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FZU Institute of Physics of the Czech Academy of Sciences

Accurate structure refinement from 3D ED data

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Significance of the project:

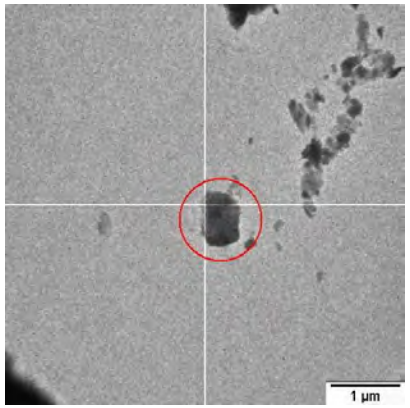
Electron interaction with matter is much stronger than X-ray's due to dynamical effects

We need to further **test and optimize** the dynamical refinement strategy by comparing various types of

- Detectors(CCD and HPD)
- Data collection methods(continuous rotation and Precession)
- Materials

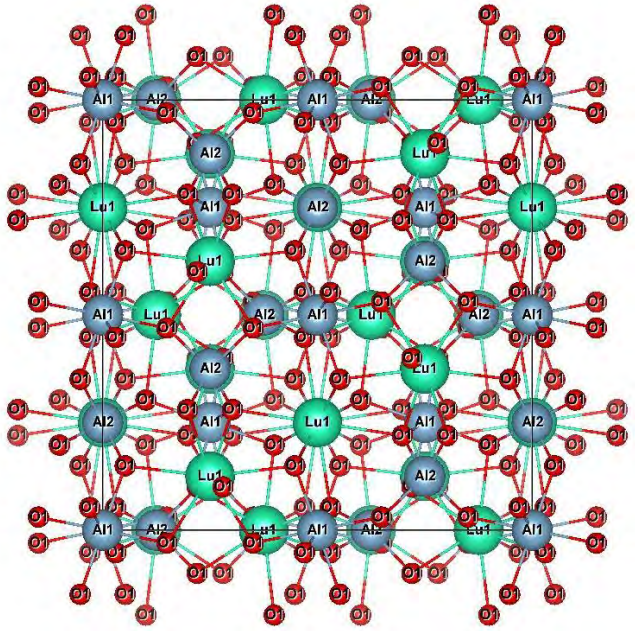
Identify the key effects that lead to the decreased quality of the fit between model and experimental data

Comparison of the Detectors(Olympus SIS Veleta and ASI cheetah) on Lutetium Aluminum Garnet



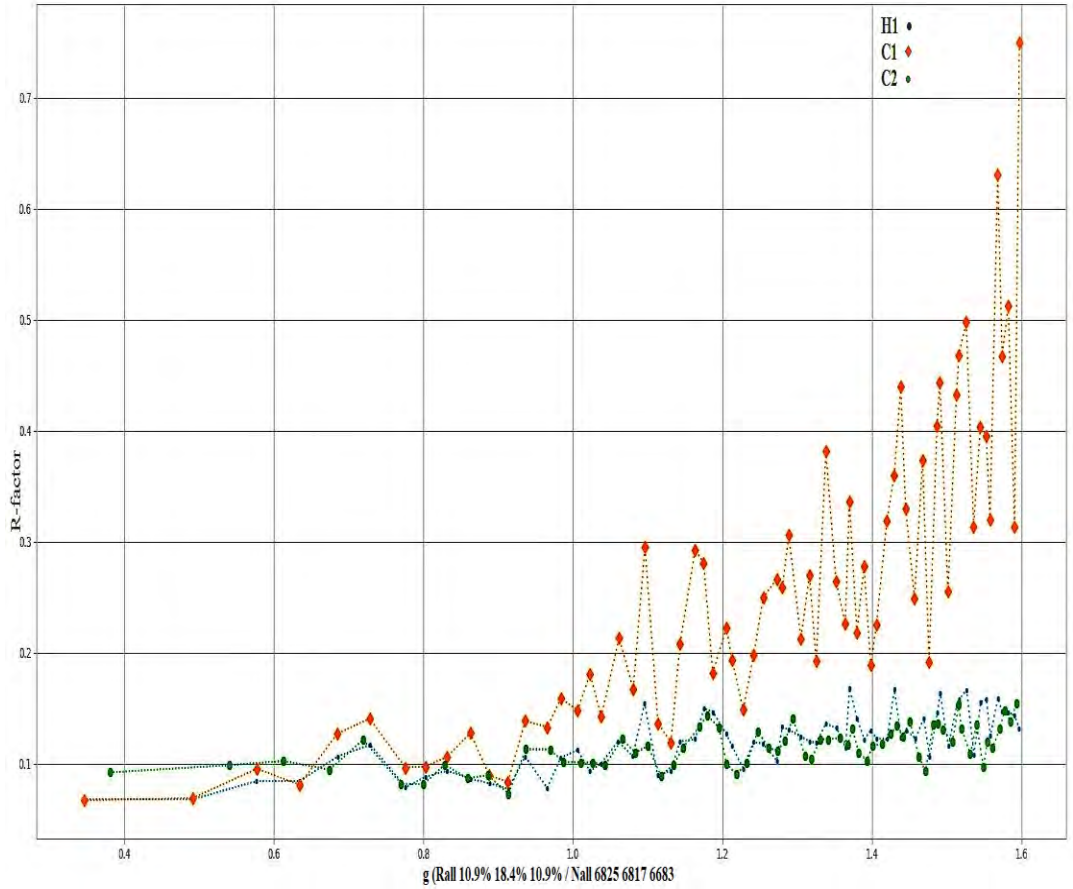
Data collection:(-50 to +50 degrees)

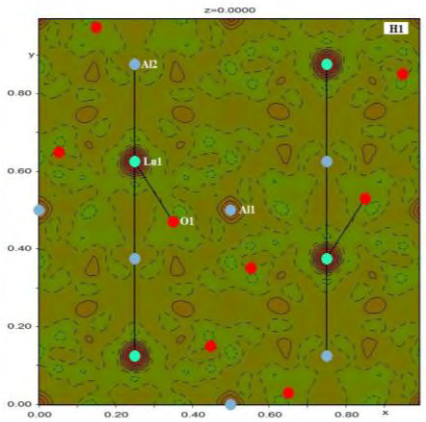
Name	Detector	Tilt step (deg)	Exposure time (ms)	Frames
H1	HPD	0.5	500	200
C1	CCD	0.5	1000	200
C2	CCD	0.5	2828	200

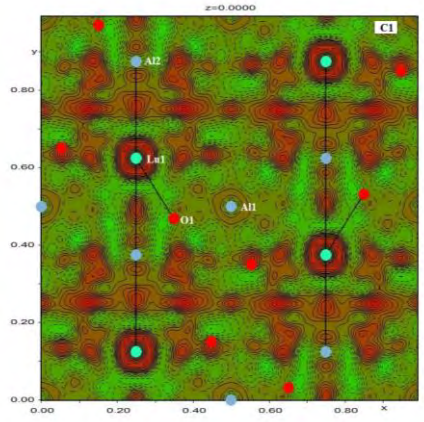


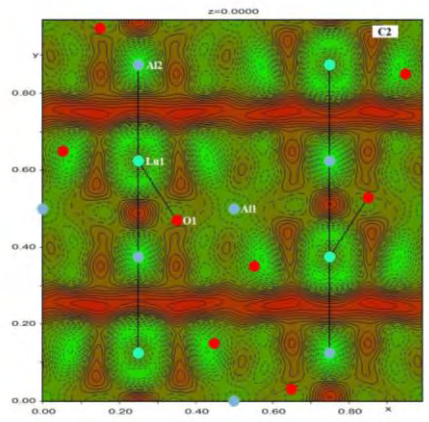
Structural parameters

CRYSTAL STRUCTURE	CUBIC
a=b=c	11.912 Å
$\alpha=\beta=\gamma$	90°
Space group	Ia-3d(space group 230)
RC width	0.0013(rec. Å)
Mosaicity	0.07(deg)









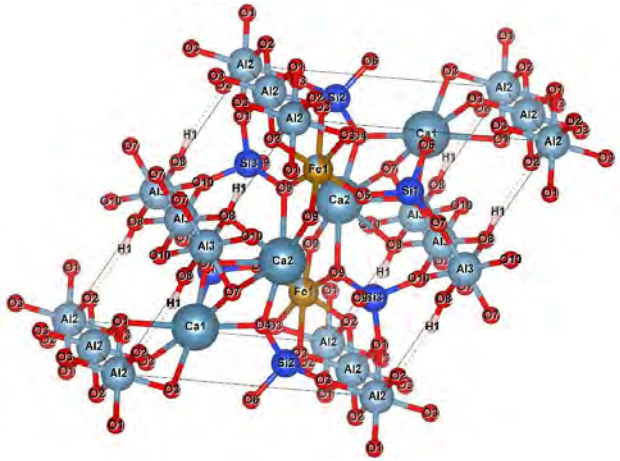
	Kinematical			Dynamical		
	H1	C1	C2	H1	C1	C2
N(obs)	310	231	310	6503	1827	6606
N(all)	310	310	310	6825	6817	6683
ref.parameters	8	8	8	66	66	66
GOF(obs)	31.43	10.45	44.33	3.58	2.3	6.28
GOF(all)	31.43	9.11	44.33	3.5	1.28	6.24
R(obs)	30.16	24.34	32.88	10.75	8.81	10.84
wR(obs)	40.64	25.71	46.49	12.02	8.87	12.8
R(all)	30.16	26.85	32.88	10.85	18.44	10.86
wR(all)	40.64	25.89	46.49	12.04	9.49	12.8

- Increasing the exposure time in C1 and making the reflections stronger in data set C2, R factors of C2 were almost found to be identical to H1.
- More noise in the difference Fourier maps of the data sets from the CCD detector when compared to the HPD
- Similar results could be obtained with the CCD detector as with HPD (provided the material is sufficiently stable in the beam to allow for long exposure times)
- Results show that HPD is better than CCD because it can obtain the same results in much less exposure time, it has much better signal to noise ratio, and more importantly better dynamic range (and thus less saturation).

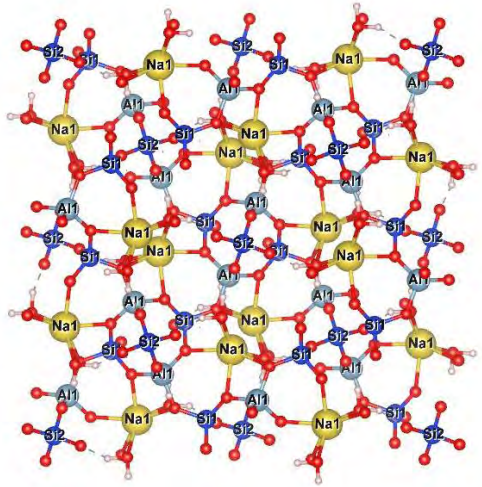
Round robin

Aim:

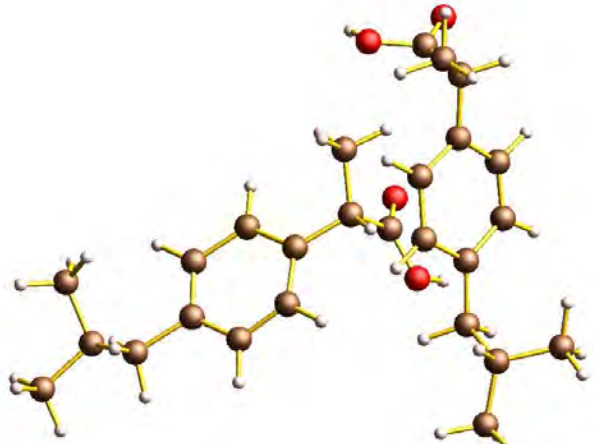
- To study and compare different data collection methods
- Perform Data processing and structure refinement of the 3 unknown samples
- Using ***thickmodel wedge command***, we have found a considerable change in the R-factors during the refinement



Epidote



Natrolite

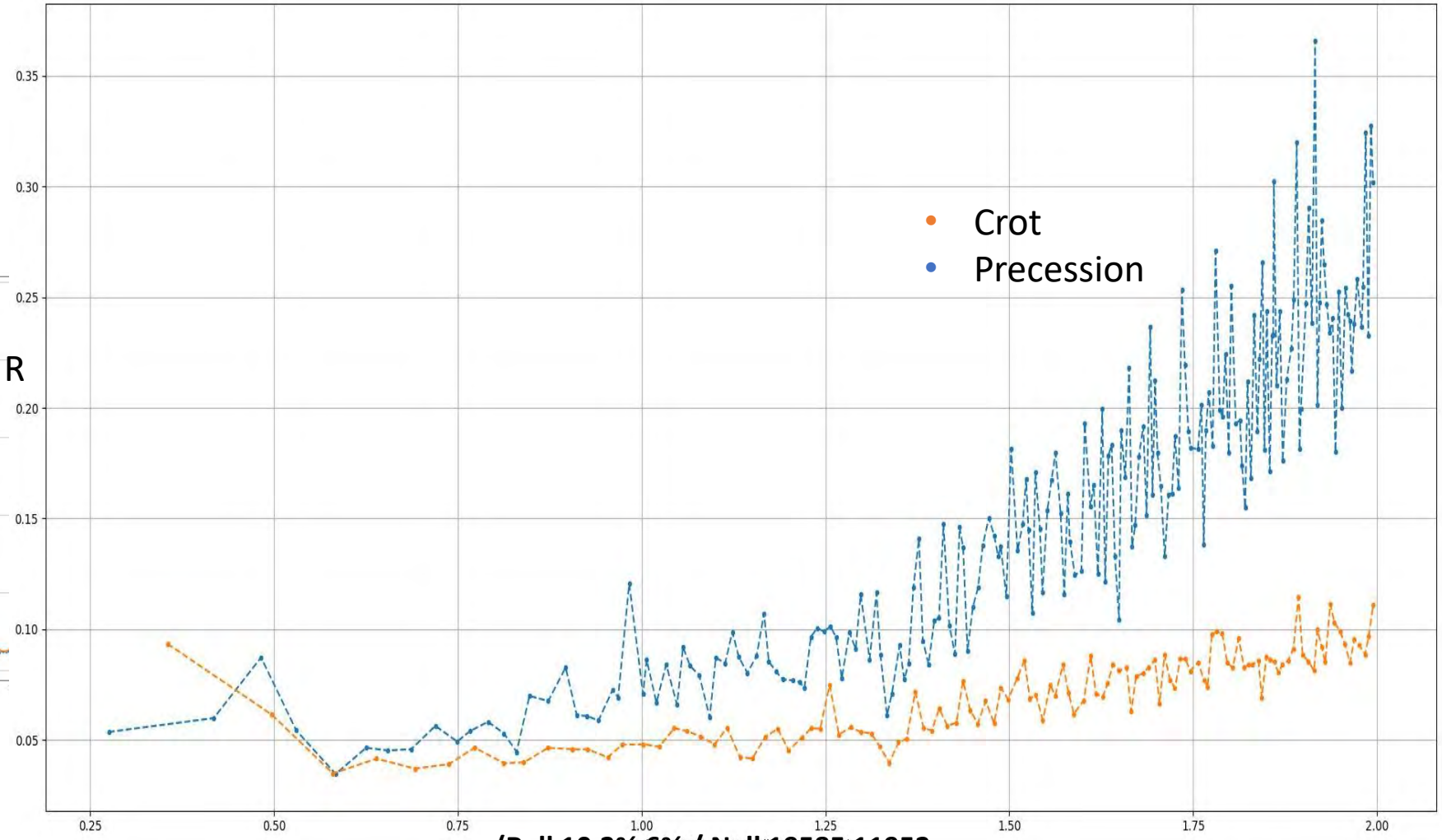


S-Ibuprofen

Comparison of the Data collection(Precession and Continuous rotation)

Natrolite-Crystal image

	Resolution 2 rec.Å	
	C.rot	**Prec**
Rsg	0.66	0.5
Dsg	0.0015	0
N(obs)	10852	7797
N(all)	11952	19585
refined parameters	152	214
GOF(obs)	2.73	1.68
GOF(all)	2.61	1.19
R(obs)	5.86	6.61
wR(obs)	6.99	6.99
R(all)	6.04	10.27
wR(all)	7.01	7.75
Thickness	846.746	755.602



Challenges faced during data collection of Ibuprofen

The sample was challenging, from the beginning of the data collection till its structure refinements. This allowed us to learn and employ different strategies and solutions to overcome the challenges.

Challenges faced	Strategies used
Repulsion of the crystals during data collection due to the charging of the grids	Used ionized grids and the data collection was done at a low temperature of -176^{o} C
Sublimation of the crystals in the vacuum	Cooling the crystals fast to prevent sublimation.
Smaller crystals dying and not diffracting over time	Used bigger crystals and low doses for data acquisition.
Low completeness of data collected	Collected data from a large number of crystals, found crystals which complemented each other and merged the datasets in PETS2.
Inability to solve the structure	The merged data set (with good completeness) was used to solve the structure
Determination of the absolute structure	A comparison in the R-factors between two enantiomorphs was performed using the results of the dynamical refinements in Jana 2020

Determination of the absolute structure

Merging the data sets in PETS2

Kinematical Refinement

	Enantiomorph-1	Enantiomorph-2
N(obs)	1458	1458
N(all)	2224	2224
Refined parameters	121	121
GOF(obs)	2.58	2.58
GOF(all)	2.26	2.26
R(obs)	19.66	19.66
wR(obs)	25.60	25.61
R(all)	23.85	23.86
wR(all)	26.98	26.99

Refined the processed datasets in individual blocks in JANA2020

Dynamical Refinement

	Enantiomorph-1	Enantiomorph-2
Rsg	0.66	0.66
Dsg	0.0015	0.0015
N(obs)	2699	2669
N(all)	5689	5689
refined parameters	246	246
GOF(obs)	2.45	2.73
GOF(all)	1.86	2.05
R(obs)	10.6	11.87
wR(obs)	10.76	12.02
R(all)	16.70	18.10
wR(all)	12.05	13.33

Frame scaling

Aim: Correct determination of frame scales in presence of appreciable dynamical effect

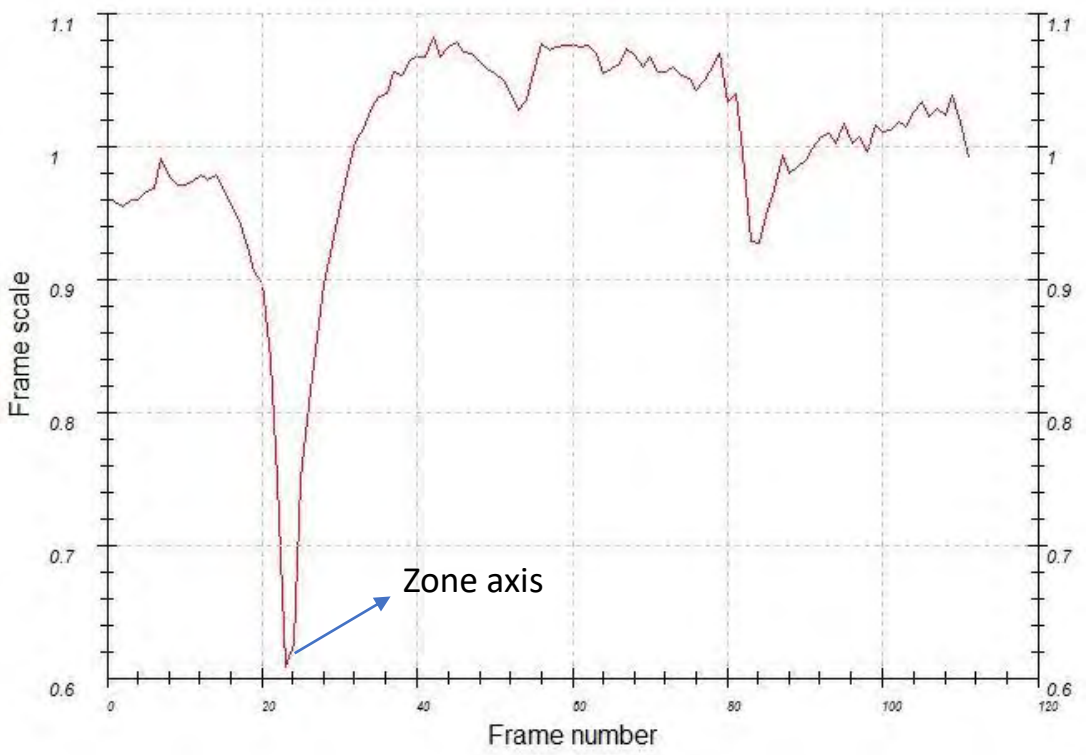
- Intensities obtained from integration of the diffraction images must be corrected for experimental effects in order to place all intensities on a common scale

$$F_i = \sum_{all} \sum_{1} (I_m - S_i I_f)^2$$

The best least-squares estimate is derived from the data by minimizing F with respect to S

$$\frac{\sum Si}{N} = 1$$

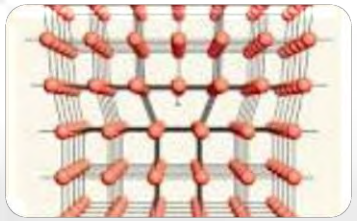
Where i-Frame, N –Total number of frames



CONCLUSION

- HPD is better than CCD because it can obtain the same results in much less exposure time, it has much better signal to noise ratio, and more importantly better dynamic range (and thus less saturation).
- Precession data collection has weaker Intensities compared to Continuous rotation
- Although the sample 3 of Roundrobin presented some challenges, the strategies employed helped to collect adequate data for structure solution, good refinements and absolute structure determination
- Dynamical refinement helps in absolute structure determination
- Frame scaling is challenging but solvable

Upcoming goals:



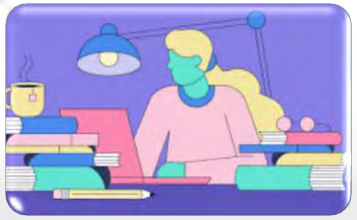
Analysis of effects of crystal imperfections on the quality of dynamical refinement by analyzing with simulated data

CHARLES UNIVERSITY

PhD studies at Charles University

Secondments

- **CNRS**: 3D ED on thin films **Supervisor:** P. Boullay
- **UA**: in situ 3D ED **Supervisor:** J. Hadermann
- **EST:** Synchrotron powder x-ray diffraction. **Supervisor:** J. Plaisier
- **BASF:** Electron diffraction on pharmaceutical **Supervisor:** P. Müller



Results Dissemination.

THANK YOU