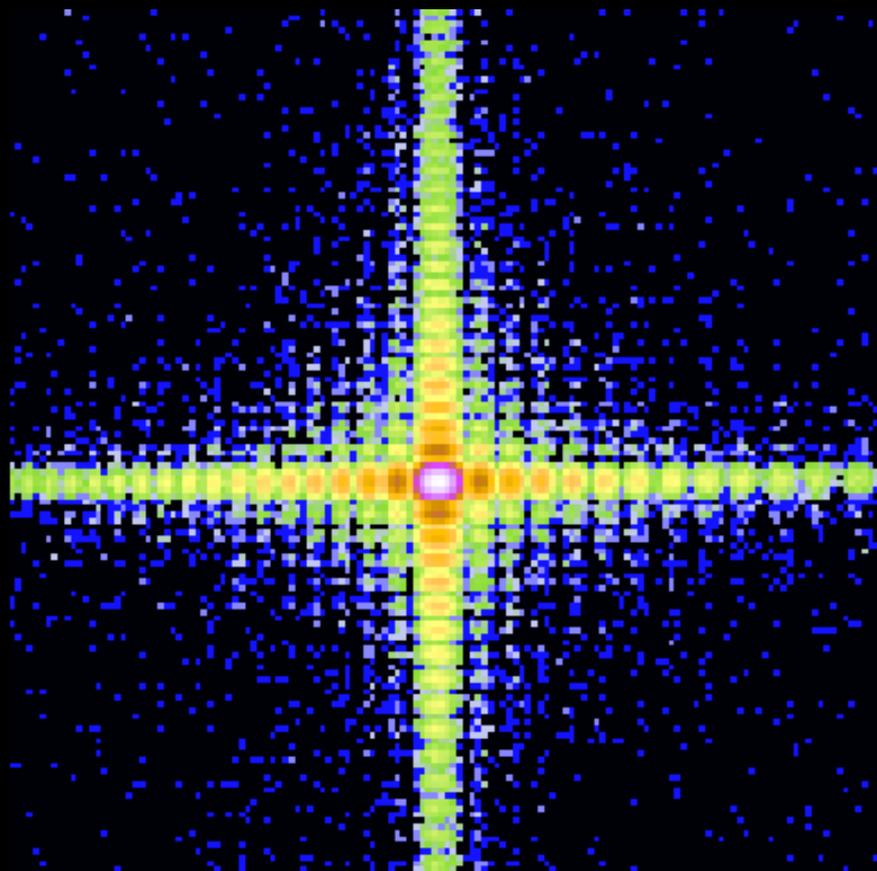


# Diffraction au **Synchrotron** **SOLEIL**



**Sylvain RAVY**

**Ligne CRISTAL**  
**Synchrotron SOLEIL**  
**Saint Aubin**  
**91192 Gif-sur-Yvette**  
**France**

# Les lignes de SOLEIL



**DIFFABS (D. Thiaudière) :**  
Dipôle (3-25 keV)  
• Diffraction-Absorption X

**PROXIMA 1 (A. Thompson)**  
**PROXIMA 2 (B. Shepard) :**  
Onduleur U20,U26 (5-15 keV)  
• Cristallographie des protéines

**SWING (J. Perez) :**  
Onduleur U20 (5-15 keV)  
• Diffusion aux petits angles,  
GISAXS

**CRISTAL (S. Ravy) :**  
U20 (4-30 keV)  
• Diffraction matière condensée

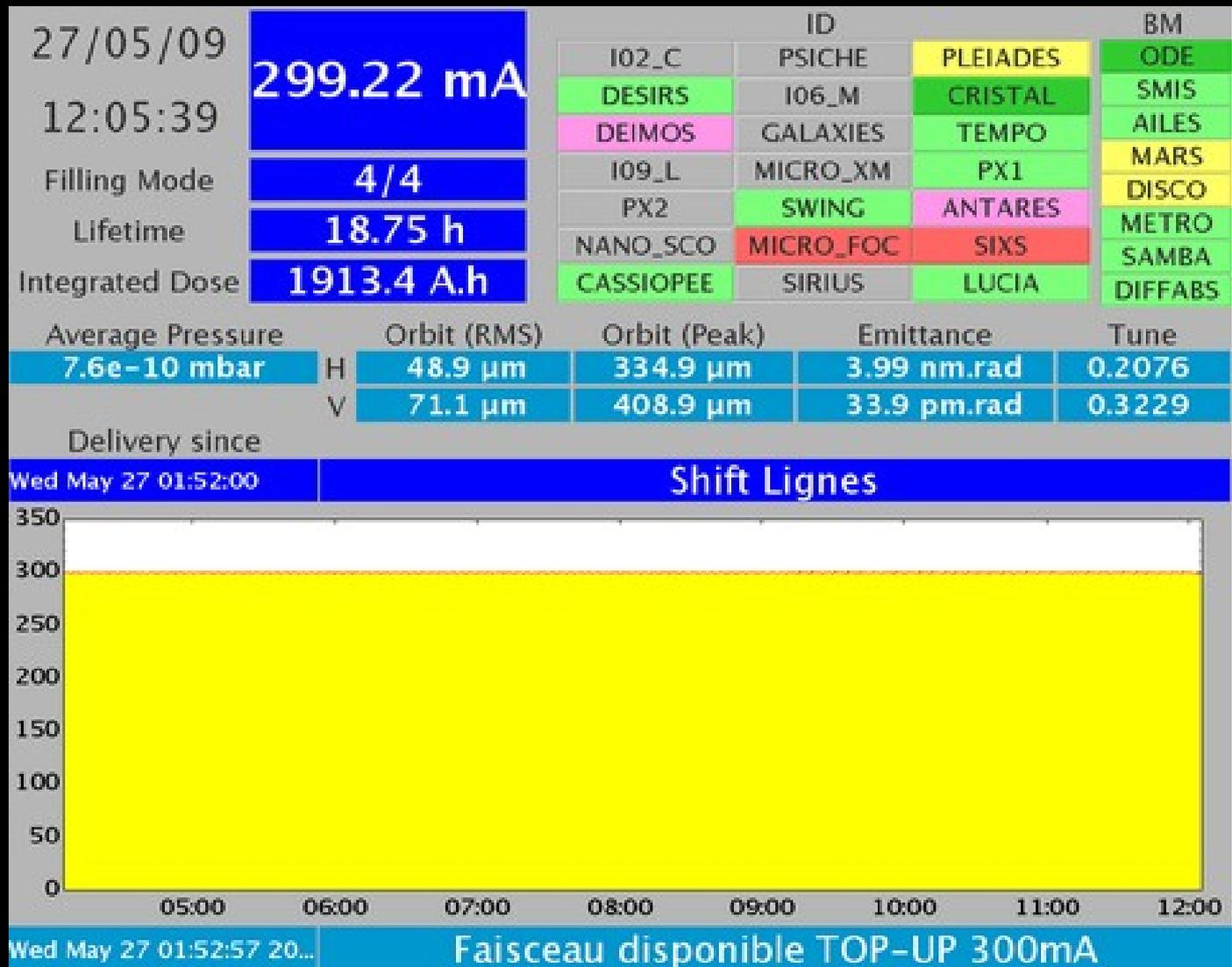
**MARS (B. Sitaud) :**  
Dipôle (5-30 keV)  
• Diffraction et Absorption  
• Matériaux radioactifs

**SIXS (Y. Garreau) :**  
Onduleur U20 (4-20 keV)  
• Diffraction sur des systèmes 2D  
• Diffraction magnétique 2D

**SIRIUS (Ph. Fontaine) :**  
Onduleur HU34 (2-10 keV)  
• Diffraction résonante et non rés.  
• Interfaces « molles » et  
magnétiques

**H<sup>te</sup> Pression (J.-P. Itié) :**  
Wiggler (10-70 keV)

# 20 Lignes ont pris du faisceau Mise en service du mode « Top-



# Calendrier de fonctionnement

janv 2009	févr 2009	2009	avr 2009	mai 2009	juin 2009	juil 2009	août 2009	sept 2009	oct 2009	nov 2009	déc 2009
jeu 01	dim 01	dim 01	mer 01	ven 01	lun 01	mer 01	sam 01	mar 01	jeu 01	dim 01	mar 01
ven 02	lun 02	lun 02	jeu 02	sam 02	mar 02	jeu 02	dim 02	mer 02	ven 02	lun 02	mer 02
sam 03	mar 03	mar 03	ven 03	dim 03	mer 03	ven 03	lun 03	jeu 03	sam 03	mar 03	jeu 03
dim 04	mer 04	mer 04	sam 04	lun 04	jeu 04	sam 04	mar 04	ven 04	dim 04	mer 04	ven 04
lun 05	jeu 05	jeu 05	dim 05	mar 05	ven 05	dim 05	mer 05	sam 05	lun 05	jeu 05	sam 05
mar 06	ven 06	ven 06	lun 06	mer 06	sam 06	lun 06	jeu 06	dim 06	mar 06	ven 06	dim 06
mer 07	sam 07	sam 07	mar 07	jeu 07	dim 07	mar 07	ven 07	lun 07	mer 07	sam 07	lun 07
jeu 08	dim 08	dim 08	mer 08	ven 08	lun 08	mer 08	sam 08	mar 08	jeu 08	dim 08	mar 08
ven 09	lun 09	lun 09	jeu 09	sam 09	mar 09	jeu 09	dim 09	mer 09	ven 09	lun 09	mer 09
sam 10	mar 10	mar 10	ven 10	dim 10	mer 10	ven 10	lun 10	jeu 10	sam 10	mar 10	jeu 10
dim 11	mer 11	mer 11	sam 11	lun 11	jeu 11	sam 11	mar 11	ven 11	dim 11	mer 11	ven 11
lun 12	jeu 12	jeu 12	dim 12	mar 12	ven 12	dim 12	mer 12	sam 12	lun 12	jeu 12	sam 12
mar 13	ven 13	ven 13								ven 13	dim 13
mer 14	sam 14	sam 14								sam 14	lun 14
jeu 15	dim 15	dim 15								dim 15	mar 15
ven 16	lun 16	lun 16								lun 16	mer 16
sam 17	mar 17	mar 17								mar 17	jeu 17
dim 18	mer 18	mer 18								mer 18	ven 18
lun 19	jeu 19	jeu 19								jeu 19	sam 19
mar 20	ven 20	ven 20								ven 20	dim 20
mer 21	sam 21	sam 21								sam 21	lun 21
jeu 22	dim 22	dim 22								dim 22	mar 22
ven 23	lun 23	lun 23								lun 23	mer 23
sam 24	mar 24	mar 24								mar 24	jeu 24
dim 25	mer 25	mer 25								mer 25	ven 25
lun 26	jeu 26	jeu 26								jeu 26	sam 26
mar 27	ven 27	ven 27								ven 27	dim 27
mer 28	sam 28	sam 28								sam 28	lun 28
jeu 29		dim 29								dim 29	mar 29
ven 30		lun 30								lun 30	mer 30
sam 31		mar 31								mar 31	jeu 31

4 432 heures faisceau Lignes  
 + 152 heures pour les tests RP  
 +1 440 heures pour les tests Machine  
 = 36 semaines de fonctionnement



# CRISTAL Beamline: Undulator (4-30 keV) Diffraction

**Sylvain Ravy, Erik Elkaïm, Pierre Fertey**

**El-Eulmi Bendeïf, Vincent Jacques, Fabien Legrand**

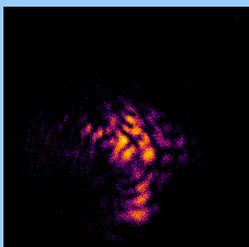
## 6-circles



**Newport-6-circle diffractometer**  
Kappa, SOC 60  $\mu\text{m}$

**15 kg samples**  
Versatile instrument

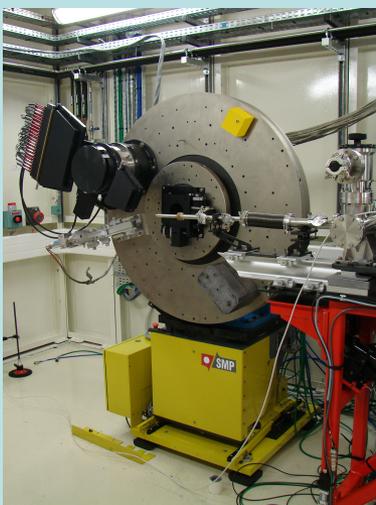
**Cryostat 4 K**



**Out-of-Bragg**  
and  
**Coherent**  
Diffraction

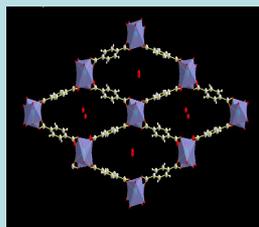
## 2-circles

**Powder diffraction**



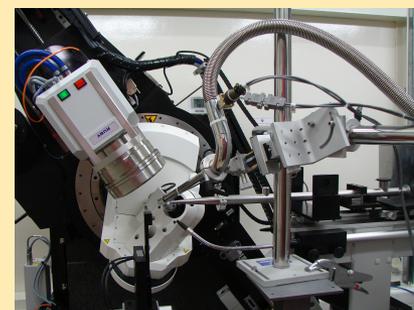
**Diffractomètre SMP**  
2'' résolution

**21 analyzers/detectors**



**High-résolution**  
**ab initio struct.**

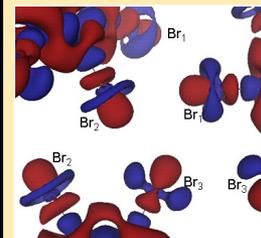
## 4-circles



**Newport-Oxford Diffraction**  
4-circle diffractometer  
Kappa, SOC 8  $\mu\text{m}$

**Oxford CCD ATLAS detector**

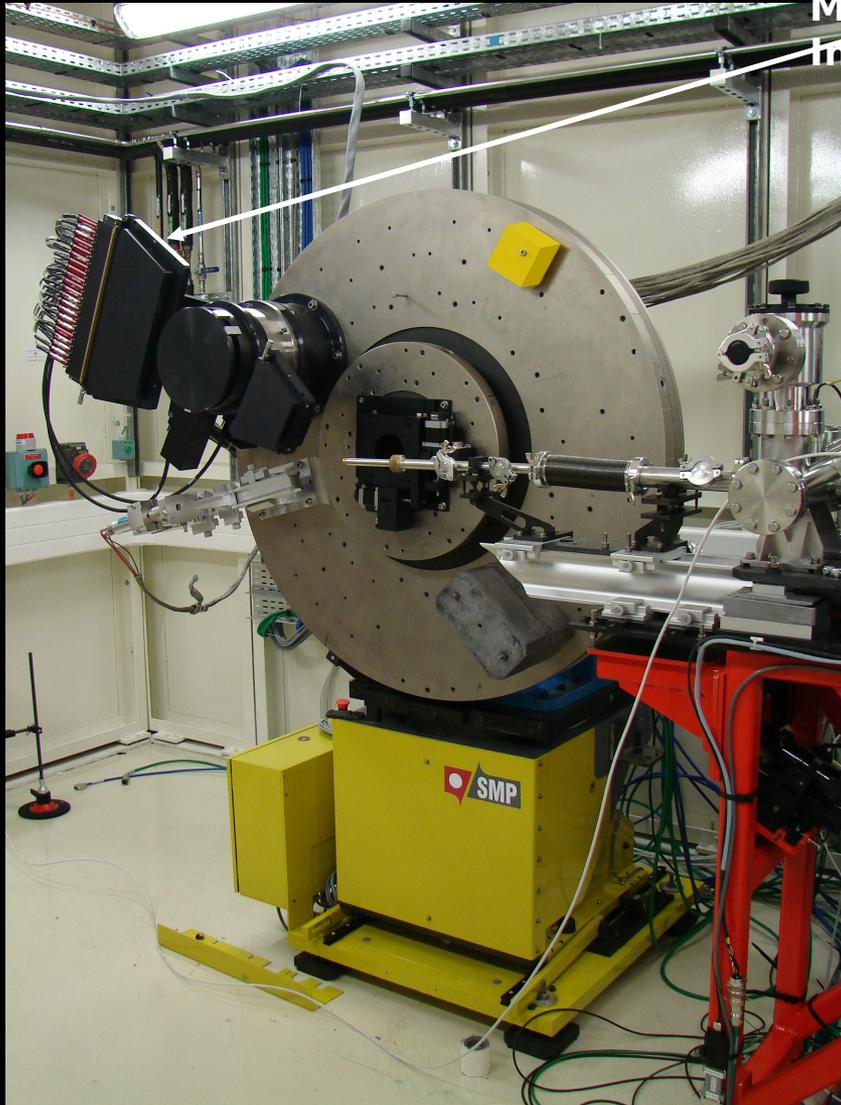
**N<sub>2</sub>/He Blower**



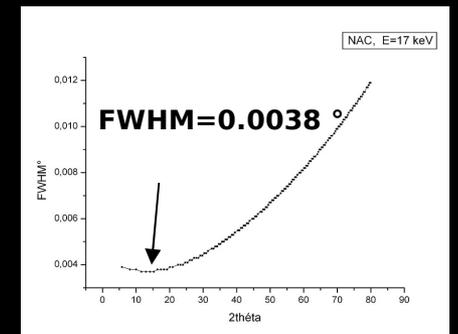
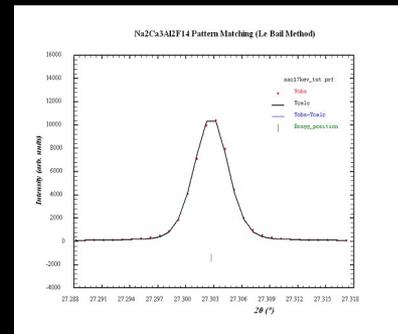
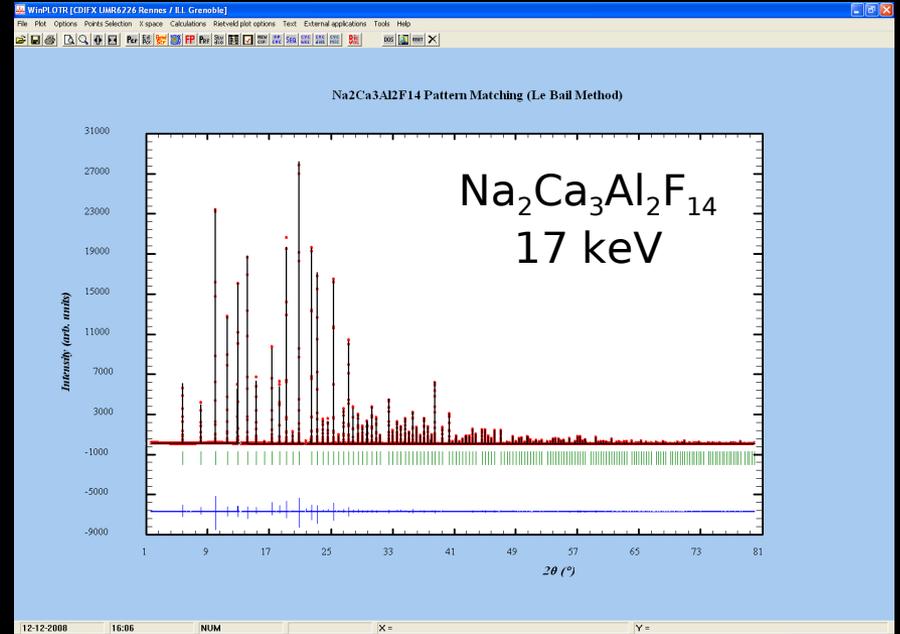
**Crystallography**  
**electron density**



# 2-circles diffractometer



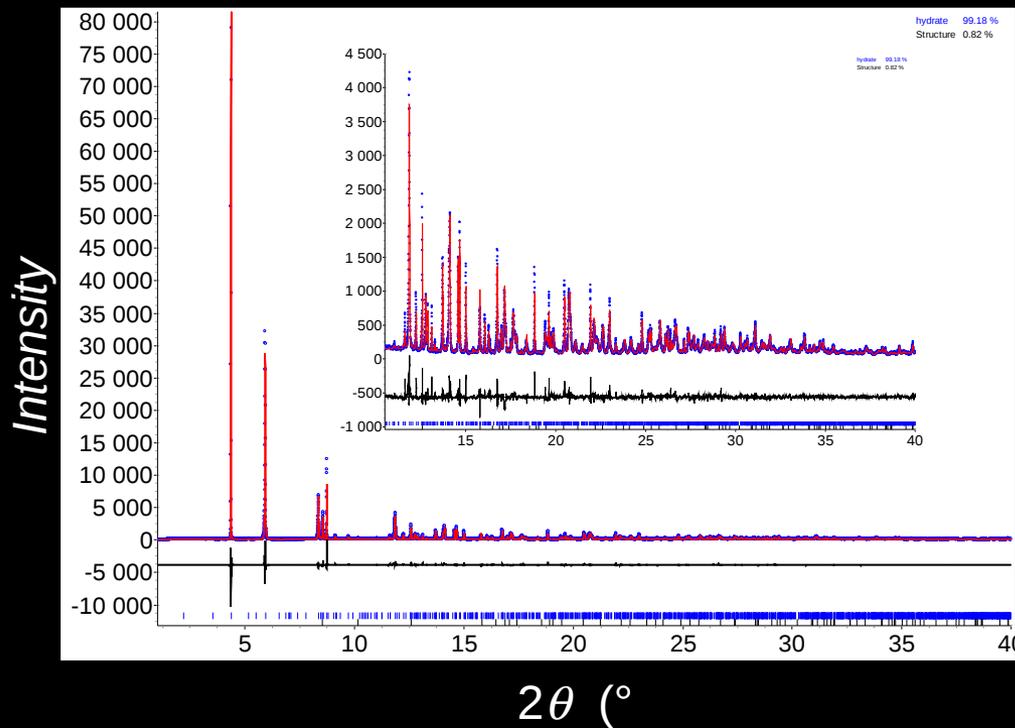
Multi-analyser: 21 detectors in use  
In continuous scanning mode: 1 diagram ~2hours



# XRD and IR structural investigations of a special breathing effect in the MOF-type gallium terephthalate MIL-53(Ga)

Christophe Volkringer, Thierry Loiseau, Nathalie Guillou, Gérard Férey, Erik Elkaïm and Alexandre Vimont  
Institut Lavoisier (Versailles) and Laboratoire de catalyse et spectrochimie (Caen).

To be published in Dalton Trans.



2 hours data acquisition on 2-circles

$R_B = 4.01\%$   
atoms

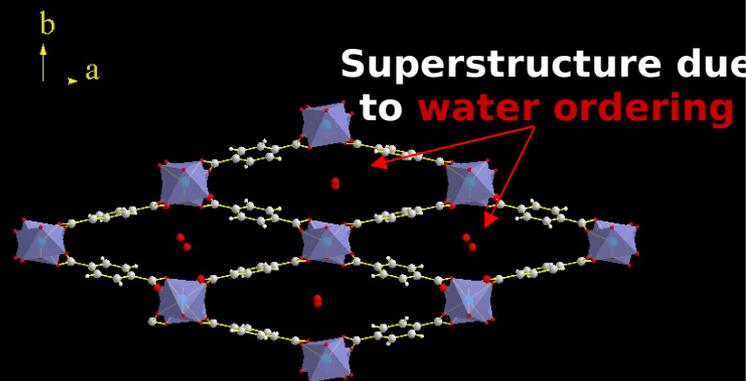
$R_{wp} = 12.18\%$

gof = 1.94 %

31 independant non-hydrogen

treated as rigid bodies

Nano-porous material

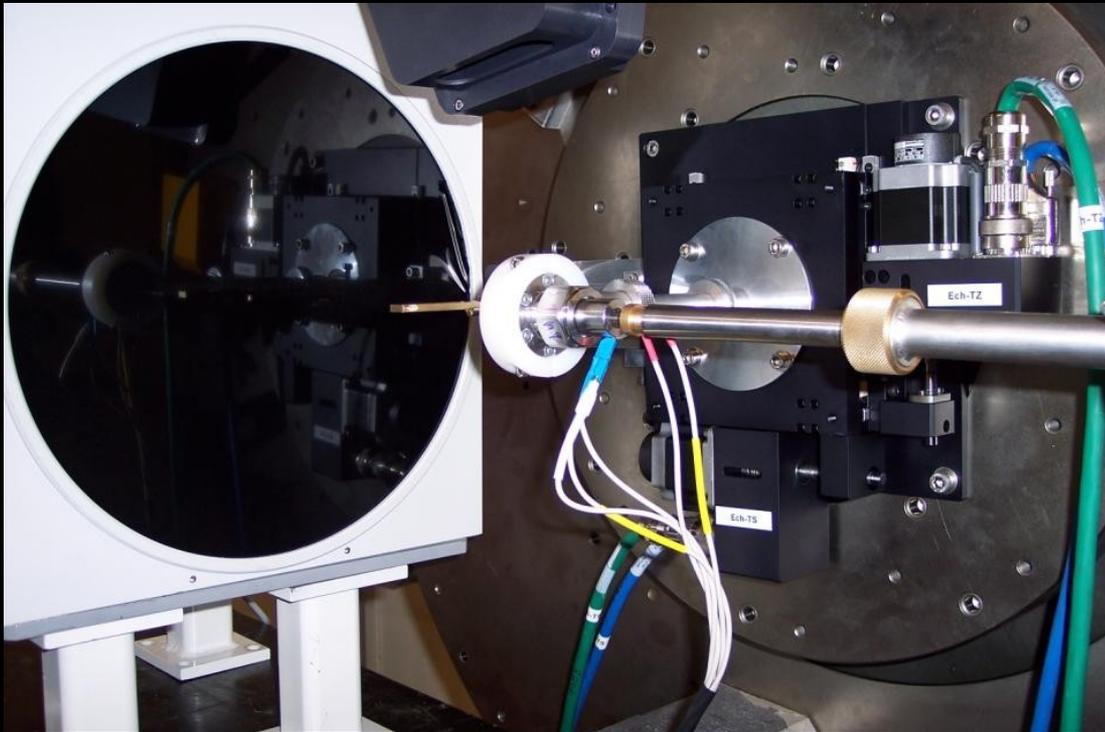


$a = 19.7053(2) \text{ \AA}$   
 $b = 15.16417(4) \text{ \AA}$   
 $c = 6.68117(9) \text{ \AA}$   
 $\beta = 103.7936(8)^\circ$   
 $V = 1938.85(7) \text{ \AA}^3$

Space group  $P2_1/c$

**In operando X-ray diffraction of a  $\text{LiFePO}_4$  battery**  
**ANR PULSSE Ch. Masquelier, Amiens**

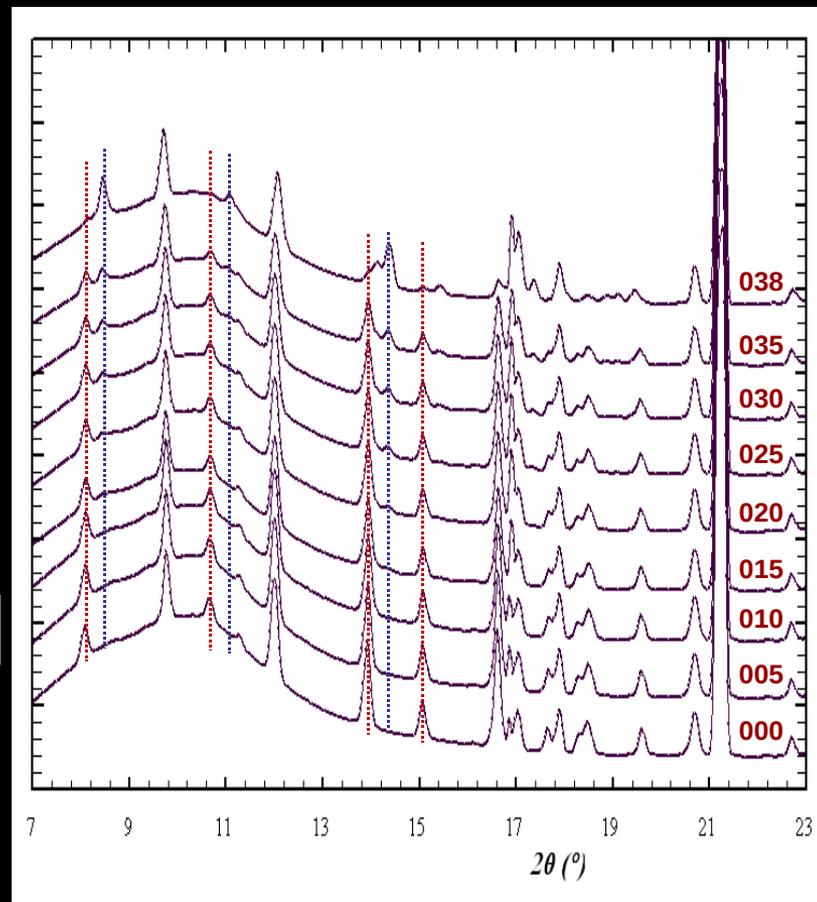
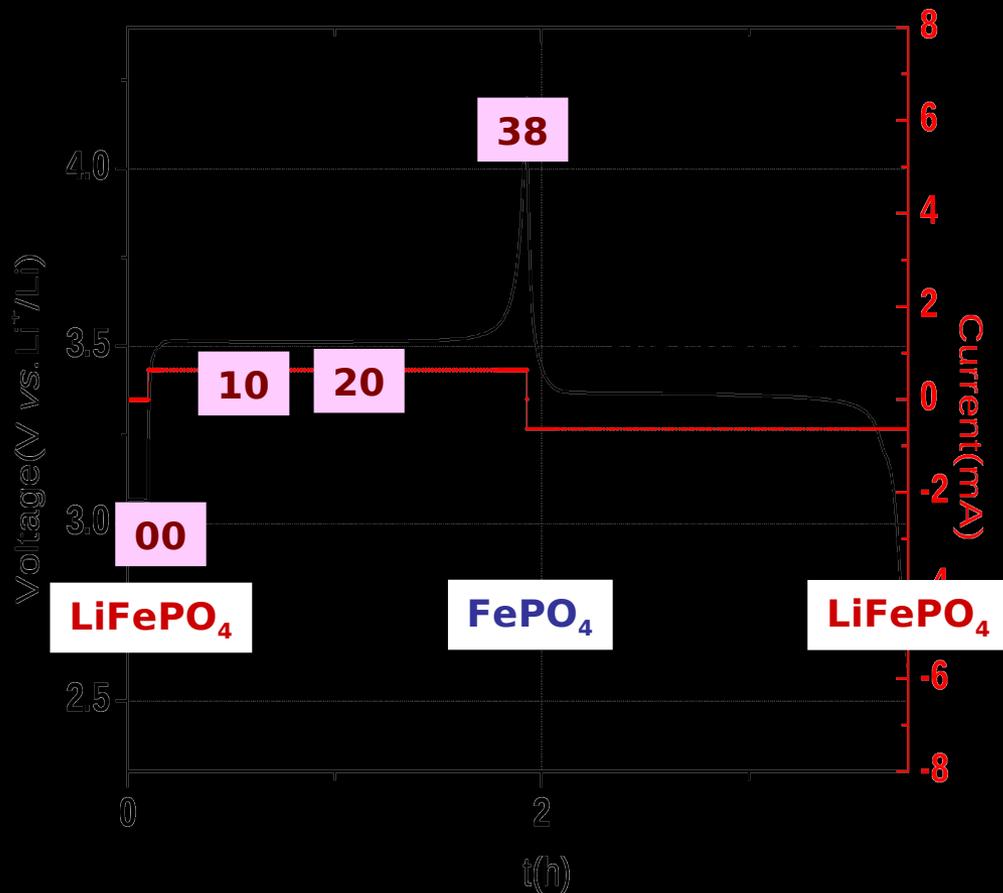
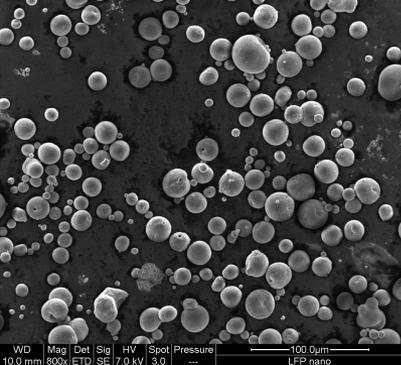
Use of the **MAR 345** to decrease acquisition time  
**1 diagram / 3 mn**



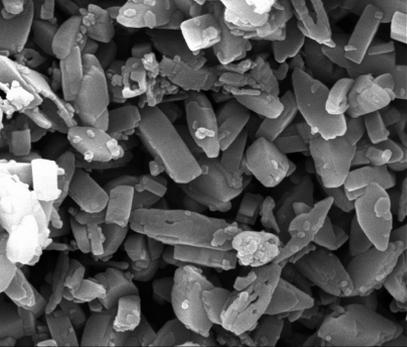
**Electrochemical cell for**  
***in operando* XRD or XAS in**  
**transmission geometry**

# Batteries Li / Electrolyte / $\text{LiFePO}_4$

One **XRD pattern** (recorded within 10 sec.) **every 3 min.**  
Wavelength :  $\lambda = 0.727 \text{ \AA}$



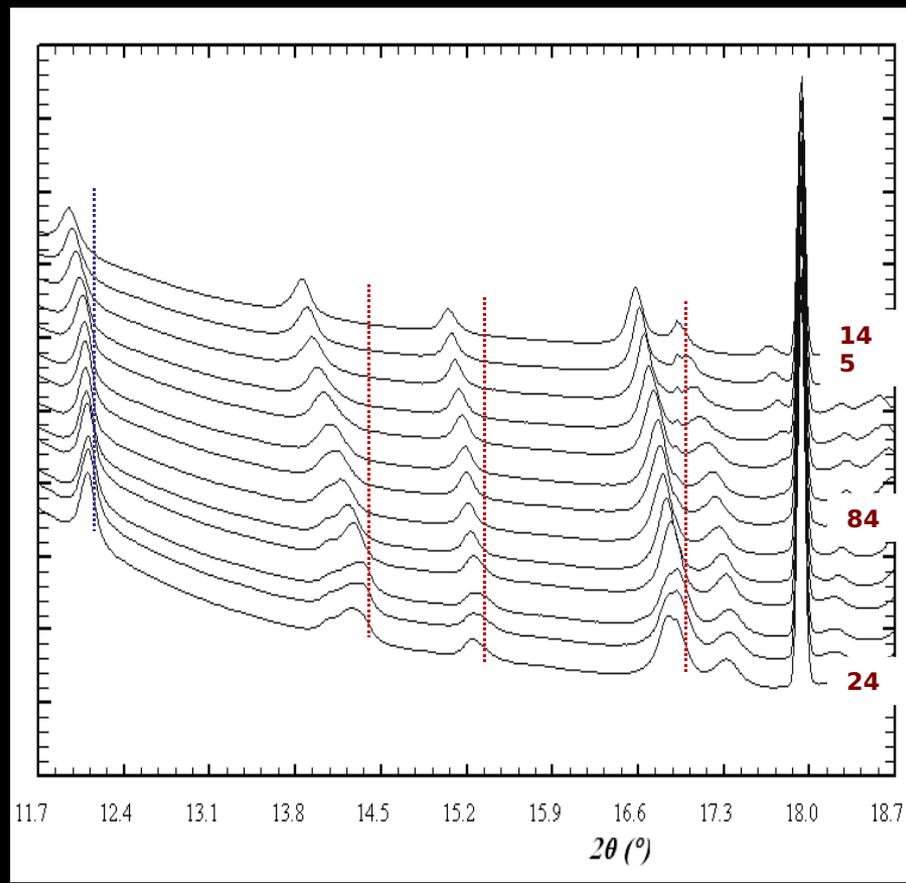
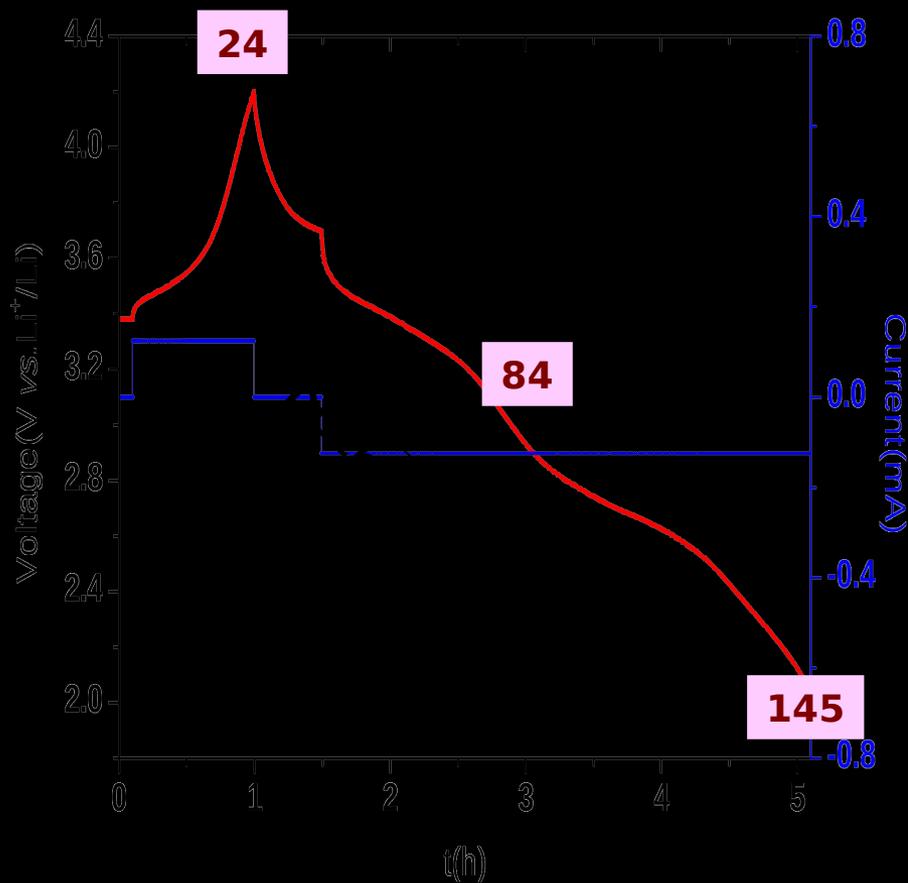
- Intercalation plateau associated with a **two-phase reaction** : classical
- **Late crystallization of second phase** (delay) observed at high rate : **NEW !!**



# Complete **solid-solution** behaviour during Li<sup>+</sup> insertion into **defective Li<sub>x</sub>FePO<sub>4</sub>** : **NEW !!**

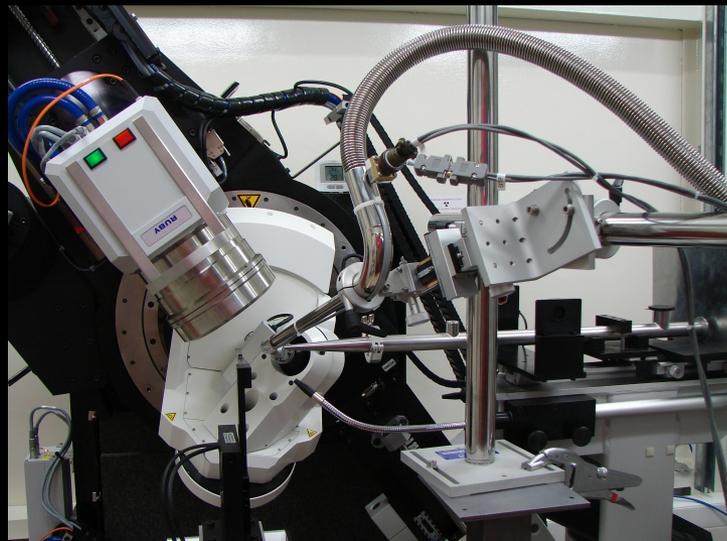
**No late crystallisation this time ! interesting**

12.20 kV 100 000 x ETO SE 6.0 mm 7.91e-6 Torr 1 μm LFPBAT820c





# 4-circles diffractometer

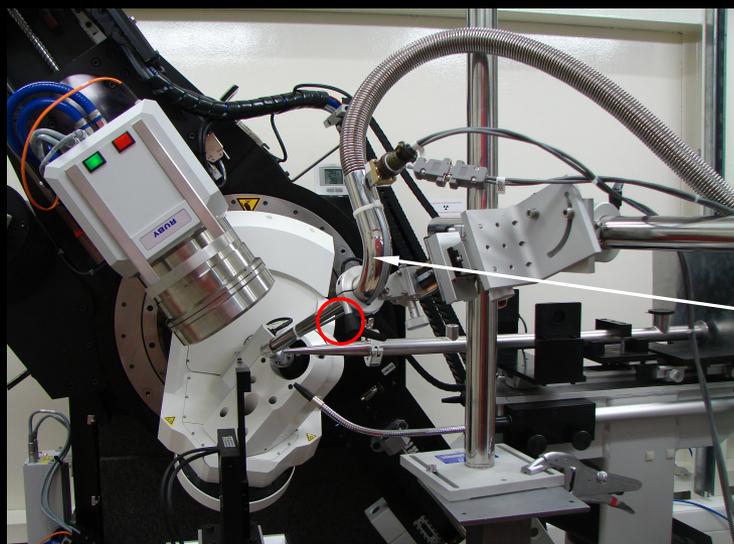


**Electron density studies**

**Incommensurate crystals**

# Topological Analysis of Experimental Electron-Densities of Halogen...X Interactions (X = Halogen, Lewis base)

Slimane DAHAOUI, CRM<sup>2</sup> Nancy



« Newport-Oxford Diffraction »  
4 circle diffractometer  
Detector upgrade: Atlas

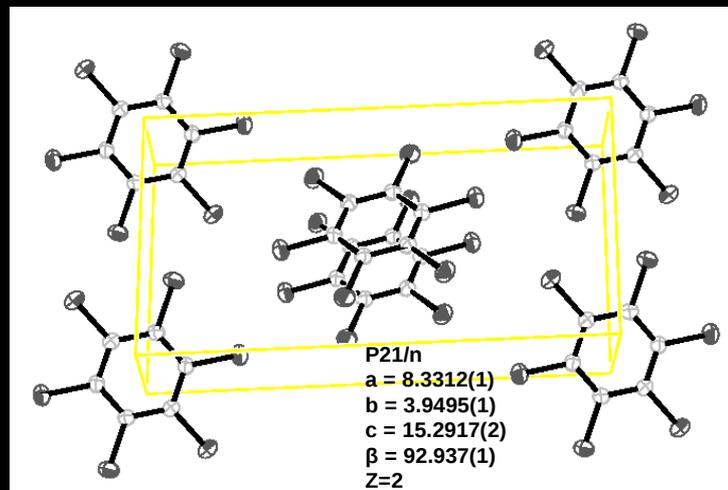
N<sub>2</sub> blower, T=100 K

Hexabromobenzene - C<sub>6</sub>Br<sub>6</sub>

3 shifts data acquisition @ 30 keV  
 $0.066 \text{ \AA}^{-1} < s = \sin\theta/\lambda < 1.530 \text{ \AA}^{-1}$

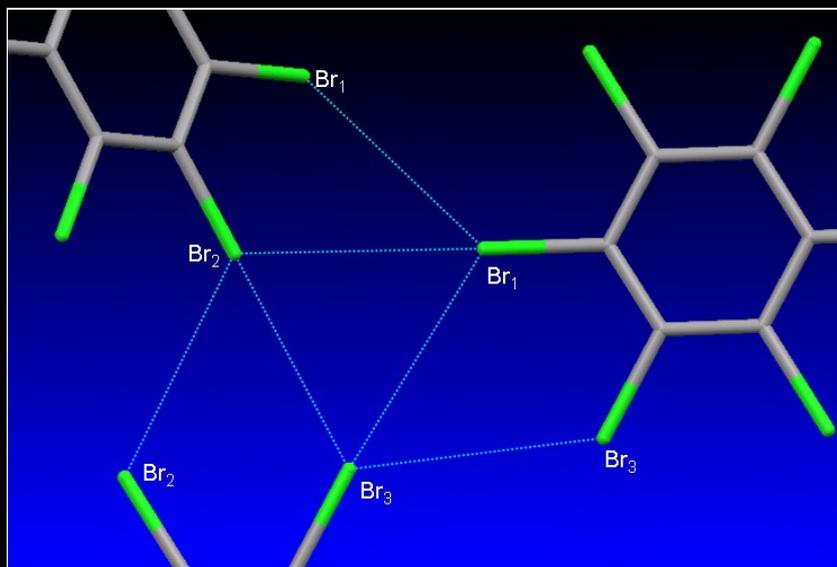
162360 Total measurements  
14690 unique reflections

Overall completeness = 97.8 %

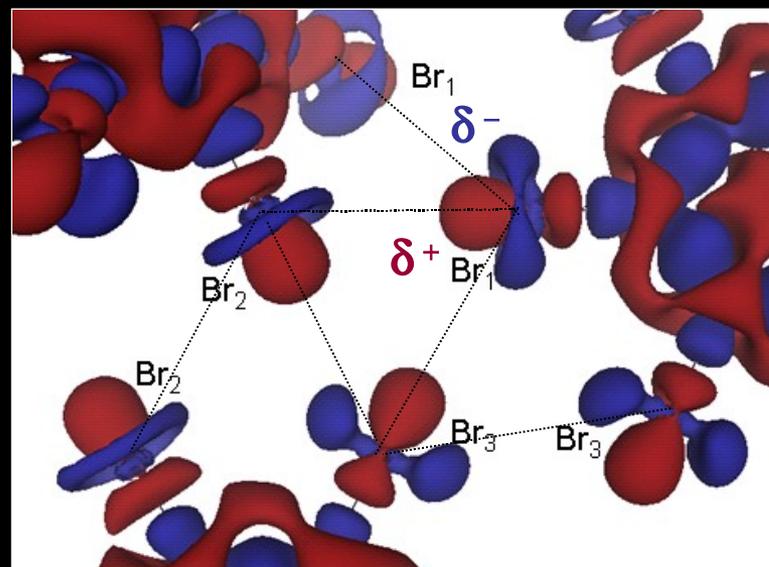


# Multipolar expansion of electron density Hansen-Coppens model

Synthon System



Static deformation map



$$\Delta\rho_{\text{stat}}(r) = \rho_{\text{multipole}}(r) - \rho_{\text{spherical}}(r)$$

The **anisotropic distribution** of electron density  
and halogen atom is the **origin of the halogen bonding interaction**

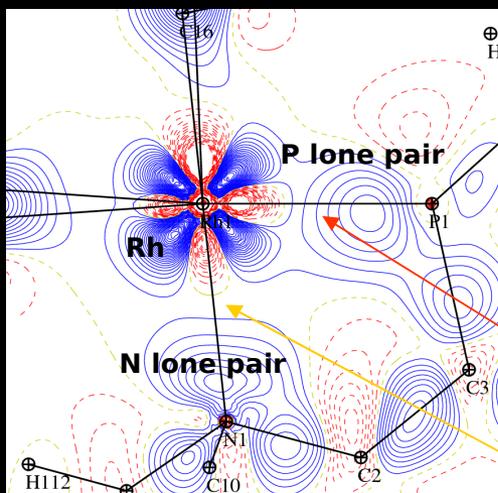
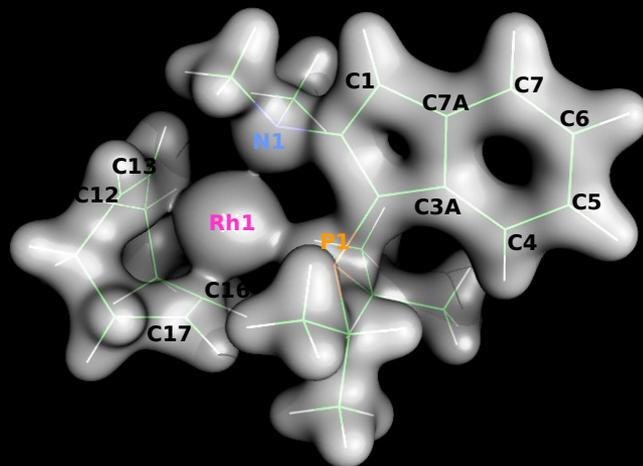
# Electron density study of metal-ligand interactions in a new Rhodium complex :



El-Eulmi Bendeif (CRISTAL), Cherif Matta (Halifax, CA)

**First use**  
of the He blower on CRISTAL  
T=30 K  
E=22.651 keV < Rh K edge

**Total electron density**  
From ~800.000 Bragg  
Resolution  $\sin\theta/\lambda = 0.3 \text{ \AA}^{-1}$



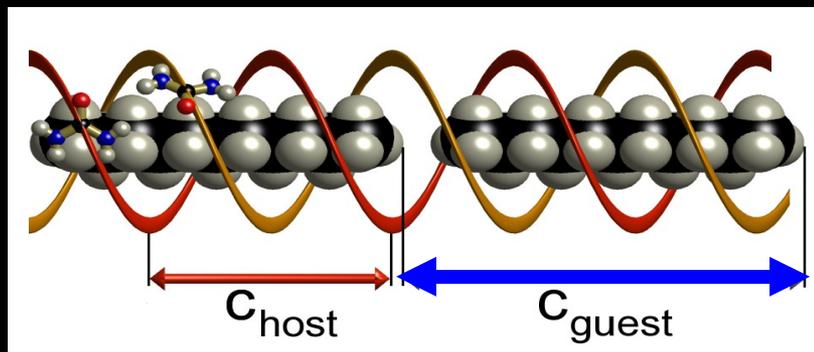
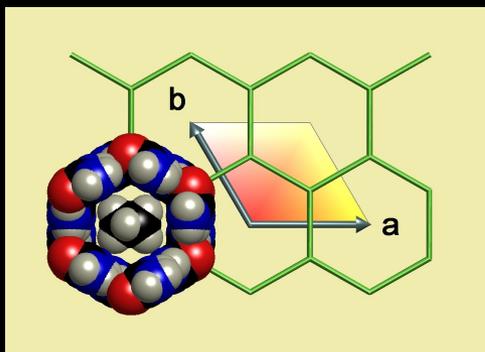
Static **deformation** map  
(total minus spherical)  
around **heavy Rh atom**

Study of **interactions** between  
Rh and N, P, C

**P-Rh** bond  
stronger  
than  
**N-Rh** one

# Phase transition in a superspace: Tetracosane-urea $C_{24}H_{50}$ -urea

B.Toudic, P. Rabiller, M. Huard and M.D. Hollingsworth  
 Institut de Physique de Rennes and Université de Manhattan, Kansas,  
 USA



Incommensurability parameter  $\alpha = c_{\text{host}}/c_{\text{guest}}$

Depending on **the alkane**, these compounds stabilize interesting **incommensurate phases**

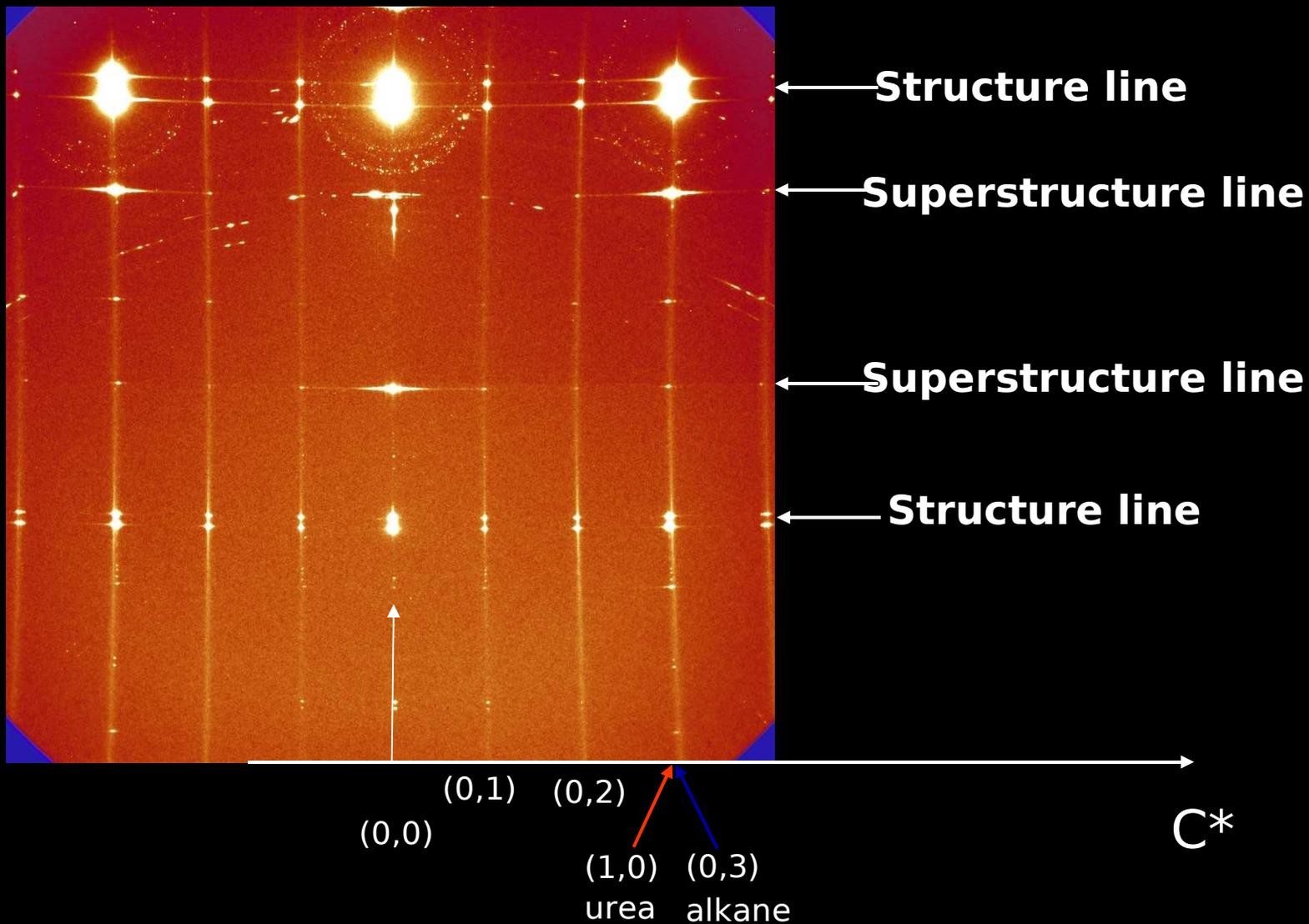
Example: Discovery of a **phase transition in the superspace** in  $C_{19}H_{40}$ -urea

	<p>Hidden Degrees of Freedom in Aperiodic Materials          Bertrand Toudic, <i>et al.</i>  <i>Science</i> 319, 69 (2008);          DOI: 10.1126/science.1146745</p>
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Issue, when  $\alpha$  is **close to 1/3** is there a **lock-in phase transition?**

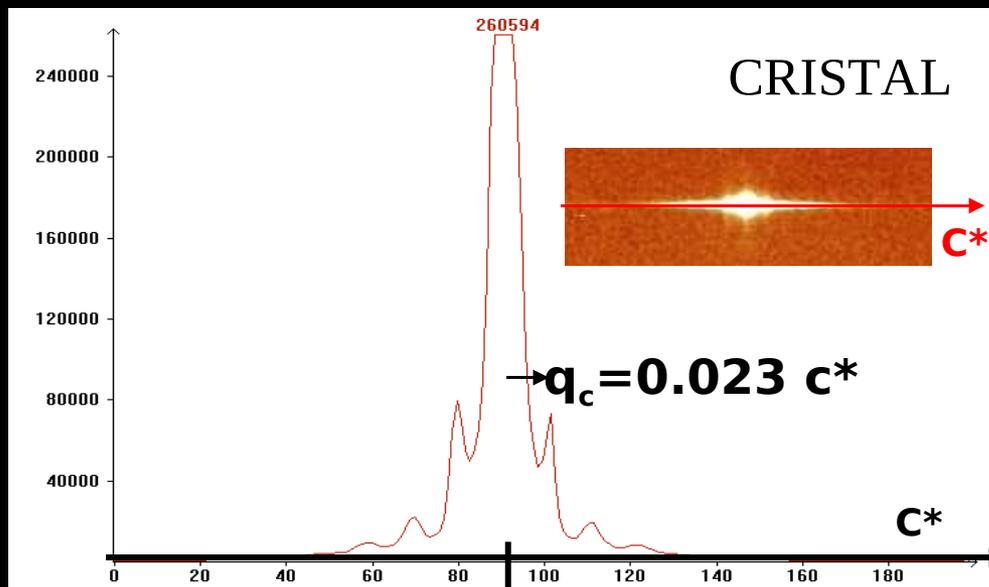
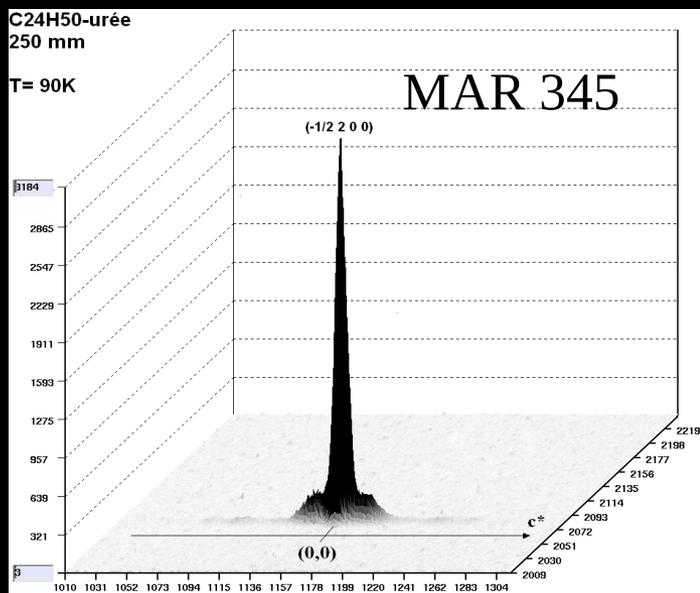
# Phase transition in a superspace: Tetracosane-urea $C_{24}H_{50}$ -urea

T=90 K  
8 keV





**No lock-in: the crystal remains aperiodic even if  $\alpha$  is so close to  $1/3$  (0.335)**



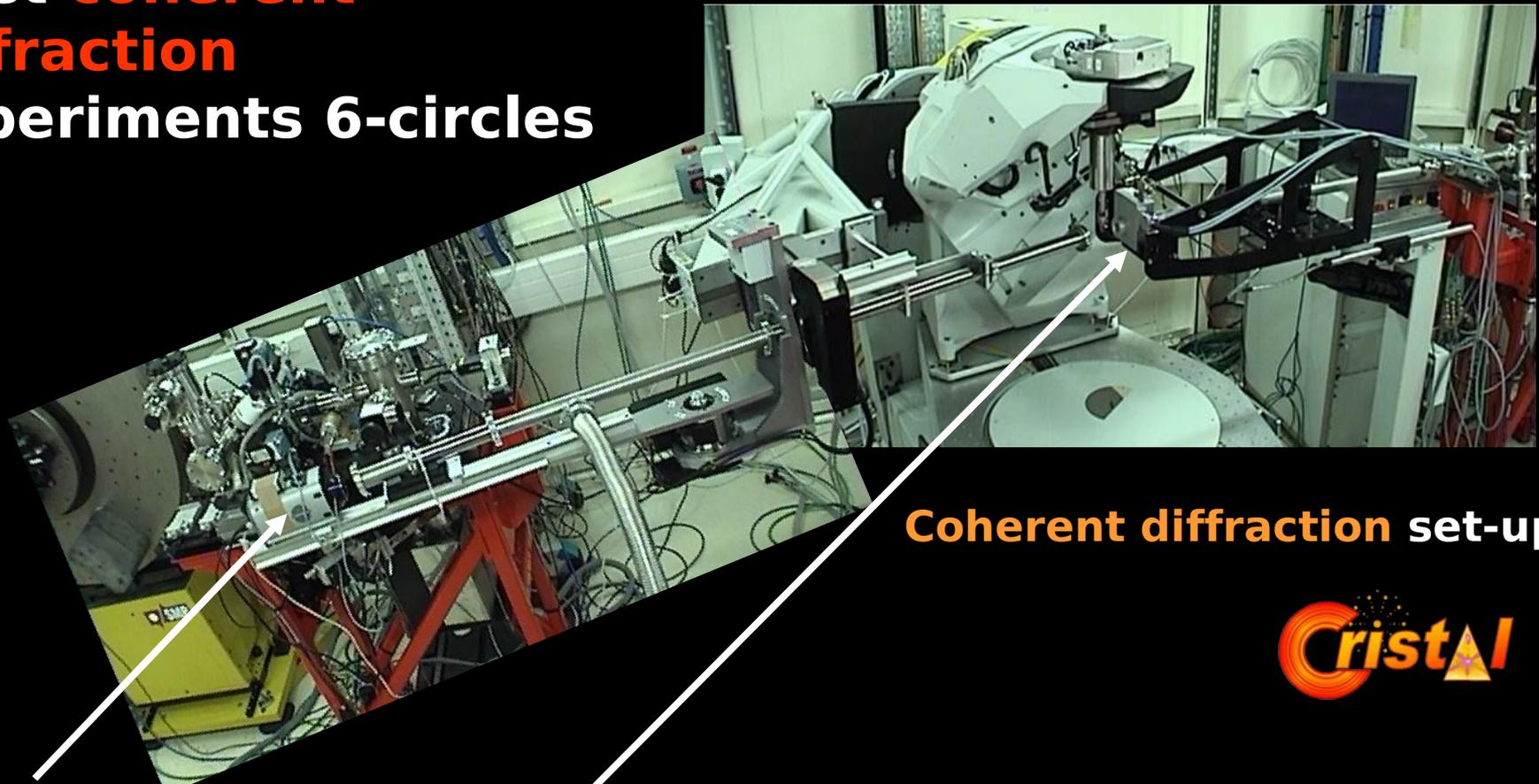
**Discovery of a new characteristic length  $\sim 270 \text{ \AA}$  below  $T_c$**

**corresponding to  $q_c = 0.023 c^*$**

**A phase transition from dimension 4 to dimension 5**

**Resolution is needed for such measurements**

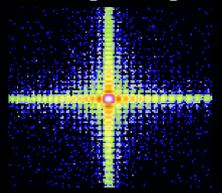
# First coherent diffraction experiments 6-circles



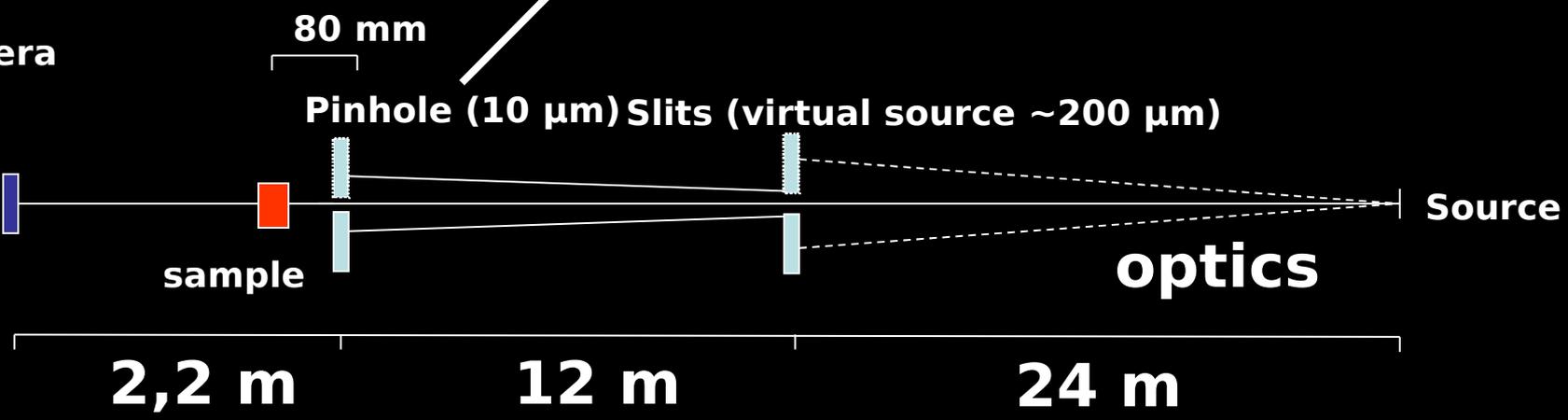
Coherent diffraction set-up



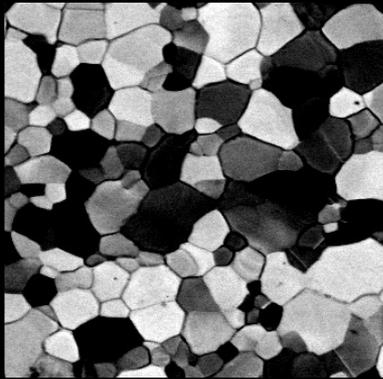
Detector  
CCD Camera  
13  $\mu\text{m}$  px



Degree of Coherence  
 $\beta = 45\%$

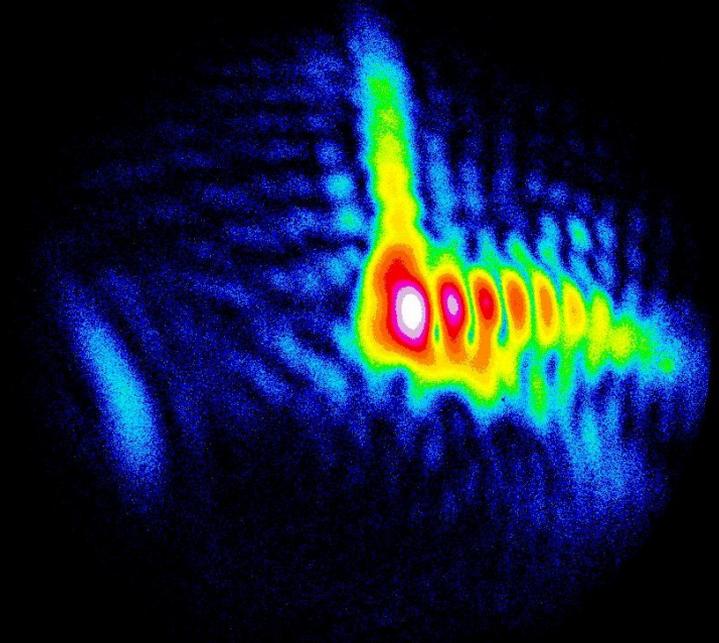


Study of **strain** in Au thin films (S. Labat, N. Vaxelaire, IM2NP Marseille)  
**RISTAL** beamline, SOLEIL



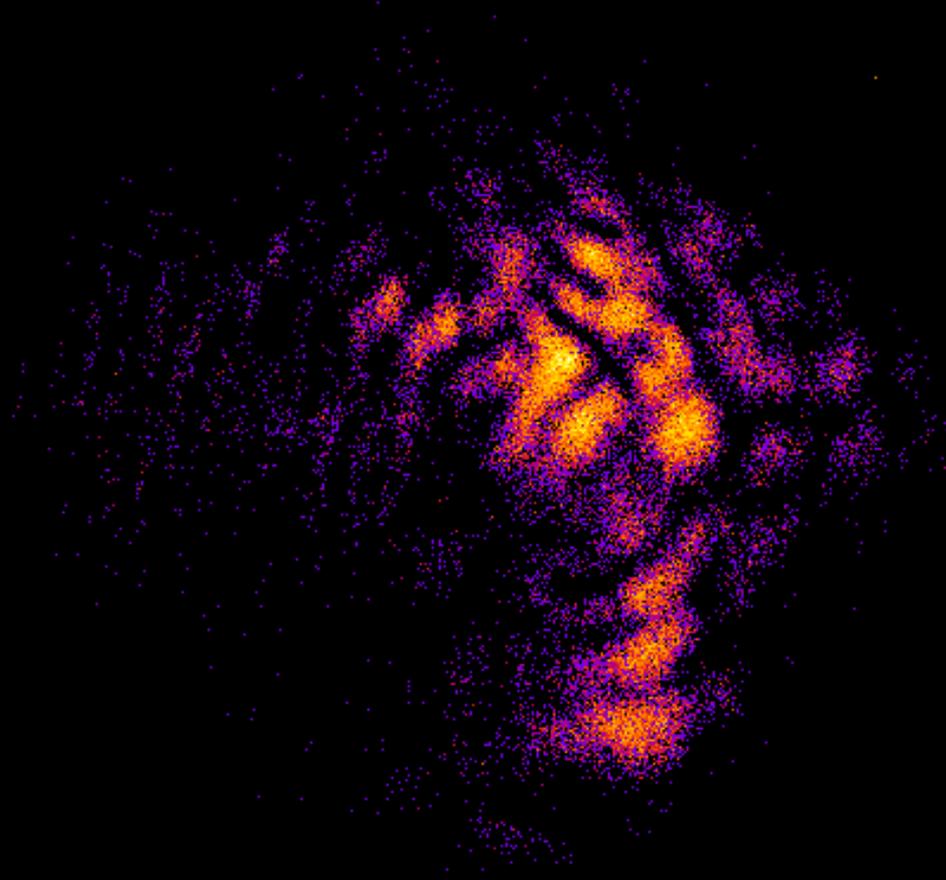
10  $\mu\text{m}$

**Asymmetry** of fringes  
due to **strain**



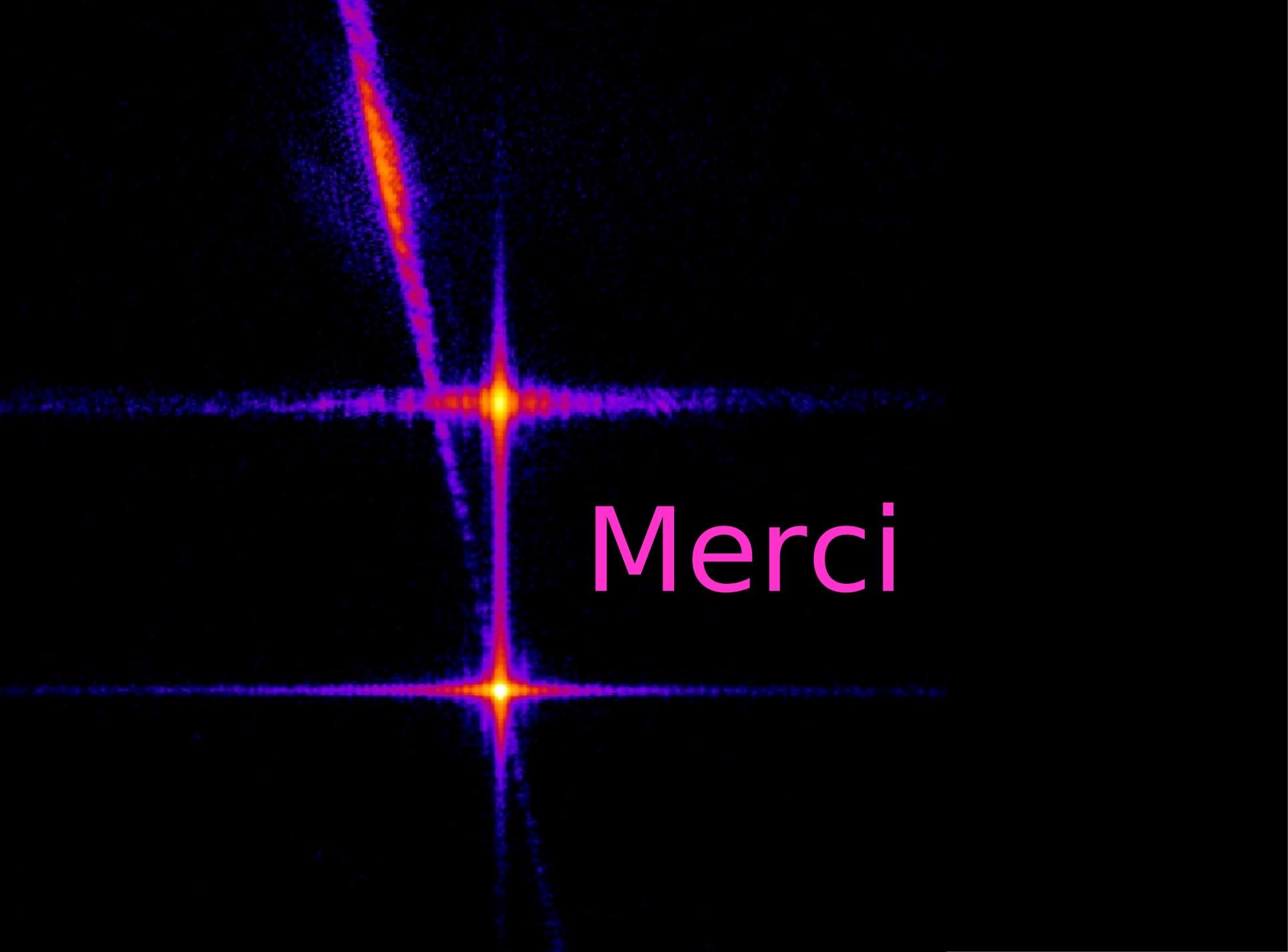
Main difficulty:  
**Select only one grain!**

**(111) « rocking curve » (20 x 0.015°) @5.2 keV**  
**of a ~ 800 nm x 800 nm x 200 nm grain**  
**Selected by 10 μm x 10 μm slits**



**8 h data acquisition**

**To be reconstructed!**



Merci