



UNIVERSITÉ DE  
GRENOBLE

# *De la diffraction sur poudre à l'étude de nano-structures uniques de semi-conducteurs*

*Vincent Favre-Nicolin*

*CEA/INAC/SP2M & Université Grenoble-Alpes, France  
Institut Universitaire de France*



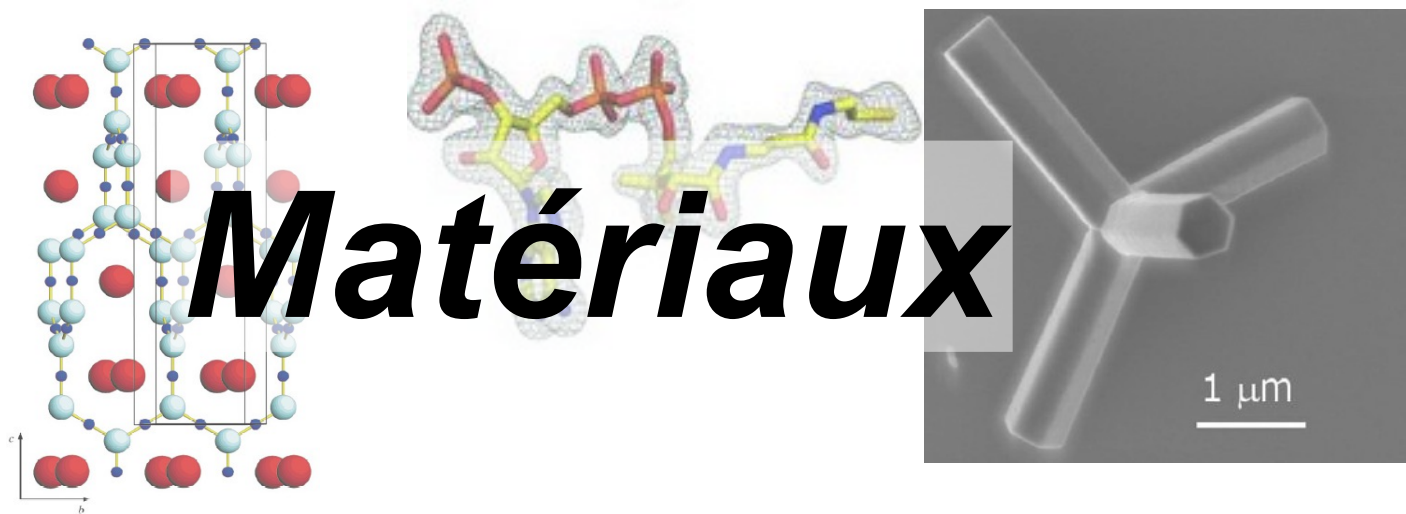
# Piliers de la Cristallographie

## ***Théorie***

*Tables internationales  
journals.iucr.org*

## ***Instrumentation***

*Laboratoire  
Synchrotron, neutrons, XFEL*



## ***Algorithmes & Logiciels***

*Open Source  
Open data*

# Cristallographes : architectes & explorateurs de la matière

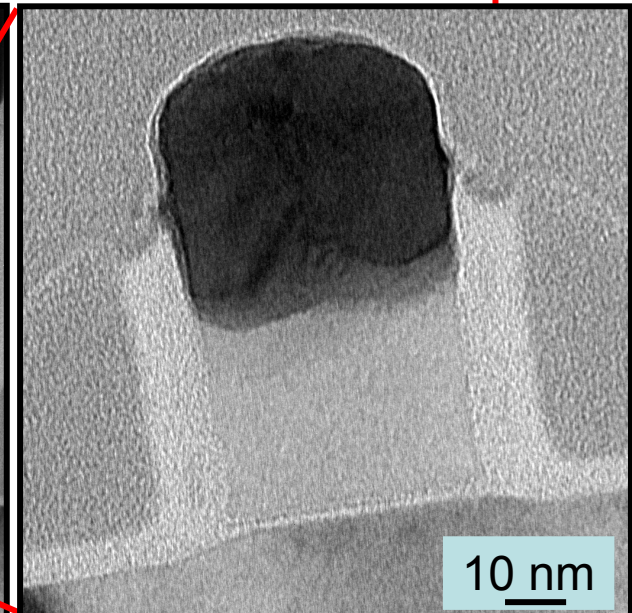
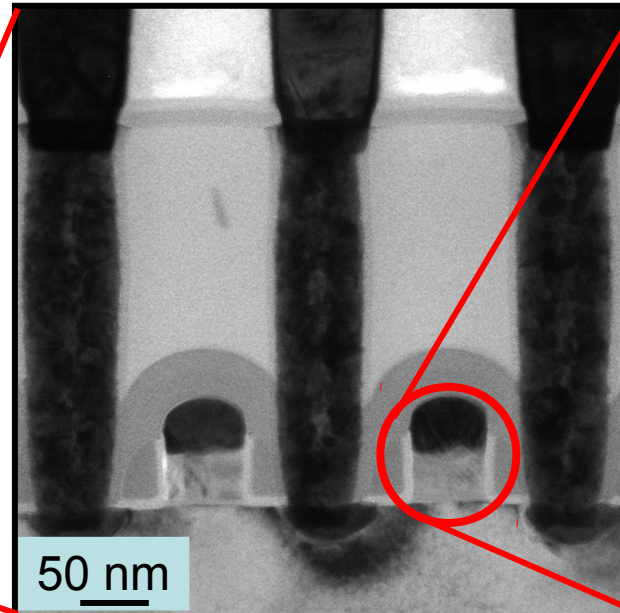
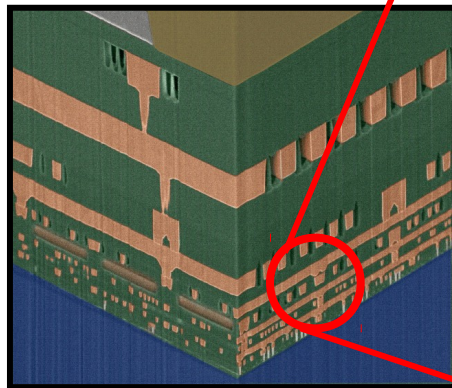


Monocristaux

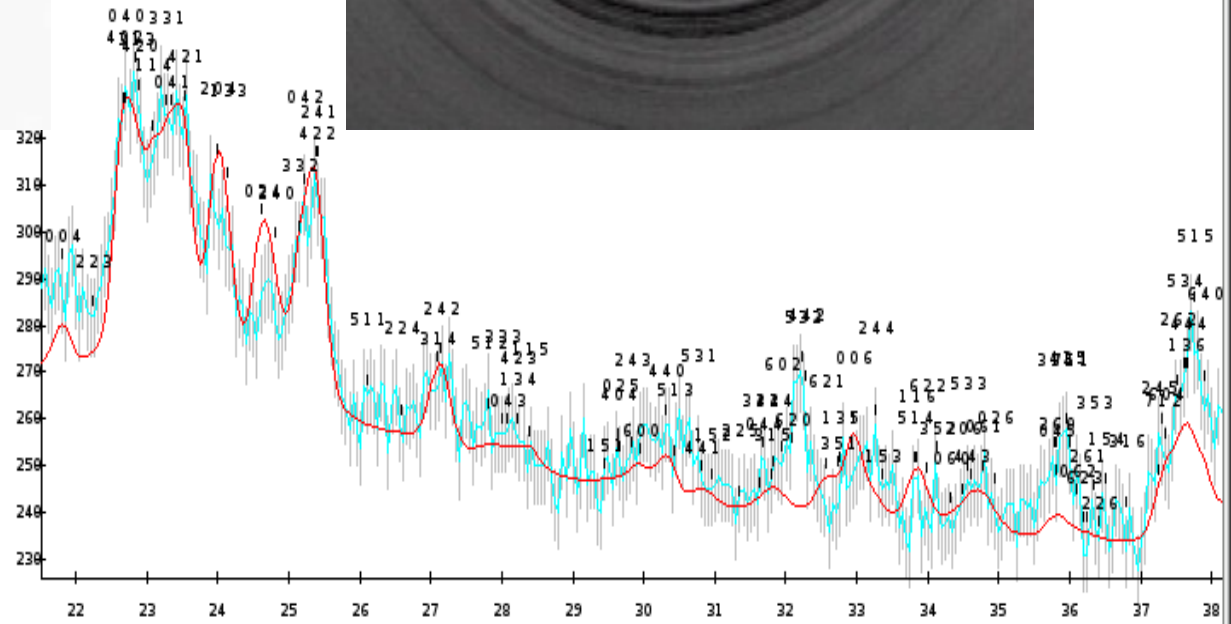
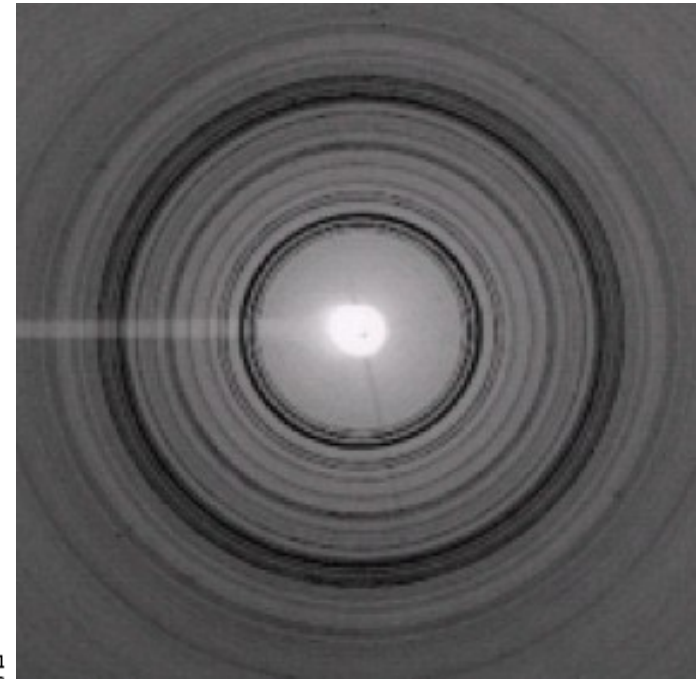
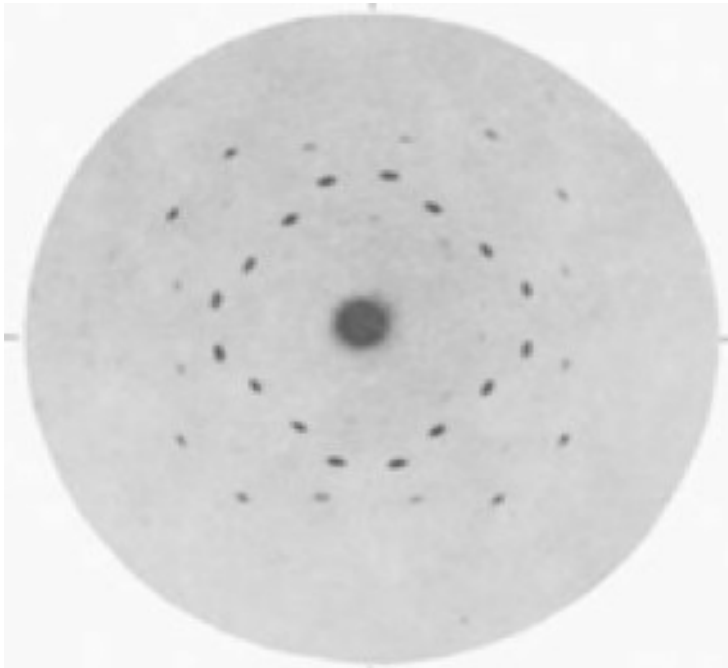


Poudre

## Nano-structures



# Diffraction sur monocristal / poudre







# 2014 : diffraction sur poudre → structure

(Film)

FOX: Free Objects for Xtal structures v1.9.8-#1350

Crystals Powder Diffraction Single Crystal Di... Global Optimization FOXGrid

List of all PowderPattern objects

PowderPattern Powder Pattern #1

Data Export Parameters Phases Radiation Pattern

Use Integrated Profiles Yes (recommended)

Radiation X-Ray Spectrum Monochromatic WavelengthR  L  1.5290

ZeroR  L  0.000000 2ThetaDisplR  L  0.000000 2ThetaTranspR  L  0.000000

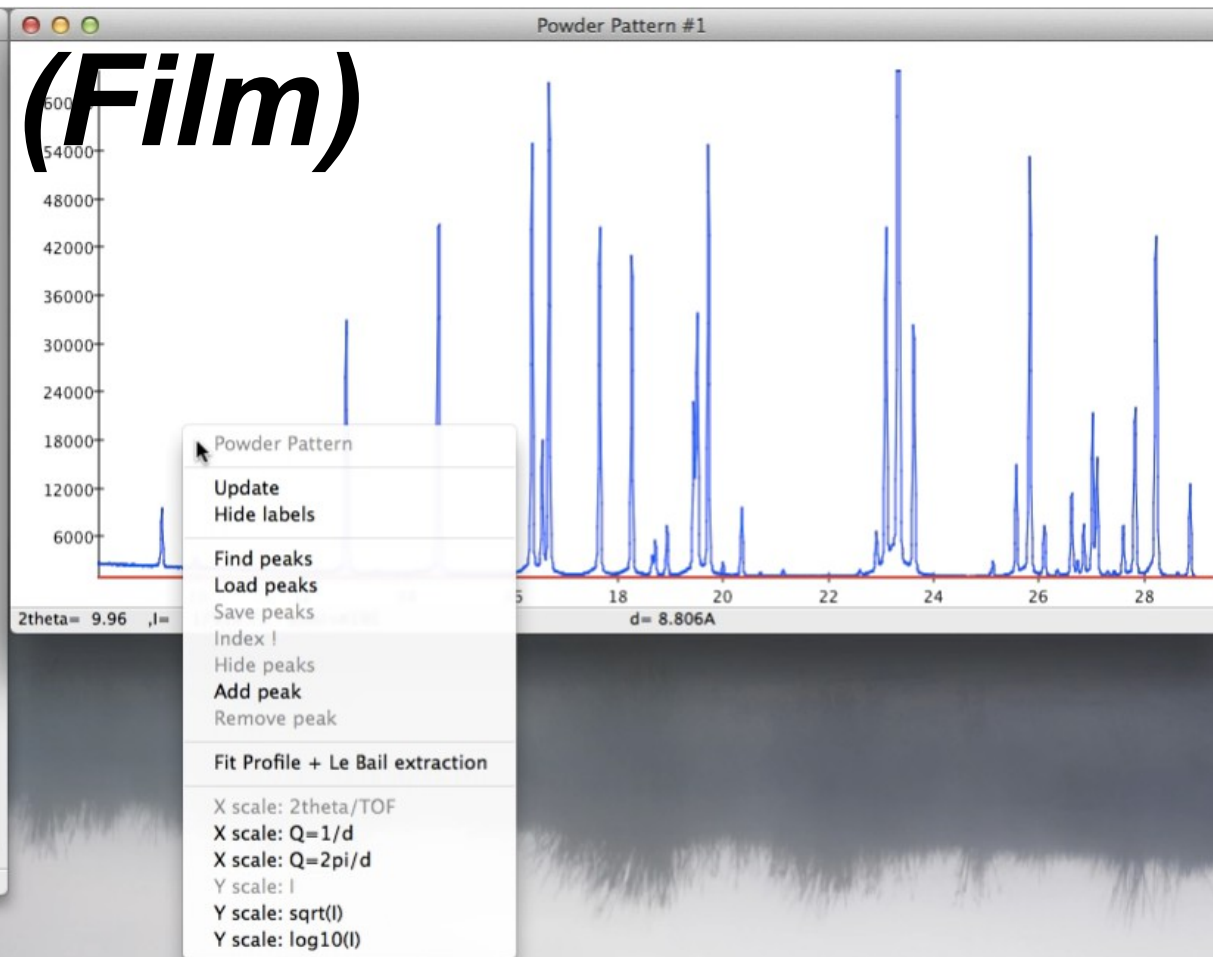
DIFCR  L  48277.14 DIFAR  L  -6.70000

Max Sin(theta)/lambda: 0.4000

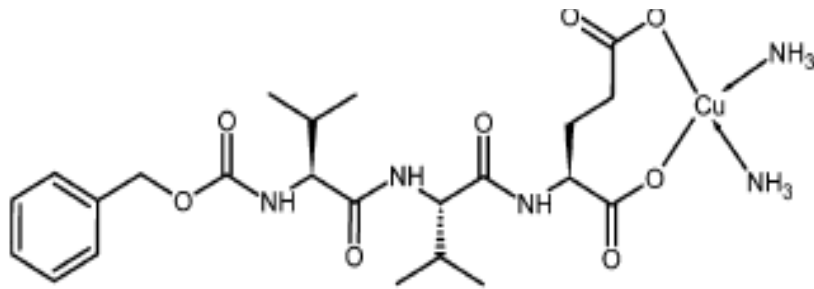
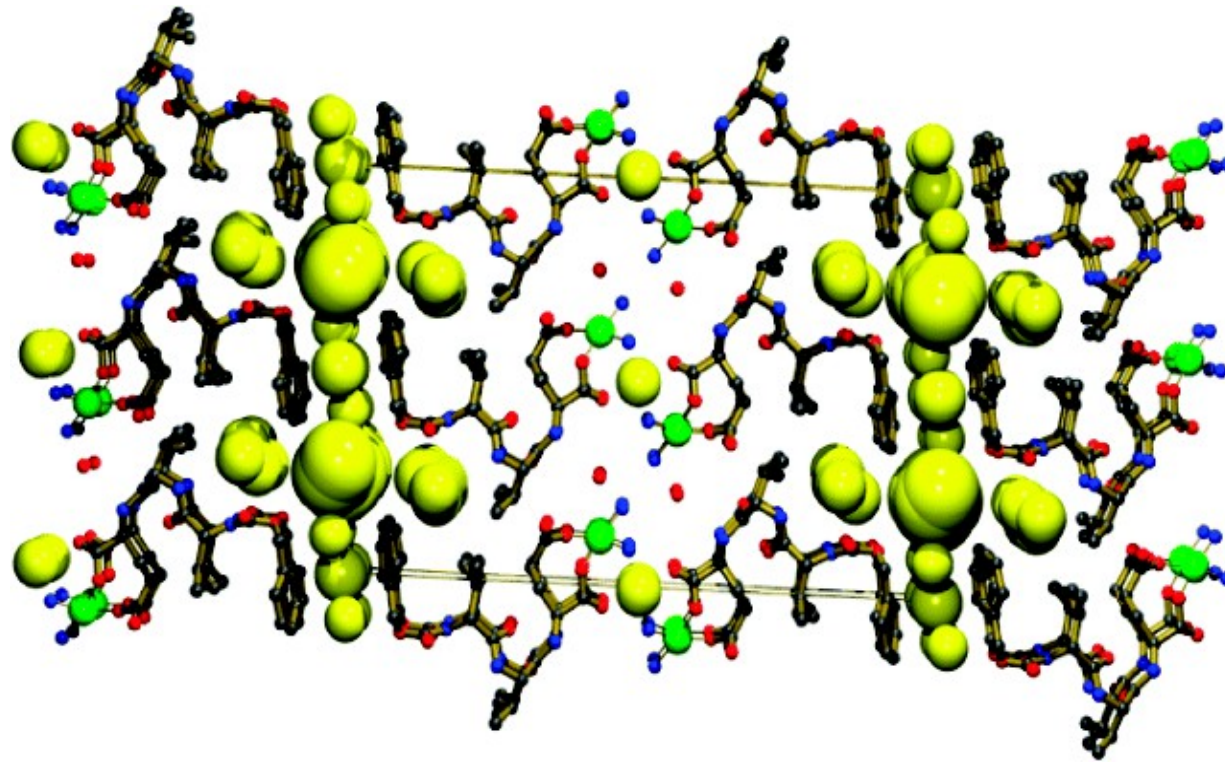
Chi^2 0.00 GoF 0.000 Rwp 0.0000 Rp 0.0000

Powder Pattern Components

Imported powder pattern: 7699 points, 2theta = 8.010 -> 84.990, step = 0.010



# Diffraction sur poudre - Exemples



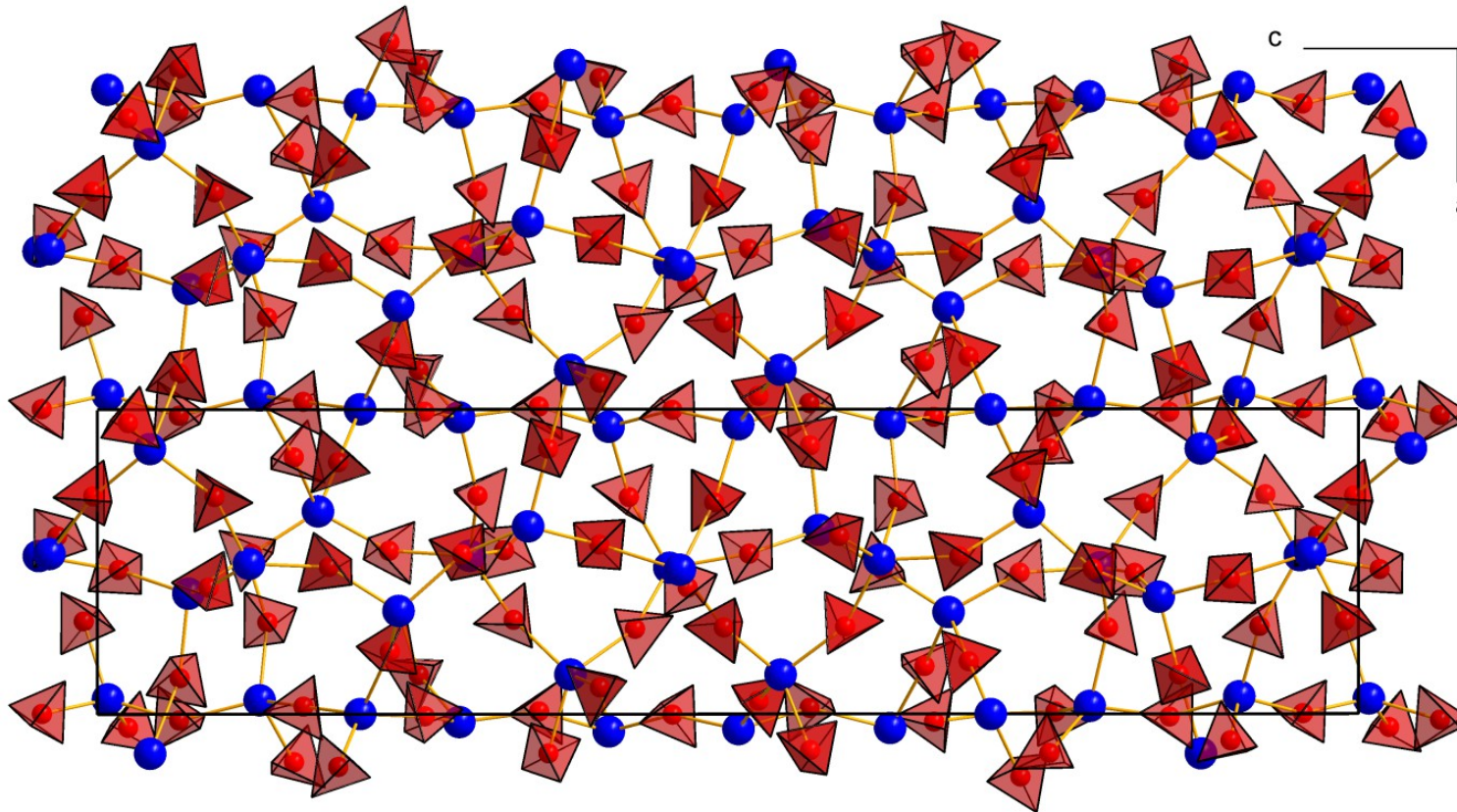
**MPF-9**

JACS 130 (2008), 2517

**“Hybride” organo-métallique**  
Approche architecturale  
de la synthèse de nouveaux matériaux



# Diffraction sur poudre - Exemples

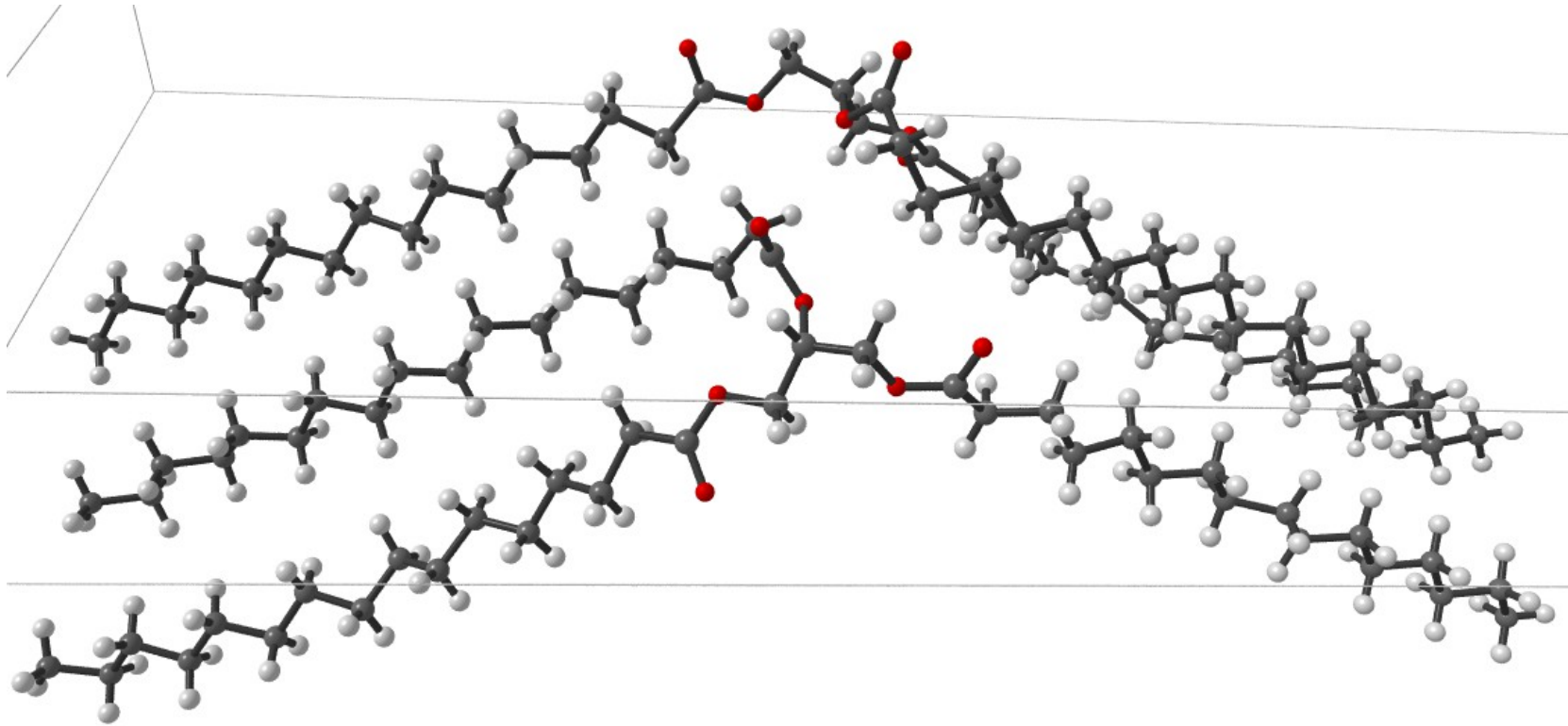


*Ang. Chemie Int. Ed. 2007, 46, 5765-5767, Acta Cryst. 2007, B63, 561-568*

## Hydrure - Stockage de l'hydrogène

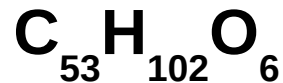


# Diffraction sur poudre - Exemples



*Triglycéride*

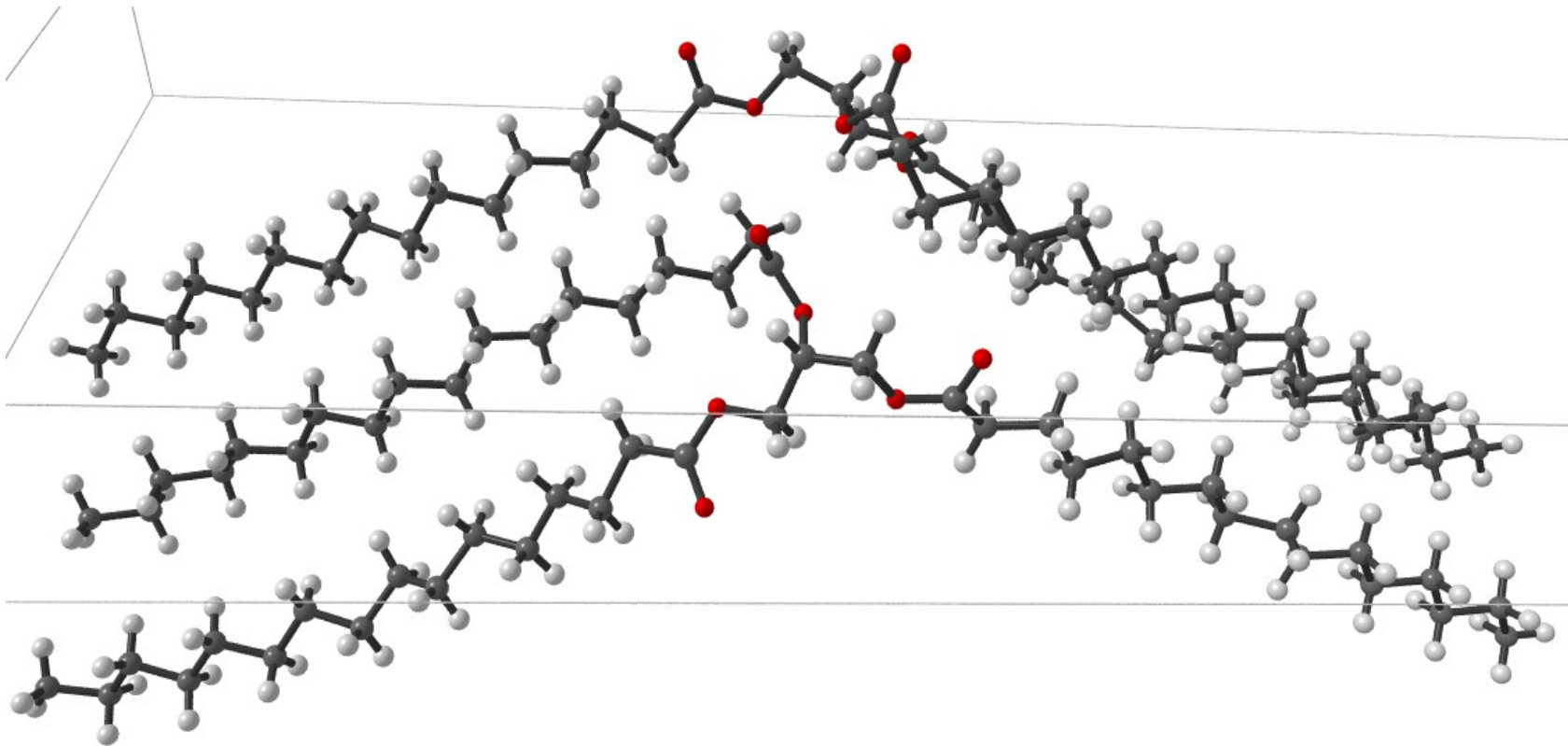
*$\beta'$  PSP (1,3-di-n-hexadecanoyl-2-n-octadecanoyl glycerol)*



*J. Phys. Chem. B* 108, 15450 (2004)

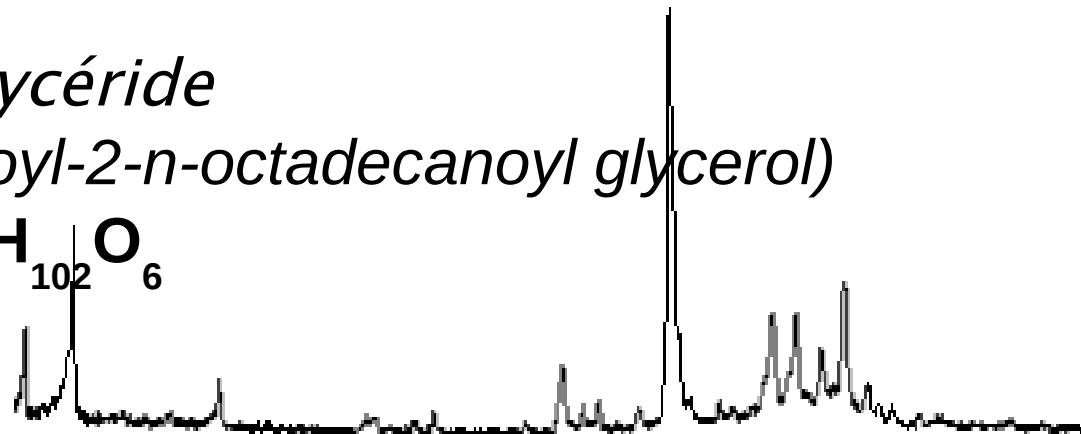
*Acta Cryst B* 64, 771 (2008)

# Diffraction sur poudre - Exemples



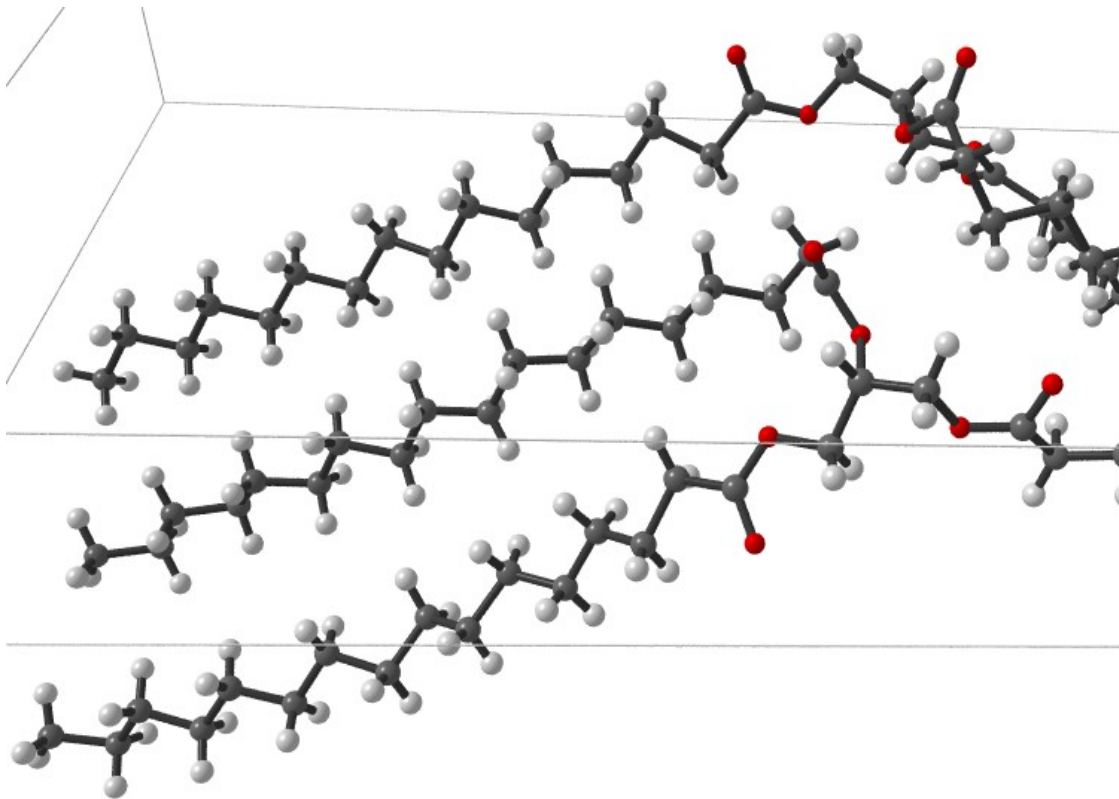
*Triglycéride*

*$\beta'$  PSP (1,3-di-n-hexadecanoyl-2-n-octadecanoyl glycerol)*



*J. Phys. Chem. B* 108, 15450 (2004)  
*Acta Cryst B* 64, 771 (2008)

# Diffraction sur poudre - Exemples



*Triglycéride*  
 $\beta'$  PSP (1,3-di-n-hexadecanoyl-2-n-octadecanoyl glycerol)



R. Peschar, M. Pop, D. De Ridder,  
J. van Mechelen, R. Driessen, H. Schenk

Triacylglycerol structures and  
the chocolate fat bloom mechanism

A high resolution powder diffraction study



Jan van Mechelen





# 2014 : diffraction sur poudre → structure

**Résolution de structure “ ab initio ”  
à partir de diffraction sur poudre : Facile ?**

**Oui, si :**

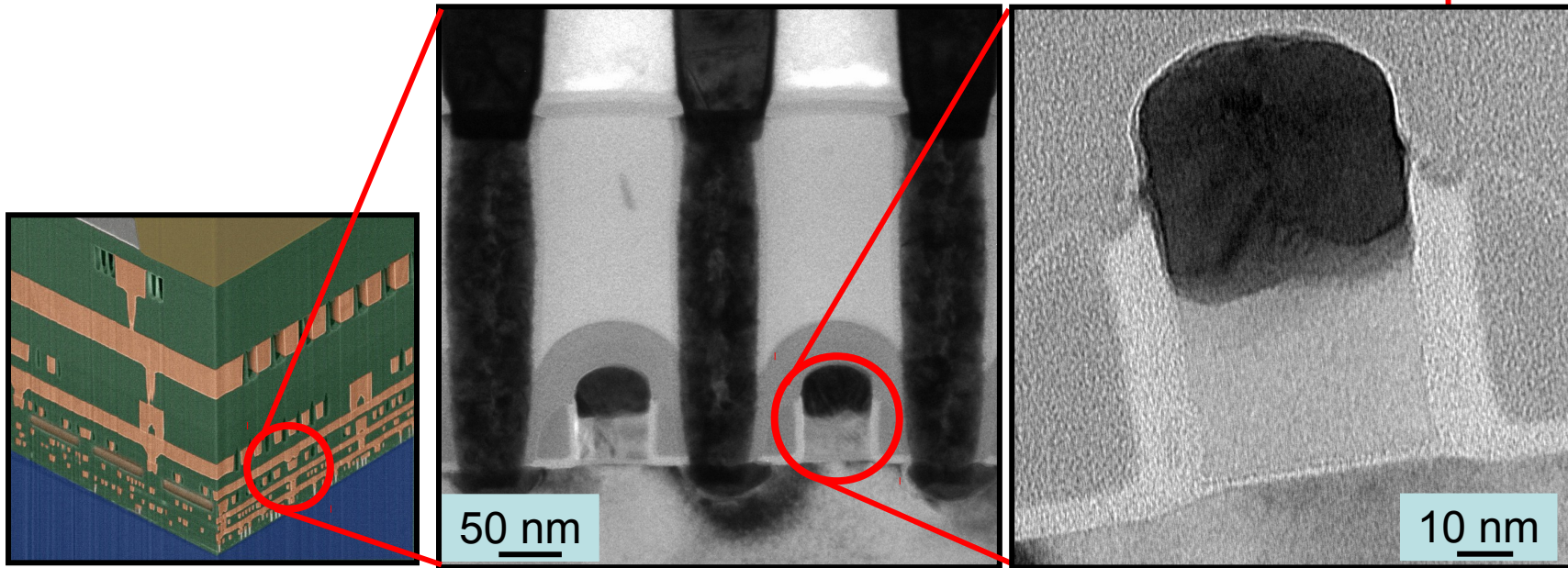
- Échantillon bien cristallisé
- Bonnes données de diffraction (pas de texture)
  - Jusqu'à 20-30 atomes indépendants
  - Composition connue

**Avec de nombreux programmes existants :**

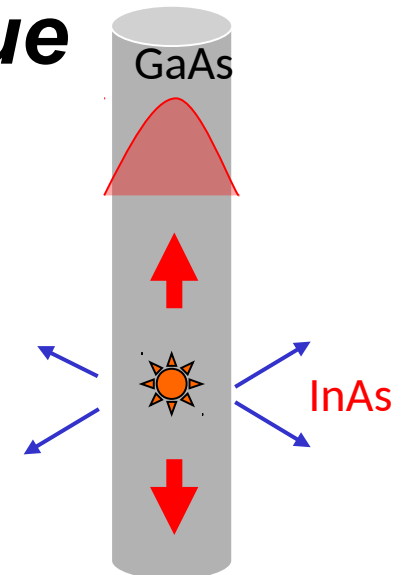
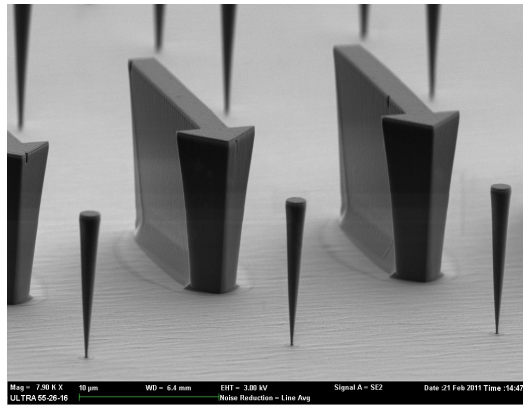
- Fox, Dash, Topas, EXPO, Superflip,...

**Sinon... Une boîte noire ne suffit plus...  
Contactez votre cristallographe !**

# Nanostructures

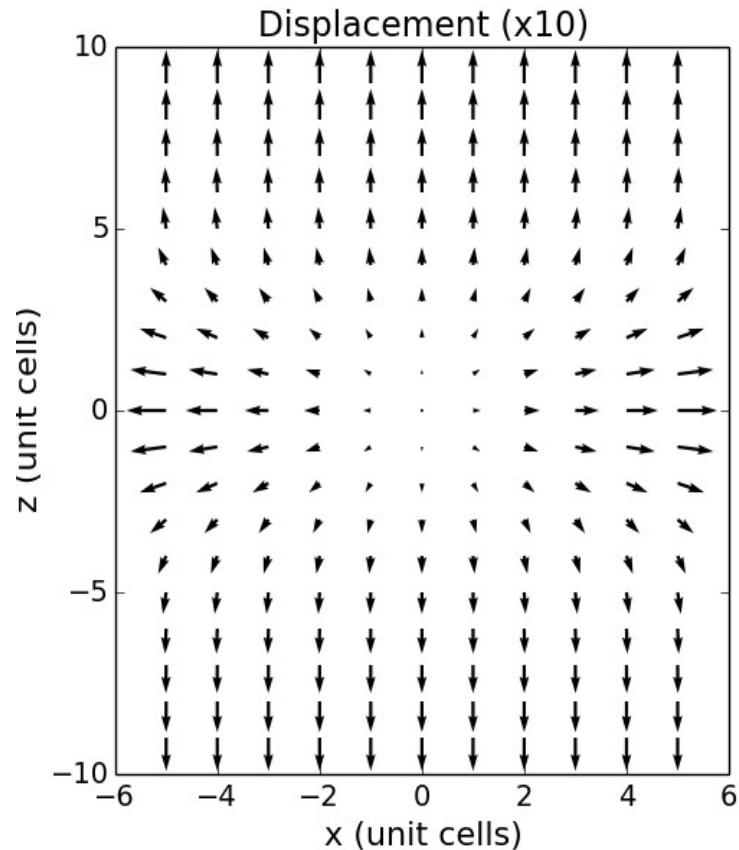


## Électronique, photonique



# Nanostructures: diffraction

$$A(\vec{k}) \approx FT [\Omega(\vec{r}) e^{2i\pi \vec{k} \cdot \vec{u}}]$$

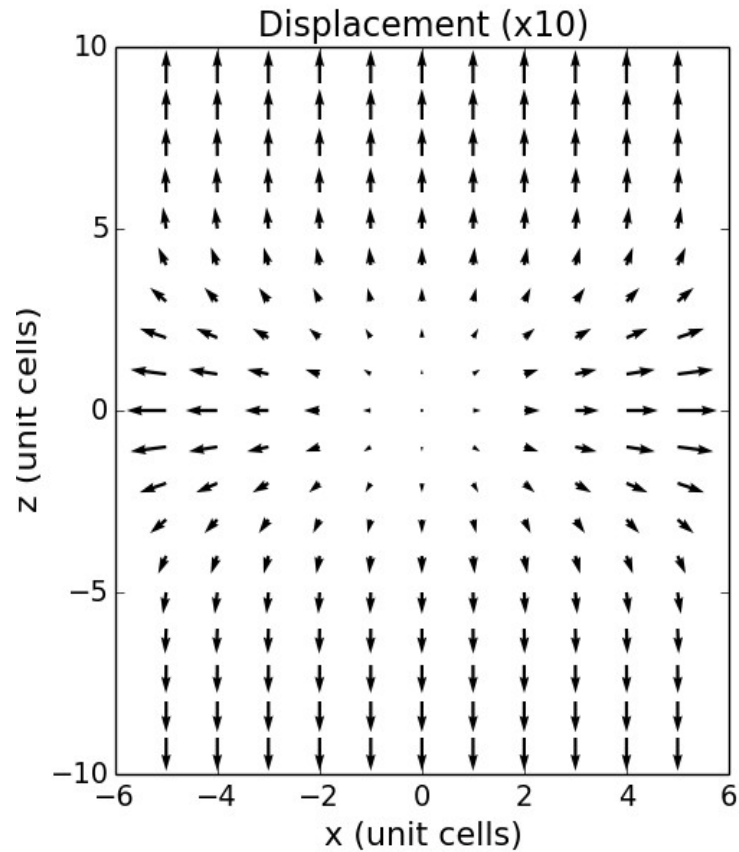


**Simulation déformation liée à une insertion le long d'un nanofil**  
- 2% déformation le long de x

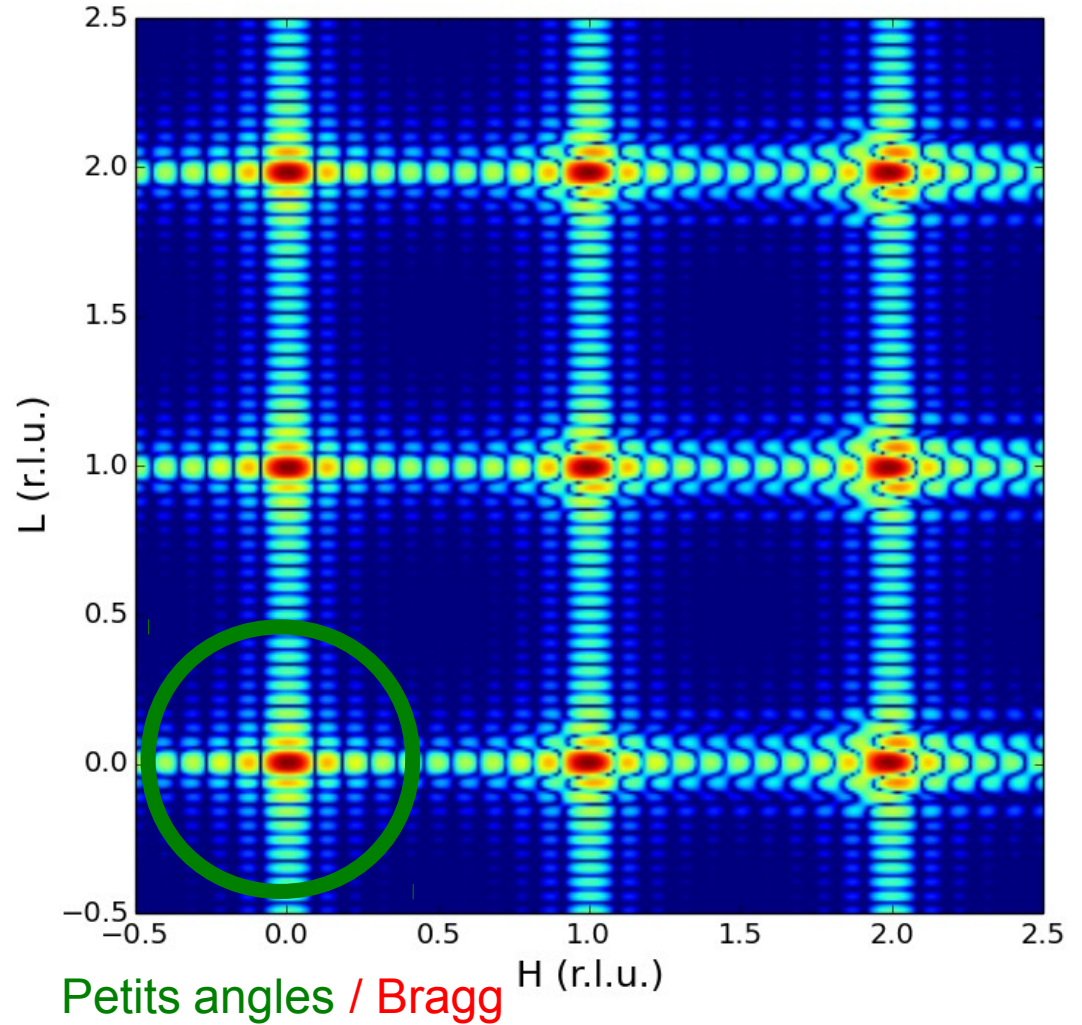


# Nanostructures : diffraction

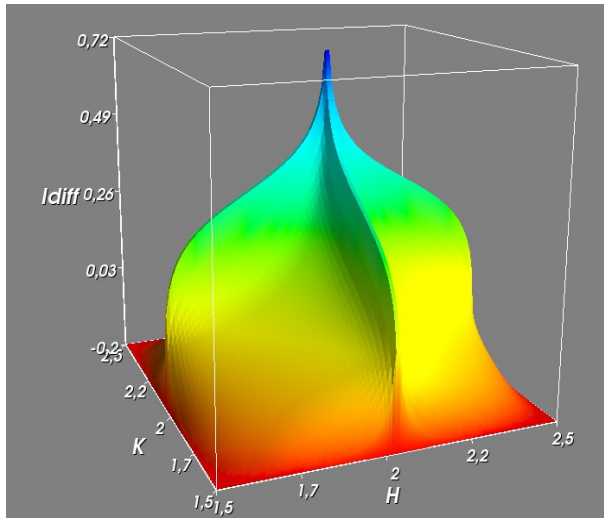
$$A(\vec{k}) \approx FT [\Omega(\vec{r}) e^{2i\pi \vec{k} \cdot \vec{u}}]$$



**Simulation déformation liée à une insertion le long d'un nanofil**  
- 2% déformation le long de x



# Nanostructures : diffraction



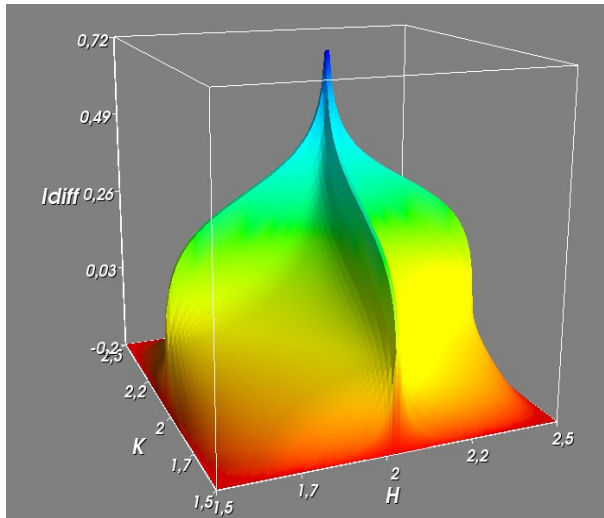
**Substrat (monocristal)**

**pic Bragg**

**+**

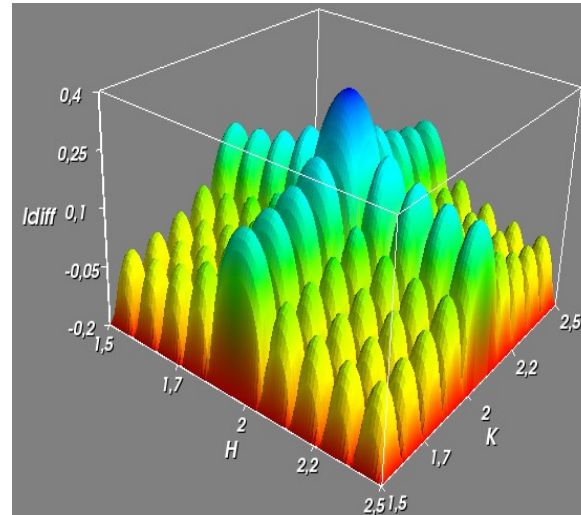
**tiges troncature**

# Nanostructures : diffraction



**Substrat (monocristal)**

**pic Bragg  
+  
tiges troncature**

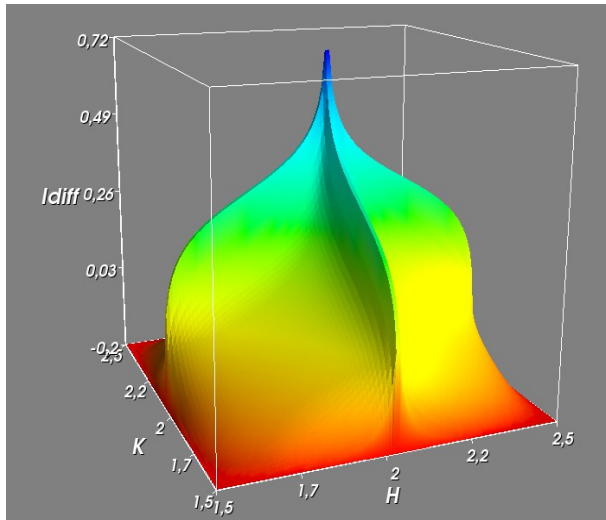


**NanoCrystal parfait**

**pic élargit,  
oscillations de taille finie**

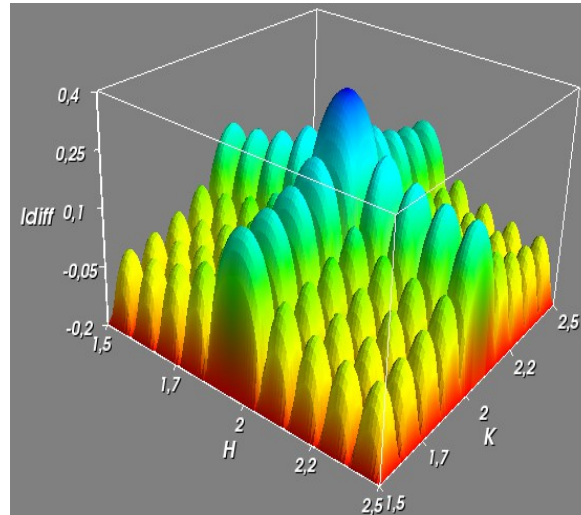


# Nanostructures : diffraction



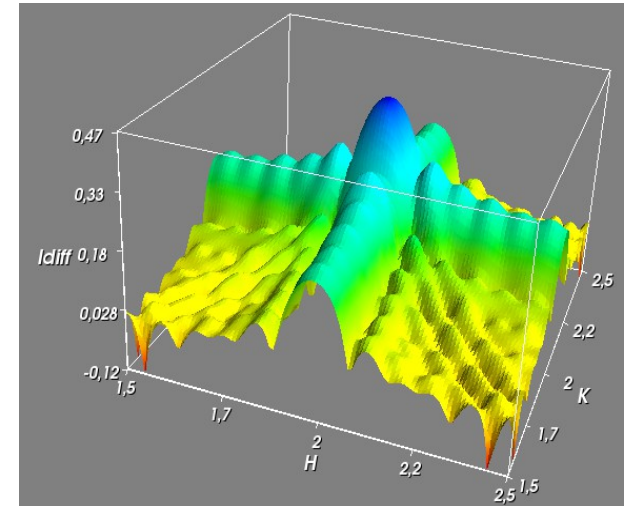
**Substrat (monocristal)**

**pic Bragg  
+  
tiges troncature**



**NanoCrystal parfait**

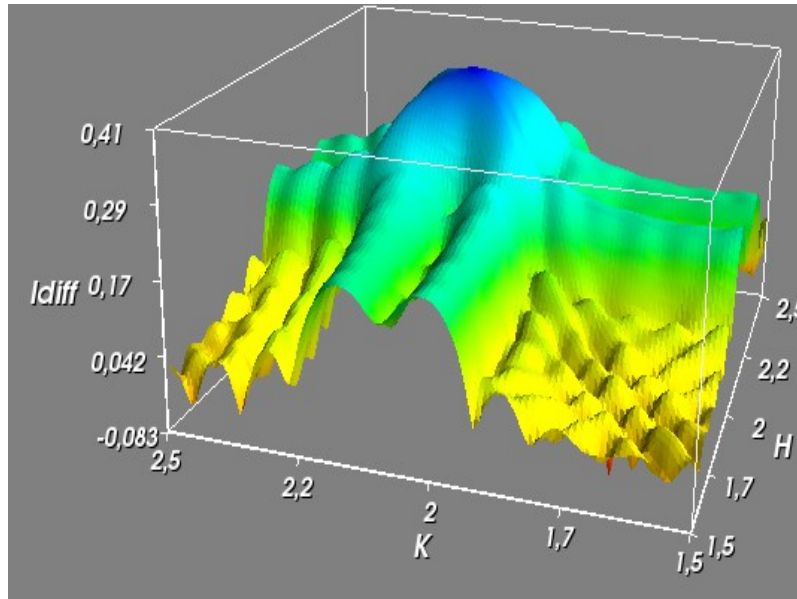
**pic élargit,  
oscillations de taille finie**



**Nanocristaux parfaits  
avec *distribution de tailles***

**Pic élargit  
ocsillations amorties**

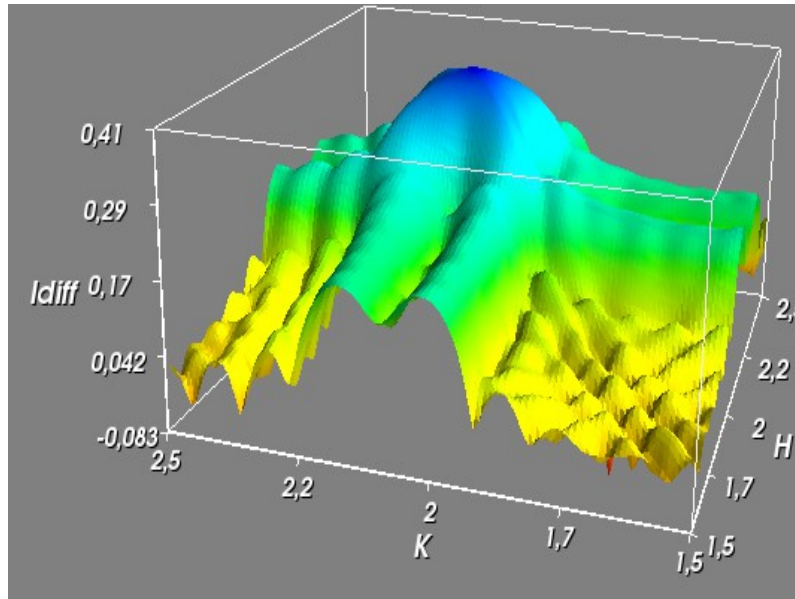
# Nanostructures : diffraction



**Nanocristaux**  
avec **champ de déformation**  
& **distribution de tailles**

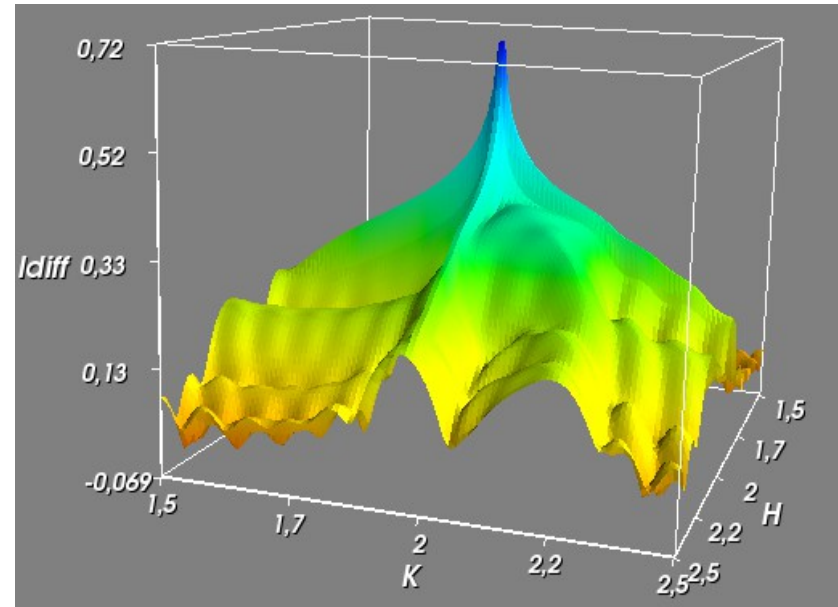
**Pic élargit, déplacé,**  
**oscillations + amorties**

# Nanostructures : diffraction



**Nanocristaux**  
avec **champ de déformation**  
& **distribution de tailles**

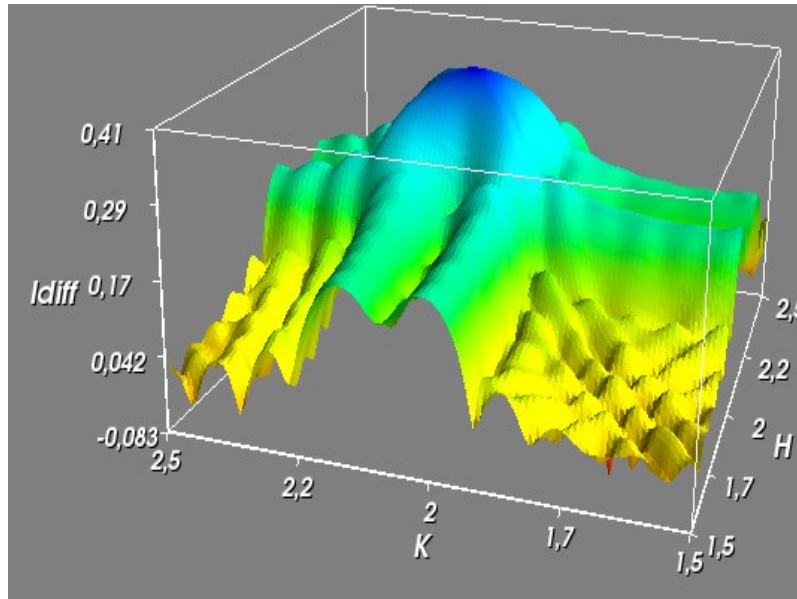
**Pic élargit, déplacé,**  
**oscillations + amorties**



**Nanocristaux**  
avec **champ de déformation**  
& **distribution de tailles**  
+ **substrat**

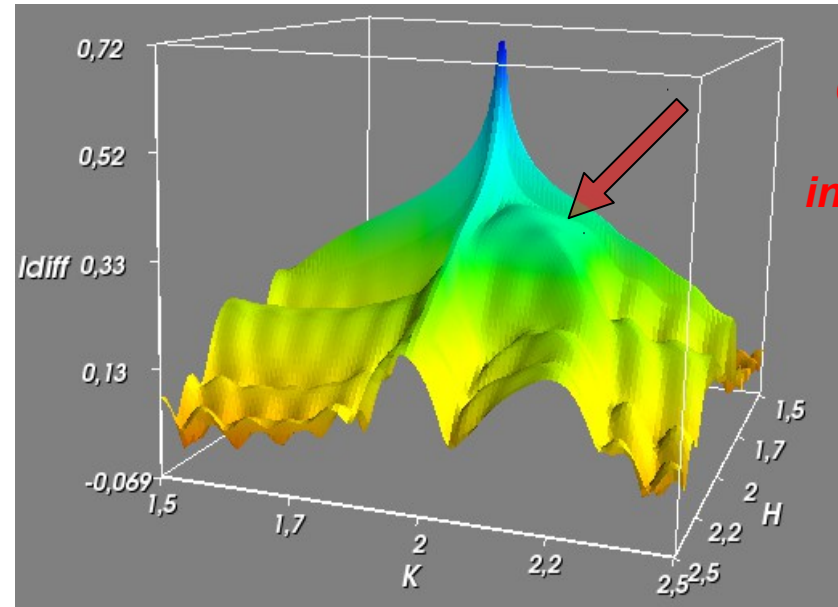
...

# Nanostructures : diffraction



**Nanocristaux**  
avec **champ de déformation**  
& **distribution de tailles**

**Pic élargit, déplacé,**  
**oscillations + amorties**



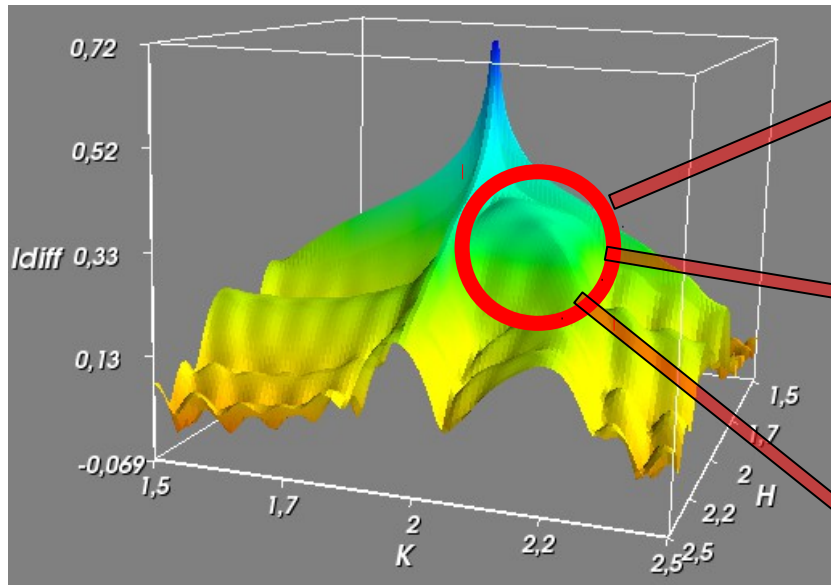
**Ce qui**  
**nous**  
**intéresse**

**Nanocristaux**  
avec **champ de déformation**  
& **distribution de tailles**  
+ **substrat**

...

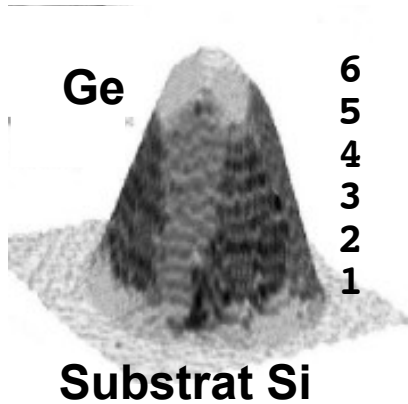


# Nanostructures : diffraction

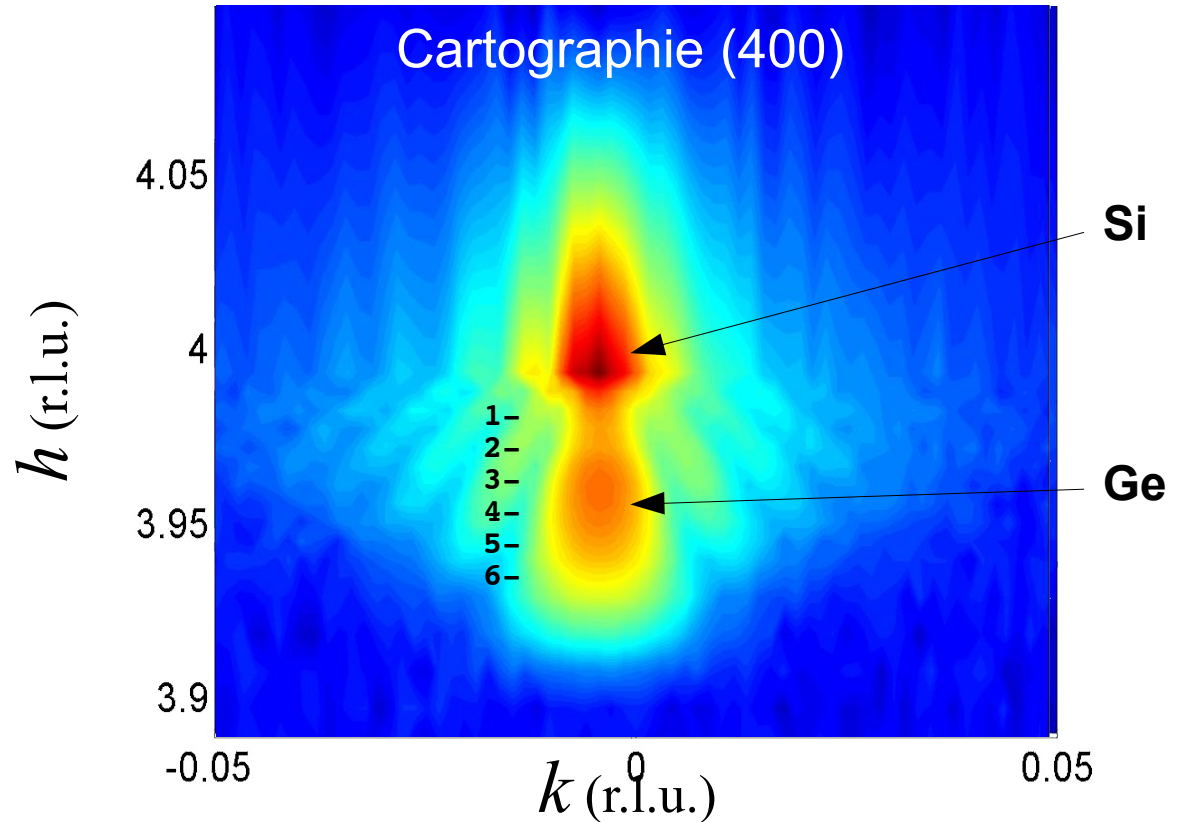


- **Cartographie** de diffraction 2D/3D (poudres : profil complet de diffraction 1D)
- **Diffraction résonante** (sensible à l'élément chimique) pour séparer nanostructures & substrat + **diffraction en incidence rasante**
- **Nano-diffraction** sur objets uniques

# Nanostructures : îlots Ge / Si



120 nm ( $\varnothing$ ) x 15 nm (h)



## Cartographie de diffraction en incidence rasante :

- État de contrainte de Ge (relaxation) ?
- Séparation des différentes couches de l'îlot
- Interdiffusion Ge / Si ?

Thèse M-I Richard

# Diffraction résonante (anomale)

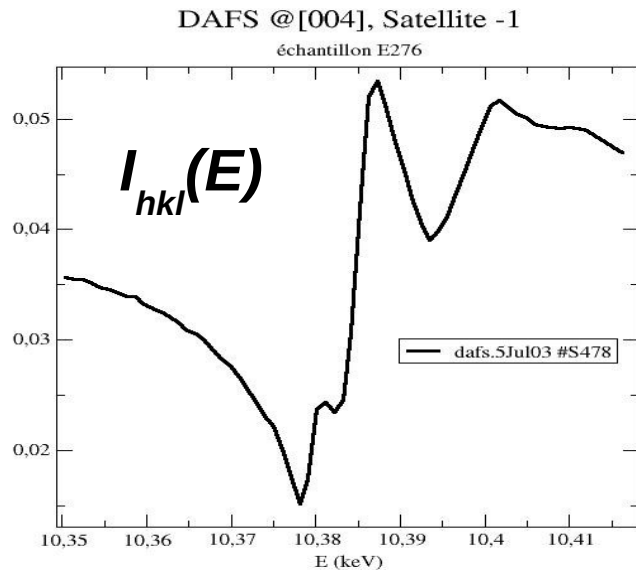
## Facteur de structure

$$I \propto |F(hkl)|^2$$

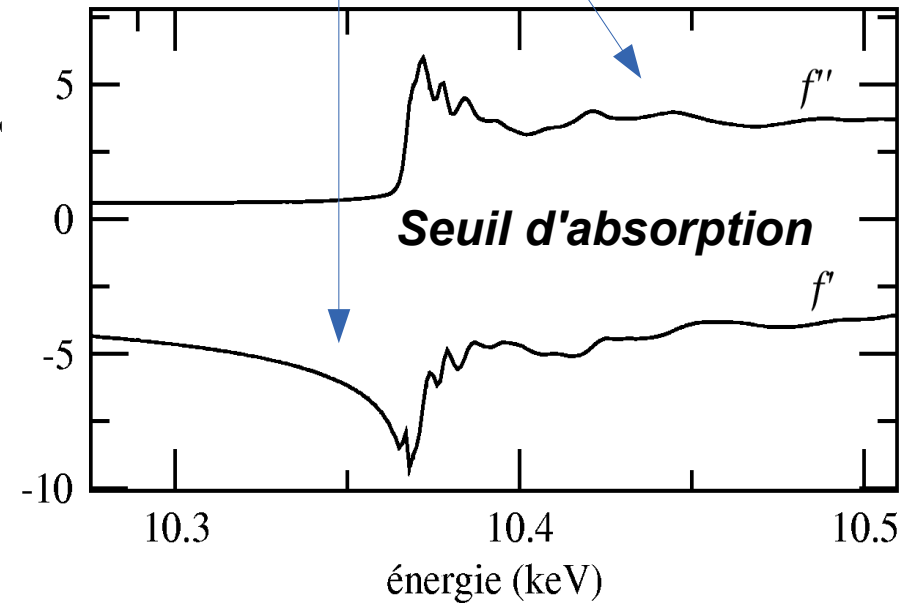
$$F(\vec{k}) = \sum f_i e^{2i\pi\vec{k}\cdot\vec{r}_i}$$

## Facteur de diffusion atomique

$$f = f^0(\vec{k}) + f'(\vec{k}, E) + f''(\vec{k}, E)$$



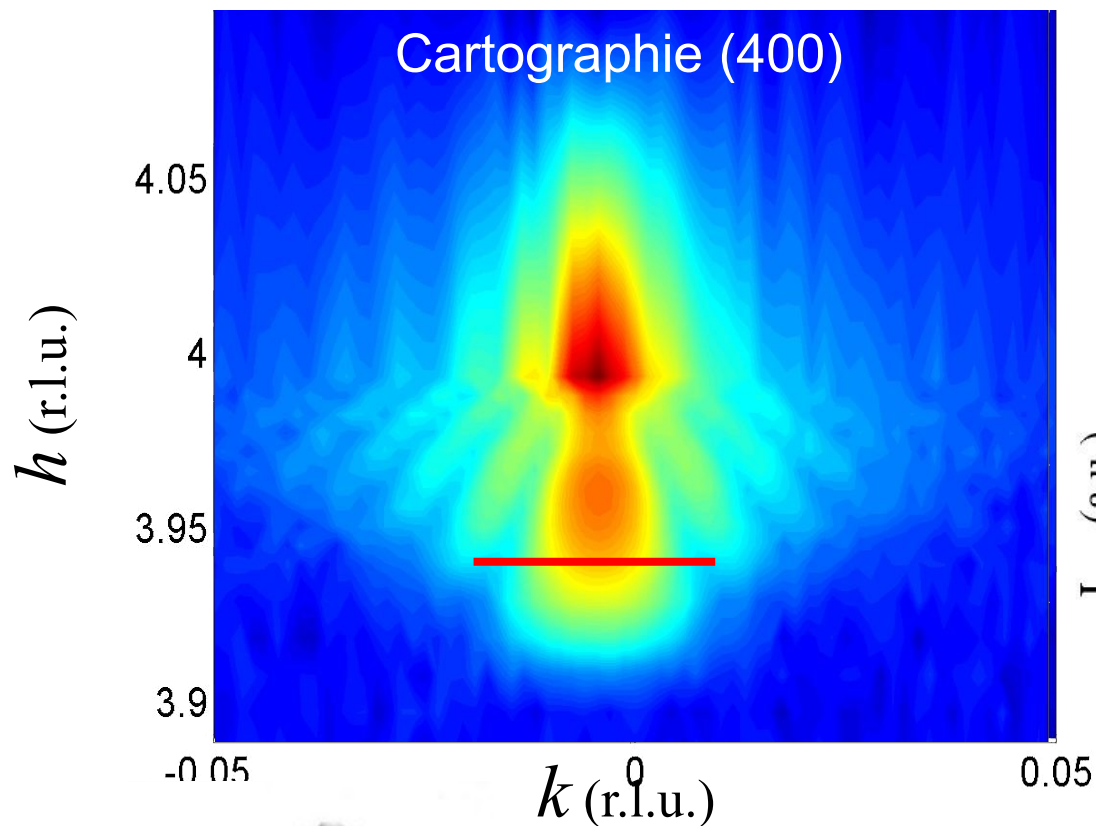
f (unités électroniques)



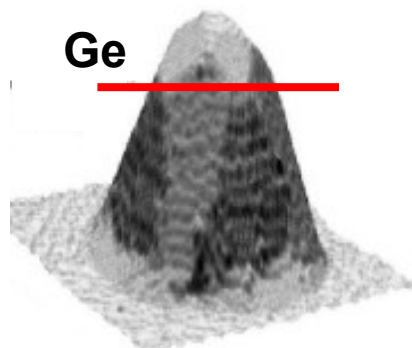
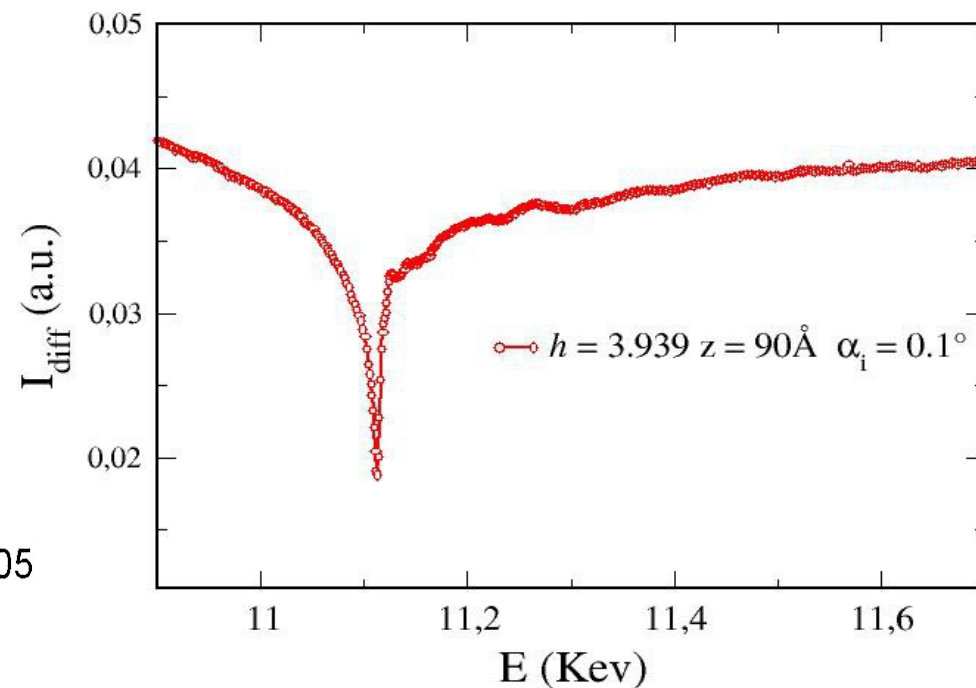
## Informations obtenues :

- Proportion de l'atome résonant
- Distance avec les premiers voisins

# Îlots Quantiques Ge/Si



GI-DAFS spectrum @  $h=3.939$



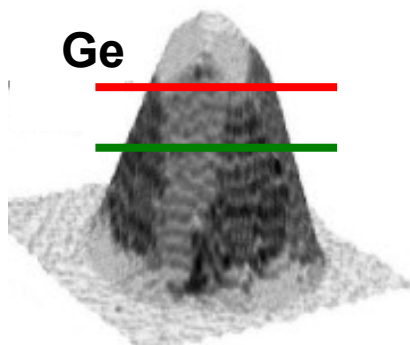
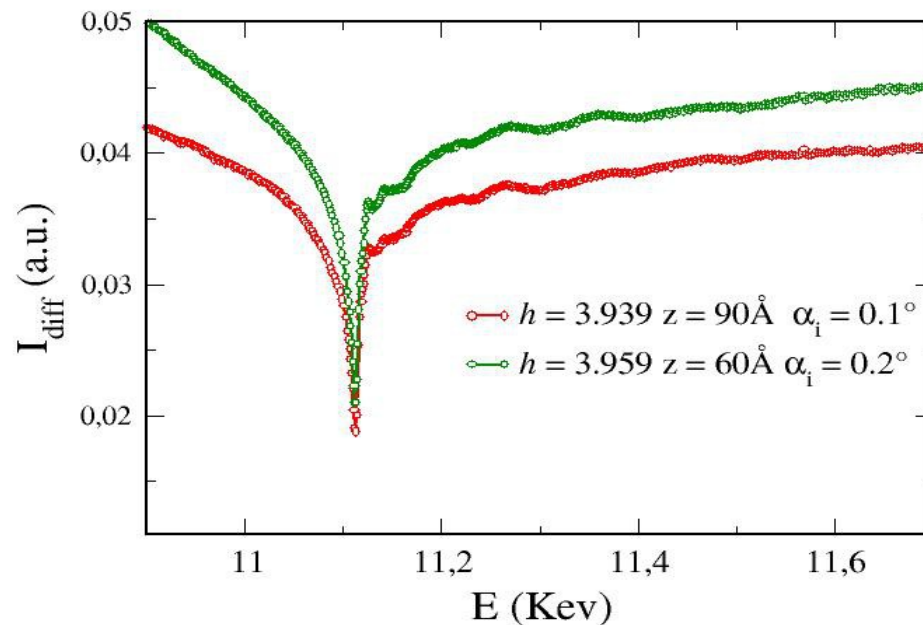
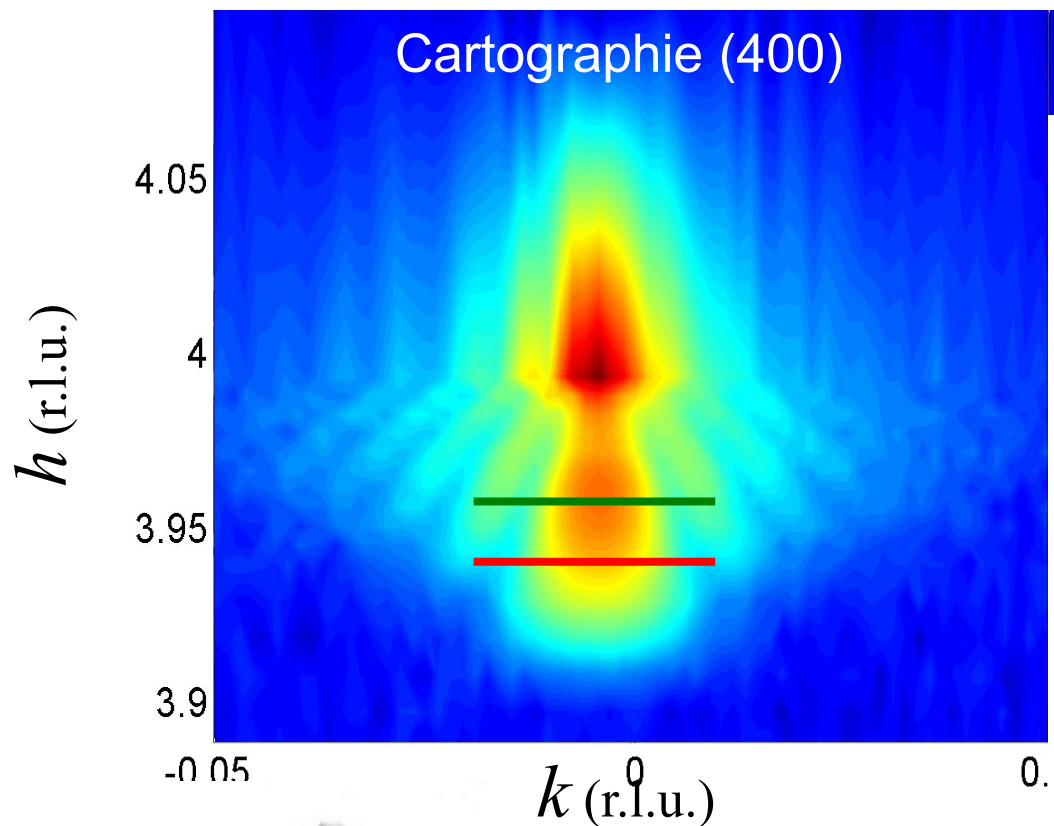
$h=3.939$   
 $z=9\text{nm}$

Si

J. Phys.: Conf. Series **190** (2009), 012129



# Îlots Quantiques Ge/Si



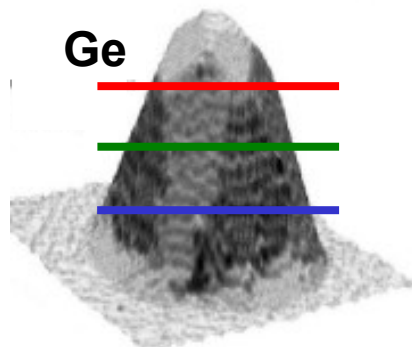
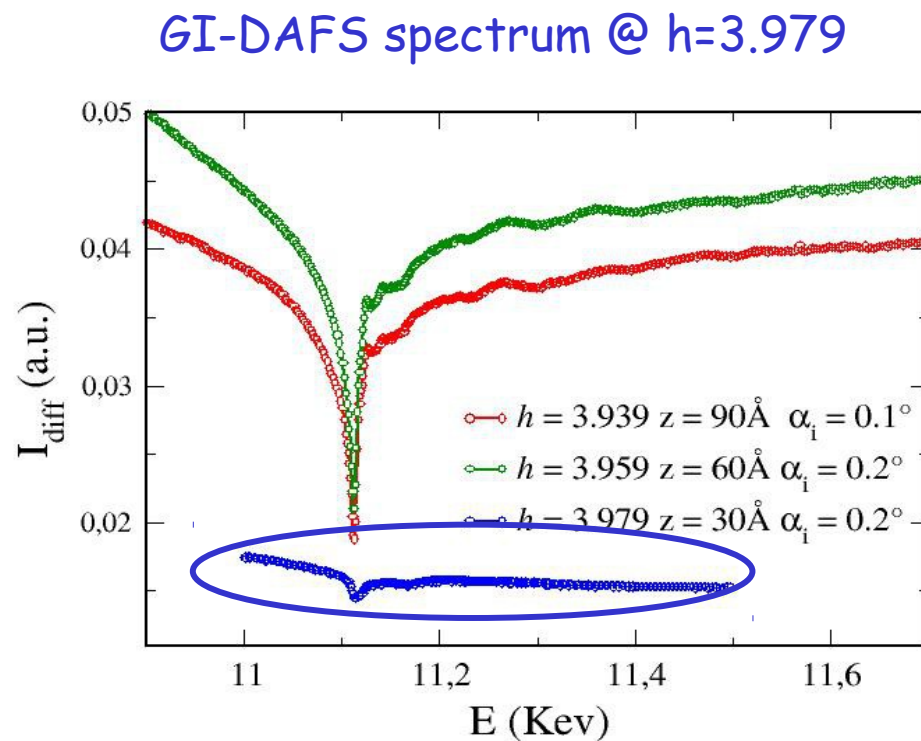
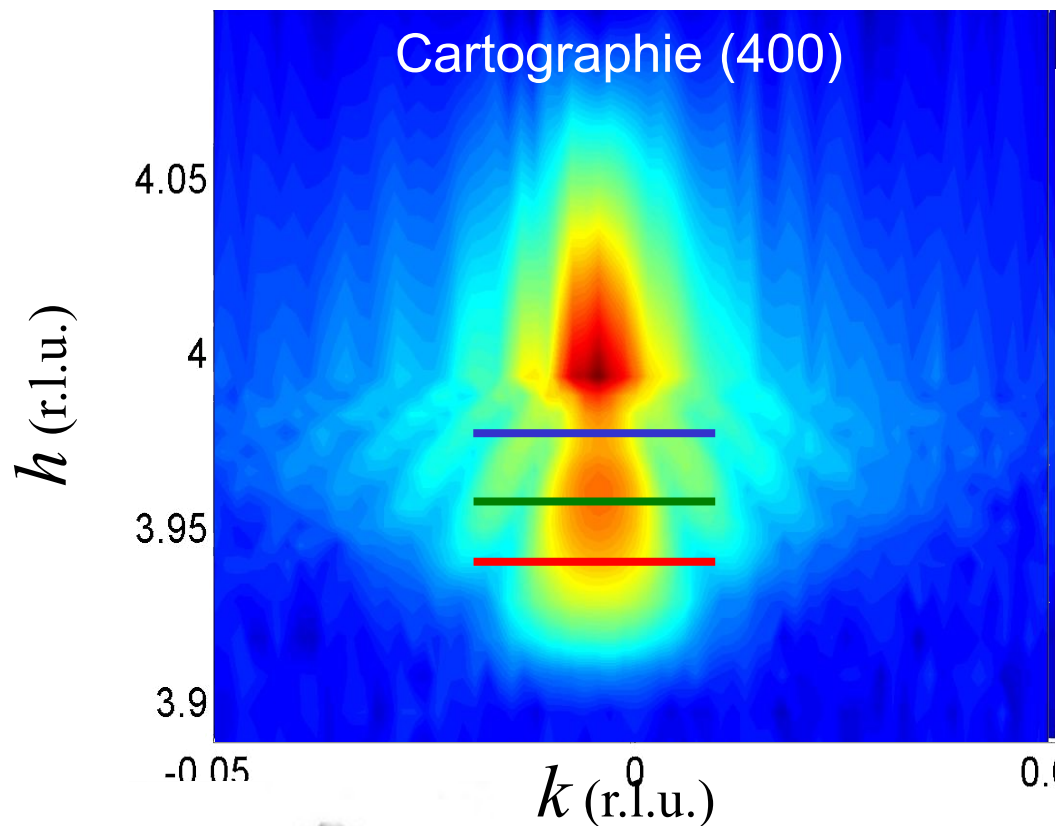
$h = 3.939$   
 $z = 9 \text{ nm}$

$h = 3.959$   
 $z = 6 \text{ nm}$

Si

J. Phys.: Conf. Series **190** (2009), 012129

# Îlots Quantiques Ge/Si



$H=3.939$  /  $z=9\text{nm}$

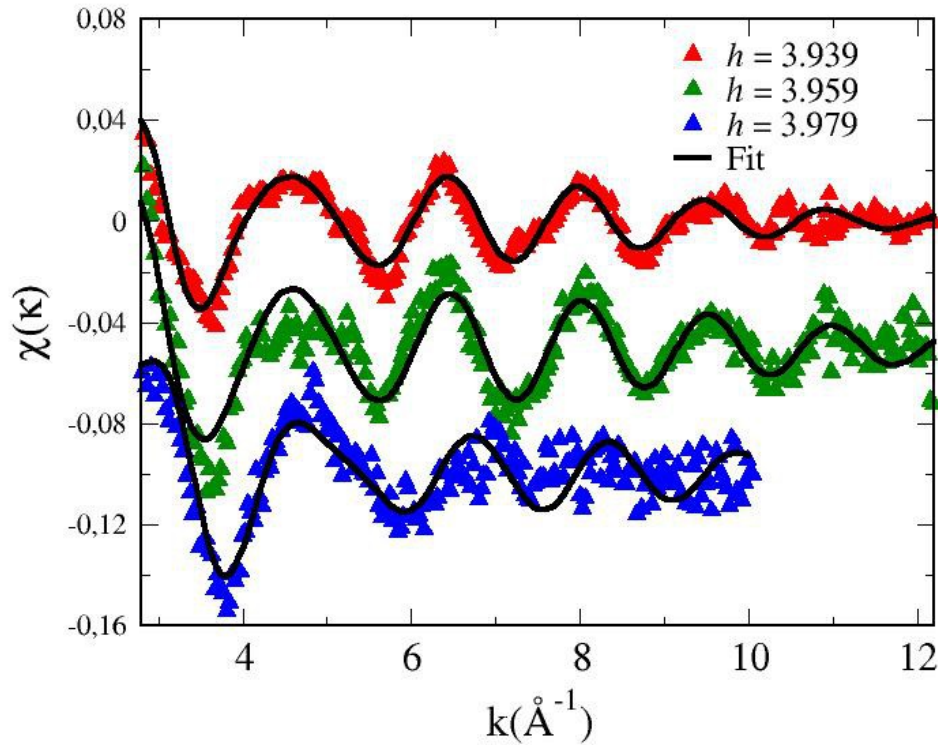
$H=3.959$  /  $z=6\text{nm}$

$H=3.979$  /  $z=3\text{nm}$

Si

J. Phys.: Conf. Series **190** (2009), 012129

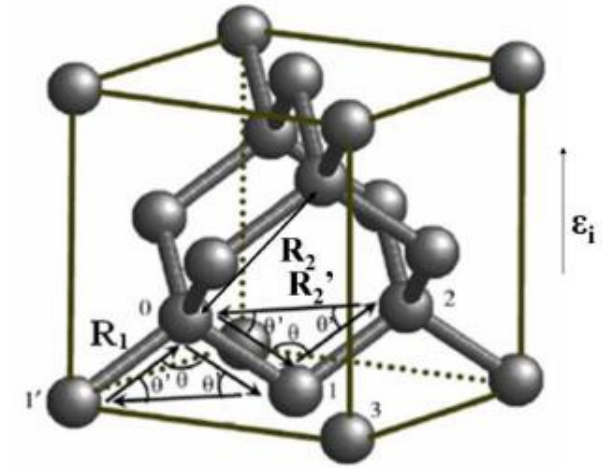
# Îlots Quantiques Ge/Si



$H=3.939 / z=9\text{nm}$

•  $H=3.959 / z=6\text{nm}$

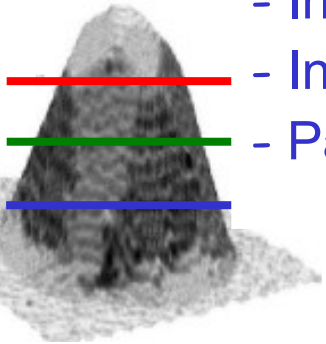
•  $H=3.979 / z=3\text{nm}$



	<i>Ge-Ge</i>	<i>Ge-Si</i>	$X_{Ge}$ (%)
massif	2.45	2.35	-
$z \approx 9\text{nm}$	2.44	2.41	60
$z \approx 6\text{nm}$	2.42	2.40	57
$z \approx 3\text{nm}$	2.41	2.40	54
$Ge_{0.5}Si_{0.5}$ rel. alloy	2.435	2.402	50

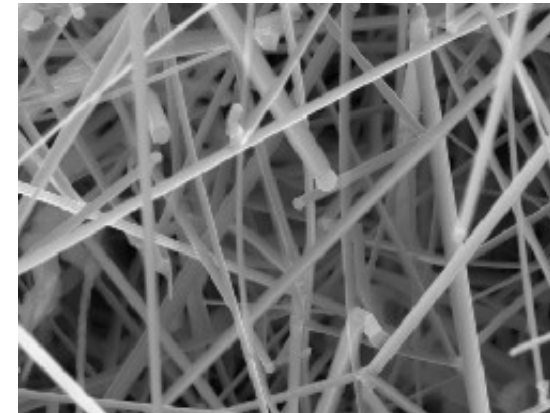
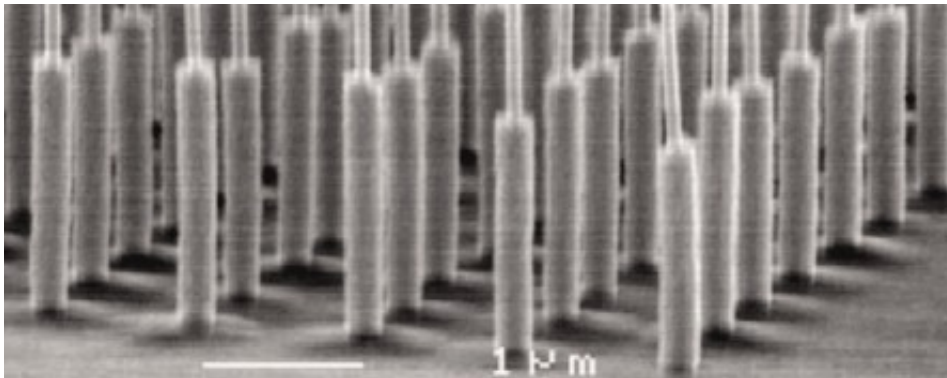
## Analyse :

- Interface abrupte Ge/Si
- Interdiffusion  $\sim 40-45\%$  Si
- Pas de cœur en Si



J. Phys.: Conf. Series **190** (2009), 012129

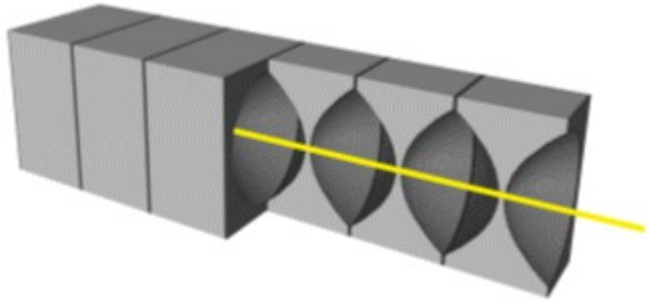
# ***Nanostructures : Dispersion de structures & propriétés***



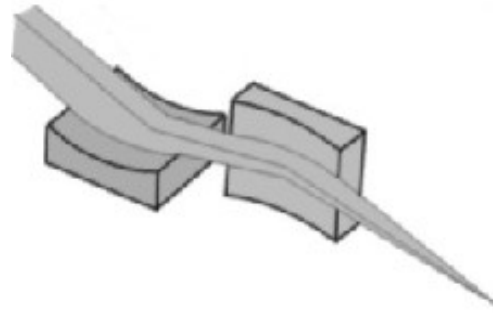
➔ **Besoin de diffraction sur objet unique**



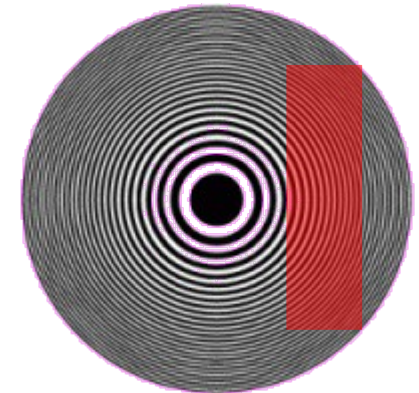
# Optiques pour nano-diffraction



Lentilles réfractives



Miroir Kirkpatrick-Baez  
(achromatique)



Lentille de Fresnel

## Longueur de cohérence (Si 111):

- transverse :  $\sim 20\text{-}40$  (horiz.)  $\times$   $\sim 60\text{-}100$  (vert.)  $\mu\text{m}^2$
- longitudinale :  $0.5\text{-}1 \mu\text{m}$  (*Optics Express* 17 (2009), 15853)

## Taille de faisceau:

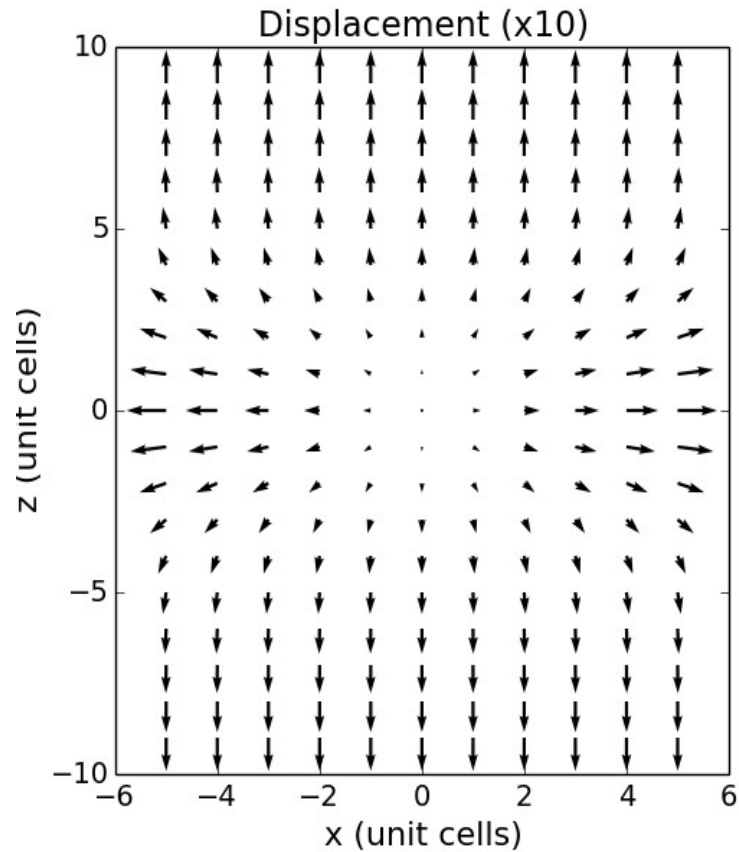
- moins que  $100 \text{ nm}$  (latéral)
- taille utile de  $100 \text{ nm}$  à quelques  $\mu\text{m}$  (garder échantillon dans faisceau !)

## Flux:

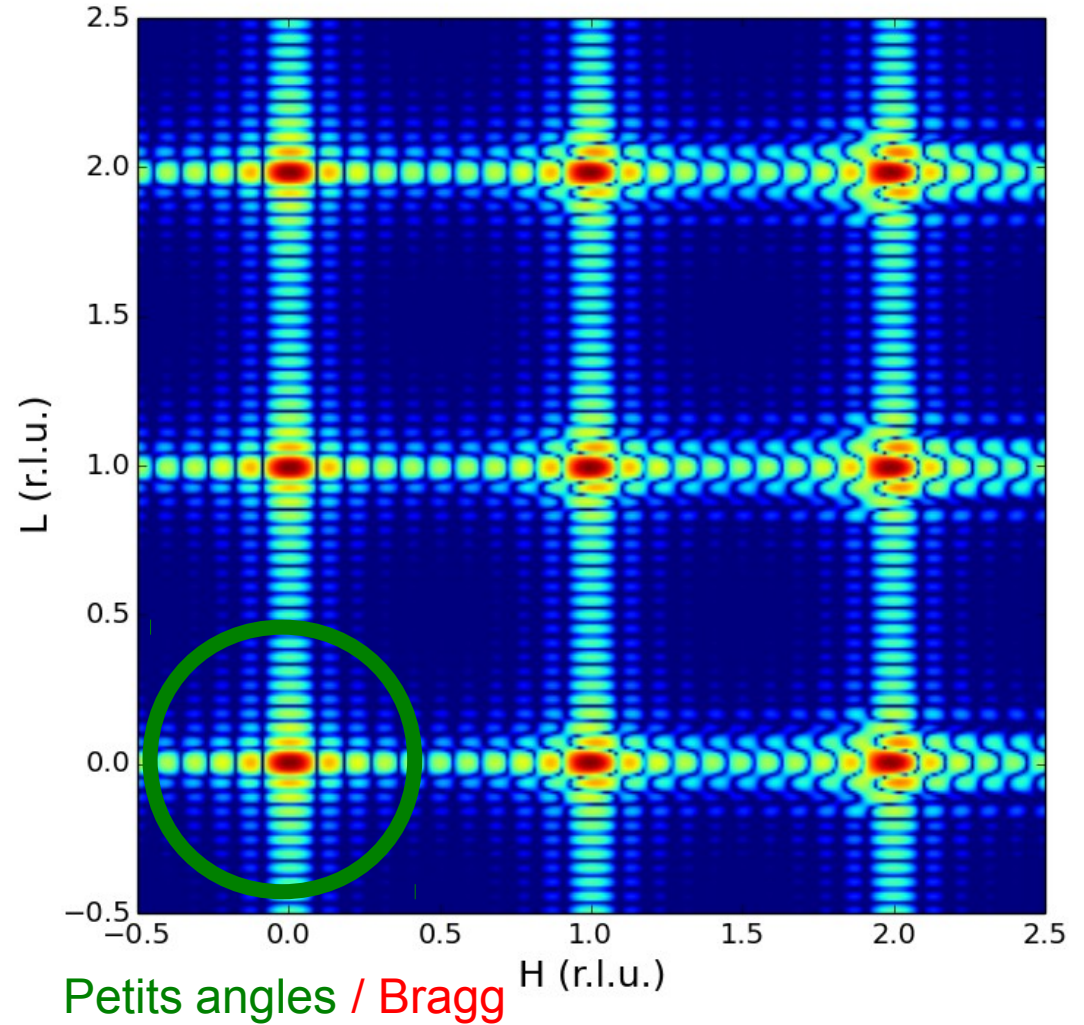
$$10^4\text{-}5 \times 10^5 \text{ ph/s/nm}^2$$

# Nanostructures : diffraction

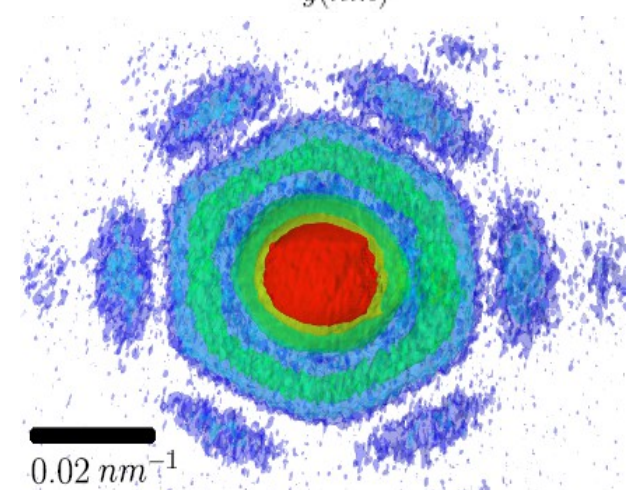
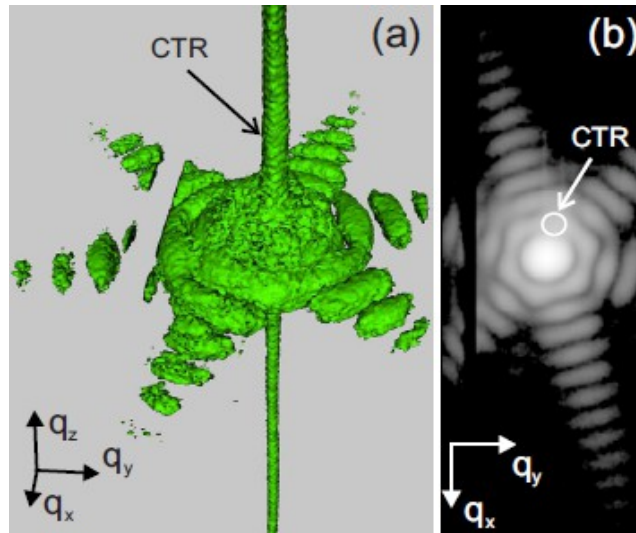
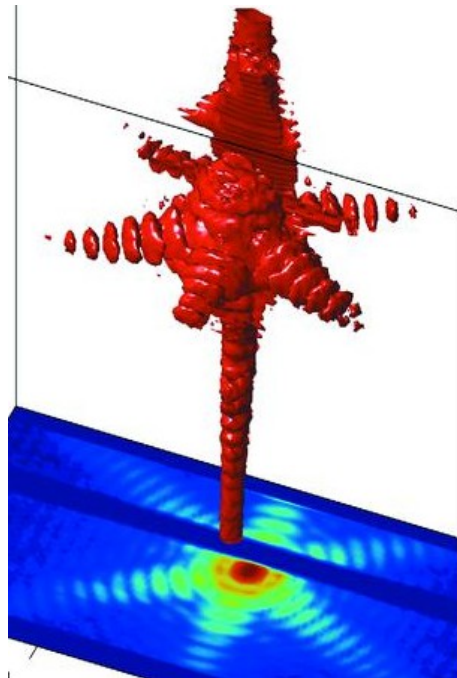
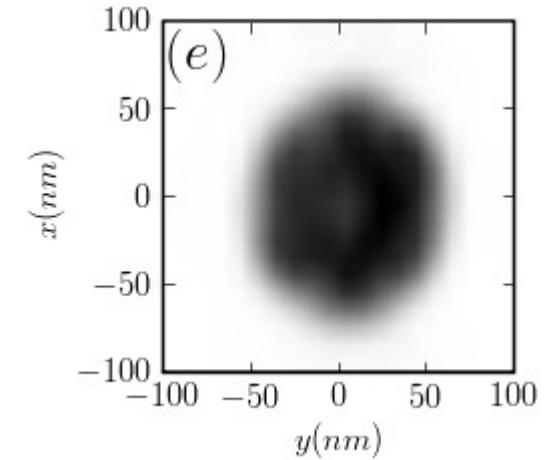
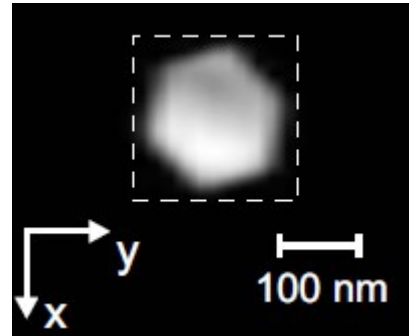
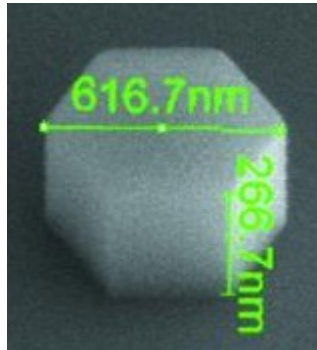
$$A(\vec{k}) \approx FT [\Omega(\vec{r}) e^{2i\pi \vec{k} \cdot \vec{u}}]$$



**Simulation déformation liée à une insertion le long d'un nanofil**  
- 2% déformation le long de x



# Limite en nano-diffraction (Bragg) ?



*J. Synchrotron Rad.* (2009). 16  
Biermanns et al  
GaAs  $\varnothing \sim 600 \text{ nm}$

*Phys. Rev. B* 79, 125324 (2009)  
Diaz et al  
InAs  $\varnothing \sim 150 \text{ nm}$

*Phys. Rev. B* 79, 195401 (2009)  
Favre-Nicolin et al  
Si  $\varnothing \sim 95 \text{ nm}$

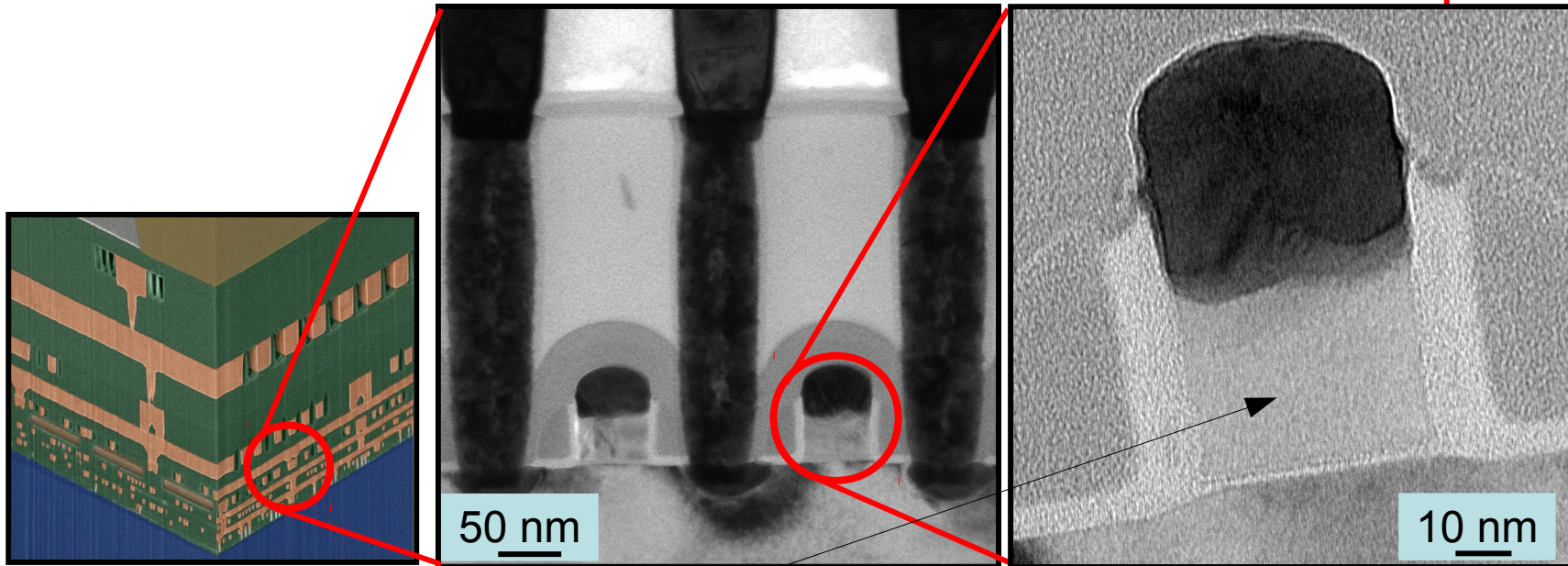
## Idée

La nano-diffraction avec un faisceau X permet de mesurer :

- **La taille & la forme de l'objet**
  - **Tout écart de cet objet à un “ réseau parfait ”**  
(déformation, dislocation, macles...)
- mesure de densité électronique & déplacements atomiques

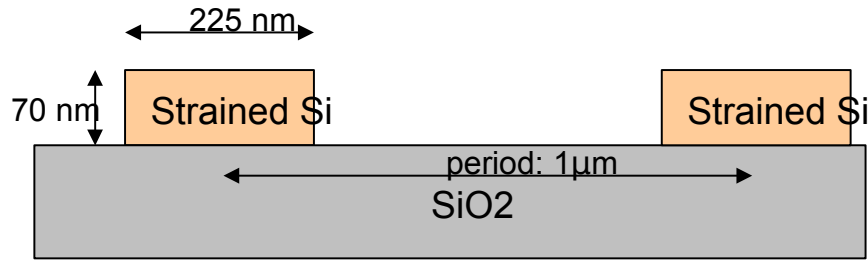


# Nanostructures : Micro-électronique

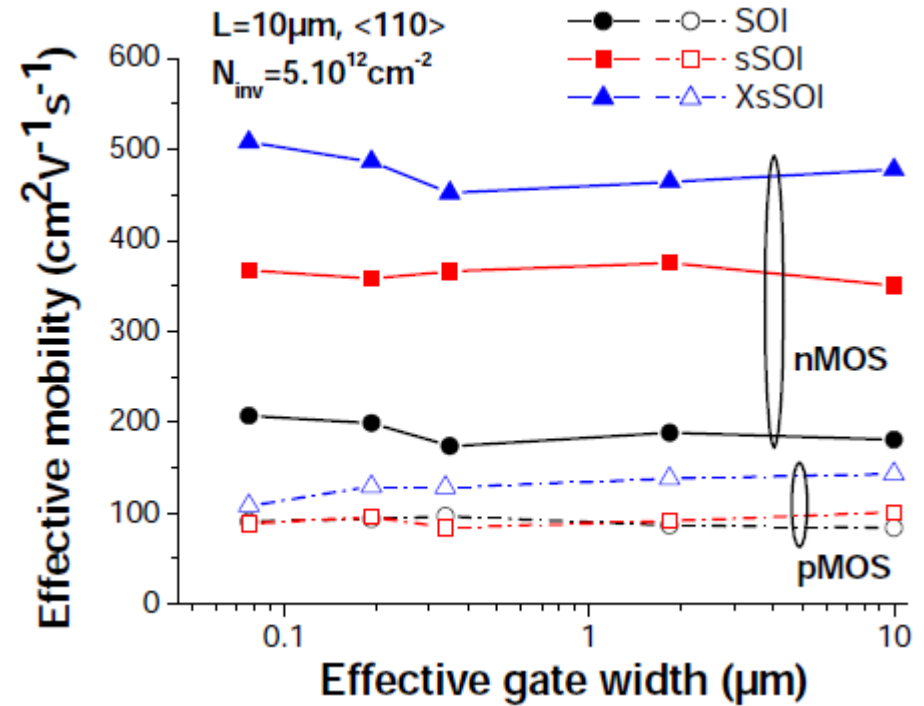
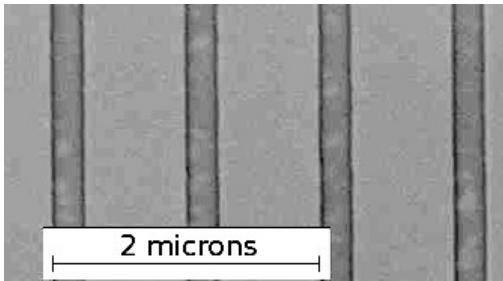


Canal en silicium : utilisation de contrainte pour  
améliorer les performances

# Lignes de silicium-sur-isolant (SOI) contraintes



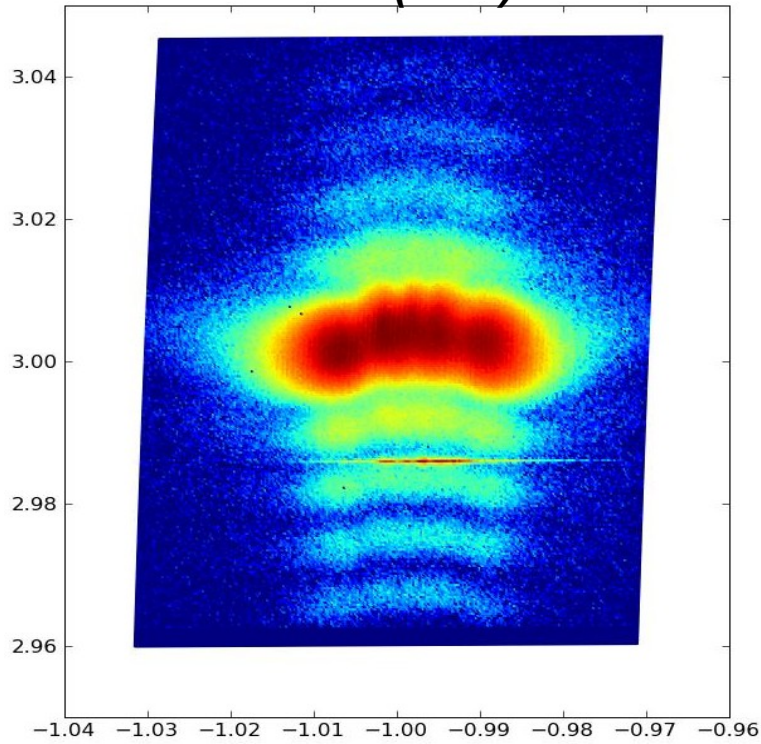
Lignes sSOI: J. Appl. Phys. 105, 114302 (2009)



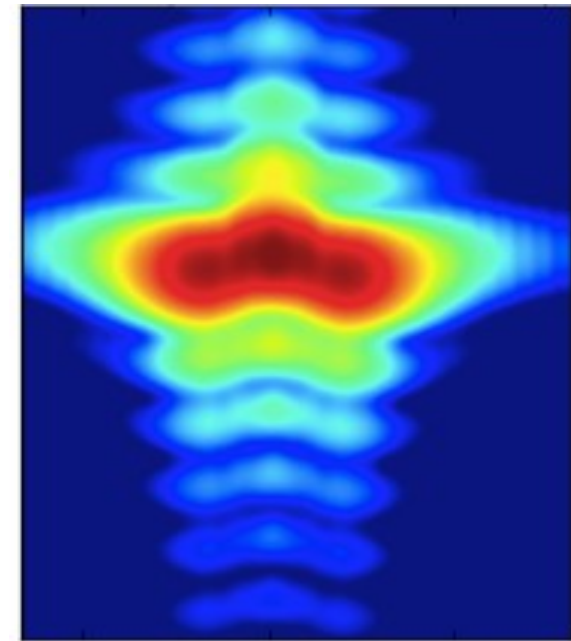
- Silicium contraint (strained Silicon-On-Insulator) = augmentation de la mobilité des porteurs de charges (x2,5)
- Besoin de connaître la déformation de lignes *individuelles*
- Nano-faisceau de RX ( $300 \times 500 \text{ nm}^2$ ) => diffraction de lignes individuelles

# Lignes de silicium-sur-isolant (SOI) contraintes

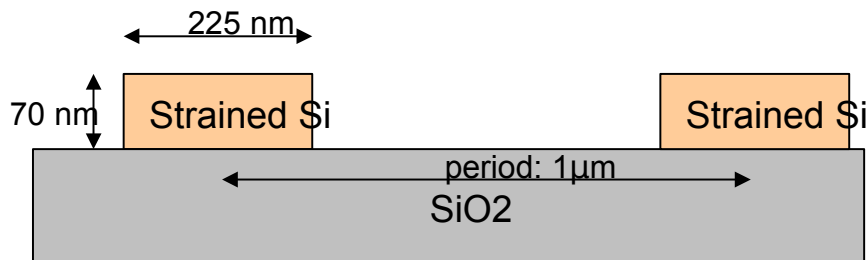
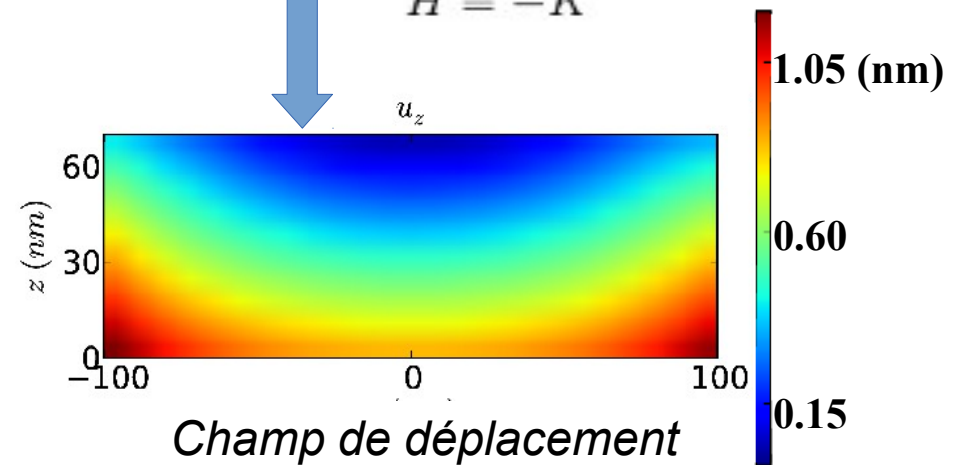
Raie (-113)



Reconstruction  
d'un modèle



$$H = -K$$

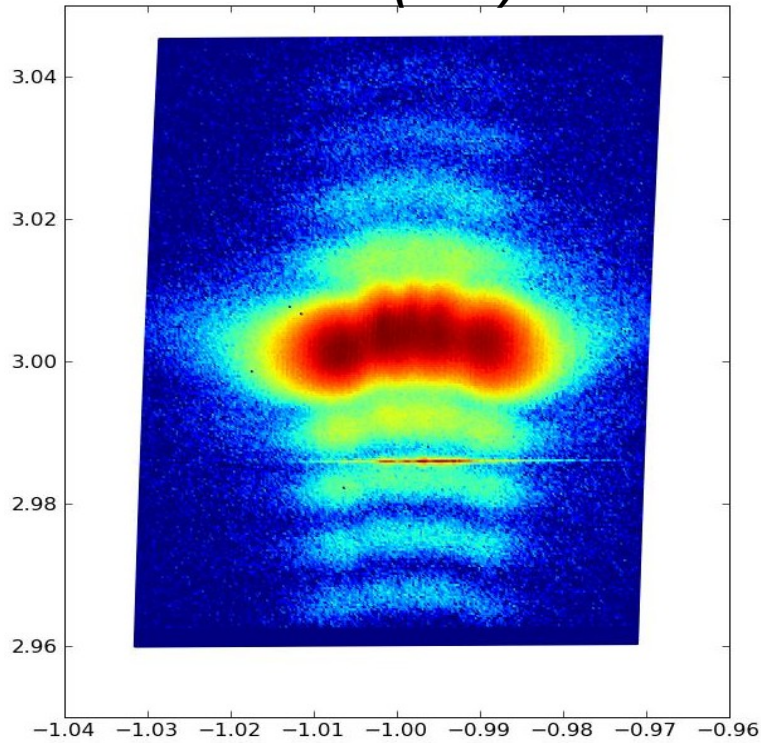


Phys. Rev. Lett. 111 (2013), 215502

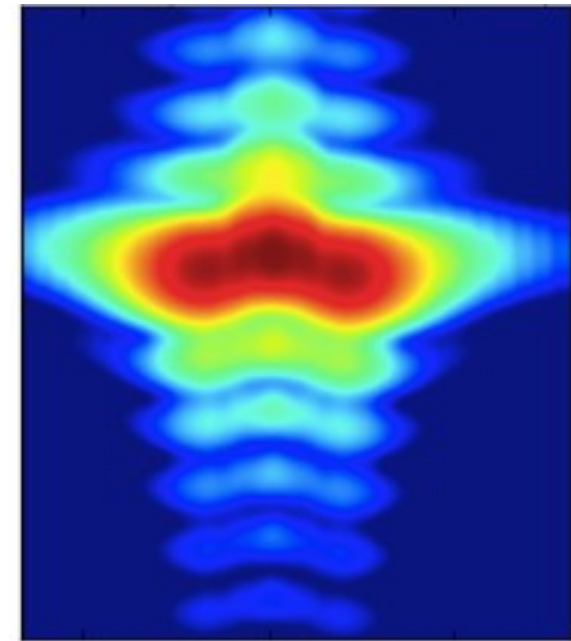


# Lignes de silicium-sur-isolant (SOI) contraintes

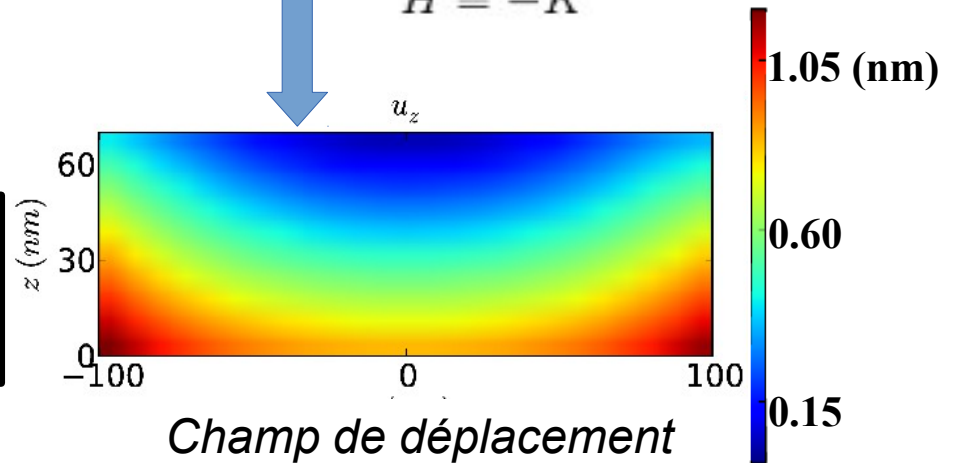
Raie (-113)



Reconstruction  
d'un modèle



$$H = -K$$

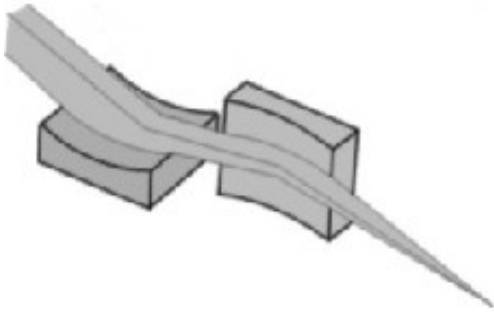


**Reconstruction de la déformation d'une ligne, avec une résolution de  $\sim 10$  nm et une précision des déplacements  $< \sim 0,01$  nm**

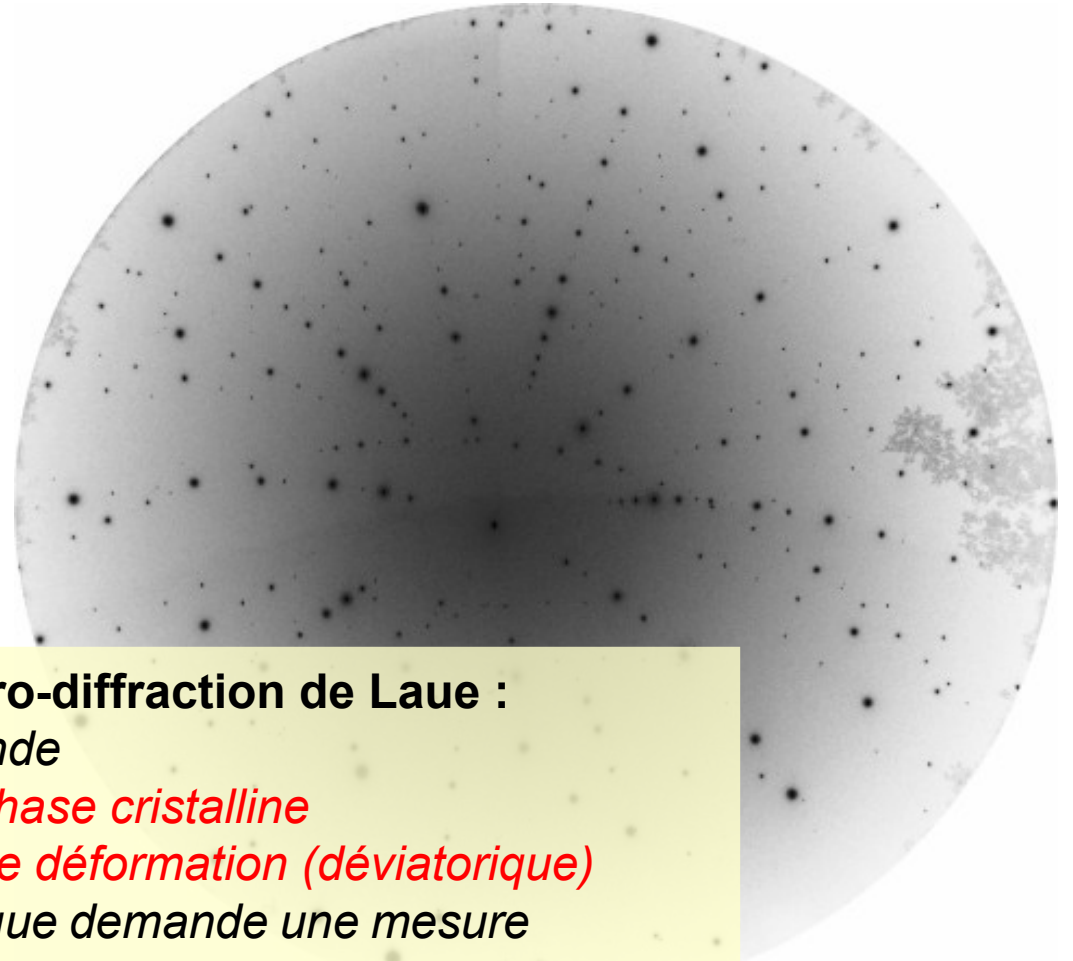
Phys. Rev. Lett. 111 (2013), 215502



# Diffraction micro-Laue



Miroir Kirkpatrick-Baez  
→ Faisceau blanc  
4-25 keV



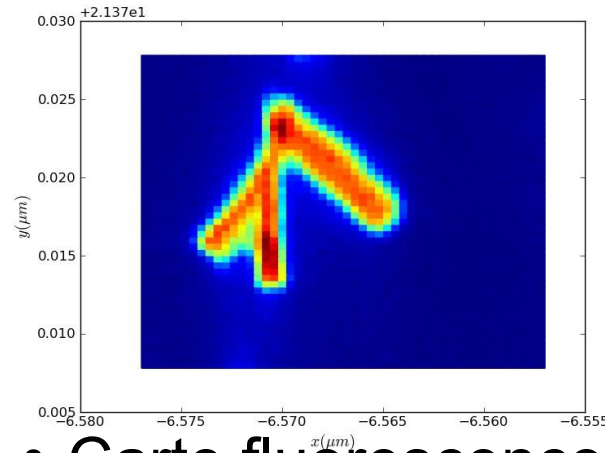
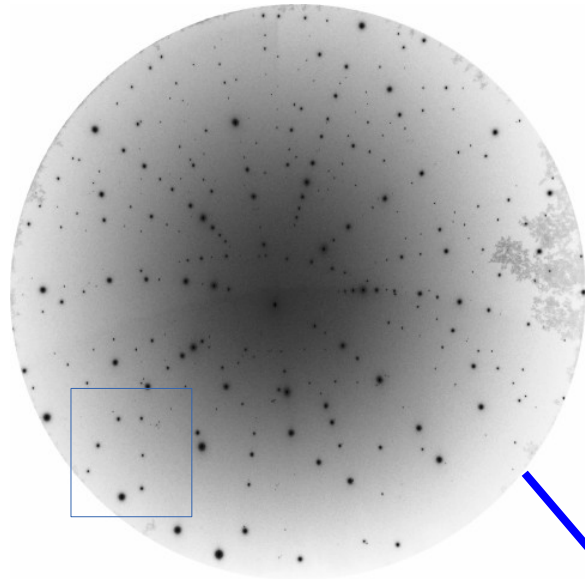
## Une seule image de micro-diffraction de Laue :

- est mesurée en une seconde
- permet de déterminer *la phase cristalline*
- donne accès *au tenseur de déformation (déviatorique)*
- (la déformation hydrostatique demande une mesure monochromatique)
- taille de faisceau  $250 \times 250 \text{ nm}^2$

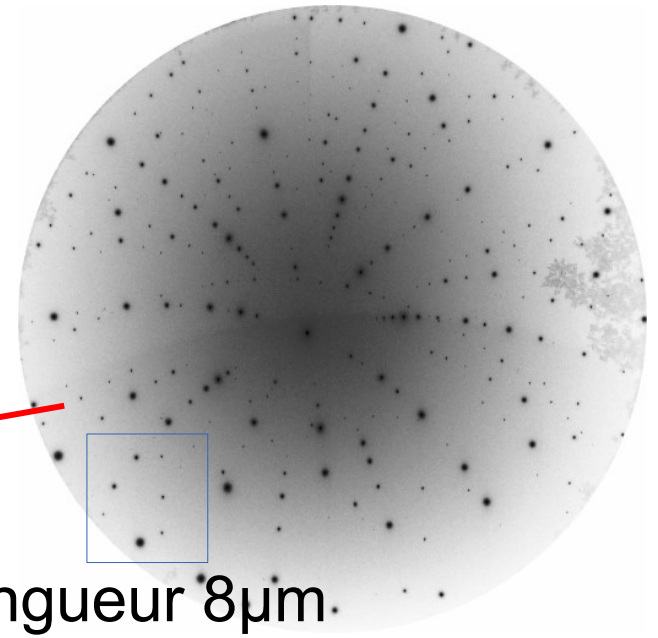
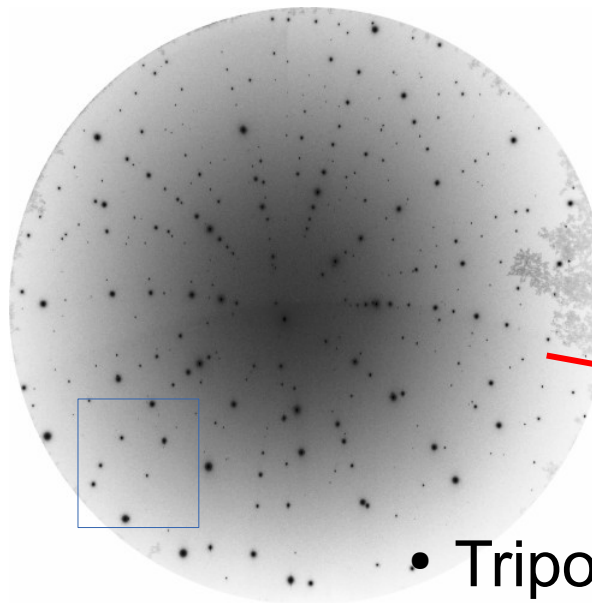
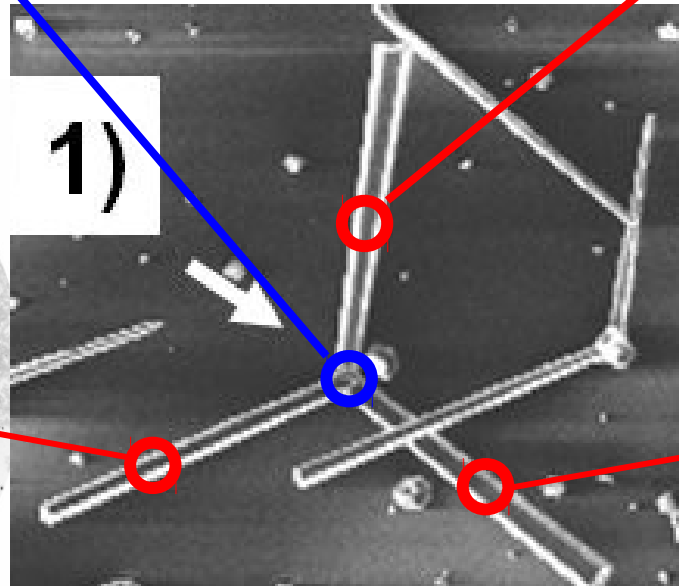
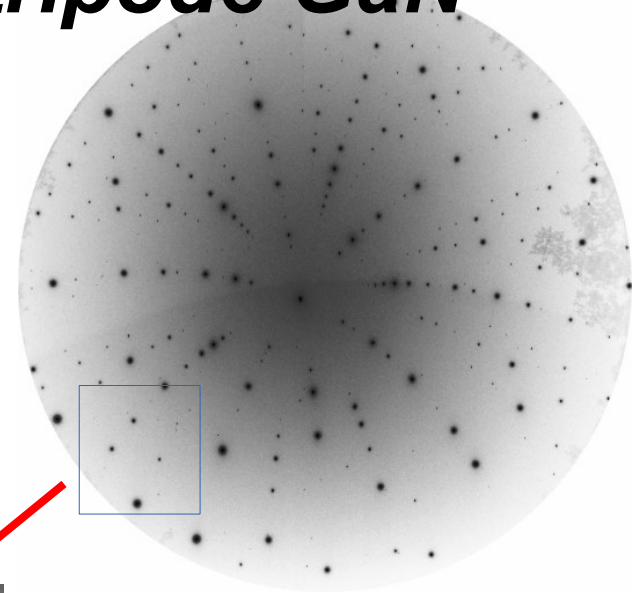
→ cartographie de déformation rapide

→ études *in-situ* (électromigration, micro-mécanique,...)

# Diffraction Micro-Laue : tripode GaN



• Carte fluorescence



• Tripode: diamètre 500 nm, longueur 8  $\mu\text{m}$ .

# Remerciements

Résolution de structures / diffraction sur poudre :

*Radovan Černý*

Lignes SOI :

*F. Mastropietro, J. Eymery, S. Baudot, F. Andrieu*

Diffraction résonante Ge/Si :

*H. Renevier, M. G. Proietti, M-I Richard, N Katcho, C. Leclère,  
G. Bauer, G Chen, J Zhang*

ESRF ID1:

*D. Carbone, T. Metzger, T. Cornelius, P. Boesecke, A. Diaz, T. Schüll*

ESRF CRG-D2AM:

*J-F. Bézar, N. Boudet, B. Caillot, S. Arnaud*

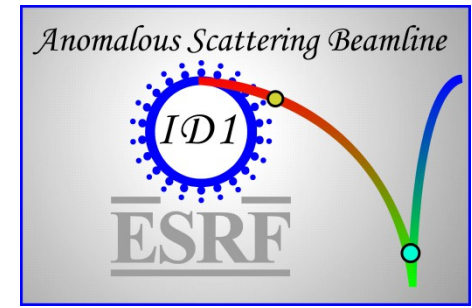
ESRF CRG-BM32 micro-Laue:

*O. Robach, O. Ulrich, JS Micha*

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**Projet ANR JC XDISPE project**

**Institut Universitaire de France**



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GRENOBLE

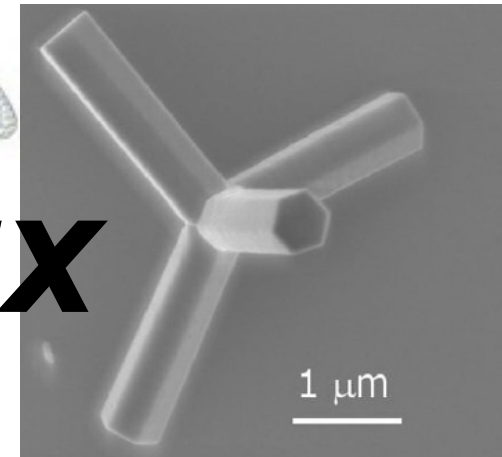
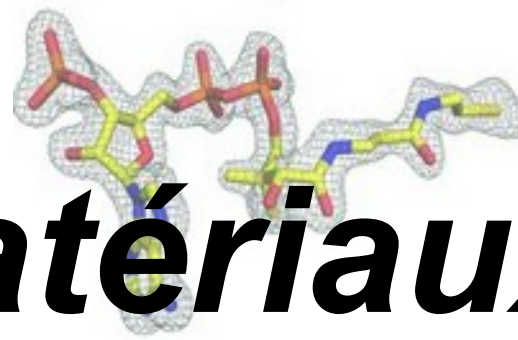
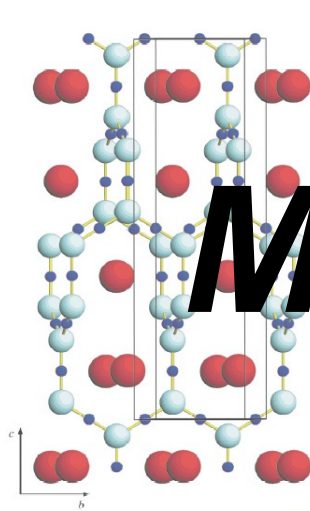
# Cristallographie

## ***Théorie***

*Tables internationales  
journals.iucr.org*

## ***Instrumentation***

*Laboratoire  
Synchrotron, neutrons, XFEL*



# ***Matériaux***

## ***Algorithmes & Logiciels***

*Open Source  
Open data*