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FZU
Institute of Physics of the
Czech Academy of Sciences

WP3 Accurate crystallography of complex nanomaterials

Lukáš Palatinus, Institute of Physics (FZU), Prague, Czechia

WP3 in a nutshell

WP3 = (more) accurate structures from 3D ED data

T3.1: Data collection strategies and their computational aspects (ESR4/FZU; ESR5/FZU, ESR6/ULM, ESR9/JGU)

How to get the best data for the best structures?

T3.2: Dynamical refinement on imperfect crystals (ESR3/UA, ESR4/FZU, ESR9/JGU)

How can we incorporate the crystal imperfections into the calculations?

T3.3: Determination of absolute structure and Flack parameter (ESR2/IIT, ESR4/FZU)

Accurate Flack needs unbiased refinements – we need to reach them!

T3.4: Charge density analysis (ESR5/FZU)

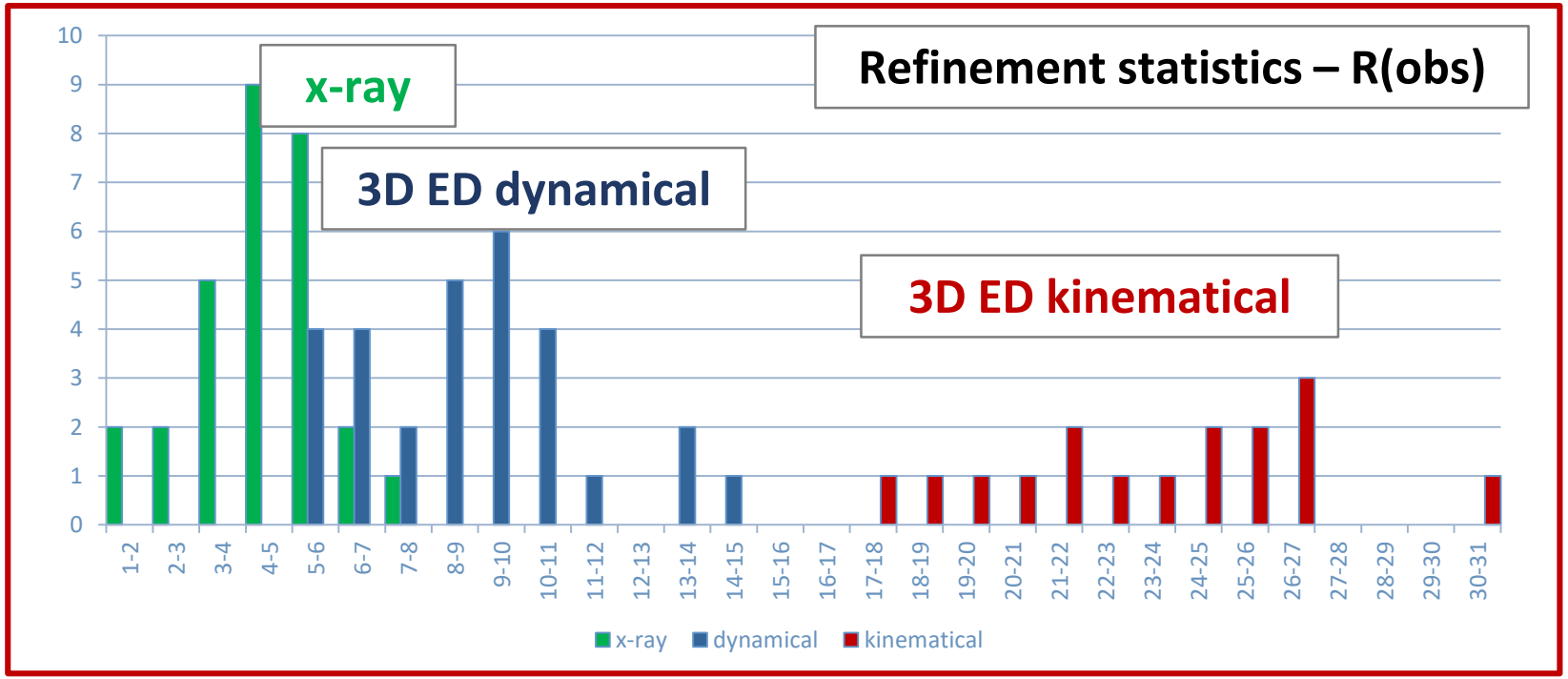
Pushing the limits, exploiting the advantages of electrons over x-rays

T3.5: Structure evolution during in situ experiments (ESR3/UA, ESR8/JGU)

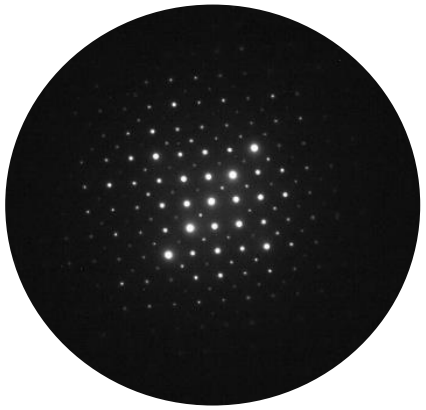
Difficult data need special treatment…

Structure analysis of inorganic and small molecule structures by 3DED – state of the art

1) Several well established data collection strategies and data types
2) Obtaining initial model usually not very dificult
3) Structure refinement: questions remain



Electron diffraction - caveats



experimental ED pattern

kinematical simulation

Kinematical approximation:

$$I_{\mathbf{h}} \propto |F_{\mathbf{h}}|^2$$

Dynamical theory:

1) Find all reflections that contribute to diffraction

2) Build structure matrix A:

$$a_{ii} = 2KS_{\mathbf{g}_i}, i = 1, N_{beams}$$

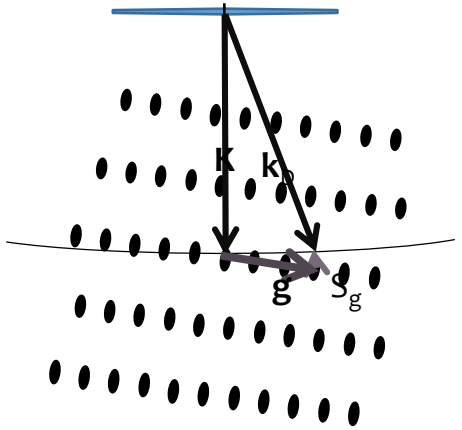
$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$

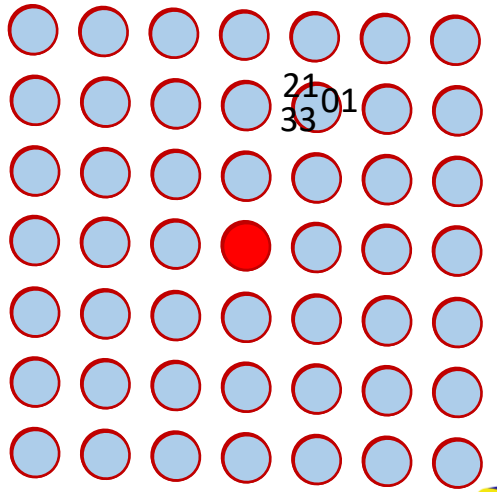
3) Calculate scattering matrix S:

$$\mathbf{S} = \exp\left(\frac{2\pi i t \mathbf{A}}{2K_n}\right)$$

4) Calculate intensities from the first column of **S**:

$$I_{\mathbf{h}_i} = |s_{i1}|^2$$

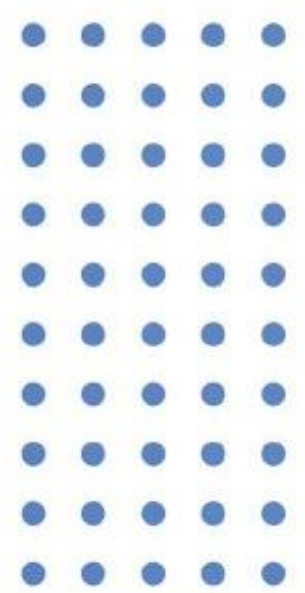


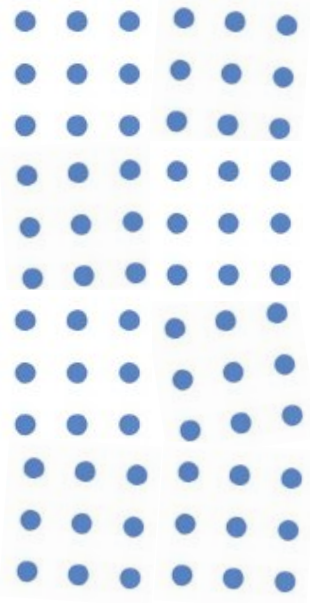


Electron diffraction - caveats

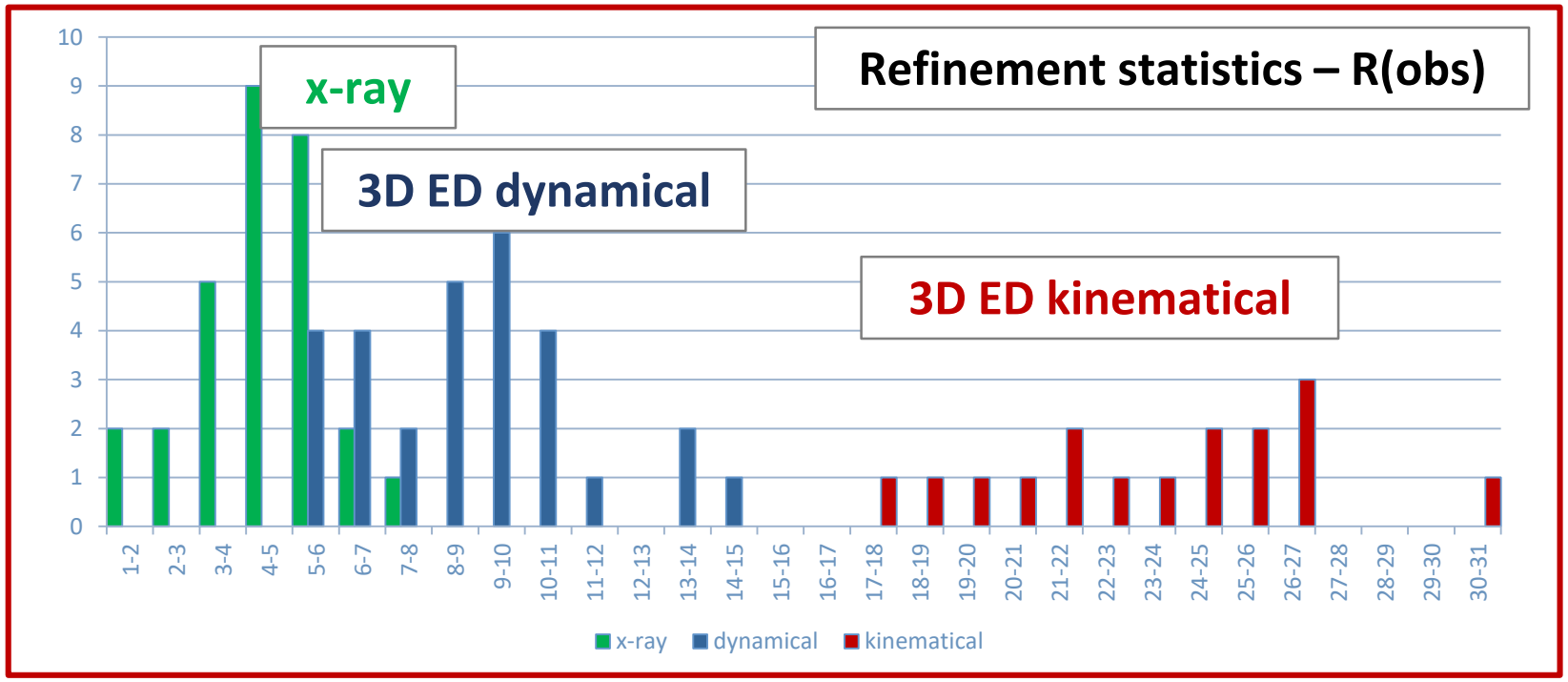
- Dynamical diffraction = effects arising from strong interaction of electrons with the crystal

Case 1: perfect crystal	Case 2. imperfect crystal
- Effects „strong“ - Theory well established - Experimentally very well confirmed - Computation effort moderate	- Effects „weak“ - Theory basically available - Experimentally not very well studied - Computation effort very high



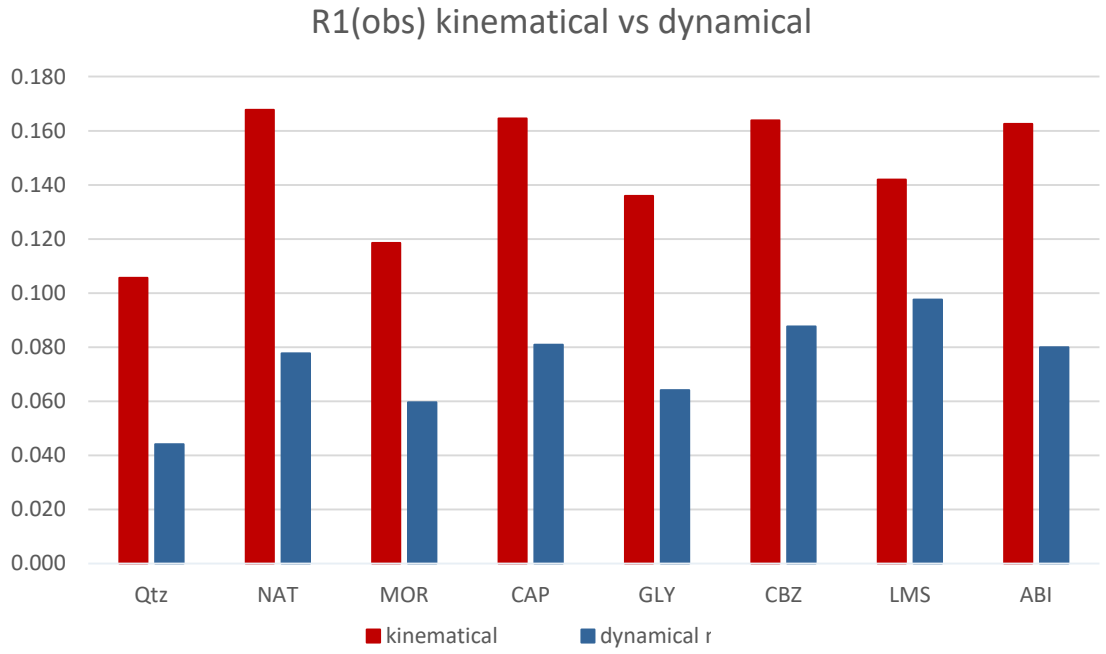


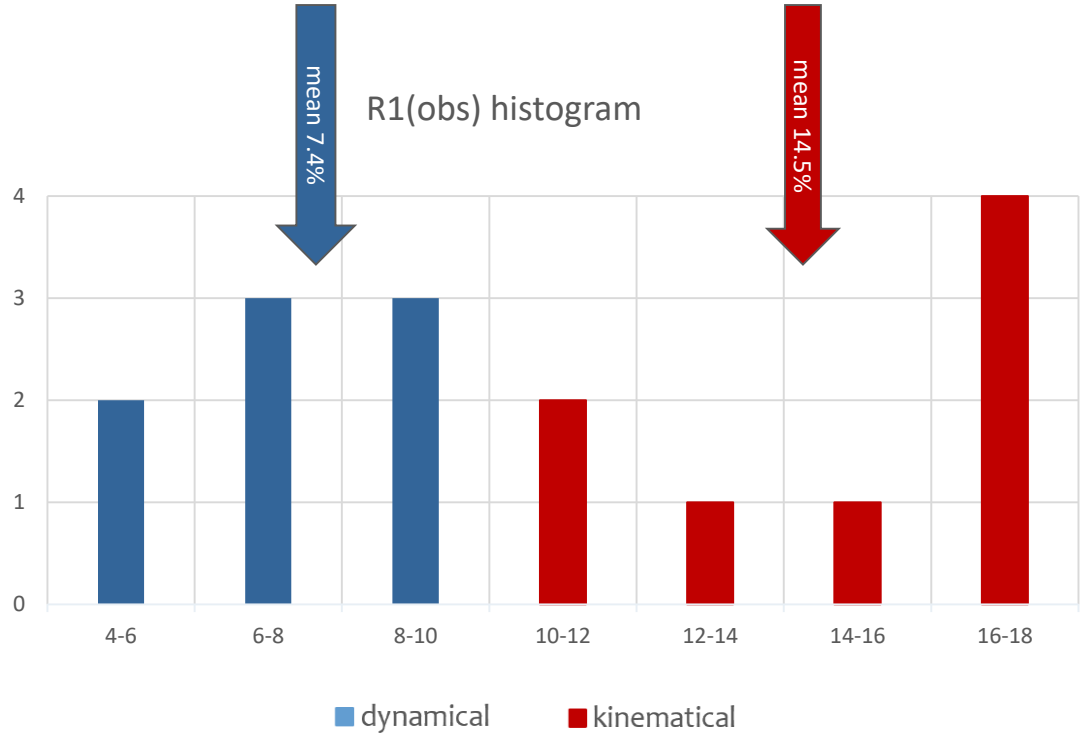
Electron diffraction - caveats



Electron diffraction - caveats

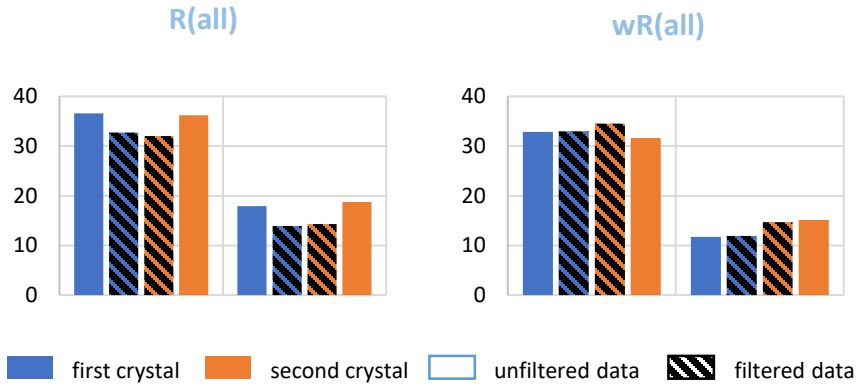
8 structures carefully refined kinematically and dynamically from the same experimental data

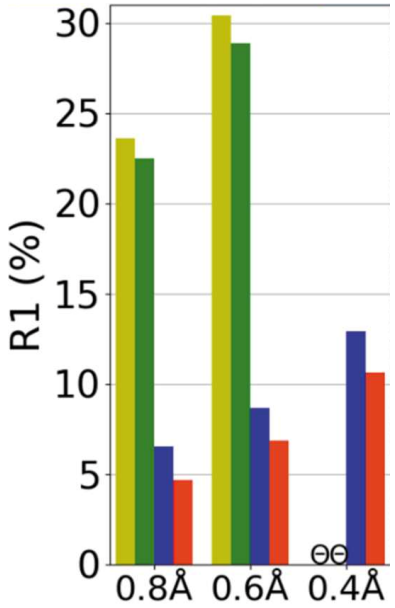




Electron diffraction - caveats

- Other possible problems:
  - Effect of inelastic scattering – visible, but small





- Charge density effects – visible, but small

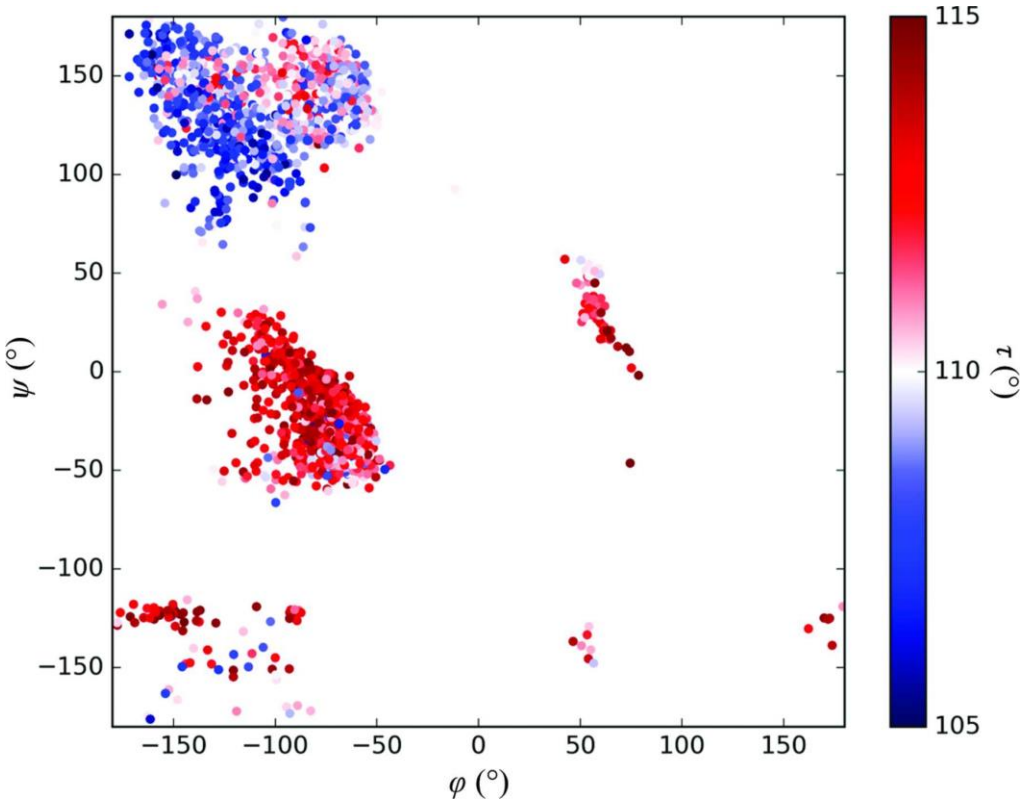
- radiation damage…

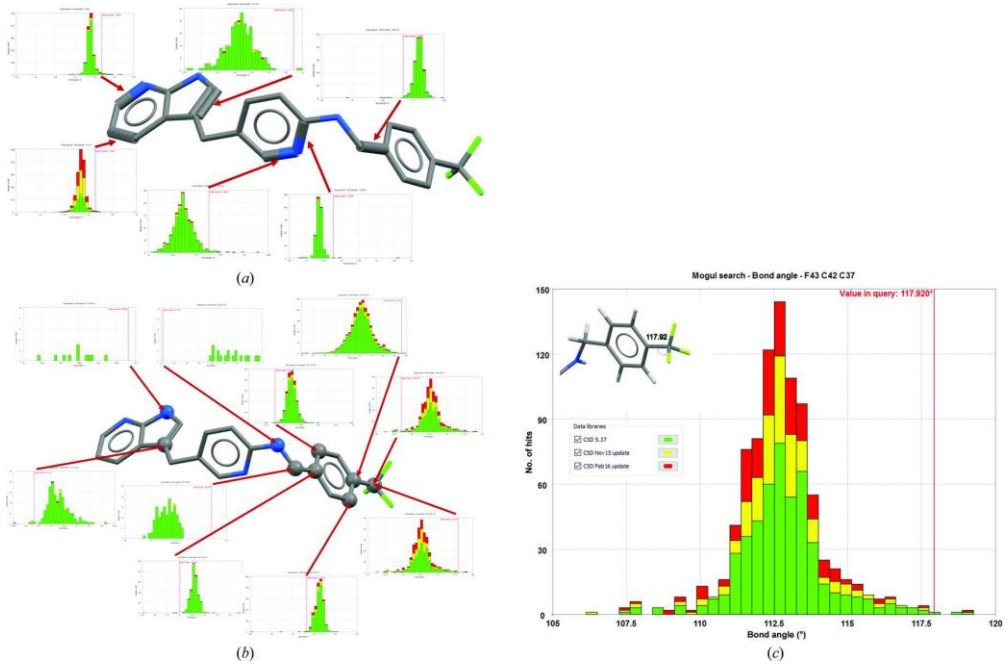
From Gruza et al., Acta Cryst. A , 92–109

10.11107/S2053273319015304

WP3 mission – close the R-factor gap!

- But why?! Aren‘t the currently available 3D ED structures good enough?





Using more than 801 296 small-molecule crystal structures to aid in protein structure refinement and analysis

- Cole *et al.*

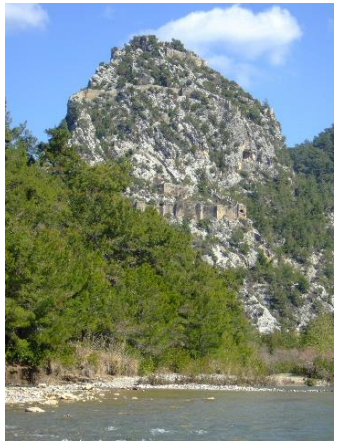
Acta Cryst D STRUCTURAL BIOLOGY

- Volume 73 | Part 3 | March 2017 | Pages 234–239 | 10.11107/S2059798316014352

WP3 mission – close the R-factor gap!

- So should I spend months getting my factors down a bit?

We should use the ALARA principle:



*Findable, Accessible, Interoperable, Reusable

ESR 4 – accurate structure refinement

Project title and related WP: Accurate structure refinement from 3D ED data (WP1,WP3)
Objectives: (1) Test and optimize the dynamical refinement strategy for various types of materials and data collection methods; (2) Generalize the dynamical refinement to include the effect of crystal imperfections, leading to the improvement of the fit to data from real crystal and to the accuracy of extracted structure models; (3) optimize the determination of absolute structure of non-centrosymmetric crystals, develop and verify the calculation of Flack parameter from 3D ED data

Challenges: help to optimize data collection strategies for the best results
remove the bias from the intensity calculations
extract most from the electron difraction data
move the absolute structure determination to the next level:
any crystal size, any composition

Motto: Data are not bad just because we can‘t fit them!

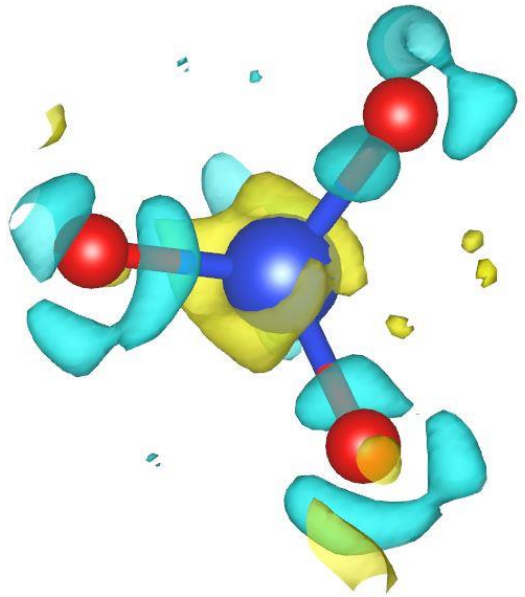
Most likely interactions: ESR2(IIT), ESR3(UA), ESR5(FZU), ESR6(ULM), ESR8(JGU), ESR9(JGU), ESR11(SU)

ESR 5 – charge density analysis from 3D ED data

Project title and related WP: Charge density analysis from 3D ED data (WP1, WP3)

Objectives: (1)Optimize data collection and data reduction strategies necessary for obtaining data suitable for charge density studies, analyse the accuracy required to provide charge density refinement; (2)Perform multipole refinements on a number of test samples from both organic and inorganic materials, compare the results with reference charge density studies from x-ray diffraction data; (3)apply the method to the analysis of interesting structures of organic and inorganic materials

Challenges:
- proof of principle for charge density studies
- explore the limits and possibilities
- establish the proper refinement of hydrogen atoms
- check, what part of the observed bias is due to the ignored bonding effects



Most likely interactions: ESR2(IIT), ESR4(FZU), ESR6(ULM)

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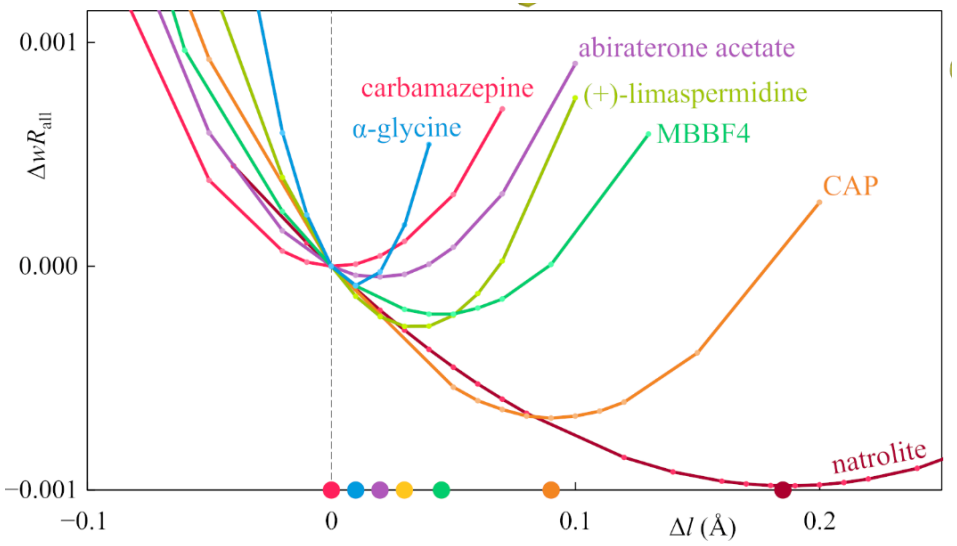

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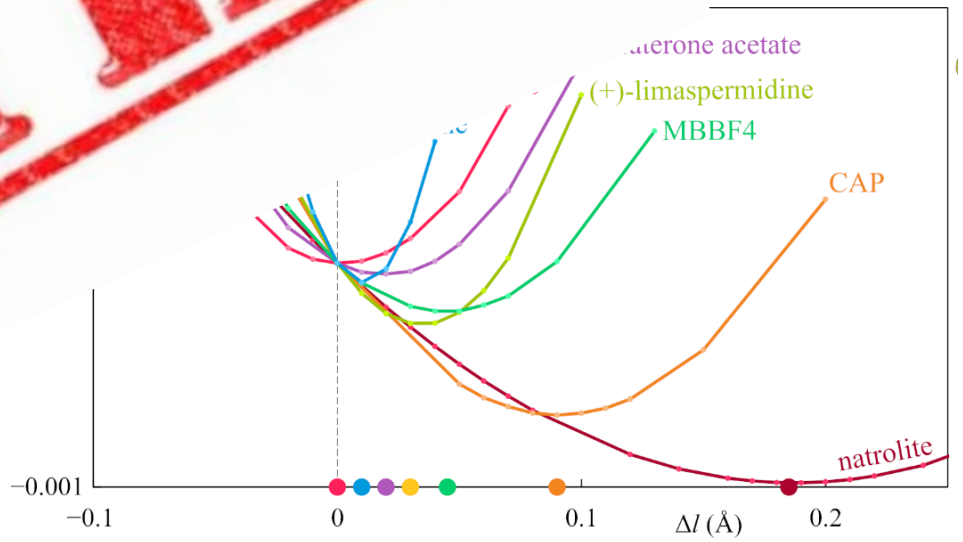

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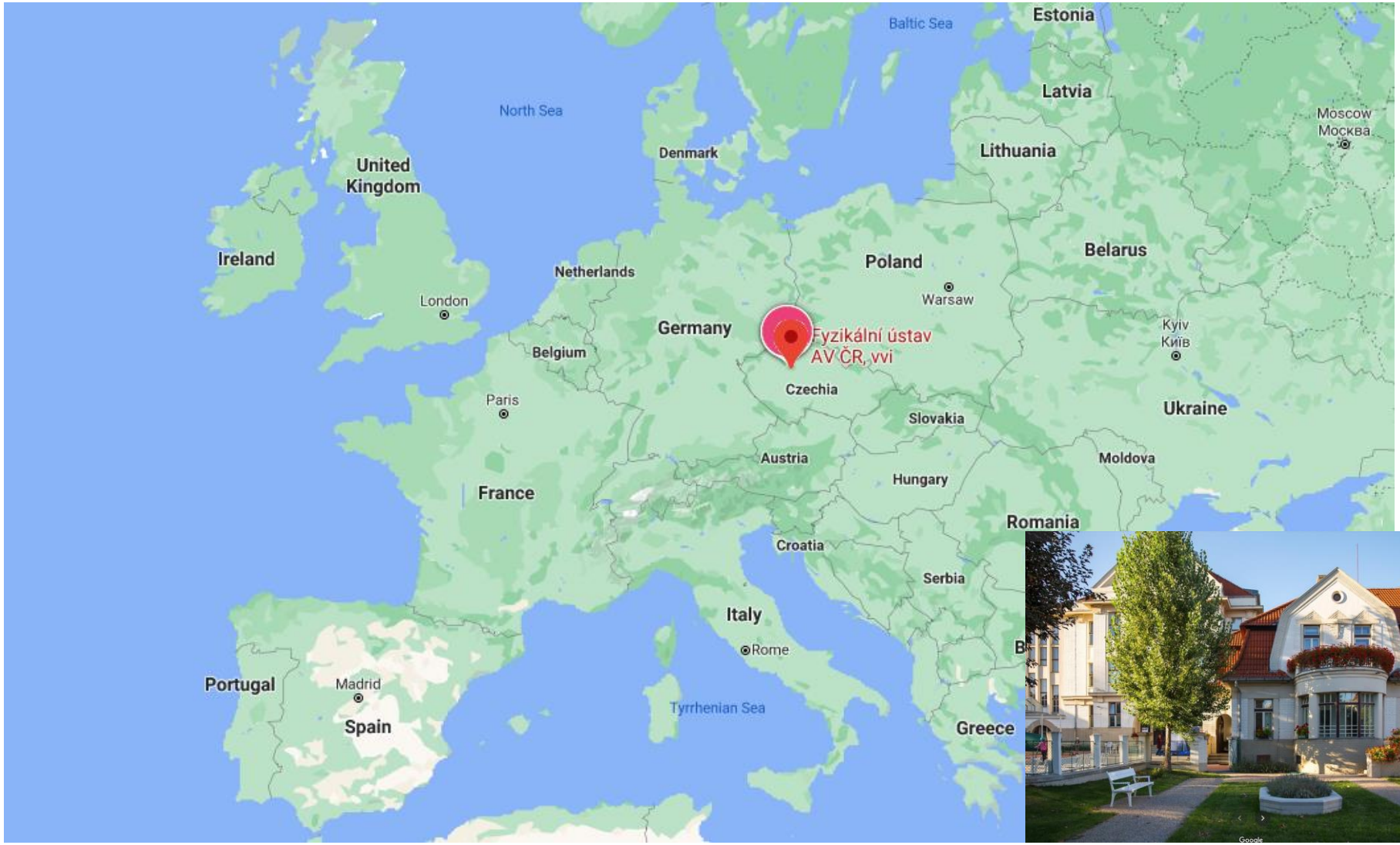


Laboratory of electron crystallography, FZU, Prague

Established 2009

Part of a crystallographic lab with 70 years of history

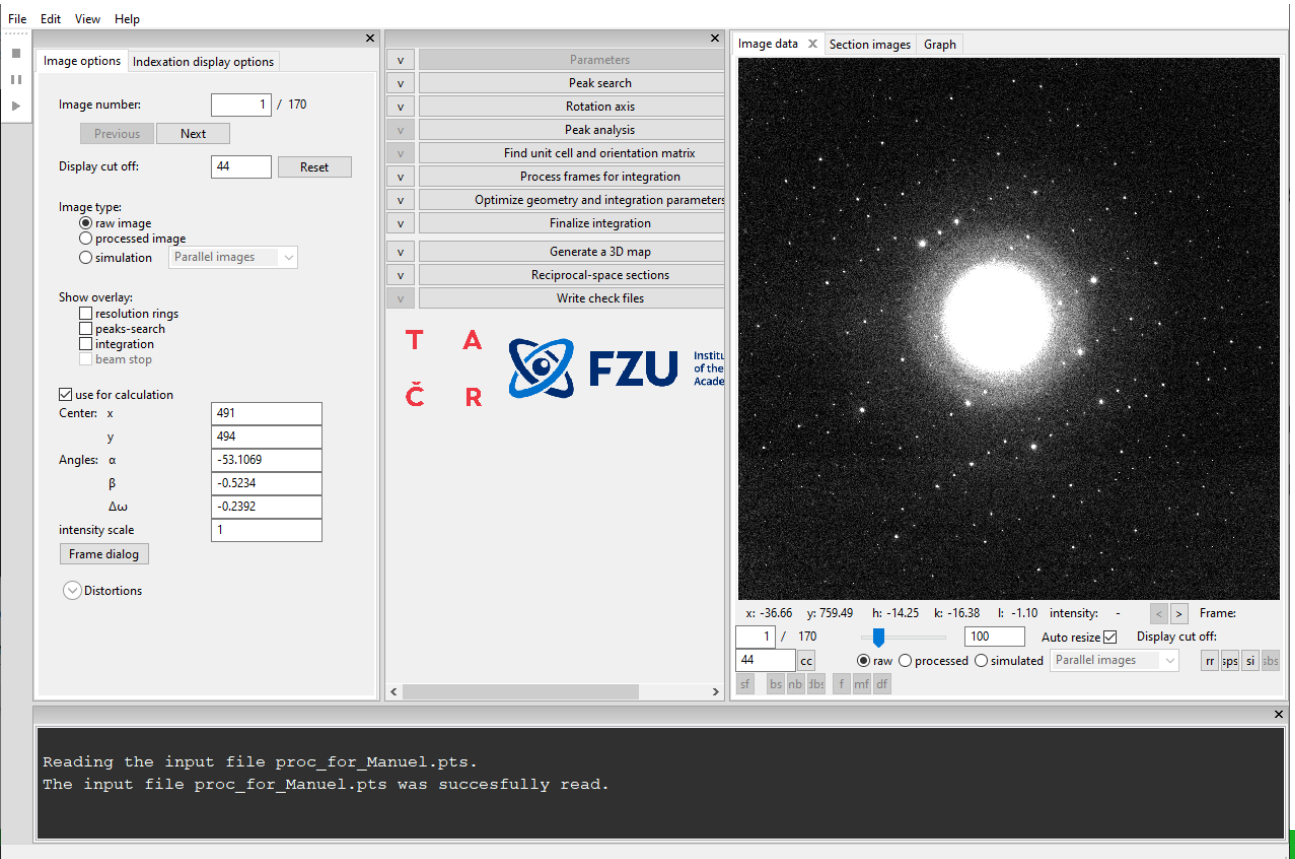
~10 researchers in methods and applications of 3D ED

TEM Tecnai G2 20, precession, HPD ASI Cheetah

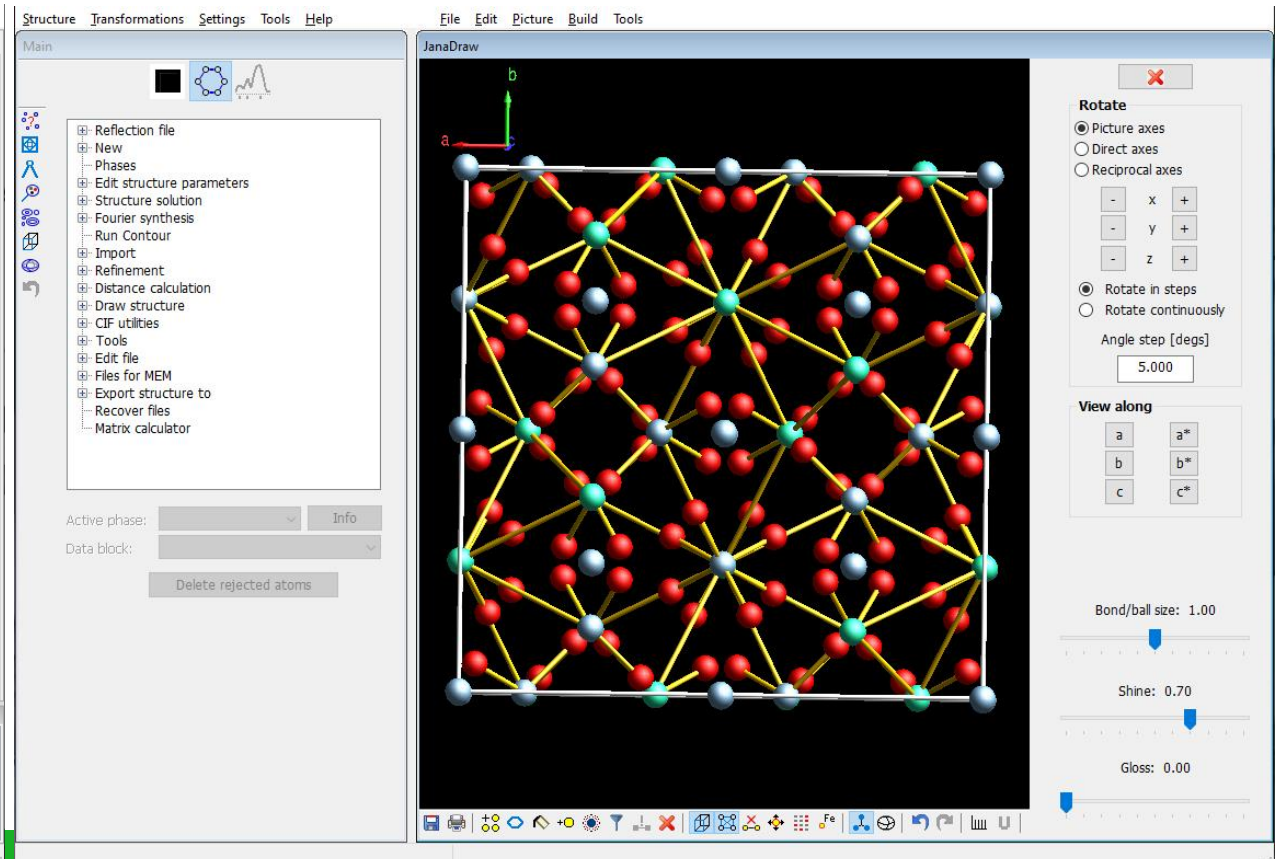
Home of the software Superflip, PETS2, Jana2006/Jana2020

Laboratory of electron crystallography, FZU, Prague

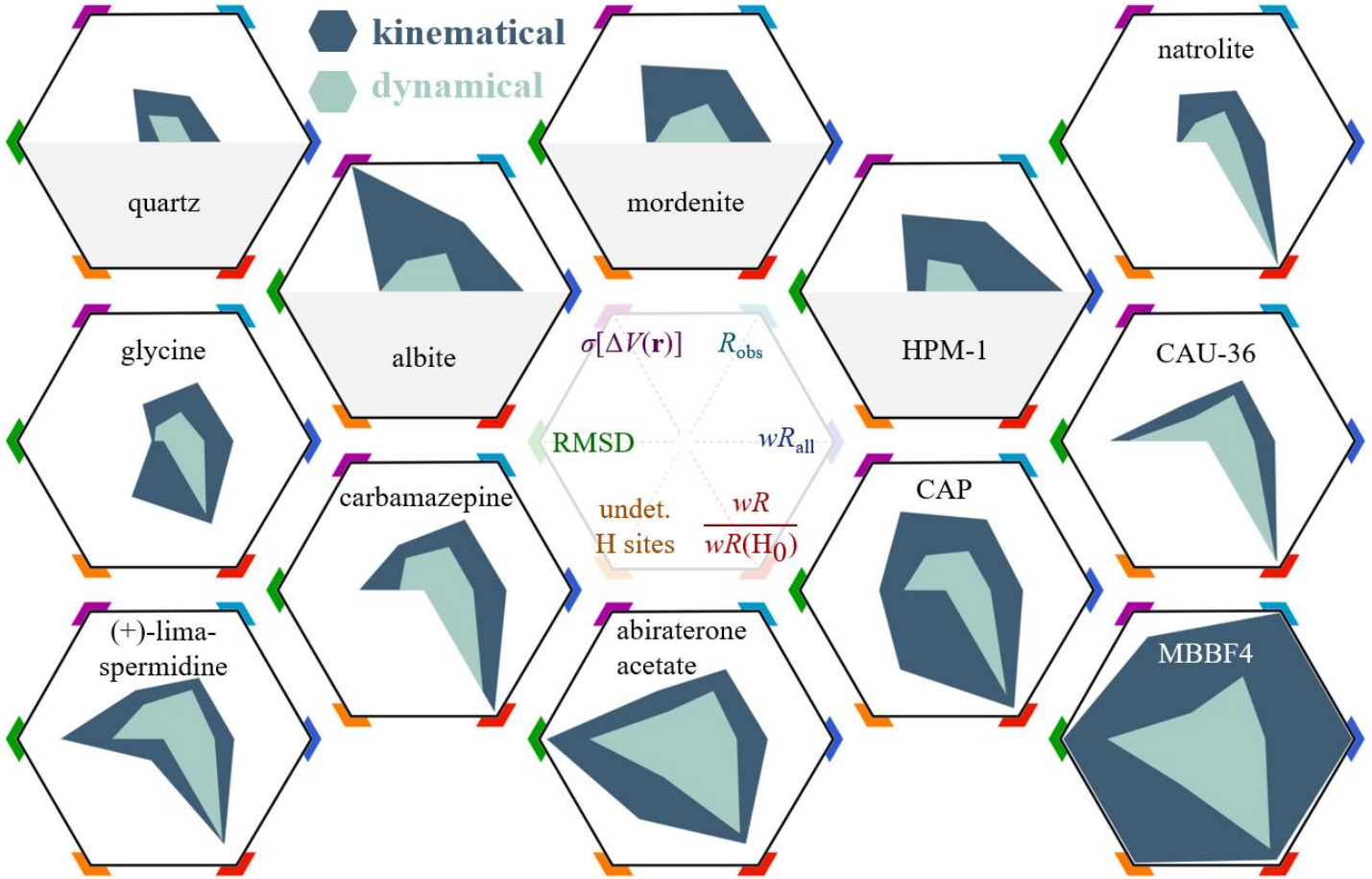
PETS2



Jana2020



Research highlights – improving the accuracy of 3D ED structures by dynamical refinement



Klar et al.: https://doi.org/10.26434/chemrxiv-2021-4jh14

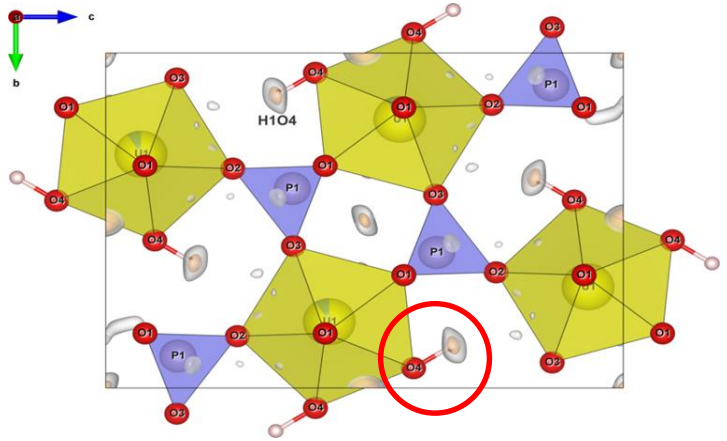
Research highlights - hydrogens

Hydrogens scatter relatively more in electrons than in x-rays.

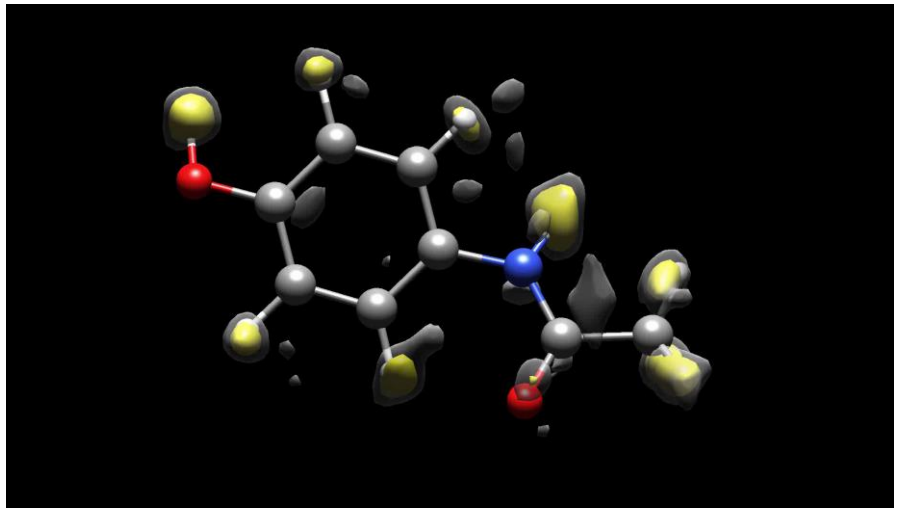
Despite of that for a long time difficult to see.

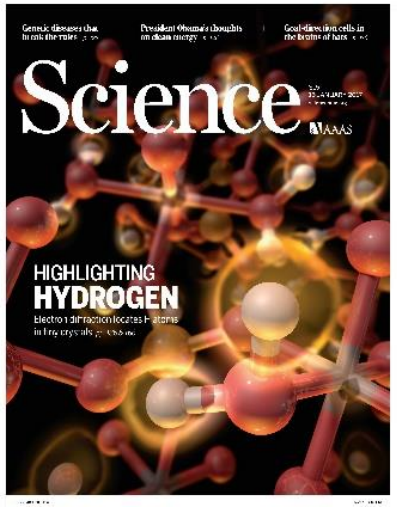
The possibility demonstrated and analyzed in detail in 2017 by Palatinus et al. (2017)

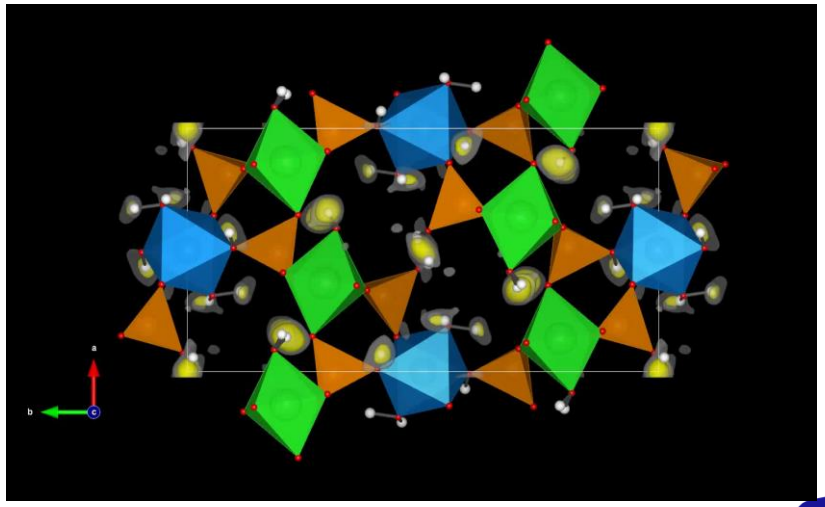
Now almost routine for organic materials, less routine for inorganics, dynamical refinement helps a lot



Steciuk, G. et al. (2021). American Mineralogist, DOI: 10.2138/am-2021-7875







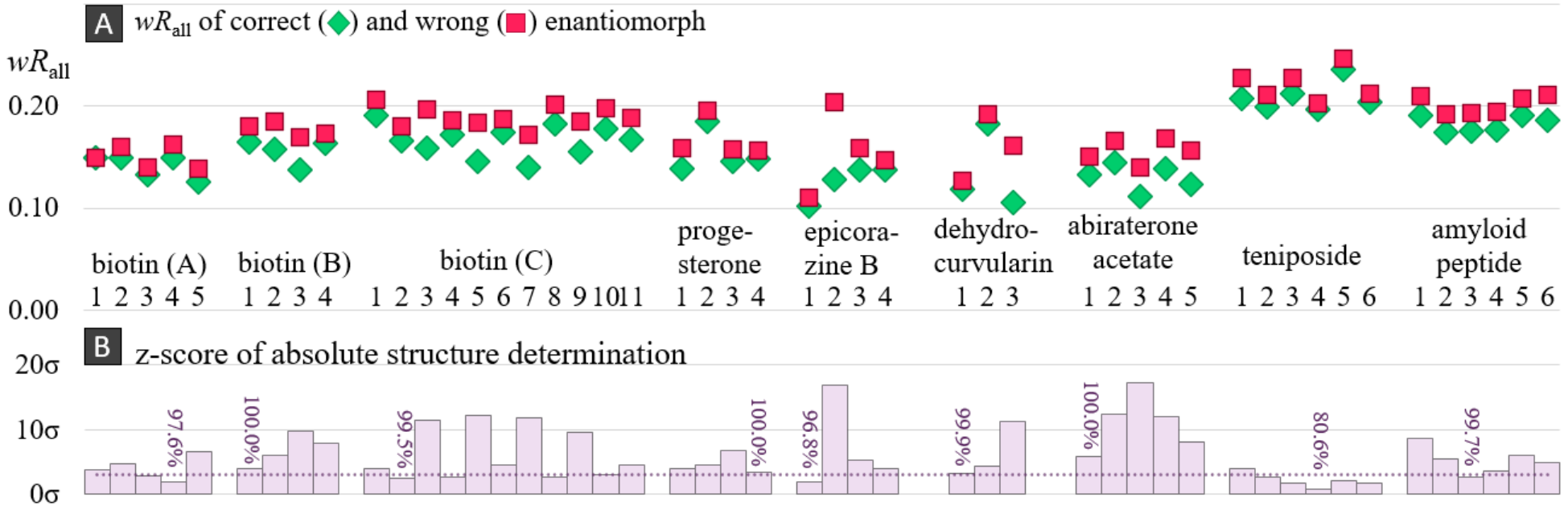
Palatinus et al. (2017), *Science 355*

Research highlights – absolute structure

Absolute structure determination = distinction between two inversion-related variants of a non-centrosymmetric structure

In electron diffraction only possible by exploiting dynamical diffraction effects

Very reliable method, does not require particularly high-quality data



Brázda et al. (2019), *Science 364; Klar et al. (2021): https://doi.org/10.26434/chemrxiv-2021-4jh14*