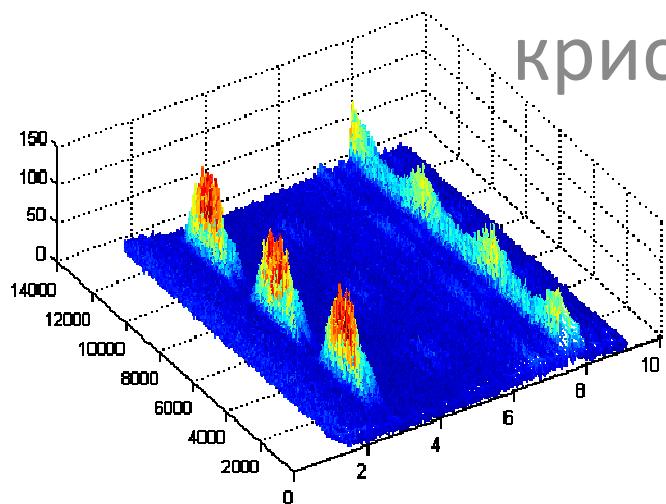


# Модуляционная дифракция

Новый способ изучения  
кристаллических и магнитных  
структур



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Лаборатория нейтронных исследований ФТИ им. А.Ф. Иоффе РАН 2010



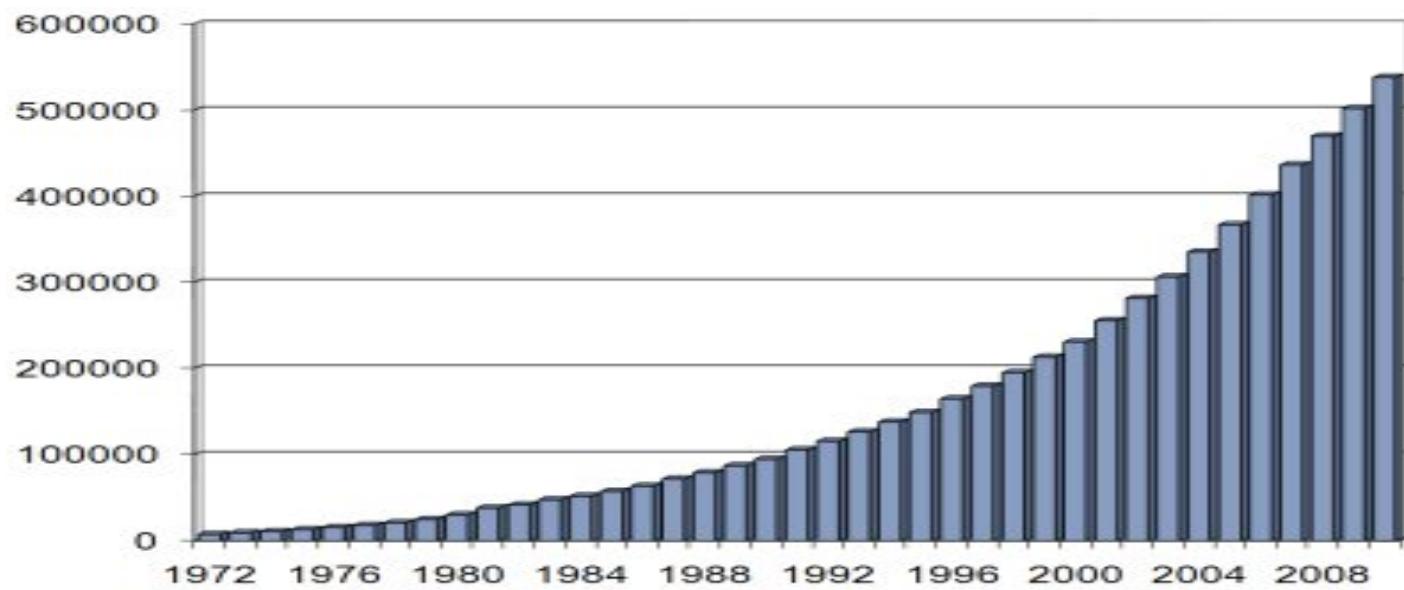
# 100 лет назад



Max Theodor Felix von Laue

The very first diffraction pattern. 1912

# сегодня



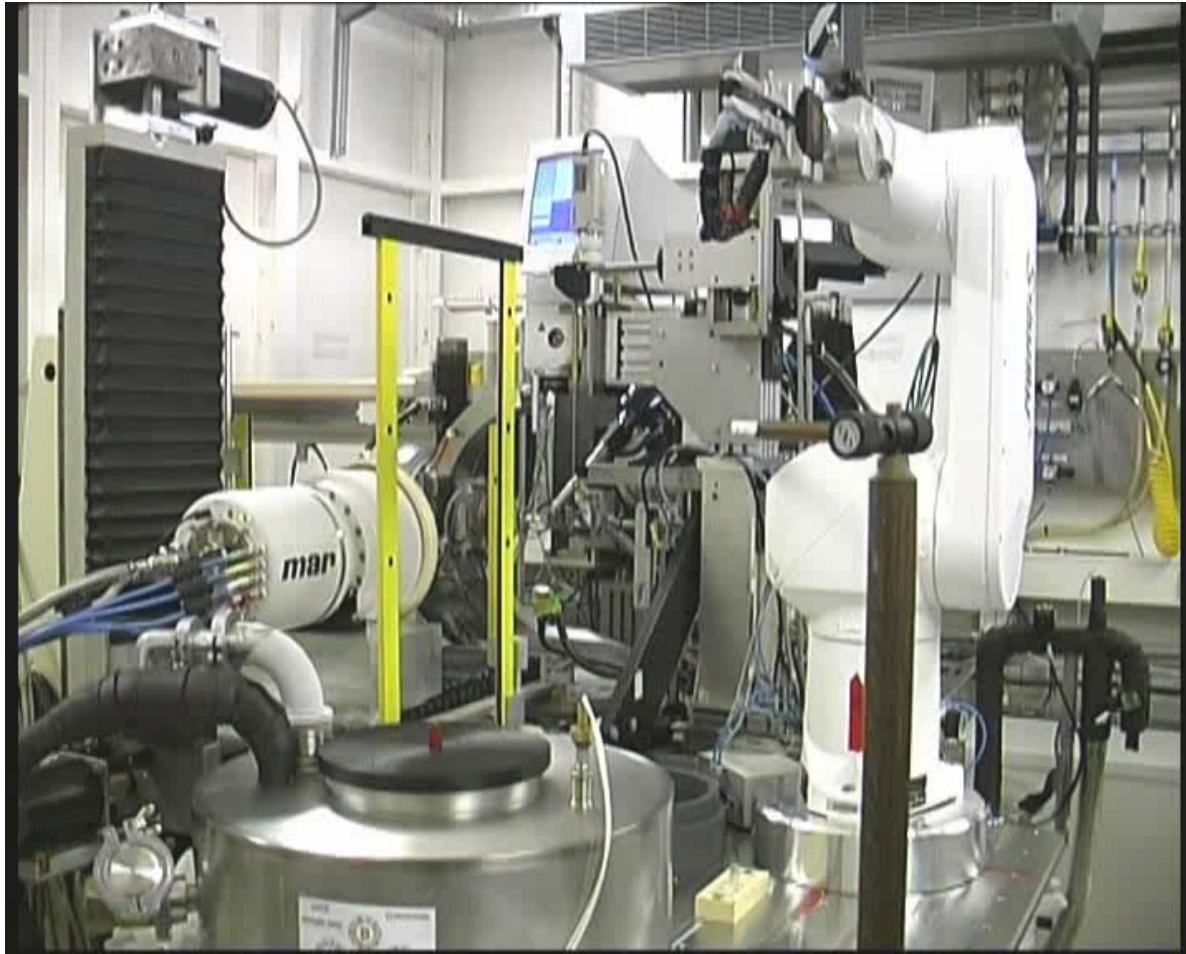
Number of published crystal structures

# Современные источники рентгеновского излучения



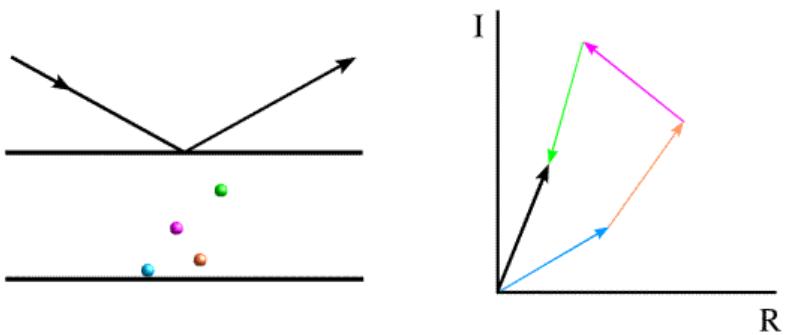
- ※ Большая яркость, быстрое детектирование рассеянного излучения
- ※ Возможность измерять слабые сечения рассеяния
- ※ Временная эволюция образца
- ※ Imaging, coherency, nanofocusing и пр.

# Автоматизация экспериментов

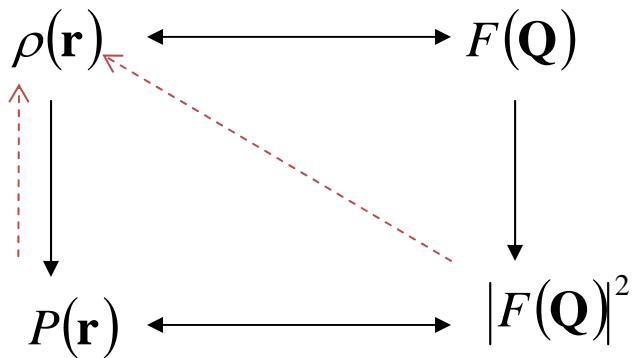


# Проблема Кристаллографии

## 1<sup>я</sup> - фазовая



$$I(\mathbf{Q}) = \left| \sum_1^N \mu_j f_j \exp(i\mathbf{QR}_j) \right|^2 = |F(\mathbf{Q})|^2$$



- \* Измерения дифракционных интенсивностей дают только модуль структурной амплитуды. Фазы не определяются.
- \* Даже измерив много рефлексов (много больше числа атомов) координаты атомов вычислить нельзя.
- \* Но координаты атомов все же можно определить – статистическими методами.

# Проблема 2<sup>я</sup> – разделение вкладов

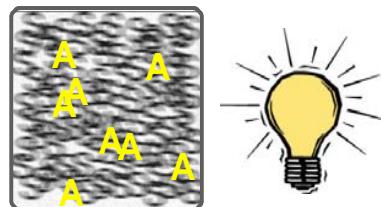
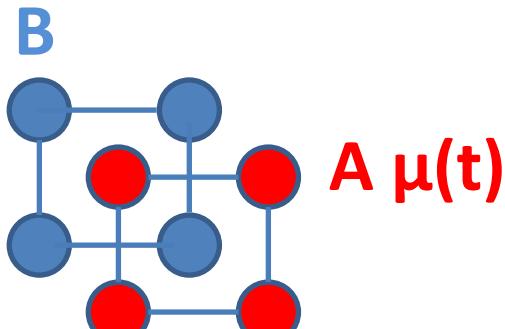
$$\rho(\mathbf{r}) = \rho_S(\mathbf{r}) + \rho_A(\mathbf{r})$$

$$I(t) = \left| \sum_1^A \mu_j f_j \exp(i\mathbf{QR}_j) + \sum_1^S \mu_j f_j \exp(i\mathbf{QR}_j) \right|^2 = |F_A + F_S|^2 = (F_A + F_S)(F_A^* + F_S^*) = \\ = |F_A|^2 + |F_S|^2 + F_A F_S^* + F_A^* F_S$$

Невозможно разделить вклады от разных подрешеток и  
интерференционный вклад.

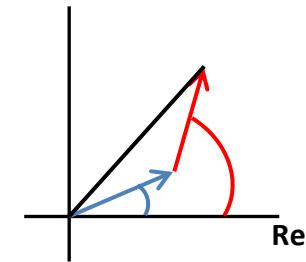
(в нейтронной дифракции можно занулить вклады от подрешеток для нескольких элементов используя смесь изотопов – «нуль матрица»)

# Простое решение



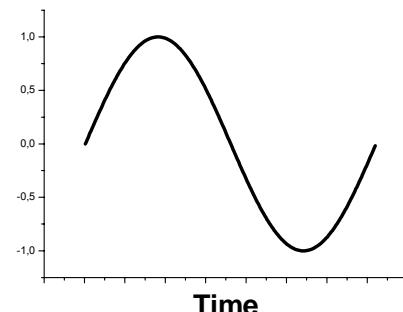
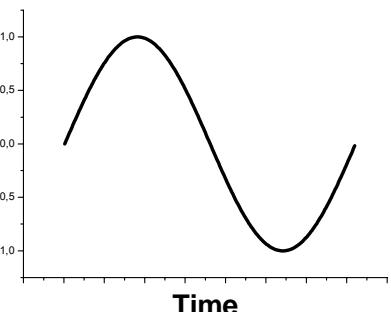
In detector

$$|F_B + \mu F_A|^2$$

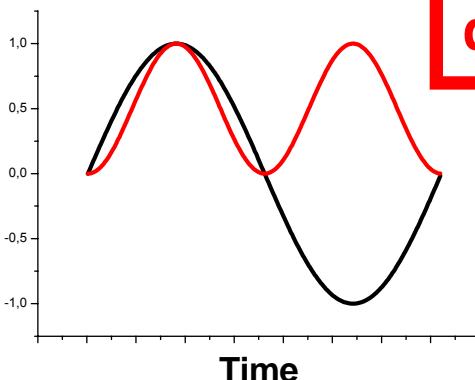


$$F_B^2 + 2\mu F_A F_B \cos(\phi_a - \phi_b) + \mu^2 F_A^2$$

Time dependence X no      ↑ yes



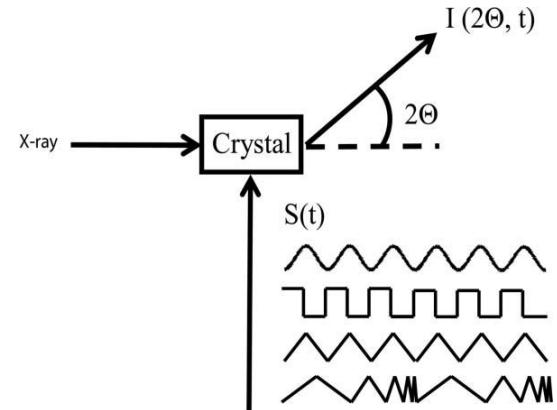
=



**Frequency  
doubling!**

# Periodic stimulus can act upon

- Occupancy 
- Scattering factor 
- Atomic positions
- Atomic Displacement Parameters

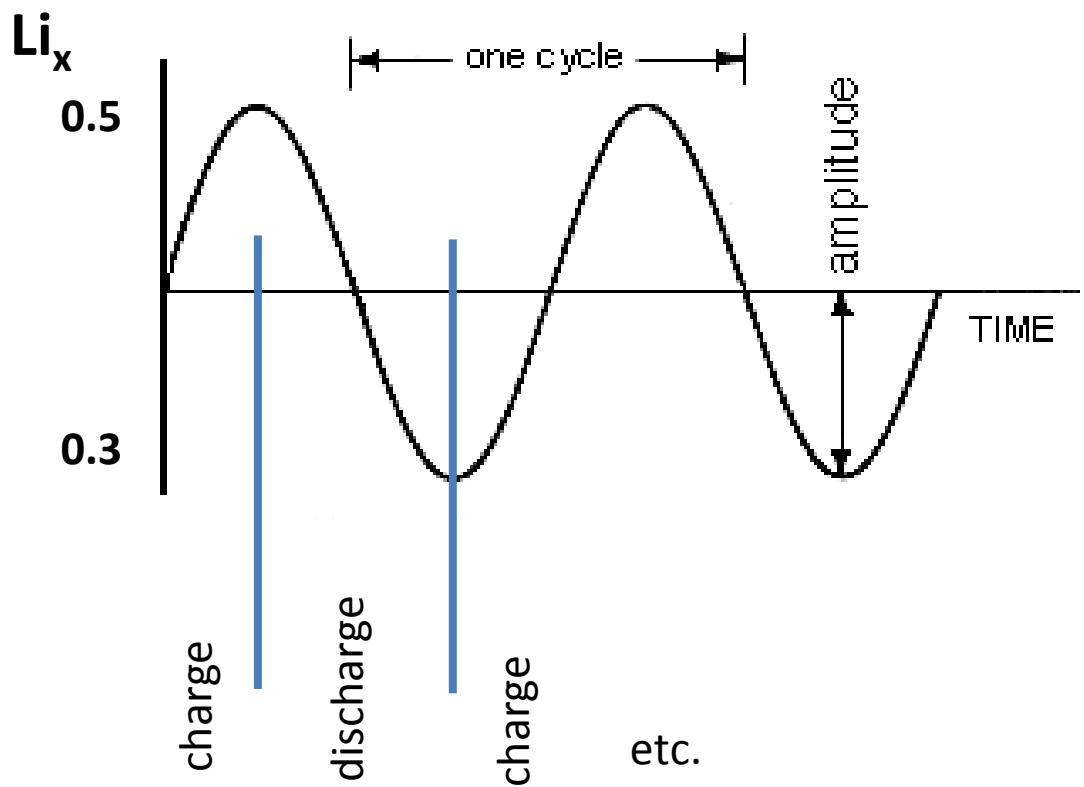


# Модуляционная дифракция Modulation Enhanced Diffraction MED

- ※ Модельные расчеты (компьютерная симуляция экспериментов)
- ※ Построение теории и формулировка требований к эксперименту
- ※ Экспериментальная проверка

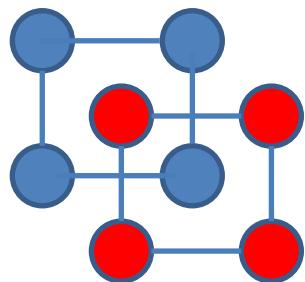
# Модельные расчеты (компьютерная симуляция экспериментов)

Li Occupancy variation in  $\text{Li}_x\text{CoO}_2$   $0.3 > x < 0.5$

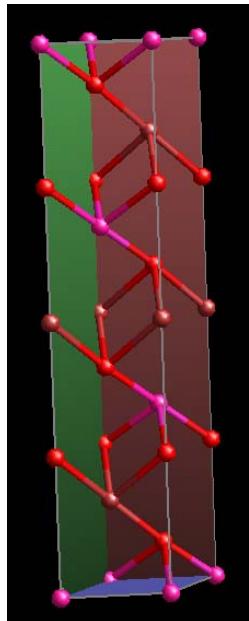


# $\text{LiCoO}_2$ , Li intercalation/de-intercalation

B



A  $\mu(t)$



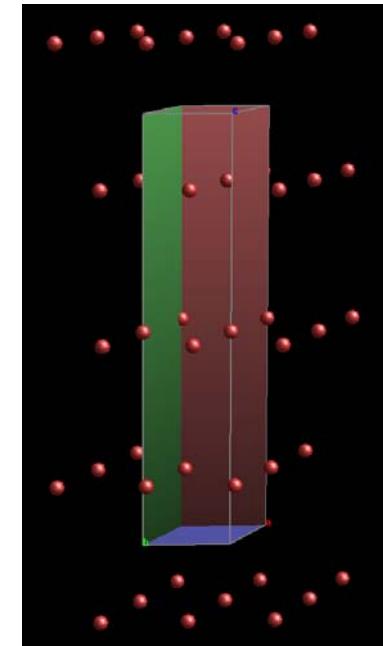
Li Sinusoidal  
Occupancy  
variation from  
0.3-0.5

Simulation

Time

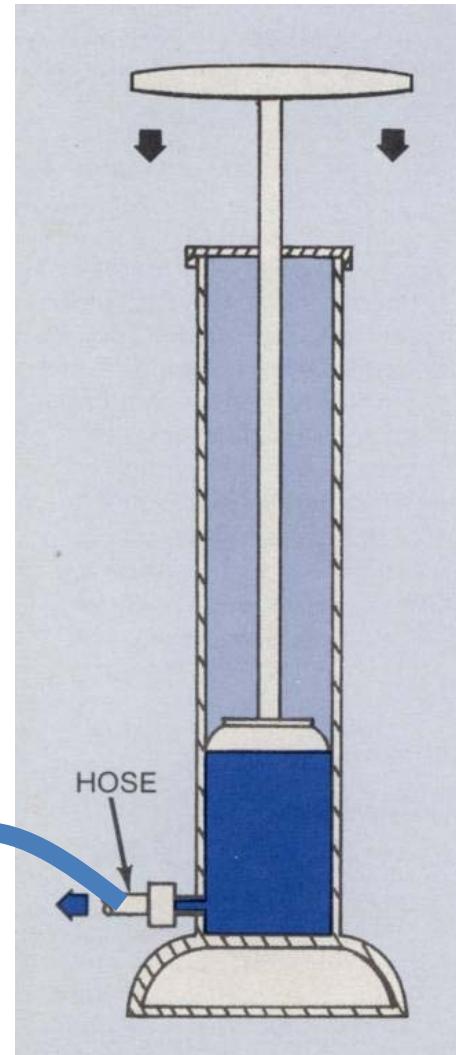
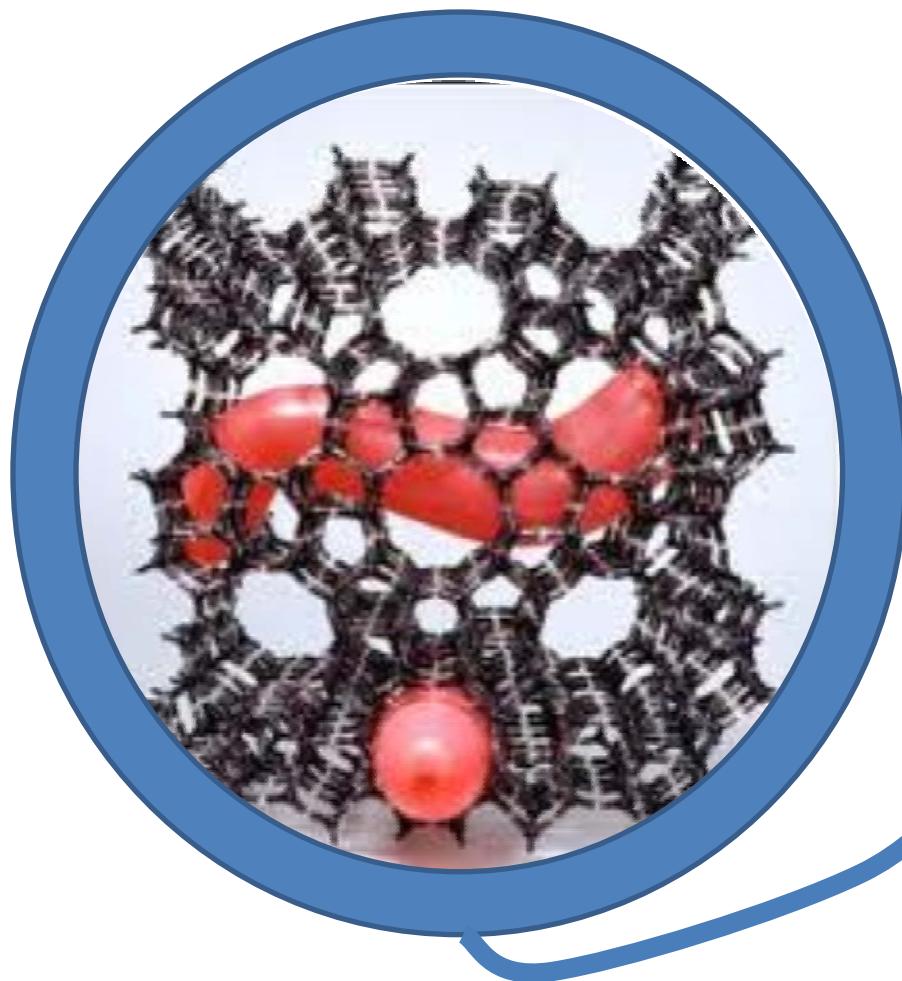
Theta

$2\omega \text{ FT}$



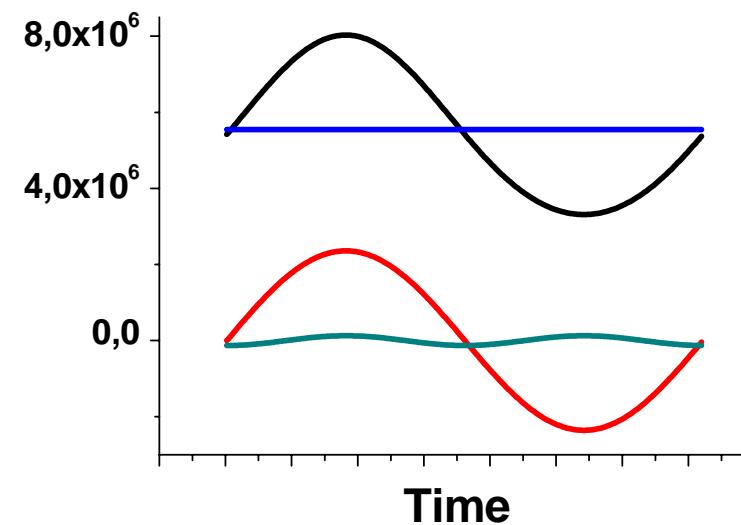
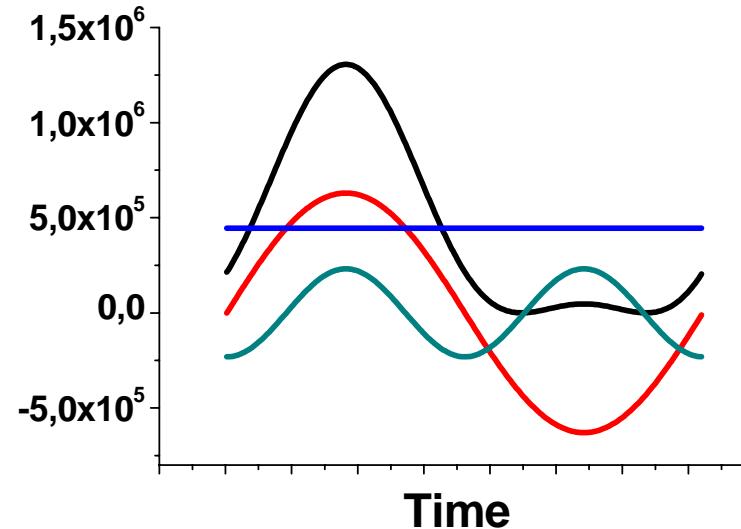
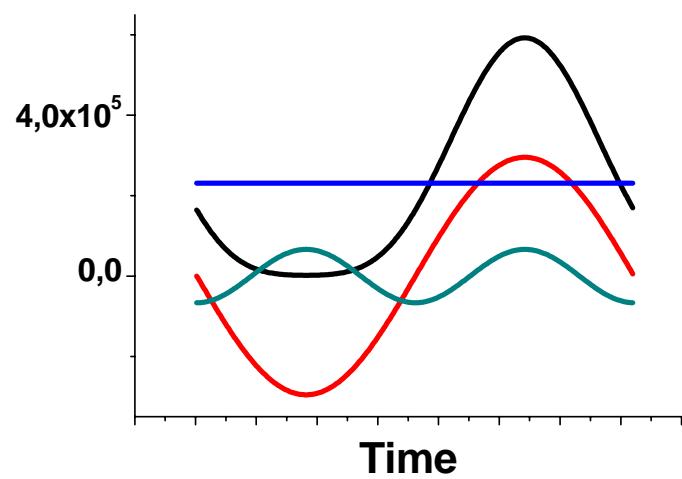
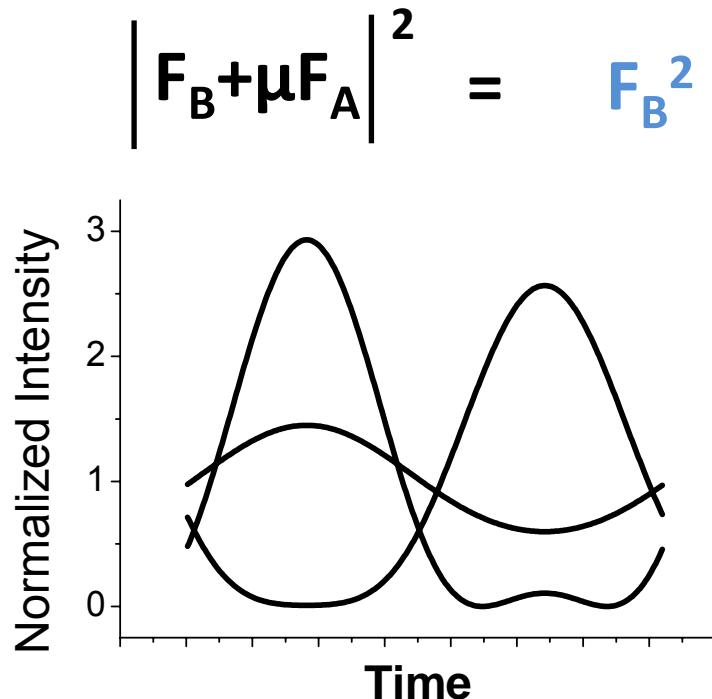
$$\cancel{F_B^2 + 2\mu F_A F_B \cos(\phi_a - \phi_b) + \mu^2 F_A^2}$$

# Xenon occupancy modulation in Zeolite

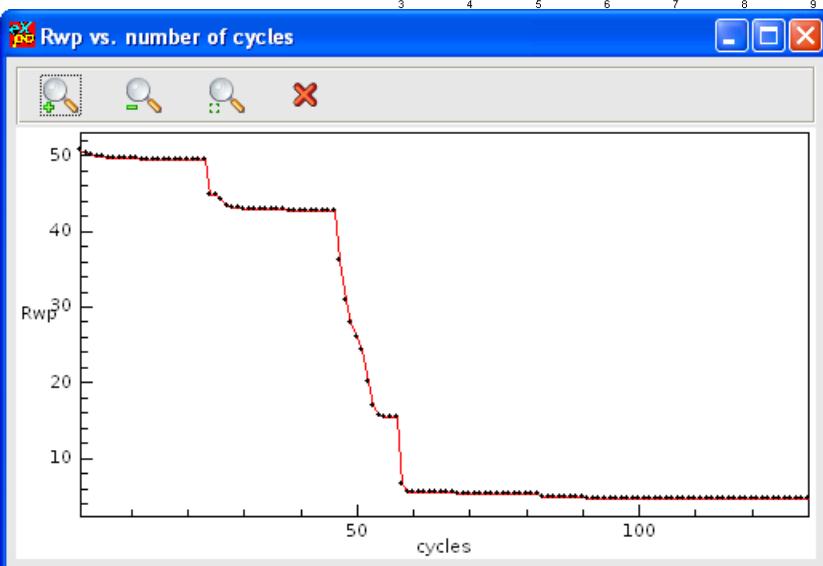
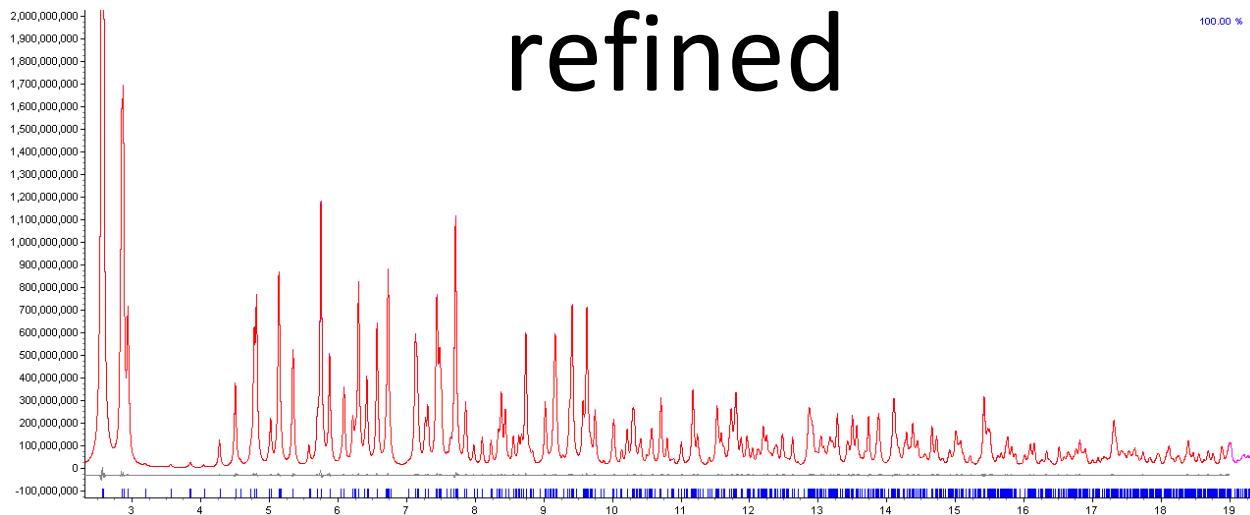


Measured in detector

# Simulation: 3 Peaks (time)



# Simulation - Direct Methods : 2 omega pattern solved and refined



List of Atoms

Atom	Height/10	X	Y	Z	Occ	B[iso]	U[iso]
Xe1	23852	0.500	0.250	0.502	0.500	3.472	0.0440
Xe2	22674	0.500	0.000	0.500	0.500	3.980	0.0504
Xe3	17384	0.685	0.250	0.660	0.500	4.905	0.0621
Xe4	16429	0.916	0.250	-0.319	0.500	5.743	0.0727

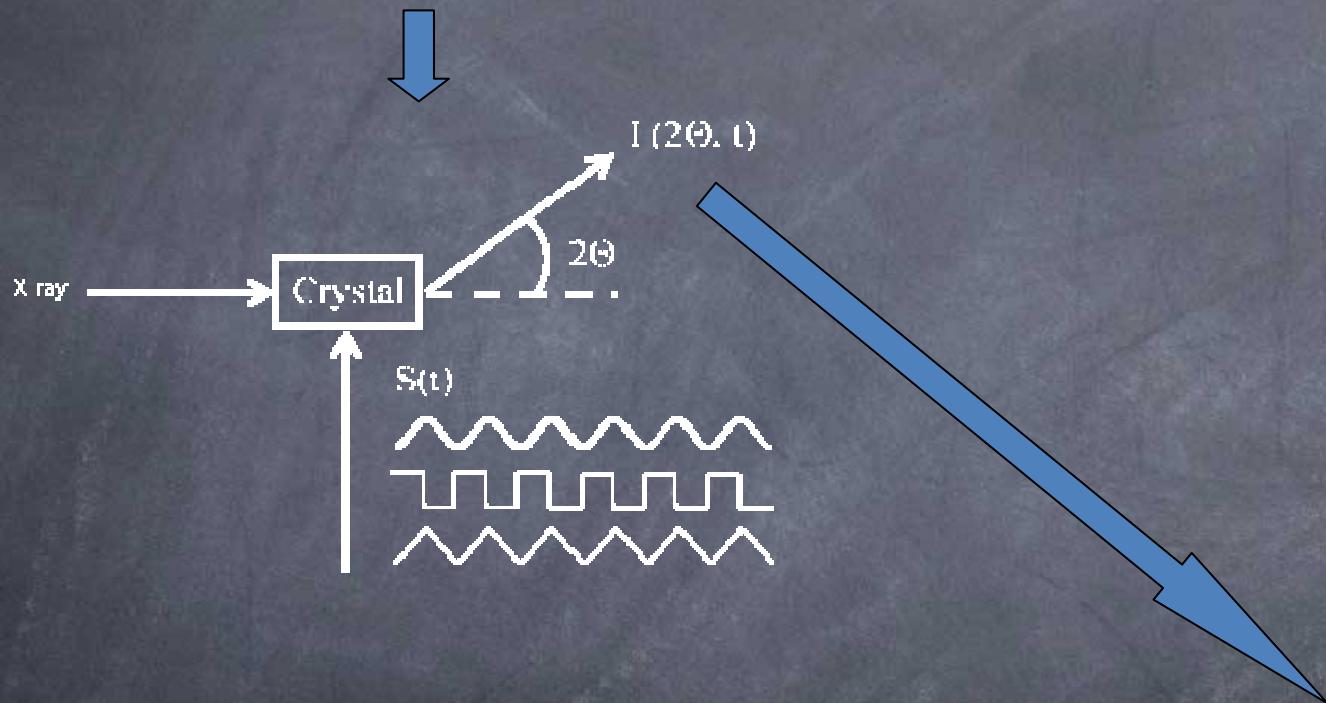
# Построение теории и формулировка требований к эксперименту

- What does the modulation do with a structure?
- How does crystal structure manifest itself in the diffraction experiment?
- What does the modulation do with diffraction intensity?

Back to the roots...

# Silent and Active

$$\rho(\mathbf{r}, t) = \rho_S(\mathbf{r}) + \rho_A(\mathbf{r}, t) = \rho_S(\mathbf{r}) + \overline{\rho_A(\mathbf{r})} + \delta\rho_A(\mathbf{r}, t)$$



$$I(t) = \left| \sum_1^A \mu_j f_j \exp(i\mathbf{QR}_j) + \sum_1^S \mu_j f_j \exp(i\mathbf{QR}_j) \right|^2 = |F_A(t) + F_S|^2 = |\overline{F_A} + \delta F_A(t) + F_S|^2$$

# What does the modulation do with diffraction intensity?

$$I(t) = \left| \overline{F_A} + F_S \right|^2 + \left| \delta F_A(t) \right|^2 + \delta F^* A(t) \left( \overline{F_A} + F_S \right) + \delta F_A(t) \left( \overline{F^*}_A + F^* S \right)$$

Fourier transform

from time to frequency domain

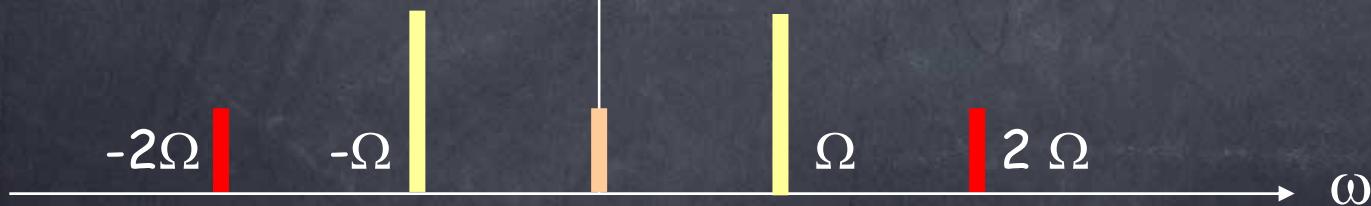
$$\tilde{I}(\omega) = FT \left\{ \left| \delta F_A(t) \right|^2 \right\} + \left( \overline{F_A} + F_S \right) \cdot FT \left\{ \delta F^* A(t) \right\} + \left( \overline{F^*}_A + F^* S \right) \cdot FT \left\{ \delta F_A(t) \right\}$$

We assume simplest periodic response

$$\delta F_A(t) = \delta F^* A(t) \propto S(t) = A \cos(\Omega t)$$

$$\tilde{I}(\omega) \propto \frac{\pi A^2}{2} (\delta(\omega) + \delta(\omega - 2\Omega) + \delta(\omega + 2\Omega)) + 2\pi A \left( \text{Re}(\overline{F_A}) + \text{Re}(F_S) \right) (\delta(\omega - \Omega) + \delta(\omega + \Omega))$$

$$I(\omega)$$



# "linear response"

$$\delta F_A = \frac{\partial F_A}{\partial S} \delta S + \frac{\partial^2 F_A}{\partial S^2} (\delta S)^2 + \dots$$

$$\delta S^\omega(t) = S(t) - \overline{S(t)} = S_0 \sum_{-\infty}^{\infty} p_r \exp(ir\omega t)$$

$$\delta F^\omega_A(t) = F_0 \sum_{-\infty}^{\infty} q_r \exp(ir\omega t)$$

$$q_r \propto p_r$$

# direct and inverse problems



- We know time dependence of a response and we want to know underlying structural changes
- We assume linear response and partitioning the atoms on Active and Silent do hold.

- We know structural changes and we want to know time evolution of the response
- linear response is not necessary
- partitioning the atoms on Active and Silent does hold.

---

Both stimulation and response may be much more complex than a simple cosine. As periodic functions they can always be expressed as a Fourier series.

# Stimulation and response expressed as Fourier series

$$\delta S^\omega(t) = S(t) - \overline{S(t)} = S_0 \sum_{-\infty}^{\infty} p_r \exp(ir\omega t) \quad p_r = \frac{1}{S_0 T} \int_0^T S^\omega(t) \exp(ir\omega t) dt$$

$$\delta F_A^\omega(t) = F_0 \sum_{-\infty}^{\infty} \hat{q}_r \exp(ir\omega t) \quad \hat{q}_r = \frac{1}{F_0 T} \int_0^T F_A^\omega(t) \exp(ir\omega t) dt$$

If the response is delayed by the time  $\tau_A$

$$|F_A^\omega(t)| = F_0 \sum_{-\infty}^{\infty} q_r \exp(ir\omega t) \exp(ir\omega \tau_A) \quad q_r \exp(ir\omega \tau_A) = \hat{q}_r$$

Useful formula for the squared term

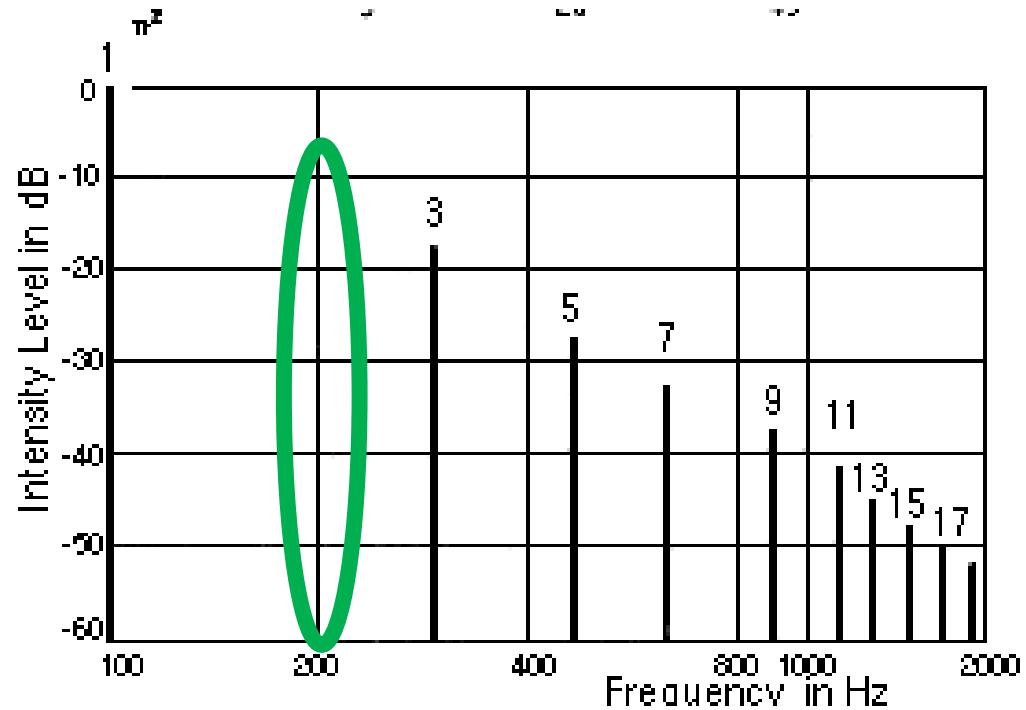
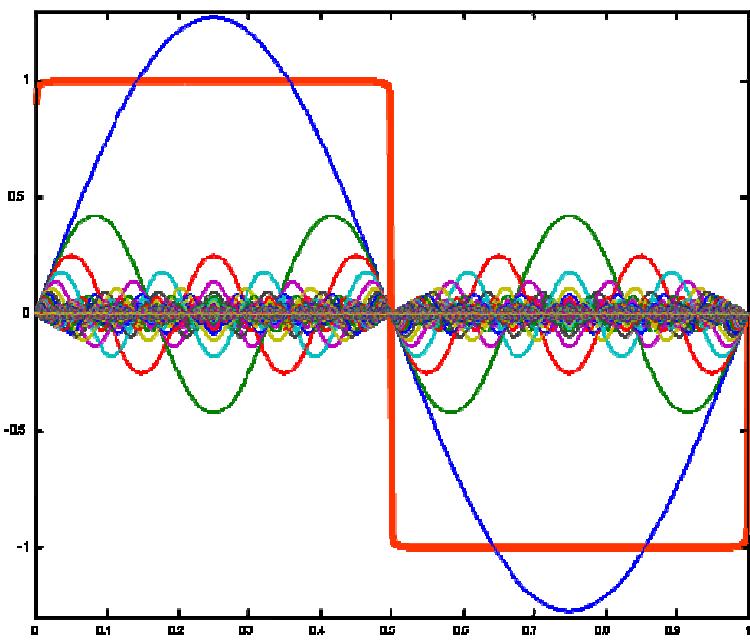
$$|\delta F_A^\omega(t)|^2 = |F_0|^2 \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} q_r q_n \exp(i\omega \tau_A(r+n)) \exp(i\omega t(r+n))$$

For a linear response of the active sub-lattice  $r$  and  $n$  are also only odd, and  $m$  is necessarily even

Remember  
 $\Omega$  and  $2\Omega$

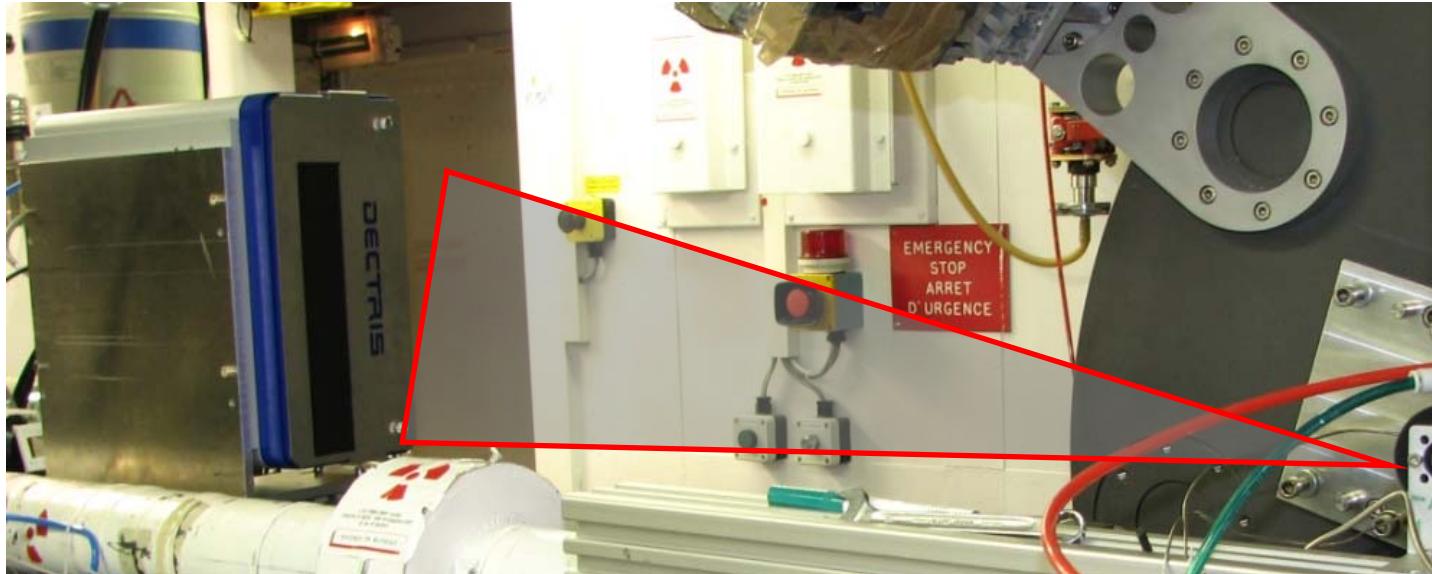
# Essential conditions for theory to hold

$$\text{square wave} = \frac{4}{\pi} \left( \sin \omega t + \frac{1}{3} \sin 3\omega t + \frac{1}{5} \sin 5\omega t + \dots + \frac{1}{(2n-1)} \sin (2n-1)\omega t + \dots \right)$$



- The stimulus has to have a symmetric shape.
- The sample has to have a linear response to the stimulus.

# MED development setup

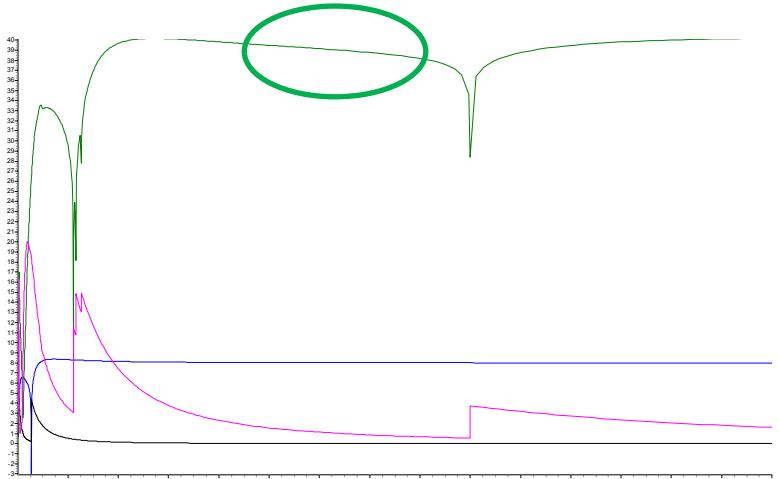


Detector: Pilatus 300K-W

Modern detectors not only increase the amount of data but can also provide access to new information.

# $\text{ZrO}_2$ f' modulation

$$f(\theta, \lambda) = f_o \left( \frac{\sin \theta}{\lambda} \right) + f'(\lambda) + i f''(\lambda)$$

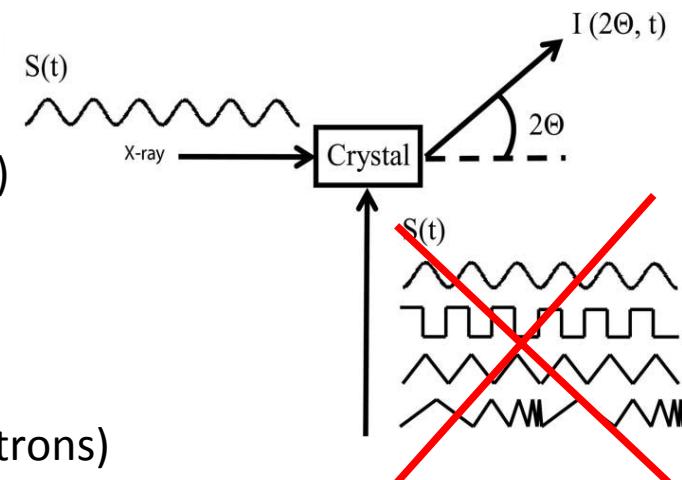


$f' \text{ Zr}$  (3 electrons)

$f' \text{ O}$  ( $\sim 0.002$  electrons)

$f'' \text{ Zr}$  - pink

$f'' \text{ O}$  - black



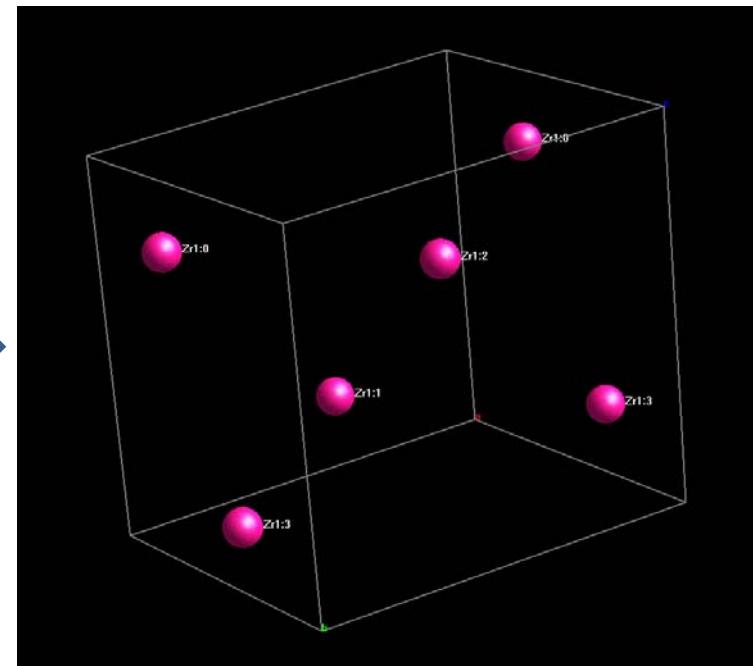
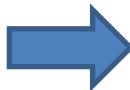
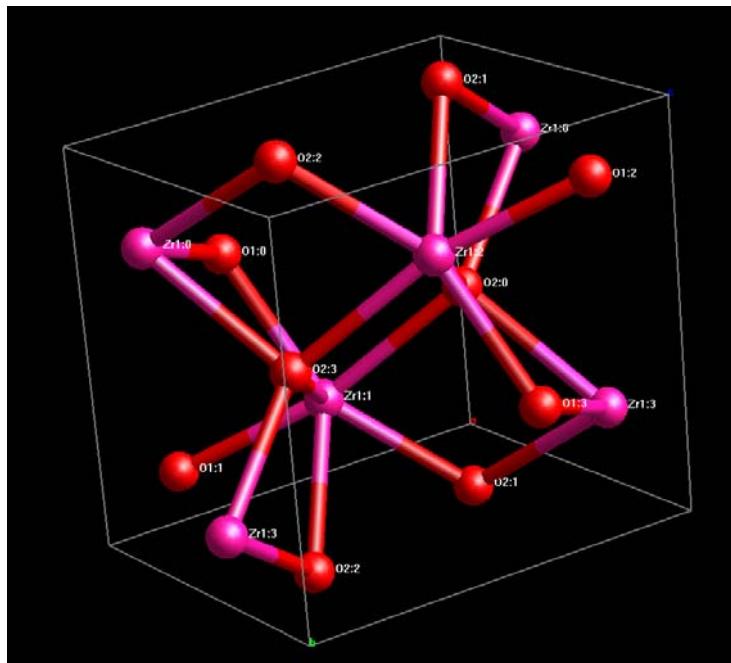
**Hypothesis:**

**Before the edge  $f''$  Zr and  $f'$  Oxygen can be neglected**

# $f'$ modulation hypothesis visual

$ZrO_2$

We expect to find only the Zr sub-lattice in 2 omega channel

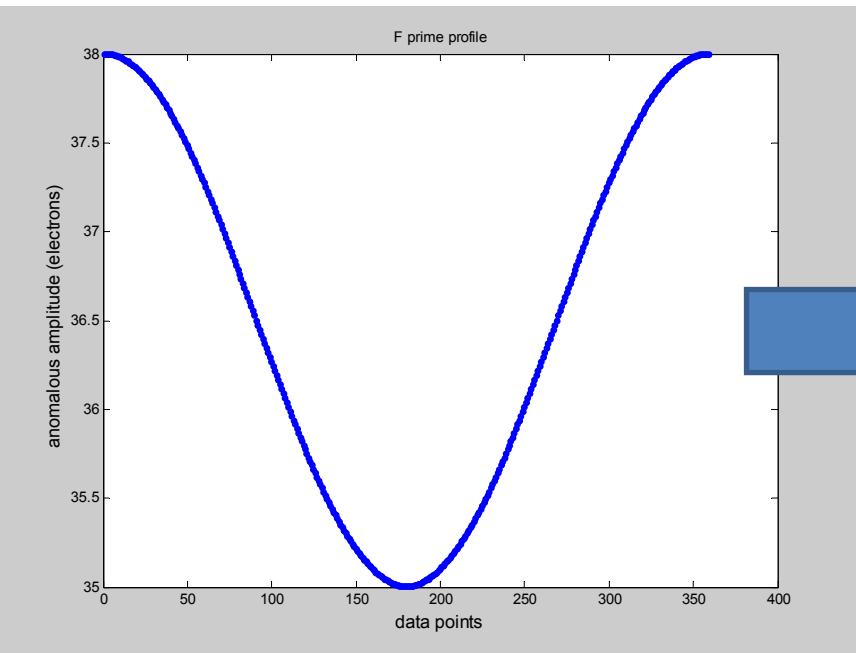


**Hypothesis:**

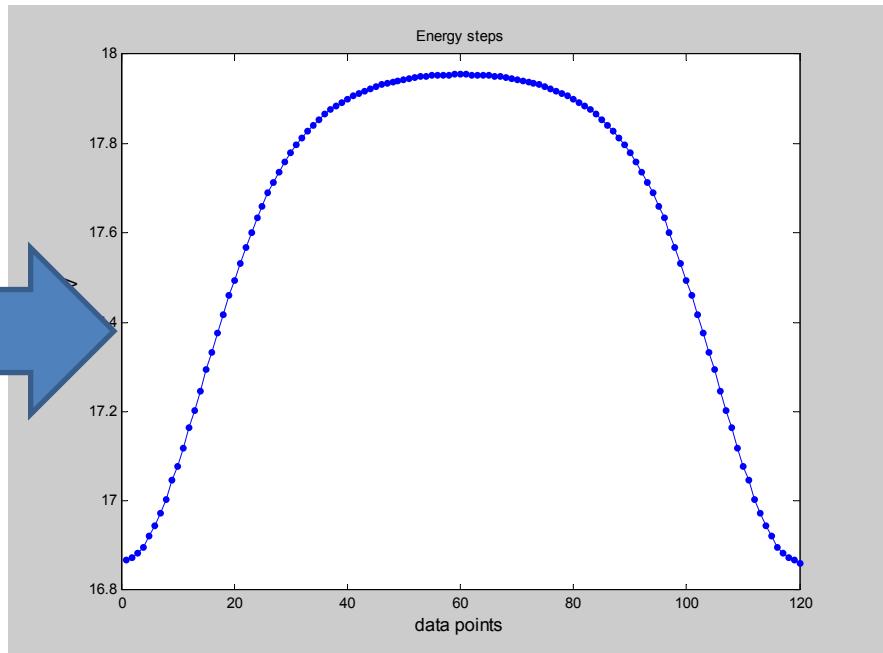
**Before the edge  $F''$   $Zr$  and  $F'$  Oxygen can be neglected**

We force a cosinusoidal  $f'$  shape and calculate the Monochromators energy profile

$f'$  Anomalous amplitude  
(electrons)



X-ray Energy (keV)

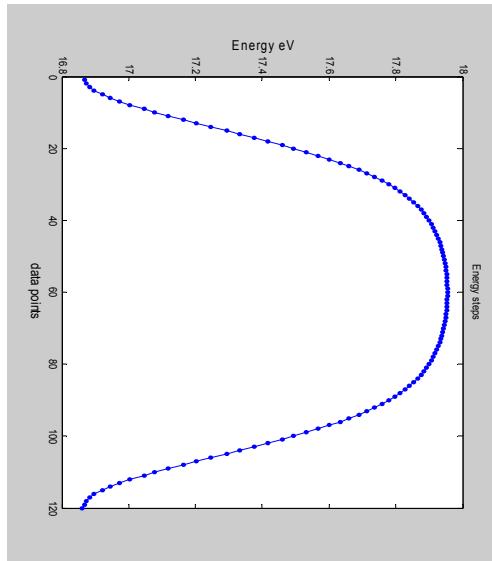


Energy (keV)

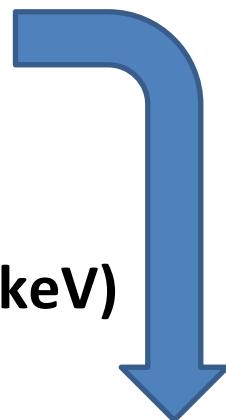
Time(seconds)

# $f'$ modulation experiment

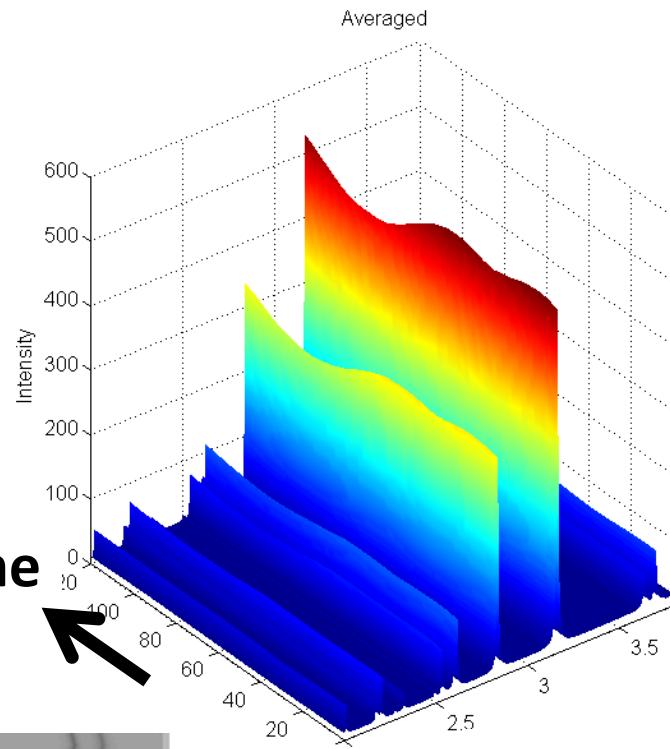
Time  
↑



X-ray energy (keV)



Time

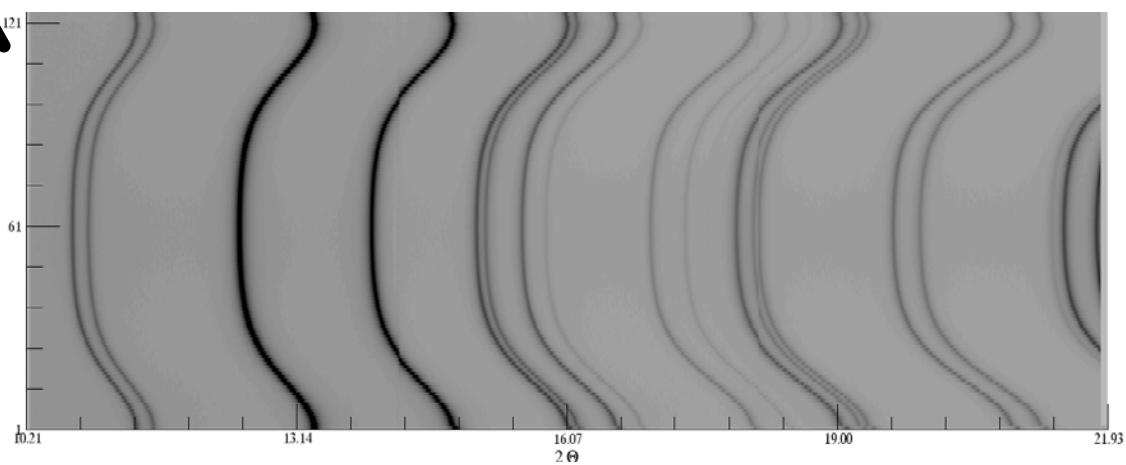


d-spacing



2 theta

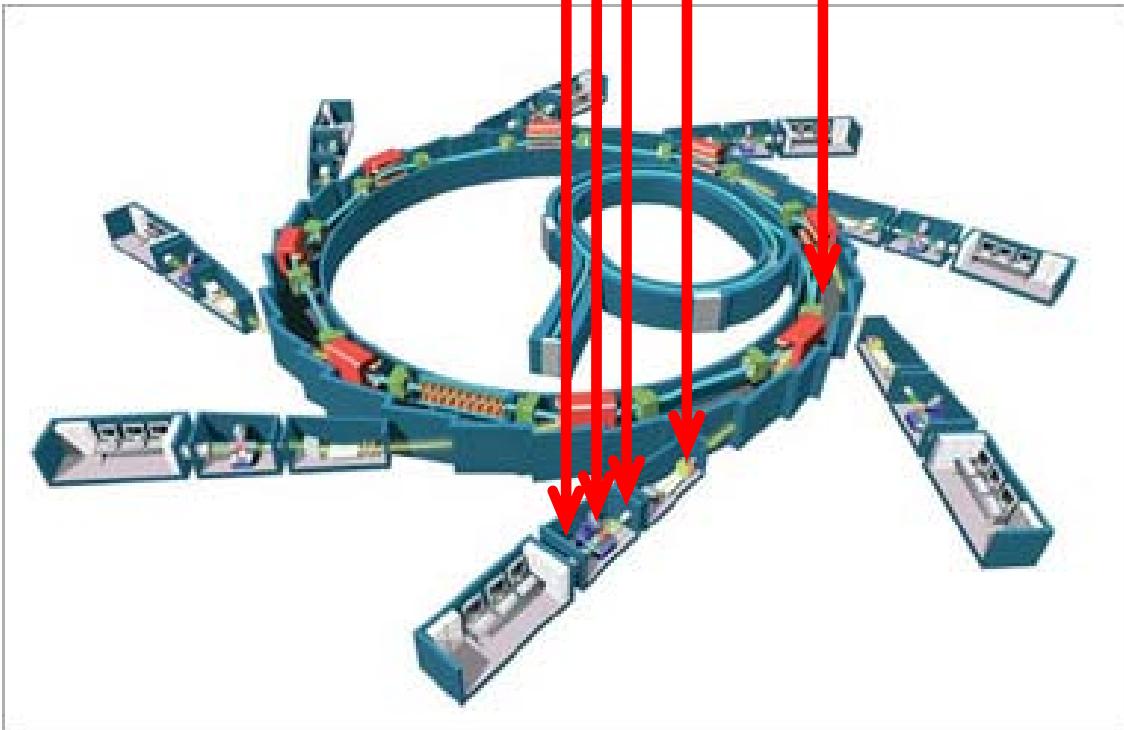
Time  
↑



# Other time = X-ray energy dependent factors

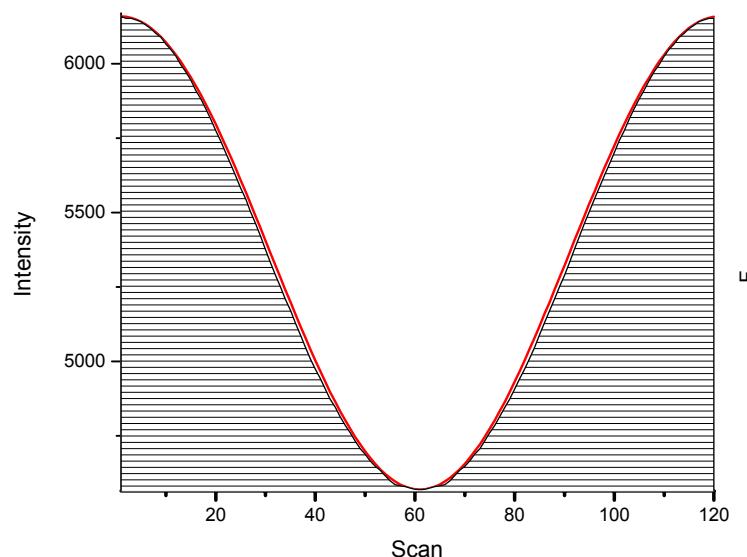
Source (E)  
Monochromator(E)  
Monitor (E)  
Sample (E)  
Detector (E)

Diffracted Intensity proportional  $\Lambda^3$

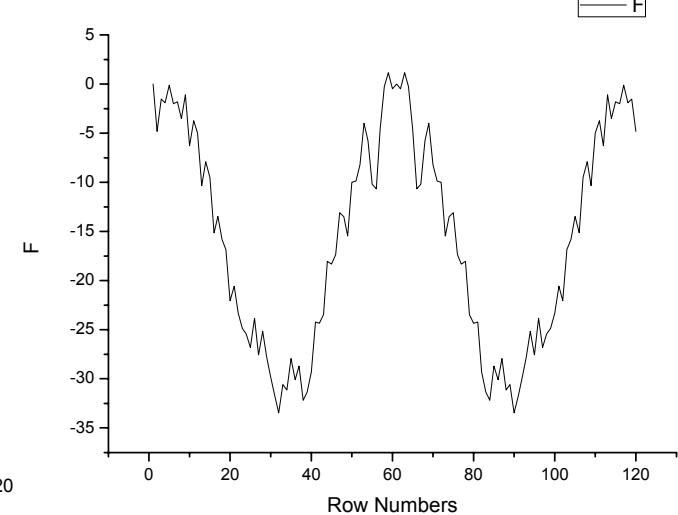


$\text{ZrO}_2$   
58 electrons

O       $8e^-$   
O       $8e^-$   
        $3e^-$   $S(t)$   
Zr       $37e^-$



1 omega term 98%



2 omega term 2%

$$F_A^2 + 2\mu F_A F_B \cos(\phi_a - \phi_b) + \mu^2 F_B^2$$



# MED: New tool to untangle scattered intensities

## Status

- Theory
- Simulations
- Experiments



## Ongoing theoretical and experimental developments:

- *Structure Solution / linear response for  $2\omega$  term*
- $1\omega$  term Development new phasing tools
- $2\omega$  term Existing phasing tools, active sub-lattice, selectivity
- *Kinetics / Non linear response*
- Fourier coefficients analysis
- Correlation multi-dimensional analysis

# Thanks to the MED Team, this is how we progress and thank you

Hermann  
Emerich

Marco  
Milanesio

Atsushi  
Urakawa

Luca  
Palin

Davide  
Viterbo

Dmitry  
Chernyshov

Rocco  
Caliandro

