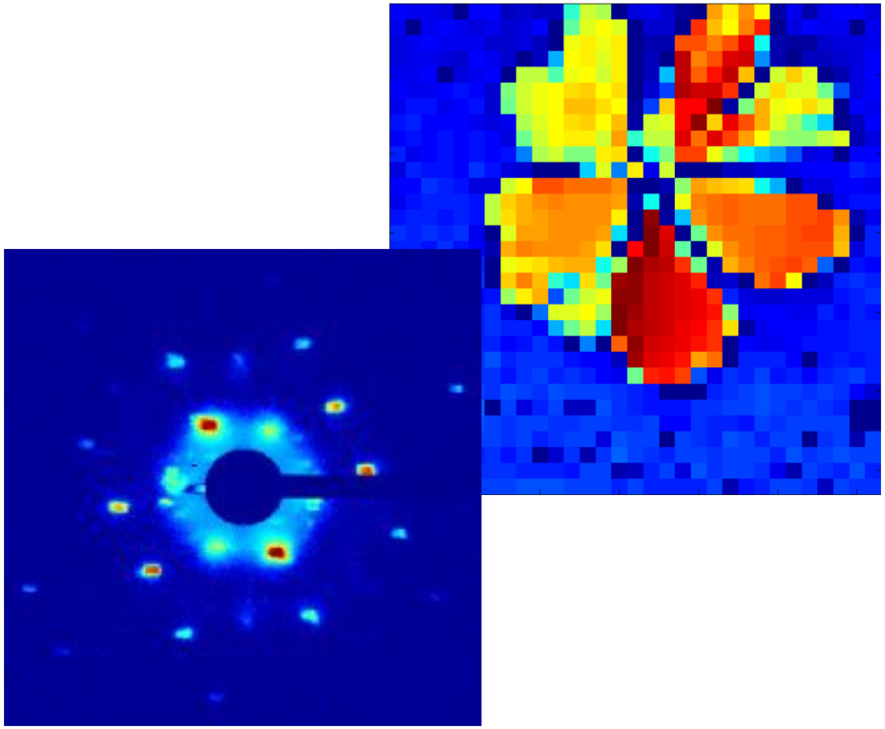
X-ray cross-correlation analysis of mesocrystals



Sample “Flower”

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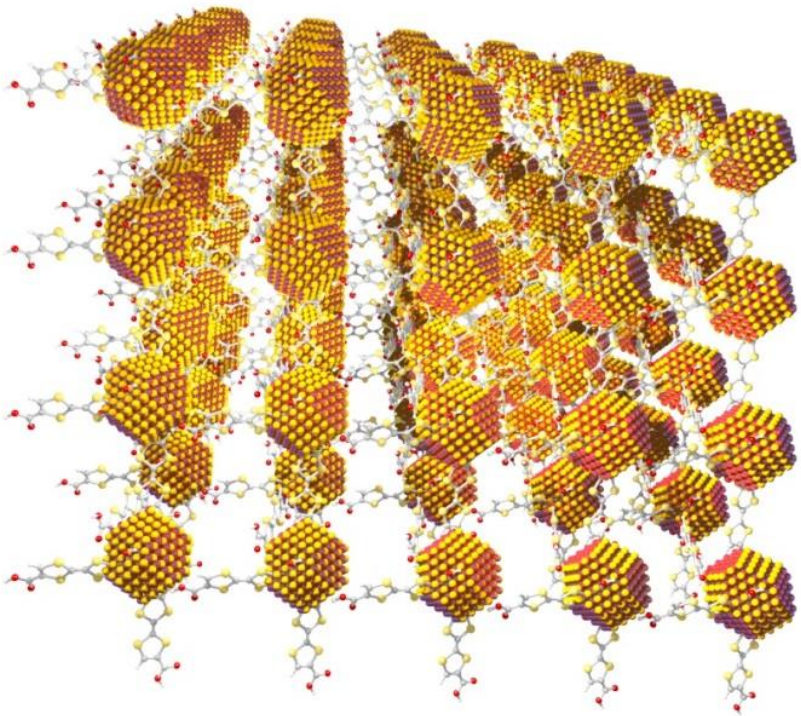
Summer Student

Supervised by Nastasia Mukharamova,
Ivan Vartaniants

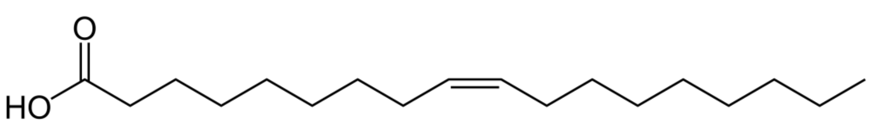
HELMHOLTZ ASSOCIATION

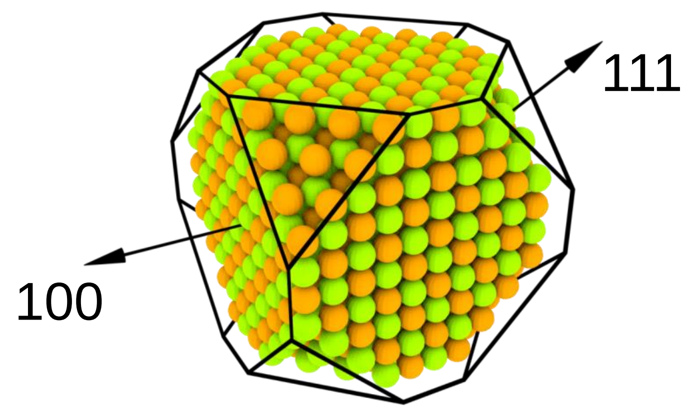
DESY

COINS: Coupled organic-inorganic nanostructures



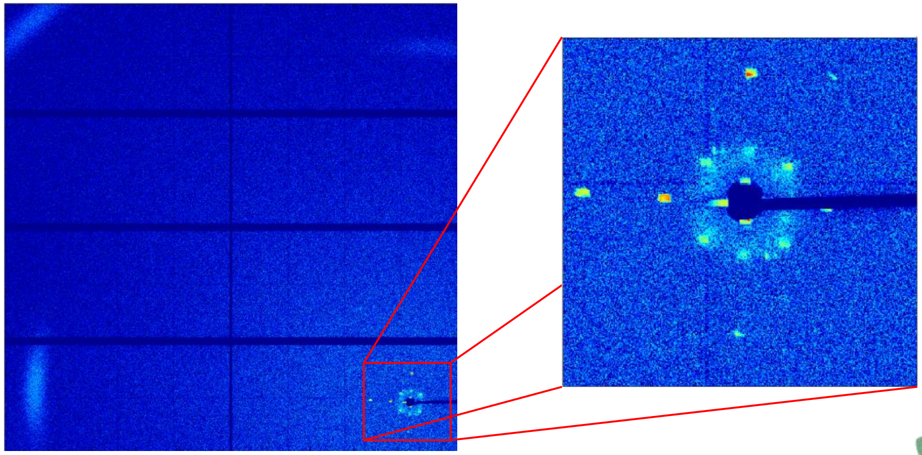
Coupled organic-inorganic nanostructures (COIN) provide a new approach to applications of semiconductor nanocrystals (NC) for power conversion. A typical COIN consists of periodically alternating NCs and organic semiconductor molecules, promoting carrier transport across the lattice.

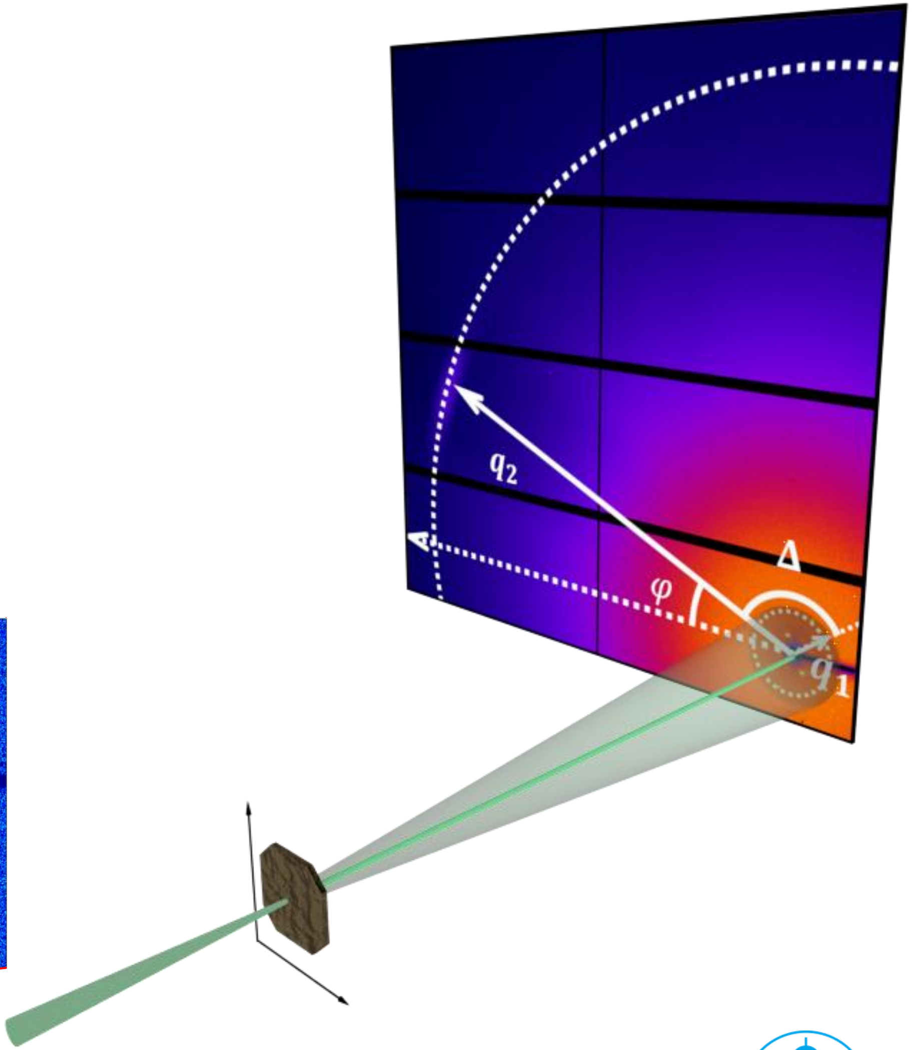




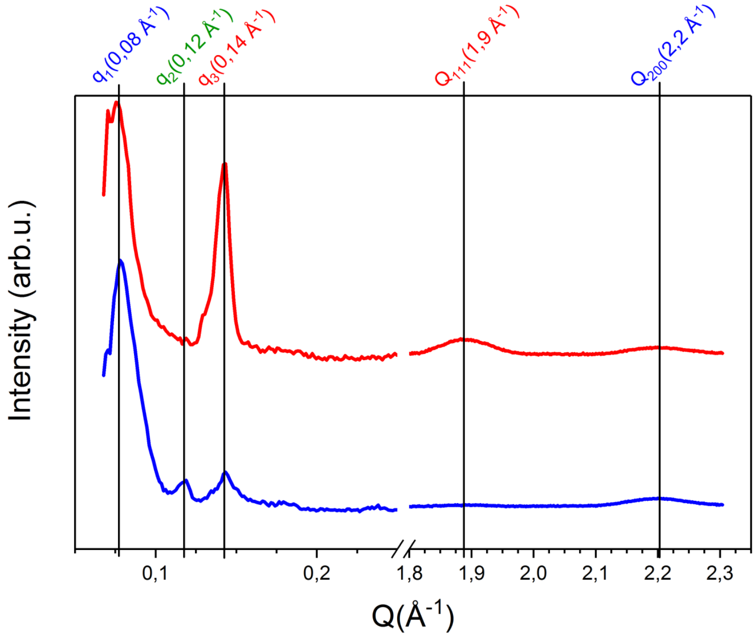
Experiment (P10 beamline, PETRA III)

- **Substrate:** Si_3N_4-membrane, 0.5x0.5 mm^2, 50 nm thick
- **X-ray beam:**
  E = 13.8 keV
  Size = 400x400 nm^2
  Flux = 10^{10}-10^{11} ph/sec
- **Spatial scanning:** 31x31 points with 1 μm resolution.





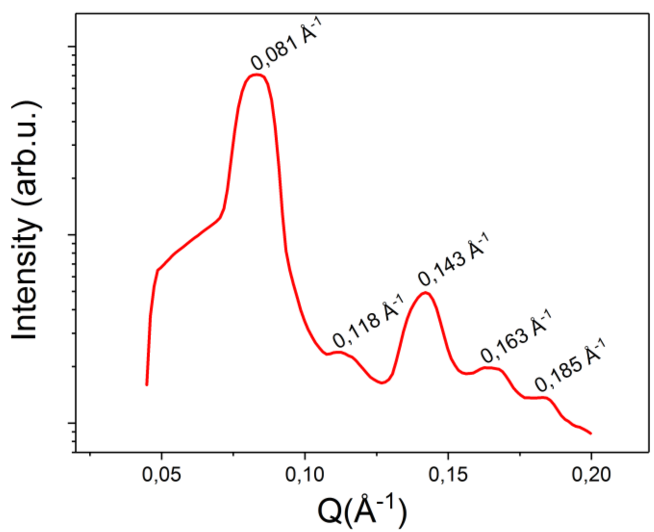
Superlattice structure

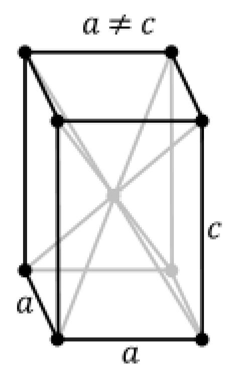


q_{exp}, $Å^{-1}$	h	k	l	$q_{predict}$, $Å^{-1}$	h+k+l
0,081	1	1	0	0,081	2
0,118	2	0	0	0,114	2
0,143	1	0	3	0,145	4
0,163	2	2	0	0,162	4
0,185	1	2	3	0,184	6

h+k+l are even -> body-centered

Radial average (log scale)

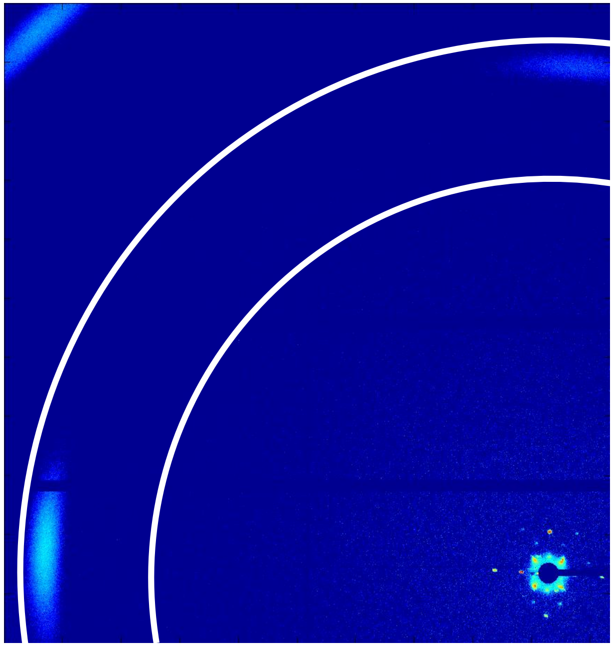




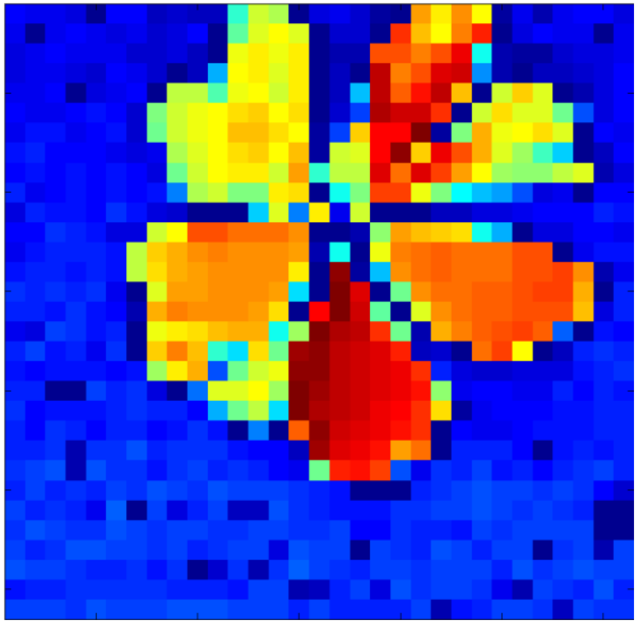
bct lattice with
a = 110 Å
c = 142 Å
c/a= 129 %

NC size ~ 70 Å

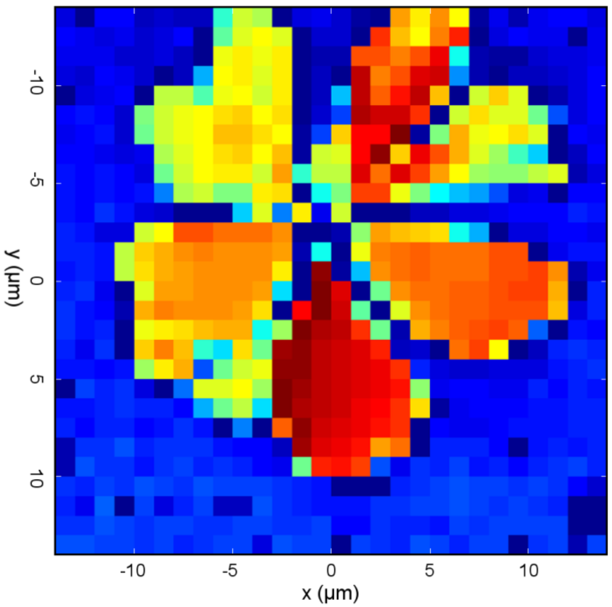
Sample-containing regions

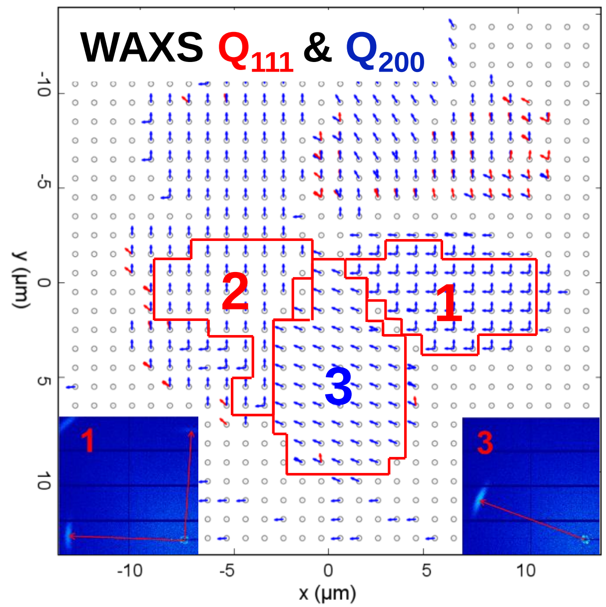


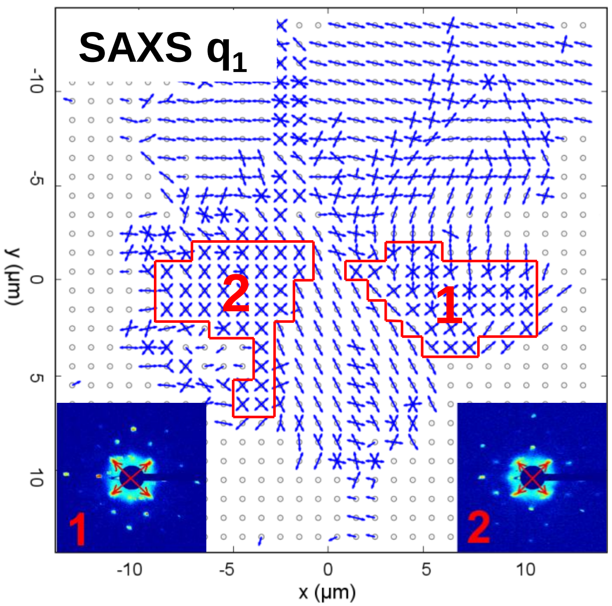
Integrate intensity in WAXS region ($|q| = 1,8 – 2,3$ Å^{-1})

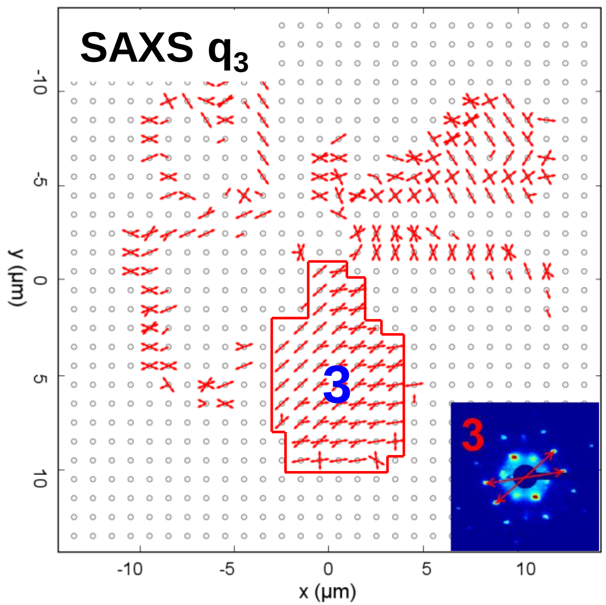


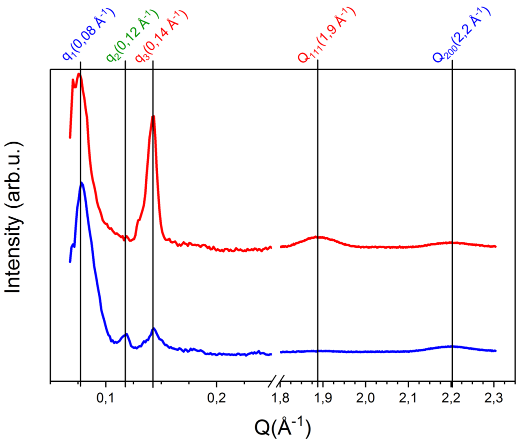
Spatial resolved maps





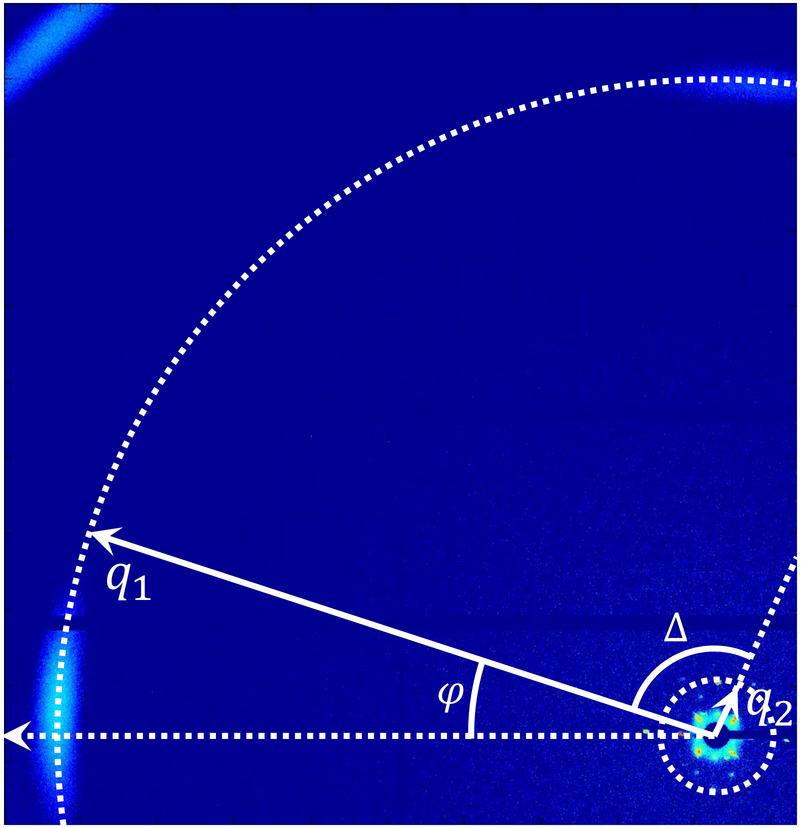






DESY

Cross-Correlation Analysis



CCF calculation

$$C(q_1,q_2,\Delta)=\frac{1}{2\pi}\int_{-\pi}^{\pi} I(q_1,\varphi)I(q_2,\varphi+\Delta)d\varphi$$

$$=\frac{\int_{-\pi}^{\pi} I(q_1,\varphi)W(q_1,\varphi)I(q_2,\varphi+\Delta)W(q_2,\varphi+\Delta)d\varphi}{\int_{-\pi}^{\pi} W(q_1,\varphi)W(q_2,\varphi+\Delta)d\varphi}.$$

Mask

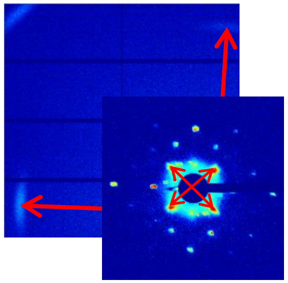
$$W(q,\varphi)=\begin{cases}0, & \text{gaps, beamstop, detector edges}\\ 1, & \text{otherwise}\end{cases}$$

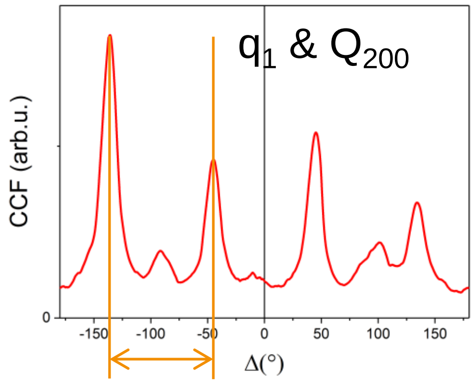
Averaging

$$\langle C(q_1,q_2,\Delta)\rangle_M=\frac{1}{M}\sum_{i=1}^{M} C^i(q_1,q_2,\Delta)$$

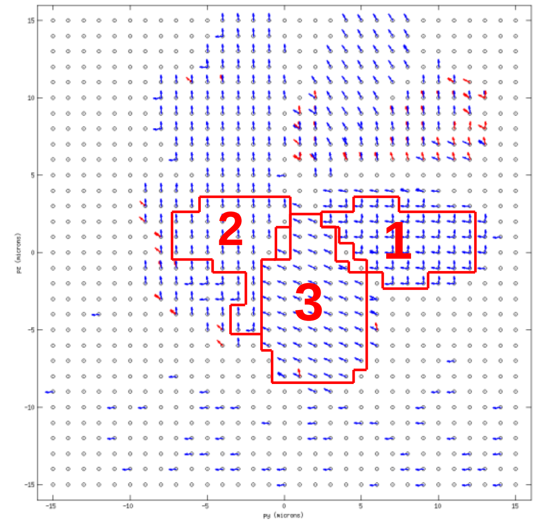
Cross-Correlation Analysis

Region 1

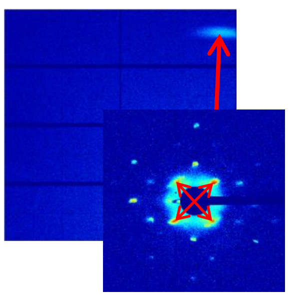


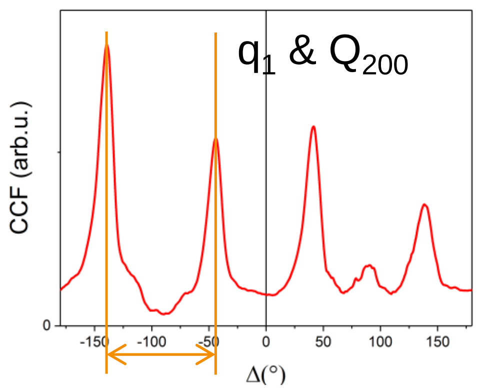


90º - no distortion!



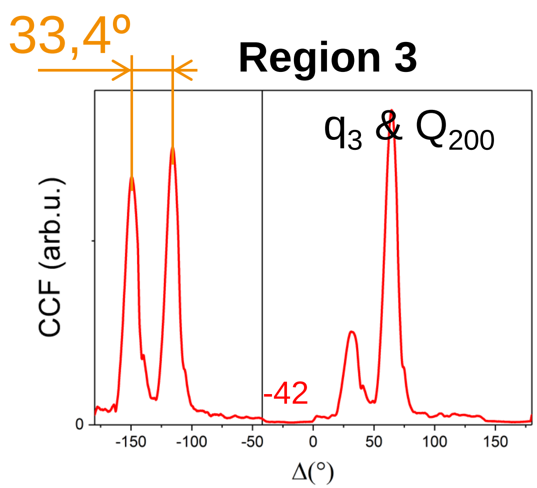
Region 2

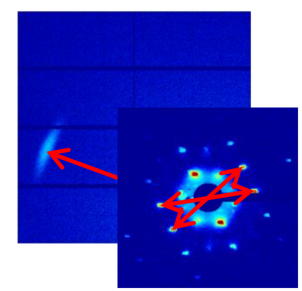




89º - no distortion!

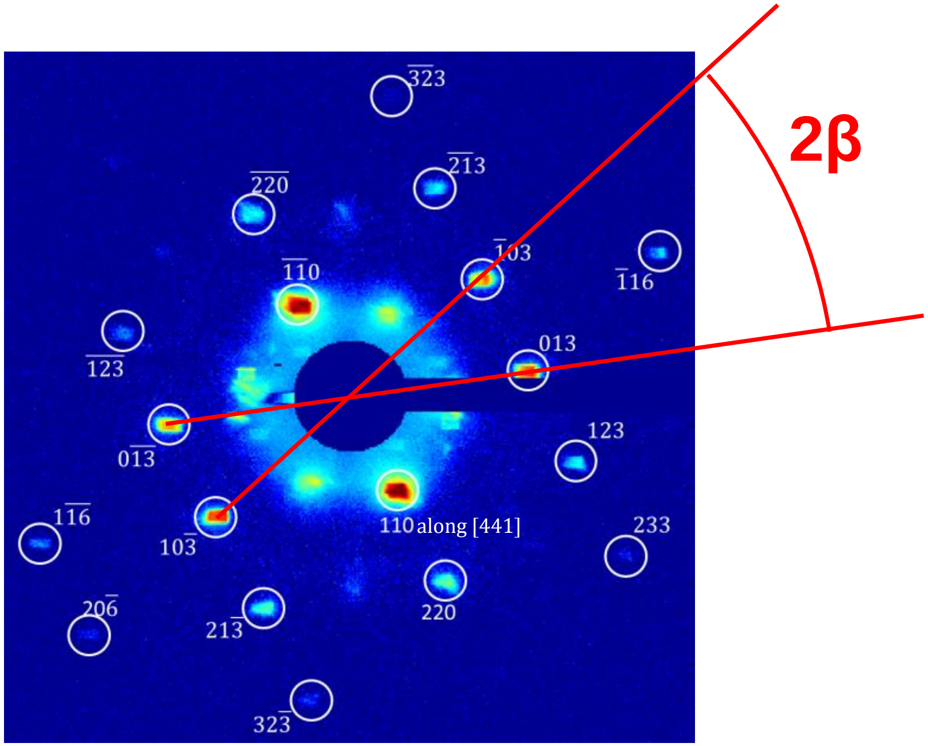
Region 3





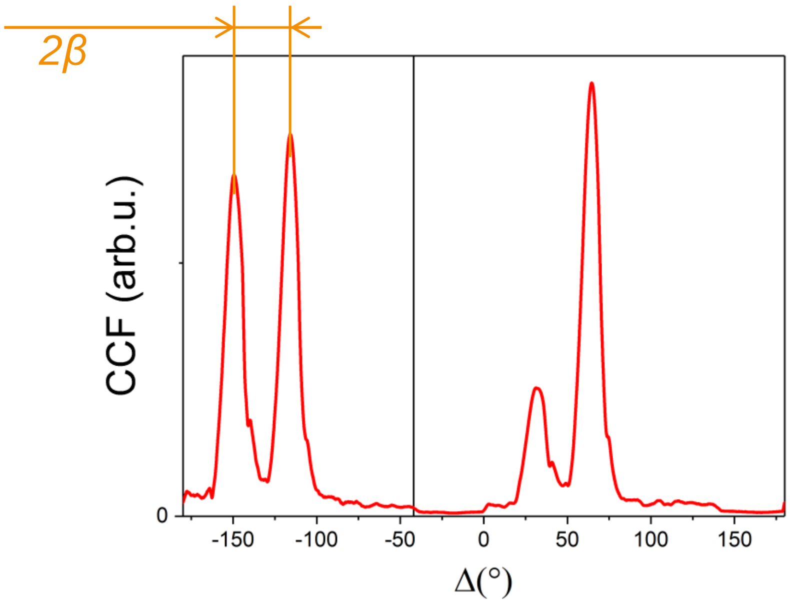
DESY

Superlattice structure



SAXS:
bct lattice with
$a = 110$ Å
$c = 142$ Å
$$\frac{c}{a} = 129\%$$

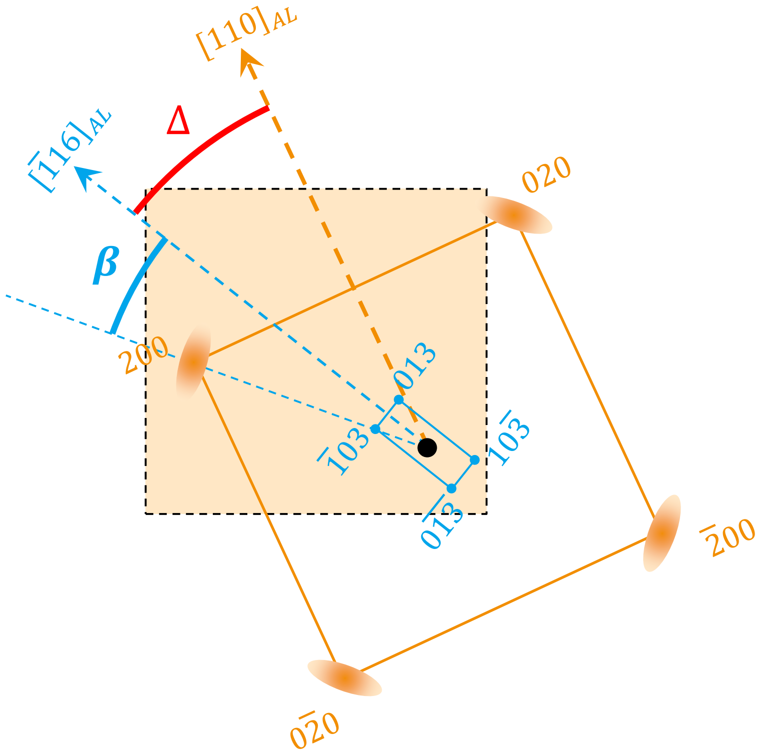
$$\frac{a}{c} = 3\sqrt{\frac{1}{\cos^2 2\beta} - 1}$$



From the XCCA data: $2\beta = 33{,}4°$

$$\frac{c}{a} = 133\%$$

CCF simulation



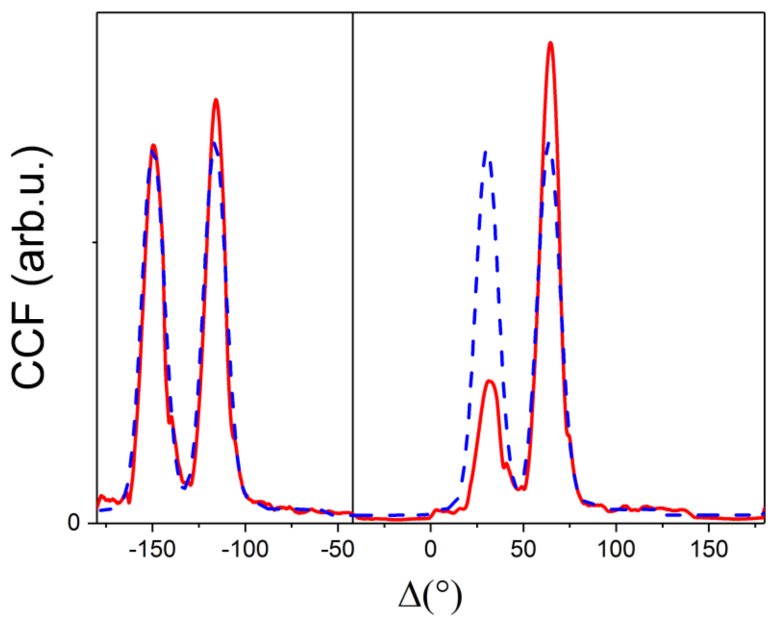
$\mathrm{tg}(\beta = 16.7°) = 0.3$

Distortion value $\frac{c}{a} = 133\%$ obtained by XCCA was approved

SAXS/WAXS peaks:

$$I_{\frac{SAXS}{WAXS}}(\varphi) = A_{\frac{SAXS}{WAXS}} \cdot \exp\left(-\frac{\left(\varphi - \varphi^{i}_{\frac{SAXS}{WAXS}}\right)^2}{2\sigma^2_{\frac{SAXS}{WAXS}}}\right)$$

$$\boxed{CCF_{sim}(\Delta) = \int_{-\pi}^{\pi} I_{SAXS}(\varphi) I_{WAXS}(\varphi + \Delta) W(\varphi + \Delta)\, d\varphi}$$



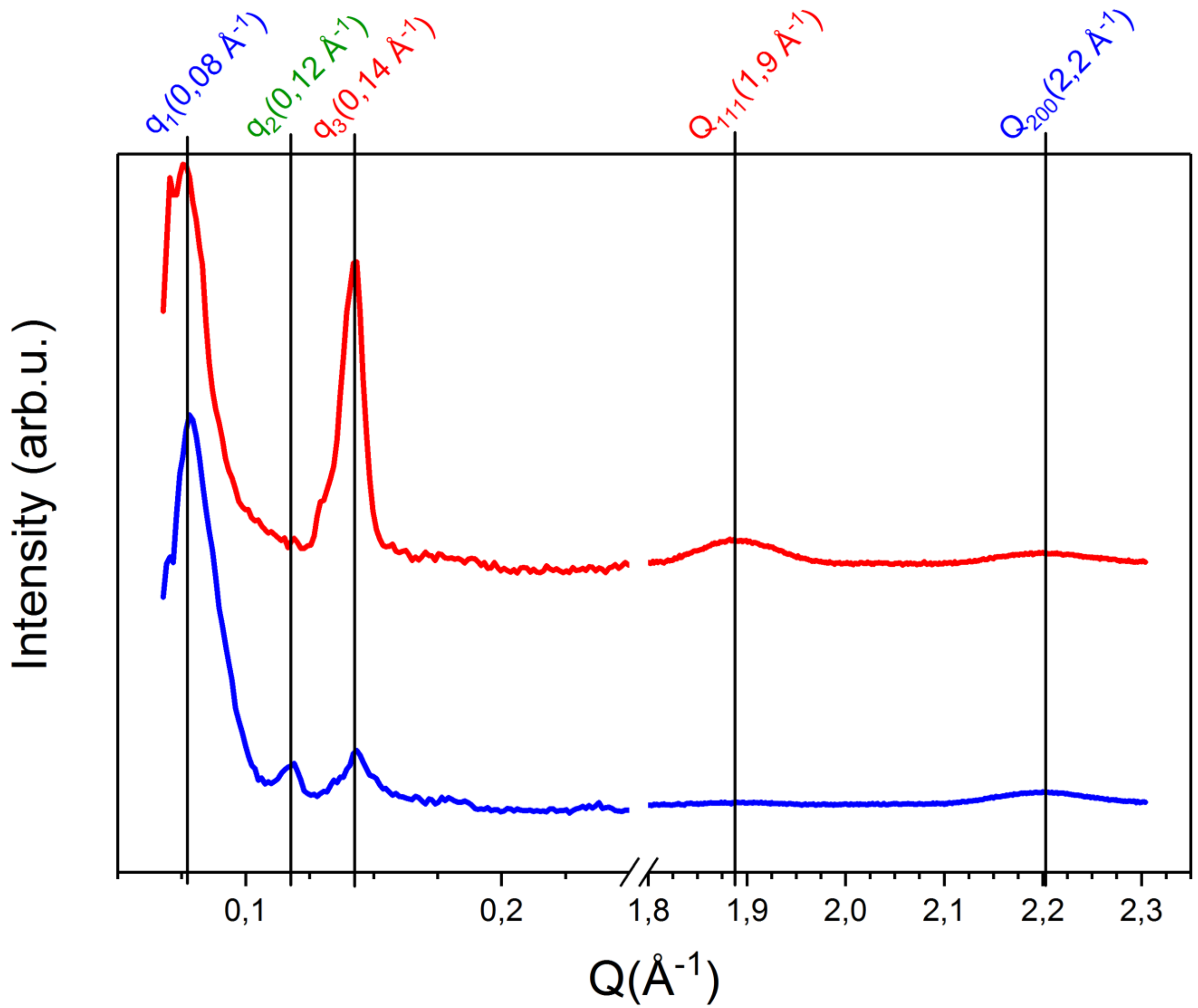
Conclusions

- Experimental data on the COIN samples (PbS-OA) was processed.
- Domains with different crystalline structure were defined from the diffraction map and the spatial-resolved peak positions map.
- Each domain was studied by the X-ray Cross-Correlation Analysis
- Unit cell parameters was evaluated from the radial average intensity and from the XCCA analysis.
- Obtained results are in good agreement:
  - bct lattice with a=b=110 Å, c = 142 Å and tetragonal distortion c/a=1.29 from RA
  - tetragonal lattice with distortion c/a=1.33 from XCCA

Thank you for your attention!

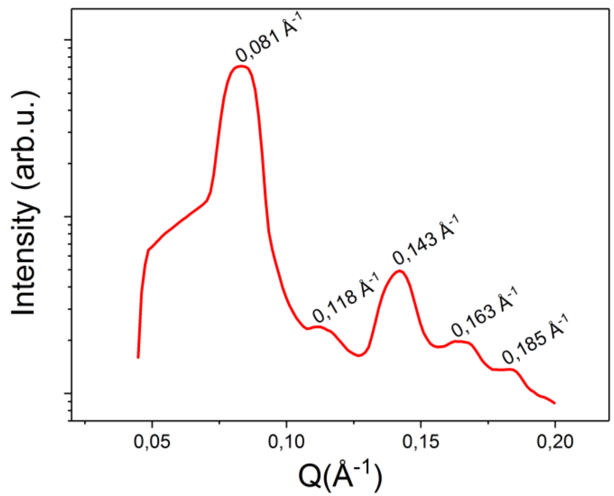
Special thanks to my supervisors and
the whole Coherent X-Ray Scattering and Imaging Group

Radial average



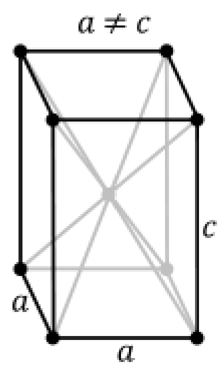
Superlattice structure

Radial average (log scale)



q_{exp}, Å^{-1}		h	k	l		$q_{predict}$, Å^{-1}	h+k+l
0,081		1	1	0		0,081	2
0,118		2	0	0		0,114	2
0,143		1	0	3		0,145	4
0,163		2	2	0		0,162	4
0,185		1	2	3		0,184	6

h+k+l are even -> body-centered



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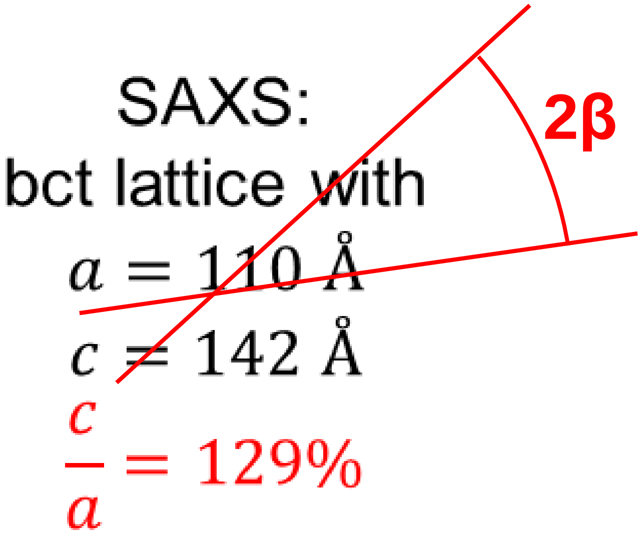


Gramian matrix for the reciprocal space

$$G = 2\pi \begin{pmatrix} \frac{1}{a^2} & 0 & 0 \\ 0 & \frac{1}{a^2} & 0 \\ 0 & 0 & \frac{1}{c^2} \end{pmatrix}$$

For angle 2β between 013 and $\bar{1}03$ reflections

$$\cos 2\beta = \frac{u^T G v}{\sqrt{u^T G u}\sqrt{v^T G v}},$$

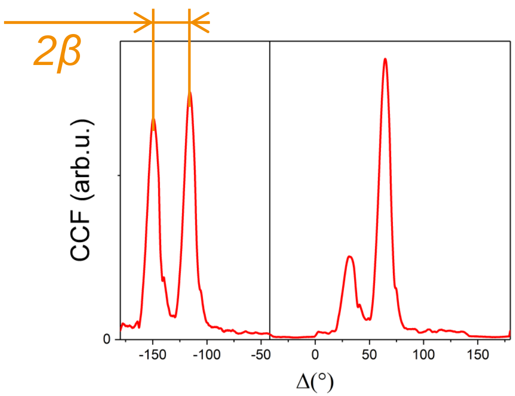
where $u^T = (0 \quad 1 \quad 3)$ and $v^T = (-1 \quad 0 \quad 3)$.

SAXS:
bct lattice with
$a = 110$ Å
$c = 142$ Å
$\frac{c}{a} = 129\%$

Thus, $\boxed{\frac{c}{a} = 3\sqrt{\frac{1}{\cos^2 2\beta} - 1}}$

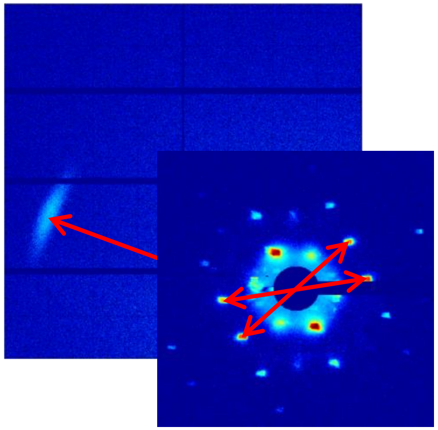
From the XCCA data: $2\beta = 33{,}4°$

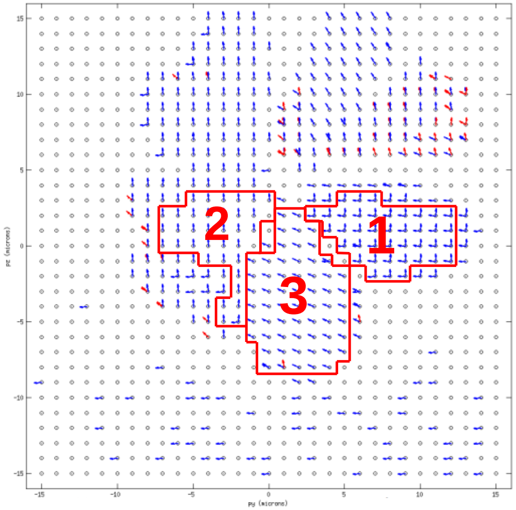
and $\frac{c}{a} = 133\%$

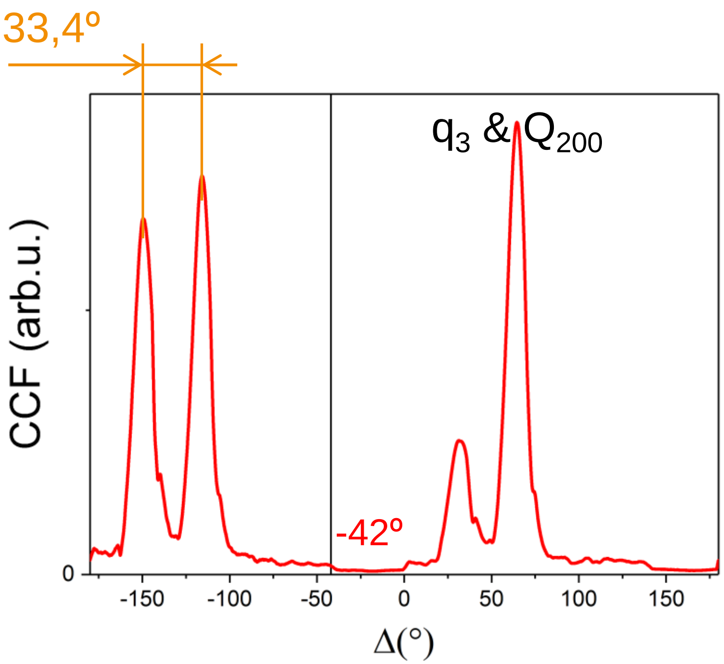


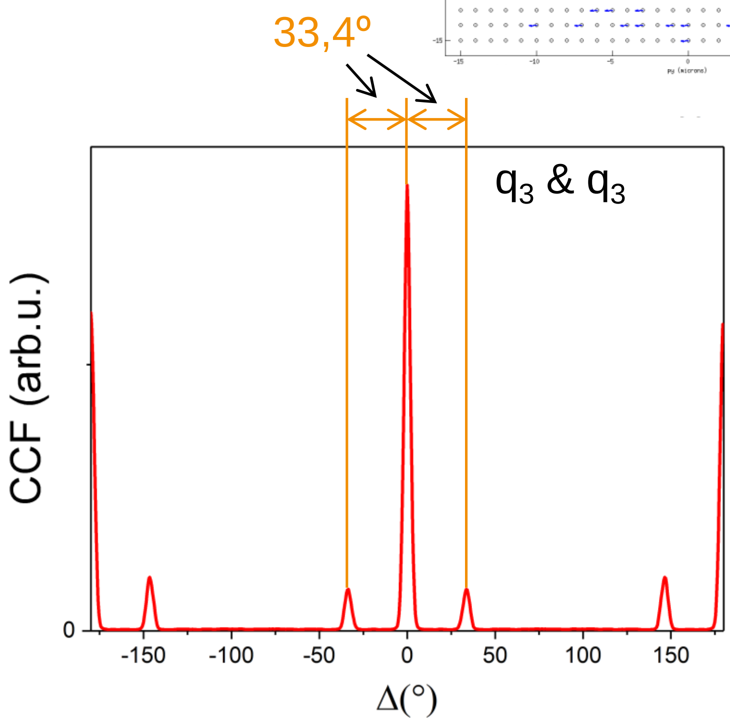
Cross-Correlation Analysis

Domain 3

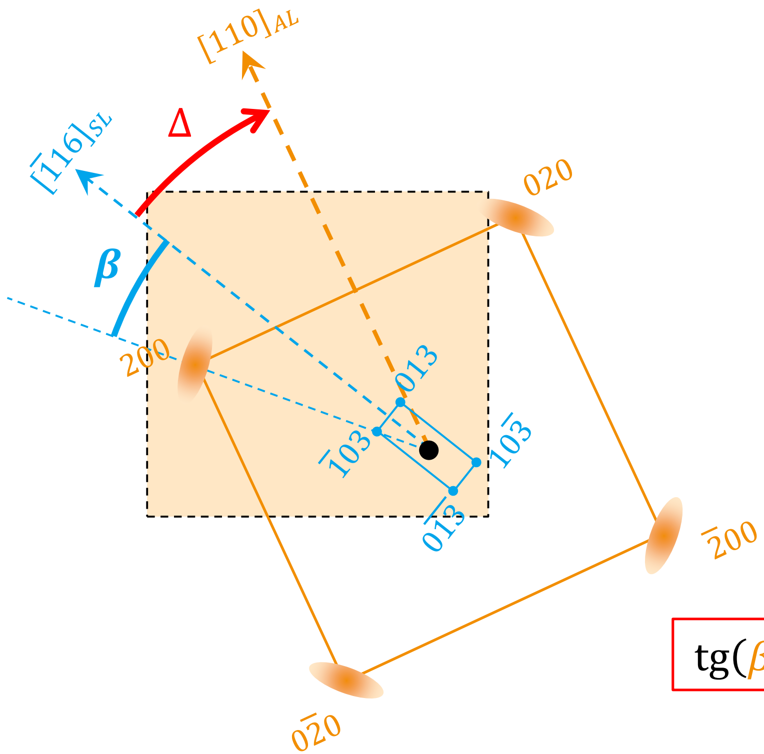








CCF simulation



SAXS/WAXS peaks:

$$I_{\frac{SAXS}{WAXS}}(\varphi) = A_{\frac{SAXS}{WAXS}} \cdot \exp\left(-\frac{\left(\varphi - \varphi^{i}_{\frac{SAXS}{WAXS}}\right)^2}{2\sigma^2_{\frac{SAXS}{WAXS}}}\right)$$

$A_{SAXS} = 50$	$A_{WAXS} = 20$
$\sigma_{SAXS} = 0.03\ (1.72°)$	$\sigma_{WAXS} = 0.1\ (5.72°)$
φ^{i}_{SAXS}: $\pm \operatorname{atan}(0.3)$, $\pi \pm \operatorname{atan}(0.3)$	φ^{i}_{WAXS}: $\pm\frac{\pi}{4}$, $\pi \pm \frac{\pi}{4}$

$$\boxed{\operatorname{tg}(\beta = 16.7°) = 0.3}$$

Mask: $W(\varphi) = \begin{cases} 1, \frac{\pi}{12} < \varphi < \frac{2\pi}{3} \\ 0, otherwise \end{cases}$

$$\boxed{CCF_{sim}(\Delta) = \int_{-\pi}^{\pi} I_{SAXS}(\varphi) I_{WAXS}(\varphi + \Delta) W(\varphi + \Delta)\, d\varphi}$$