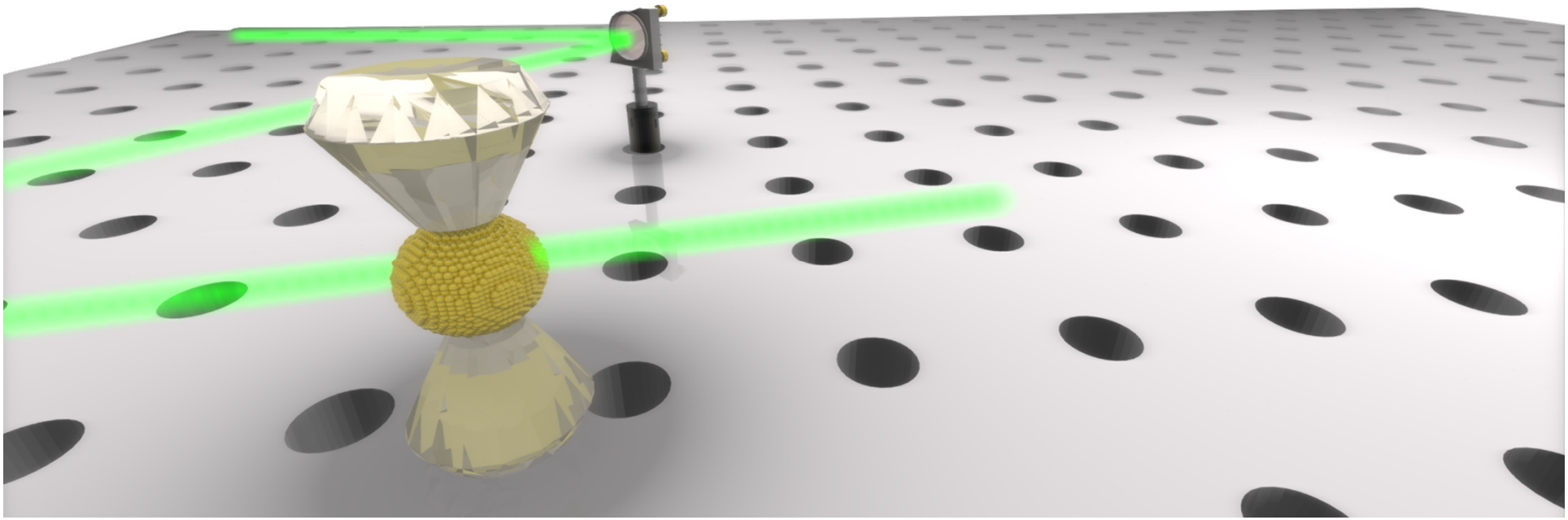
INSTITUT LUMIÈRE MATIÈRE

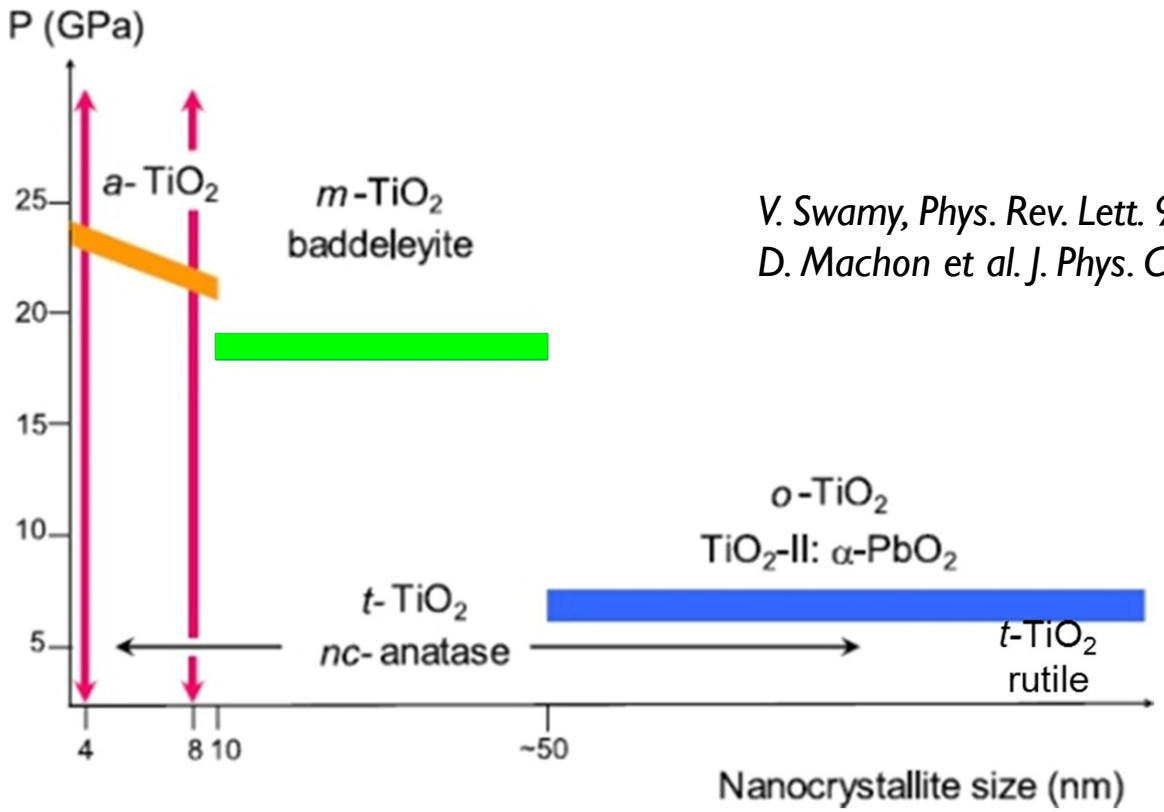
Pressure-induced phase transitions in nanomaterials

A thermodynamics panorama

Denis Machon



Combination of Pressure and size: A perfect cocktail

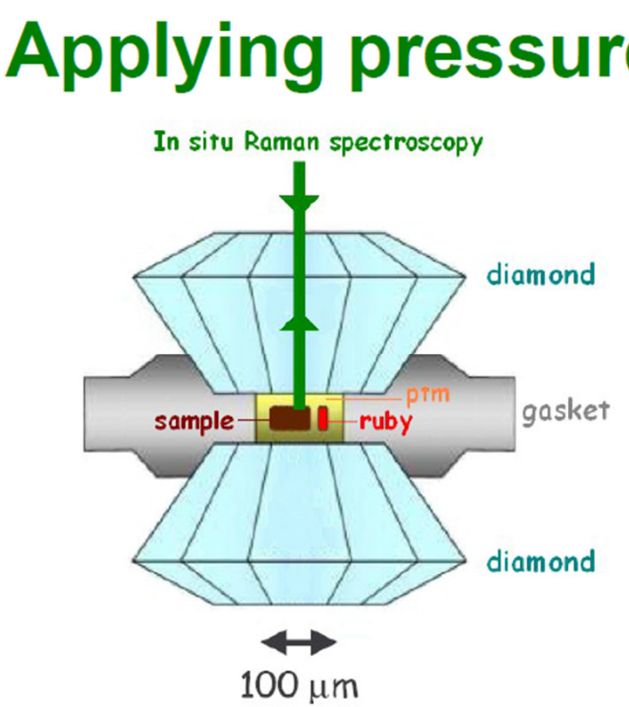


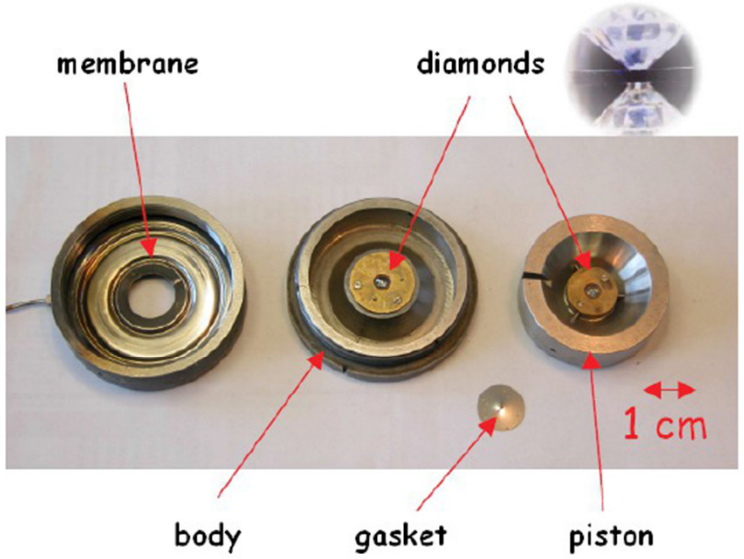
V. Swamy, Phys. Rev. Lett. 96, 135702 (2006)
D. Machon et al. J. Phys. Chem C 115, 22286 (2011)

Pressure-size phase diagram:
Interface Energy Impact on Phase Transitions

Stabilizing new materials by these combined effects

Experimental set-up



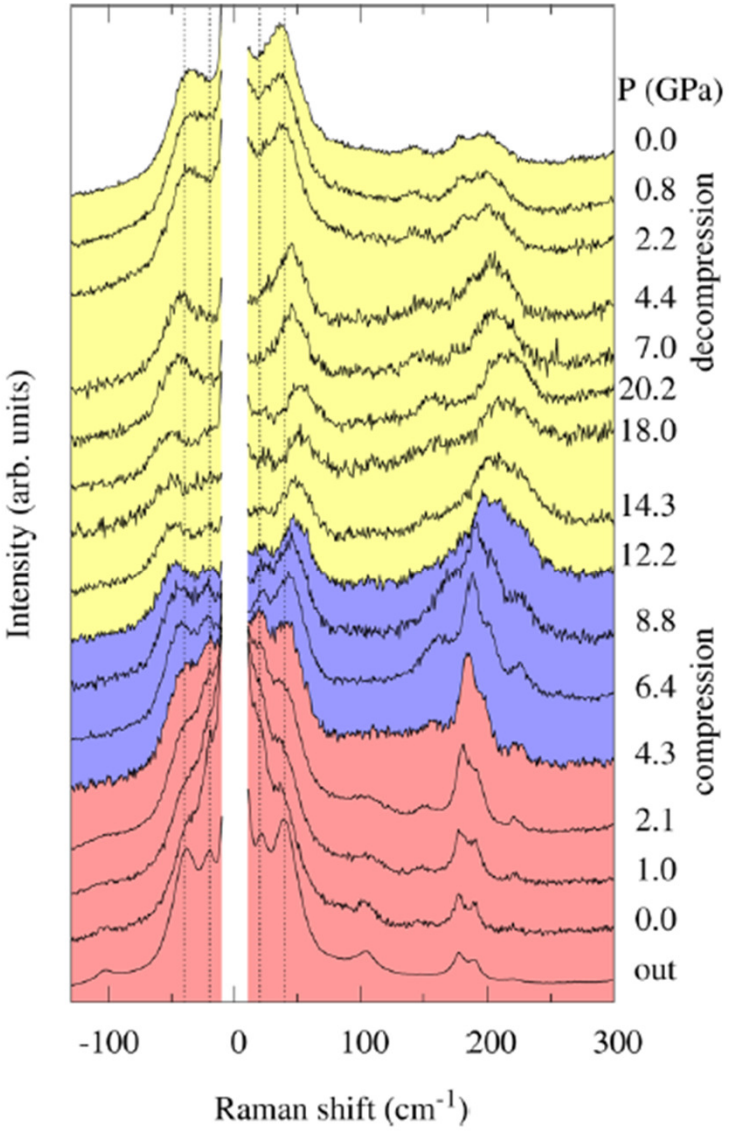


Diamond-anvils cell

Idea: At constant force, drastically reduce the surface

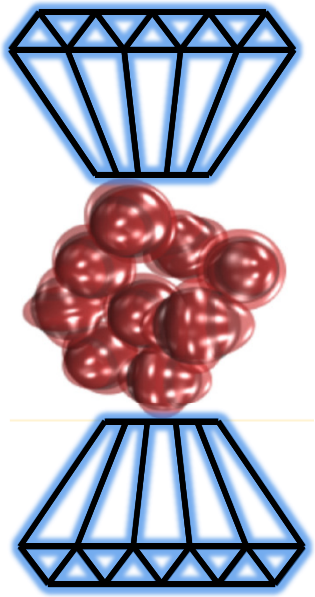
+ Raman spectroscopy / X-ray diffraction

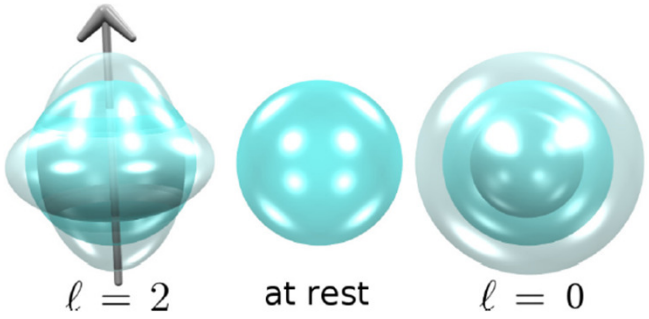
Are we sure that the nanoparticles remain nano at high-pressure?



ZrO_2 – 4 nm

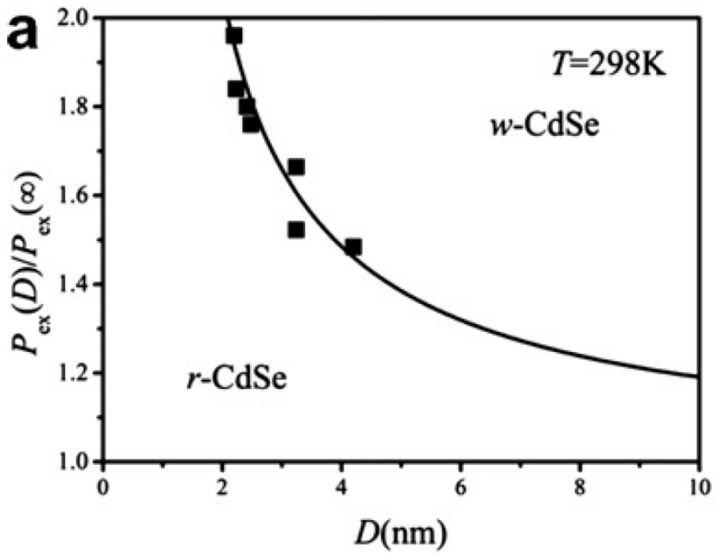
Nanoparticles as an elastic sphere

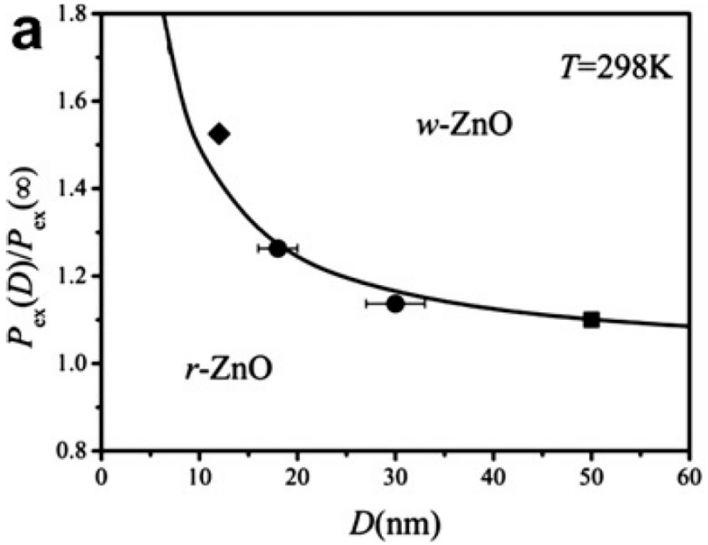




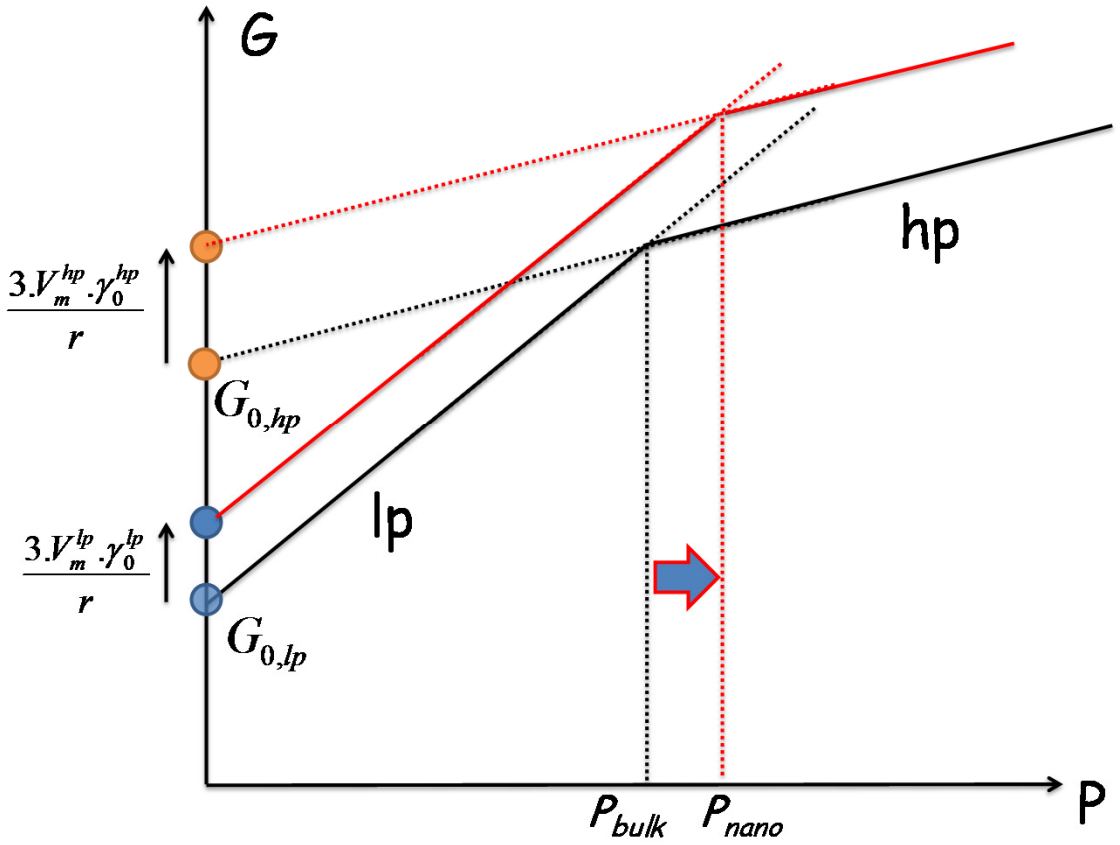
L. Saviot et al. J. Phys. Chem. C 116, 22043 (2012)
L. Saviot et al. J. Phys. Chem. C 118, 10495 (2014)

First size effect in the literature: shift of the transition pressure





S.H. Tolbert & A.P. Alivisatos, J. Chem. Phys.102, 4542 (1995)
S. Li et al., Scripta Materiala 59, 526-529 (2008)



γ_0: interfacial energy

D. Machon & al. Nanoletters 14, 269 (2014)
D. Machon & al. PCCP DOI: 10.1039/C4CP04633A

An Alternative description: Landau theory of phase transition

Shift of the transition line:

the surface energies are considered as secondary order parameter

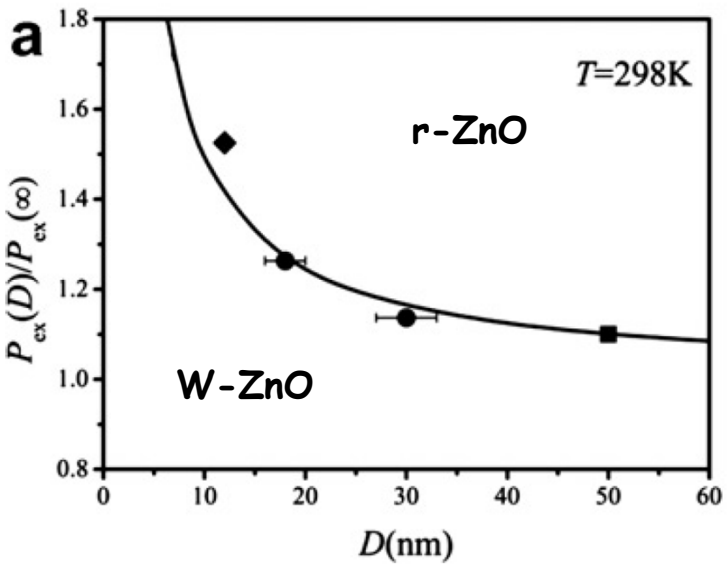
$$F = F_0 + \alpha\eta^2 + \beta\eta^4 + \delta\frac{\gamma_{hp} - \gamma_{lp}}{V}.S.\eta^2$$

Coupling term

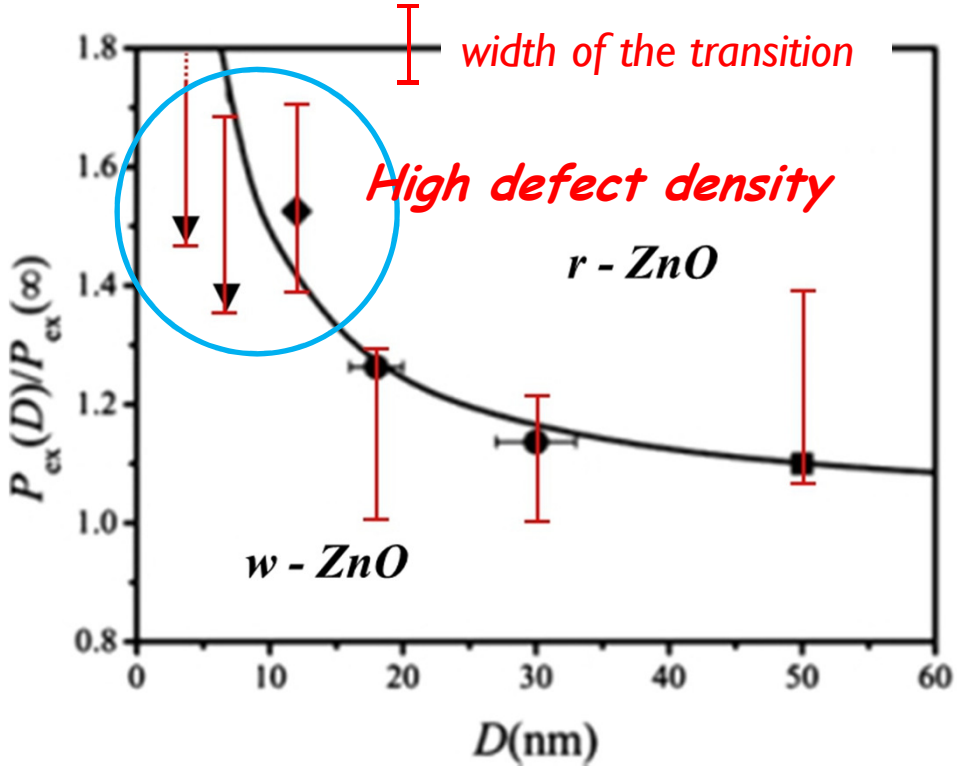
Landau: $P_{T(nano)} = P_{T(bulk)} + \alpha.\frac{\Delta\gamma}{r}$

Gibbs: $P_{T(nano)} = P_{T(bulk)} + \frac{3\delta\Delta\gamma}{\alpha.r}$

D. Machon & al. Nanoletters 14, 269 (2014)



How is defined the transition pressure?

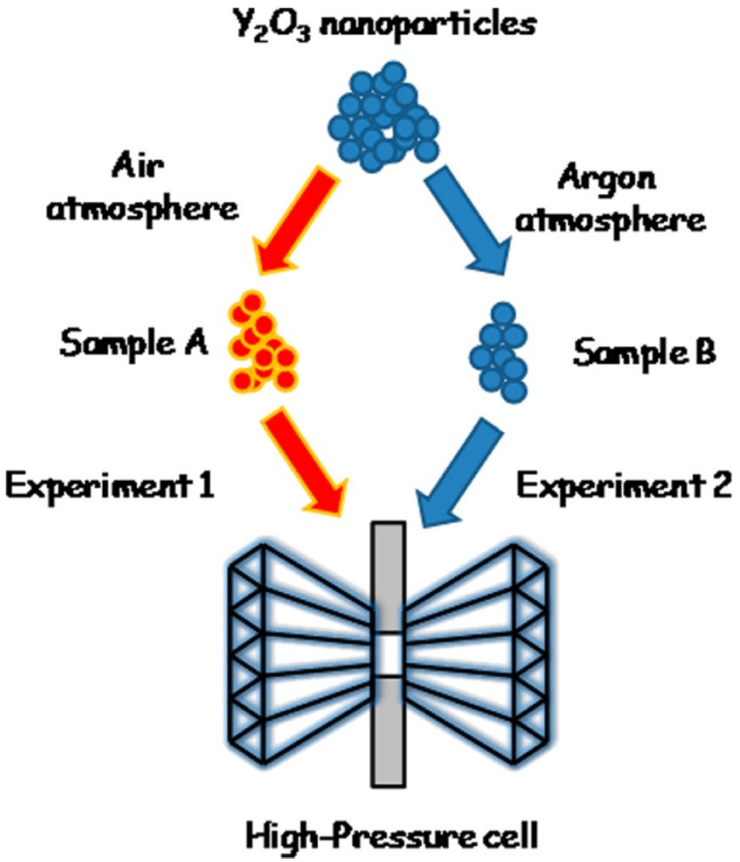


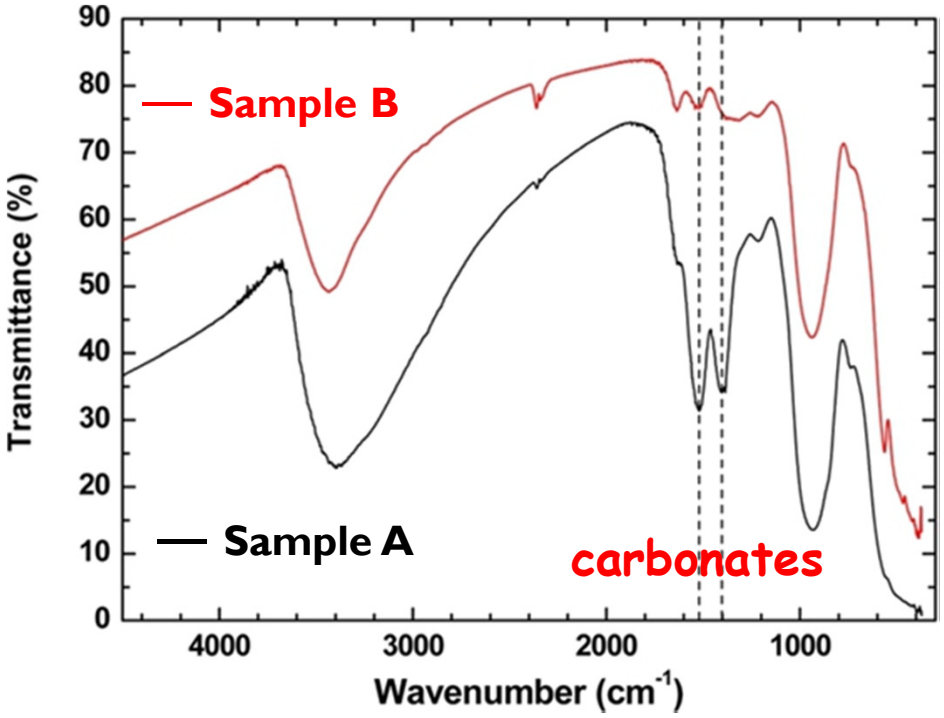
Shift of the transition? Spreading of the transition?

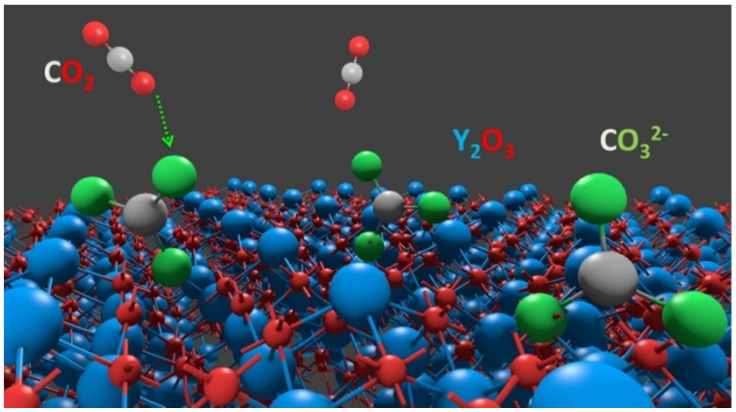
Only a size-effect? Other factors?

Strong dependence on the interface energy (surface state)

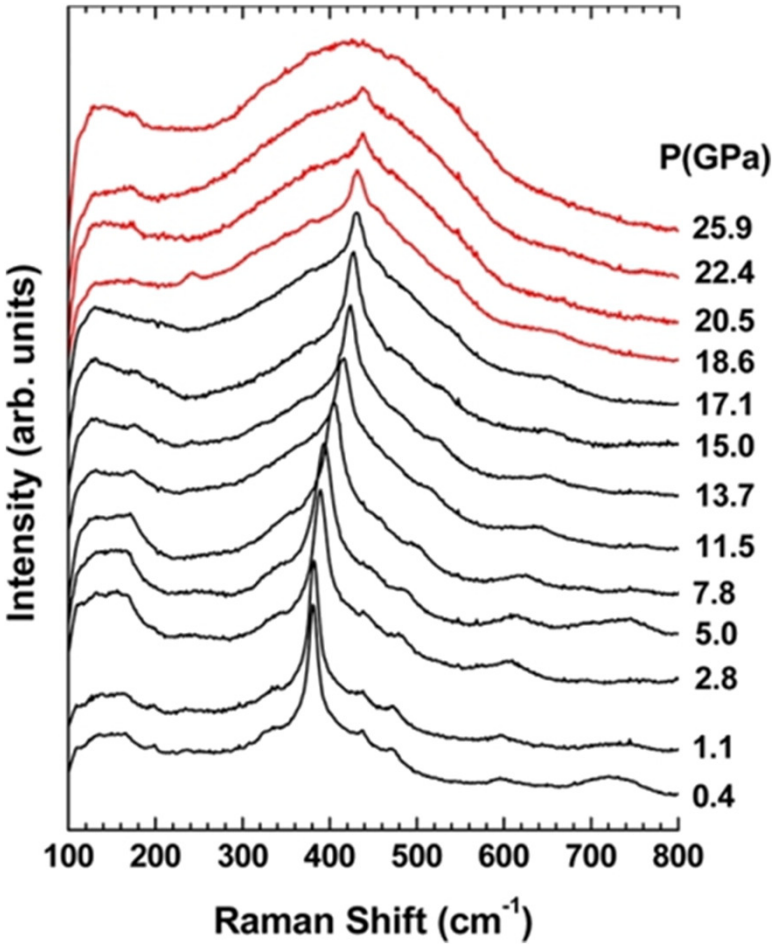
Example: 7-nm particles of Y_2O_3



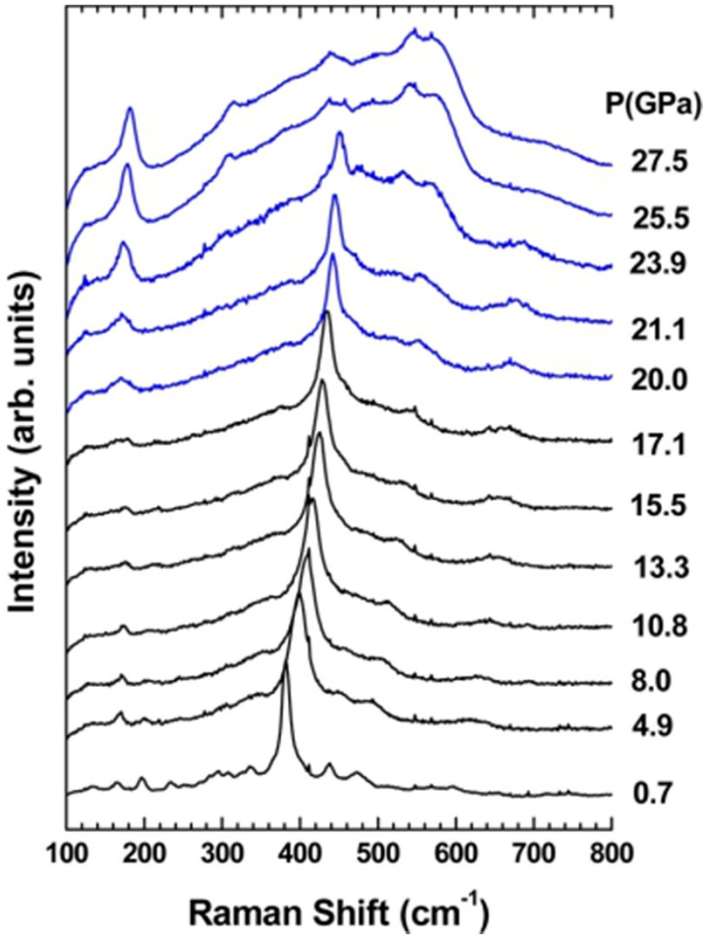




Exposed to air

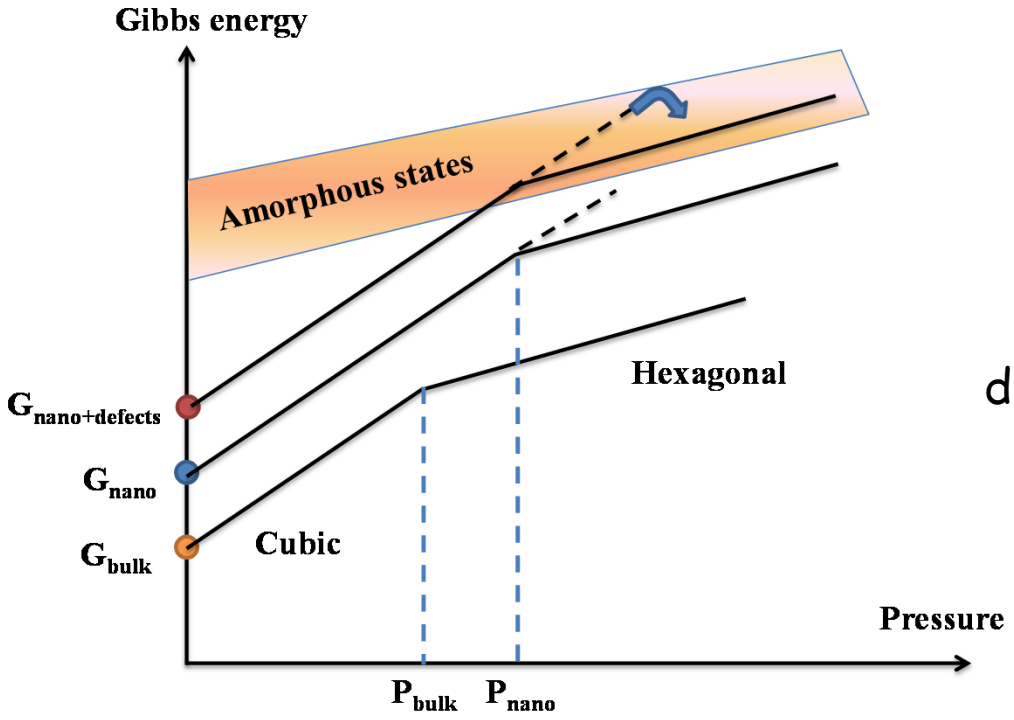


Argon Atmosphere
(Loaded in glove box)



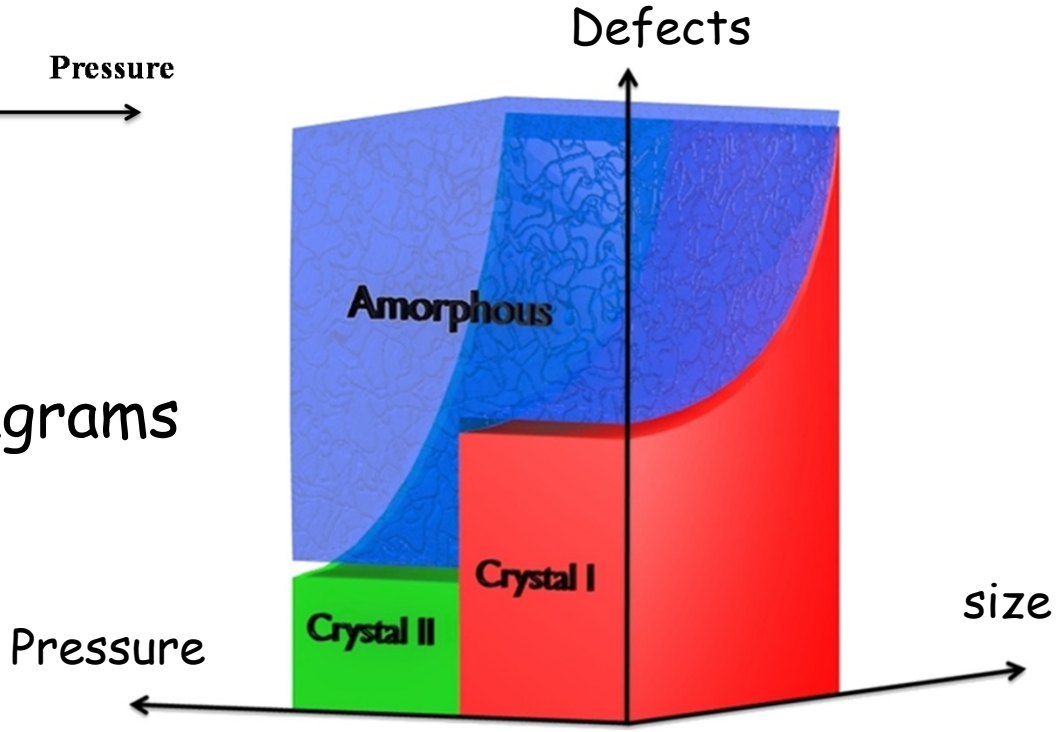
Amorphization

Polymorphic transition



Energizing processes

defects, interfacial and elastic energies



Multidimensional phase diagrams (surface-related effects)

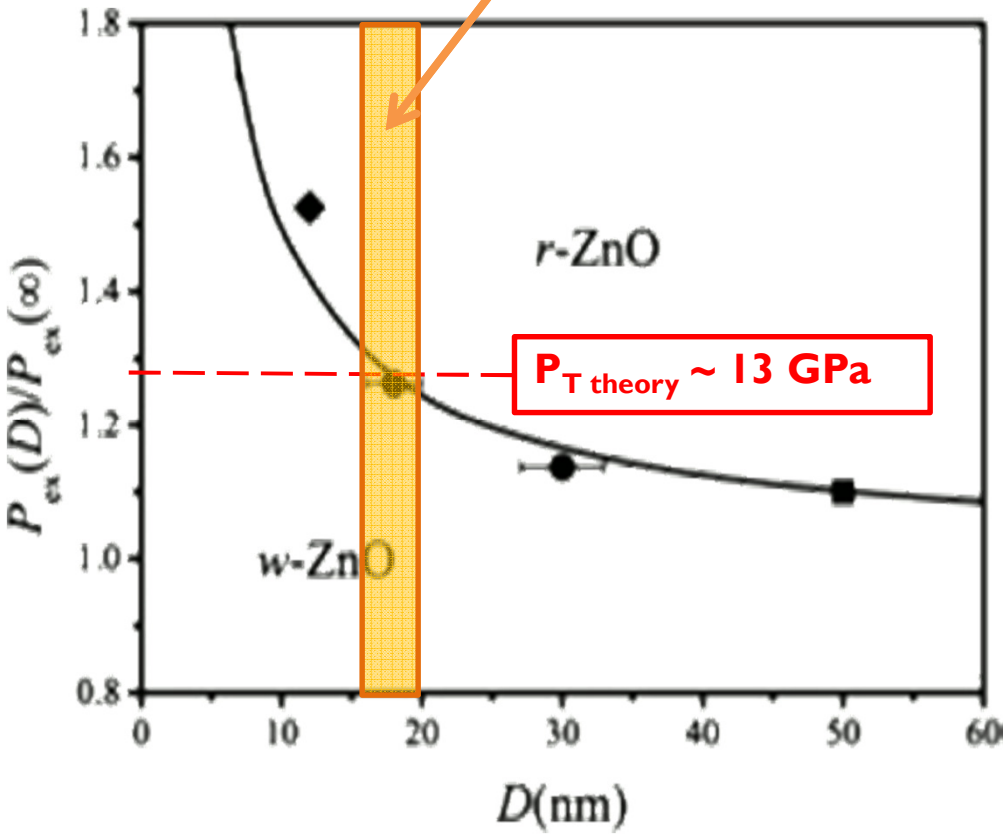
L.Piot & al. J. Phys. Chem C 117, 11133 (2013)
D. Machon & P. Mélinon, PCCP DOI: 10.1039/C4CP04633A

The case of ZnO nanoparticles

Approach:

- ❑ **Size control:** D ~ 16 - 20 nm (TEM, XRD)
- ❑ **Influence of the surface state**

→ **Samples from different synthesis routes**

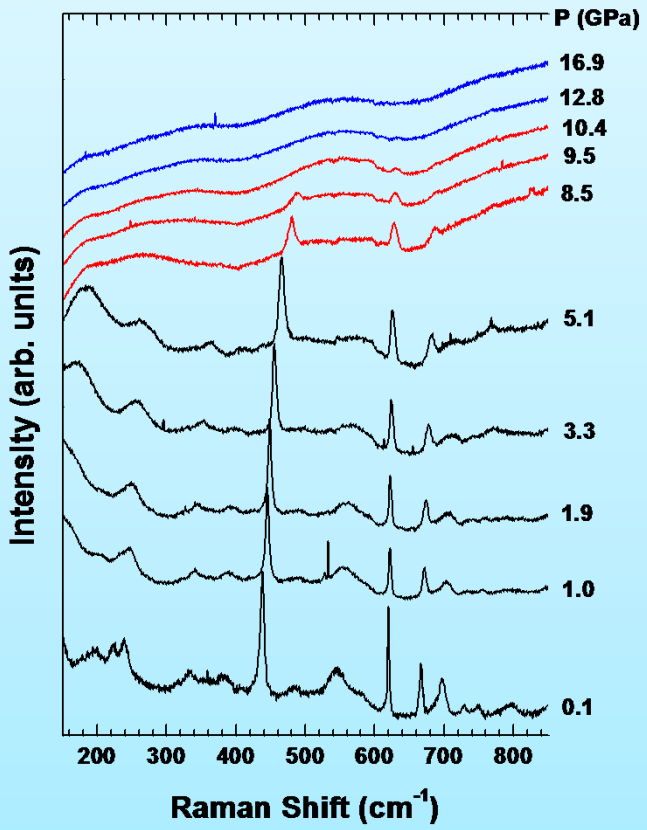


1) LECBD (Physical method) Defect-free
2) Sol-gel
3) Hydrothermal
4) Polyol

❑ **Analysis of the surface state (Luminescence, Raman, …)**

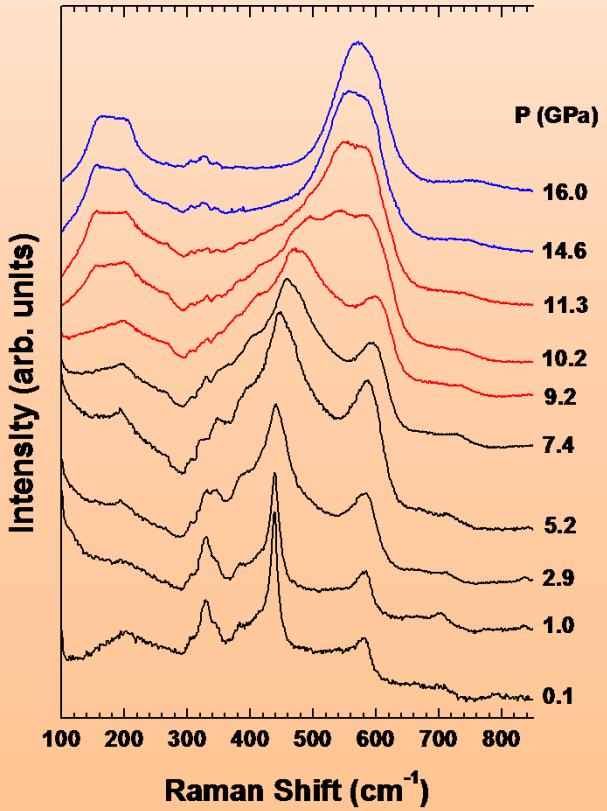
Low Energy Cluster Beam Deposition

Defect-free nanoparticles
(checked by luminescence)



Transition to the rocksalt structure
Start ~ 8.5 GPa
End > 10.4 GPa

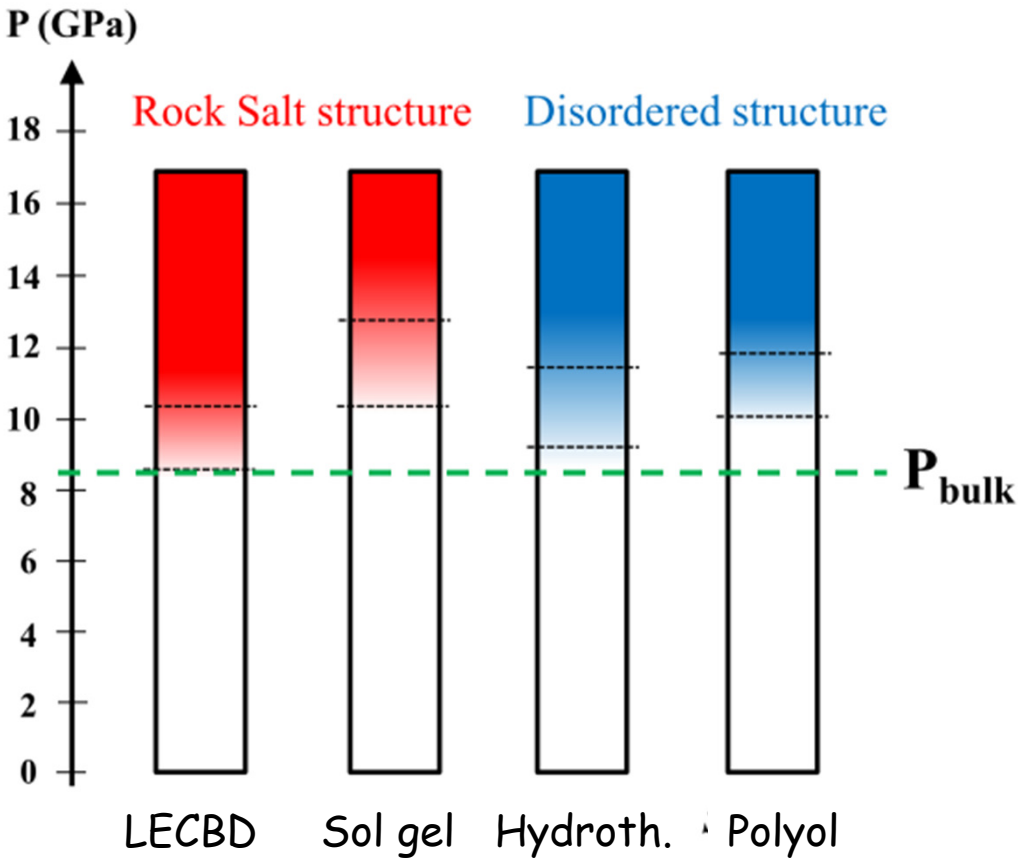
Hydrothermal synthesis



Transition to a disordered structure
Start ~ 9.2 GPa
End > 11.3 GPa

Bulk: start ~ 8.5 GPa, end < 8.9 GPa *(F. Decremps et al. PRB 65, 092101 (2002))*

Summary



4 different samples = 4 different pressure-induced behaviours

Size effect: spreading of the transition

Ginzburg-Landau theory

$$F = F_0 + \alpha\eta^2 + \beta\eta^4 + \delta\frac{\gamma_{hp} - \gamma_{lp}}{V}.S.\eta^2$$

Thermodynamics

$$+(K_{dipolar} + K_{\text{int}erface} + K_{pressure})(\nabla\eta)^2$$

Kinetics

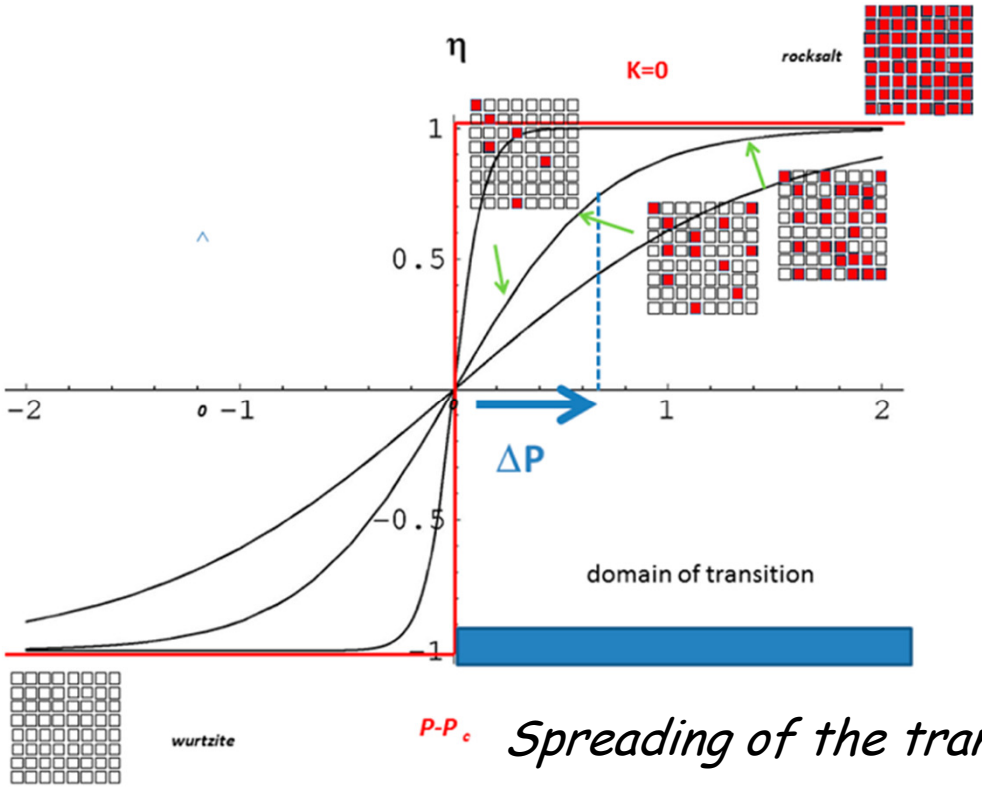
Master equation to describe
1) polymorphic transition
2) Amorphization

Ginzburg-Landau: Polymorphic transition

$$\eta(x) = \frac{e^{(\sqrt{2}/\varepsilon)x} - 1}{e^{(\sqrt{2}/\varepsilon)x} + 1}$$

$$\varepsilon \propto K^{1/2}$$

Width of the transition



Spreading of the transition

D. Machon & al. Nanoletters 14, 269 (2014)

Ginzburg-Landau: Amorphization

Radius of the amorphous region

$$r_N = \left(\frac{K}{\alpha_0}\right)^{1/2}\left[(C_0 - C_N) - \lambda\frac{\gamma}{r}\right]^{-1/2} + r_0$$

C_N: defect concentration at which the amorphous embryo nucleates

$C_c = C_0 - \lambda\frac{\gamma}{r}$ critical concentration for merging of amorphous embryos

$$r_N \propto K^{1/2}$$

P. Tolédano & al. J.Phys.: Condens. Matter 17, 6627 (2005).
D. Machon & P. Mélinon, PCCP DOI: 10.1039/C4CP04633A

Polymorphism: $\varepsilon \propto K^{1/2}$ ⟹ Slowing down

Amorphization $r_N \propto K^{1/2}$ ⟹ Favorable

$$K = K_{dipolar} + K_{interface} + K_{pressure}$$

Dipolar interaction
(ZnO is non-centrosym.)

Surface state
(defects, capping, etc)

Hydrostaticity

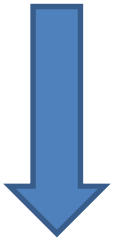
Sample

Experiment

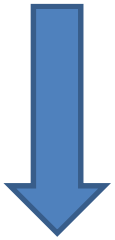
Amorphous state is kinetically favoured state

Conclusions

Point defects, capping molecules



Interface energy impact on the phase transitions



Behavior at high pressure:
a quality control test for the nanoparticles

Acknowledgments

Sylvie Le Floch, Patrice Mélinon, Dimitri Hapiuk

Bruno Masenelli

Stéphane Daniele

Lucien Saviot, Frédéric Demoisson,
Romain Piolet, Moustapha Ariane

Samir Farhat

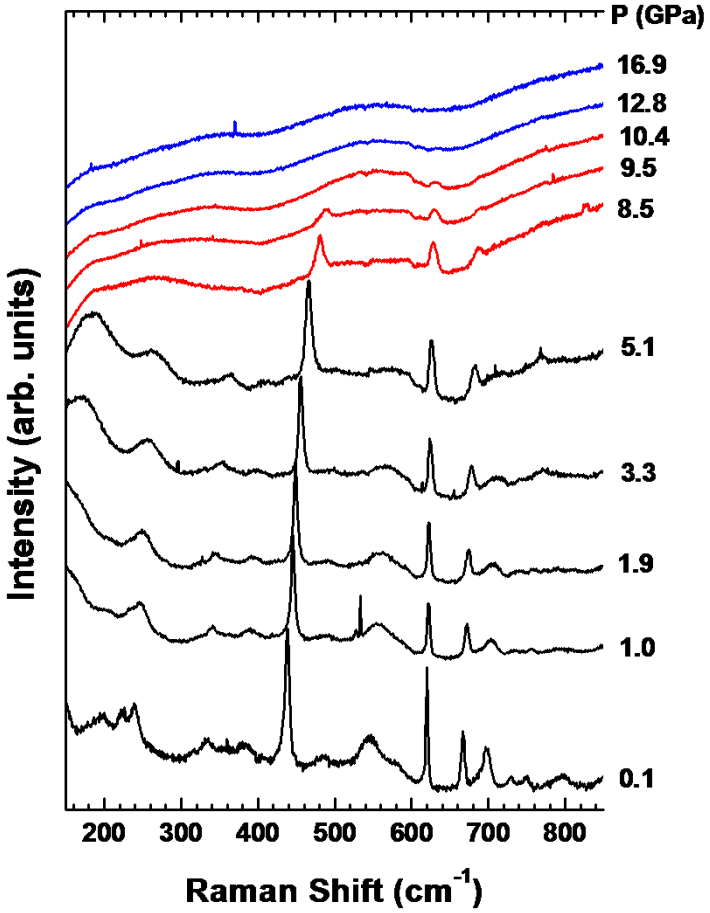
Nanotek organizers

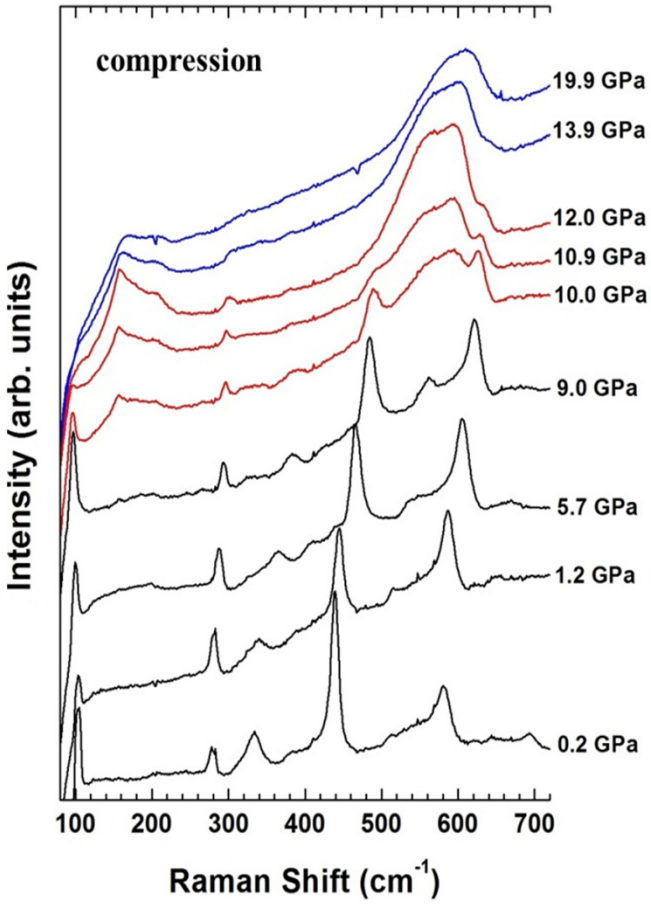
Thank you for your attention

Nanoparticles LECBD
Free-defect (out of equilibrium)

Annealing 400K

Defect density
(equilibrium)





Conclusions

- **Thermodynamics**

Landau: $P_{T(nano)} = P_{T(bulk)} + \alpha . \frac{\Delta\gamma}{r}$

Gibbs: $P_{T(nano)} = P_{T(bulk)} + \frac{3\delta\Delta\gamma}{\alpha . r}$

Different approaches,

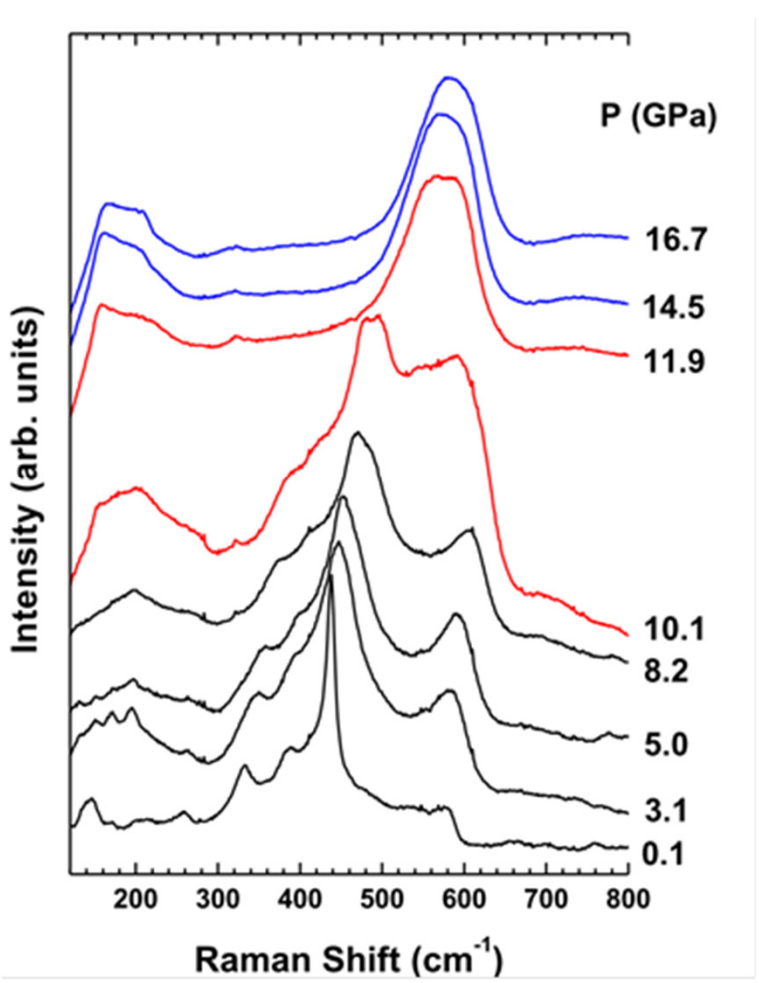
Similar results

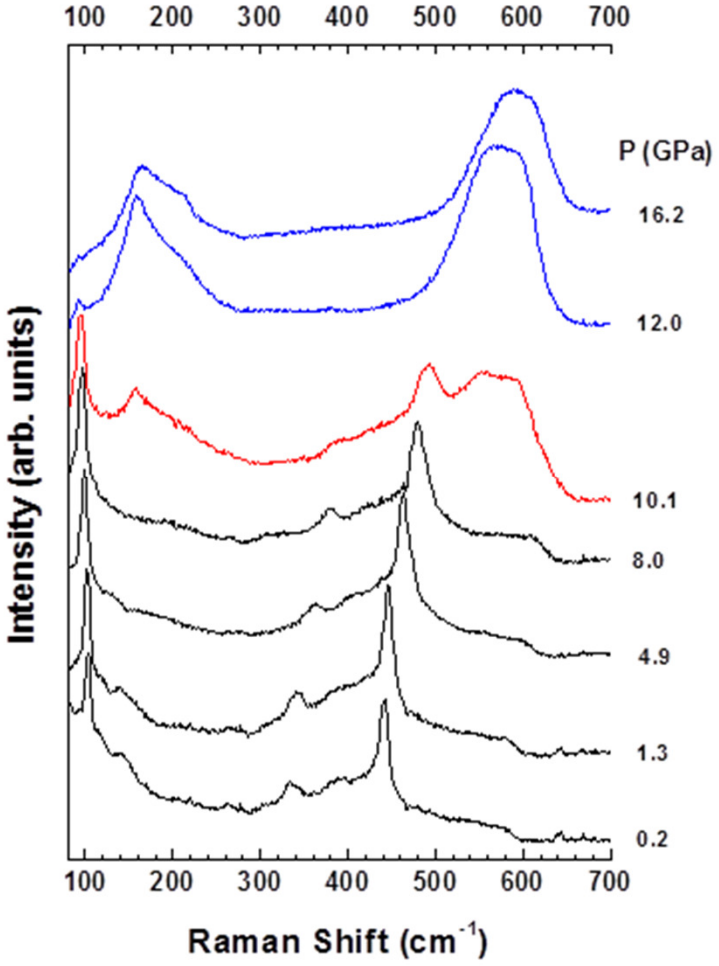
- **Kinetics: Ginzburg-Landau theory**

→ Describe the spreading of the transition

→ Competition between polymorphic transition and Amorphization

Interfacial energy impact on the phase transitions





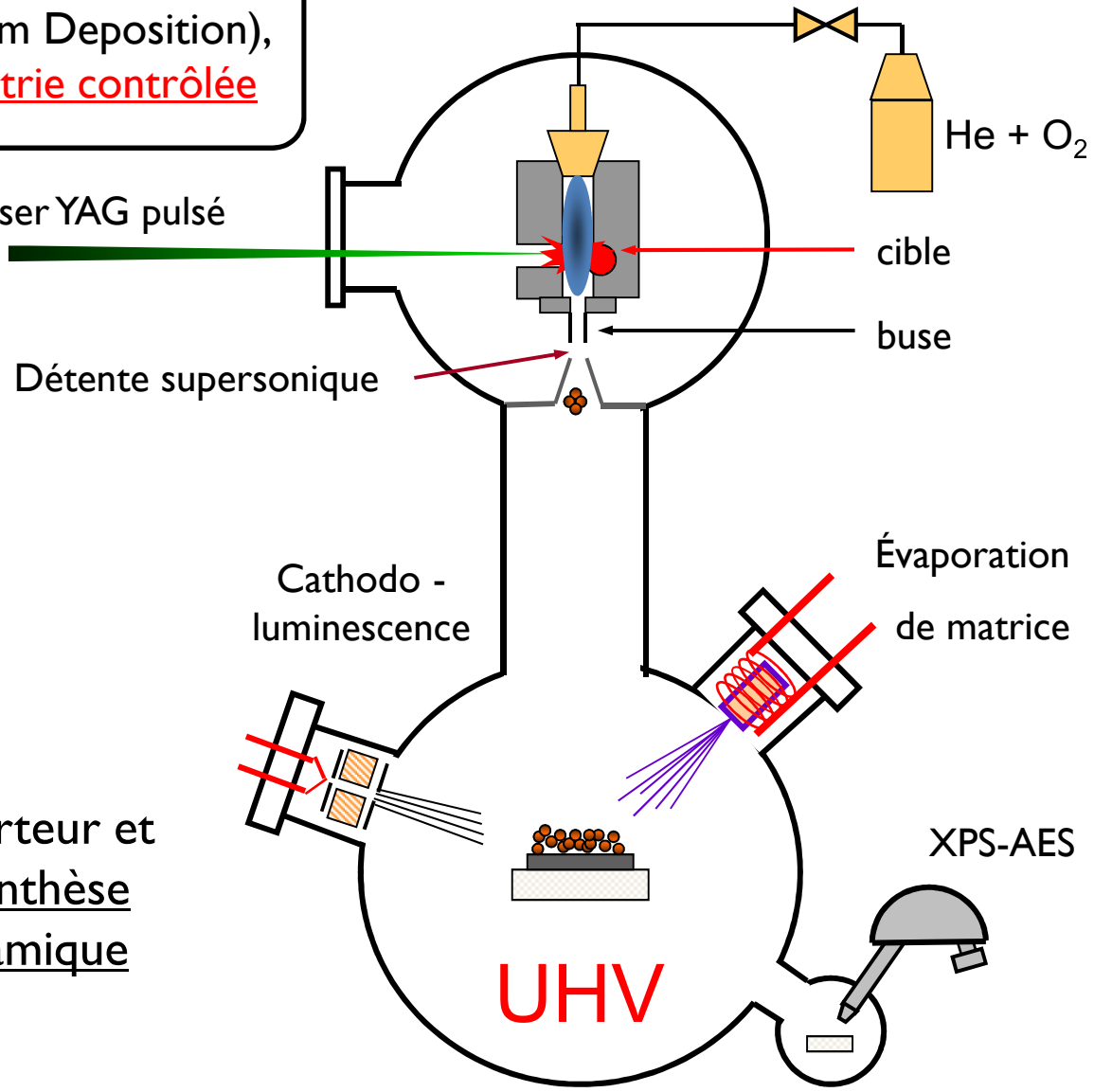
No PTM

PTM: Methanol/Ethanol

Voies de synthèses (physique)

LECBD (Low Energy Cluster Beam Deposition), D ~ 16 nm (*DRX, MET*), stœchiométrie contrôlée

Plateforme PLYRA



Principales caractéristiques:

- Ablation laser
- Vitesse de trempe (gaz porteur et détente adiabatique) → synthèse hors équilibre thermodynamique
- Surpression en O_2 pré-déposition