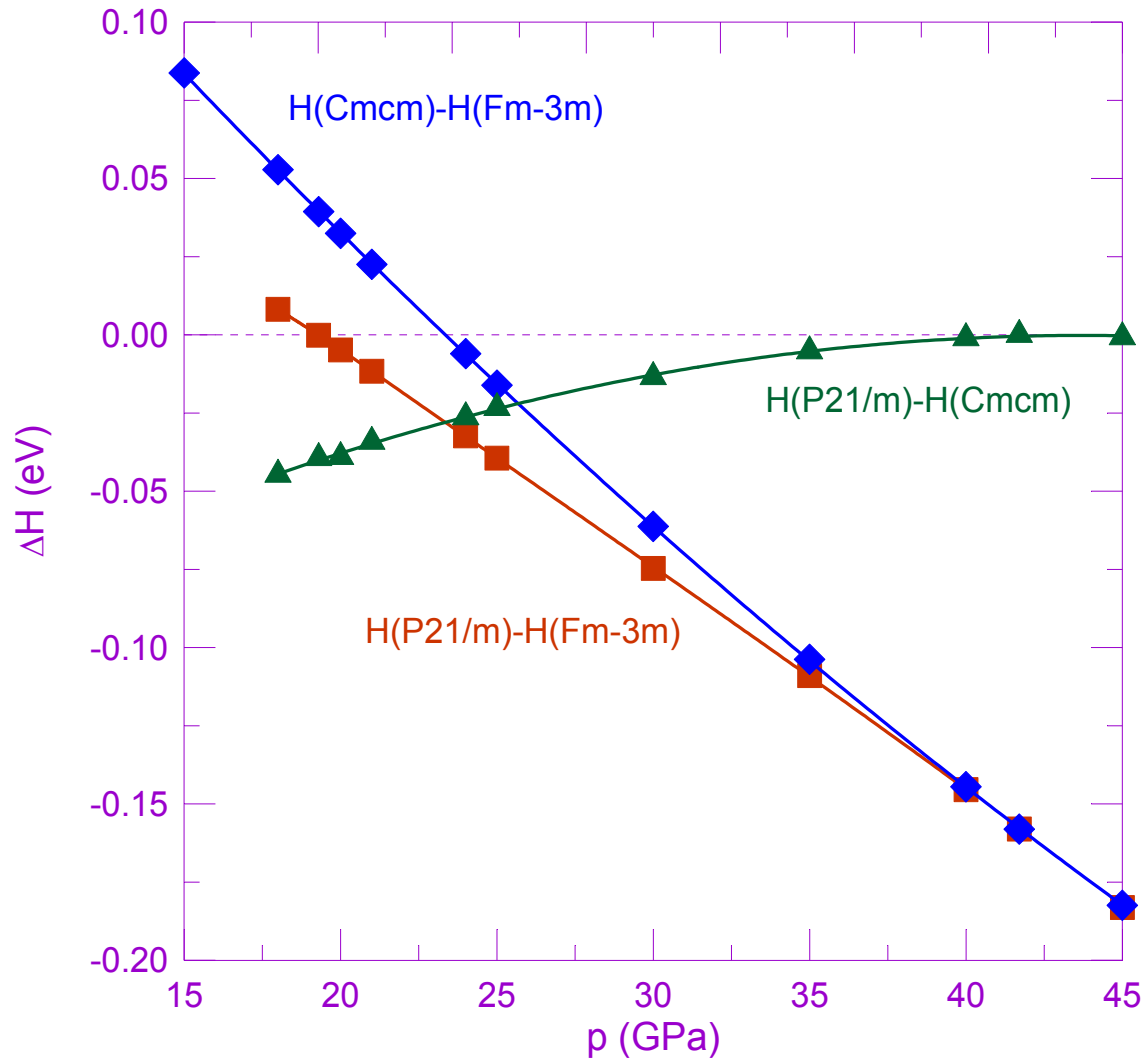
Crystal quantum-mechanical total energy: E

Enthalpy: $H = E + pV = H(\underline{a}, \underline{X}, p) = H(\underline{a}', \underline{X}', \eta, p)$

\underline{a}' and \underline{X}' : lattice constants and atomic coordinates not related to the order parameter η

- enthalpy minimized vs. \underline{a}' , \underline{X}' and η at constant p
 $\Rightarrow H(p) \Rightarrow$ equilibrium phase diagram
- enthalpy minimized vs. \underline{a}' and \underline{X}' at constant η and p
 $\Rightarrow H(\eta, p) \Rightarrow$ Landau theory analysis

Theoretical phase diagram of AgI

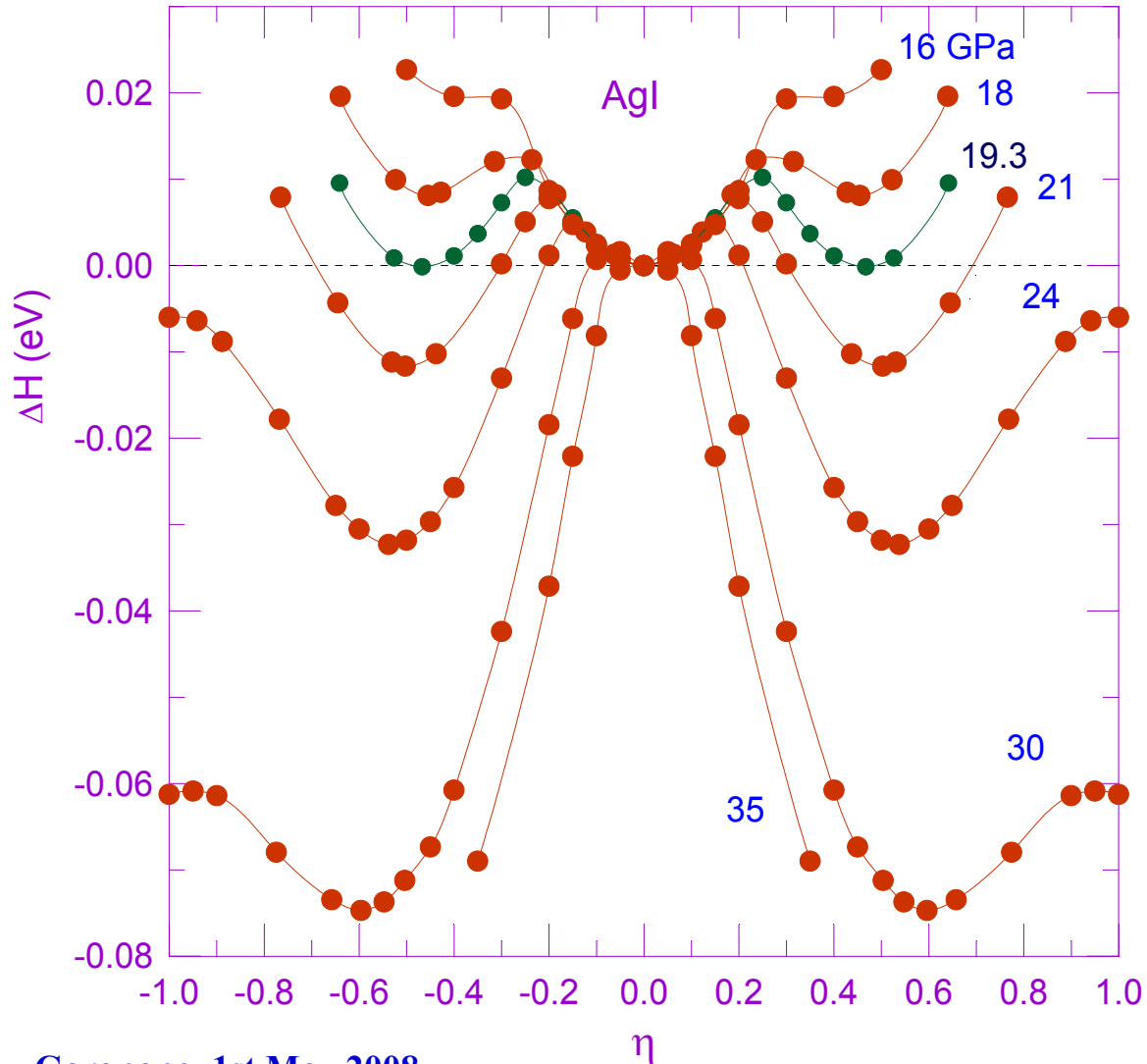


Calculated and experimental¹ phase transition pressures

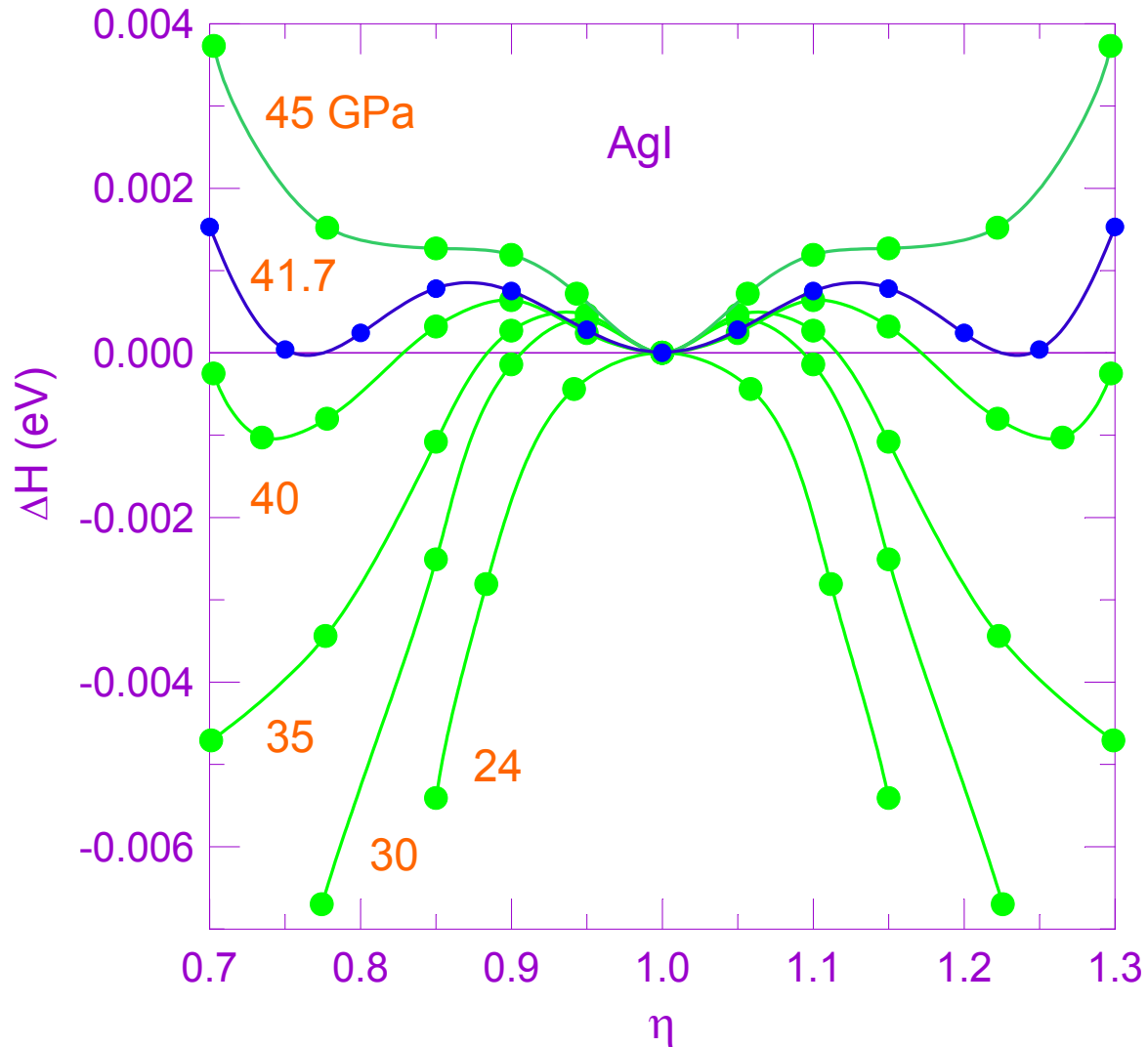
¹ Hull & Keen, Phys.Rev.B (1999)

	AgI		AgCl		
	ρ_{calc} <i>B3LYP</i>	ρ_{exp}	ρ_{calc} <i>B3LYP</i>	ρ_{calc} <i>PBE</i>	ρ_{exp}
Rocksalt- ↔ KOH-type <i>Fm-3m</i> ↔ <i>P2₁/m</i>	19	11	10	4	7 GPa
KOH- ↔ TII-type <i>P2₁/m</i> ↔ <i>Cmcm</i>	42	?	15	6	11
Rocksalt-* ↔ TII-type* (metastable)	23	----	12		----

Enthalpy of the KOH-type phase of AgI vs. order parameter (lower ρ range) - $\eta = 0$ corresponds to the rocksalt-type phase



Enthalpy of the KOH-type phase of AgI vs. order parameter (upper ρ range) - $\eta = 1$ corresponds to the TII-type phase



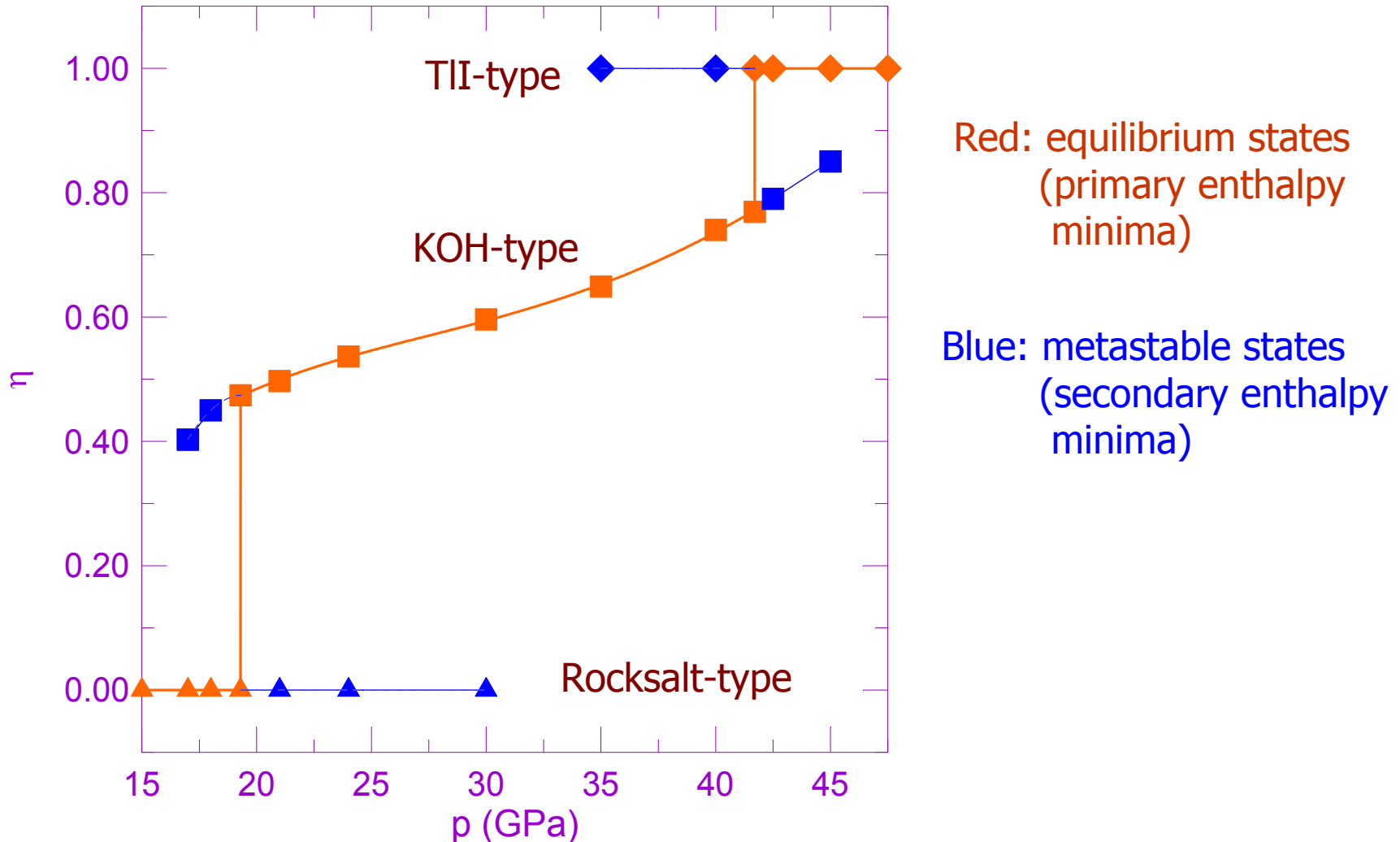
Both phase transitions show a partly discontinuous character, with activation barriers and possible metastable states; but:

- ▶ in the KOH- to TII-type case, the ΔH_a value (0.8 meV) is negligible with respect to thermal energy at RT
- ▶ in the rocksalt- to KOH-type case, the activation enthalpy is significant (10.3 meV)

Structural parameters optimized at the rocksalt-/KOH-type (19.3 GPa) and
KOH-/TII-type (41.7 GPa) phase equilibrium pressures

η	β (°)	a (Å)	b (Å)	c (Å)	x_{Ag}	z_{Ag}	x_I	z_I	ΔH (meV)
$p = 19.3$ GPa									
0	90	4.074	4.074	5.762	0.25	0.25	0.25	0.75	0
0.250	95.08	4.079	4.026	5.746	0.1914	0.2207	0.2929	0.7332	10.22
0.474	99.57	4.067	4.058	5.749	0.1491	0.1898	0.3173	0.7203	-0.15
$p = 41.7$ GPa									
0.769	105.23	3.757	4.016	5.506	0.1065	0.1776	0.3444	0.7152	0.00
0.870	107.04	3.734	4.046	5.543	0.0996	0.1768	0.3495	0.7152	0.83
1	109.37	3.716	4.071	5.602	0.0880	0.1761	0.3578	0.7155	0

Order parameter of the phases of AgI vs. pressure



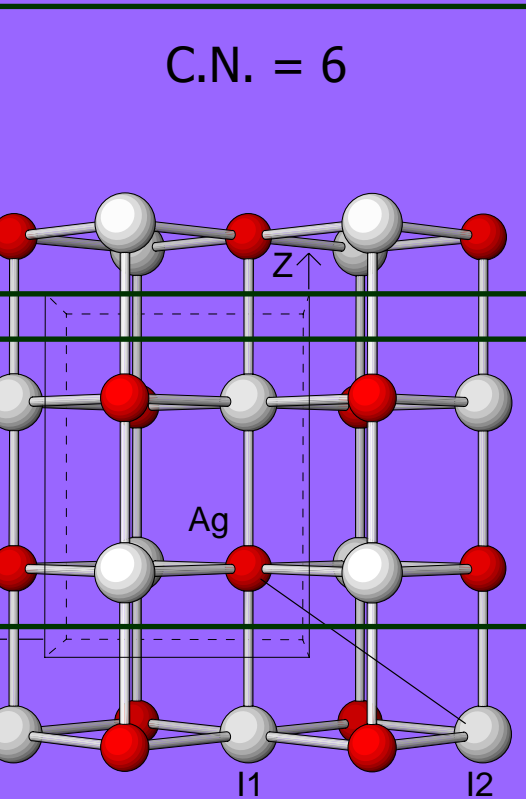
- ▶ Large jump $\Delta\eta$ of order parameter at the rocksalt-/KOH-type transition, and significant $\Delta\eta$ value also at the KOH-/TII-type transformation
- ⇓
- ▶ Relatively limited η range for the stable monoclinic KOH-type phase

Unexpected result, in view of the moderate/small enthalpy barriers for either phase transition

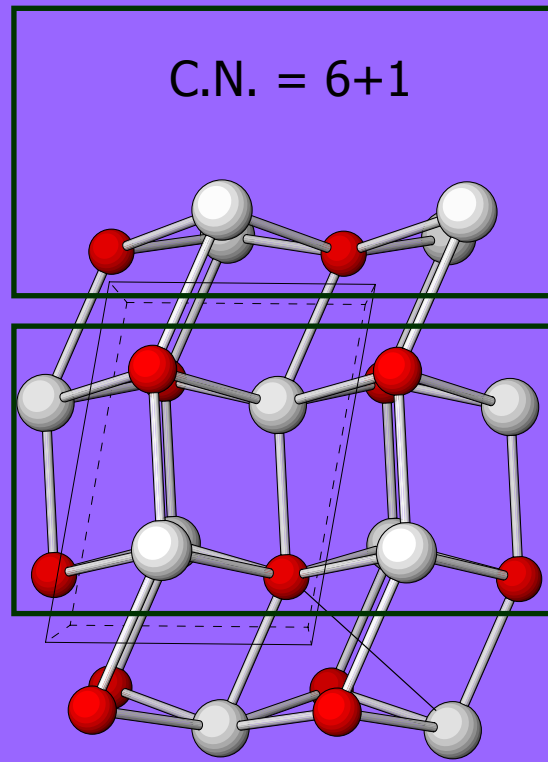
⇒ How can the large $\Delta\eta$ jump at the rocksalt-/KOH-type phase boundary be justified on structural grounds ?

Mechanism of phase transformation: slide of double (001) atomic layers along [100]

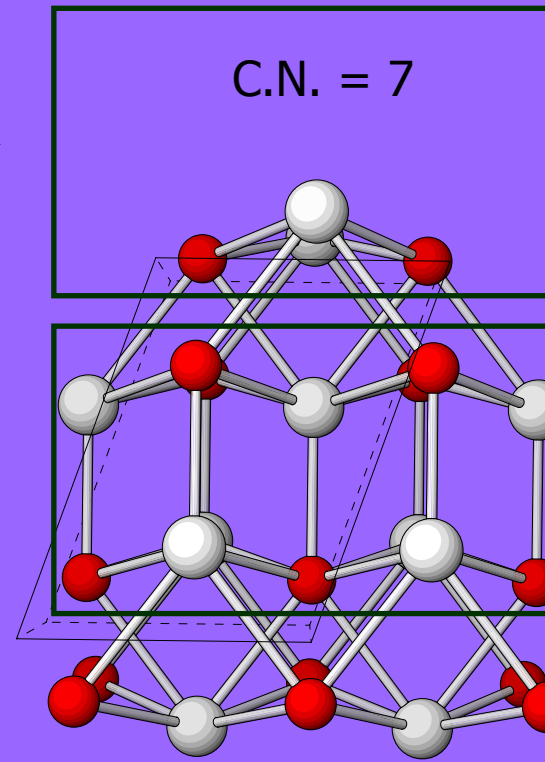
rocksalt
cubic $Fm-3m$



KOH-type
monoclinic $P2_1/m$



TII-type
orthorhombic $Cmcm$

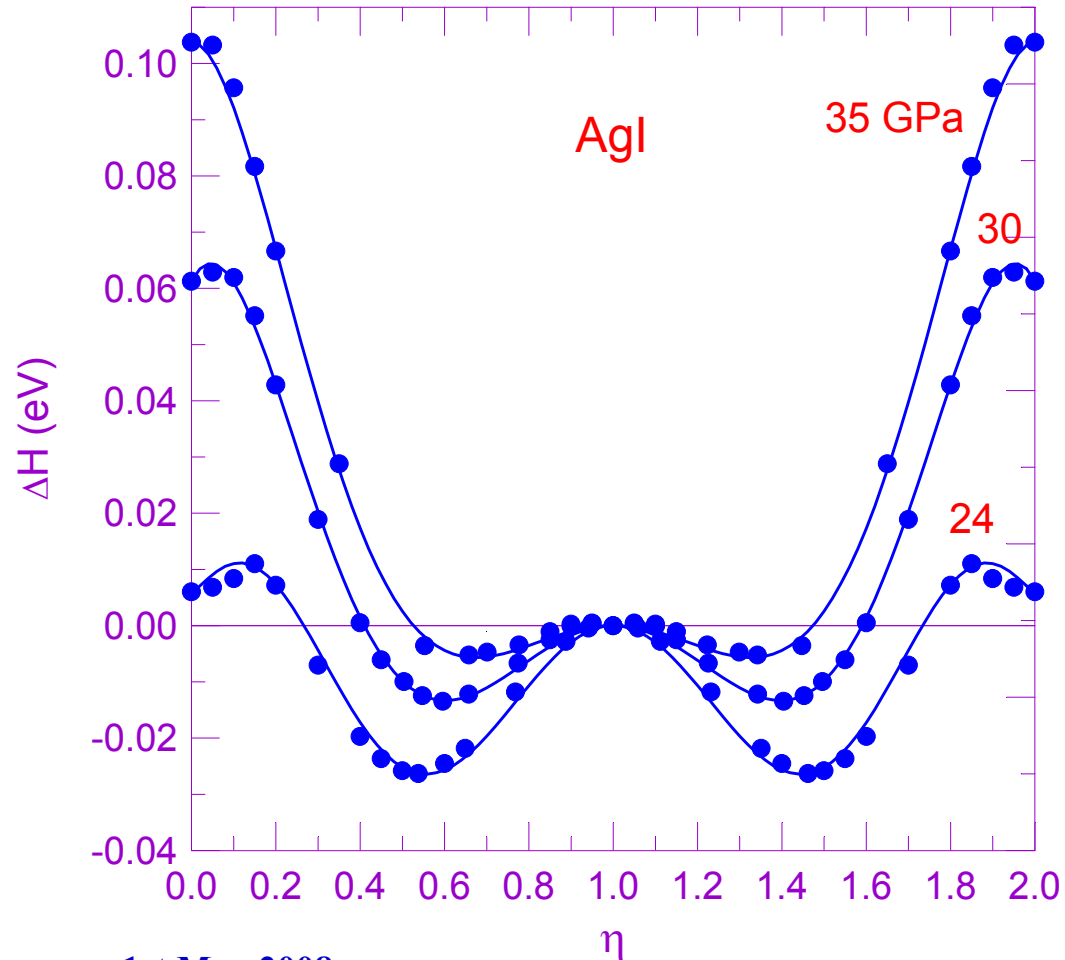


- ▶ Monoclinic KOH-type structure:
 $d(\text{Ag-I2}) \leq d(\text{I1-I2})$ in order to form the seventh Ag-I2 coordination bond
- ▶ KOH (experimental data by Jacobs et al., Z. Anorg. Allg. Chem. (1985)):
K-O2 = 3.92, O1-O2 = 3.96 Å
- ▶ AgI (19.3 GPa, this work):
Ag-I2 = 3.96, I1-I2 = 4.07 Å
- ▶ AgI (41.7 GPa, this work):
Ag-I2 = 3.31, I1-I2 = 3.76 Å

8-th order polynomial fits of the $H(\eta)$ Landau potential

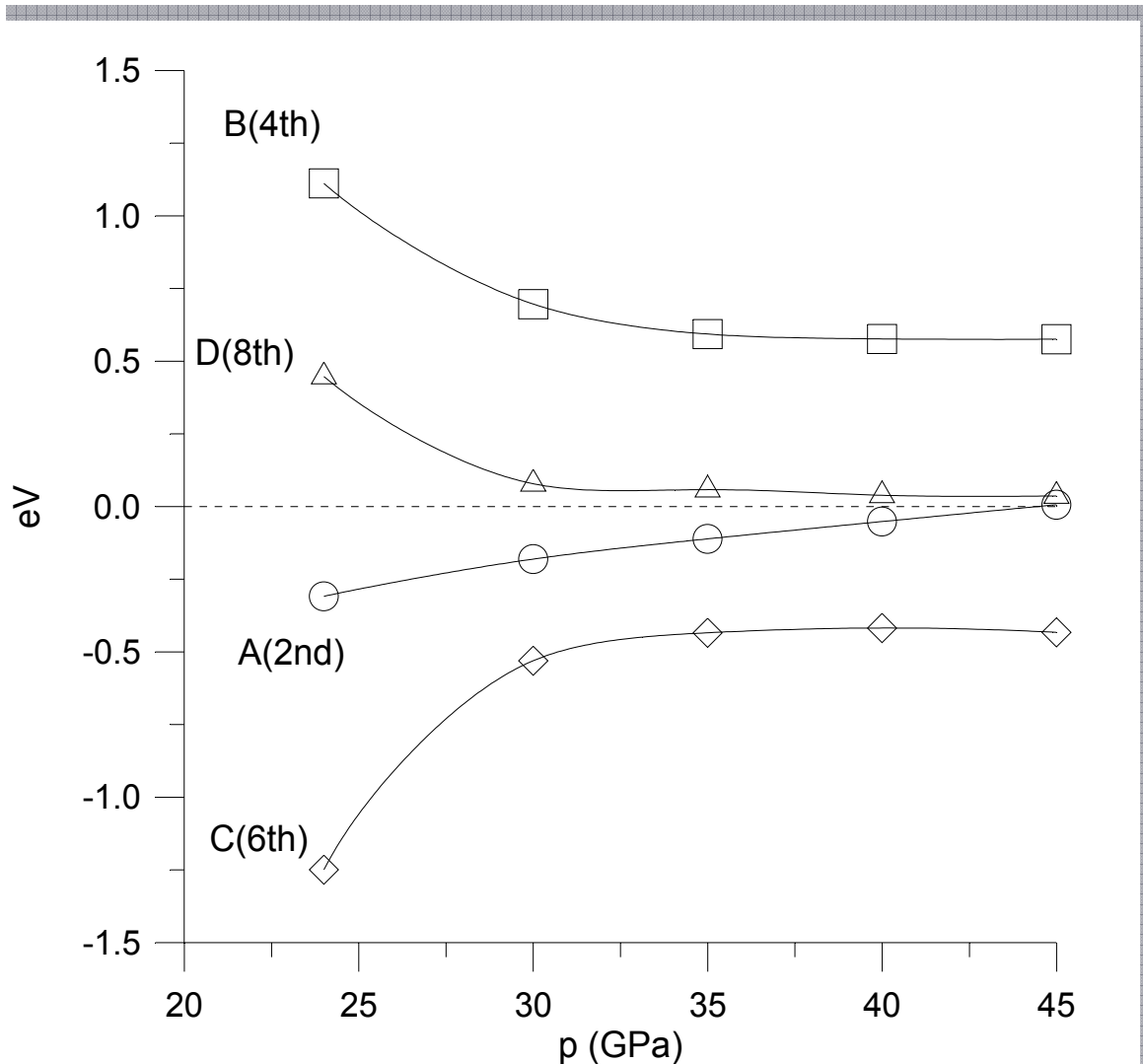
about the KOH-/TII-type phase equilibrium ($\eta = 1$)

$$\Delta H = A(\eta-1)^2 + B(\eta-1)^4 + C(\eta-1)^6 + D(\eta-1)^8$$



Pressure dependence of the Landau polynomial coefficients

$$\Delta H = A(\eta-1)^2 + B(\eta-1)^4 + C(\eta-1)^6 + D(\eta-1)^8$$



2° order A:
linear behaviour about
 p_t for KOH-/TII-type
transition

4°, 6°, and 8° order
B, C, and D:
constant behaviour about
 p_t for KOH-/TII-type
transition



Second-order phase
transition

◆ First-order transformations:

both discontinuous order parameter and significant activation enthalpy

◆ AgI phase transitions:

weak first-order (rocksalt-/KOH-type) and effective second-order (KOH-/TII-type) characters on the basis of ΔH_a values

◆ $H(\eta)$ Landau potential expanded by 8-th order even polynomial about the KOH-/TII-type phase equilibrium



correct pressure dependence of the four coefficients

A, B, C, and D

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. of 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:

$$T \subseteq T_1, \quad T \subseteq T_2$$

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).

Let P be the symmetry point group of the superlattice T .

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

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

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

Example: rocksalt ($G_1 = \text{Fm-3m}$) to CsCl-type ($G_2 = \text{Pm-3m}$) structure in NaCl under pressure

Na and Cl in Wyckoff positions (a) and (b), respectively, in both G_1 and G_2

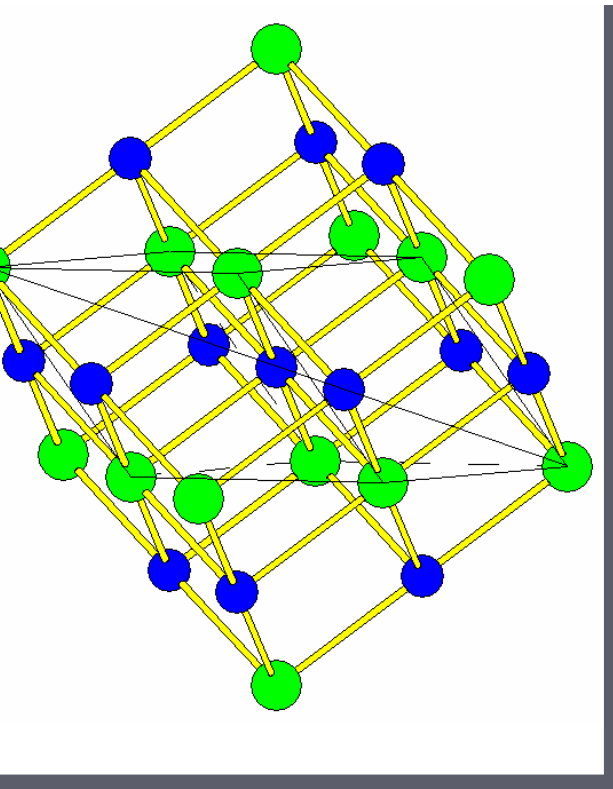
Fm-3m (B1) $Z=4$ M 0, 0, 0 (m-3m); X $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (m-3m) a_I

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

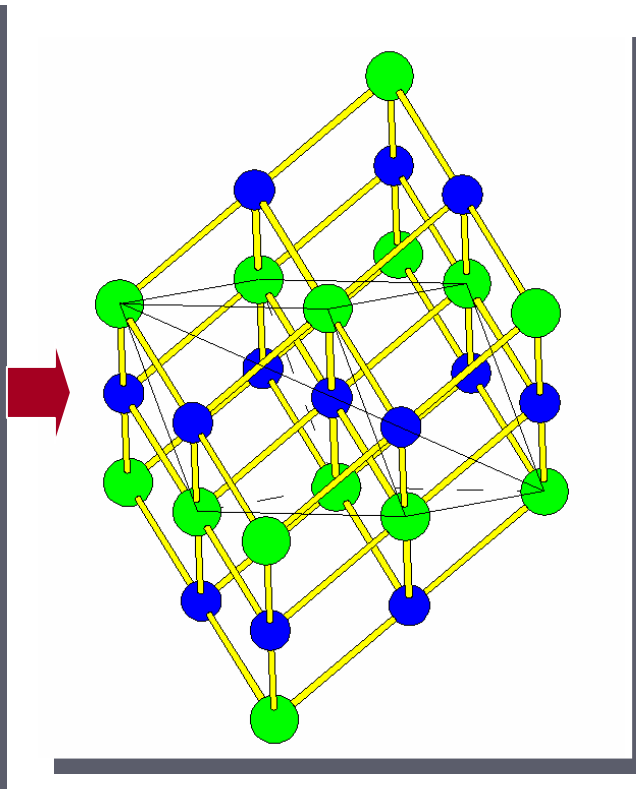
Intermediate state with common subgroup of the Fm-3m and Pm-3m space groups

- Buerger's mechanism: intermediate state with **R-3m** maximal common subgroup
(index k1)
- Watanabe's mechanism: intermediate state with **Pmmn** maximal common subgroup
(index k2)
- new mechanism: intermediate state with **P2₁/m** non-maximal common subgroup
(index k2), but subgroup of R-3m

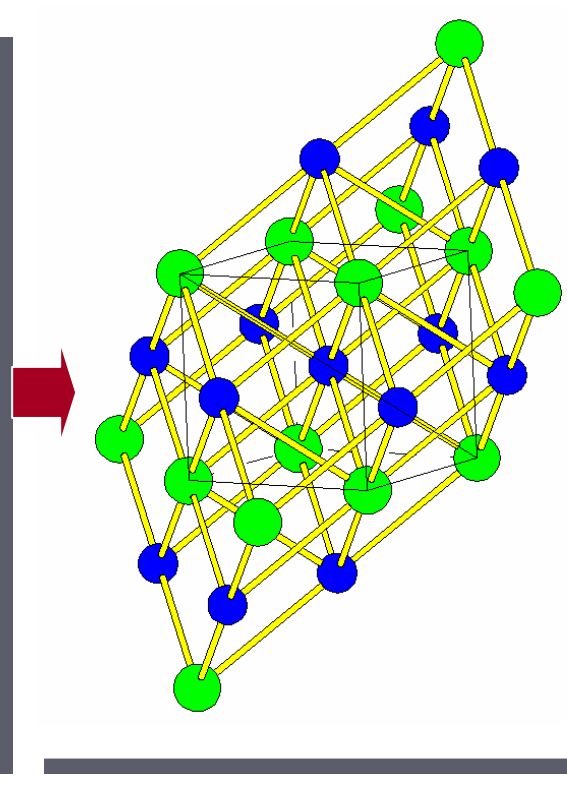
R-3m pathway of the B1/B2 phase transition



B1

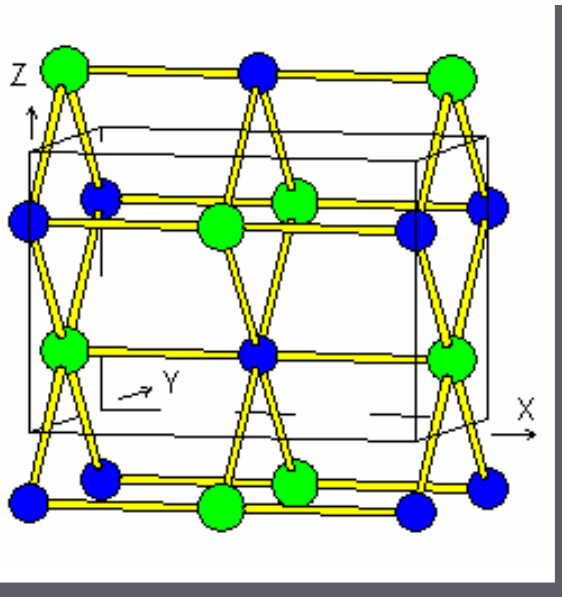


R-3m

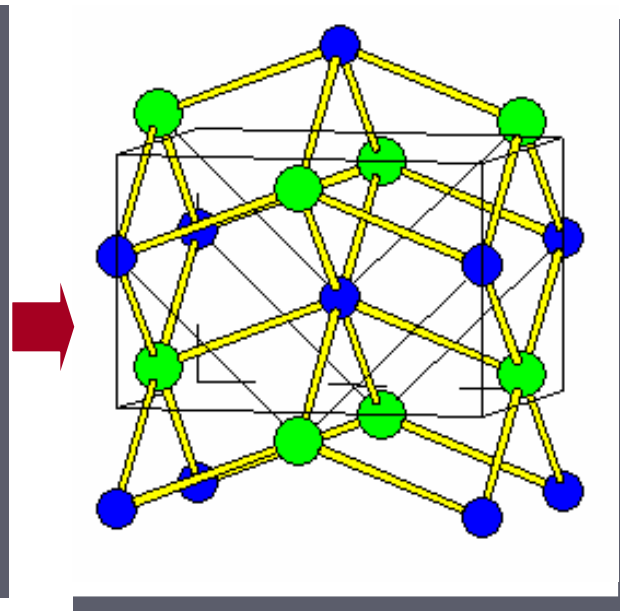


B2

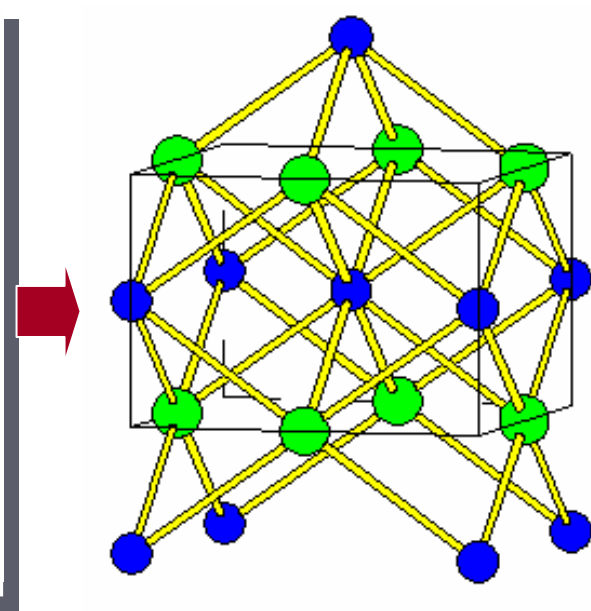
*Pm*mn pathway of the B1/B2 phase transition



B1

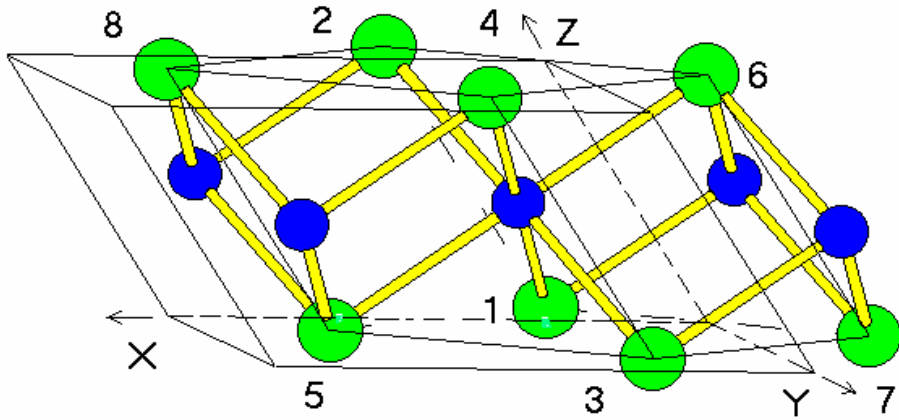


*Pm*mn



B2

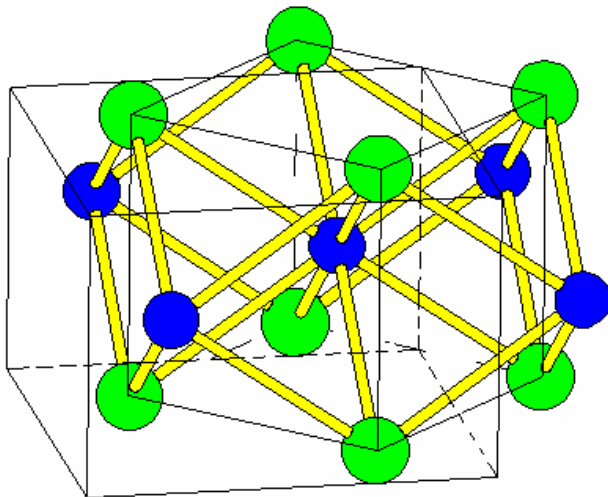
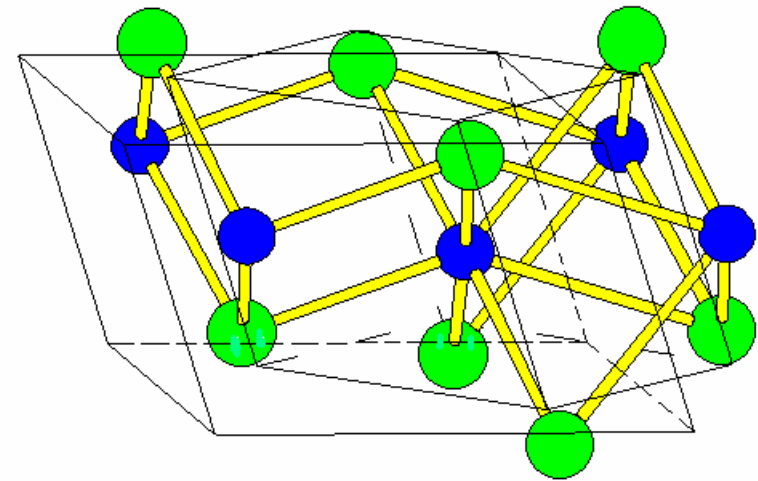
$P2_1/m$ pathway of the B1/B2 phase transition



B1



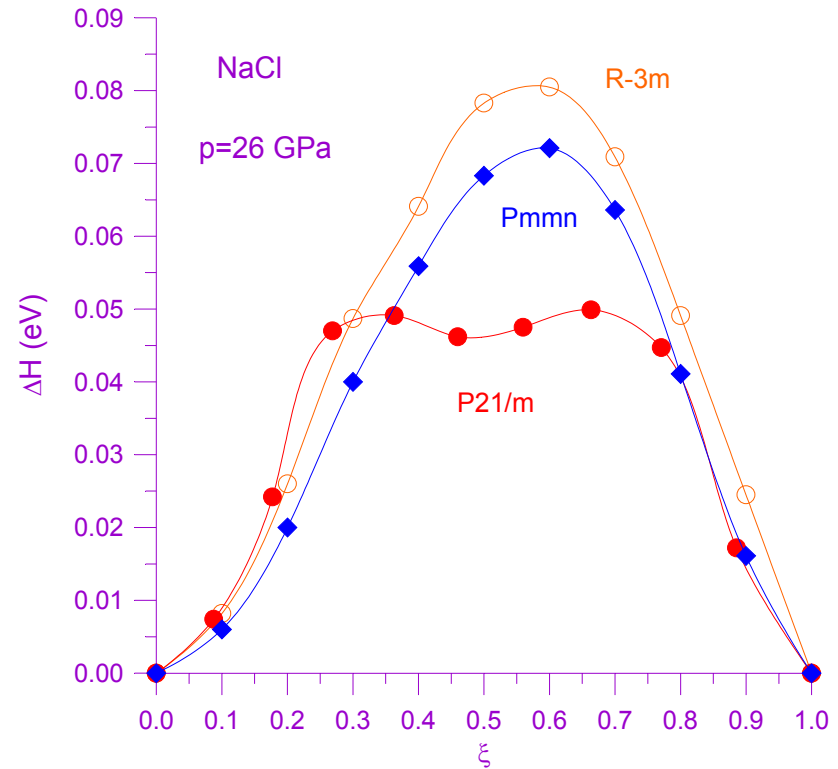
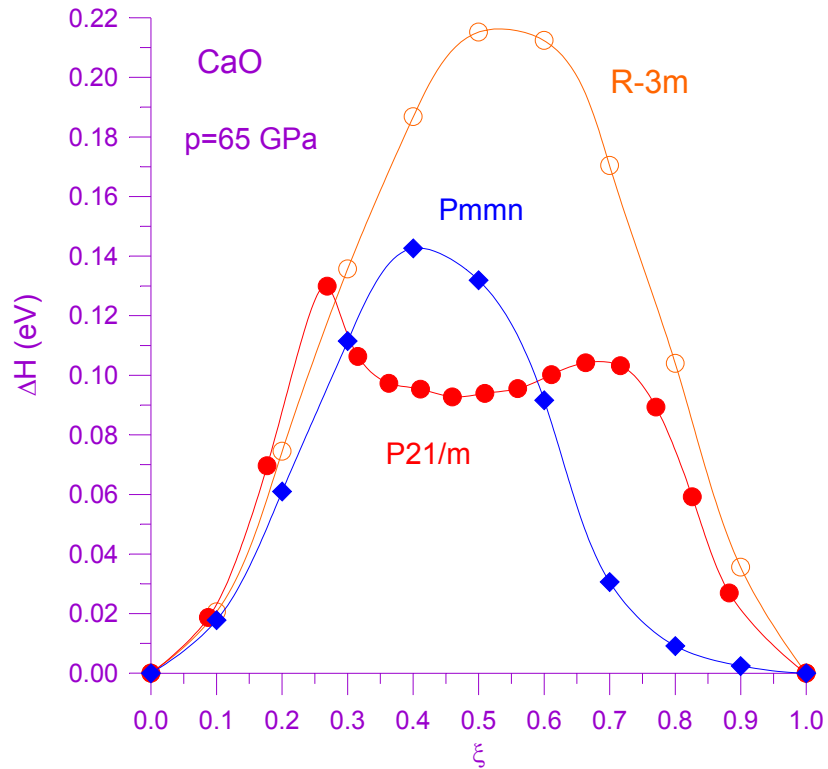
$P2_1/m$



B2



Enthalpy of intermediate states vs. reaction coordinate for the B1/B2 transition at equilibrium pressure



- The $P2_1/m$ pathway is most favoured
- Hierarchy of mechanisms: $P2_1/m > Pmmn > R-3m$
- Activation enthalpies (eV):

	$P2_1/m$	$Pmmn$	$R-3m$
CaO	0.130	0.143	0.215
NaCl	0.050	0.072	0.081

⇒ **Intermediate metastable phase in the $P2_1/m$ pathway**

- ◆ $P2_1/m$ metastable phase at $\beta = 71^\circ$:
slight monoclinic distortion of the orthorhombic $Cmcm$ TII (yellow phase) structure
- ◆ $Cmcm$ structure: stable intermediate phase in the $B1 \rightarrow Cmcm \rightarrow B2$ transition of AgCl, NaBr, NaI
- ◆ C.N. = 7 for both cations and anions, giving a peculiar stability to the structure

Only along the $P2_1/m$ pathway C.N.=7 is allowed

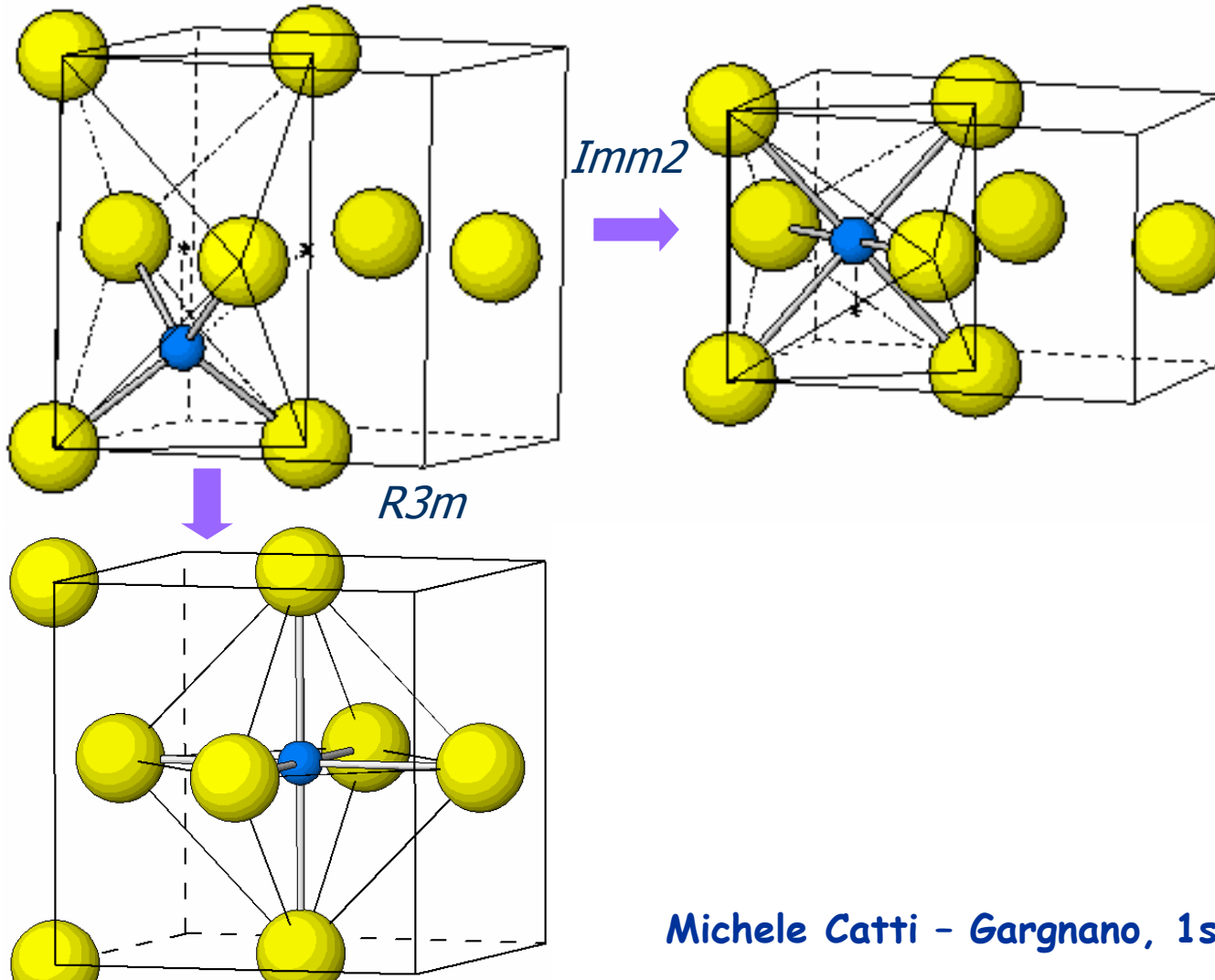
B3/B1 phase transition

- ▶ B3 structure: zinc blende-type ($F-43m$), C.N.=4
low pressure
 - ▶ B1 structure: rocksalt-type FCC ($Fm-3m$), C.N.=6
high pressure
- ZnS: $p_t = 19$ GPa SiC: $p_t = 92$ GPa

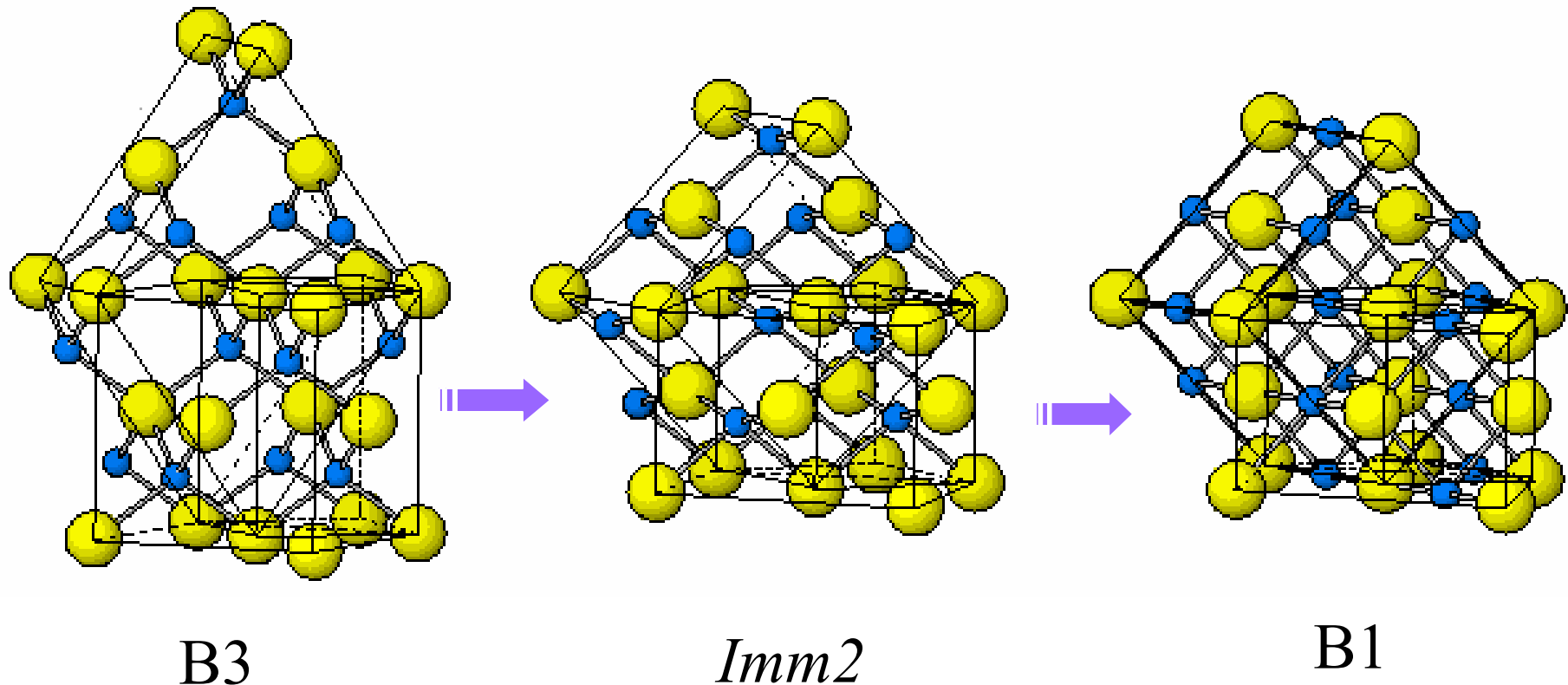
Proposed mechanisms:

- $R3m$ (Buerger, 1948)
- $Imm2$ (Catti, 2001)

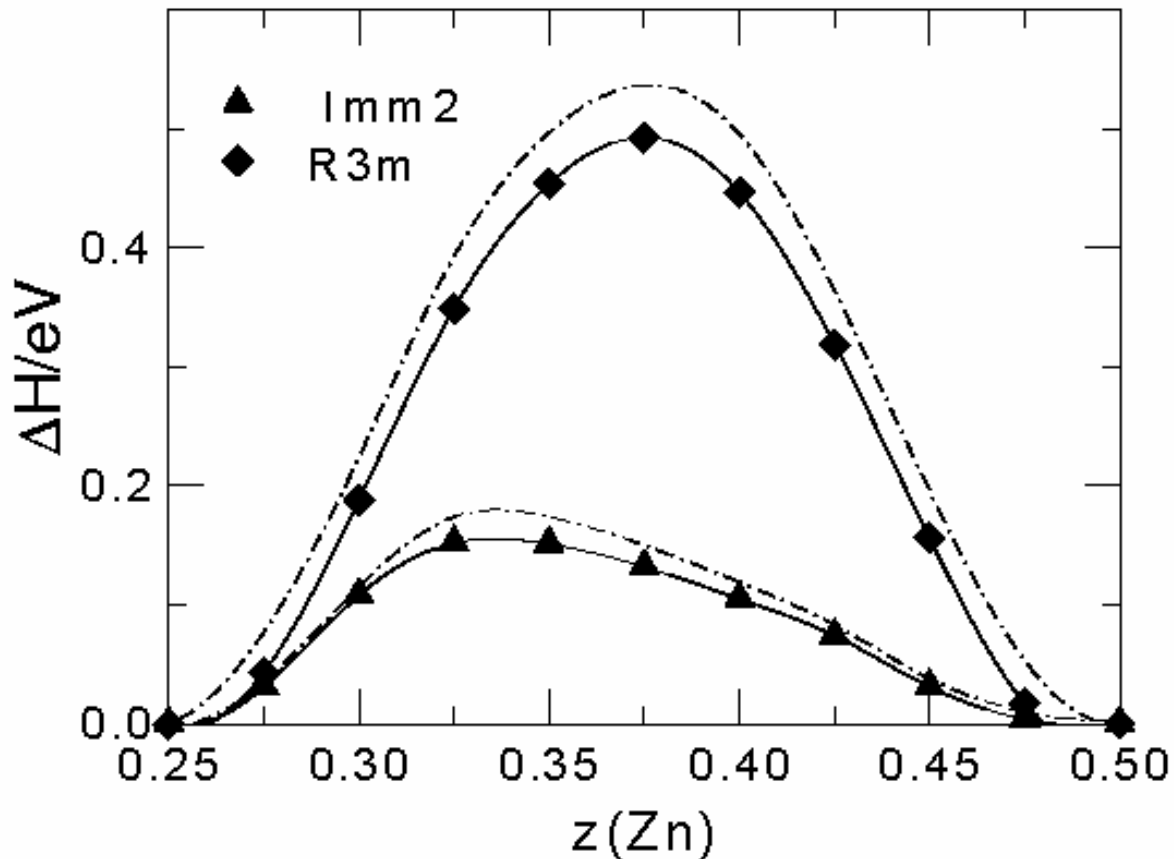
Imm2 and *R3m* mechanisms of the B3/B1 phase transition



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



Enthalpy of intermediate states vs. reaction coordinate for the B3/B1 transition of ZnS at $p_t = 19$ GPa



→ The *Imm2* mechanism is favoured over *R3m*

→ Activation enthalpies (eV):

	<i>Imm2</i>	<i>R3m</i>
ZnS	0.15	0.49
SiC	0.75	2.10

→ *Imm2*: C.N. increases from 4 to 6

R3m: C.N. decreases from 4 to 3, then increases to 6

Summary

- ◆ Ab initio simulations are a powerful tool to investigate the thermodynamics and kinetics of high-pressure phase transitions
- ◆ The first- or second-order character of displacive transitions can be assessed
- ◆ Landau theory can be applied quantitatively to displacive transformations
- ◆ Comparison of enthalpy barriers can detect the hierarchy of different kinetic mechanisms for reconstructive transitions

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