Colloidal Crystals Structure and Dynamics

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Coherent X-ray Scattering and Imaging Group at DESY

Present members:

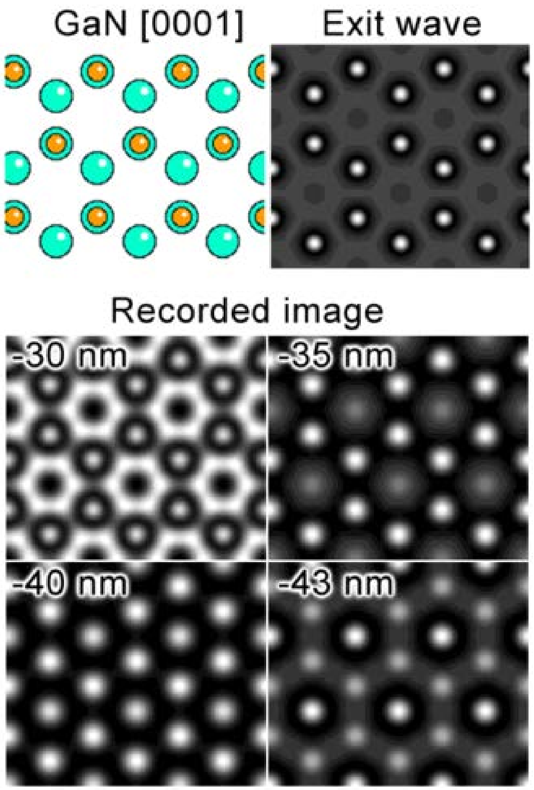
- S. Lazarev
- I. Besedin
- P. Skopintsev
- D. Dzhigaev
- I. Zaluzhnyy
- M. Rose
- O. Gorobtsov
- N. Mukharamova

Former members:

- A. Zozulya (now@PETRA III)
- A. Mancuso (now@XFEL)
- O. Yefanov (now@CFEL)
- R. Dronyak
- J. Gulden (now@FH-Stralsund)
- U. Lorenz (now@University of Potsdam)
- A. Singer (now@UCSD)
- R. Kurta (now@XFEL)
- A. Shabalin (now@CFEL)

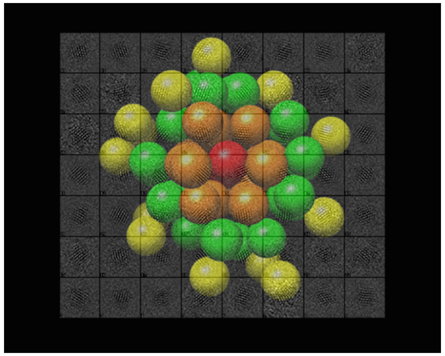
High resolution microscopy

High resolution electron microscopy



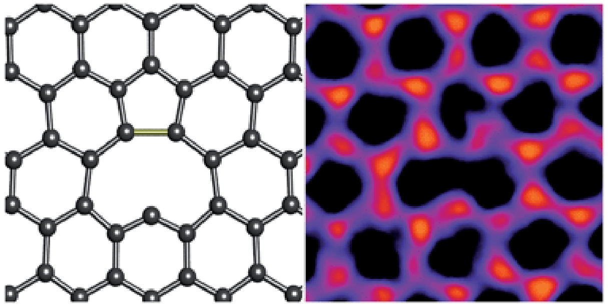
Simulated HREM images
for GaN[0001]

From: Wikipedia



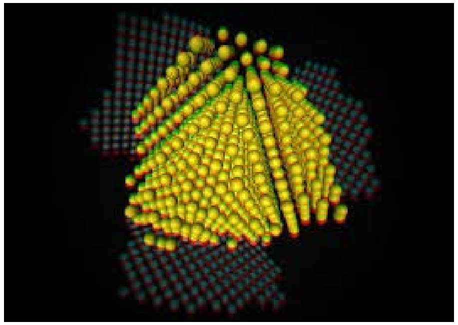
Atomic structure of the Au68 gold nanoparticle determined by electron microscopy.

M. Azubel, et al., ***Science*** 345, 909 (2014)

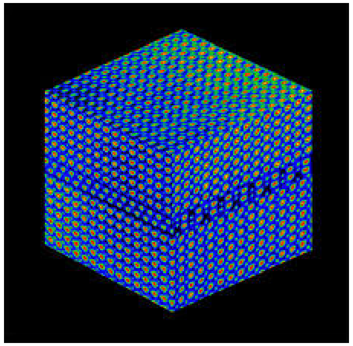


Atomic resolution imaging of graphene

A. Robertson and J. Warner, ***Nanoscale***, (2013),**5**, 4079-4093



From: Web Images



From: Web Images

Can we develop

x-ray microscope with

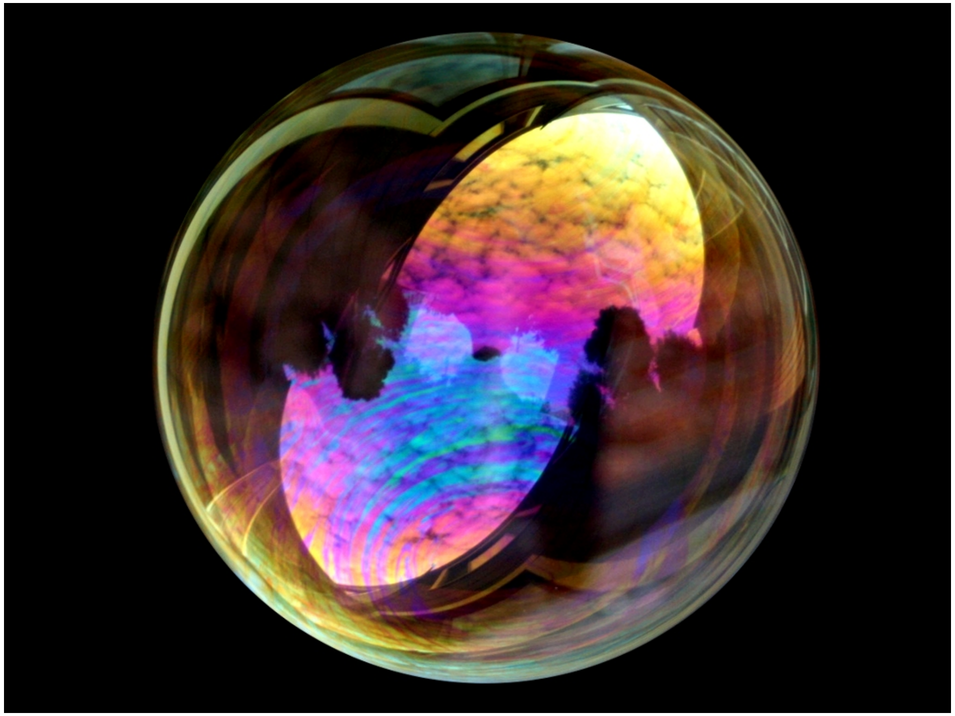
atomic resolution?

It does not work with conventional approach due to the lack of atomic resolution X-ray optics

Can coherent x-ray diffraction imaging be the way to go?

What is Coherence?

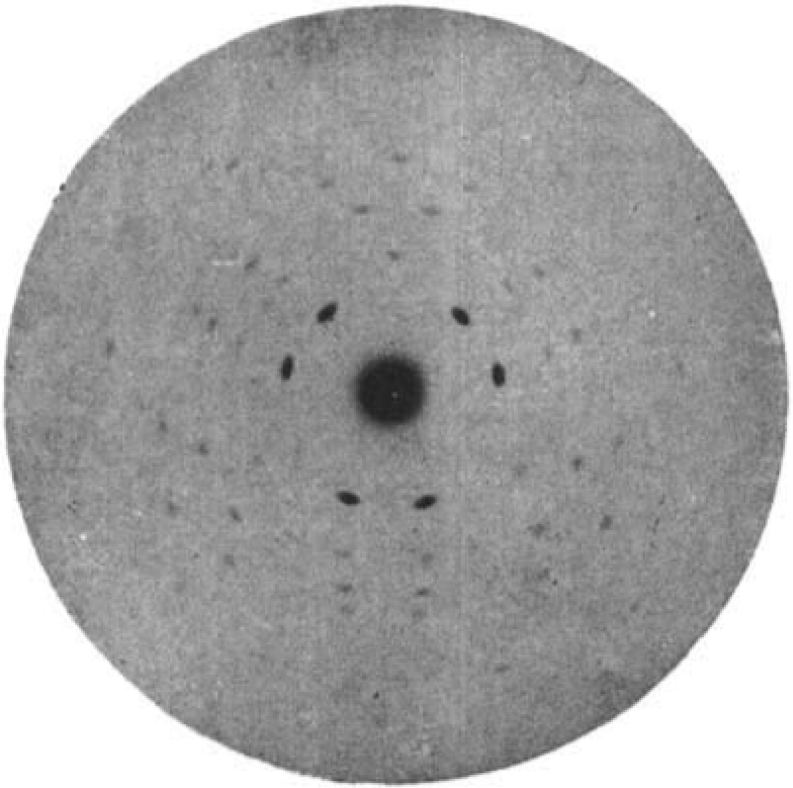
Coherence is an ideal property of waves that enables stationary interference



Soap bubble

wikipedia.org

Whether X-rays are coherent waves?



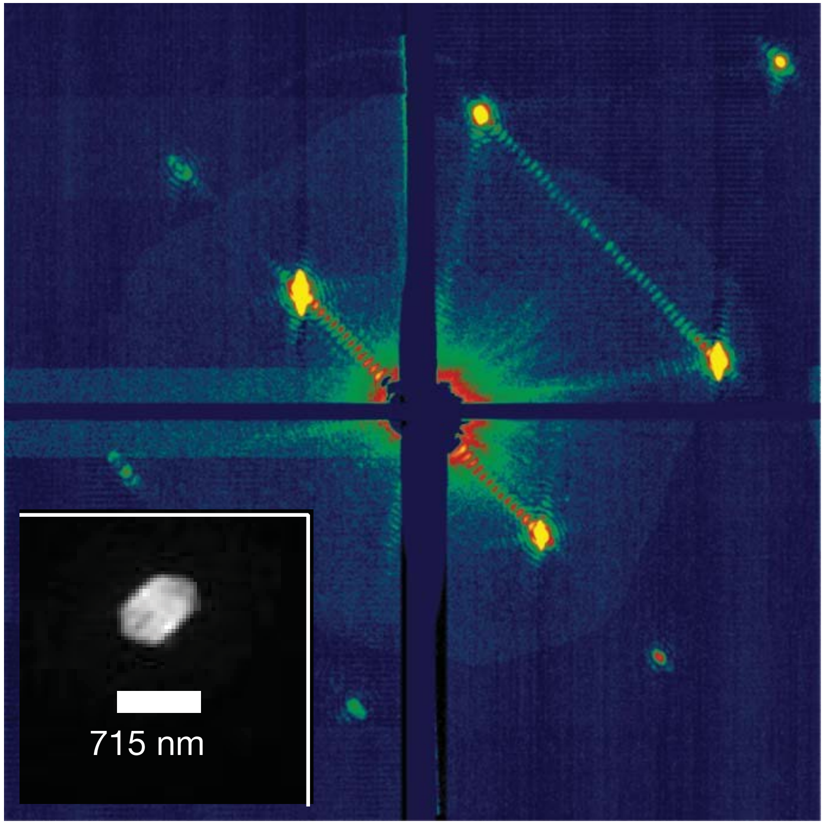
Max von Laue

Nobel Prize in Physics, 1914

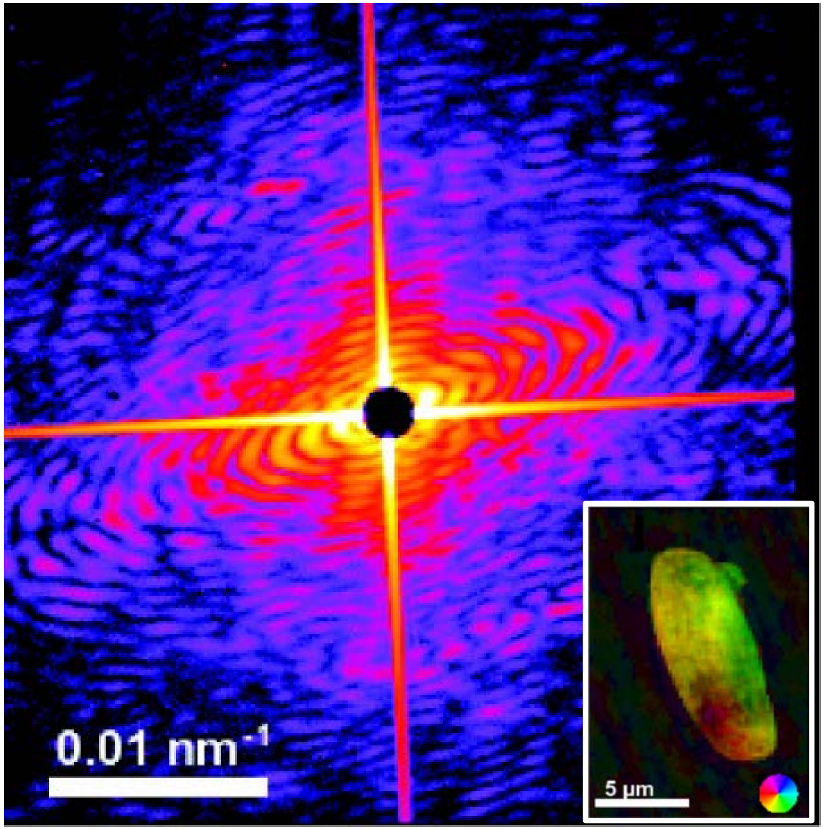
W. Friedrich, P. Knipping,
M. von Laue, Ann. Phys. (1913)

100 years later

LCLS



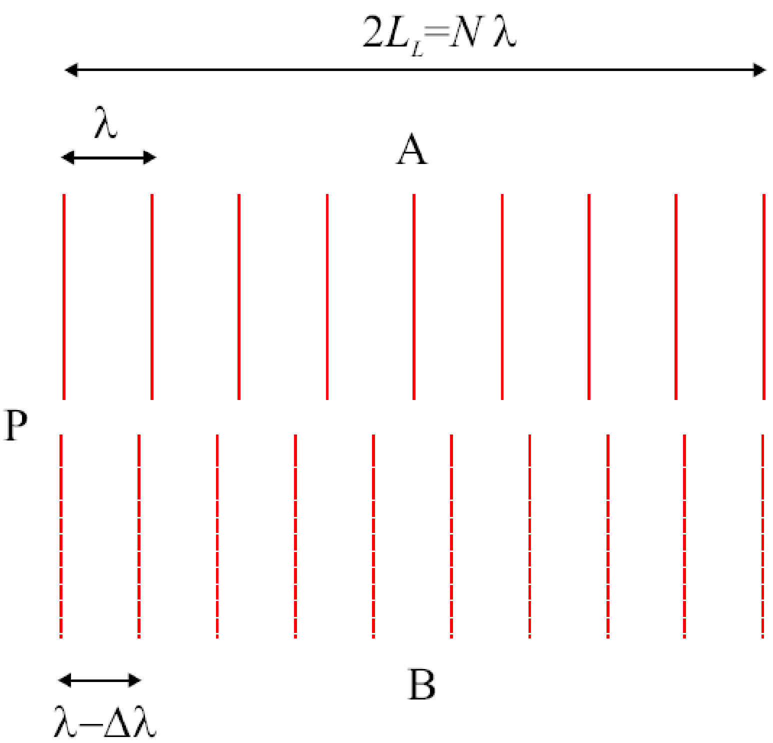
FLASH

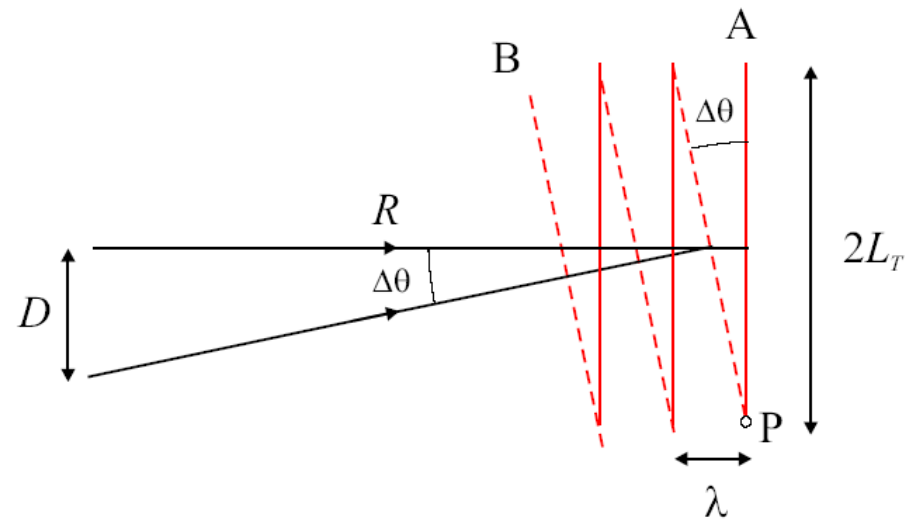


H. Chapman *et al.*,
Nature (2011)

A. Mancuso *et al.*,
New J. Physics (2010)

Coherence





$$L_L=\lambda^2/(2\Delta\lambda)$$

Longitudinal Coherence Length

$$L_T=(\lambda R/2D)$$

Transverse Coherence Length

Als-Nielsen & McMorrow (2001)

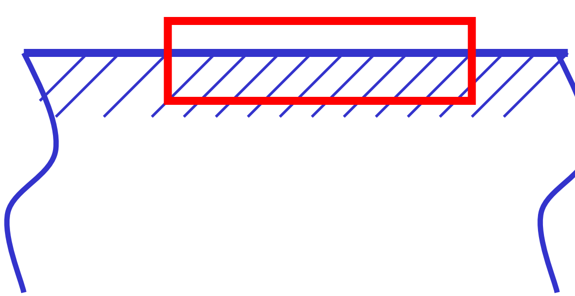
Coherence properties of 3rd generation synchrotron sources

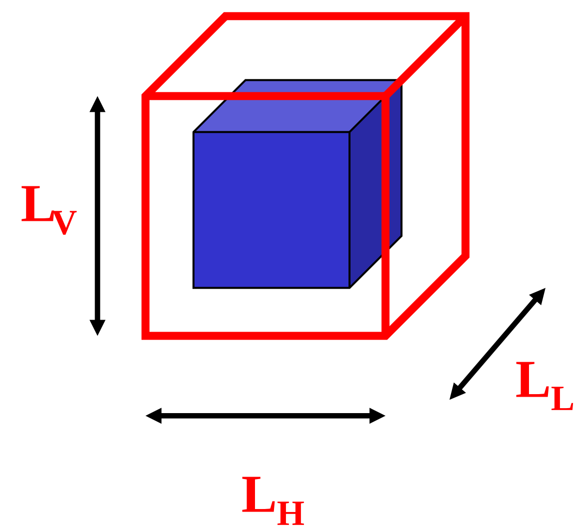
I.A. Vartanyants & A. Singer "**Coherence Properties of Third-Generation Synchrotron Sources and Free-Electron Lasers"**, Chapter in: *Handbook on Synchrotron Radiation and Free-Electron Lasers*

Coherent volume (PETRA III, E=12 keV)

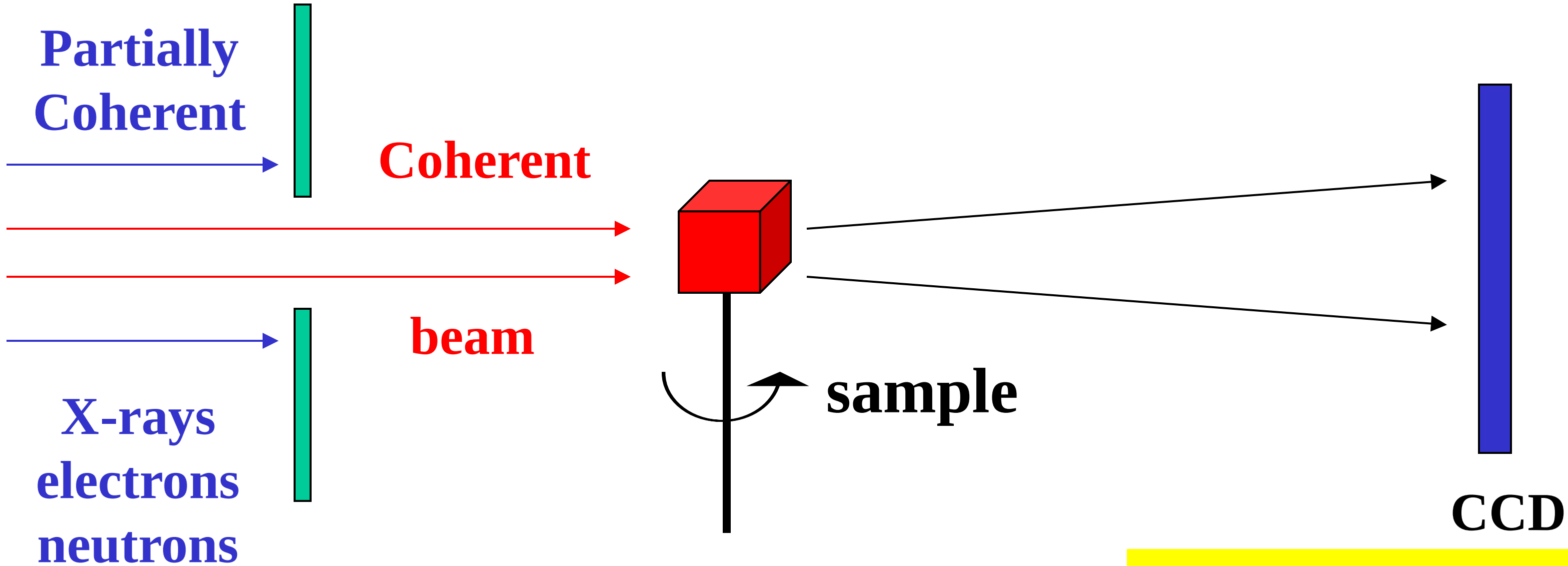
	L_V	L_H	L_L	Coh. Flux
Raw Undulator [illegible]	260 µm	40 µm	0.02 µm	6×10^{12} ph/s
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]h/s
Ra[illegible] High-β	[illegible]	[illegible]	[illegible]	[illegible]/s
DC Si (111) High-β	280 µm	10 µm	0.5 µm	2×10^{10} ph/s

We expect about two orders of magnitude more coherent flux at diffraction limited sources



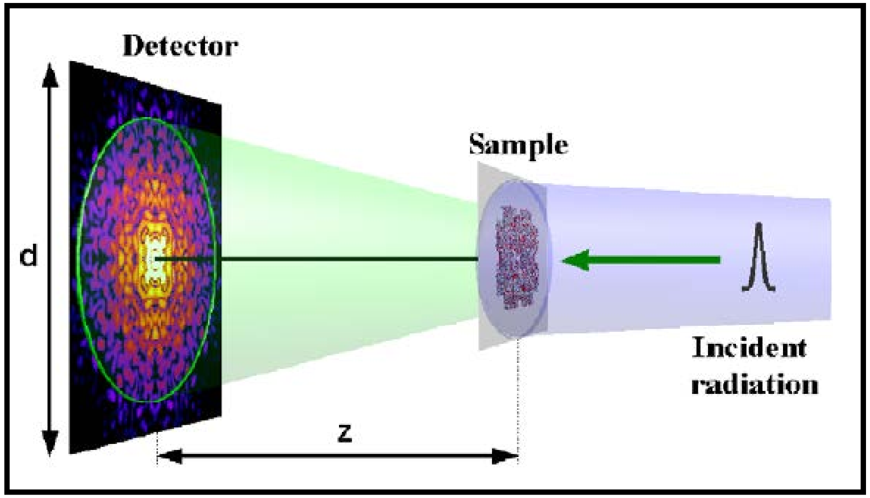


Coherent X-ray Diffraction Imaging
Lensless X-ray Microscopy



Optics: → **Phase Retrieval** → **Diffraction Limited Microscope**

Coherent X-ray Diffraction Imaging in forward direction



Mancuso *et al.* J. Biotechnol. **149** 229 (2010)

Small-angle scattering CDI

Non-crystallographic samples

Uniform distribution of electron density

Kinematical approximation:

$$A(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r}$$

q_z=0

$$A(q_x, q_y) = \int \langle \rho(x,y,z) \rangle_z e^{-i(q_x x + q_y y)}\, \mathrm{d}x\mathrm{d}y$$

$$\langle \rho(x,y) \rangle_z = \int \rho(x,y,z) \mathrm{d}z$$

Inverse Fourier transform:

$$\langle \rho(x,y) \rangle_z = \frac{1}{(2\pi)^2} \int A(q_x, q_y) e^{i(q_x x + q_y y)}\, \mathrm{d}q_x \mathrm{d}q_y$$

Unfortunately, phases of $A(q_x,q_y)$ are not known!!!

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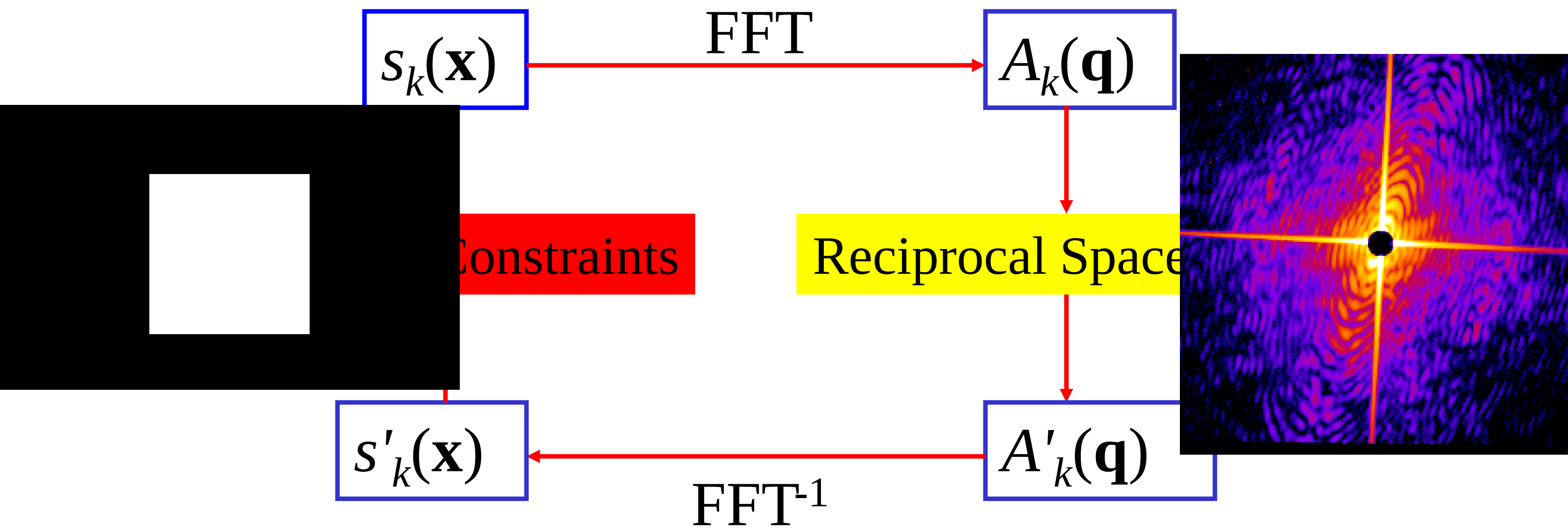
Phase retrieval

Iterative phase retrieval algorithm



Real space constraints:

use all *a priori* knowledge:

- finite support
- positivity
- …

Reciprocal space constraint:

$$\left|A_k(\mathbf{q})\right| \rightarrow \sqrt{I_{exp}(\mathbf{q})}$$

R.W.Gerchberg & W.O. Saxton, *Optic* (1972) **35**, 237

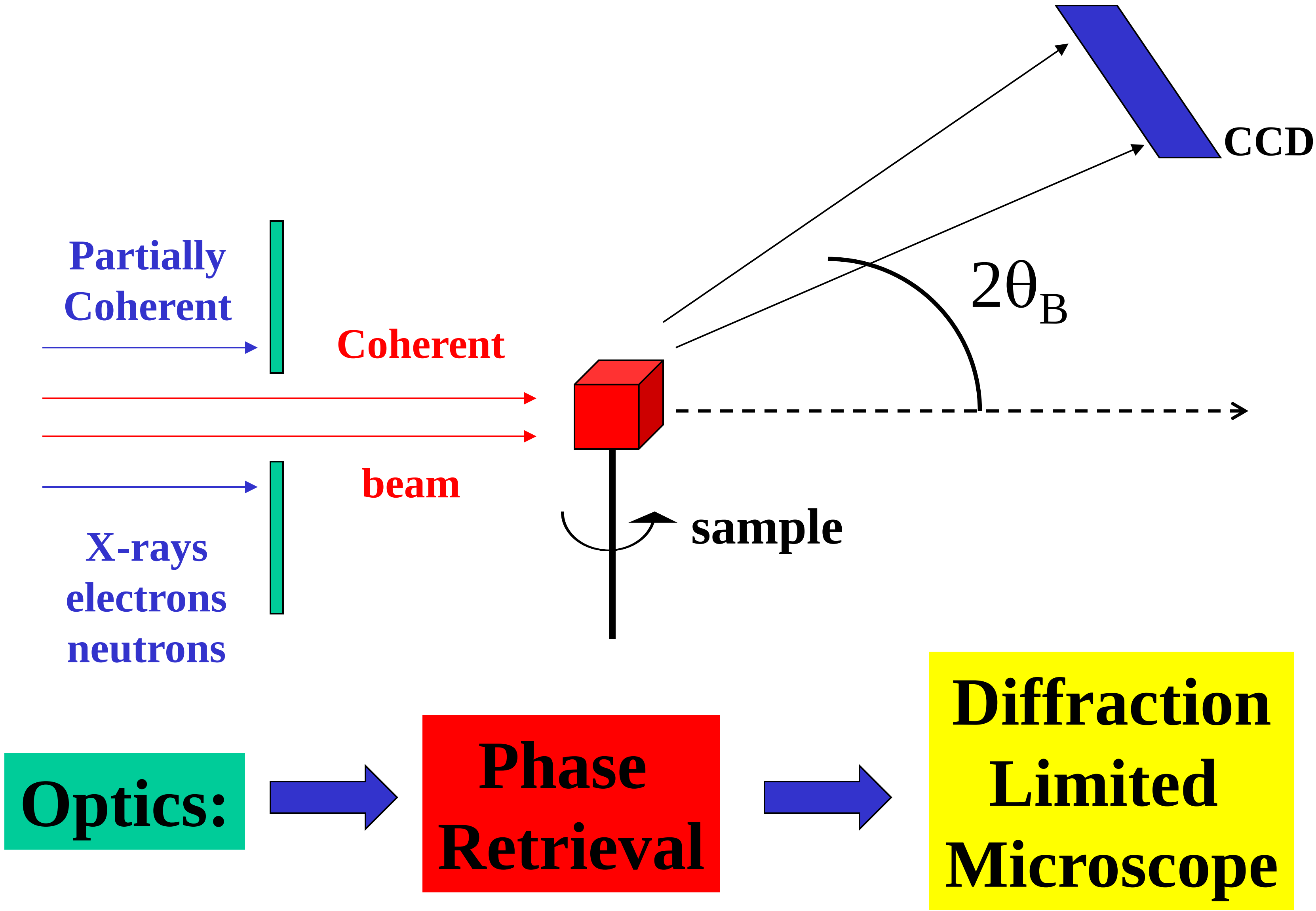
J.R. Fienup, *Appl Opt.* (1982) **21**, 2758

V. Elser, *J. Opt. Soc. Am. A* (2003) **20**, 40

Example of reconstruction (O.Yefanov)

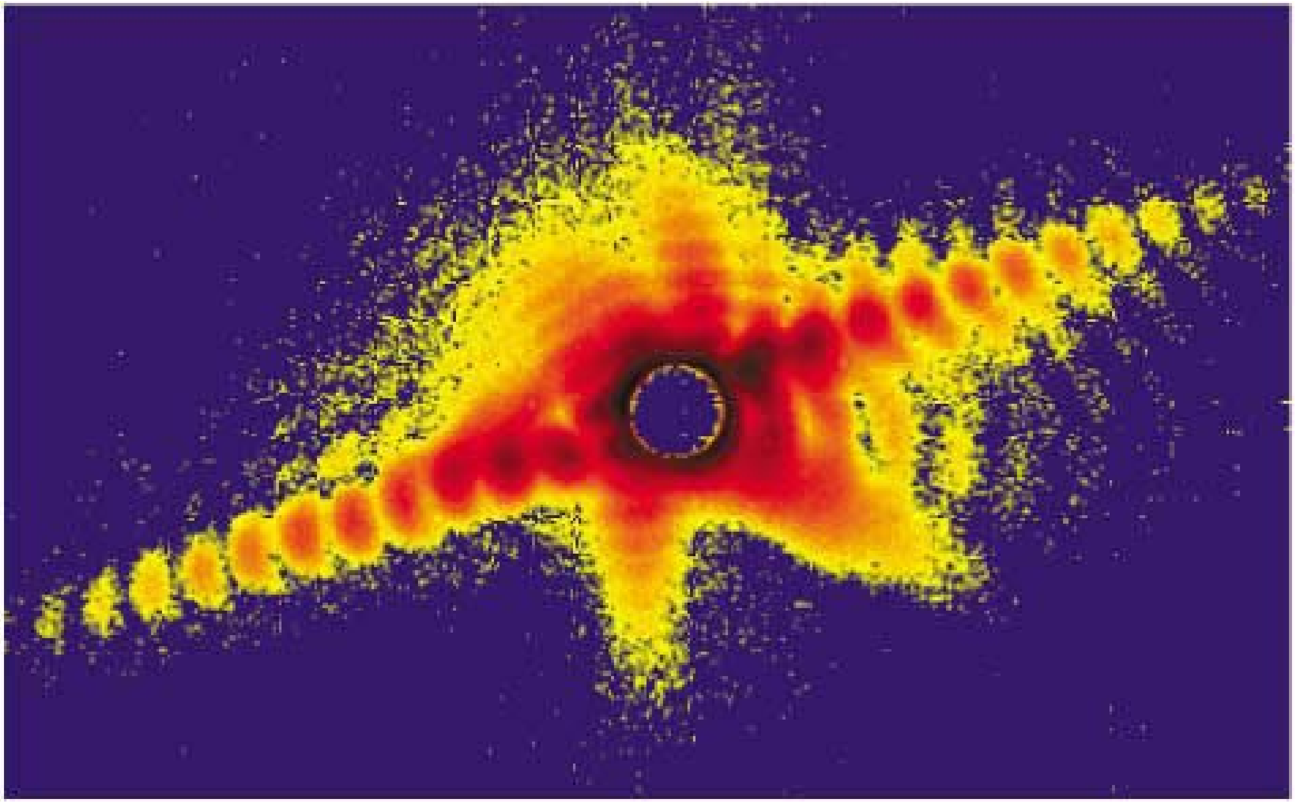
Bragg
Coherent X-ray Diffraction Imaging
(Bragg CXDI)

Coherent X-ray Diffraction Imaging
Lensless X-ray Microscopy



Coherent Scattering on Au Crystals

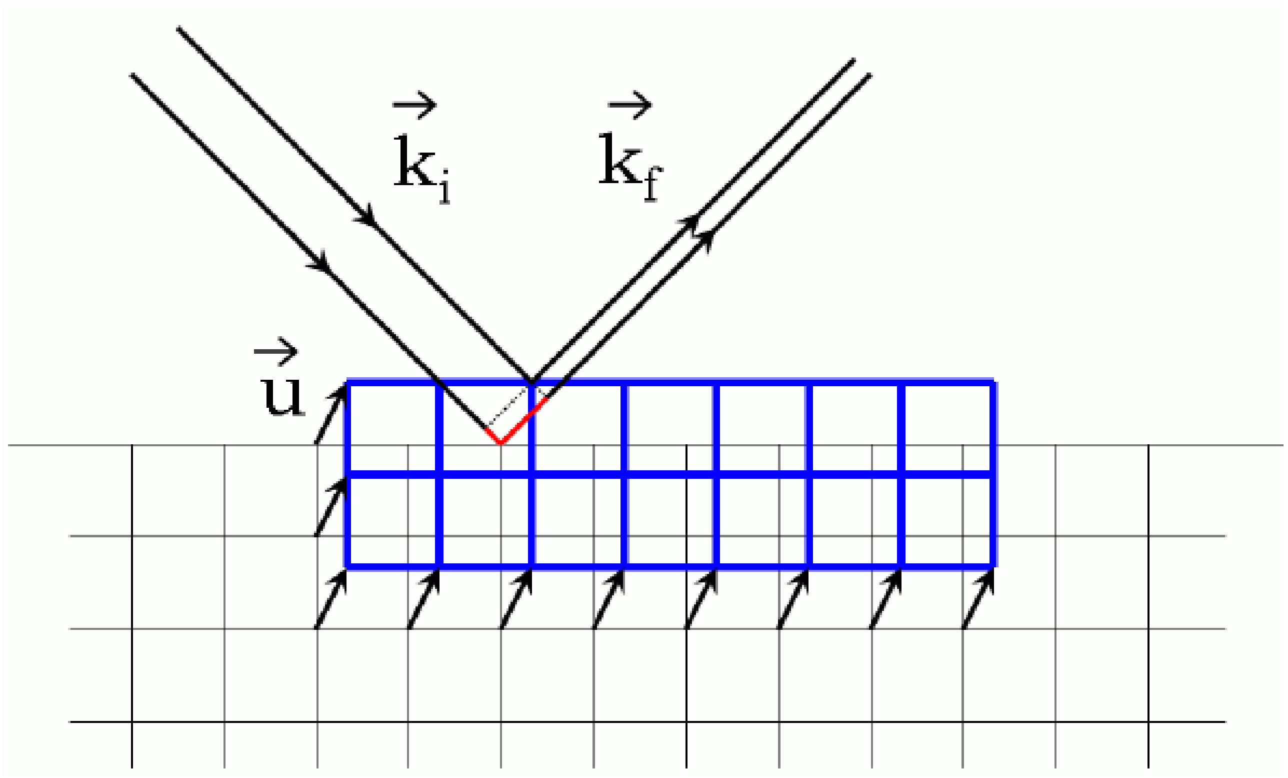
- 4 micron Au nanocrystal
- Coherent X-ray Diffraction
- Measurement at APS sector 33-ID (UNICAT)



I. Robinson, I. Vartanyants, *et al.*, PRL (2001), 87, 195505

Sensitivity to strain

$$\varphi(\boldsymbol{r}) = (\boldsymbol{k}_f - \boldsymbol{k}_i) \cdot \boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{Q} \cdot \boldsymbol{u}(\boldsymbol{r})$$



Courtesy to I. Robinson

Bragg CDI

Kinematical approximation:

$$A(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{-i\mathbf{q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r}$$

$\rho(\boldsymbol{r})$ – periodic electron density in crystal

Scattered amplitude near Bragg peak:

$$A_h(\boldsymbol{Q}) = \frac{F_h}{v} \int s(\boldsymbol{r}) e^{-i\boldsymbol{h}\cdot\boldsymbol{u}(\boldsymbol{r})} e^{-i\boldsymbol{Q}\cdot\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r}$$

F_h – structure factor

$\boldsymbol{Q} = \boldsymbol{q} - \boldsymbol{h}$

Shape function:

$$s(\boldsymbol{r}) = \begin{cases} 1, & \boldsymbol{r} \in \Omega \\ 0, & \boldsymbol{r} \notin \Omega \end{cases}$$

Phase, or projected strain field in crystal:

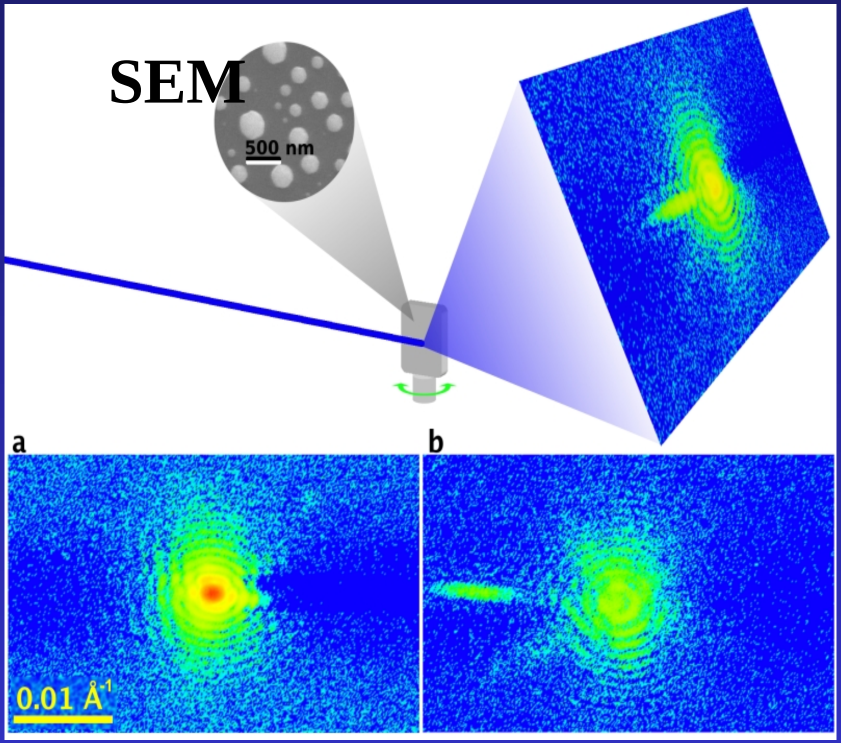
$$\varphi(\boldsymbol{r}) = \boldsymbol{h} \cdot \boldsymbol{u}(\boldsymbol{r})$$

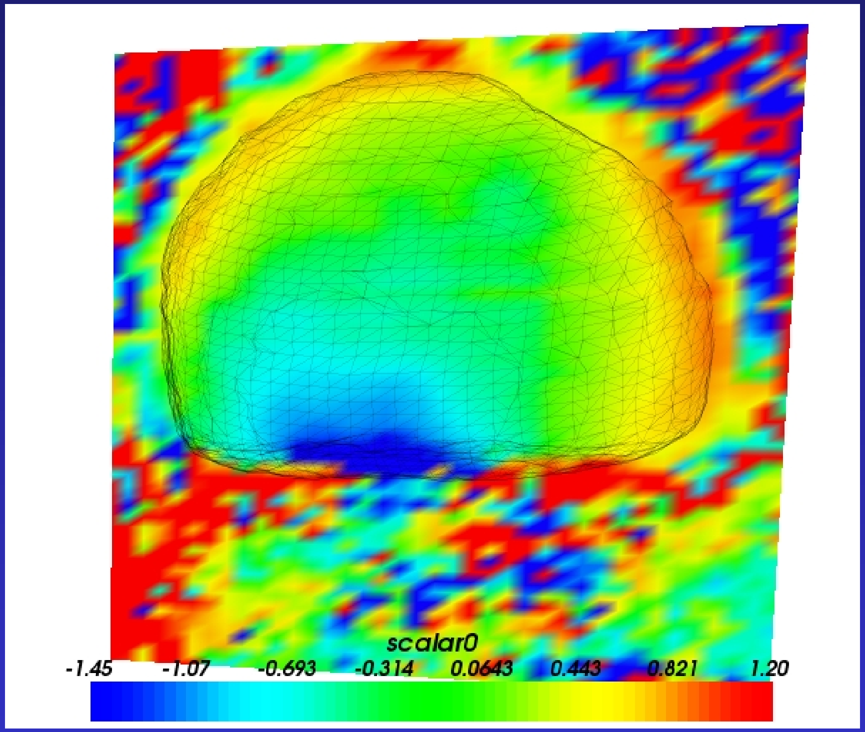
Crystallographic samples, uniform distribution of strain

I.A. Vartanyants & I.K. Robinson, JPCM **13**, 10593 (2001);

I.A. Vartanyants & O.M. Yefanov, in the book: *X-ray Diffraction Modern Experimental Techniques*. (2015), pp. 341-384.

3D mapping of a deformation field inside a nanocrystal





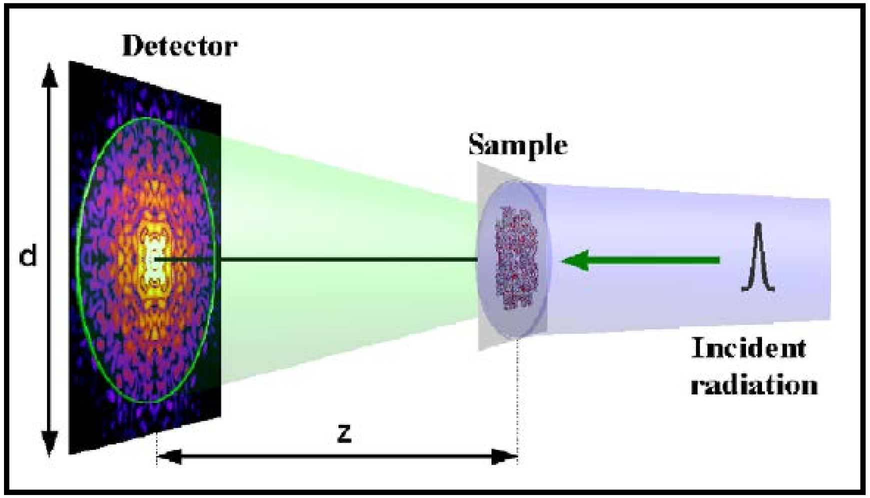
Diffraction patterns from Pb nanocrystal measured around (111) Bragg peak

Strain field shown by color gradient

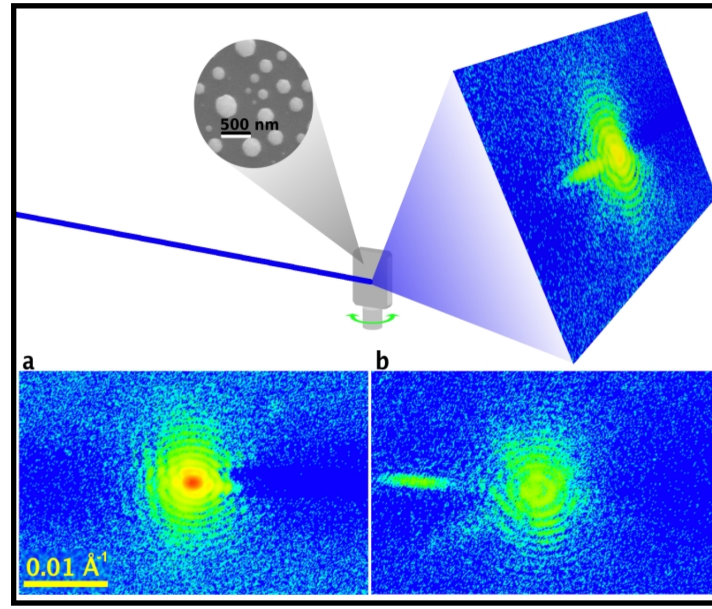
Resolution: 40÷50 nm

M. Pfeifer, *et al.*, Nature, **442**, 63 (2006),
R. Harder, *et al.*, PRB B **76**, 115425 (2007).

Coherent Diffractive Imaging



Mancuso *et al.* J. Biotechnol. **149** 229 (2010)

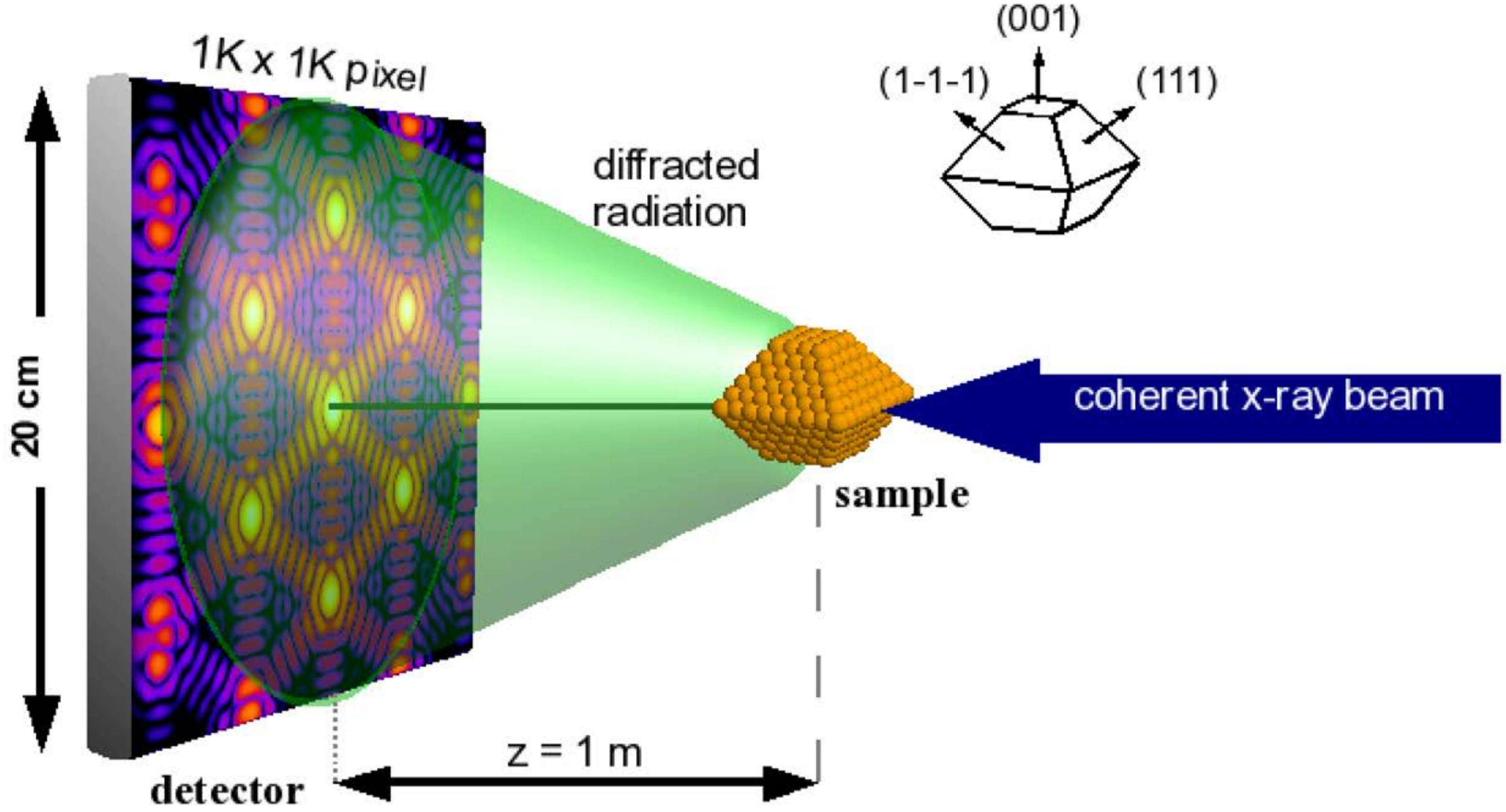


Pfeifer *et al.* Nature. **442** 63 (2006)

Small-angle scattering CDI
Non-crystallographic samples
Uniform electron density of the sample

Bragg CDI
Crystallographic samples
Uniform strain field distribution in the sample

Coherent imaging with atomic resolution



J. Gulden, et al.,
"**Imaging of Nanocrystals with Atomic Resolution Using High-Energy Coherent X-rays**", *XRM-2010 Proceedings,* AIP Conf. Proc. **1365**, 42-45 (2011)

Theory

If several Bragg peaks are measured simultaneously:

$$A(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{-i\mathbf{q}\cdot\boldsymbol{r}} \, \mathrm{d}\boldsymbol{r} = B(\boldsymbol{q}) \cdot F(\boldsymbol{q}) \cdot [\rho_\infty(\boldsymbol{q}) \otimes s(\boldsymbol{q})]$$

Here: *B(**q**)* – envelope function;
*F(**q**)* – structure factor of a unit cell;
*s(**q**)* – FT of the shape function

$$\rho_\infty(\boldsymbol{q}) = \frac{(2\pi)^3}{v} \sum_h \delta(\boldsymbol{q} - \boldsymbol{h})$$

Inverse Fourier transform of this relationship:

$$\rho(\boldsymbol{r}) = [b(\boldsymbol{r}) \otimes \rho_{uc}(\boldsymbol{r})] \otimes [\rho_\infty(\boldsymbol{r}) \cdot s(\boldsymbol{r})]$$

Here: *b(**r**)* – FT of the envelope function *B(**q**)*;
$\rho_{uc}(\boldsymbol{r})$ – electron density of a unit cell;
*s(**r**)* – shape function

$$\rho_\infty(\boldsymbol{r}) = \sum_n \delta(\boldsymbol{r} - \boldsymbol{R}_n);$$

$$\boldsymbol{R}_n = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3$$

I.A. Vartanyants & O.M. Yefanov, in the book: *X-ray Diffraction Modern Experimental Techniques*. (2015), pp. 341-384.

Theory

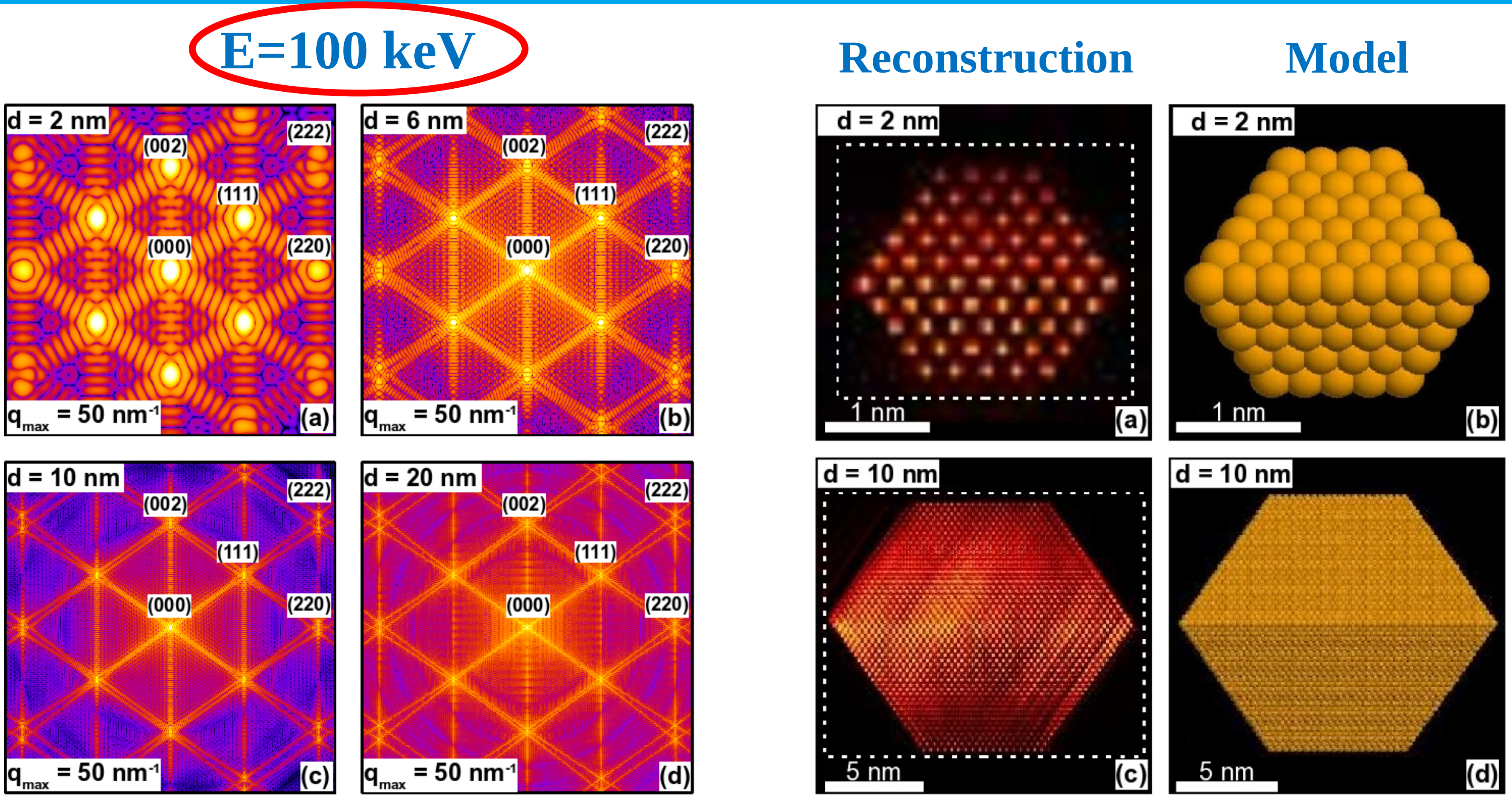
This electron density is peaking at the regular positions of the unit cell due to the function $\rho_{\infty}(\mathbf{r})$ and has an overall shape of the sample $s(\mathbf{r})$.

Most importantly, it contains the position of the atoms in the unit cell due to the reconstruction of the electron density function of a unit cell $\rho_{uc}(\mathbf{r})$.

This means the following: If the continuous intensity distribution around several Bragg peaks will be measured simultaneously and phase retrieval methods will be applied to get the phase, then, in principle, the electron density with ***atomic*** resolution will be obtained.

I.A. Vartanyants & O.M. Yefanov, in the book: *X-ray Diffraction Modern Experimental Techniques*. (2015), pp. 341-384.

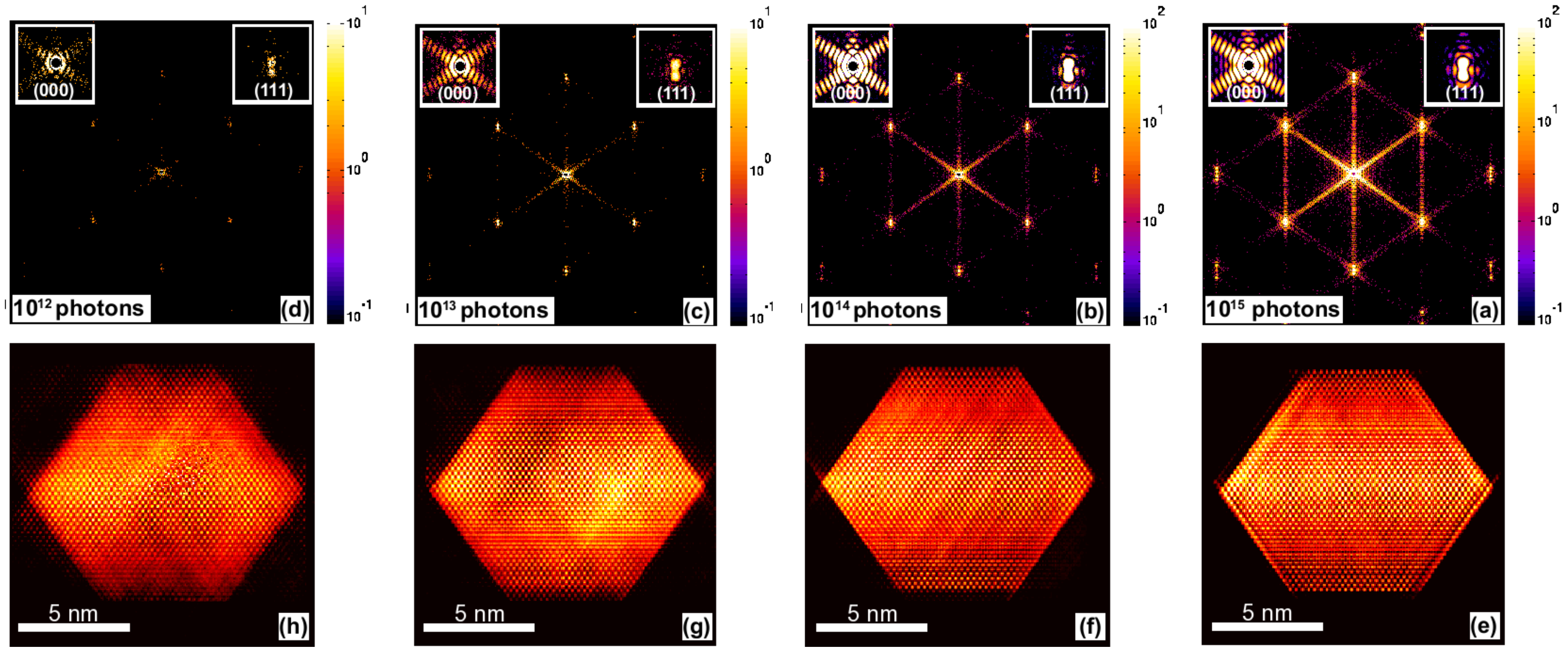
CXDI using high energy coherent X-rays



J. Gulden, et al.,
"**Imaging of Nanocrystals with Atomic Resolution Using High-Energy Coherent X-rays**", *XRM-2010 Proceedings,* AIP Conf. Proc. **1365**, 42-45 (2011)

CXDI using high energy coherent X-rays

F=10^{12} photons | F=10^{13} photons | F=10^{14} photons | F=10^{15} photons



Pd nanocrystal
10 nm size

An excellent scientific goal for

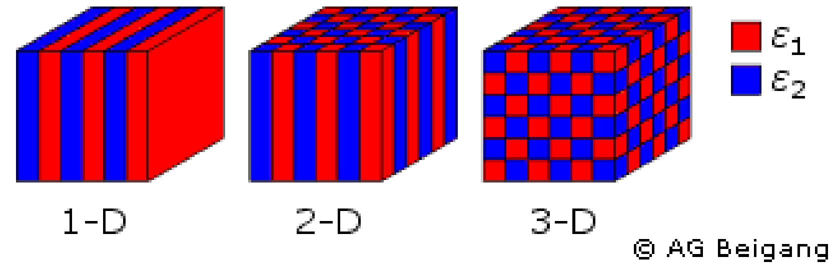
diffraction limited storage ring?

First realization of these ideas with photonic (colloidal) crystals

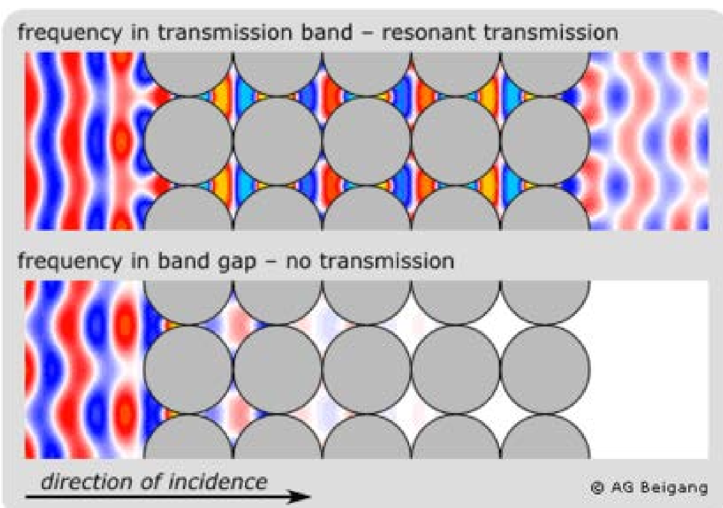
Photonic crystals

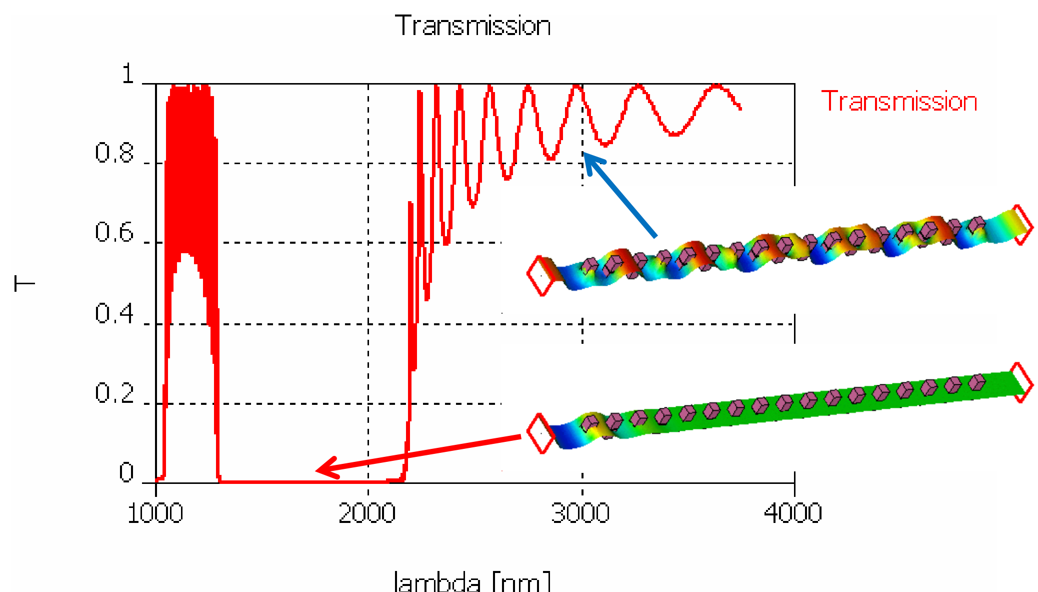
Photonic crystals in nature

Artificial photonic crystals



Photonic band gap materials

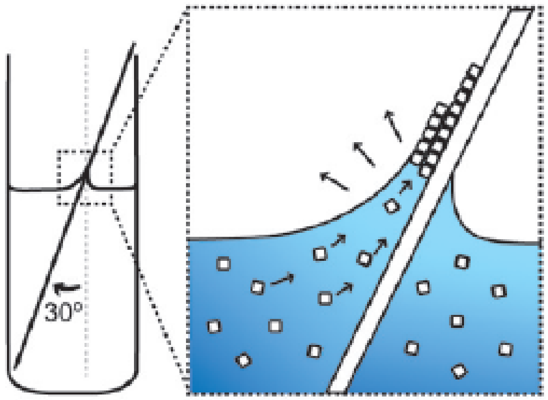


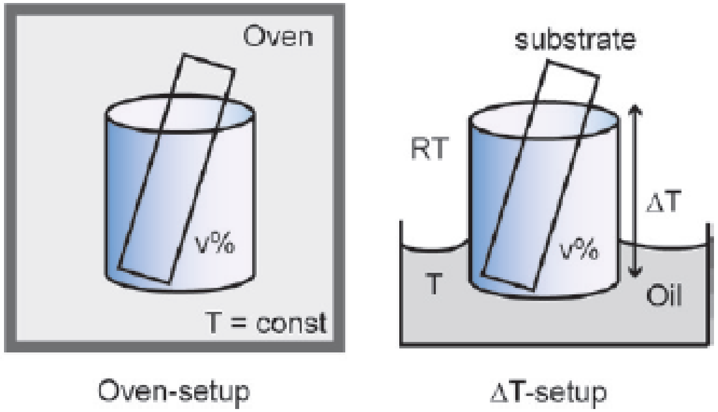


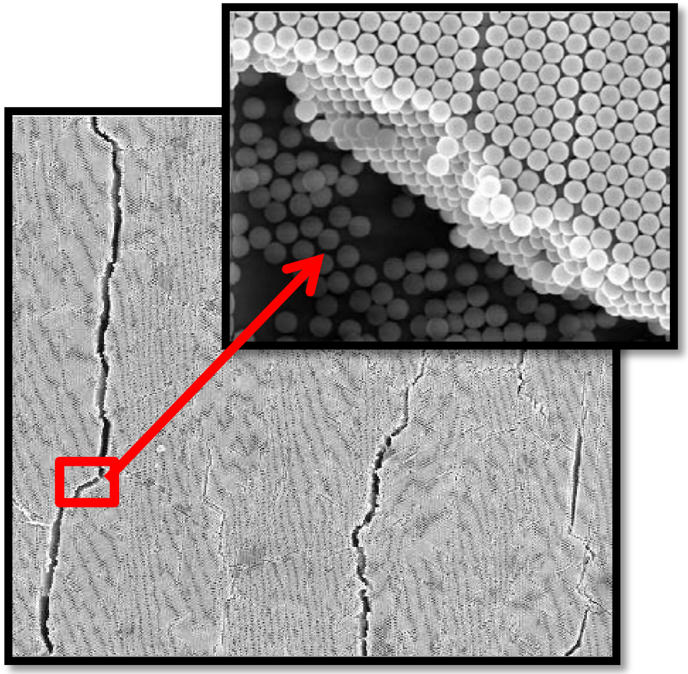
https://www.theochem.kth.se/research/phot_c
t/Photonic_Crystals.html

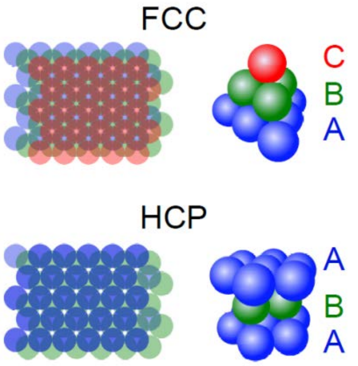
Colloidal crystals grown by self-organization

Vertical deposition method









A
B
C = RHCP
A
B

J-M. Meijer, et. al. Langmuir (**2012**), 28, 7631−7638.

Coherent x-ray imaging of defects in colloidal crystals

J. Gulden, *et al.*, Phys. Rev. B **81**, 224105 (2010)

European Synchrotron Radiation Facility
ESRF

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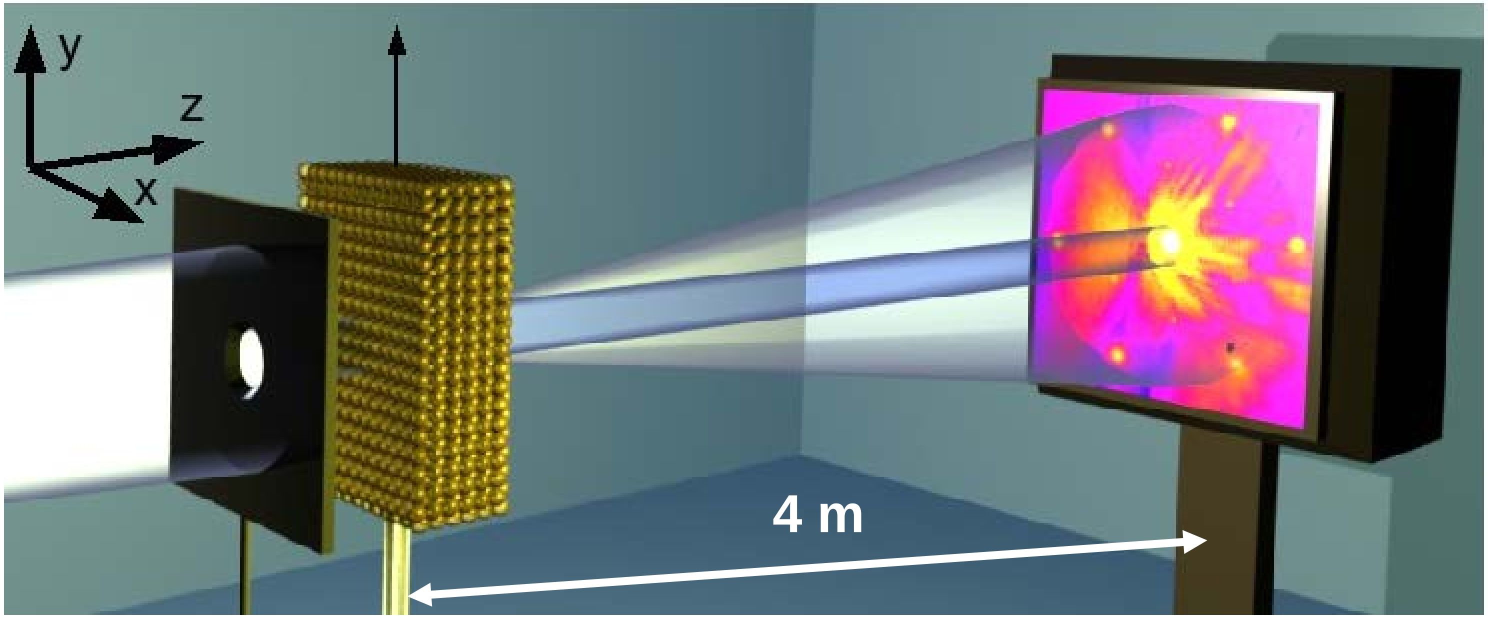
Measurements at azimuthal angle φ = 0°



Experimental conditions (ID06, ESRF):

- **Energy: E=14 keV**
- **Pinhole size 6.9 µm**
- **Sample detector distance: 3.96 m**
- **Detector pixel size: 9 µm**
- **Detector size: 4005 × 2671 pixels**

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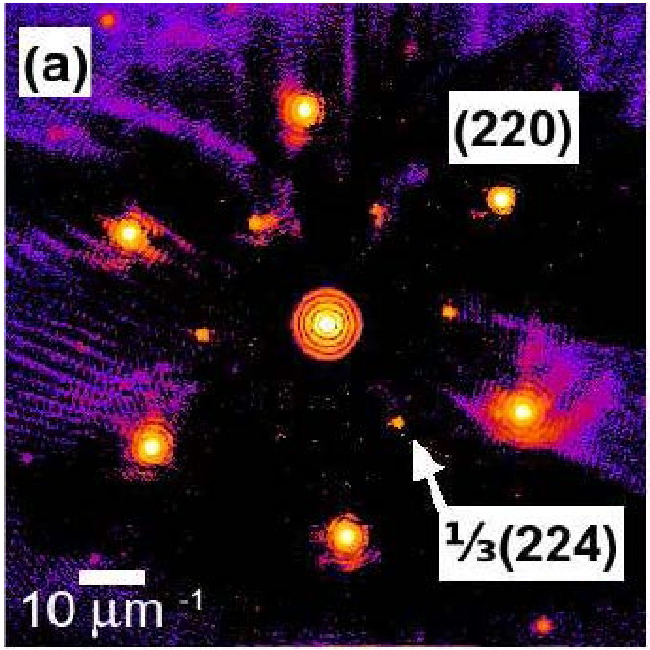
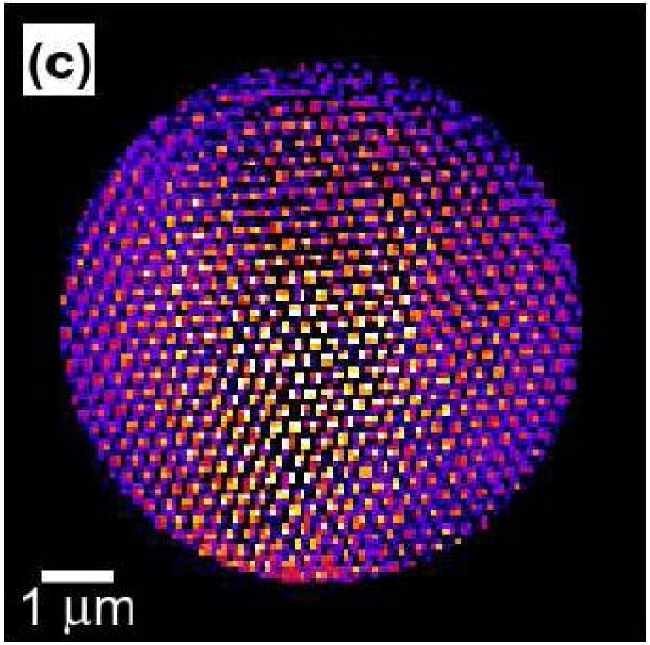
J. Gulden, *et al.*, Phys. Rev. B **81**, 224105 (2010)

Measurements at azimuthal angle φ = 0°



Diffraction pattern with the subtracted pinhole



Results of reconstruction from this diffraction pattern

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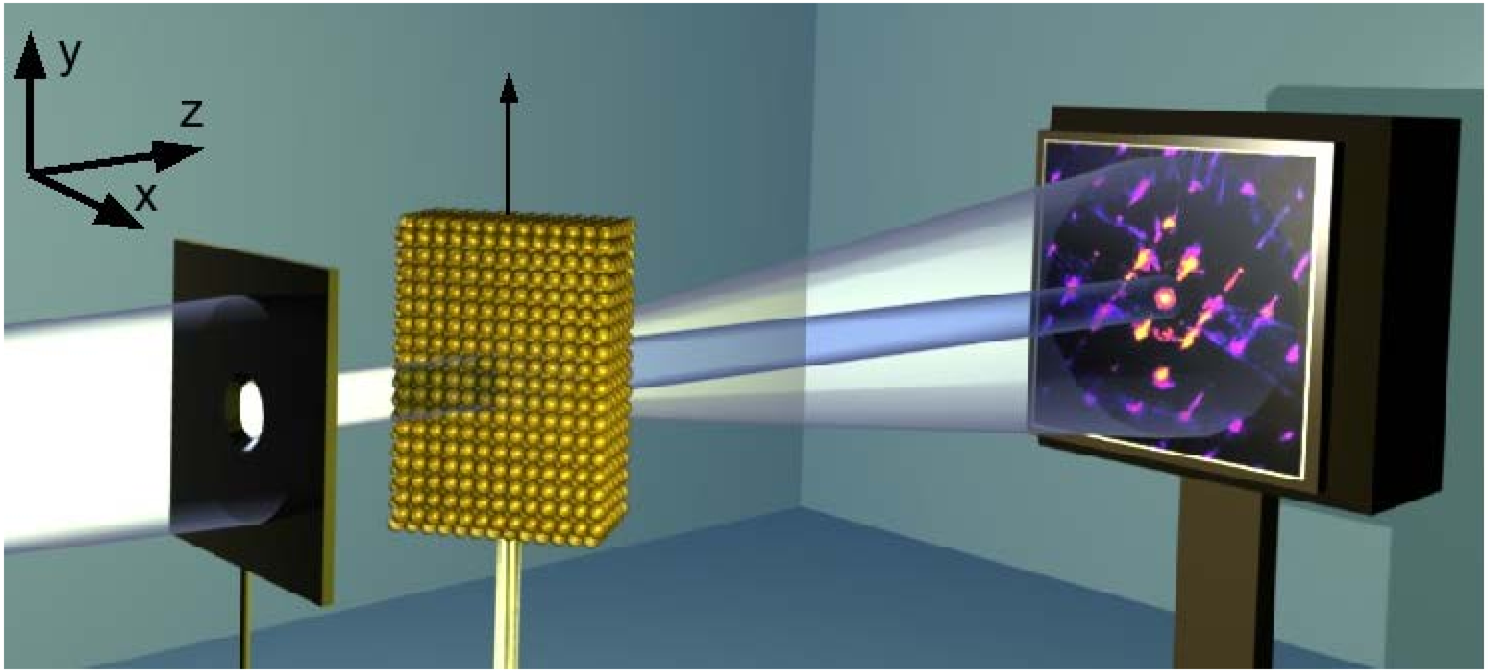
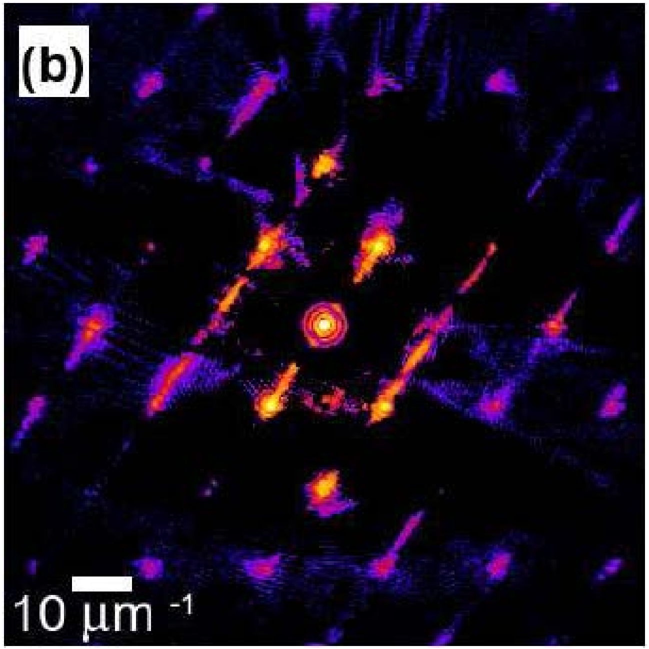
Measurements at azimuthal angle φ = 35°

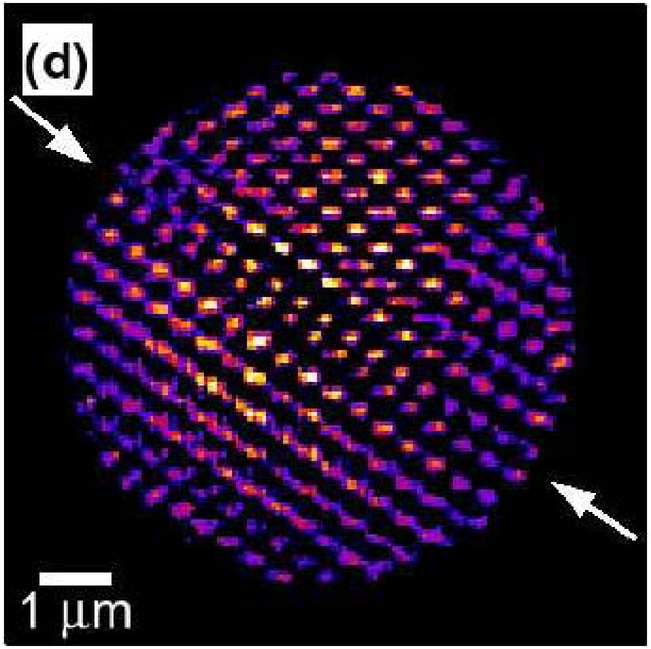


Experimental conditions (ID06, ESRF):

- **Energy: E=14 keV**
- **Pinhole size 6.9 μm**
- **Sample detector distance: 3.96 m**
- **Detector pixel size: 9 μm**
- **Detector size: 4005 × 2671 pixels**

Measurements at azimuthal angle $\varphi = 35^\circ$





For the first time defect core was directly imaged using coherent x-rays

Extension to 3D

Crystallography with coherent X-rays

J. Gulden, *et al.*, Optics Express, **20**(4) 4039 (2012)
A. Shabalin, *et al.*, (2015) (in preparation)

PETRA III

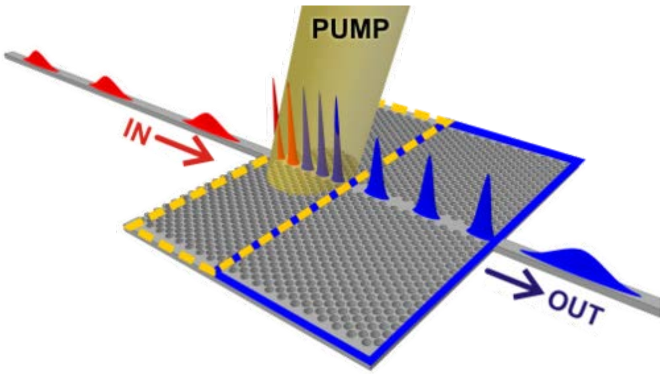
HELMHOLTZ GEMEINSCHAFT

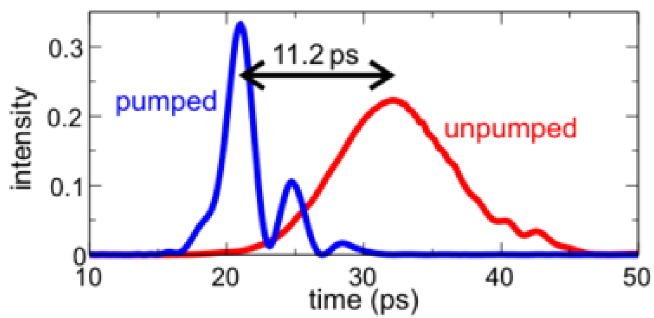
DESY

Structural evolution of colloidal crystal films in the vicinity of the melting transition

Tuning of properties by external fields

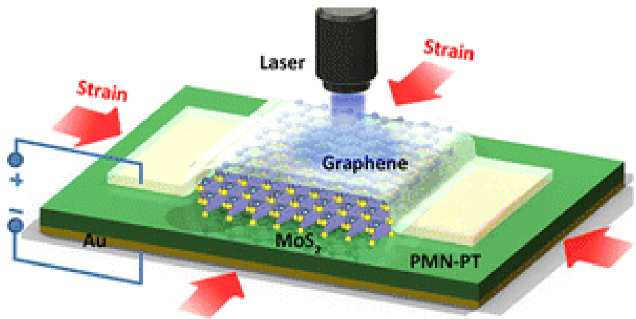
Pumping energy

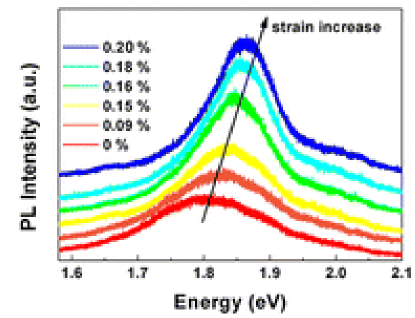




M. Daryl *et al.*, PRL 108, 033902 (2012)

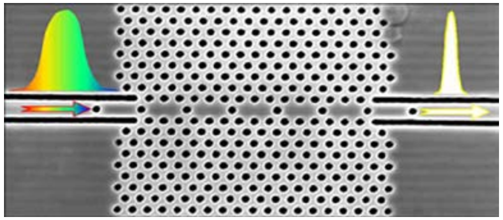
Strain field engineering





Y. Y. Hui et al., ACS Nano 7 (8), 7126 (2013)

Incremental heating

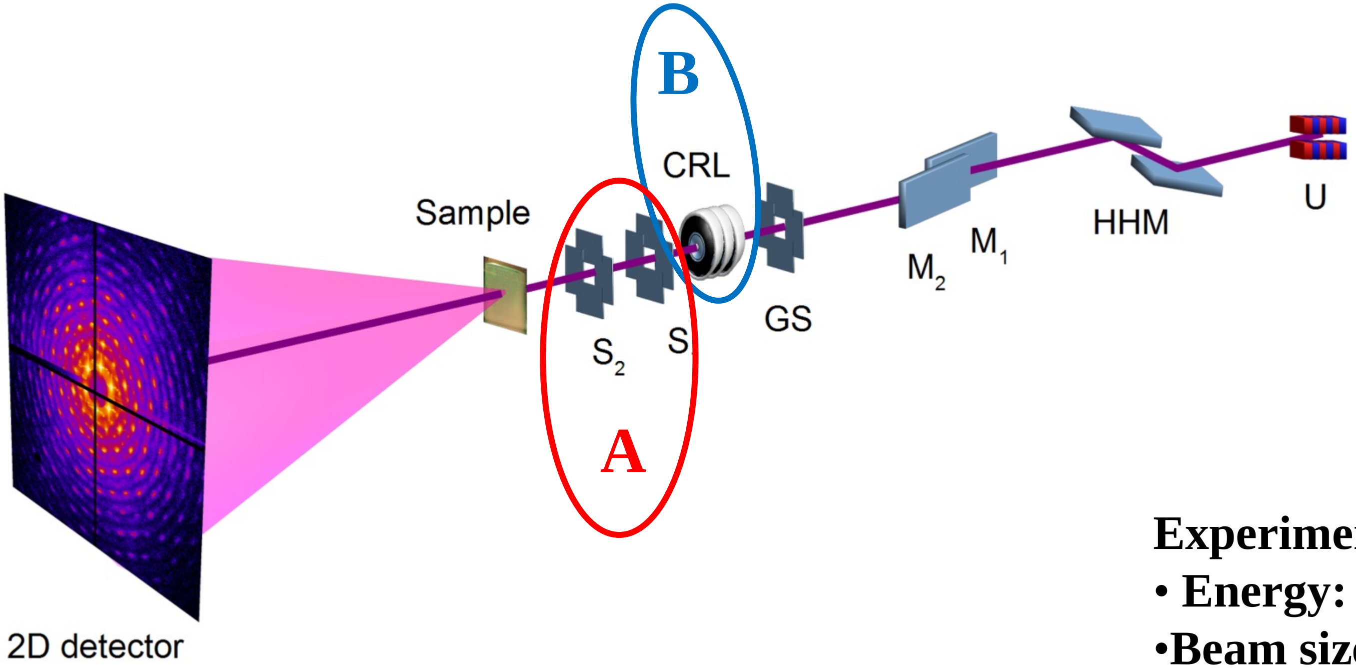


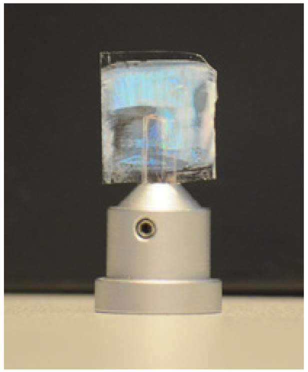
http://www.st-andrews.ac.uk/microphotonics/Gallery.php

http://www.amolf.nl/research/nanooptics/news/detailpage/artikel/pumped-photonic-crystal-accelerates-slow-light/

E. Sulyanova *et al.*, Langmuir **31**(19), 5274 (2015).

Experimental setup. P10 beamline, PETRA III

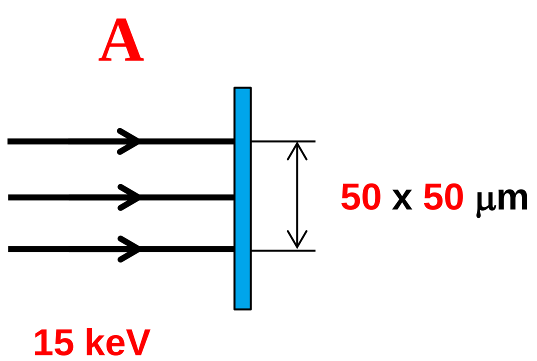


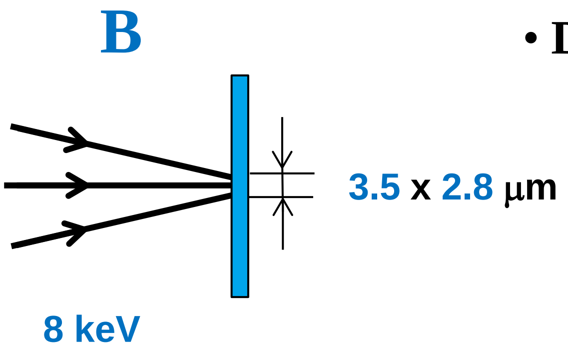


Colloidal crystal film

Experimental conditions:

- **Energy: E=15 keV, 8 keV**
- **Beam size 50x50 μm, 3.5x2.8 μm**
- **Sample detector distance: 5.1 m**
- **Detector pixel size: 55x55 μm^2**
- **Detector size: 516×516 pixels**

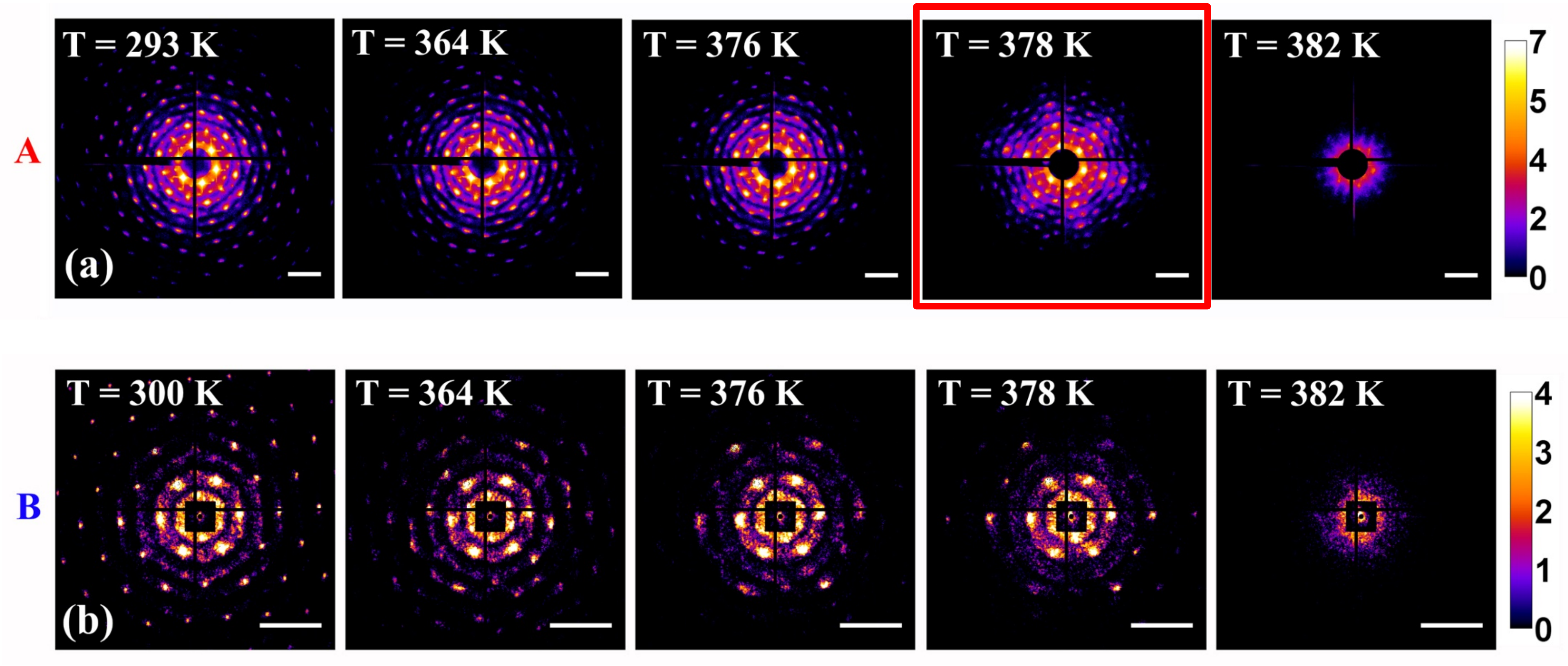




X-ray diffraction patterns measured *in situ* during incremental heating

Experiment A

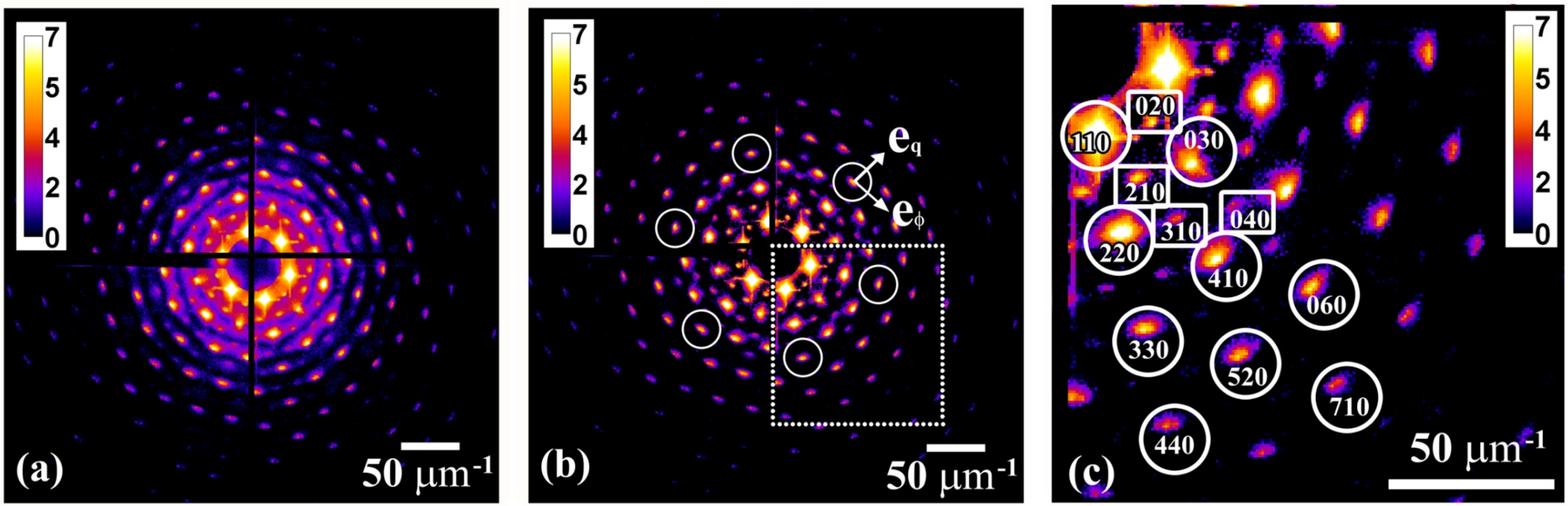
15 keV, 50 x 50 μm unfocused beam



Experiment B

8 keV, 3.5 x 2.8 μm focused coherent beam

X-ray diffraction pattern of the experiment A measured at room temperature

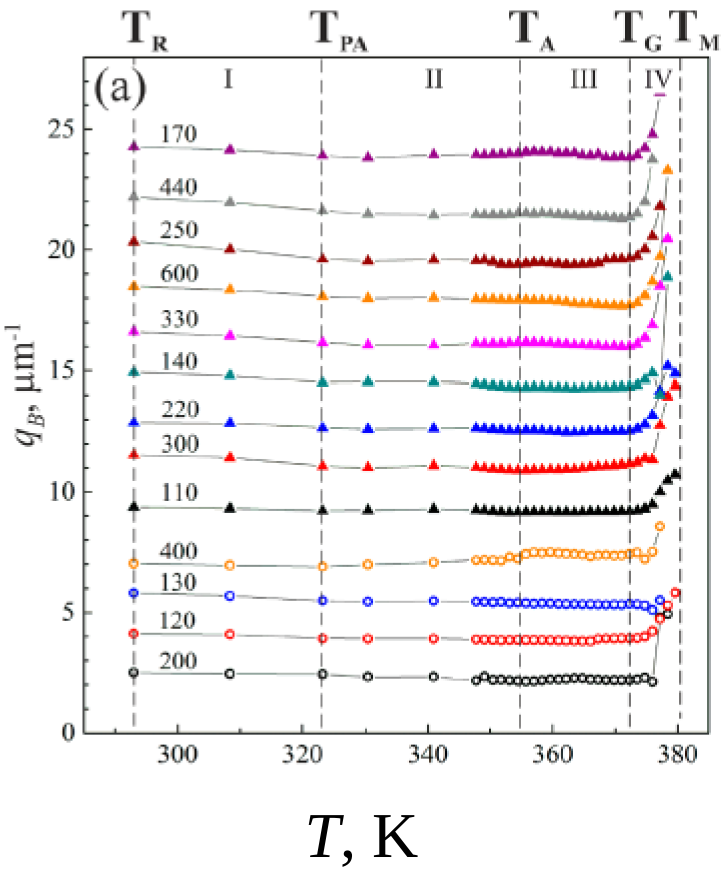


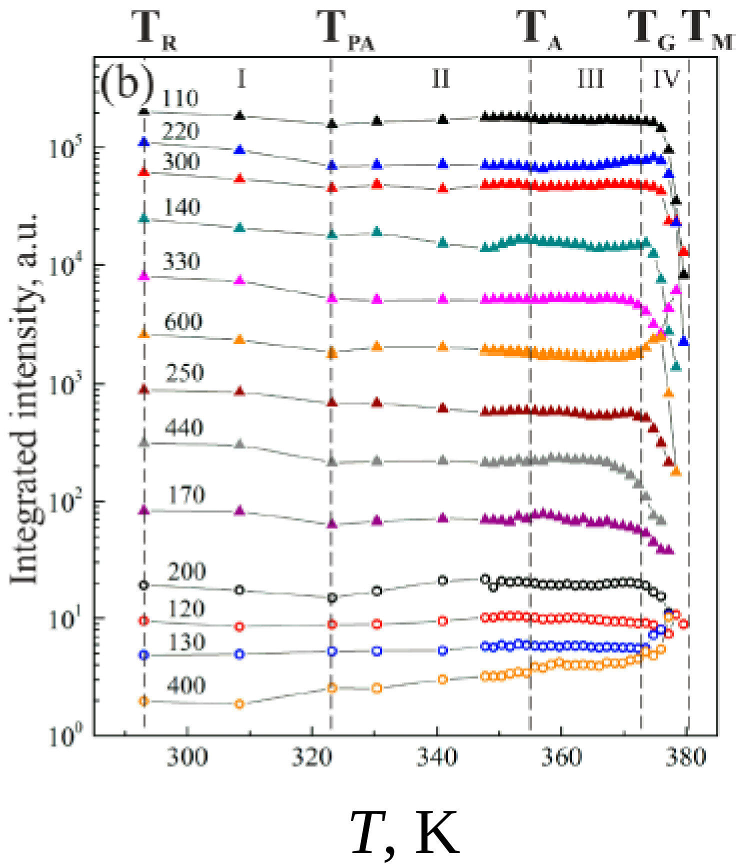
X-ray diffraction pattern of the experiment A measured at room temperature.

Same pattern with SAXS contribution subtracted.

Enlarged area of (b) showing Bragg peak indexing.

Temperature evolution of the Bragg peaks parameters experiment A

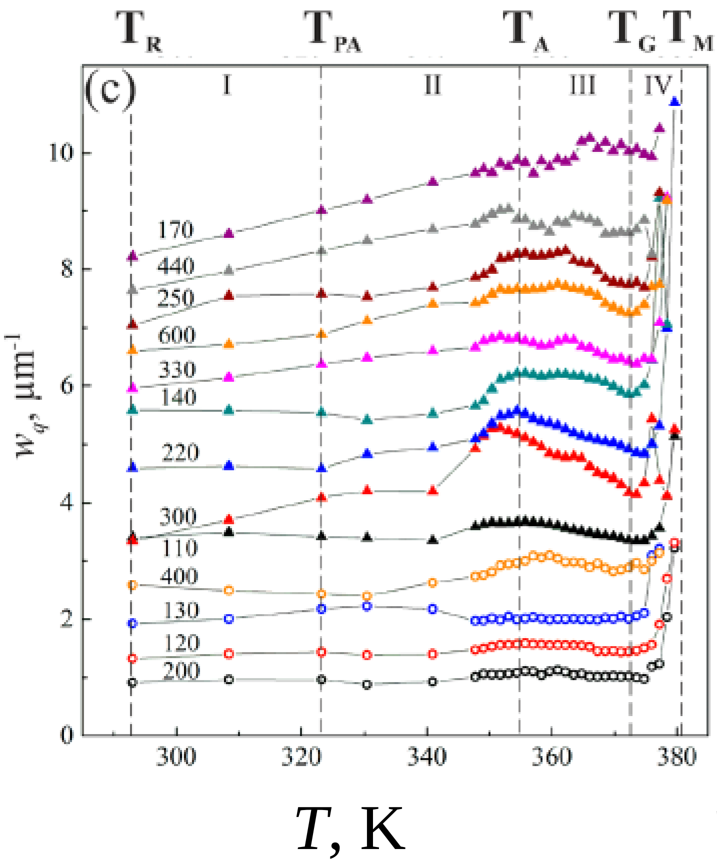




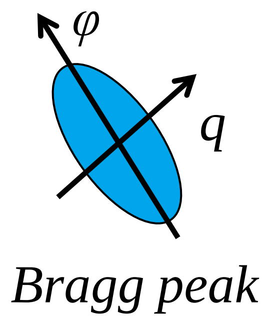
Position of the Bragg peak

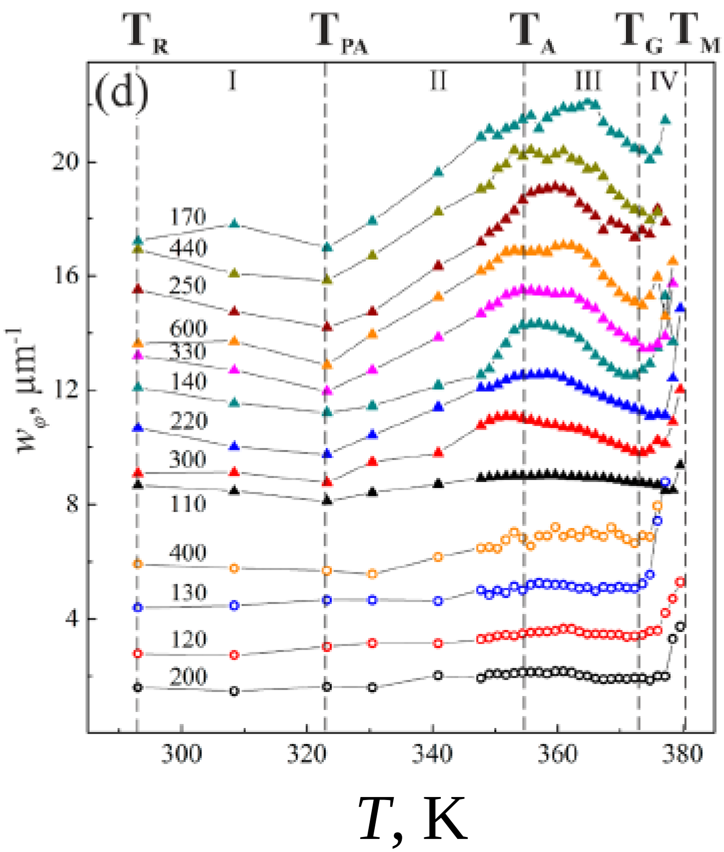
Integrated intensity

Temperature evolution of the Bragg peaks parameters experiment A



FWHM of the Bragg peak in radial direction, w_q

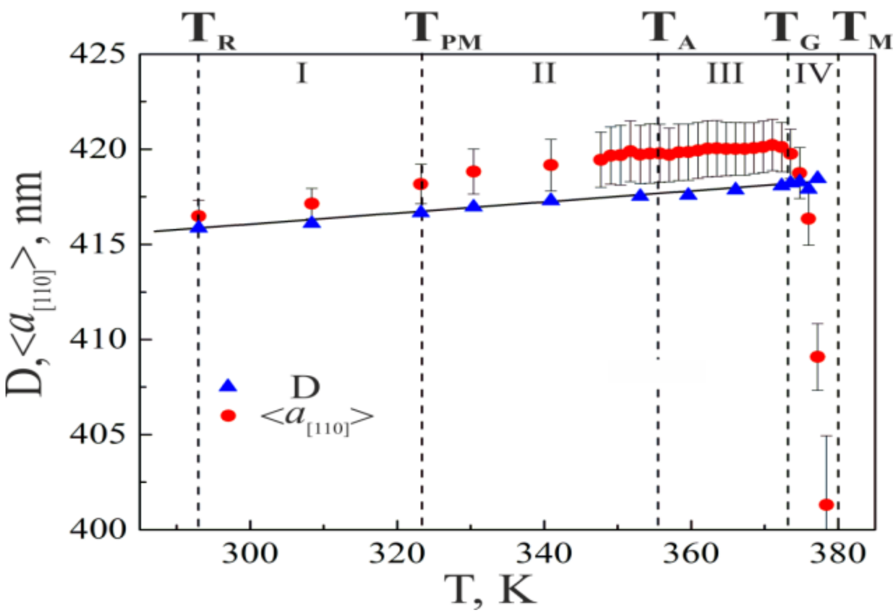




FWHM of the Bragg peak in azimuthal direction, w_φ

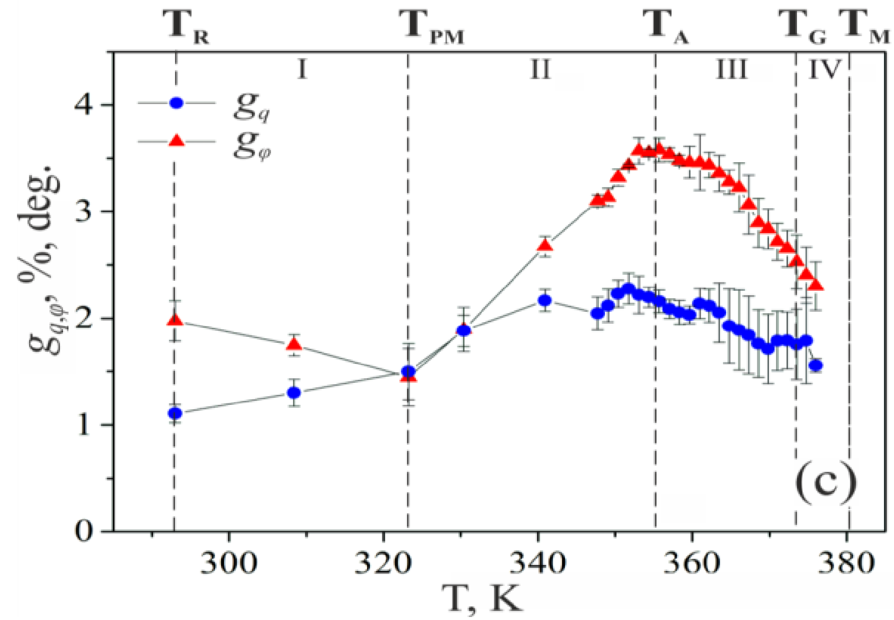
Temperature evolution

Nano- scale



Polysterene particle diameter D and average lattice parameter $<a_{[110]}>$

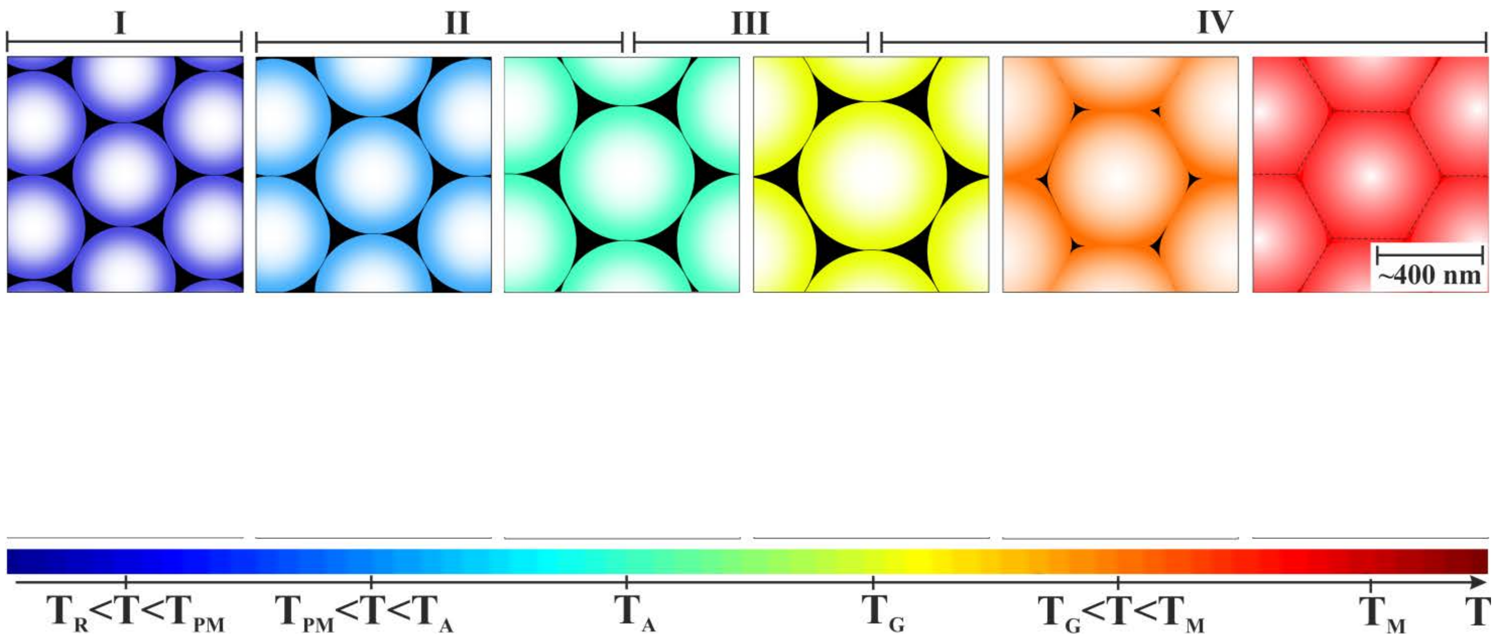
Mesoscopic scale



Lattice distortion parameter g_q and domain misorientation parameter g_φ

The model of colloidal crystal melting process

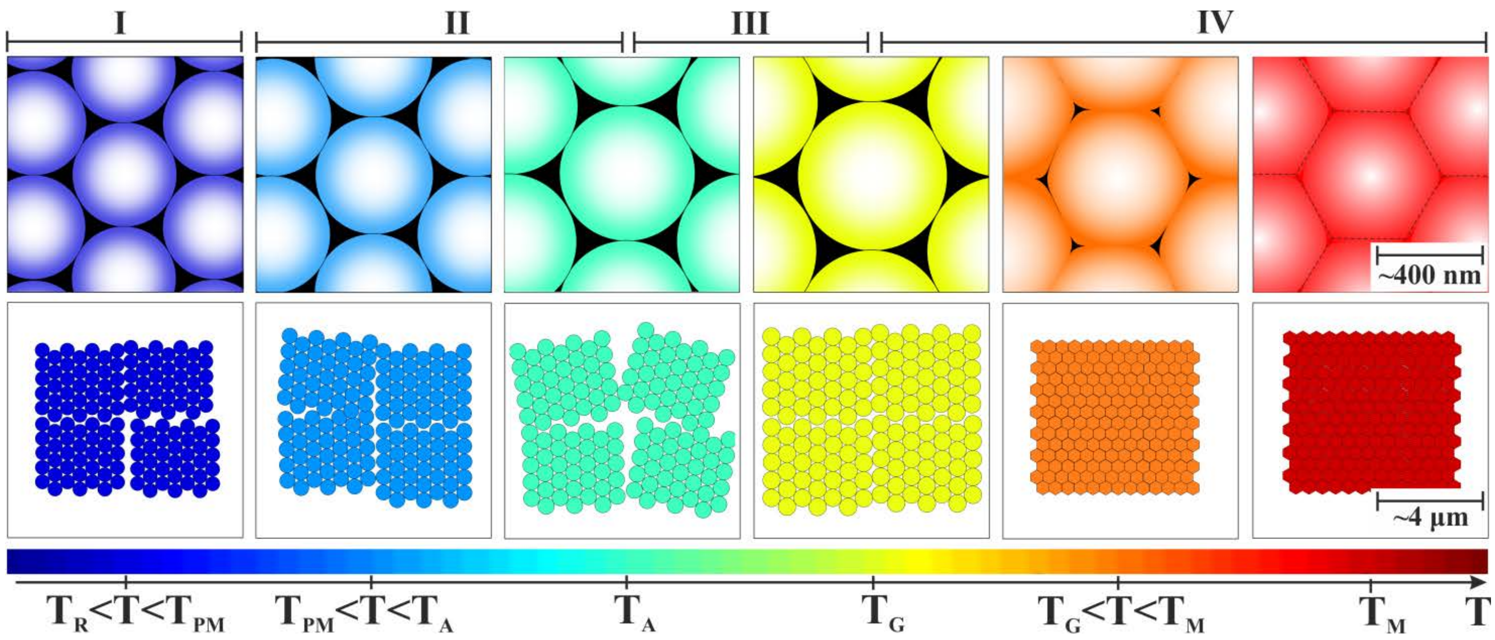
Nano- scale



Mesoscopic scale

The model of colloidal crystal melting process

Nano- scale



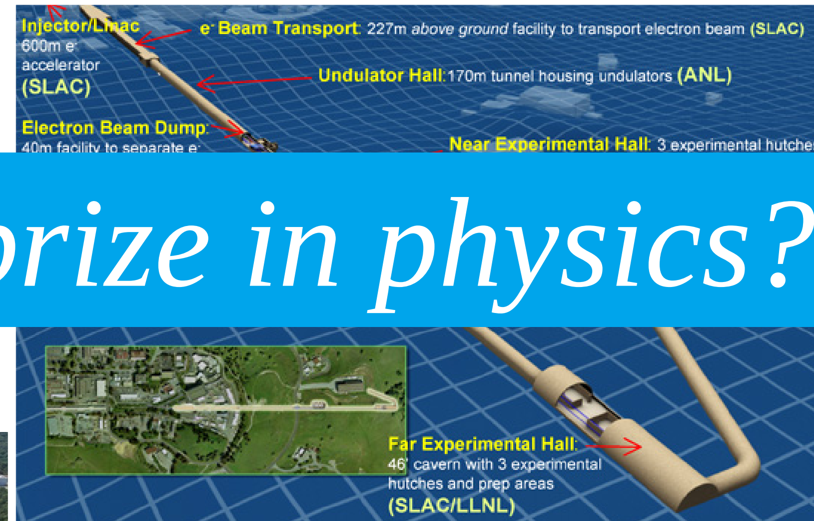
Mesoscopic scale

Free-electron lasers

We are living in exciting time !

FLASH at DESY
2005

LCLS at Stanford
2009



Sometime Nobel prize in physics?

SACLA at Spring8
2011

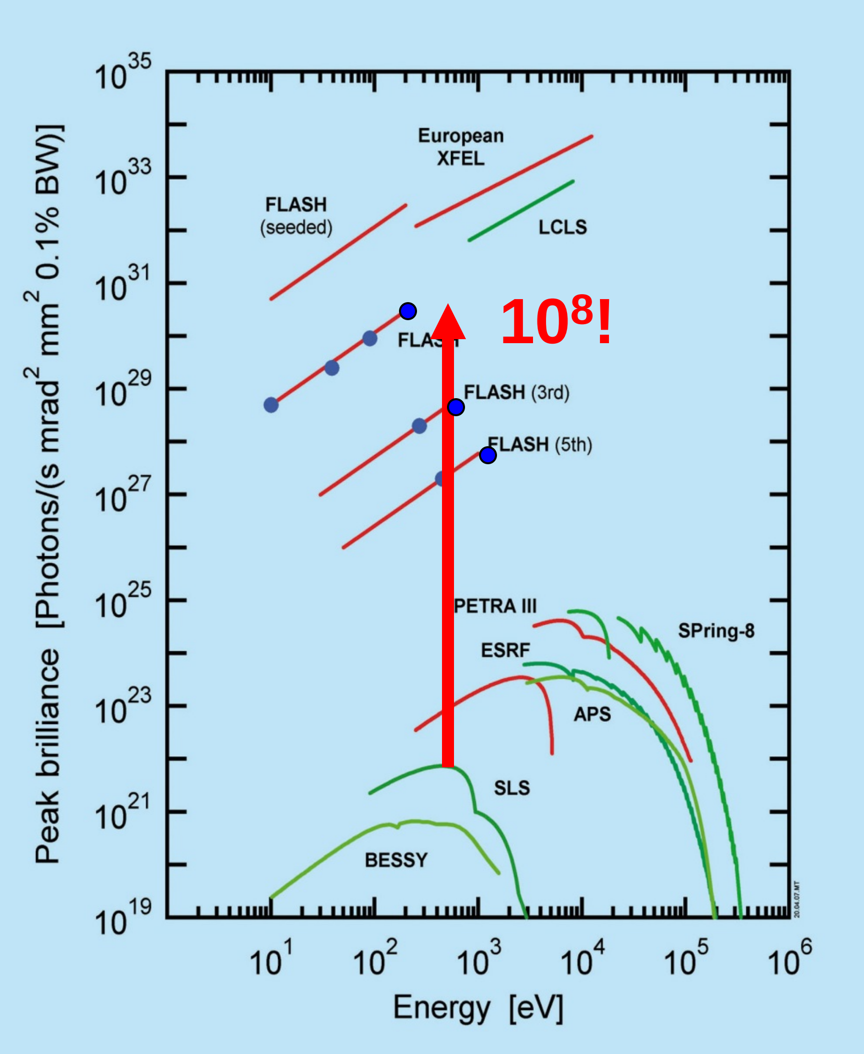
HELMHOLTZ | ASSOCIATION

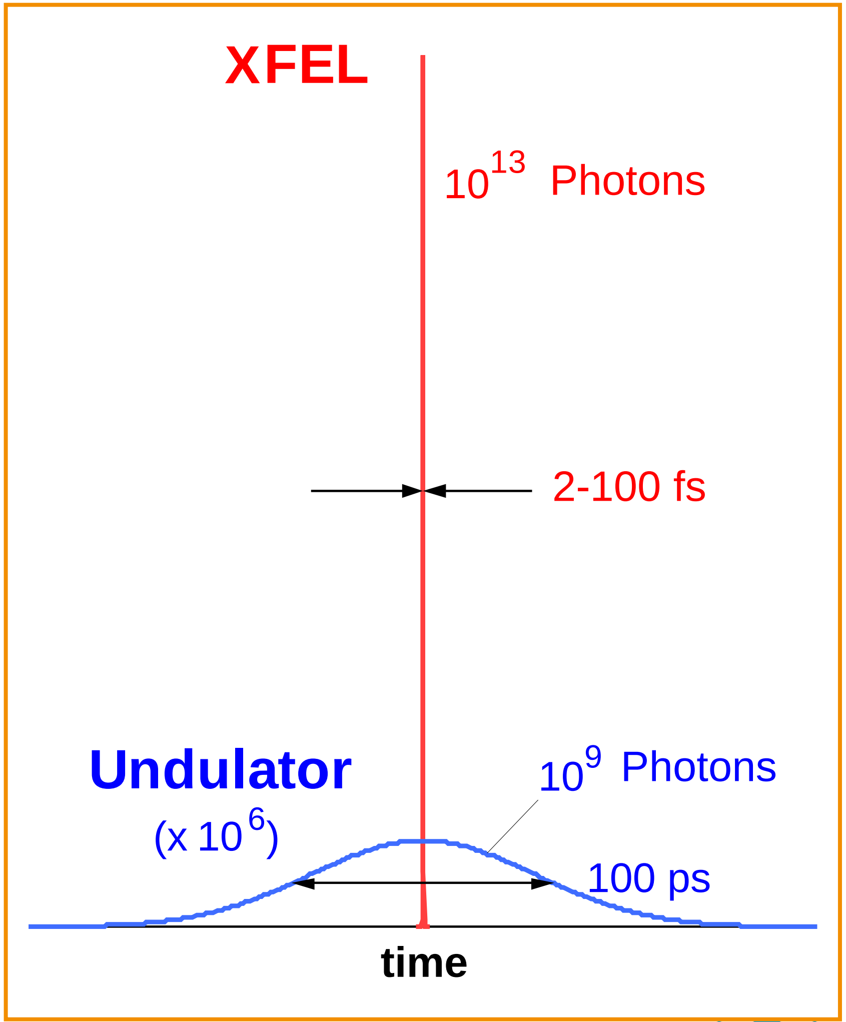
DESY

European XFEL under construction (2016-2017)

European XFEL

Comparison of 3rd and 4th generation sources



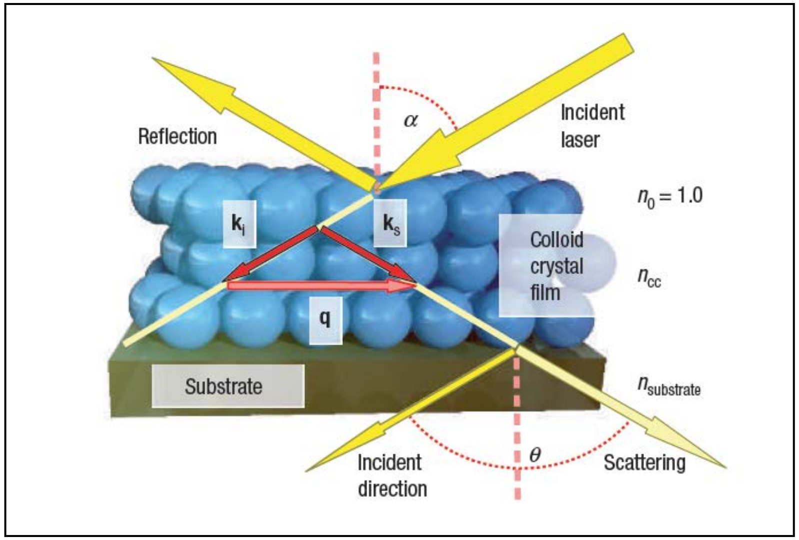


ENFMC 2012, Águas de Lindóia, 17.05.2012
Massimo Altarelli, European XFEL GmbH, Hamburg

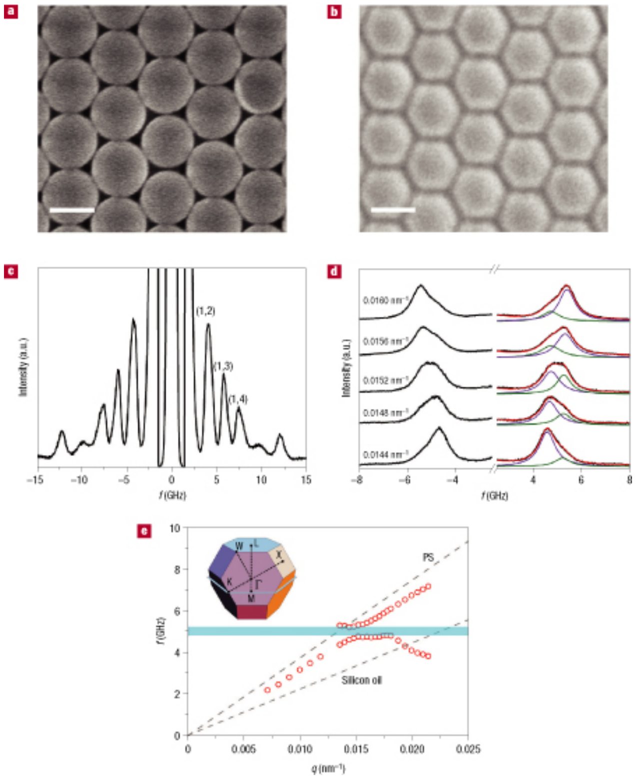
Study of dynamics in colloidal crystals

Observation and tuning of hypersonic bandgaps in colloidal crystals

- Polysterene spheres in air, glycerol, PDMS and silicon oil
- $D = 256\,nm, 307\,nm$
- Brillouin spectroscopy
- No sintering



Supported opal and scattering geometry



Brillouin light scattering spectra of dry and wet opals and phononic gap

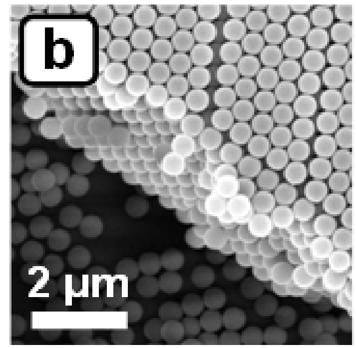
W. Cheng *et al.*, Nature Materials (2006)

Pump-probe experiment on colloidal crystals at FLASH

Pump probe experiment on colloidal crystal film at FLASH

> **Study of colloidal crystal in the temporal domain**

- ✓ Elastic vibration of the spheres (Lamb modes)
- ✓ Collective vibrations (phonons)
- ✓ Order-disorder transitions

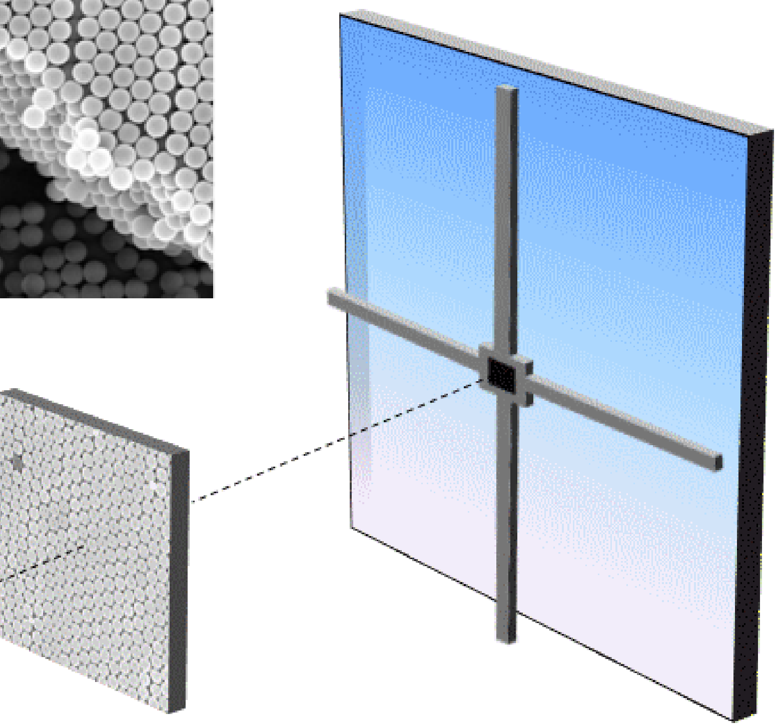


Pump-probe experiment:

> Pump: 800 nm IR laser

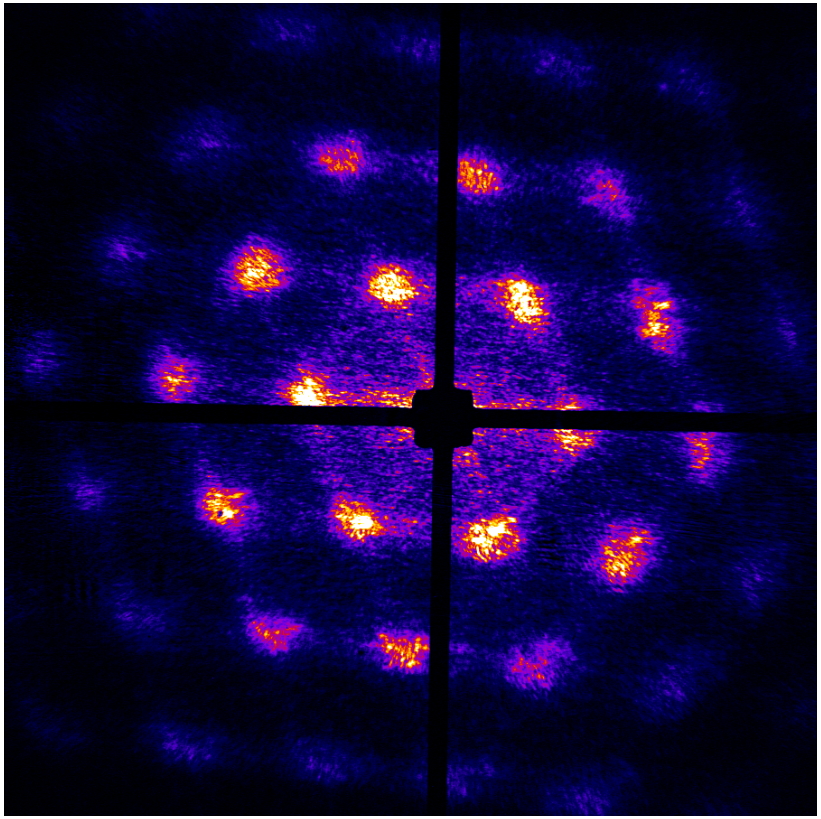
> Probe: 8 nm FEL radiation

> Time delay from -100 ps up to 1000 ps, with 50 ps steps

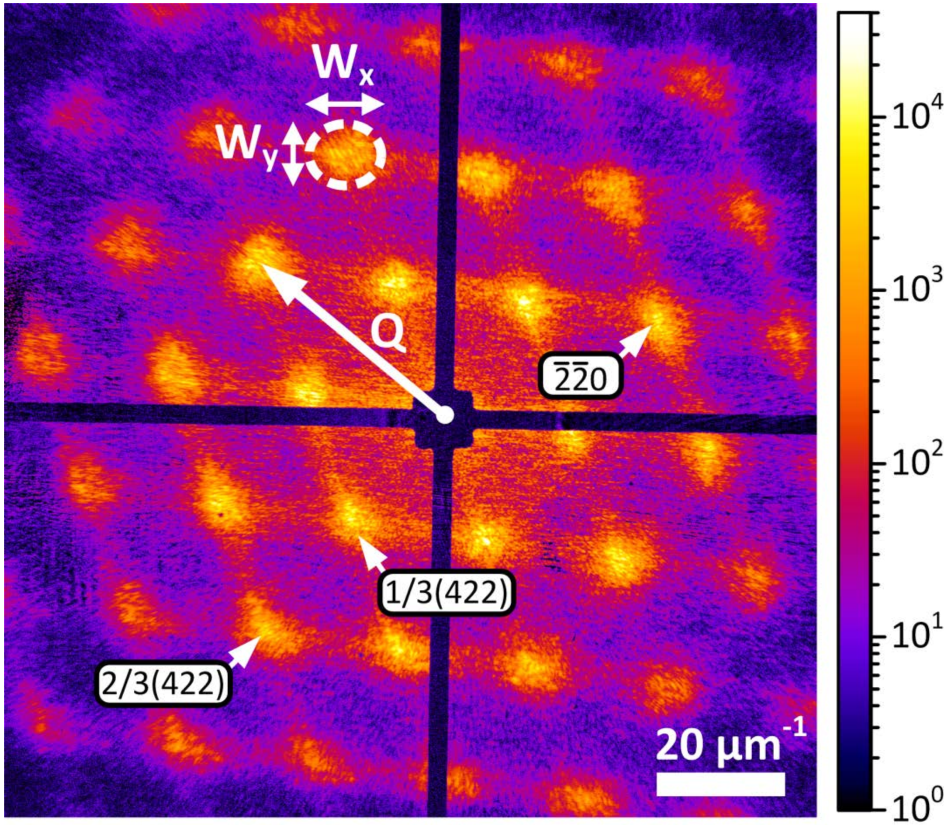


R.Dronyak et. al., Phys Rev B 86 (2012)

Pump-Probe Experiment on Colloidal Crystal Film at FLASH



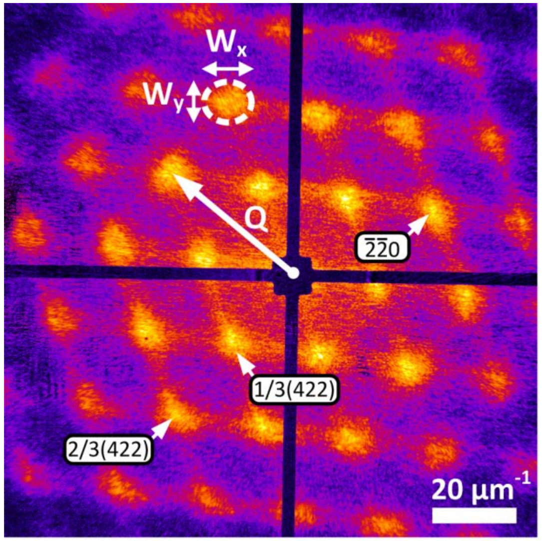
Single-shot diffraction patterns at different time delay

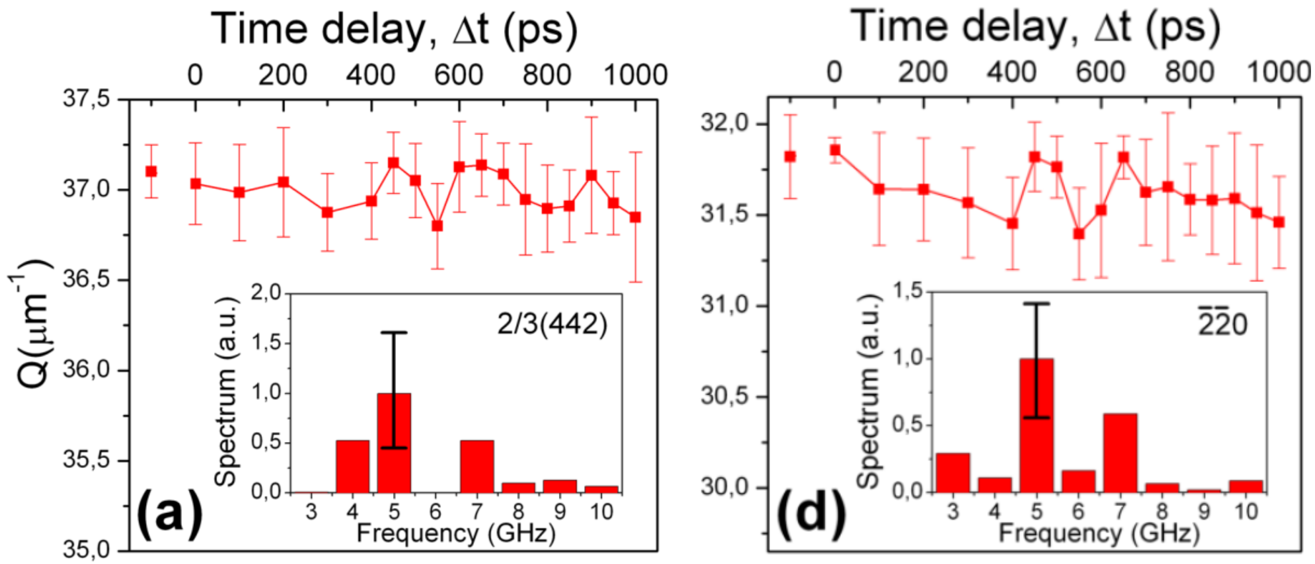


The momentum transfer vector **Q** and the horizontal W_x and vertical W_y size of the peaks were analyzed

R.Dronyak et. al., Phys Rev B 86 (2012)

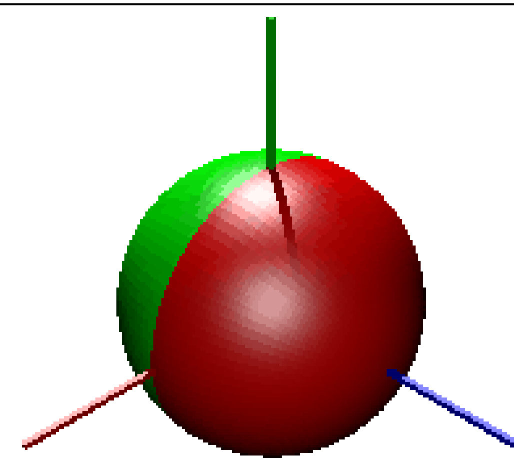
Pump-Probe Experiment on Colloidal Crystal Film at FLASH



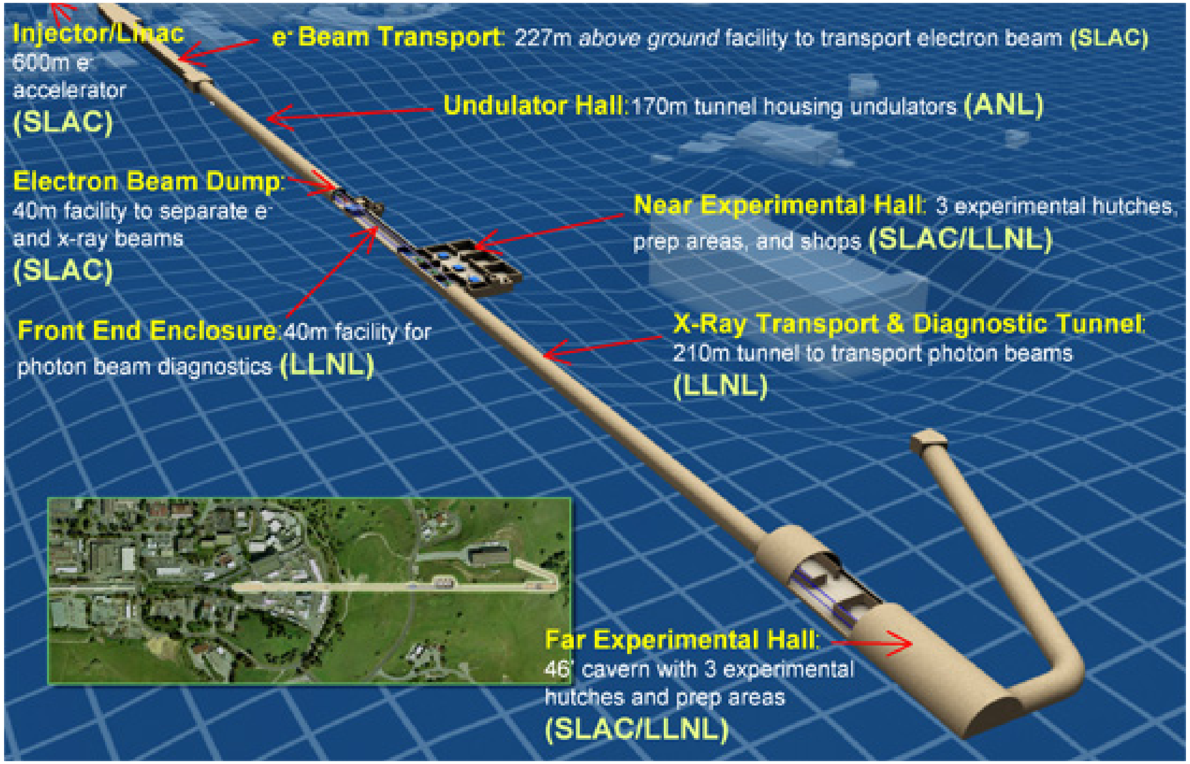


Time dependence and power spectrum of |**Q**| for the selected 2/3(422) and 220 Bragg peaks

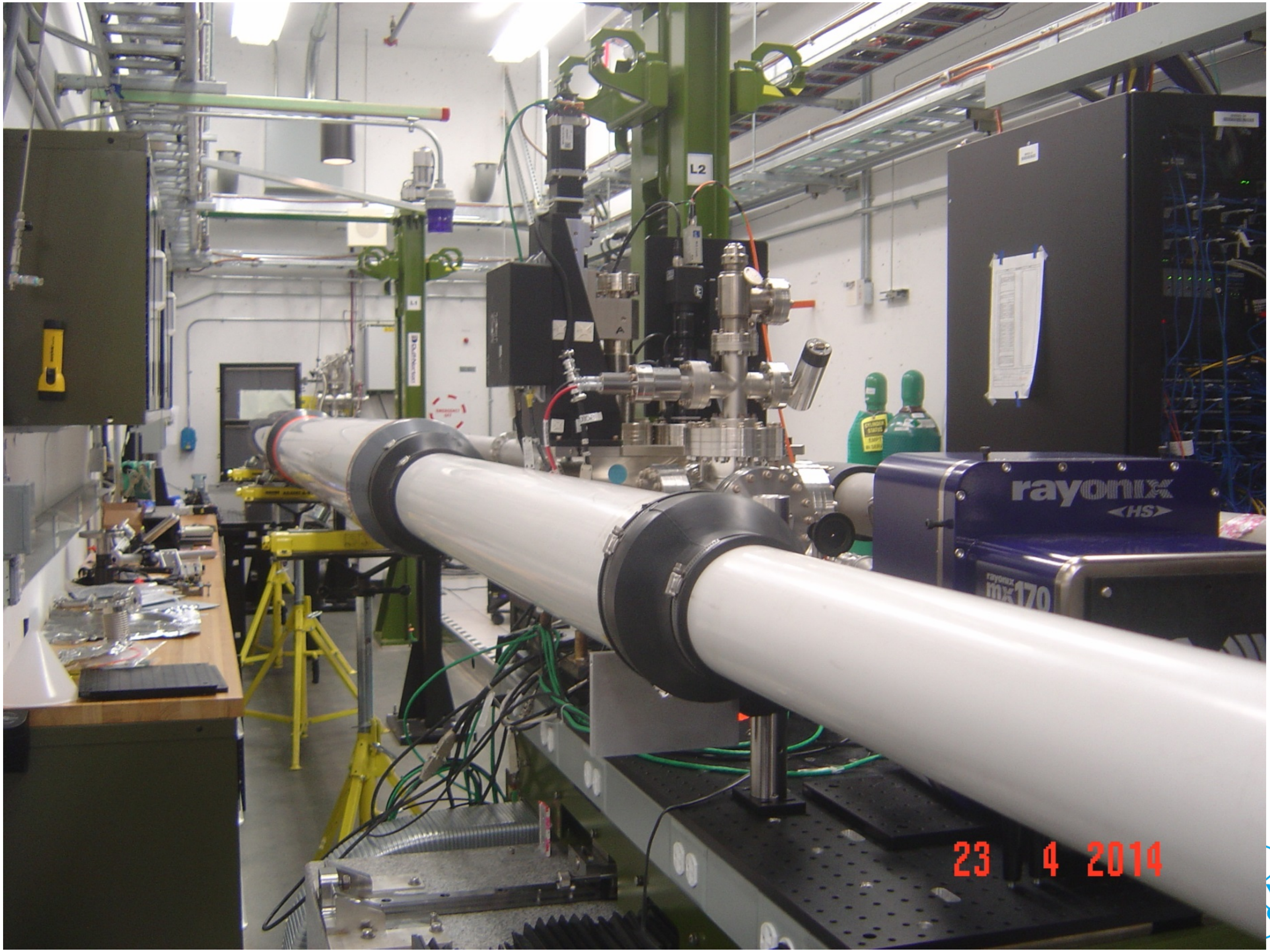
Theoretical calculations of vibrations of a 400 nm isotropic elastic sphere based on the Lamb theory reveal a 5.07 GHz eigenfrequency of the ground (breathing) mode



Pump-probe experiment on colloidal crystals at LCLS



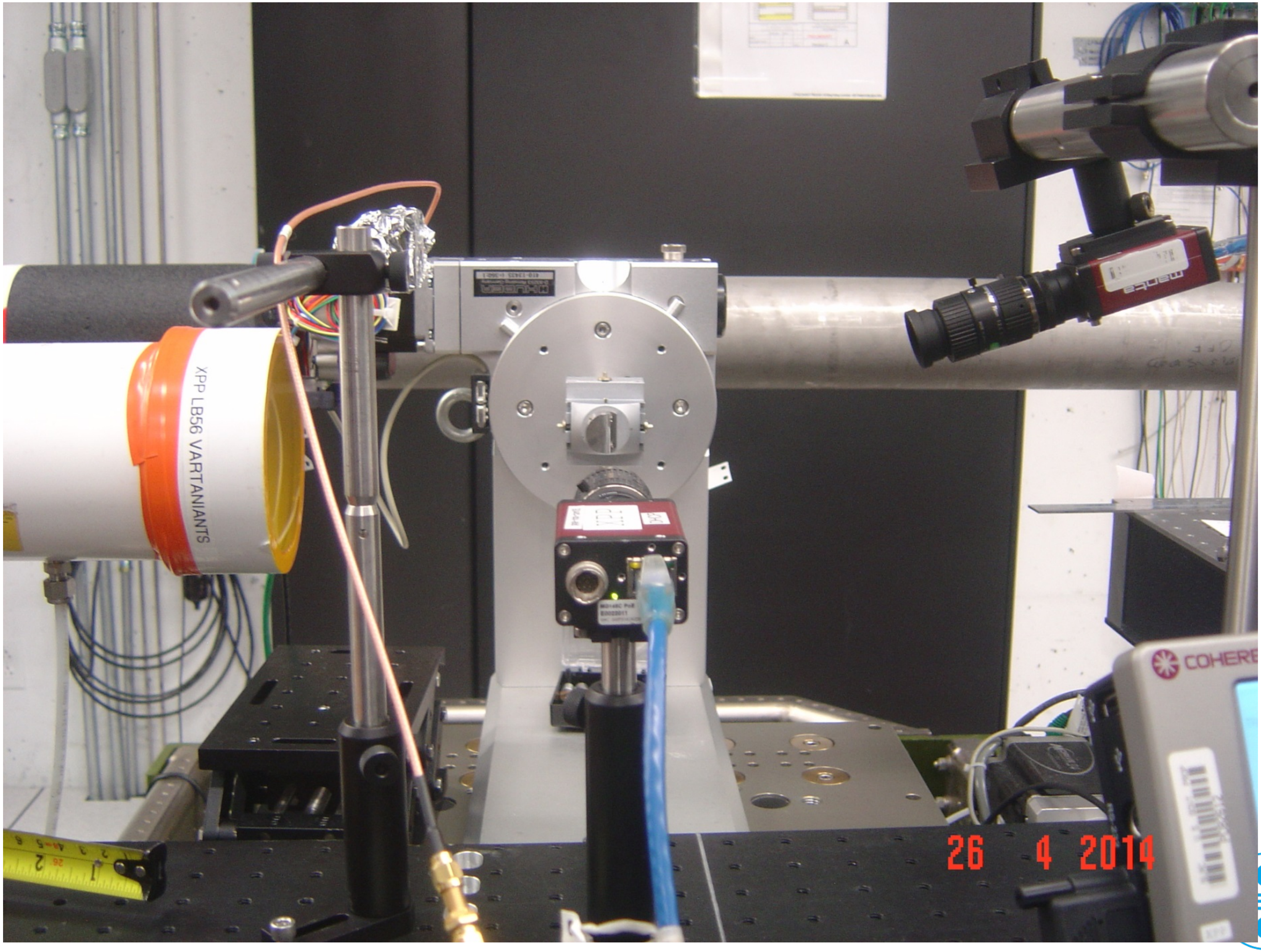
Experimental setup@XPP



Experimental setup@XPP

CSPAD detector

Experimental setup@XPP



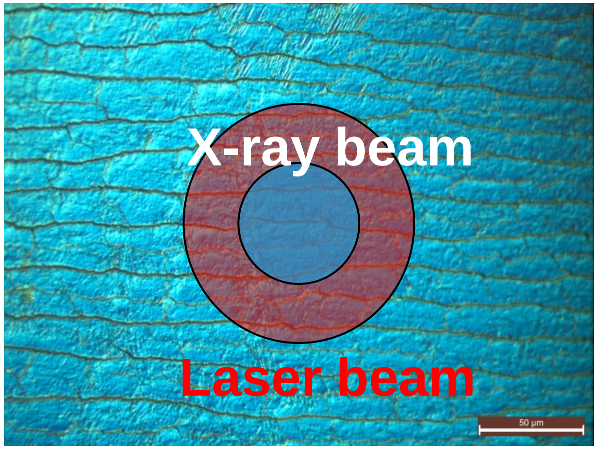
Parameters of X-ray and IR laser beams

1. X-ray beam

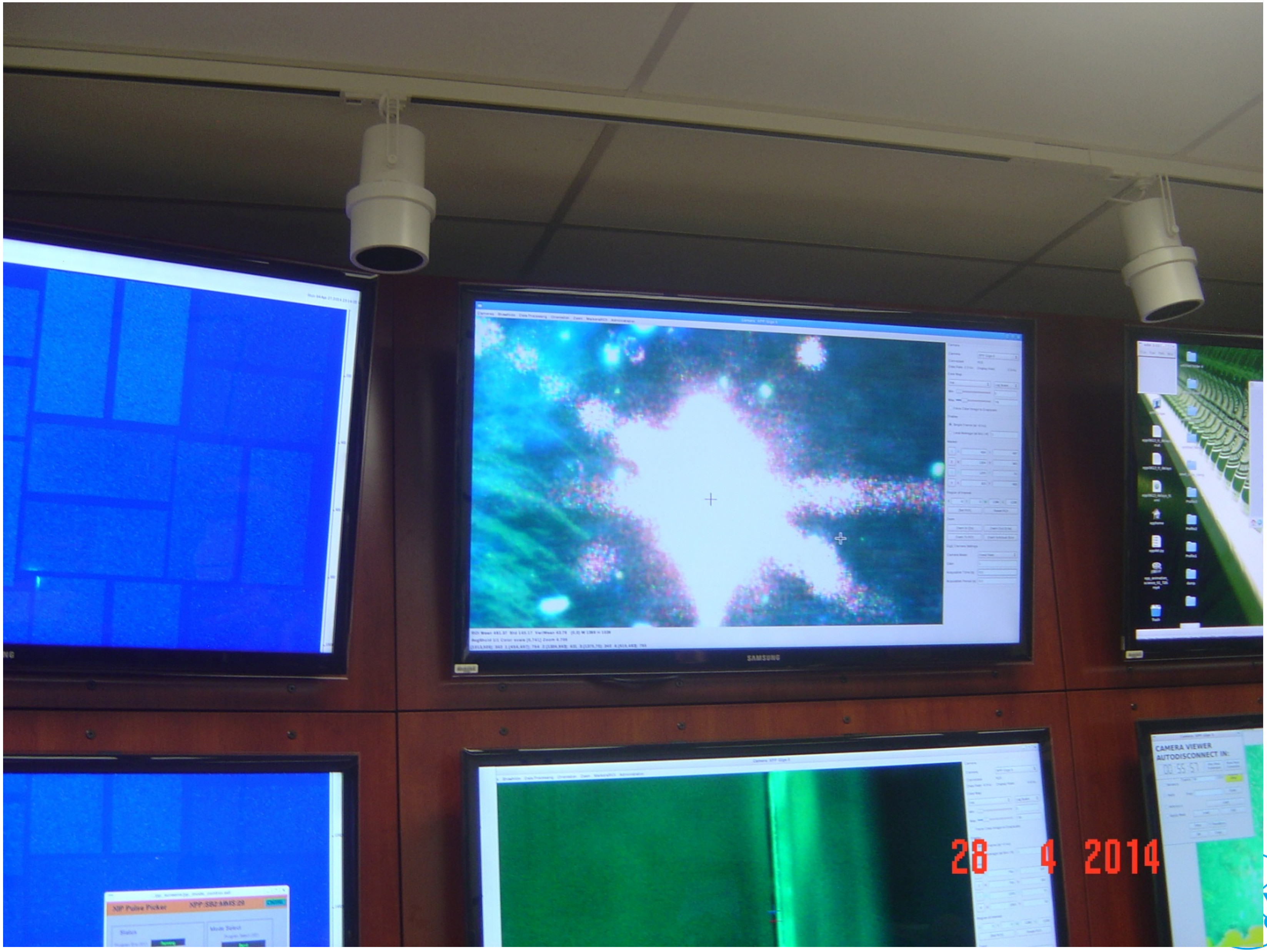
- E=8 keV
- Pulse duration: ≤ 50 fs
- $Flux_{sample}$ ~10^9 ph/pulse
- Focus ~ 50 μm
- Energy bandwidth ~10^{-4}

2. Laser beam

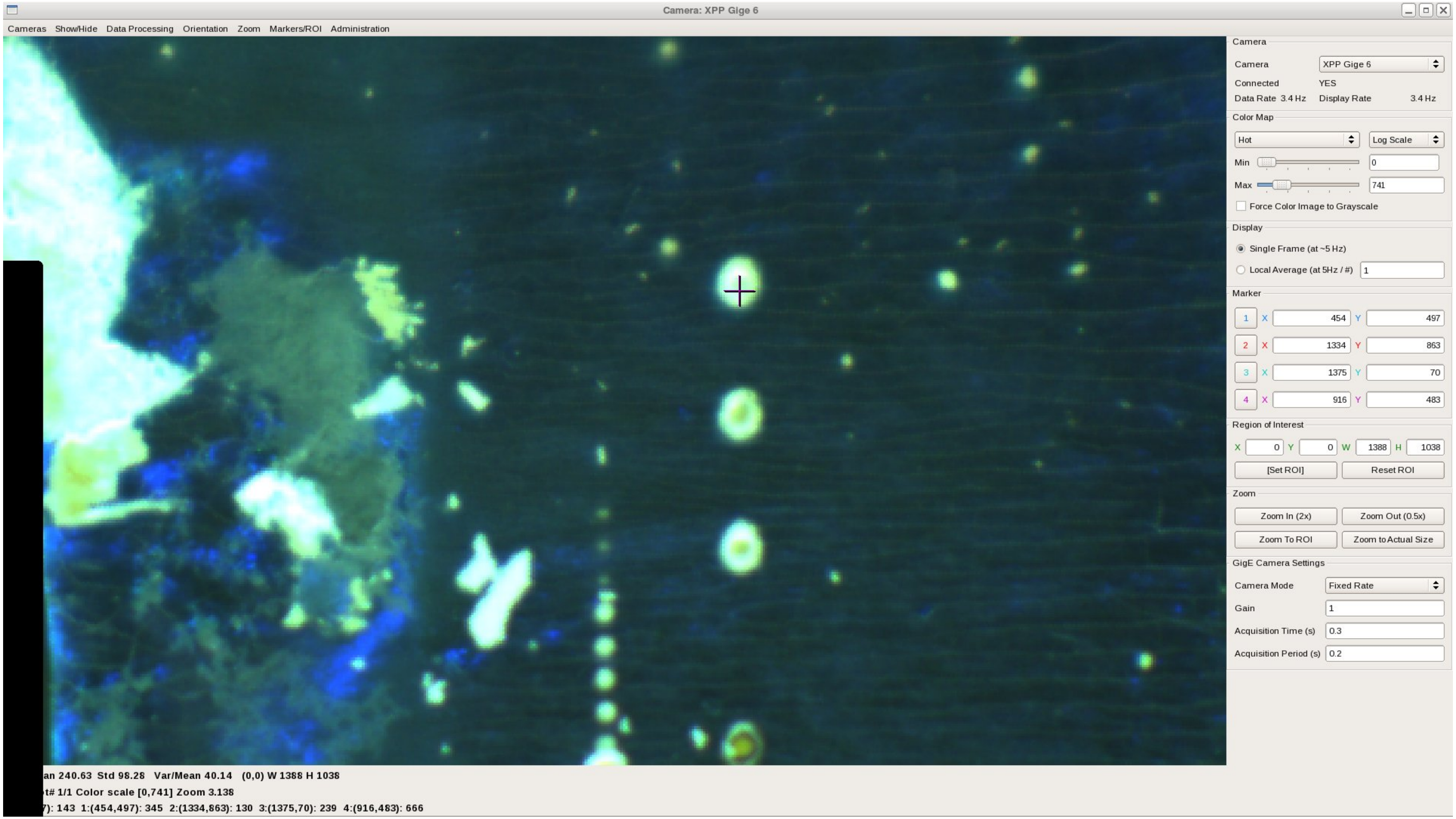
- λ_{las} = 800 nm
- Pulse duration: ≤ 50 fs
- E ~ 2 mJ
- Power: P ~ $4*10^{10}$ W
- Focus ~ 100 μm



Pump-Probe experiment on colloidal crystals



Pump-Probe on Colloidal Crystals

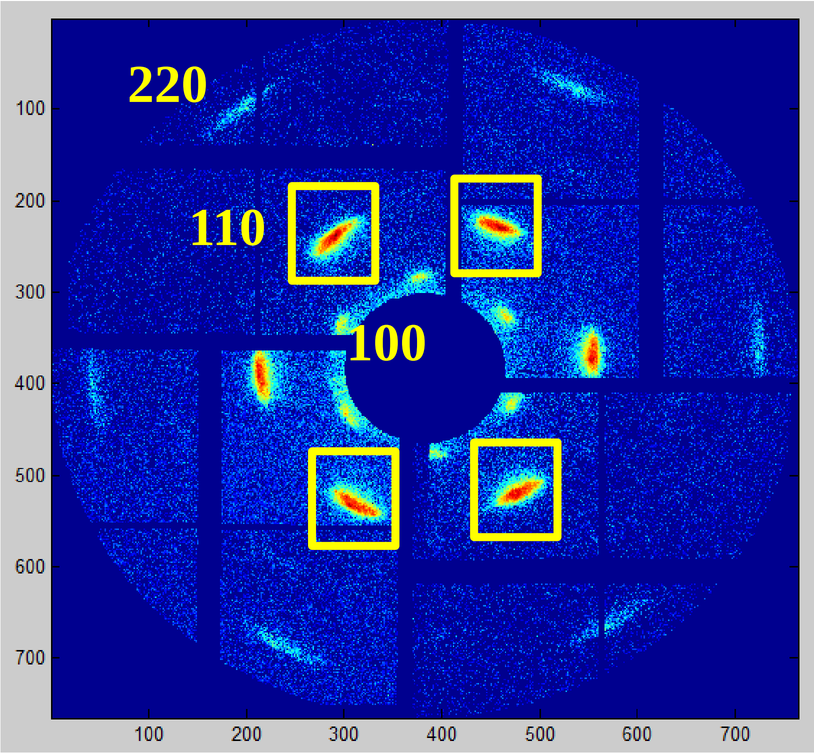


Damage produced by laser power 7° wave plate angle (~50 µJ)

Study of ultrafast melting of colloidal crystals

Decay of integrated intensity of the peaks

Diffraction pattern



Decay of integrated intensity

$$\frac{\Delta I(\tau)}{\langle I \rangle} = \frac{I_1^{on}(\tau) - \langle I^{off} \rangle}{\langle I^{off} \rangle}$$

τ - time delay between laser and X-ray pulses

$$\frac{\Delta I(\tau)}{\langle I \rangle} = A \cdot exp\left(-\frac{\tau}{\tau_0}\right) - A$$

Fit of integrated intensity decay with exponential function

Time delays from -10 ps to +1000 ps

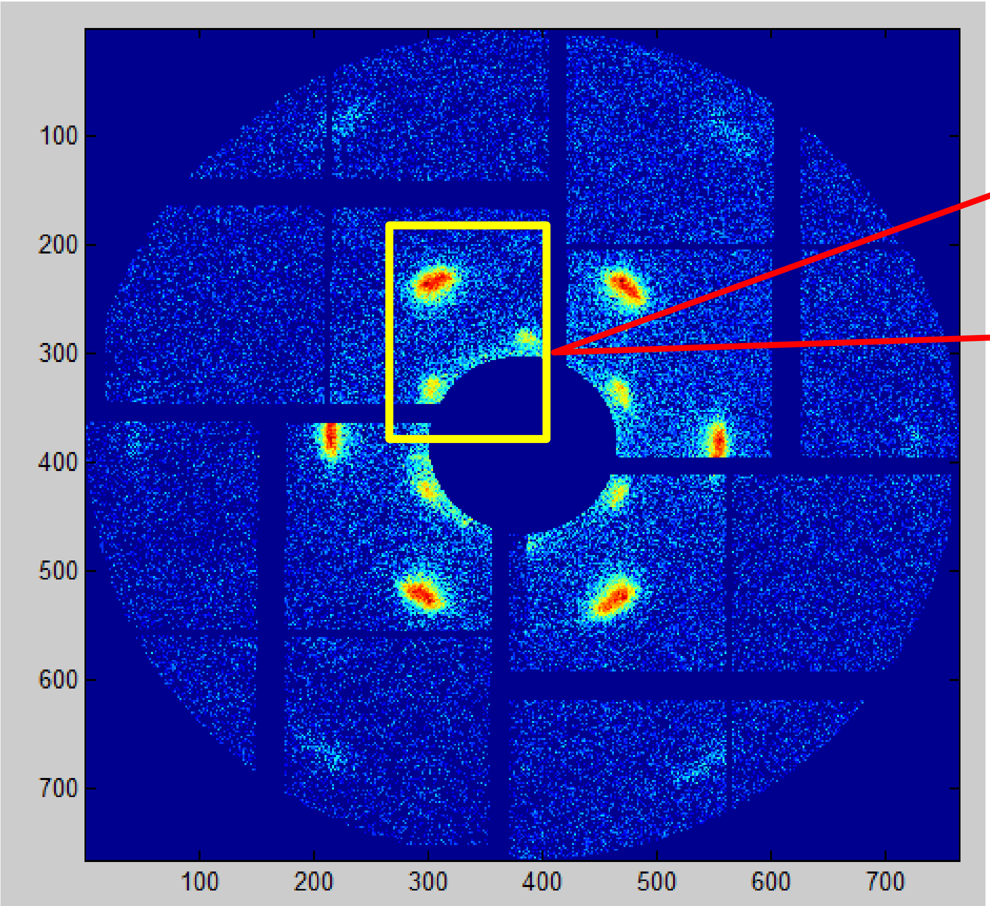
$\Delta\tau$=25.25 ps

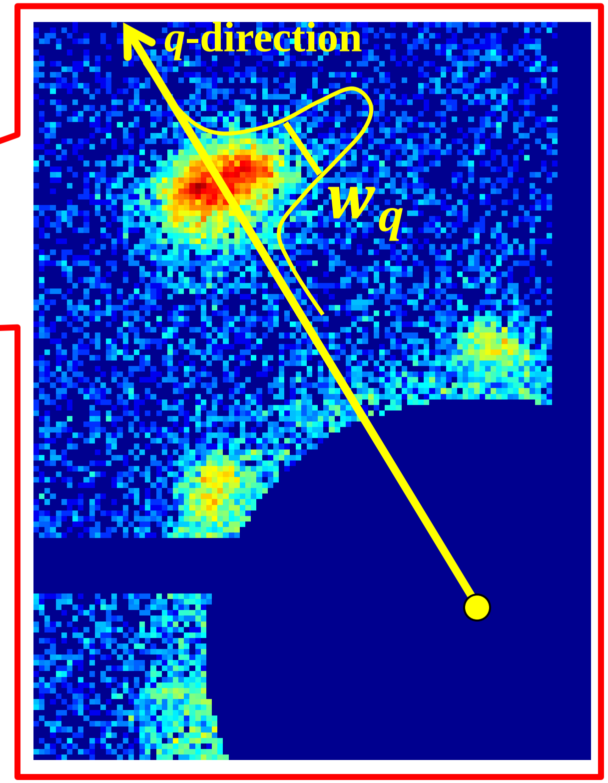
Time delays from -10 ps to +250 ps

$\Delta\tau$=6.5 ps

Bragg peak’s broadening in q-direction

Bragg peak's broadening in *q*-direction





w_q - FWHM in q-direction

$$\frac{\Delta w_q(\tau)}{\langle w_q \rangle} = \frac{{w_q}_1^{on}(\tau) - \langle {w_q}^{off} \rangle}{\langle {w_q}^{off} \rangle}$$

- τ is time delay between laser and X-ray pulses

Model of ultrafast melting of colloidal crystal

1. Energy transfer from IR laser to colloidal crystal?

2. Response of colloidal crystal lattice?
    a. Decay of Bragg peaks integrated intensity
    b. Growth of Bragg peaks FWHM

Energy transfer from IR laser to colloidal crystal

- IR wavelength: 800 nm
- Energy: 1.5 eV

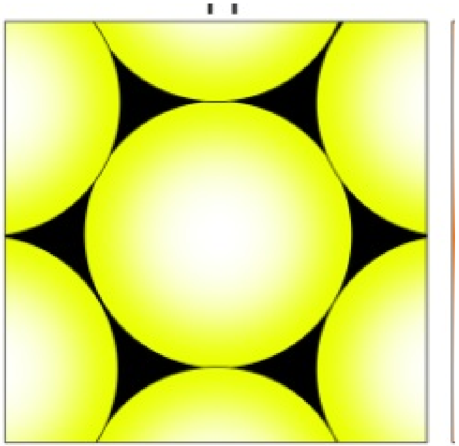
- Energy of chemical bonds: (C-C, C-H) ~3-4 eV

- Absorption coefficient of 800 nm radiation in polystyrene: 10^{-4}

- Temperature raise: one-two degrees

Response of colloidal crystal lattice

Colloidal crystal is heated above T_g in 50 fs



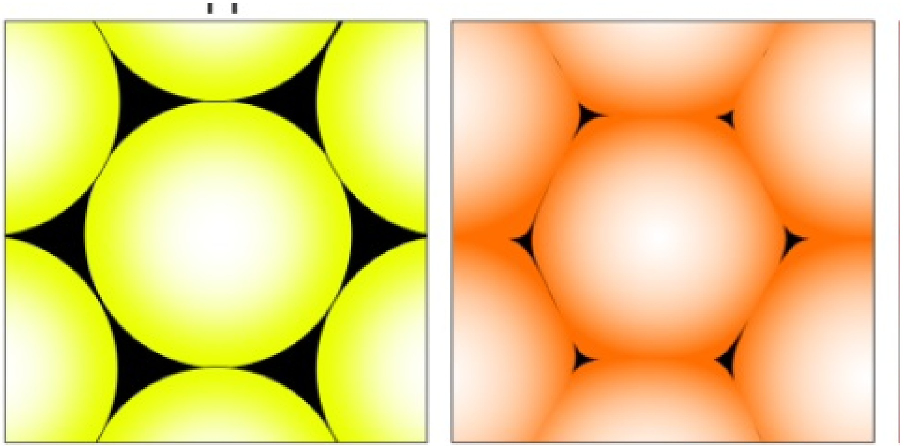
Soft PS spheres

Model of ultrafast melting of colloidal crystal

Response of colloidal crystal lattice

Colloidal crystal is heated above T_g in 50 fs

In ≤50 ps a sintering of PS spheres is going



Soft PS spheres

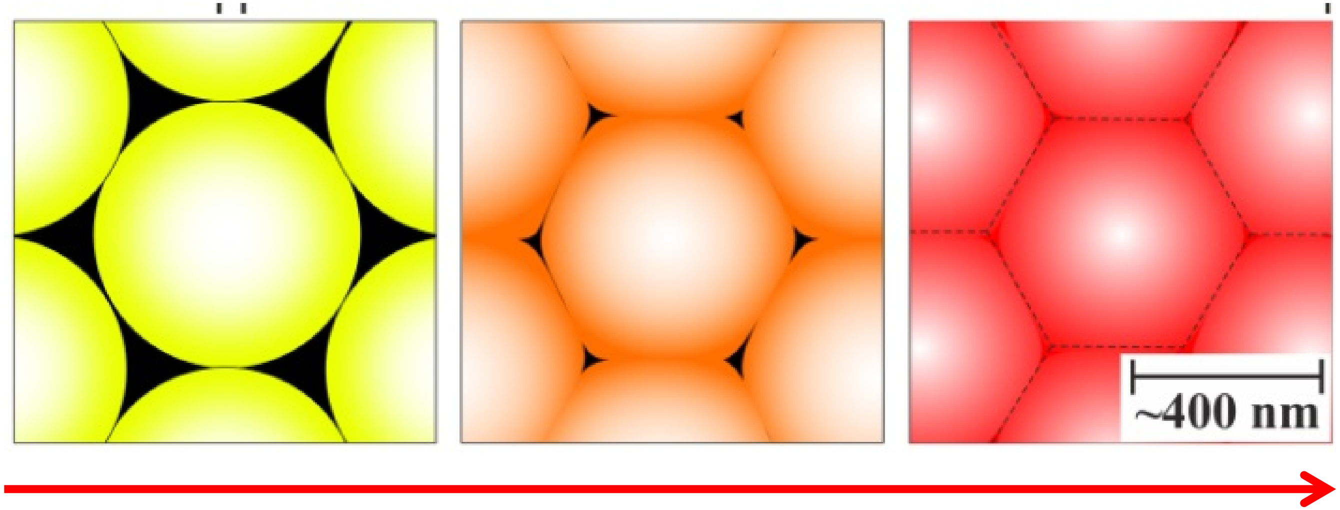
Sintering of PS spheres

Response of colloidal crystal lattice

Colloidal crystal is heated above T_g in 50 fs

In ≤50 ps a sintering of PS spheres is going

In few 100 ps PS dynamics is damped (due to viscosity)

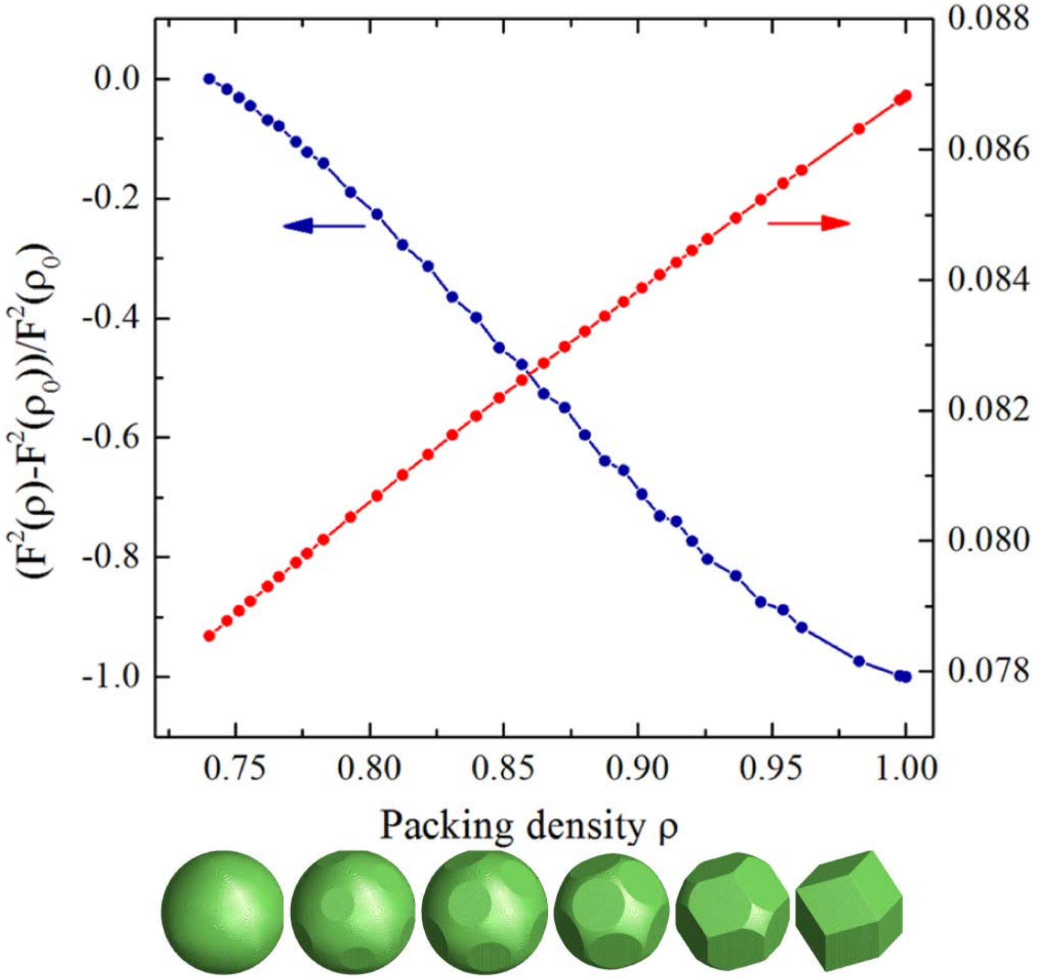


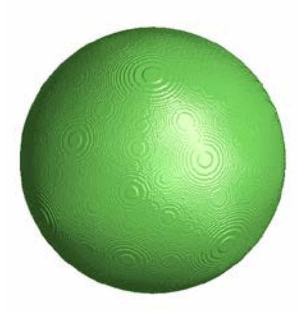
Soft PS spheres

Sintering of PS spheres

Liquid to solid transition

Variation of intensity and modulus of the scattering vector q as a function of packing density ρ



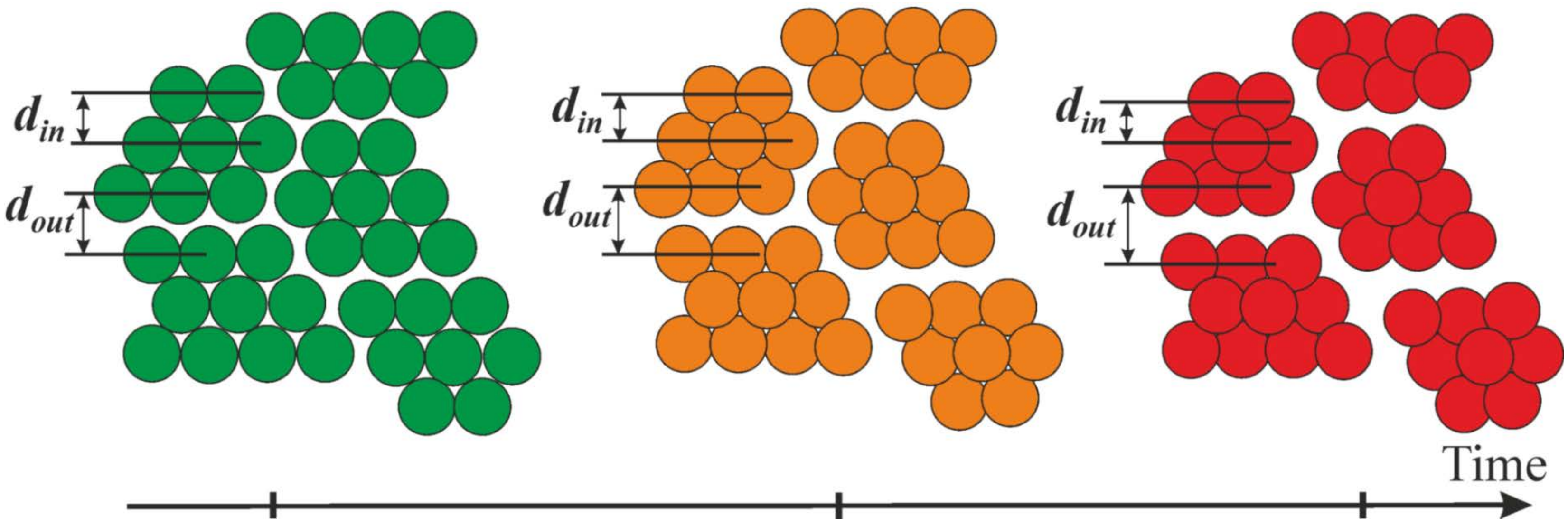


Model of ultrafast melting of colloidal crystal

This model explains decay of integrated intensity but does not explain the broadening of the Bragg peaks

Imperfections of the real colloidal crystal

The broadening of Bragg peaks can be explained by including the imperfections of the colloidal crystal lattice in the model



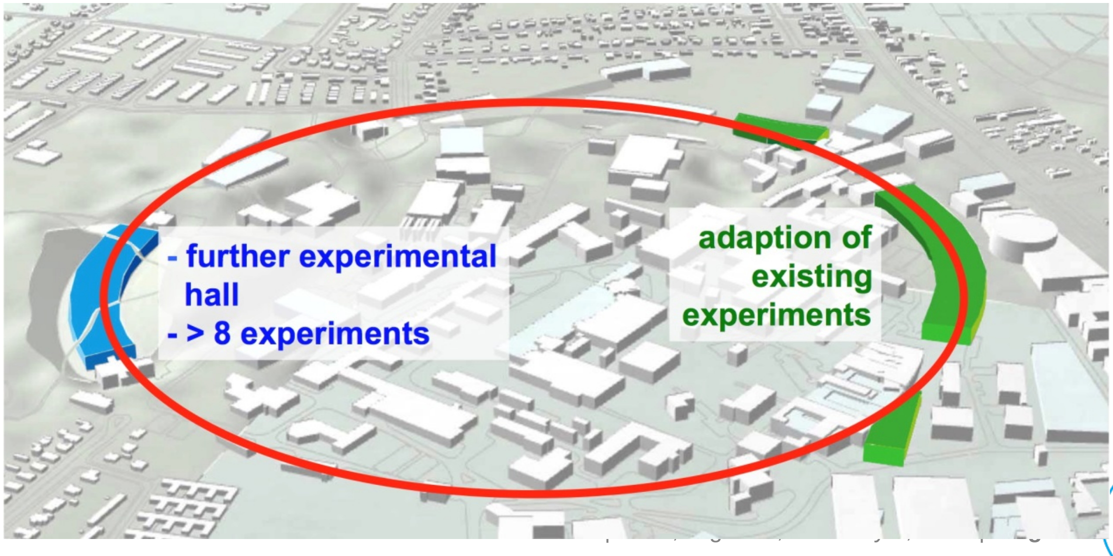
Model of ultrafast melting of colloidal crystal

Work in progress …

DESY future projects for large scale facilities

FLASH2020

PETRA IV

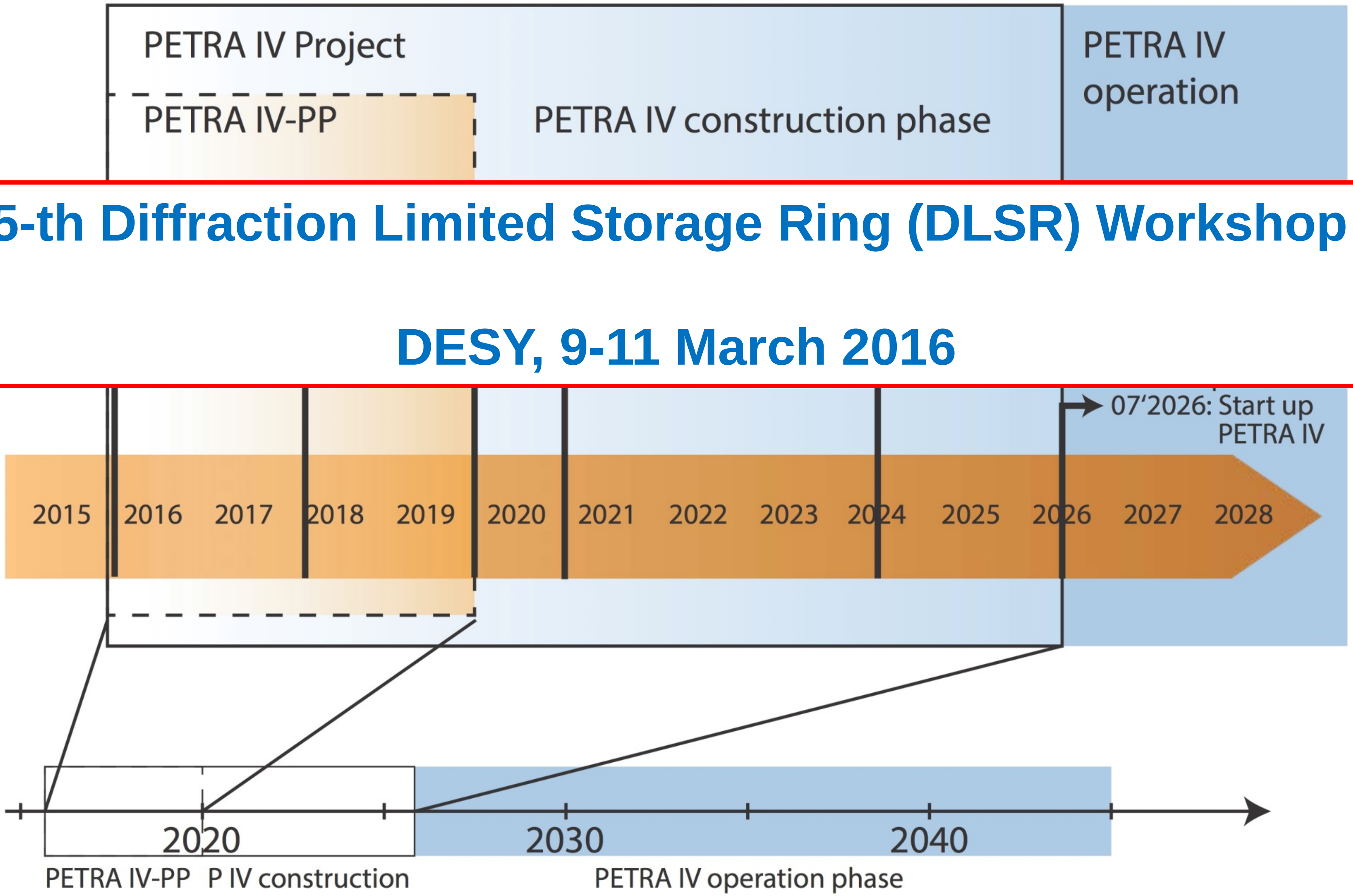


Courtesy to E. Weckert

PETRA IV: status and further development

5-th Diffraction Limited Storage Ring (DLSR) Workshop

DESY, 9-11 March 2016



DESY

Acknowledgements

- DESY
  - E. Weckert
  - Former and present members of my group
  - P10 beamline (M. Sprung, A. Zozulya)
  - FLASH team
- University of Utrecht
  - A. Petukhov
  - J.-M. Meijer
- LCLS
  - XPP beamline
- Russia
  - Institute of Crystallography RAS
  - RC “Kurchatov Institute”
  - National Research Nuclear Centre, “MEPhI”
- …

We are looking for motivated PhD students and PostDocs

Thank you for your attention!