

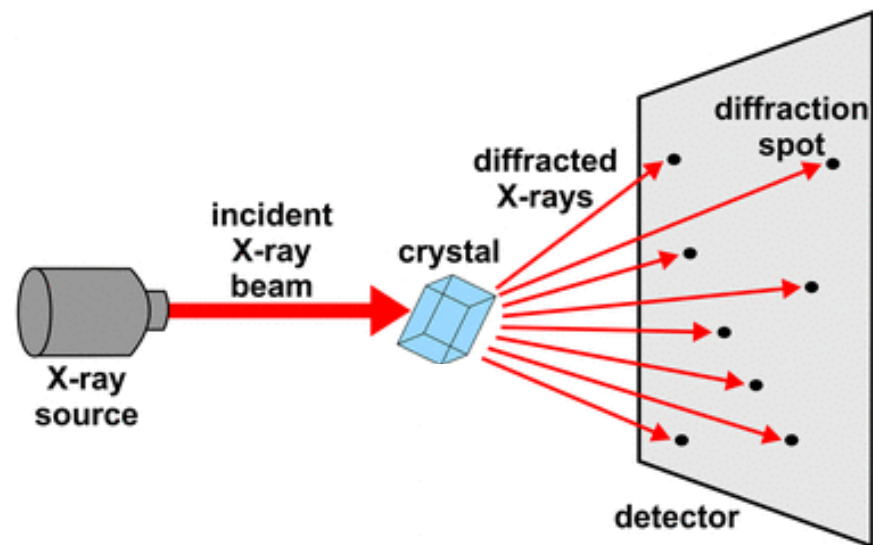
X-ray Diffraction and Imaging

From First Steps to Present Day State-of-the-Art Techniques

841. WE-Heraeus-Seminar: Important Quantum Technologies – Origins and Applications



Edgar Weckert



Layout:

➤ Introduction and motivation

Why do we want to know the atomic structure?

➤ Early work in X-ray crystallography

From the discovery of X-rays and the solution of the 'phase problem' to standard tools

➤ Latest developments in X-ray crystallography

The use of AI and almost automatic structure solution

➤ X-ray imaging of nano-objects

Application of coherent X-ray radiation

Examples of applications

➤ Use of AI and LLMs for structural studies

Some words of caution

Introduction and Motivation

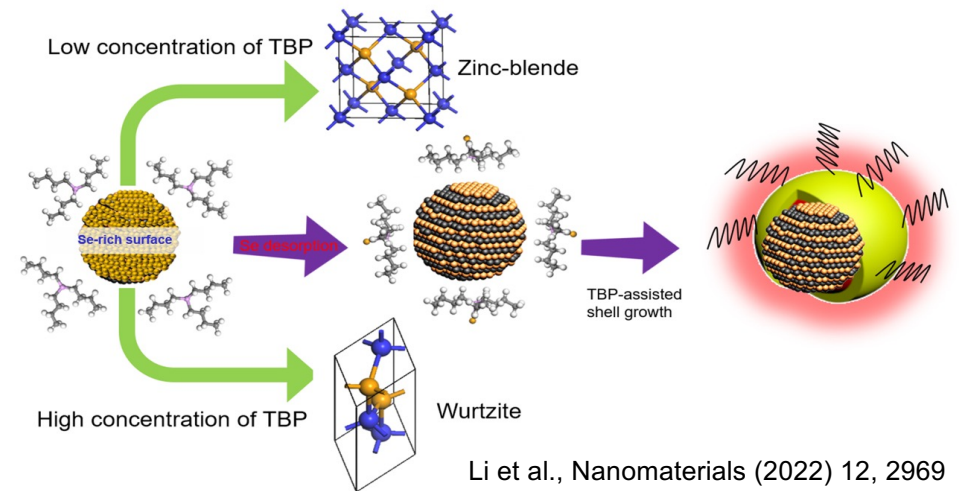
Example: understanding the properties of quantum dots

Quantum dots (QD):

- Size is comparable or smaller than the coherence length of the electrons
- Quantum effects are relevant for physical and chemical properties
- **Analytical tools:**
 - Light (laser) spectroscopy for optical properties
 - X-ray spectroscopy for oxidation states and local atomic environment
 - **X-rays** and electron microscopy for **atomic structure, size and shape**
 - ...
- **Applications:**
 - Dyes in fluorescence microscopy
 - LEDs, QD-laser
 - Single photon sources
 - Quantum computing
 - Spin valves
 - Sensors
 - QD solar cells
 - Catalysis
 - ...



(source: <https://lumenci.com>)



Li et al., Nanomaterials (2022) 12, 2969

Understanding the properties requires the knowledge of the atomic structure, shape and size

Early work in crystallography

How to obtain the atomic structure of crystals?

Some historical remarks:

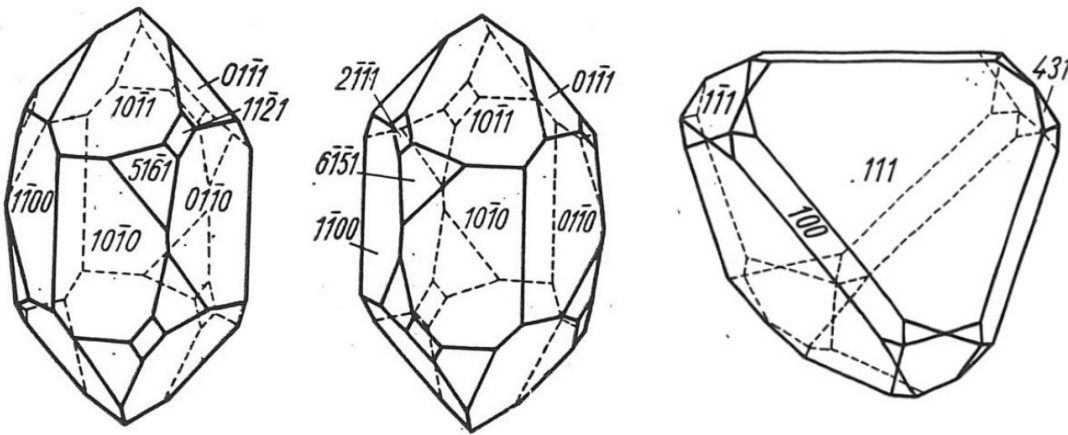
- Let's go back to the year 1900 ...
- What was known about crystals at the time ?



Pyrit, FeS



Quartz, SiO₂



- Just by looking on the **normals** (directions) of the grown crystal faces, one realized that they can be described by small integer numbers provided one uses the proper coordinate system.
- 7 different coordinate systems are required triclinic ... cubic
- There exist symmetry relations between the normals of the crystal faces and this symmetry operations form a group
- One need **32 point groups** to describe all possible combinations of coordinate systems and symmetries

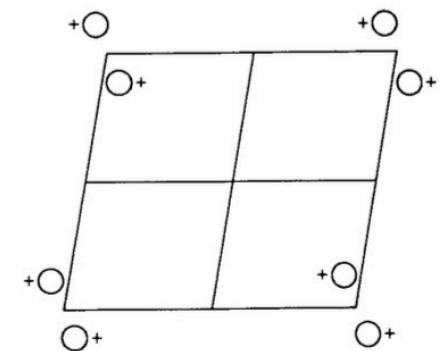
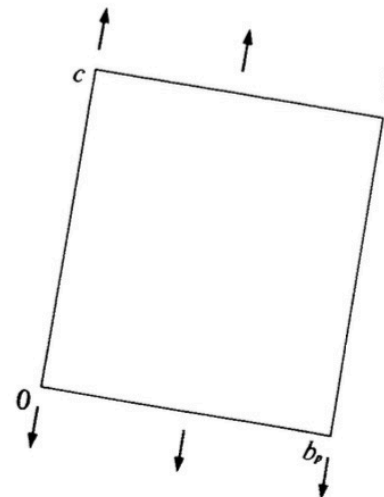
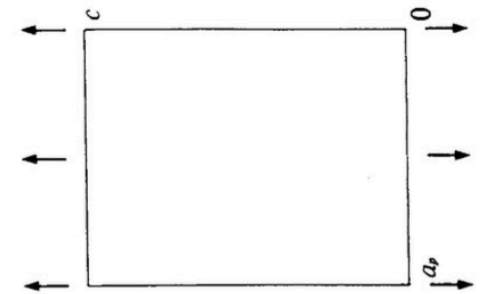
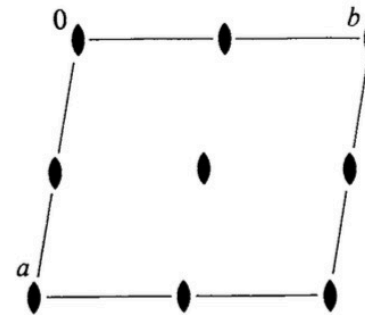
Early work in crystallography

How to obtain the atomic structure of crystals?

Further historical remarks:

- By not looking only on directions of the crystal faces but also including translations E.S. Federov (1891) and independently A.M. Schönflies (1891) and W. Barlow (1894) found out that one needs 230 so called space groups to describe the symmetry of all possible translation periodic arrangements of points in 3D.
- The smallest arrangement of points one needs to know is the so-called unit cell.
- Important: since crystallographers give priority to symmetry the selected unit cells are not always the smallest ones that one would obtain by looking only on translation equivalent points → Bravais lattices.
- These findings are the basis of all crystallographic work up to now.
- Tabulated and accessible to everyone in the International Tables for Crystallography.

Example: space group P2 (No. 3), monoclinic



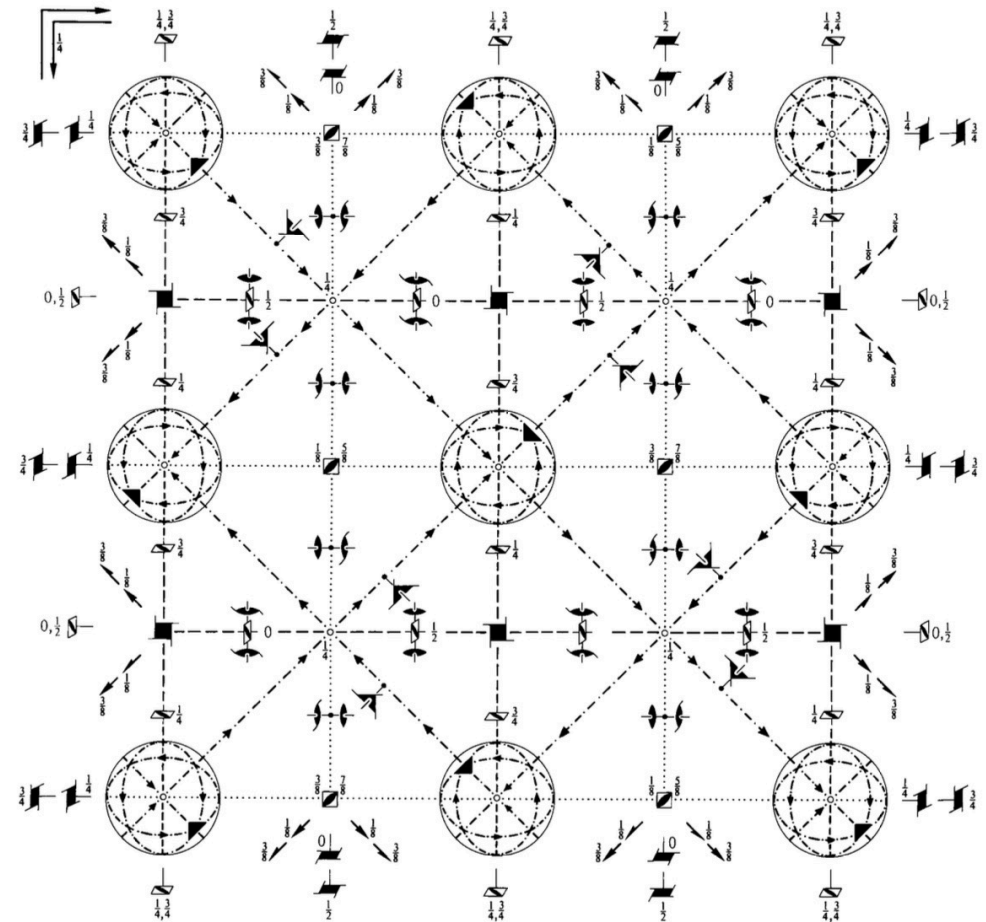
Early work in crystallography

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Example: space group $1a\bar{3}d$ (No. 230), cubic

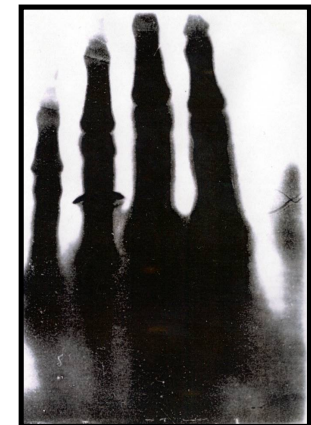
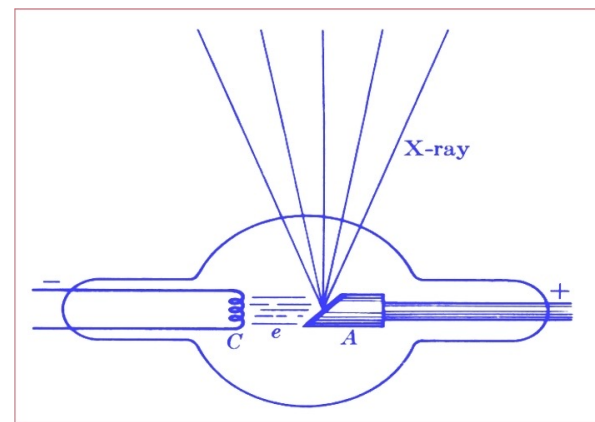
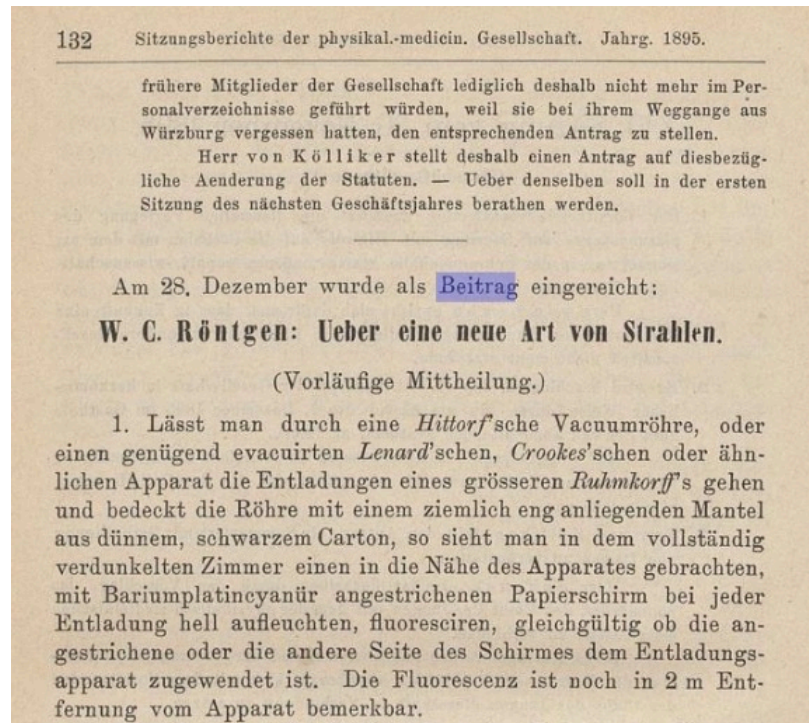


Early work on X-rays

How to obtain the atomic structure of crystals?

X-rays were discovered in 1895 by
W. C. Röntgen in Würzburg

- Many properties already characterized but no idea on wavelength and photon energy



Early work on X-rays crystallography

How to obtain the atomic structure of crystals?

1910:

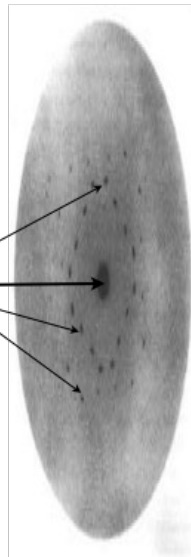
- P.P. Ewald received from Sommerfeld the thesis topic 'Dispersion und Doppelbrechung von Elektronengittern (Kristallen)' ... does an anisotropic arrangement of dipol oscillators explain these effects.
- First steps of the development of what later became the dynamical theory of X-ray diffraction.

1912:

- Discussion of M. v. Laue with Ewald on the extinction of the incident beam inside the crystals.
- At that time v. Laue was not aware of the idea that crystals may be translation periodic arrangements of atoms or molecules.
- Laue asked Ewald what happens in his theory if the incident wavelength is smaller than the translation periods.
- Laue, Friedrich and Knipping did the famous experiment demonstrating that crystals are translation periodic and that X-rays are waves with wavelengths in the 0.1nm range.



X-ray beam



Interferenz-Erscheinungen bei Röntgenstrahlen.

Von W. Friedrich, P. Knipping und M. Laue.

Vorgelegt von A. Sommerfeld in der Sitzung am 8. Juni 1912.

(SITZUNGSBERICHTE DER MATH. – PHYS. KLASSE DER K. B. AKADEMIE DER WISSENSCHAFTEN ZU MÜNCHEN 1912)

At that time, it was not clear whether the observed interferences are due to fluorescence or scattering of the incident radiation.

Early work on X-rays crystallography

How to obtain the atomic structure of crystals?

In the years to follow, based on this initial work, all the concepts were developed that we use today:

- reciprocal lattice
- Ewald construction
- Bragg's equation
- Structure factor

Relation of the measured Bragg reflection intensity on the atomic structure?

- X-rays are scattered from the electrons
- Interaction is weak → 1. Born approximation → only single scattering events

$$I(\vec{h}) = I_0 r_0^2 P \frac{\lambda^3}{\sin(2\theta)} \underbrace{\left[\sum_{\vec{g}_j} e^{2\pi i \vec{g}_j \vec{h}} \right]}_{IF} \underbrace{\left[\sum_{\vec{r}_i} \left(\int_{V_{atom_i}} \rho_e^i(\vec{x}) e^{2\pi i \vec{h} \vec{x}} d\vec{x} \right) e^{2\pi i \vec{h} \vec{r}_i} \right]}_{F(\vec{h})}^2$$

$f_i(\vec{h})$

$f_i(\vec{h})$: atomic form factor (tabulated)

P: polarization factor (known from the experiment and used radiation)

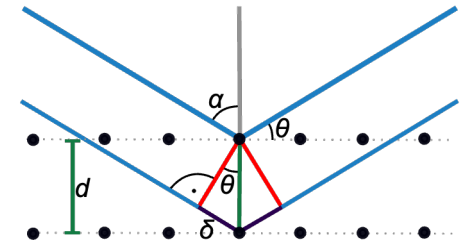
r_0 : classical electron radius $O(10^{-15} \text{ m})$, natural constant

IF: interference function: for large N_{uc} , meaningful amplitudes only at reciprocal lattice points $\sim V_{cr}/V_{uc}^2$ (constant)

$F(\vec{h})$: structure factor: scattering amplitude of one unit cell (what we are looking for)

\vec{g}_j : vector to the origin on the unit cells $\vec{g}_j = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$

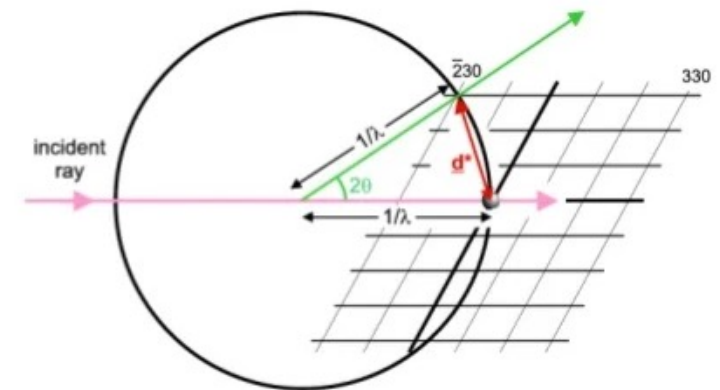
$$n\lambda = 2d \sin \theta$$



$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{V_{uc}}, \quad \vec{b}^* = \frac{\vec{a} \times \vec{c}}{V_{uc}}, \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{V_{uc}}$$

$$\vec{h} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$|\vec{h}| = 1/d_{hkl} = |\vec{d}^*|$$



Ewald construction: geometric solution of Bragg's equation in 3D

Early work on X-rays crystallography

How to obtain the atomic structure of crystals?

If $F(\vec{h})$ would be known: $\rho_{uc}(\vec{r}) = 1/V_{uc} \sum_{\vec{h}} F(\vec{h}) e^{-2\pi i \vec{h} \cdot \vec{r}}$

Easy, but what we have is: $|F(\vec{h})|^2 = I(\vec{h}) / \text{Const}(\lambda, \theta)$

We cannot measure the phase of the complex $F(\vec{h})$... ☹

$$F(\vec{h}) = \sum_i^{N_{atoms}} f_i e^{2\pi i \vec{h} \cdot \vec{r}_i}$$

- Things are even worse: the phase of the $F(\vec{h})$ depends on the chosen origin of the unit cell
➔ the phase of $F(\vec{h})$ is not a measurable property !
- Of course, illuminating an entire crystal with a plane wave will give a defined phase of the diffracted wave, but then we have to deal with a problem of much larger complexity which is irrelevant for the structure within a unit cell ➔ we come to that later

1913: W. L. Bragg, W. H. Bragg

Solution of simple structures like NaCl, KCl, CaF_2 , and Diamond by just analyzing extinct reflections and trial and error.

(W.L. Bragg, Proc. R. Soc. Lond. Ser. A, **89**(1913), 248)

Evaluation of the correctness of the model:

Minimize: $R = \frac{\sum_{\vec{h}} |C \cdot F_{obs}^2(\vec{h}) - |F_{calc}(\vec{h})|^2|}{\sum_{\vec{h}} C \cdot F_{obs}^2(\vec{h})}$

by iterative non-linear least-square methods. R from 2 to 5% are excellent, for many large protein structures 10 – 30% are common.

1935: A. L. Patterson

Calculation of the Patterson function:

$$P(\vec{u}) = 1/V_{uc} \sum_{\vec{h}} |F(\vec{h})|^2 e^{-2\pi i \vec{h} \cdot \vec{u}} = \int_{V_{uc}} \rho_e(\vec{r}) \rho_e(\vec{r} + \vec{u}) d\vec{r}$$

The $|F(\vec{h})|^2$ encode the autocorrelation of the electron density of the unit cell, meaning the interatomic distances
Problem: N atoms give rise to $N(N-1)$ distances ... ☹

(A.L. Patterson, Physical Review, **46**(1934), 372)

Early work on X-rays crystallography

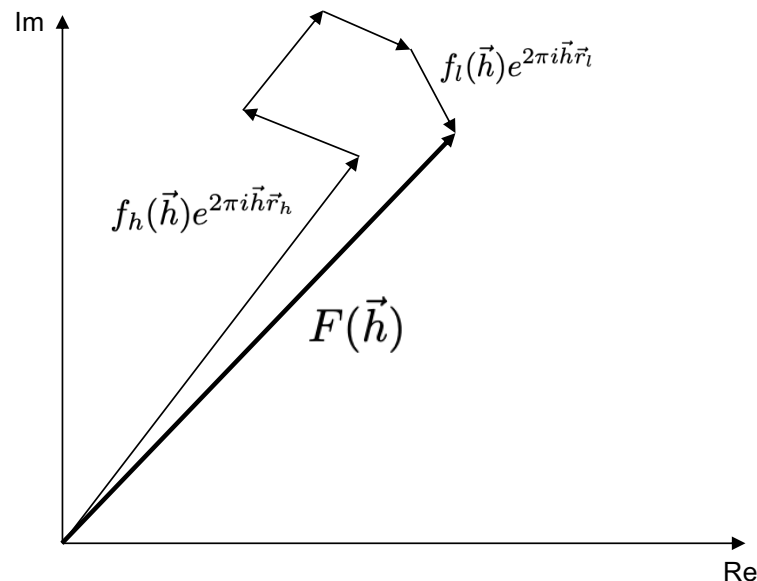
How to obtain the atomic structure of crystals?

Patterson function: the first systematic approach

➤ Let's look on

$$F(\vec{h}) = |F(\vec{h})|e^{i\phi(\vec{h})}$$

for a structure with one strong scatterer and many weaker ones.



If the interatomic vectors of heavy atoms could be identified and their scattering contribution is dominant the phase of $F(\vec{h})$ will be close to the one of the substructure of heavy atoms.

$$\rho(\vec{r}) = 1/V_{uc} \sum_{\vec{h}} \left(|F_{exp}(\vec{h})| e^{2\pi i\vec{h}\vec{r}_h} \right) e^{-2\pi i\vec{h}\vec{r}}$$

$\rho(\vec{r})$ will contain information on the missing atoms of the model

- ➔ update the model
- ➔ refine positions by non linear LSQ
- ➔ calculate new model phases
- ➔ calculate next electron density map, look for missing atoms
- ➔ iterate until the model is complete

For very long time the Patterson based methods were the methods to solve large and complex protein structures:

- ➔ either use already present or introduce heavy atoms in the molecule ➔ then proceed as before
- ➔ in case of isomorphous substitution: additional information is available in form of native $I(\vec{h})$

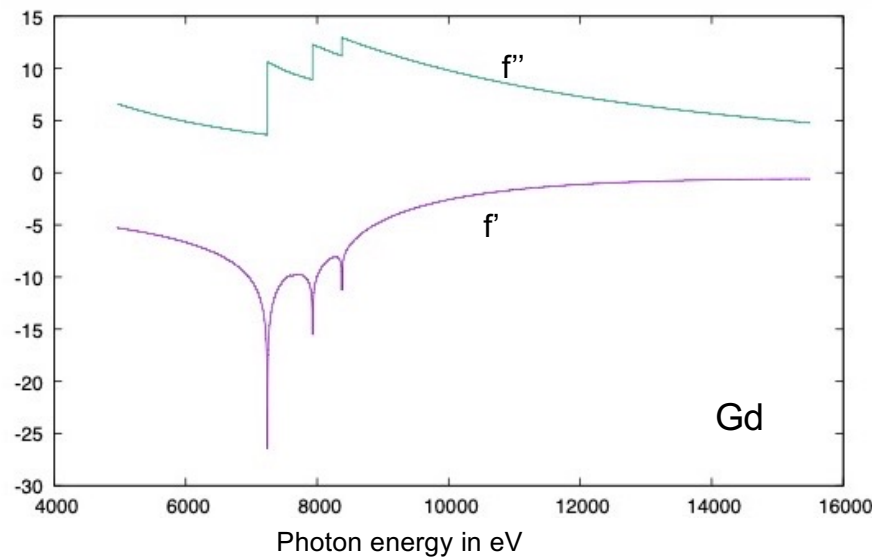
Early work on X-rays crystallography

How to obtain the atomic structure of crystals?

How did the use of synchrotron radiation change the situation?

- More brilliant and intense beams:
 - ➔ faster experiments, smaller crystals, larger unit cells
- Tunable wavelengths:
 - ➔ 'manipulate' the scattering of heavier atoms, multi wavelength anomalous dispersion (**MAD**)

$$f(h) = f_0(h) + f'(E) + if''(E)$$

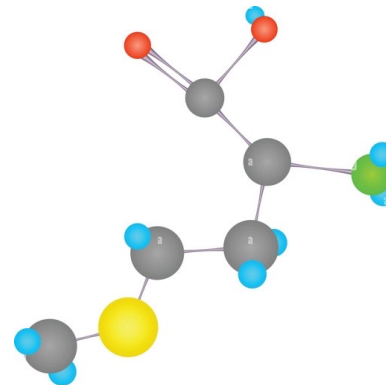


MAD – procedure:

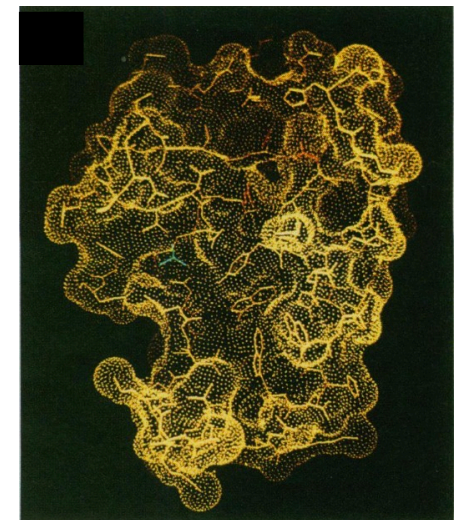
- Measurement of data sets before, at, and after the absorption edge
- $F(h)$ has parts that are dependent and independent of the photon energies
- With the known values for f' and f'' it is possible to determine the quantities: $|F_A(\vec{h})|$, $|F_T(\vec{h})|$, $\phi_T(\vec{h}) - \phi_A(\vec{h})$
- From $|F_A(h)|$ the structure of the anomalous scattering atoms can be determined ➔ phase estimates for all reflections for a first model ➔ LSQ

(W. Hendrickson, Science, **254**(1991), 51)

For the last 2-3 decades MAD was the most powerful method to solve large crystal structures, why?



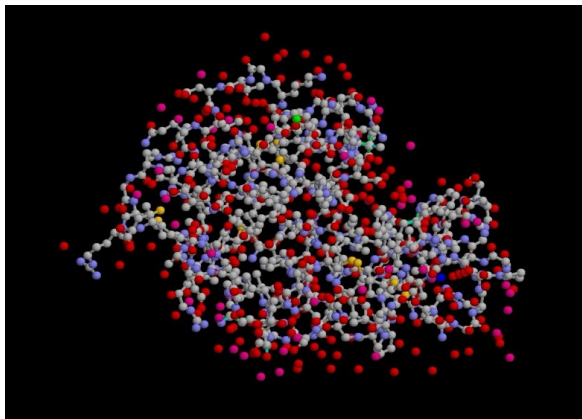
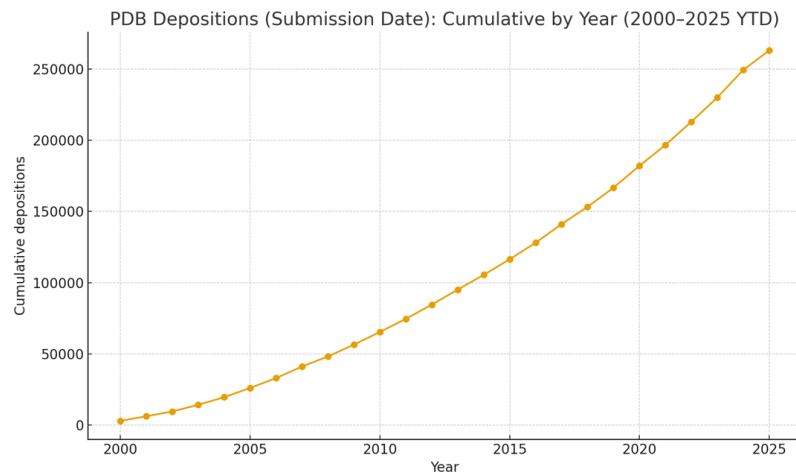
The S-atom in the amino acid Methionine can be replaced by Se ➔ intrinsic heavy atom for MAD experiments



Early work on X-rays crystallography

How to obtain the atomic structure of crystals?

Let's stay for the moment with large molecules



molecular
structure of
hen-egg white
lysozyme

- More than 250.000 protein structures are meanwhile deposited in the PDB.
- The likelihood that the molecular coordinated of a related or similar protein is already deposited is steadily increasing.
- Here sets a method in that has been called 'Molecular Replacement'
(M. Rossmann, D. Blow, Acta Cryst. **15**(1962)24)
 - ➔ take the coordinates of the best matching molecule from the data base
 - ➔ place it into the unit cell of the unknown structure and apply the symmetry operations
 - ➔ from this molecule calculate model $F_M(h)$
 - ➔ rotate and translate the model molecule until one gets the best match between $|F_{obs}(h)|$ and $|F_M(h)|$
 - ➔ use the corresponding phases and $|F_{obs}(h)|$ to calculate a first electron density model
 - ➔ use non-linear LSQ to refine the model

Latest developments in X-rays crystallography

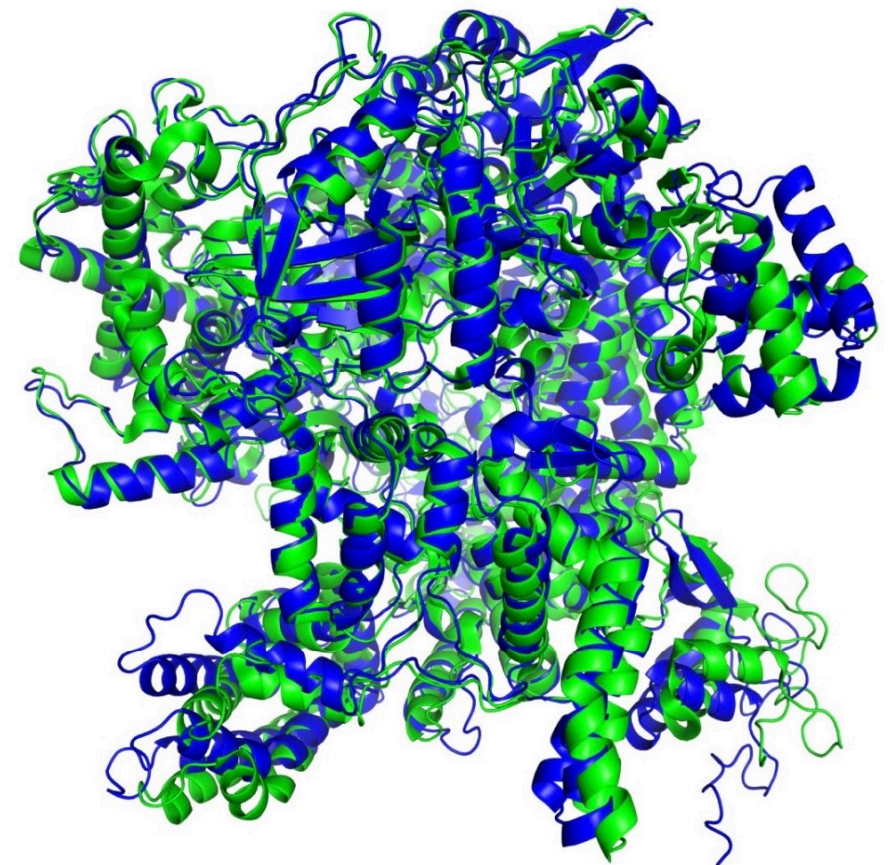
How to obtain the atomic structure of protein crystals in the era of AI

A long-standing problem in biological science:

- Given the sequence of a protein, how does it fold to a 3D molecule as we observe it
- Idea: train a neural network with the more than 250.000 3D protein structures from the PDB (Google DeepMind)
- Use the trained neural network to predict the 3D structure for a given protein sequence (**AlphaFold II**)
- This method has revolutionized structural biology
- For more than 80% of the cases the prediction is good enough to serve as a starting model for the molecular replacement method

Senior et al., Nature **577**(2020)706
Jumper et al., Nature **596**(2021)583

DESY. X-ray Diffraction and Imaging: ... | Edgar Weckert | 1-4 September 2025



AlphaFold Experiment
r.m.s.d.₉₅ = 2.2 Å; TM-score = 0.96

Latest developments in X-rays crystallography

How to obtain the atomic structure of small molecules

- Due to the computing power available today the solution of small (O(100)) independent non-H atoms is fairly straight forward
- The method of choice is called 'Direct Methods'
- The basics have already been established in the mid 1950-ies by Karle and Hauptmann
 - Hauptman, H. A.; Karle, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. American Crystallographic Association Monograph No. 3
 - Hauptman & Karle, "Structure Invariants and Seminvariants for Non-Centrosymmetric Space Groups," *Acta Cryst.* 9, 45–55 (1956).
- Many have contributed to the development and success: Woolfson (York), Schenk (Amsterdam), Giacovazzo (Bari), **Sheldrick** (Göttingen), many more
- Success through easy-to-use software packages to solve and refine crystal structures
- Mostly used: shelxs, shelxl, ...

What is the basic idea behind the 'Direct Methods' ?

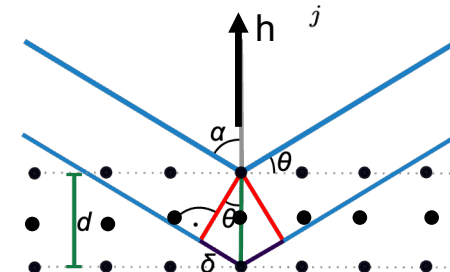
- Exploit structure factor statistics and symmetry
- What is the expectation value for $|F(h)|^2$ for a random arrangement of atoms?

$$F(\vec{h})F^*(\vec{h}) = \sum_j f_j(\vec{h})^2 + 2 \sum_{j \neq k} f_j(\vec{h})f_k(\vec{h}) \cos(2\pi\vec{h}(\vec{r}_j - \vec{r}_k)) \approx \sum_j f_j(\vec{h})^2$$

$$|E(\vec{h})| = |F(\vec{h})| / \sqrt{\sum_j f_j(\vec{h})^2}$$

What actually does $|E(h)|$ mean?

- $|E(h)| \gg 1$: atoms are mainly on a plane
- $|E(h)| \sim 1$: atoms are randomly distributed
- $|E(h)| \ll 1$: atoms are on planes with half of the periodicity

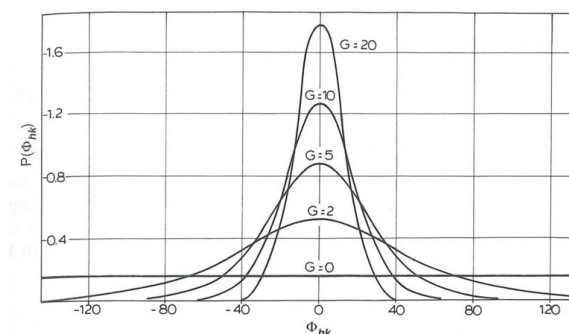


$$E(-\vec{h})E(\vec{k})E(\vec{h} - \vec{k}) = |E(-\vec{h})E(\vec{k})E(\vec{h} - \vec{k})|e^{i(\phi_{-h} + \phi_k + \phi_{h-k})}$$

$\Phi_{hk} = \phi_{-h} + \phi_k + \phi_{h-k}$ is a so-called triplet phase and invariant of origin choices

$$G_{hk} = (2/\sqrt{N_{at}})|E_{-h}E_kE_{h-k}|$$

$$P(\Phi_{hk}) \propto \exp(G_{hk} \cos \Phi_{hk})$$



- ➔ Statistical estimates for phase relations between reflections
- ➔ Compute est. phases for the largest $F(h)$, multiple solutions need to be evaluated
- ➔ Refine phases by Sayre's equation: $E(\vec{h}) \propto \sum_{\vec{k}} E(\vec{k})E(\vec{h} - \vec{k})$
- ➔ First model electron density map ➔ interpretation ➔ refinement ...

D. Sayre, *Acta Cryst.* 5(1952)60

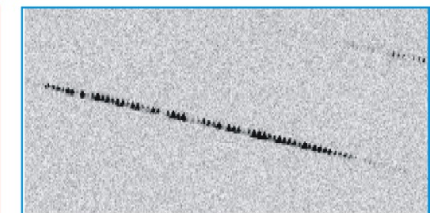
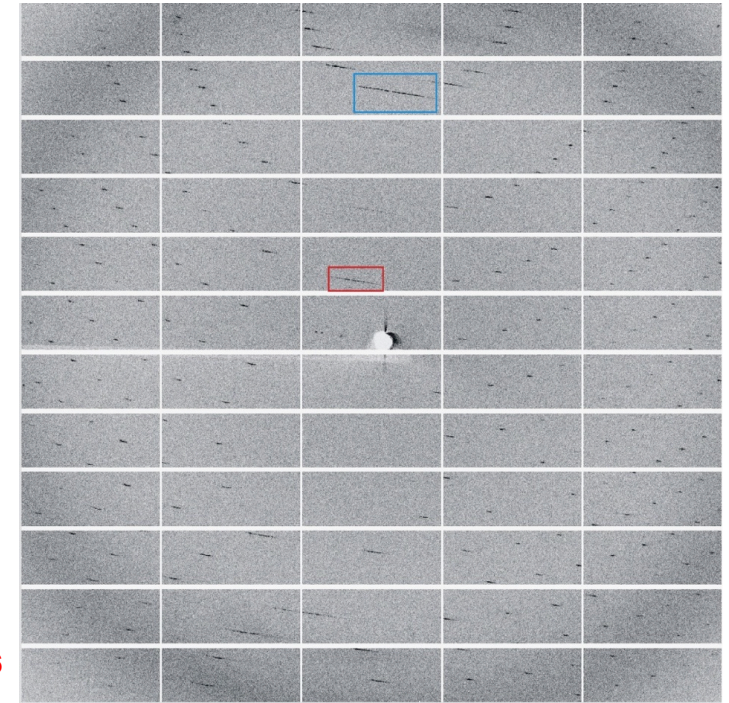
X-ray imaging and diffraction from nano objects

The use of coherent X-ray radiation to study structure and function of nano objects

- Up to now we know how to determine the atomic structure of a crystal
- We have not yet discussed the requirements for the X-ray beam
- For a homogeneous crystal the divergence of the beam and the wavelength spread need to be such that the reflections do not overlap at the detector
 - Large unit cells (e.g. large complexes or viruses) require better collimated beams
→ SR light
 - For MAD one needs to be able to tune the wavelength and the wavelength spread should be small compared to the f' and f'' changes as not to spoil the anomalous signal
- In summary: almost any beam will do provided it has enough flux density

Unit cell in Å: 98.54 98.54 1288.26
in deg. 90. 90. 120.

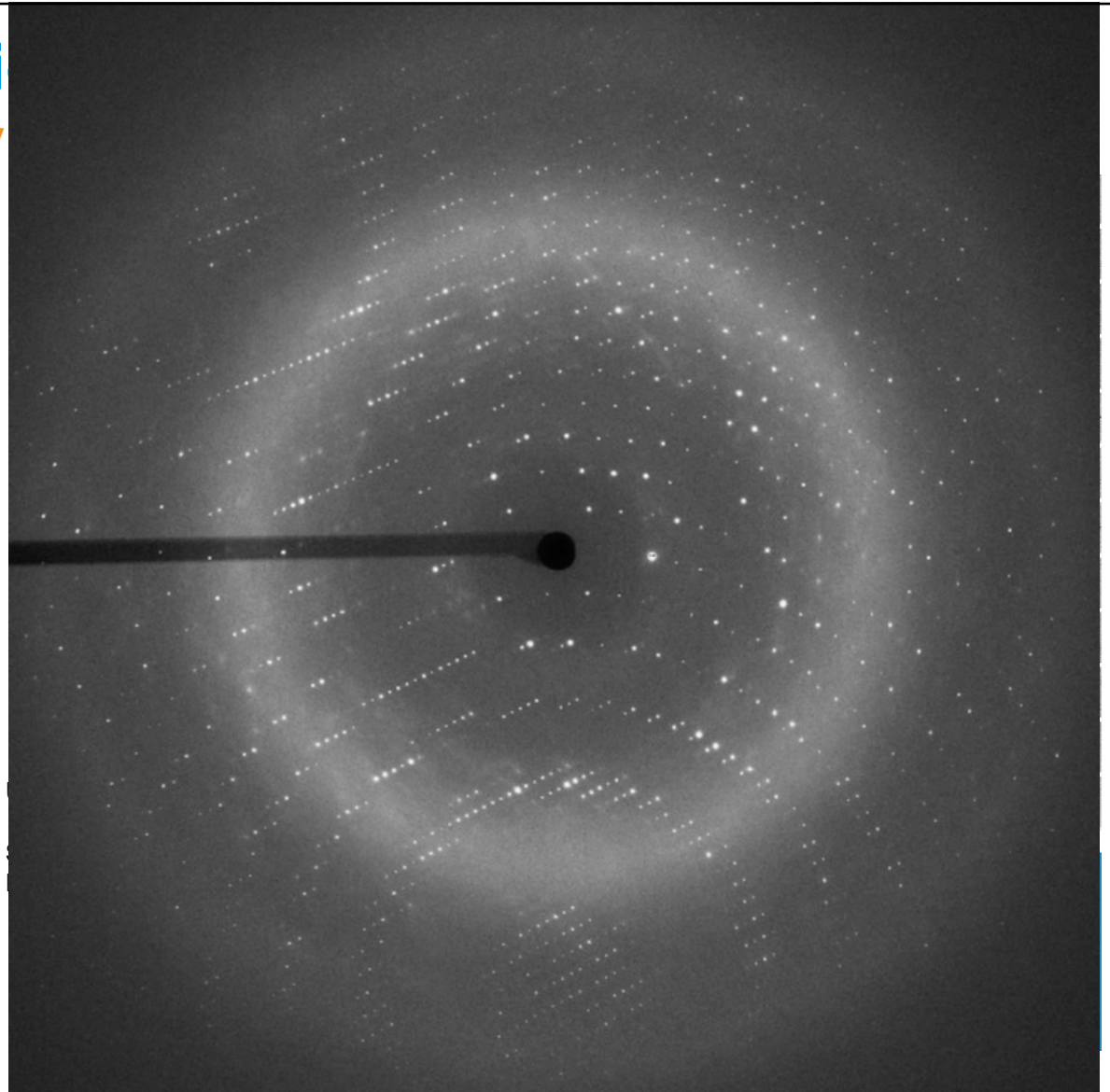
Space group: P 6₁ 2 2
Beamline P11@PETRA III



X-ray imaging and diffraction

The use of coherent X-ray radiation to study

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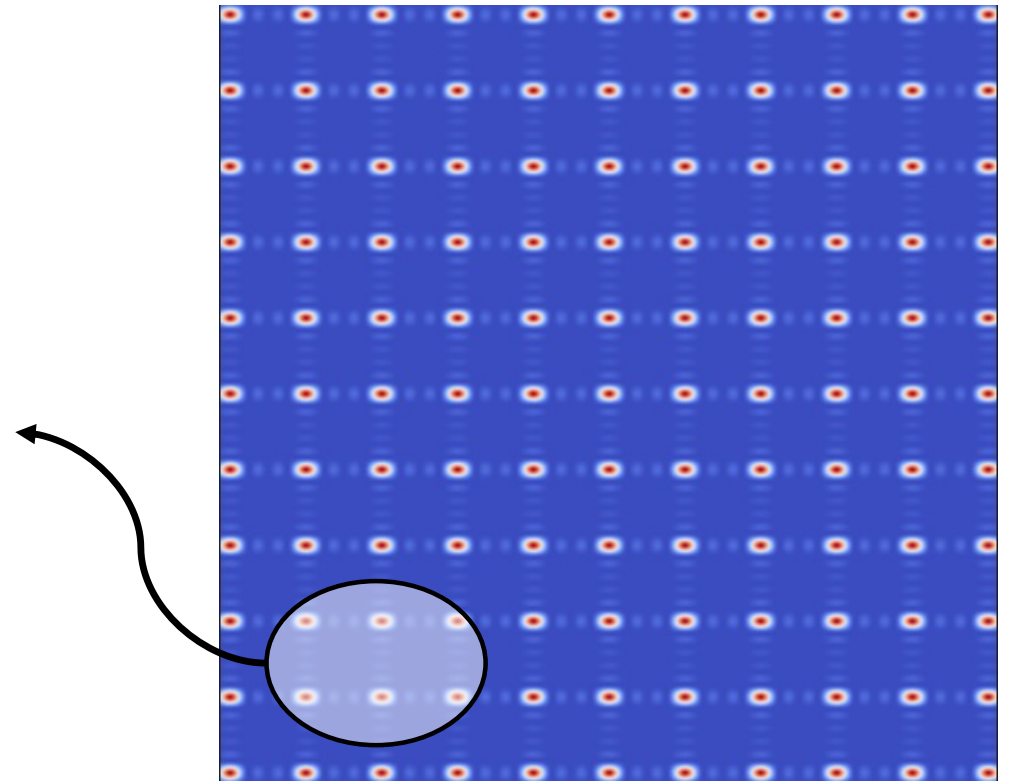
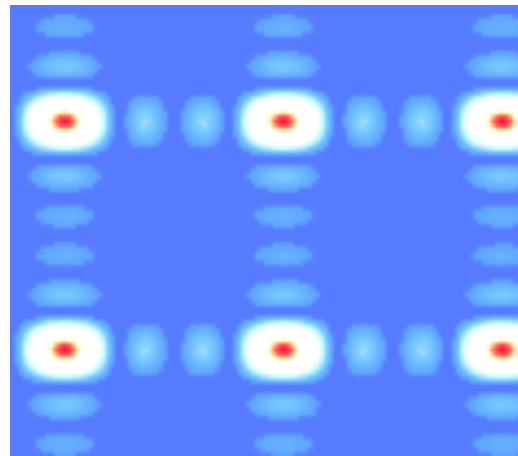
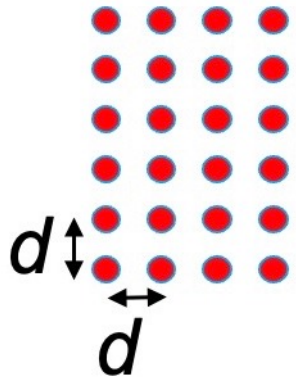
X-ray imaging and diffraction from nano objects

The use of coherent X-ray radiation to study structure and function of nano objects

What happens if we carry out X-ray diffraction from nano-object ?

$$I(\vec{h}) = I_0 r_0^2 P \frac{\lambda^3}{\sin(2\theta)} \left| \sum_{\vec{g}_j}^{N_{uc}} e^{2\pi i \vec{g}_j \vec{h}} \left[\sum_{\vec{r}_i}^{N_{atoms-uc}} \left(\int_{V_{atom_i}} \rho_e^i(\vec{x}) e^{2\pi i \vec{h} \vec{x}} d\vec{x} \right) e^{2\pi i \vec{h} \vec{r}_i} \right] \right|^2$$

For small N, the interference function shows side maxima which encode the sample shape



X-ray imaging and diffraction from nano objects

The use of coherent X-ray radiation to study structure and function of nano objects

What are the requirements for the incident radiation to observe these side maxima?

- The particle needs to be illuminated coherently
- The coherence lengths l_c for an incoherent source at a given distance L from the source of size D is given by:

$$l_c \approx \frac{\lambda L}{D} \quad l_t \approx \frac{\lambda^2}{\Delta\lambda}$$

PETRA III: (emittance: 1.1 nmrad, 1% coup.)

- source size (FWHM): 220 μm x 9 μm (h x v)
- wavelength: 0.1 nm
- L: 80 m
- ➔ $l_c \sim 36 \mu\text{m}$ x 880 μm

PETRA IV: (emittance: < 20 pmrad, 100% coup.)

- source size (FWHM): 9 μm x 9 μm (h x v)
- wavelength: 0.1 nm
- L: 80 m
- ➔ $l_c \sim 880 \mu\text{m}$ x 880 μm

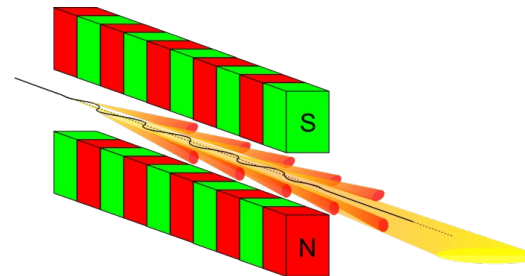
l_t depends on monochromator: $\sim 1 \mu\text{m}$

Already the lateral coherence length of modern 3rd generation synchrotron radiation storage rings is sufficient to illuminate nano – optics coherently in the X-ray regime.

Sources for coherent X-rays (12 keV):

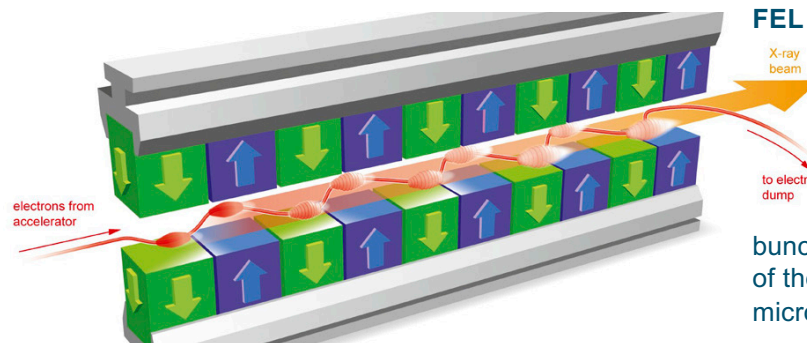
- 3rd generation storage rings: coherent fraction $\sim 0.1 \%$
- 4th generation storage rings: coherent fraction up to 40%
- (X-ray) FELs: coherent fraction: $\sim 50 - >90\%$

Khubbutdinov et al., JSR, **26**(2019)1811
Khubbutdinov et al., Struct. Dyn., **8**(2021)44305
Vartanyants et al., PRL **107**(2011)144801



Undulators in a storage ring:

angular deviation of the electron beam needs to be smaller than the emitted radiation cone at each magnet ➔ constructive interference of the emitted radiation at each pole



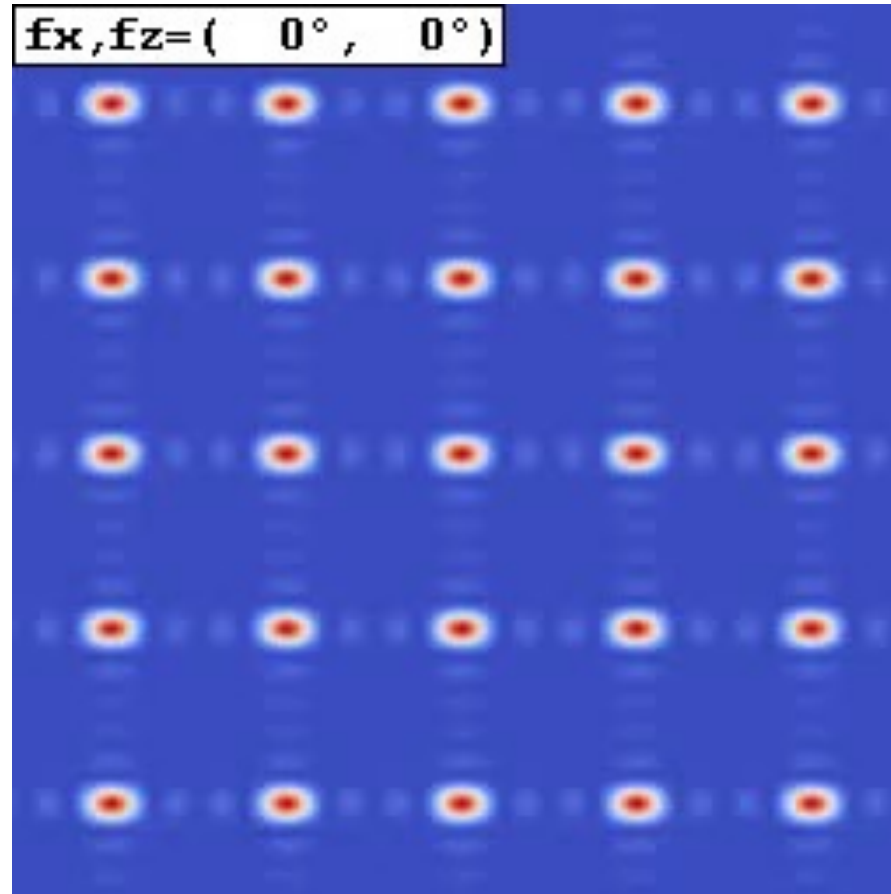
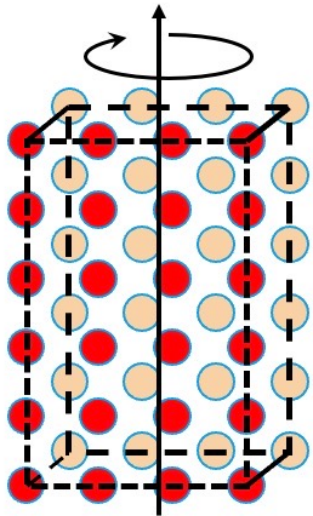
FEL undulators:

same as in a storage ring, but the emittance of the electron beam is so small, that the interaction of the emitted radiation with the electron beam causes micro bunching ➔ constructive interference of the emitted radiation within each microbunch

X-ray imaging and diffraction from nano objects

The use of coherent X-ray radiation to study structure and function of nano objects

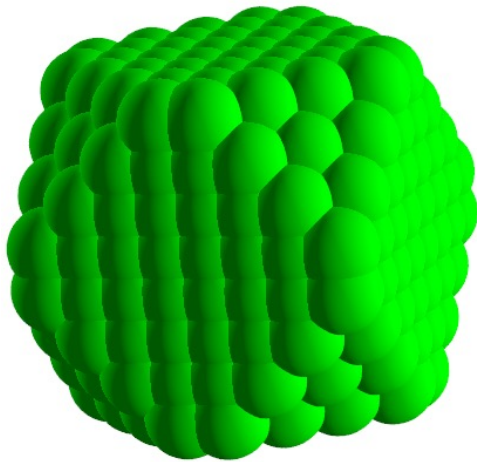
Let's rotate a hypothetical nano crystal about the vertical axis



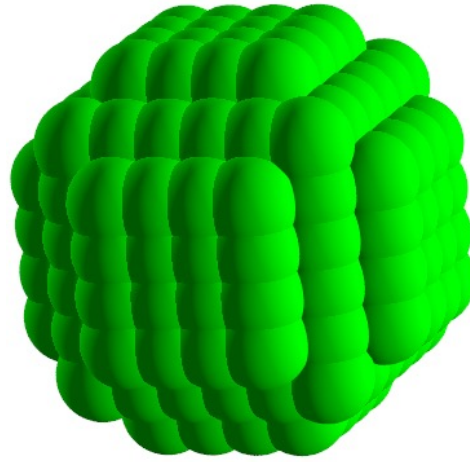
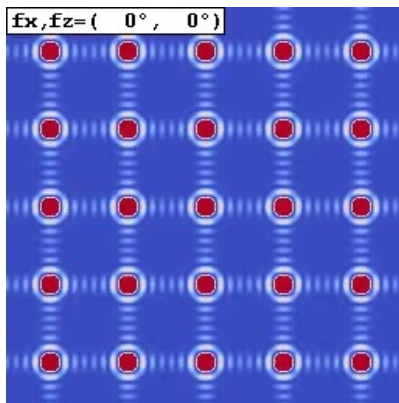
- Positions of the main peaks depends on the crystal lattice of the underlying crystal structure
- Intensity of the main peaks depend on $F(h)$ and encode the chemical content of the unit cell
- Maxima and minima between the main peaks depend on the shape of the nano crystal
- The video show slice through reciprocal space (curvature of the Ewald sphere has not been modelled)

X-ray imaging and diffraction from nano objects

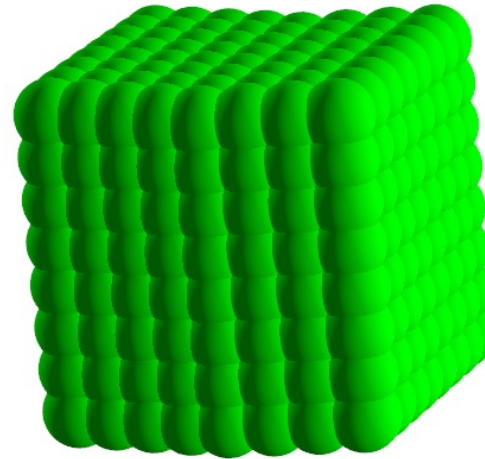
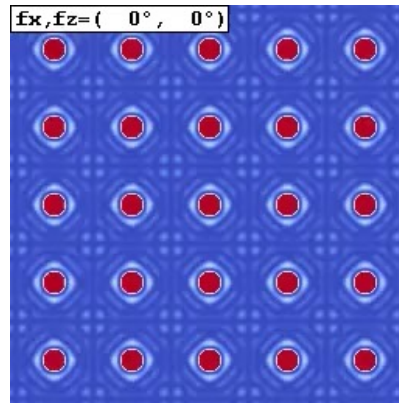
The use of coherent X-ray radiation to study structure and function of nano objects



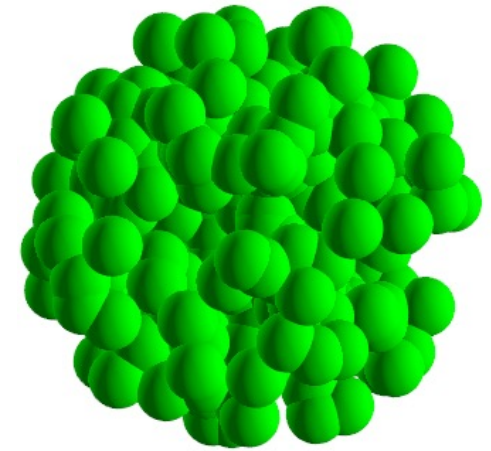
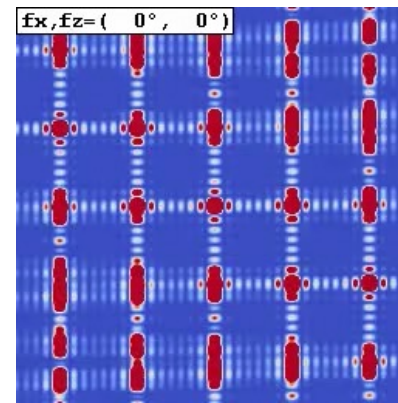
Facets in 111 directions



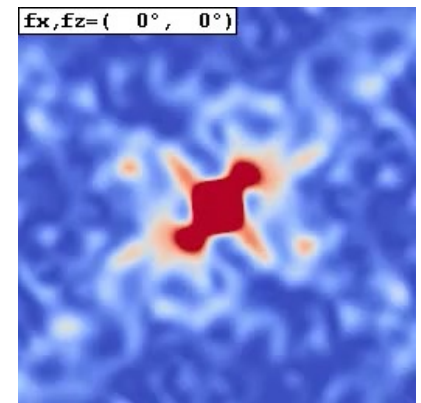
Facets in 110 directions



strained cube



512 random particles

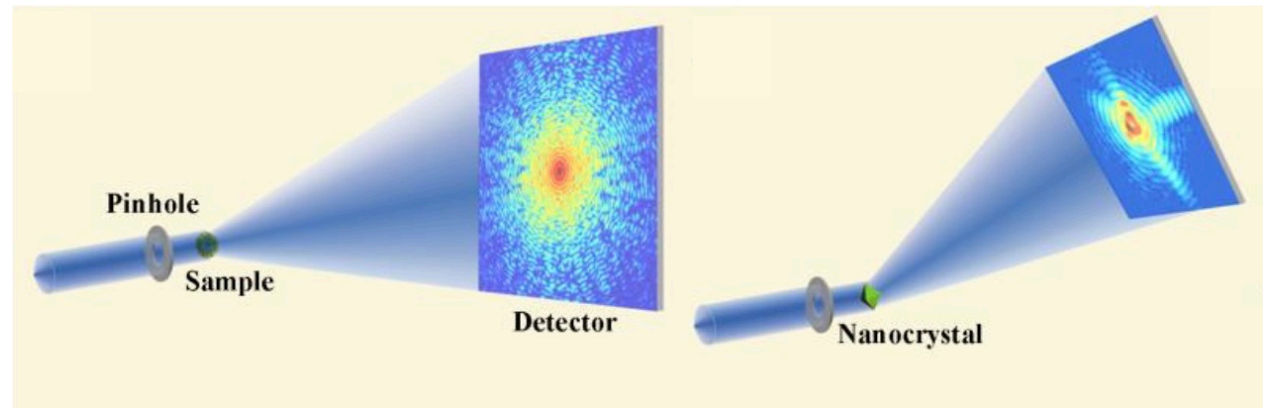


X-ray imaging and diffraction from nano objects

Structural studies on nano-wires: how does it work at all?

- Also, in this case we can not measure the phases of the diffracted wavefield
➔ direct inversion is not possible
- Crystal: The directions of the Bragg reflections represent exactly the minimal required number of sampling point according to the Nyquist criteria
- Coherent X-ray Diffractive Imaging (CXDI): continuous diffraction pattern can be oversampled
➔ sufficient information for inversion
- Iteration btw. real and reciprocal space applying respective constrains

Gerchberg, Saxton, Optik, **35**(1972)237
Fienup, Optics Letter **3**(1978)27
Miao, Sayre, Chapman, J. Opt. Soc. Am. A **15**(1998)1662
Miao, ..., Sayre, Nature, **400**(1999)342
Robinson et al., PRL, **87**(2001)195505
Miao et al., Science, **348**(2015)530



Exit wavefield after the sample:

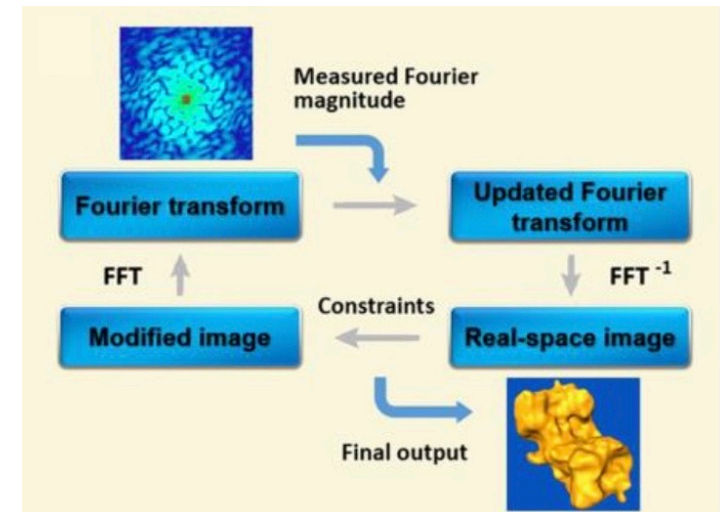
$$\Psi(\vec{r}) = P(\vec{r})O(\vec{r})$$

$P(r)$: complex illumination function
 $O(r)$: sample transmission function

Observation in the far field is the Fourier transform of $\Psi(\vec{r})$

Most important real space constraint:
- so called support taking into account the expected sample size

Problem: exact knowledge of $P(r)$



X-ray imaging and diffraction from nano objects

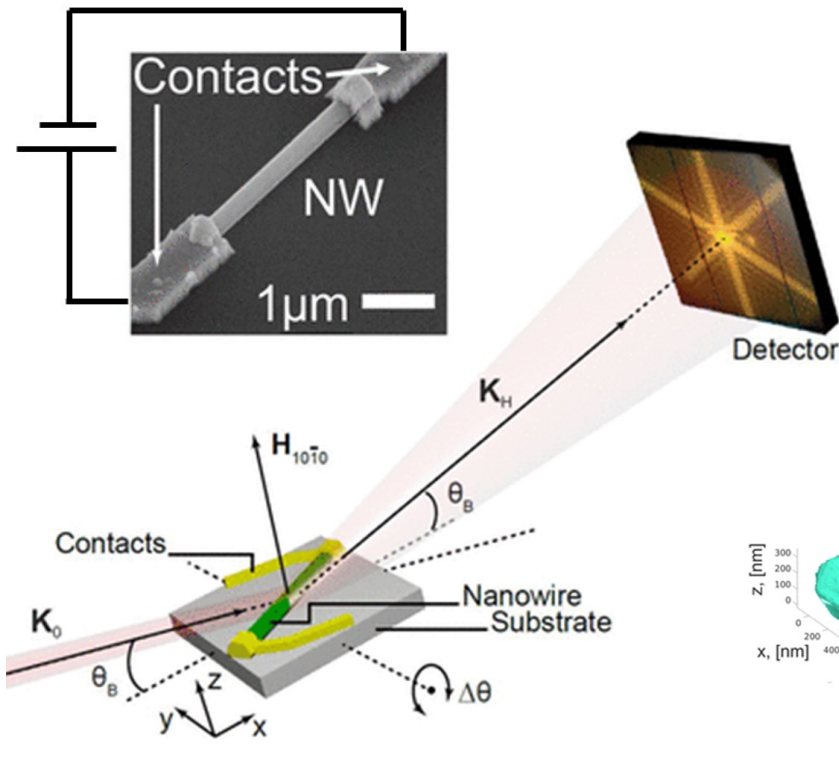
Structural studies on nano-wires

Structural changes in a single GaN nanowire under applied voltage bias

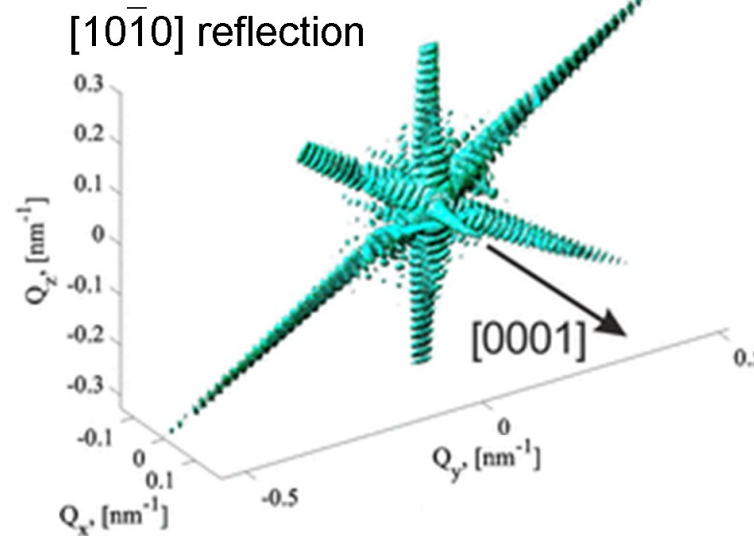
S. Lazarev et. al., Nano Lett. 18, 5446 (2018)

P10@PETRA III

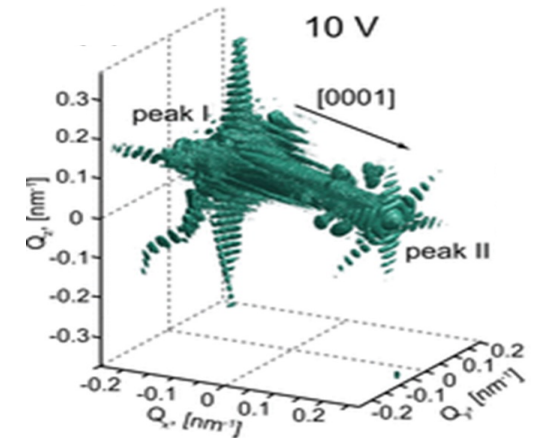
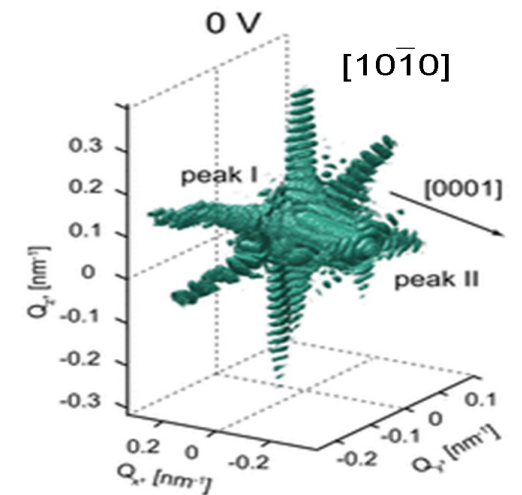
Heating a nanowire and measuring the strain & shape



unstrained nanowire, not mounted

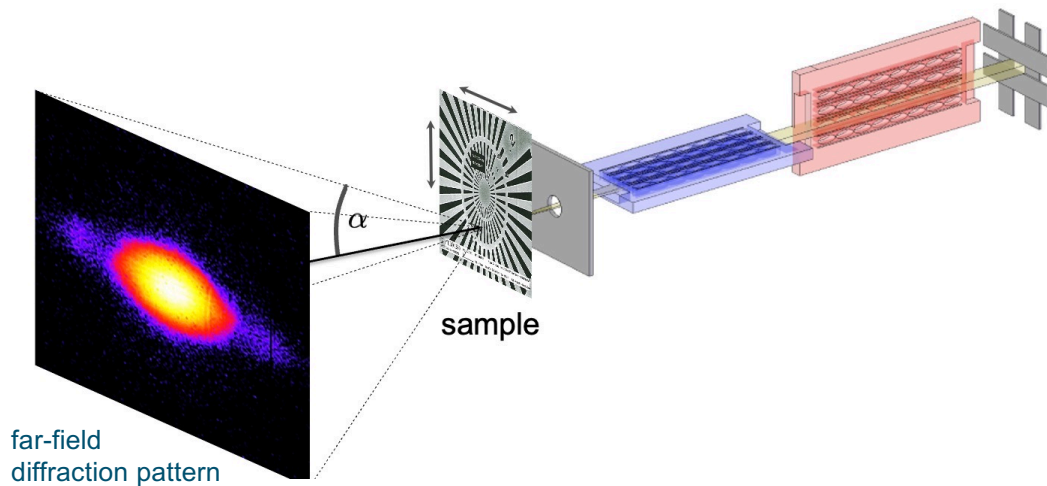


reconstruction from [1010] reflection



X-ray imaging and diffraction from nano objects

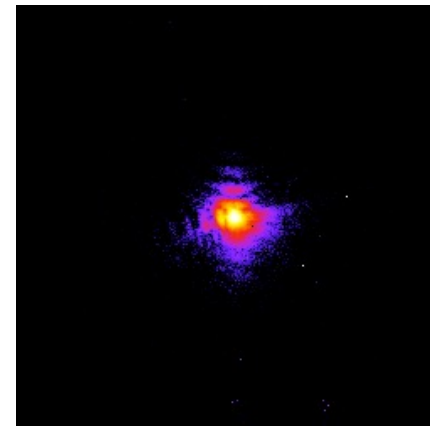
X-ray ptychography allows for imaging larger objects



- > Sample is raster scanned through confined beam
- > At each position of scan: diffraction pattern is recorded
- > Overlap in illumination between adjacent points

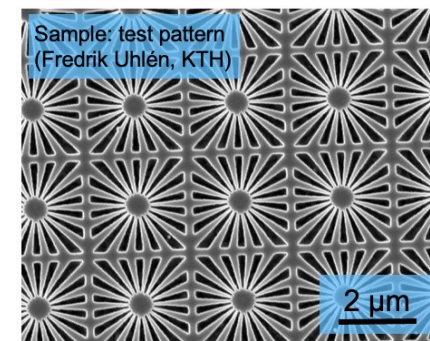
J. Rodenburg, H. Faulkner, *Appl. Phys. Lett.* **85**, 4795 (2004),
P. Thibault, et al., *Science* **321**, 379 (2008),
A. Schropp, et al., *Appl. Phys. Lett.* **96**, 091102 (2010),
M. Dierolf, et al., *Nature* **467**, 436 (2010).

DESY. X-ray Diffraction and Imaging: ... | Edgar Weckert | 1-4 September 2025



Nanofocusing lenses at
P06@PETRA III

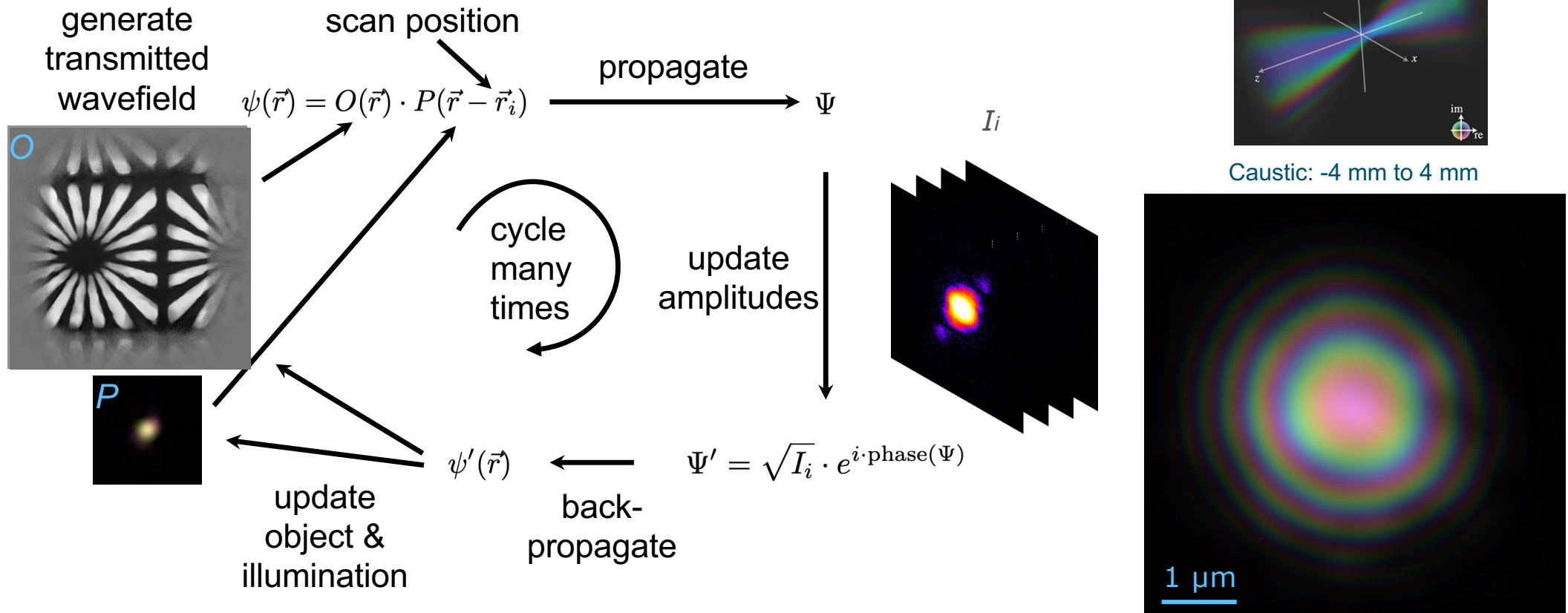
$E = 8.0$ keV
25 x 25 steps of 80×80 nm²
 2×2 μ m² FOV
exposure: 1.0 s per point
detected fluence: 120 ph/nm²



A. Schropp, et al., *Appl. Phys. Lett.* **96**, 091102 (2010).
C. G. Schroer, et al., *Proc. SPIE* **8848**, 884807 (2013).

X-ray imaging and diffraction from nano objects

X-ray ptychography allows for imaging larger objects



Maiden & Rodenburg, Ultramicroscopy **109**, 1256 (2009).

DESY. X-ray Diffraction and Imaging: ... | Edgar Weckert | 1-4 September 2025

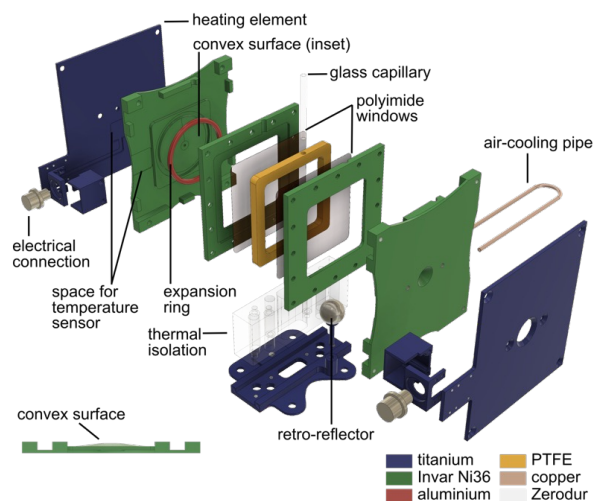
A. Schropp, et al., Appl. Phys. Lett. **96**, 091102 (2010).

C. G. Schroer, et al., Proc. SPIE **8848**, 884807 (2013).

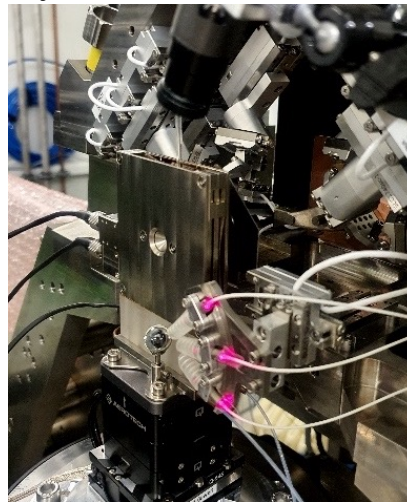
X-ray imaging and diffraction from nano objects

Chemical reactors and multi-slice ptychography allow in-situ observation of nanostructure formation

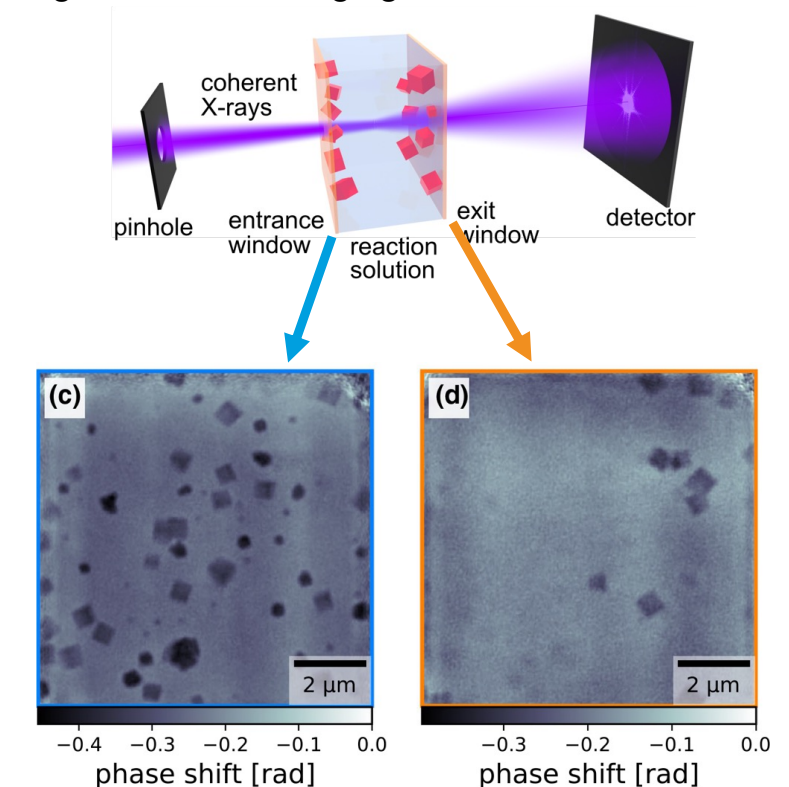
chemical reactor for nanoparticle growth from the liquid phase



chemical imaging at PtyNAMI at beamline P06



Multi-slice ptychography: simultaneous high-resolution imaging of two reactor windows

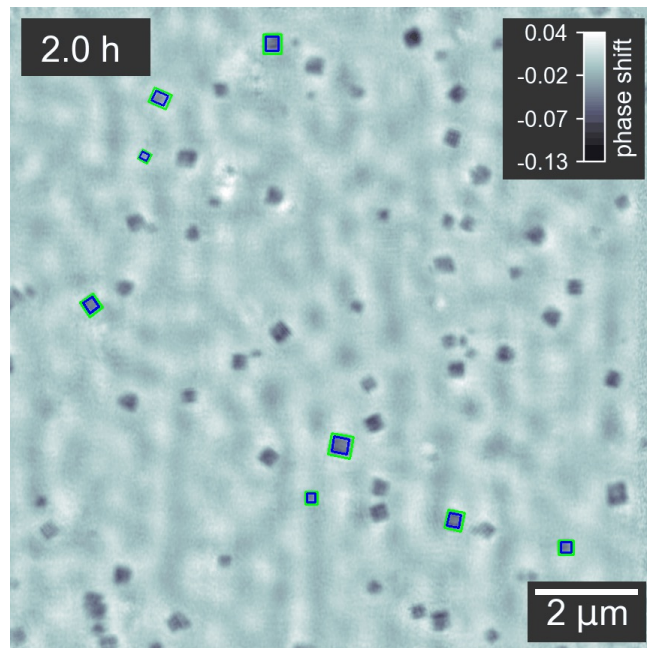


L. Grote, *et al.*, Nat. Commun. **13**, 4971 (2022).

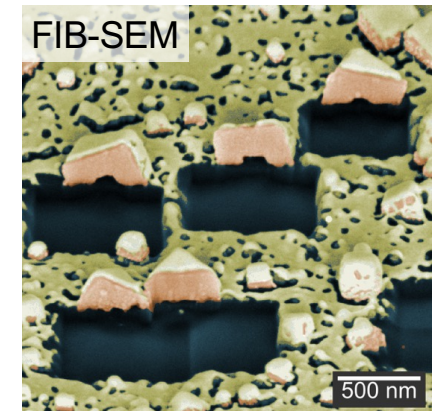
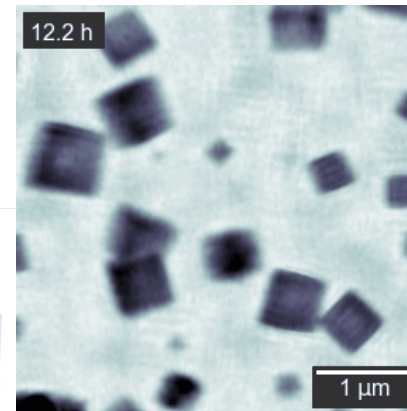
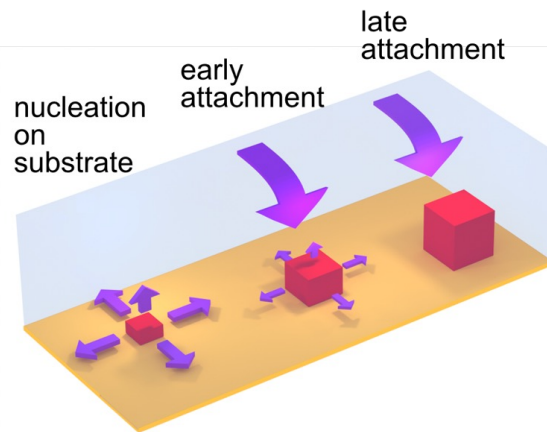
M. Kahnt, *et al.*, Sci. Rep. **11**, 1500 (2021).

X-ray imaging and diffraction from nano objects

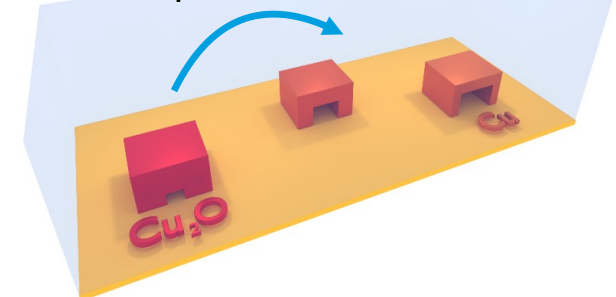
The growth and hollowing of CuO nanocubes is followed quantitatively by in-situ multi-slice ptychography



→ particle in 3D:
thickness evolution



surface-protected conversion



L. Grote, et al., Nat. Commun. **13**, 4971 (2022).

Structure of Quantum Dots for single photon sources

Use a combination of ptychography, SEM, X-ray fluorescence and X-ray diffraction

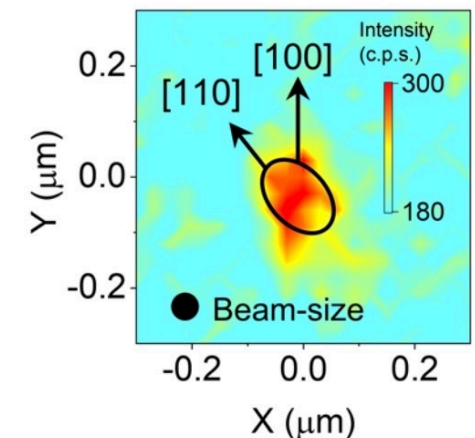
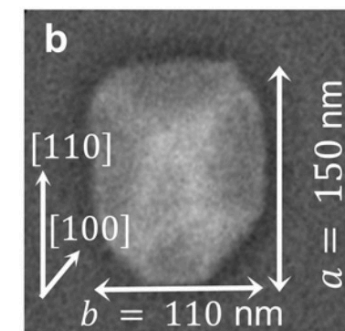
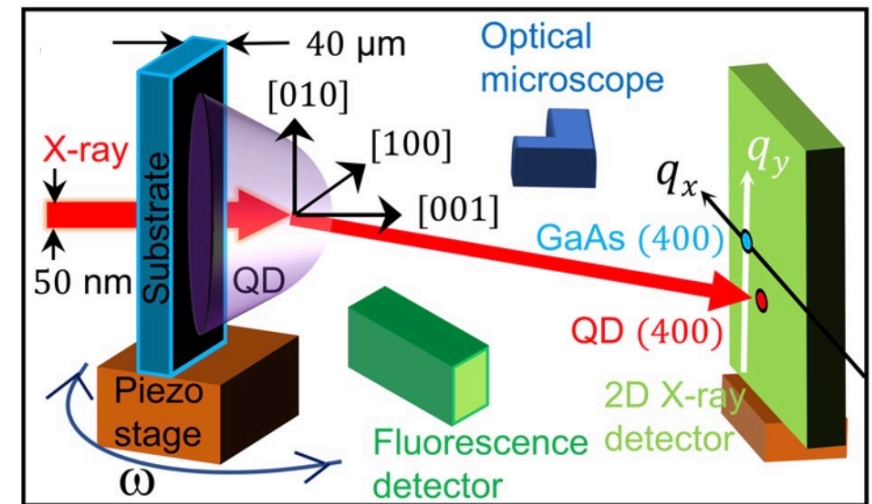
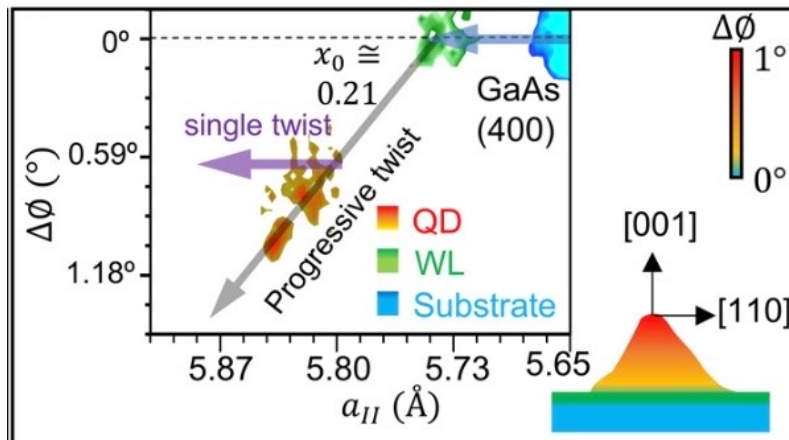
Culling a Self-Assembled Quantum Dot as a Single-Photon Source Using X-ray Microscopy

Arka Bikash Dey,* Milan K. Sanyal,* Andreas Schropp, Silvio Achilles, Thomas F. Keller, Ian Farrer, David A. Ritchie, Florian Bertram, Christian G. Schroer, and Oliver H. Seeck

Cite This: *ACS Nano* 2023, 17, 16080–16088

Read Online

- MBE growth of InSb Q-dots on GaAs (001), self assembly of Q-dots
- A combination of nano X-ray diffraction and fluorescence analysis as well as X-ray ptychography was able to unravel the internal structure of the Q-dots
- Information on chemical gradients (In) and lattice strain and rotations need to be feed in into procedures to optimize optical performance



Use of AI and LLMs for structural studies

Some words of caution

- We have learned that **AlphaFold II** is a very powerful tool to obtain a first starting model for structure refinement
 - However, >80% success rate is not 100% ... confirmation by experimental data is always needed.
- Can state of the art LLMs be used to support work in structural science?
 - The following question was sent to a ChatGPT 5, ChatGPT 4o, ChatGPT 3, Claude.ai, perplexity.ai, and ChatGPT 5 thinking:
'Given two carbon atoms C1 and C2 connected by a single electron bond. How does the bond distance between the two atoms change if one replaces an H atom connected to say C1 by a F atom'

ChatGPT 5:

Step 1: Consider the elec

- Fluorine is highly electronegative (C1).
- This reduces the electron density in the C1-C2 bond.
- Reduced electron density

Step 2: Consider orbital

- Substituting fluorine for hydrogen on C1 strengthens the C-F bond, which increases the p-character of the C1 orbital.
- In many substituted systems, the C-F bond is stronger than the C-H bond, which increases the p-character of the C1 orbital.
- More p-character → longer C-C bond.

Step 3: Compare with ex

In alkanes, C-C bond length is approximately 1.54 Å. In fluorinated alkanes (like fluoromethane), the C-C bond length is slightly longer, around 1.55 Å. So the effect is small but measurable.

ChatGPT 5:

Thought for 46s

Great question to press on—there are some nuances here. Replacing an H on C1 with F → think **ethyl fluoride**, $\text{CH}_3\text{—CH}_2\text{F}$, the adjacent C—C bond compared to ethane:

- **Ethane:** $r(\text{C—C}) \approx 1.534 \text{ \AA}$ from gas-phase electron diffraction.
- **Ethyl fluoride ($\text{CH}_3\text{—CH}_2\text{F}$):** $r(\text{C—C}) = 1.541 \pm 0.003 \text{ \AA}$

That supports the earlier statement: adding a single fluorine atom **slightly**, consistent with F's strong $-\text{I}$ (inductive) withdrawal.

Two helpful footnotes:

- In **1,2-difluoroethane**, gas-phase electron diffraction shows the effect can be small and context-dependent.
- If you keep adding fluorines (CF_3 , perfluoro systems), hyperconjugation, the gauche effect can complicate things. Fluorinated ethanes show **non-monotonic** behavior: single C—C bond, the **modest lengthening** above summarized here for context. ([Wikipedia](#))

So: yes—I'm confident about the **slight C—C bond lengthening** the sizes above as experimental anchors.

Answer: ChatGPT 4o:

✓ The C1–C2 bond distance increases slightly when you replace an H on C1 with a fluorine atom.

Why?

1. Electronegativity of Fluorine ($-\text{I}$ effect):

- Fluorine is highly electronegative.
- It pulls electron density away from C1 through the σ -bond network.
- This **reduces electron density** in the C1–C2 bond, making it slightly weaker and **longer**.

2. Hybridization Effects (Bent's Rule):

- The C–F bond prefers more **s-character** to stabilize the electronegative F.
- This pushes more **p-character** into the C1–C2 bond → a more diffuse orbital → **longer bond**.

Experimental Confirmation:

Molecule	C–C Bond Length (Å)
Ethane ($\text{CH}_3\text{—CH}_3$)	$\sim 1.534 \text{ \AA}$
Fluoroethane ($\text{CH}_3\text{—CH}_2\text{F}$)	$\sim 1.540\text{--}1.541 \text{ \AA}$

So, C–C bond lengthens by $\sim 0.005\text{--}0.007 \text{ \AA}$.

Final Summary:

Replacing an H atom on one carbon with a fluorine atom causes the adjacent C–C single bond to **increase slightly in length**. This is mainly due to fluorine's strong inductive withdrawal of electron density.

All other LLMs and google AI give the correct answer, also ChatGPT 5 thinking !!

Summary

....

- X-ray crystallography is a very mature technique for the determination of the atomic structure at high resolution
- With the advent of useful coherent X-ray fluxes at 3rd and 4th generation synchrotron and FEL radiation sources X-ray imaging methods to the single digit nm range can provide valuable information for materials design
- In general, whole set of X-ray, electron, and other methods are required to obtain the full picture
- Strength of the X-ray methods is in particular in the field of in-situ or operando experiments

Thank you for your attention

