

Thermodynamics and kinetics of solid phase transformations

Michele Catti

*Dipartimento di Scienza dei Materiali,
Universita' di Milano Bicocca, Milano, Italy*

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:

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

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

Thermodynamics: effect of temperature

Quasi-harmonic lattice-dynamical model



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

- Vibrational partition function:

$$Z = \prod_i Z_i = \prod_i \exp(h\nu_i/2k_B T) / [\exp(h\nu_i/k_B T) - 1]$$

$$F = E_{st} - RT \ln Z; \quad S = R \ln Z + RT(\partial \ln Z / \partial T)_V;$$

$$E = E_{st} + RT^2(\partial \ln Z / \partial T)_V; \quad C_V = (\partial E / \partial T)_V$$

- Quasi-harmonic equation of state:

$$p = -dE_{st}/dV - (1/V)\sum_i \{hv_i/[\exp(hv_i/k_B T)-1]\}\gamma_i$$

the vibrational frequencies ν_i are assumed to depend on volume \Rightarrow

$$\gamma_i = \partial \ln \nu_i / \partial \ln V \quad \text{Grueneisen parameter of the } i\text{-th vibrational mode}$$

Problem:

- full vibrational spectrum extended to the whole Brillouin zone
- supercell approach required to compute frequencies at $\mathbf{K} \neq 0$
- some interpolation scheme in reciprocal space is necessary

Zeroth-order approximation: Einstein model
(non-dispersive approximation for optic modes only)

optic frequencies at $\mathbf{K}=0$ are extrapolated to the whole Brillouin zone

Alternative approaches:

Debye model \Rightarrow acoustic frequencies approximate the whole vibrational spectrum

Mixed Einstein+Debye model:

Ab initio elastic constants \rightarrow Debye temperature $\Theta_{D,a}$ \rightarrow

acoustic contribution to thermodynamic functions

Ab initio zone-centre frequencies \rightarrow Einstein modes \rightarrow

optic contribution to thermodynamic functions

Debye model

$$v_D = cK_D/2\pi = c(3p/4\pi V)^{1/3} \quad \Theta_D = hv_D/k_B$$

p = number of atoms per unit-cell volume V

c = average acoustic wave velocity in the crystal = $f(C_{hk})$

density of acoustic modes:

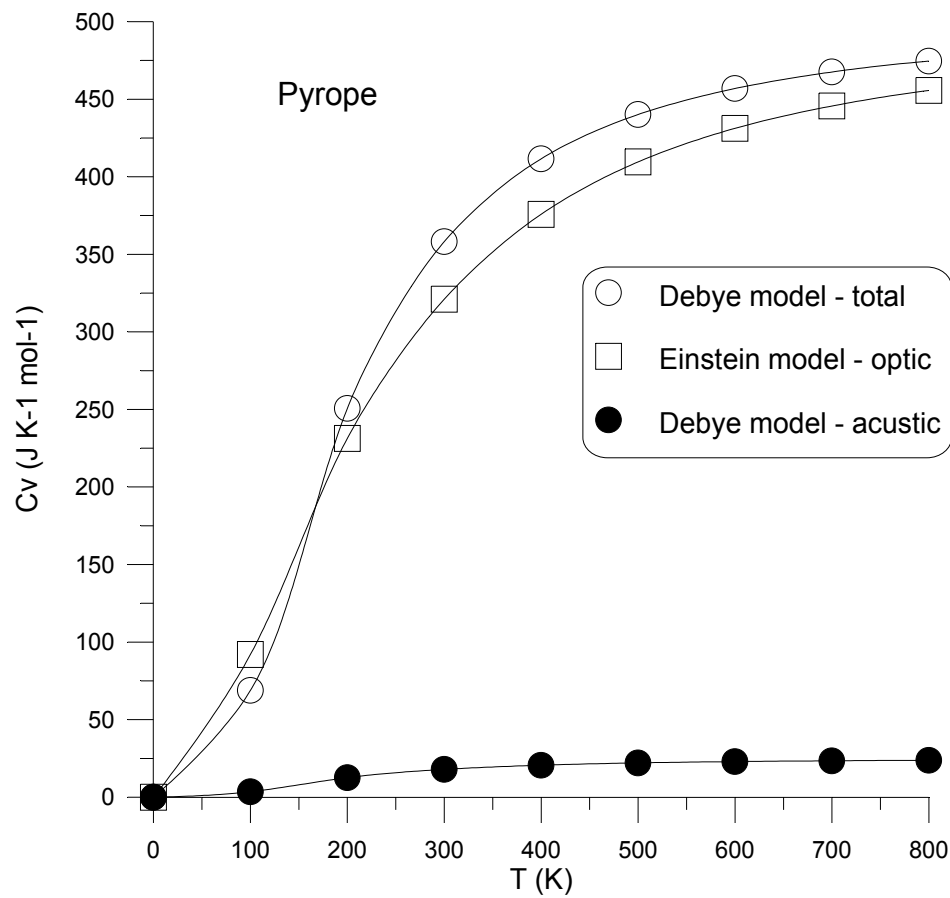
$$g(v) = 9Nv^2/v_D^3 = (6V/c^3) v^2 \quad \text{for } v \leq v_D$$

$$g(v) = 0 \quad \text{for } v > v_D$$

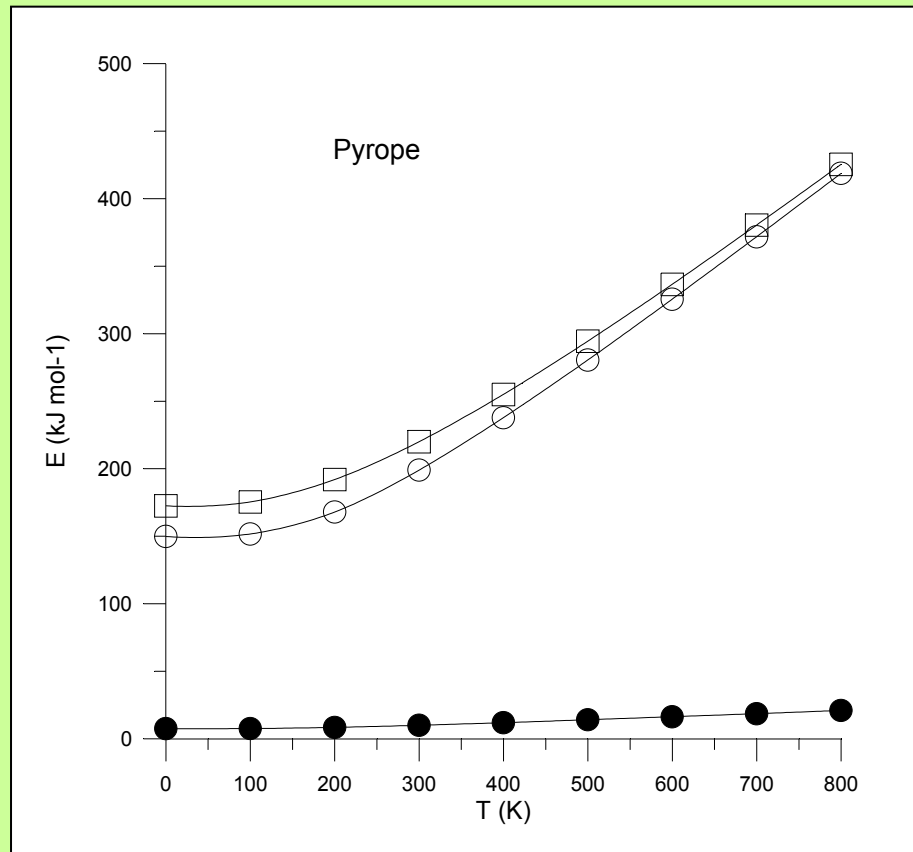
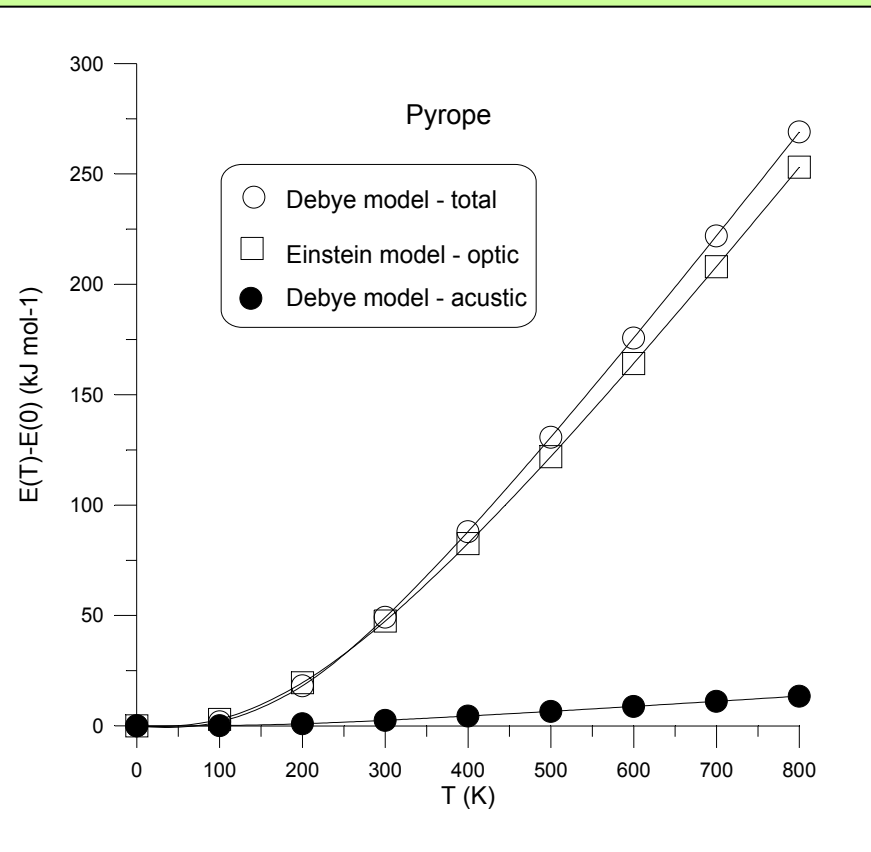
$$F(T) = \int g(v)f(v,T)dv$$

$$e(v,T) = (1/2)hv + hv/[\exp(hv/kT) - 1]$$

$$E(T) = (9/8)nR\Theta_D + 9nRT(\Theta_D/T)^{-3} \int_0^{\Theta_D/T} [x^3/(e^x-1)]dx$$



Ab initio elastic and vibrational data of pyrope



Thermodynamic functions of several phases/compounds



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



Thermodynamics of phase transitions / chemical reactions

Athermal limit case:

only pressure is considered, enthalpy replaces G function

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

Kinetics

Basic assumption:

lattice periodicity is preserved (role of defects ignored)

Example: reconstructive (first-order) phase transitions

- 1) Symmetry analysis (cf. Stokes and Hatch, PRB 2002)
 - ◆ identification of possible atomic pathways
 - ◆ the symmetry must be a subgroup of the space groups of both end phases
- 2) Calculation of the free energy or enthalpy function along the transformation coordinate (order parameter) \Rightarrow
 - activation free energy/enthalpy
 - hierarchy among different mechanisms

Transition State Theory (TST) \Rightarrow
from molecular chemical reactivity to solid state kinetics

molecular transition state (activated complex) \Rightarrow
intermediate structural state

Simplified version of Eyring equation for solid state
transformations $A \rightarrow P^* \rightarrow B$:

$$k \text{ (rate constant)} = (k_B T/h)(Z_{P^*}/Z_A)\exp(-\Delta E_0^*/k_B T)$$



Arrhenius equation:

$$k = (k_B T/h)\exp(-\Delta F^*/k_B T) = \nu_{P^*}(Z_{P^*}/Z_A)\exp(-\Delta E_0^*/k_B T)$$

From ab initio total energies:

ΔE_0^* or ΔH_0^* static activation barrier

From ab initio vibrational frequencies:

Z_{P^*} and Z_A vibrational partition functions



pre-exponential factor of the Arrhenius formula



rate constant of the transformation

Applications to static kinetic modeling of high-pressure reconstructive phase transitions

- ◆ B1/B2 transformation (NaCl, CaO):
from rocksalt-type (Fm-3m), C.N.=6, to CsCl-type (Pm-3m), C.N.=8
- ◆ B3/B1 transformation (ZnS, SiC):
from zinc blende (F-43m), C.N.=4, to rocksalt-type (Fm-3m), C.N.=6

cf. also Catti, PRL 87, 035504 (2001), PRB 65, 224115 (2002), JPCM 16, 3909 (2004), PRB 72, 064105 (2005)

B1 structure: rocksalt-type FCC (Fm-3m), C.N.=6
B2 structure: CsCl-type (Pm-3m), C.N.=8

Thermodynamics

$$V(B2)-V(B1) < 0 \quad \Rightarrow \quad B1 \leftrightarrow B2 \quad \text{at } p = p_t$$

$$p < p_t, \quad H(B2)-H(B1) > 0, \quad B1 \text{ stable}$$

$$p > p_t, \quad H(B2)-H(B1) < 0, \quad B2 \text{ stable}$$

KCl, NaCl, SrO, CaO: $p_t = 2, 27, 36, 60$ Gpa
(diamond anvil cell + X-ray diffraction)

Kinetics

Proposed mechanisms:

- R-3m (Buerger, 1948)
- Pmmn (Watanabe et al., 1977)
- $P2_1/m$ (Stokes and Hatch, 2002)

Which one is energetically favoured ?

What is the enthalpy barrier ΔH_0 ?



Arrhenius law: rate constant $\propto \exp(-\Delta H_0/kT)$

Theoretical method

- E : crystal quantum-mechanical total energy
- $H = E + pV = H(\underline{a}, \underline{X}, p)$
minimized vs. \underline{a} (lattice parameters) and \underline{X} (atomic coordinates)
at constant pressure p



ξ : reaction coordinate (one of the $\underline{a}, \underline{X}$ variables)

Computational

- DFT-GGA-PBE Hamiltonian
- all-electron localized Gaussian basis set
Ca: 8(s)6511(sp)3(d)G; O: 8(s)411(sp)1(d)G
Na: 8(s)511(sp)3(d)G; Cl: 8(s)6311(sp)G
- Computer code: CRYSTAL

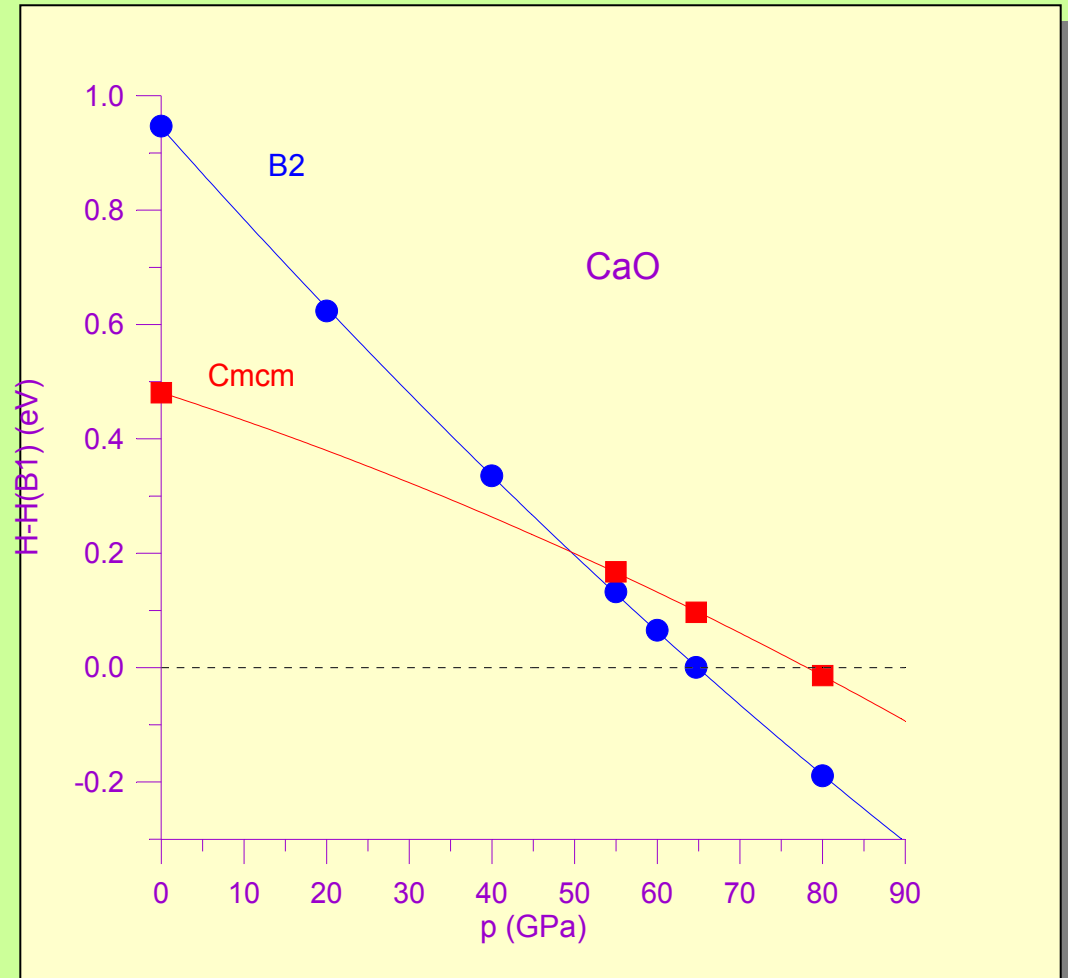
Enthalpy differences B2-B1 and Cmcm(TII-like)-B1 vs. pressure for CaO

$$\Delta H(p) = 0$$

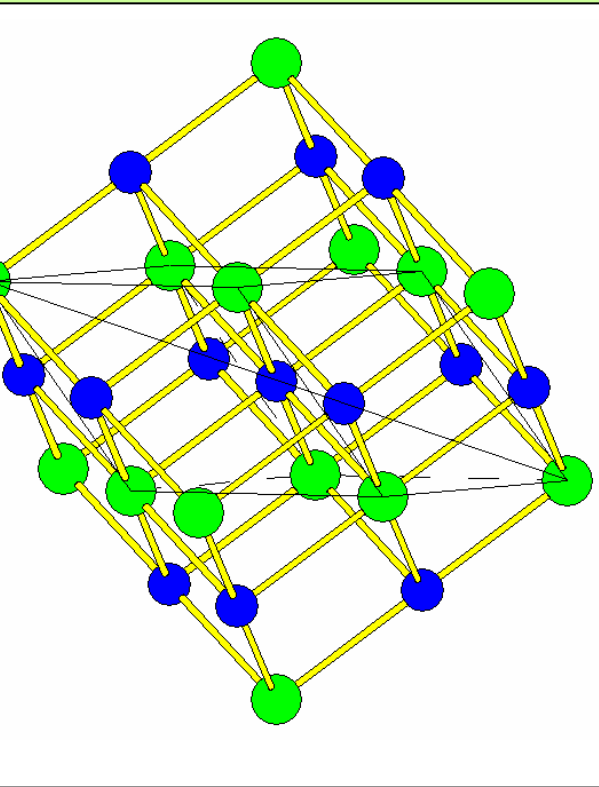
Equilibrium condition



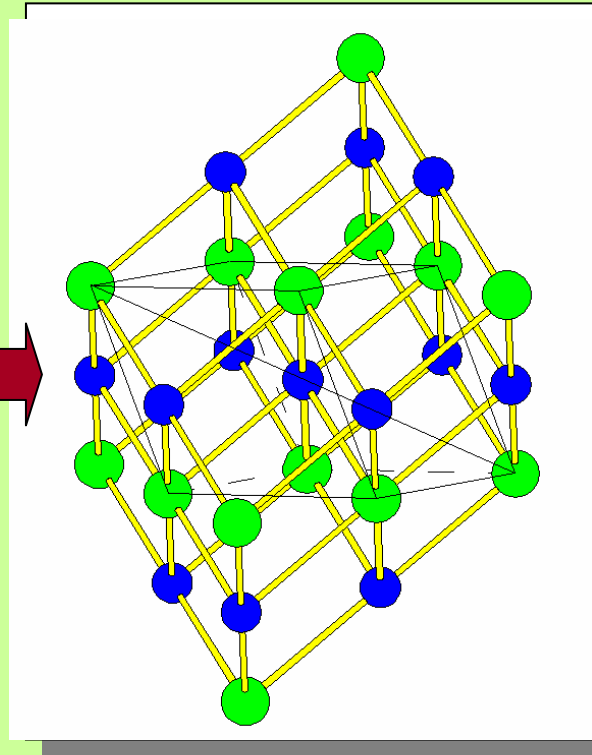
$$p = p_t$$



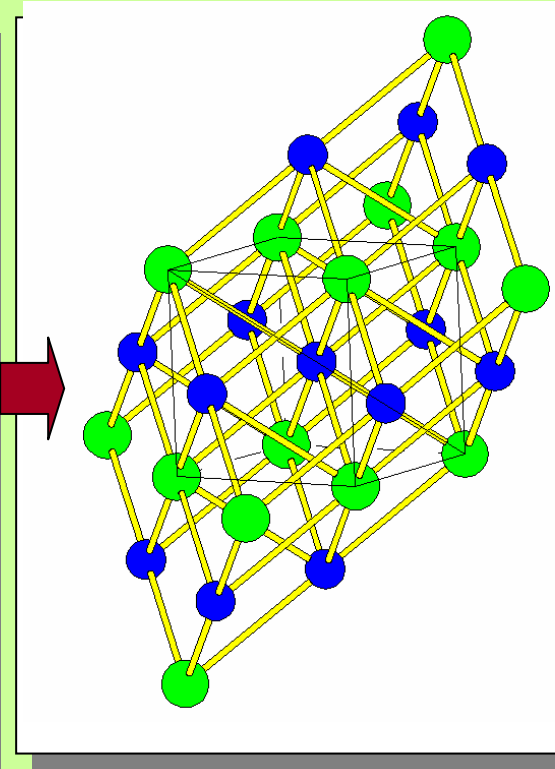
R-3m pathway of the B1/B2 phase transition



B1

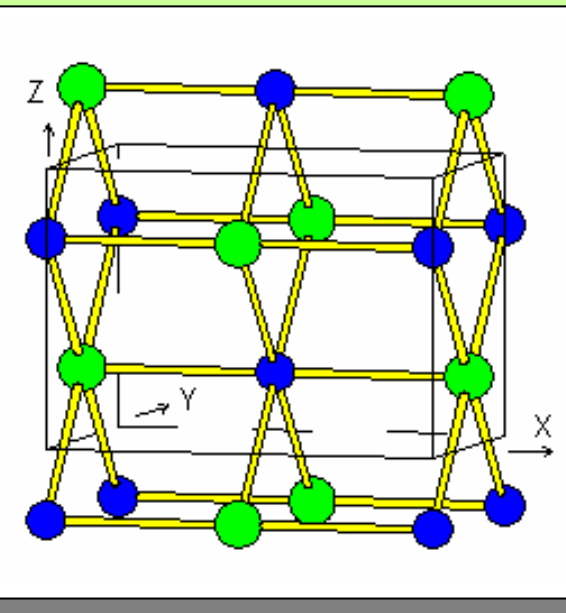


R-3m

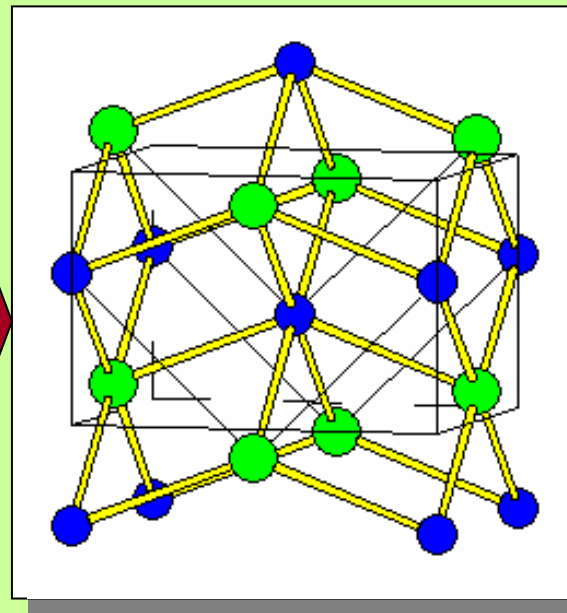


B2

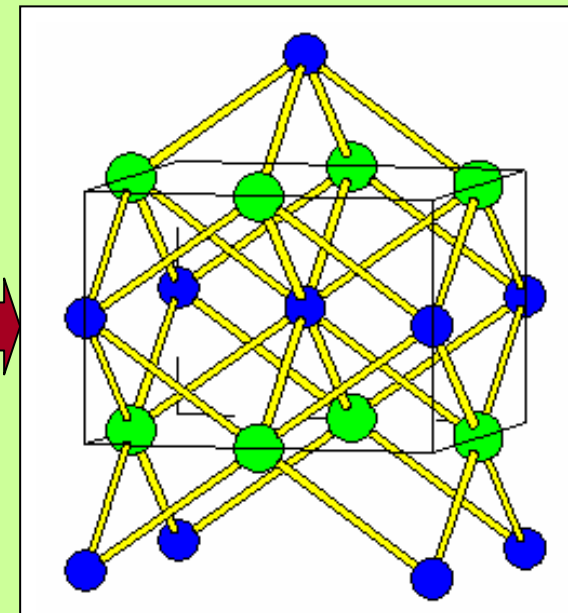
Pmnn pathway of the B1/B2 phase transition



B1



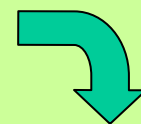
Pmnn



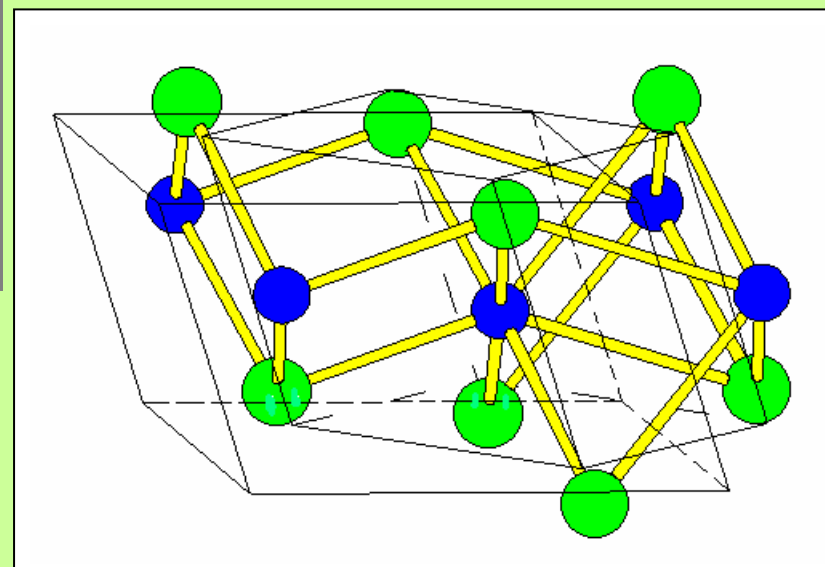
B2

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

B1

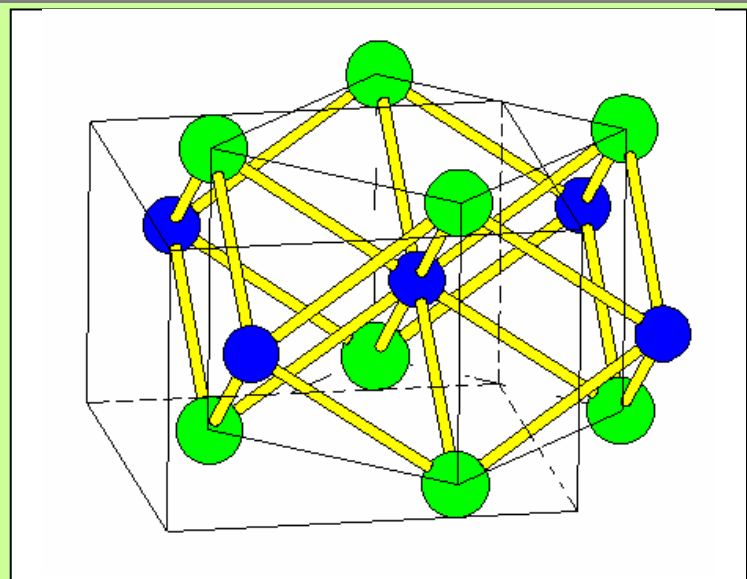
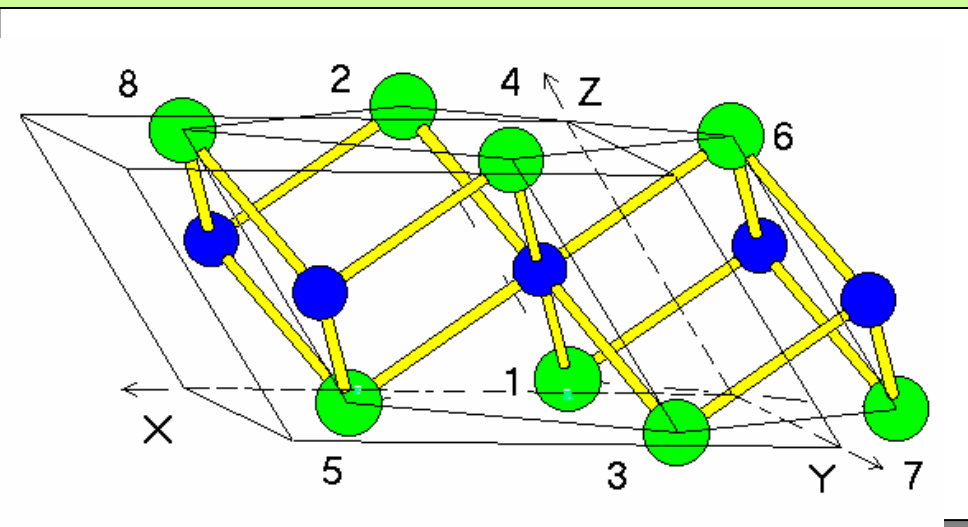


$P2_1/m$



B2

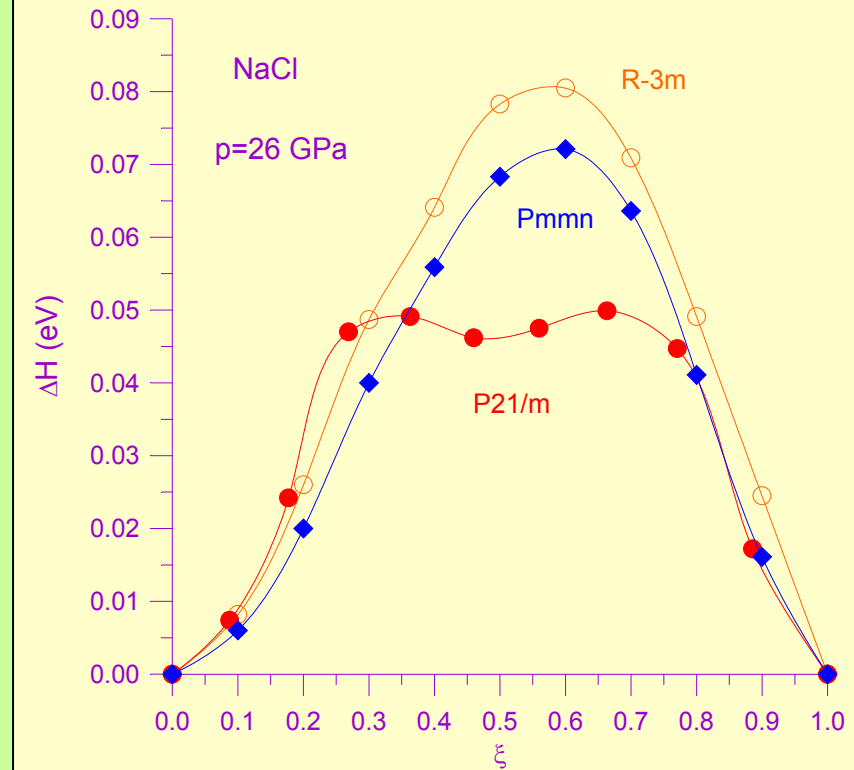
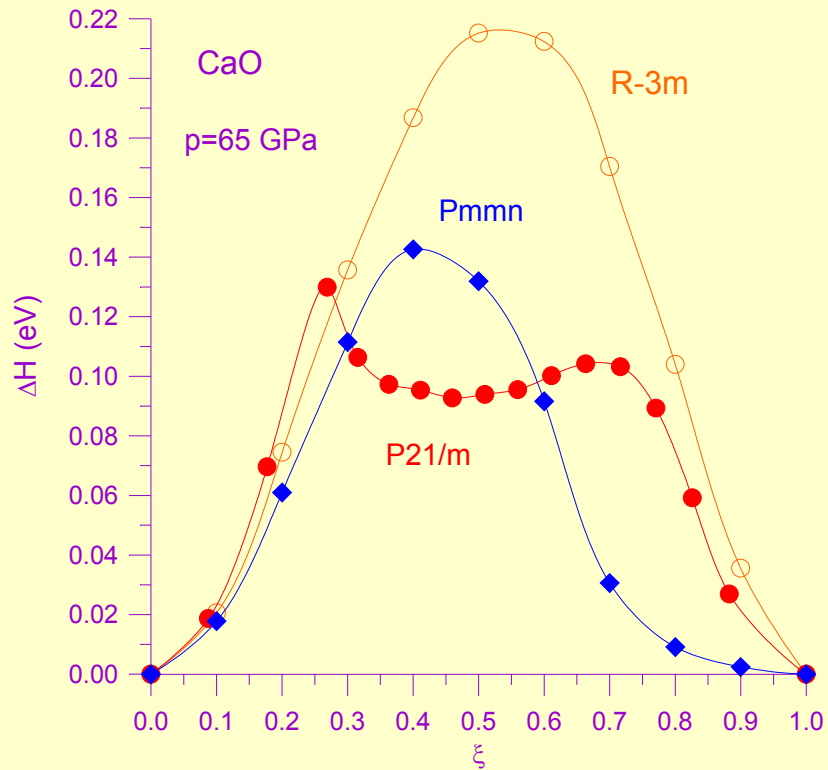
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Transformation matrices relating unit-cells

R-3m	→	Fm-3m	$[-1 \ 1 \ 1/1 \ -1 \ 1/1 \ 1 \ -1]$	}	R-3m pathway
R-3m	→	Pm-3m	$[1 \ 0 \ 0/0 \ 1 \ 0/0 \ 0 \ 1]$		
Fm-3m	→	Pm-3m	$[0 \ 1/2 \ 1/2 \ / \ 1/2 \ 0 \ 1/2 \ / \ 1/2 \ 1/2 \ 0]$		
P2 ₁ /m	→	Fm-3m	$[0 \ 1 \ 1/0 \ -1 \ 1/1 \ 0 \ -1]$	}	P2 ₁ /m pathway
P2 ₁ /m	→	Pm-3m	$[1/2 \ -1/2 \ 0/ \ 1/2 \ 1/2 \ 0/0 \ 0 \ 1]$		
Fm-3m	→	Pm-3m	$[0 \ 1/2 \ 1/2 \ / \ 1/2 \ 0 \ 1/2 \ / \ 1/2 \ 1/2 \ 0]$		
Pmmn	→	Fm-3m	$[1 \ 0 \ 0/0 \ 1 \ 1/0 \ -1 \ 1]$	}	Pmmn pathway
Pmmn	→	Pm-3m	$[1/2 \ 1/2 \ 0/0 \ 0 \ 1/ \ 1/2 \ -1/2 \ 0]$		
Fm-3m	→	Pm-3m	$[1/2 \ 1/4 \ -1/4 \ /0 \ 1/2 \ 1/2 \ / \ 1/2 \ -1/4 \ 1/4]$		

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



→ The $P2_1/m$ pathway is most favoured

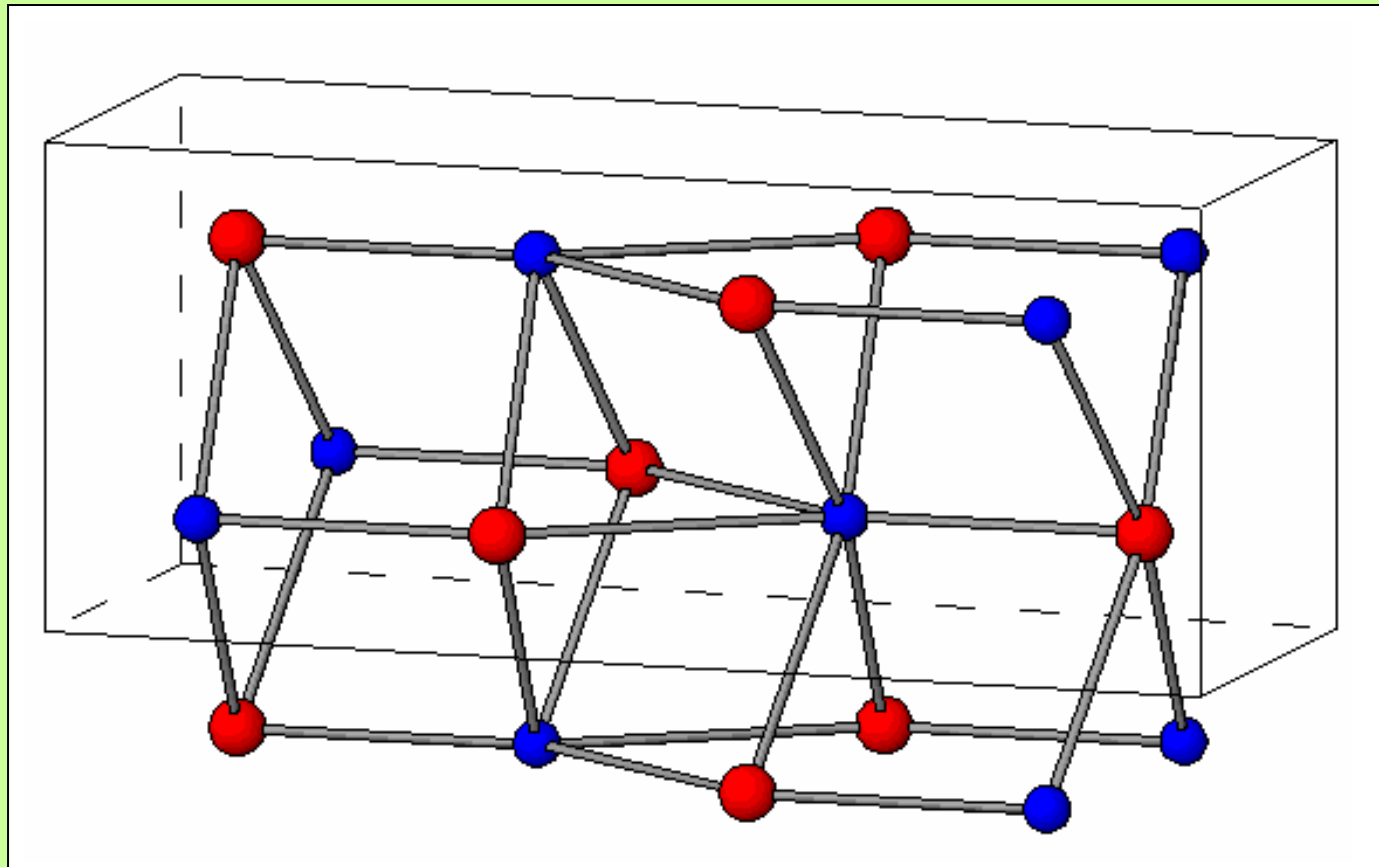
→ Hierarchy of mechanisms: $P2_1/m > Pmmn > R-3m$

→ Activation enthalpies (eV):

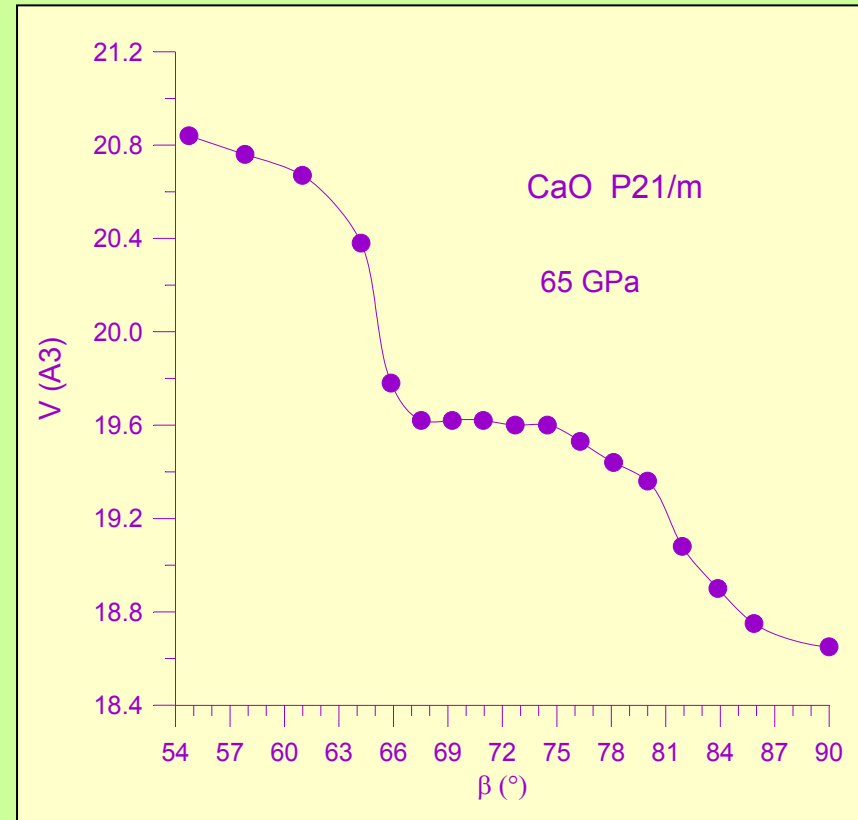
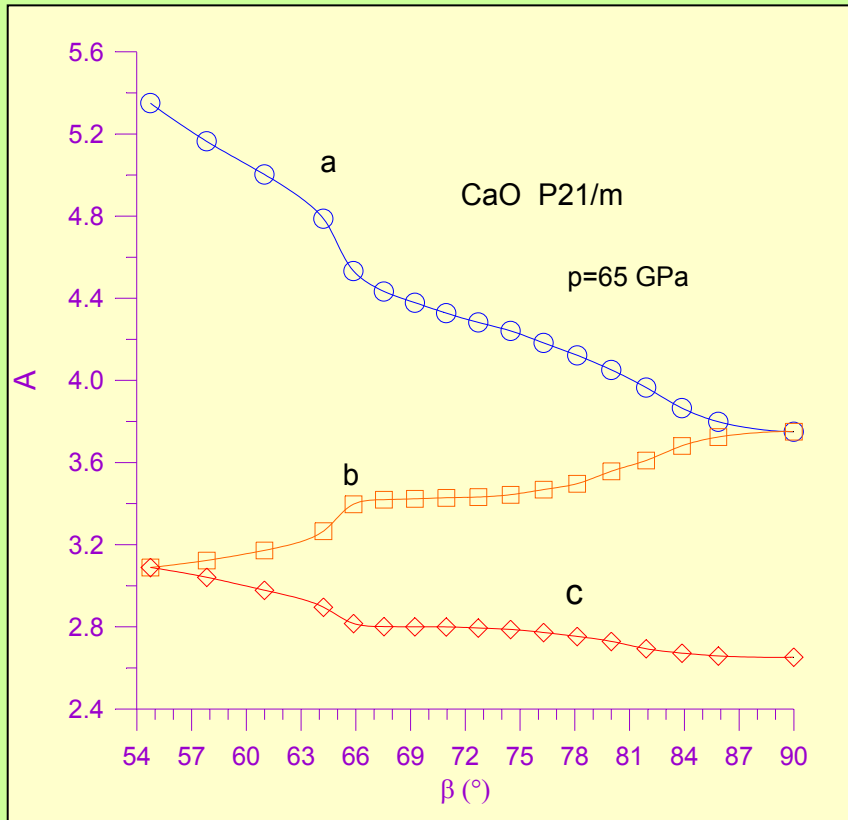
	$P2_1/m$	$Pmmn$	$R-3m$
CaO	0.130	0.143	0.215
NaCl	0.050	0.072	0.081

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

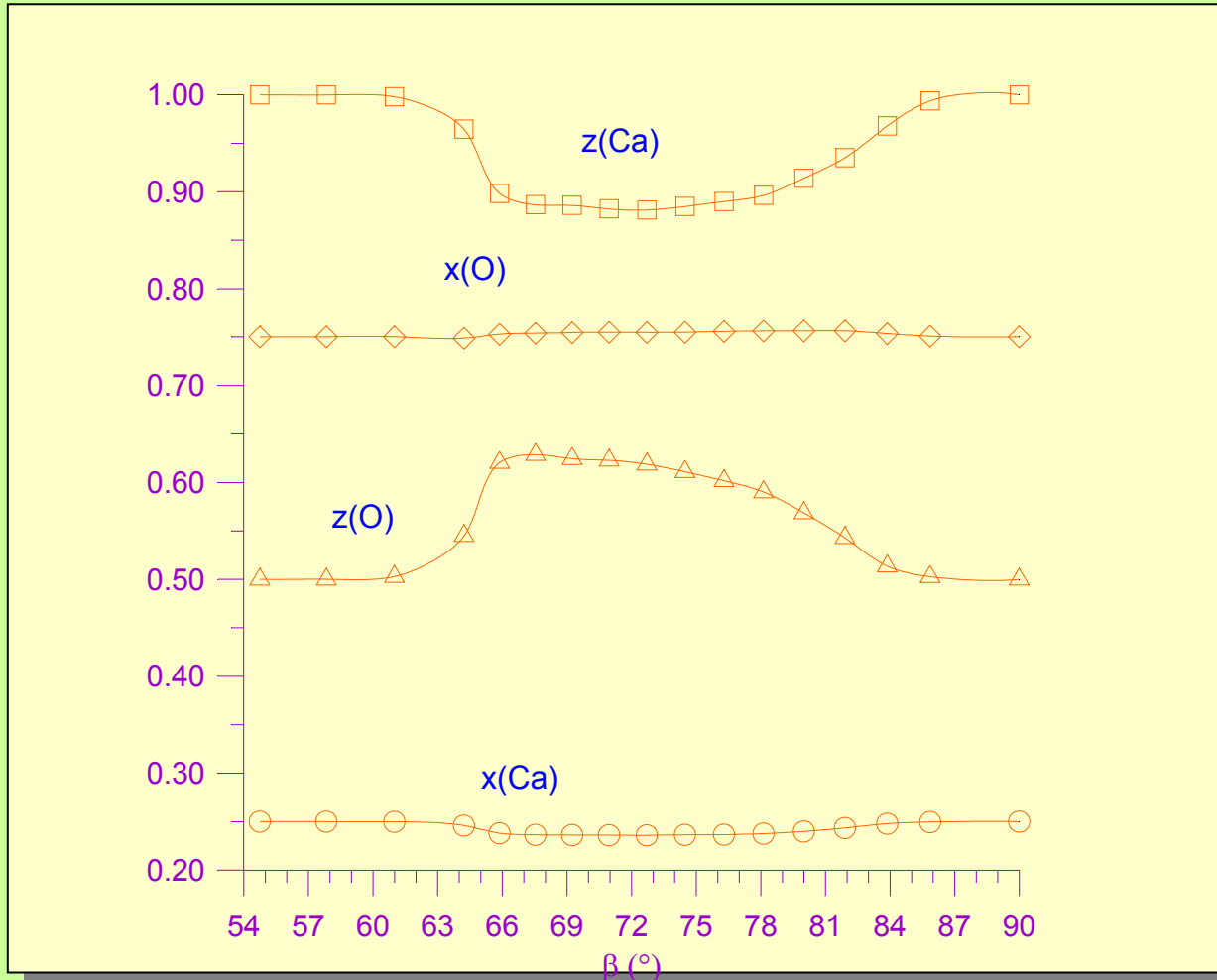
Crystal structure of Cmc₂m-TII (yellow form)



Unit-cell constants of CaO along the $P2_1/m$ path vs. the monoclinic β angle

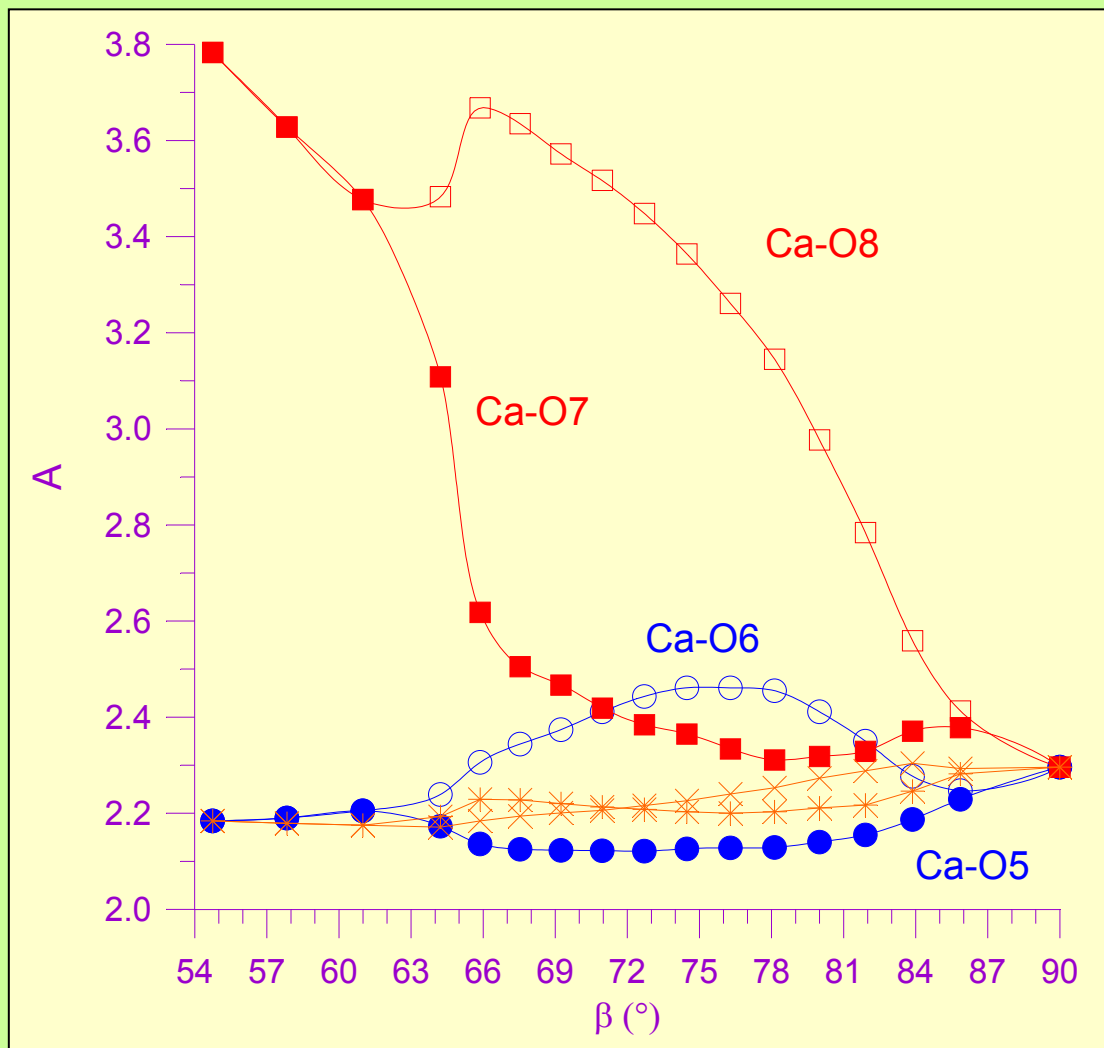


Atomic fractional coordinates of CaO along the $P2_1/m$ path



Evolution of Ca-O distances along the $P2_1/m$ path

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- ◆ $P2_1/m$ 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

- ◆ $P2_1/m$ mechanism:
(2+2+1+1)+1+1 evolution of A-B bonds
- ◆ $Pmmn$ mechanism:
(2+2+2)+2 evolution of A-B bonds
- ◆ $R-3m$ mechanism:
(6)+2 evolution of A-B bonds



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

B3/B1 phase transition

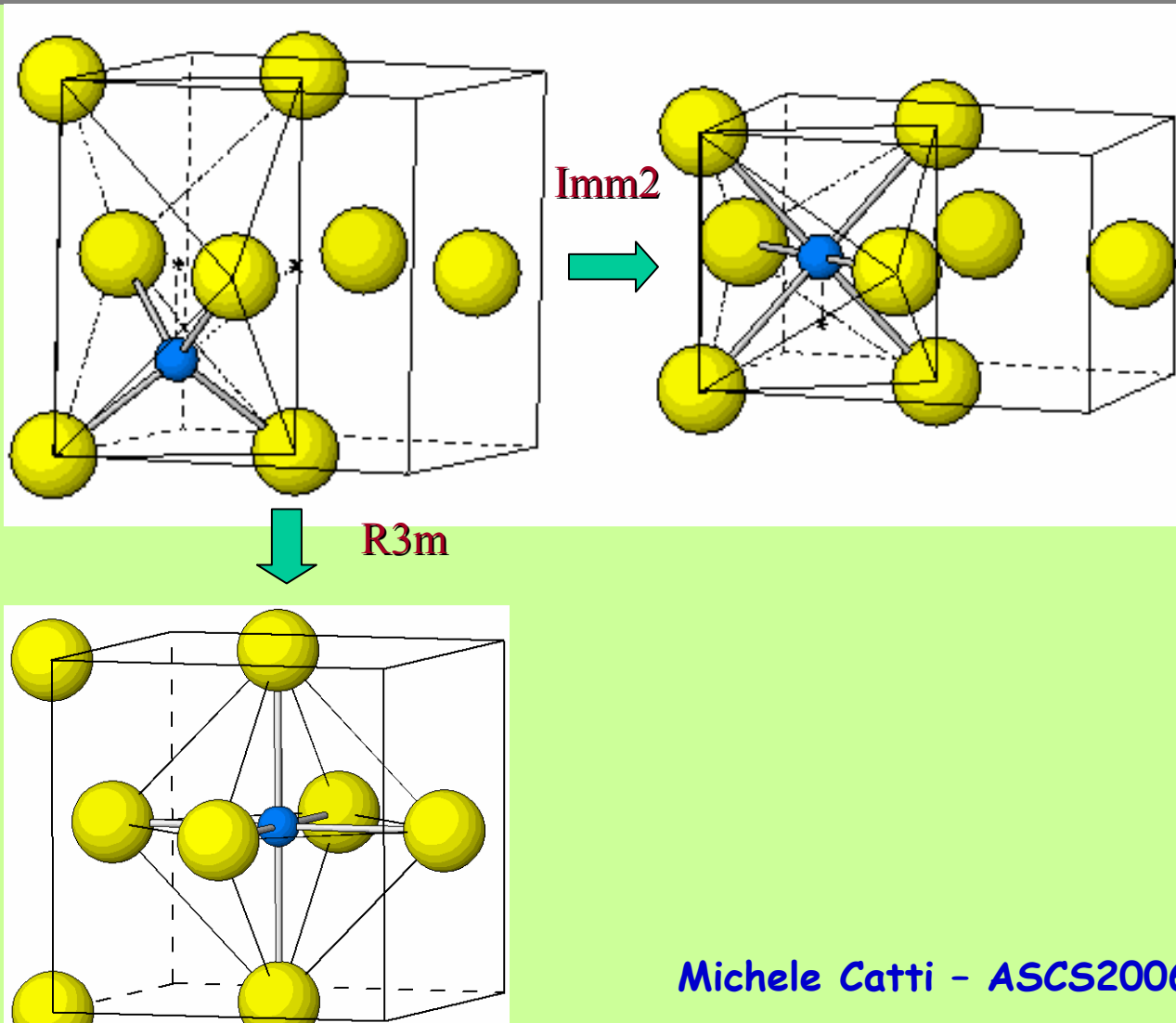
- B3 structure: zinc blende-type (F-43m), C.N.=4
low pressure
 - B1 structure: rocksalt-type FCC (Fm-3m), C.N.=6
high pressure
- ZnS: $p_t = 19$ GPa SiC: $p_t = 92$ GPa

Proposed mechanisms:

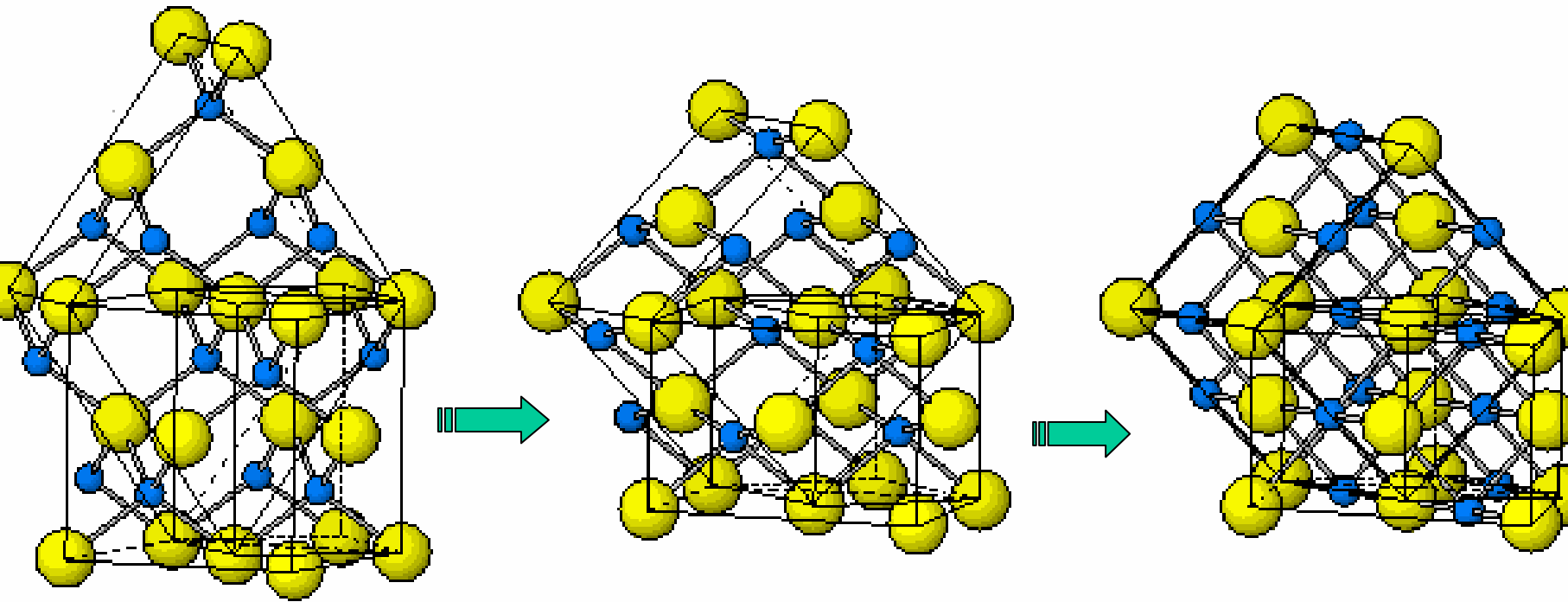
→ R3m (Buerger, 1948)

→ Imm2 (Catti, 2001)

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



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



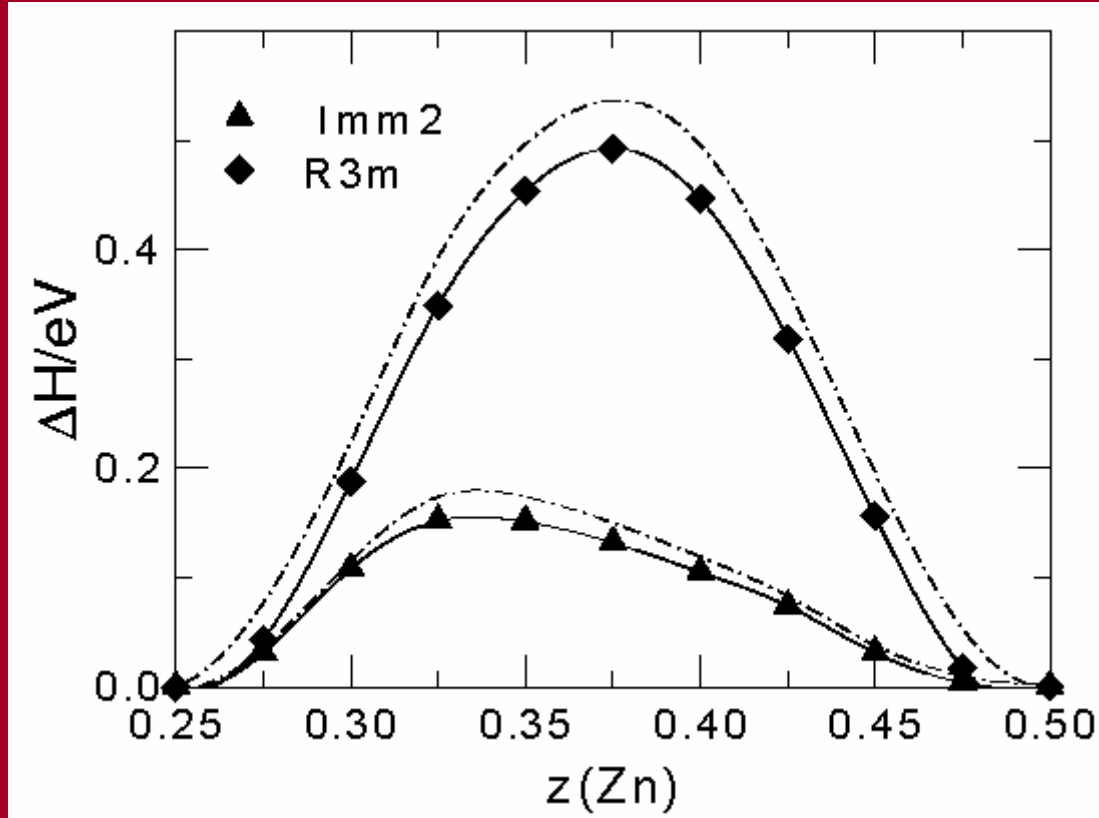
B3

Imm2

B1

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

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→ The Imm2 mechanism is favoured over R3m

→ Activation enthalpies (eV):

	Imm2	R3m
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 solid state kinetics at high pressure
- ◆ Comparison of enthalpy barriers can detect the hierarchy of different transformation pathways
- ◆ B1/B2 transition (CaO and NaCl):
 - the $P2_1/m$ mechanism is more favourable than R-3m and Pmmn
 - a metastable TII-like intermediate phase is predicted
- ◆ B3/B1 transition (SiC and ZnS):
 - the Imm2 mechanism is more favourable than R3m