Self-assembly of anisotropic colloids: microradian x-ray diffraction

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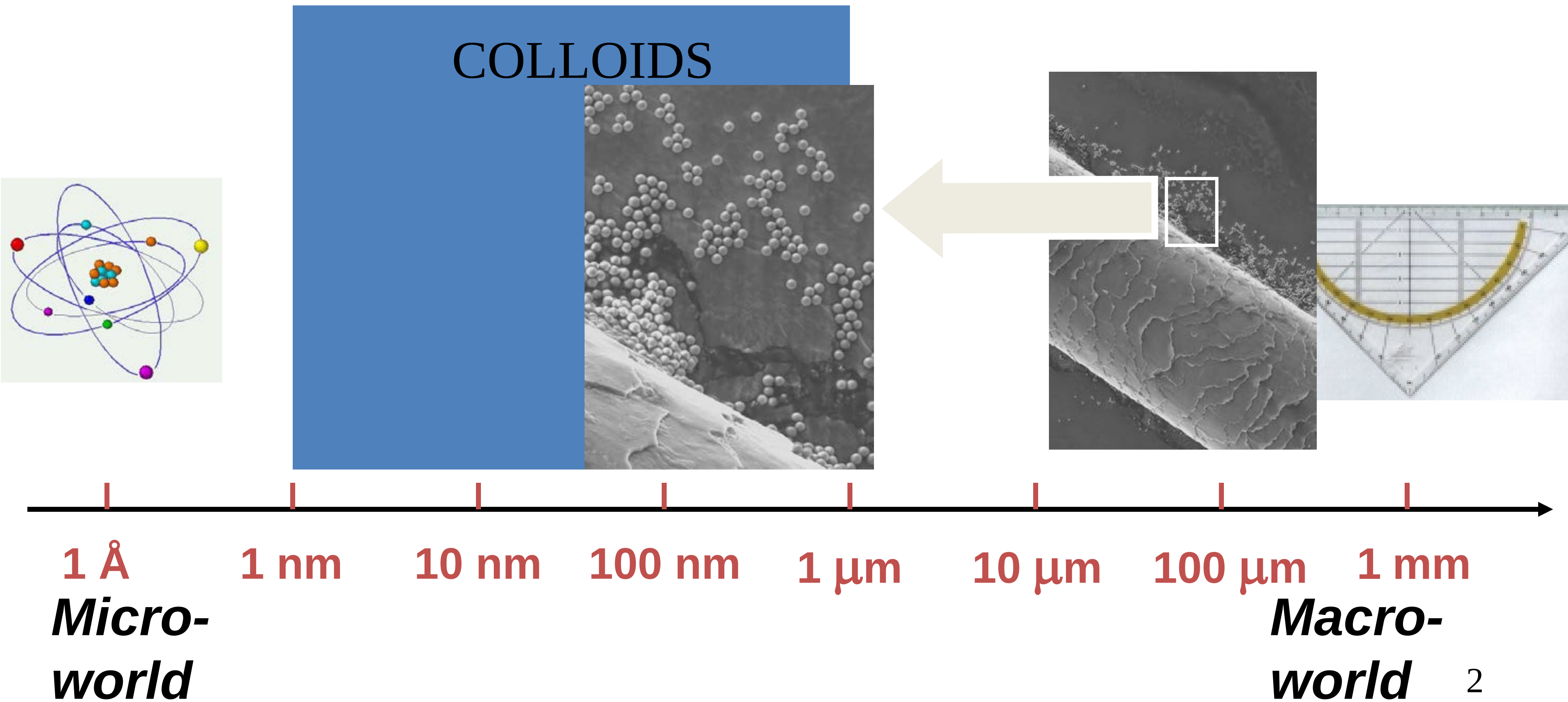
DUBBLE

What is colloid?

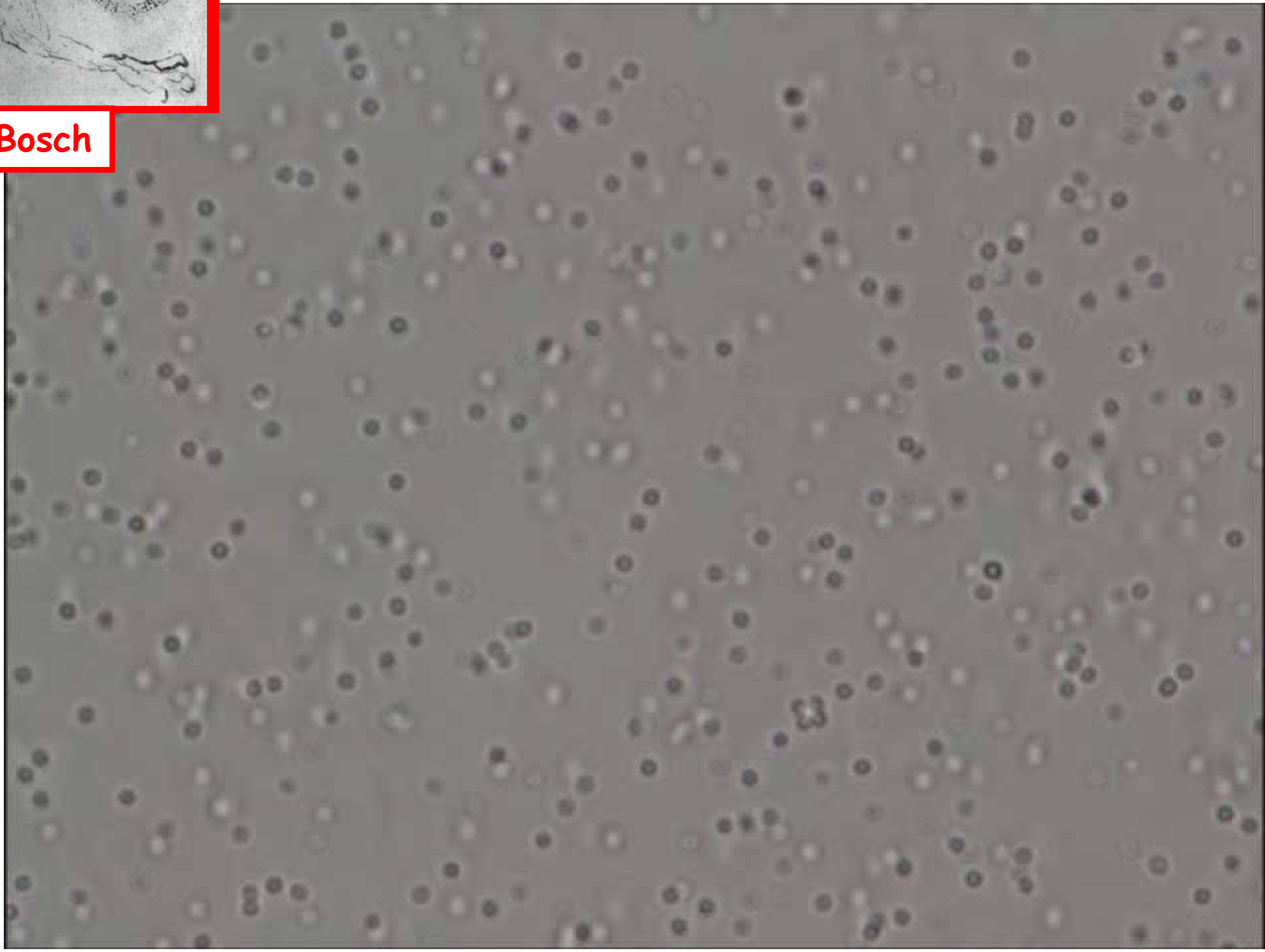
International Union of Pure and Applied Chemistry

"The term colloidal refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm."



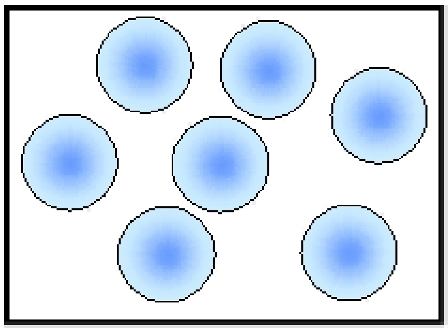
Colloids = Brownian movers

Hieronymus Bosch

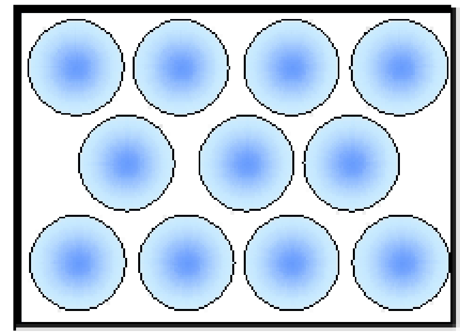


700 nm cubes in EtOH
2x real time

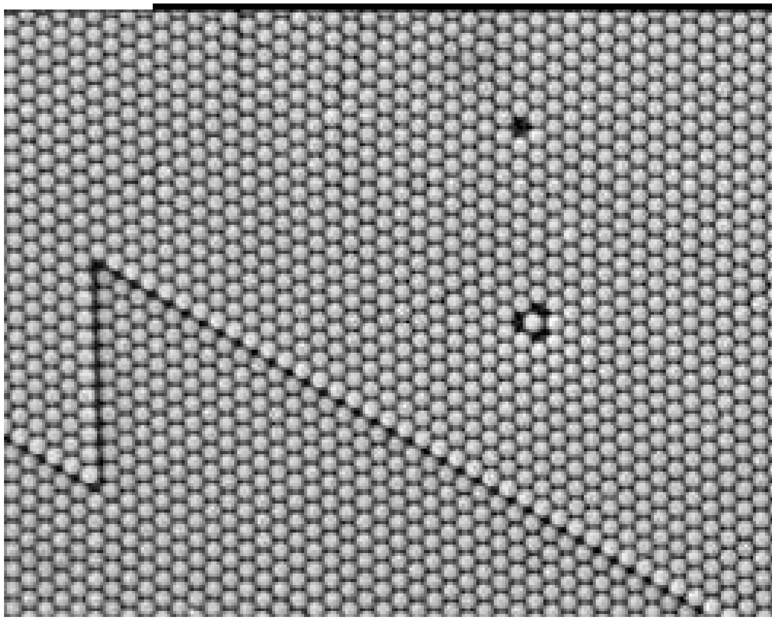
Colloid self-assembly:
Entropy-induced order



fluid

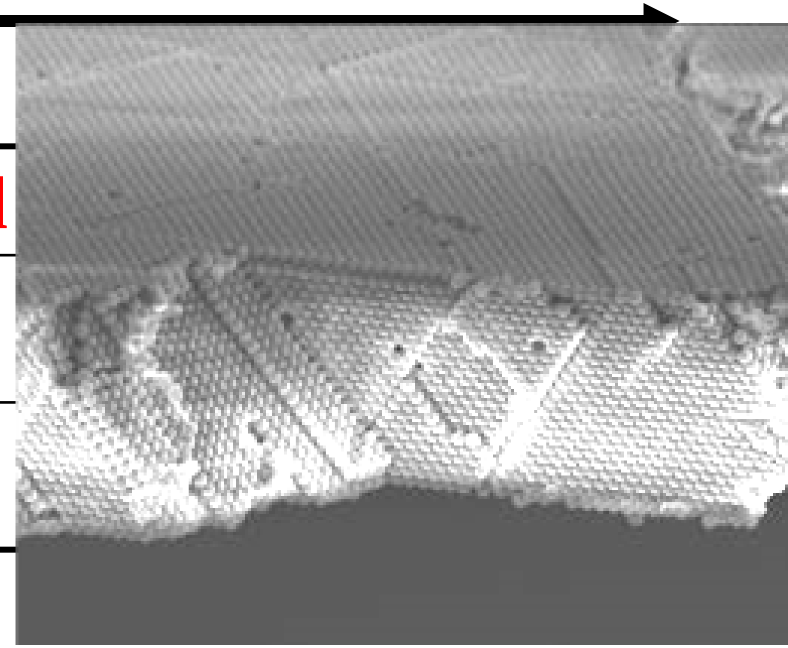


crystal

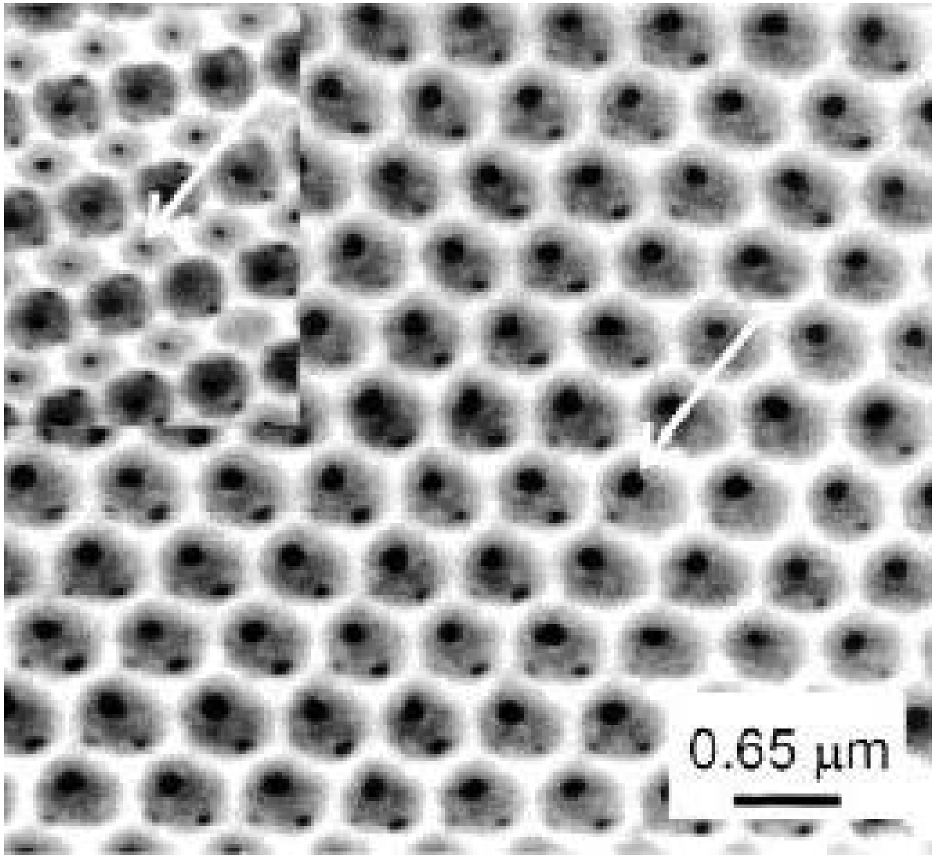


ncentration

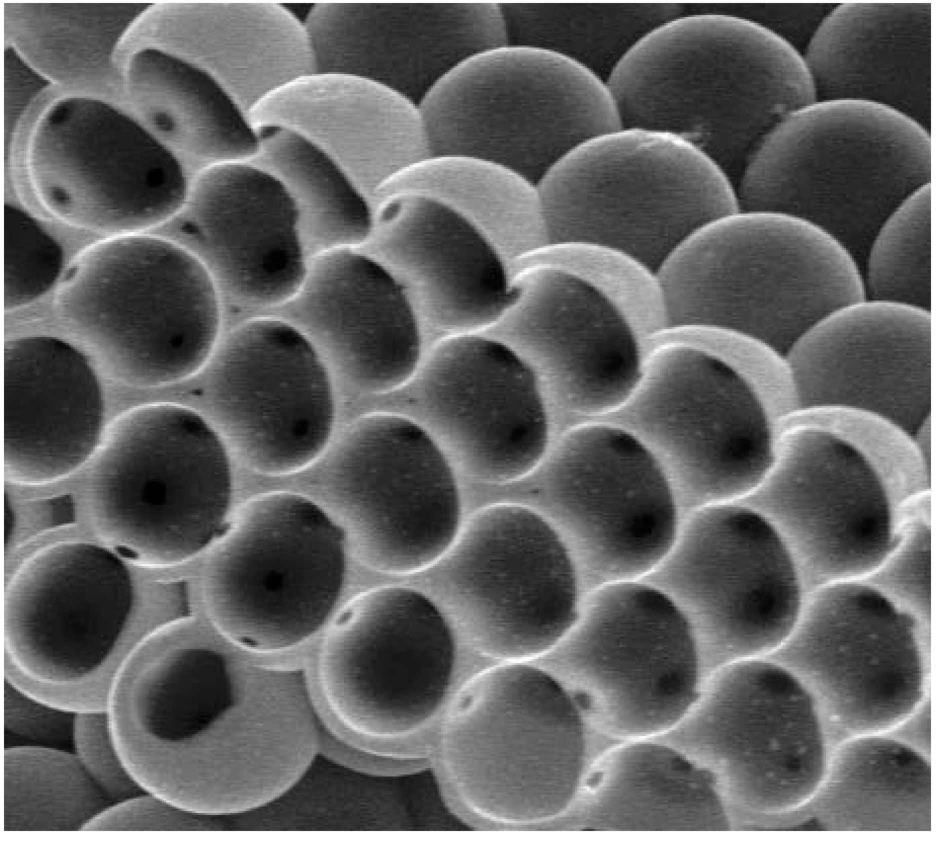
	Fluid
	high
e	low



Photonic materials



Wijnhoven & Vos

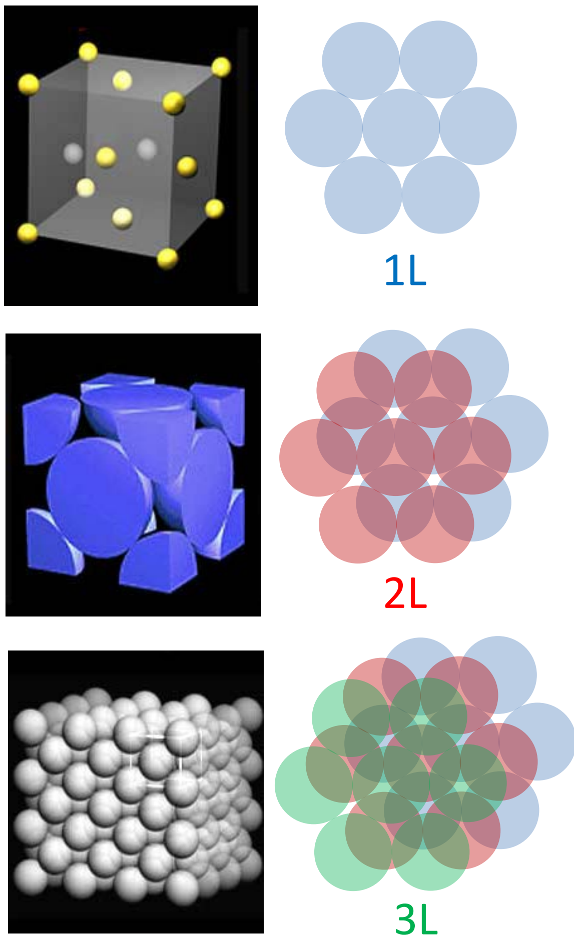


’t Hart & van Blaaderen

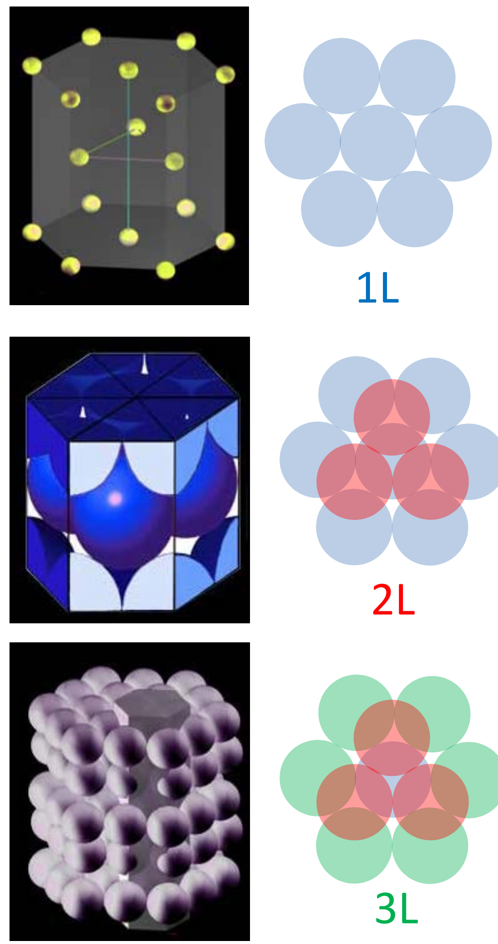
Using colloidal approach

Most studied shape of colloid is ***sphere***

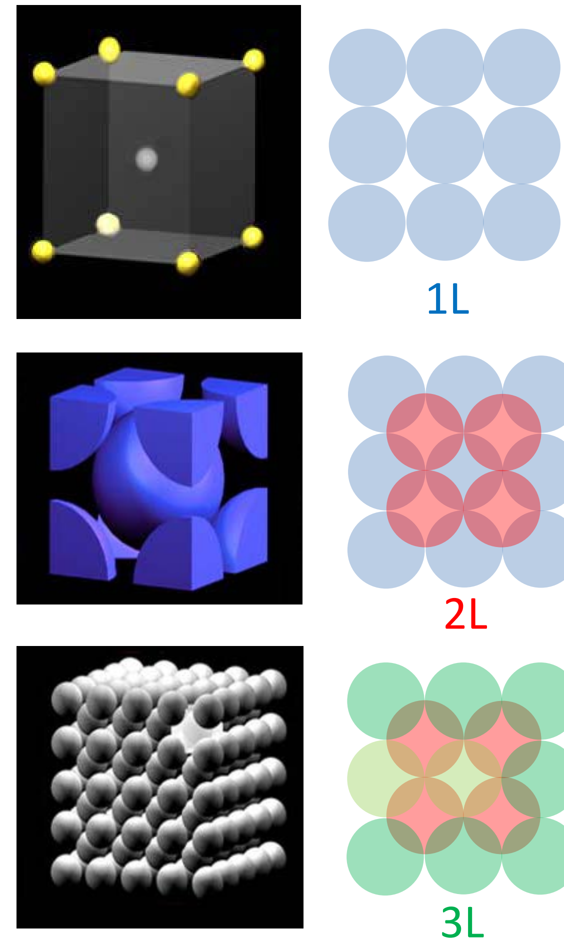
- Face Centred Cubic (FCC)



- Hexagonal Close Packed (HCP)



- Body Centred Cubic (BCC)

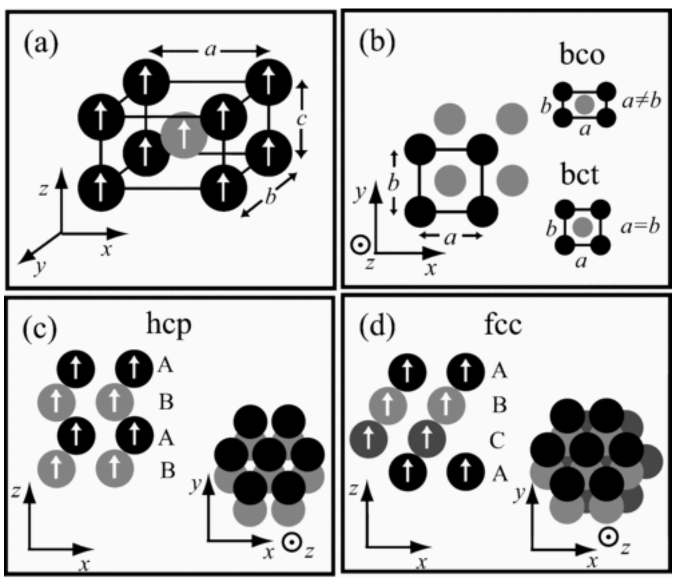


- **Random Hexagonal Close-Packed (RHCP) is often observed**

W.B Russel, Nature, 421, 490, 2003.

New architectures with other symmetries?

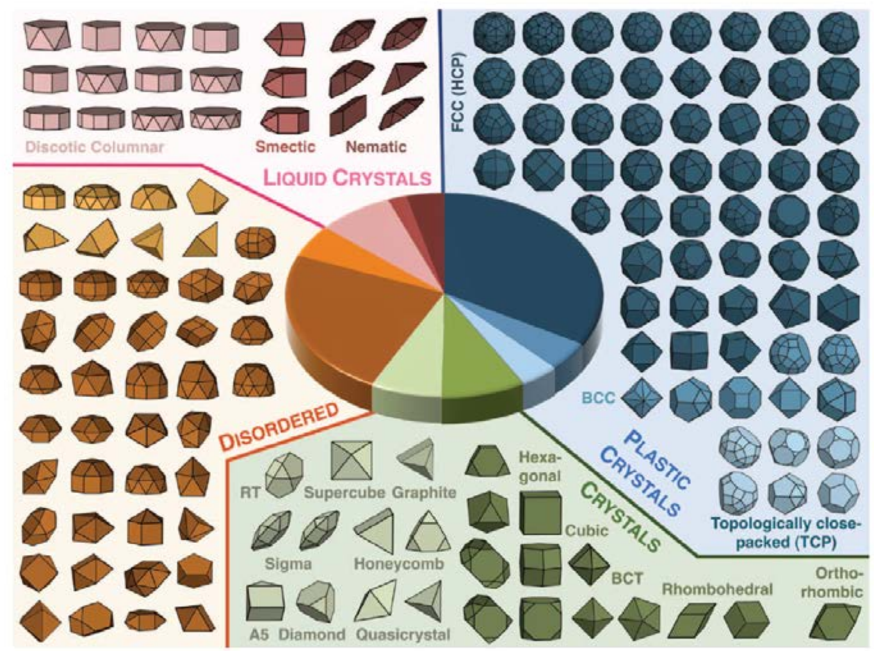
Anisotropic interactions (dipole-dipole)



A. Yethiraj & A. van Blaaderen, Nature, 421, 513, 2003.

A.P. Hynninen et.al, PRE 72, 051402, 2005.

Anisotropic shape



Damasceno *et al.,* Science 2012

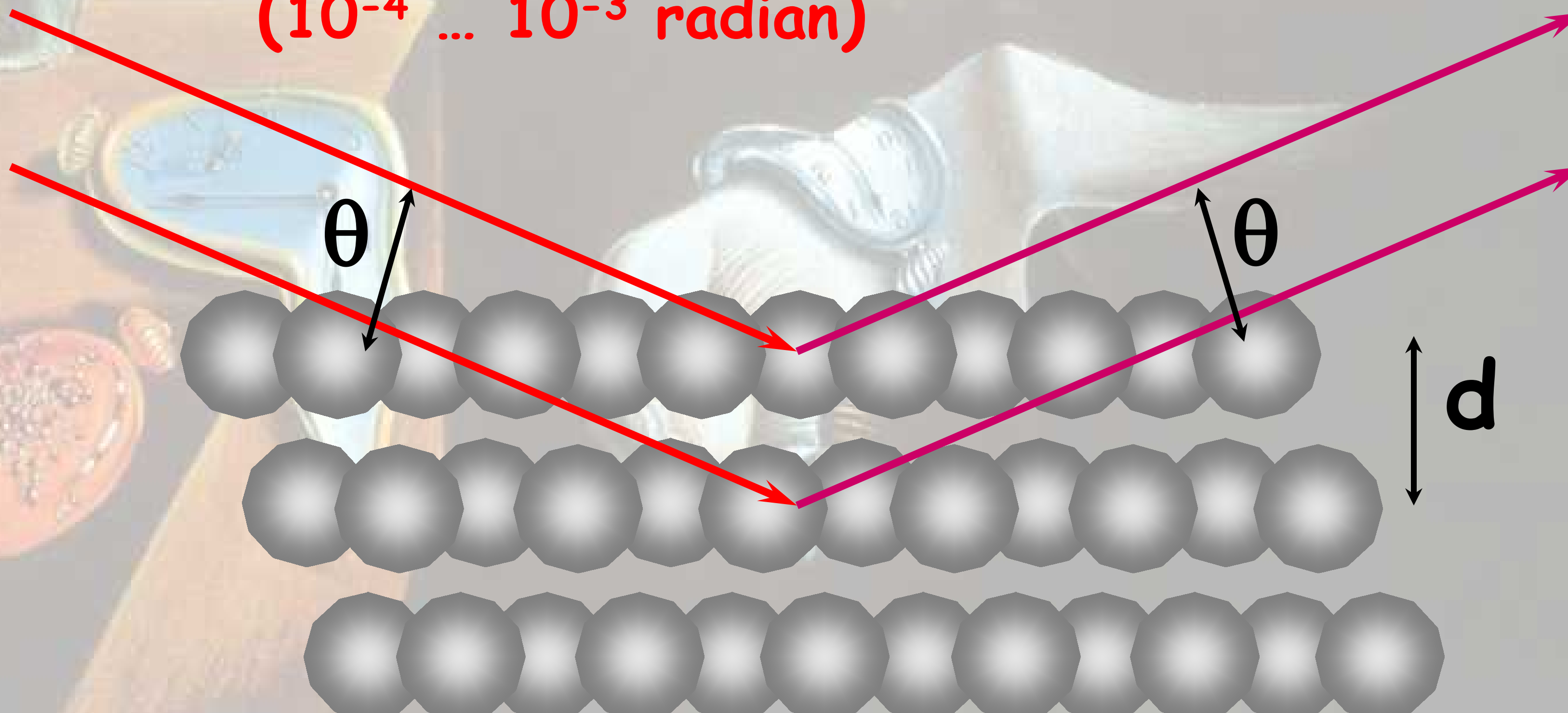
Theory: Bragg's law

Ordinary (atomic) crystals: $d \sim \lambda$
=> large diffraction angle 2θ

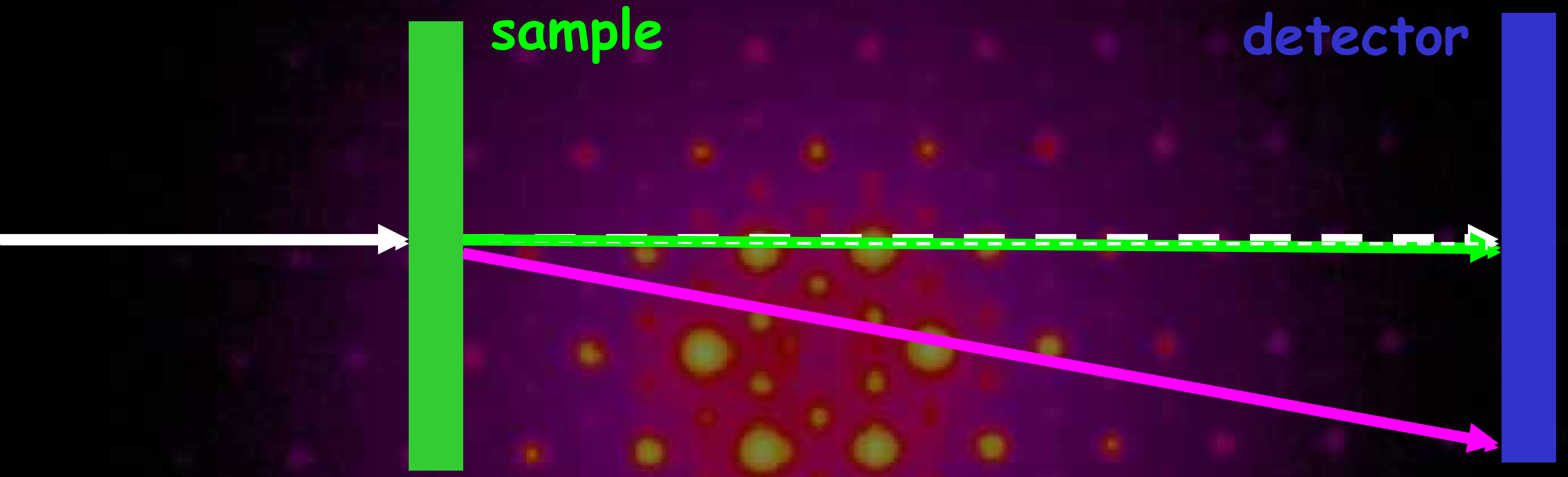
X-rays: $\lambda \sim 1$ A

Colloidal crystals: $d >> \lambda$
=> small diffraction angle 2θ
(10^{-4} … 10^{-3} radian)

$$\sin\theta = n\lambda/2d; \quad n=1,2,...$$

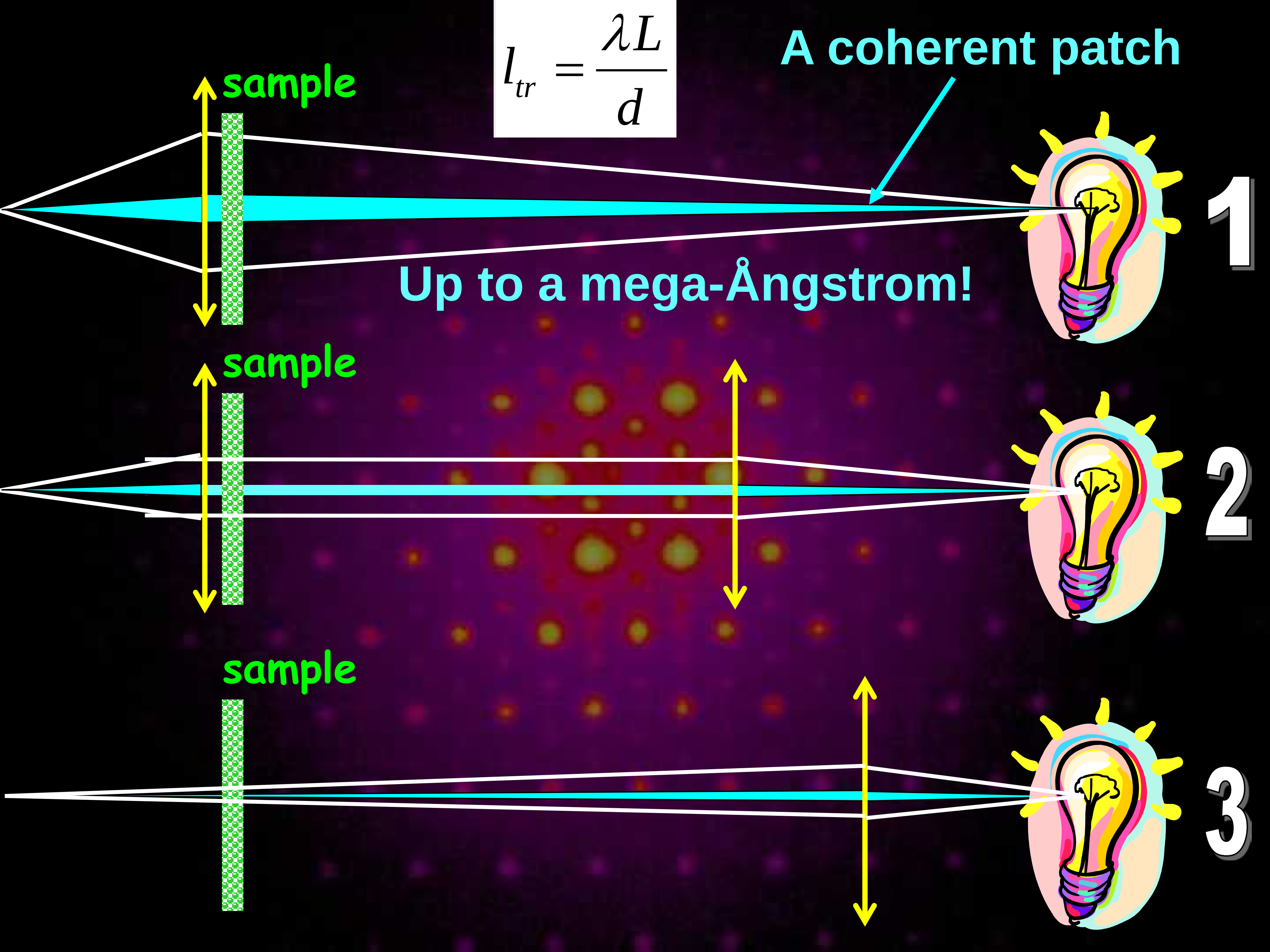


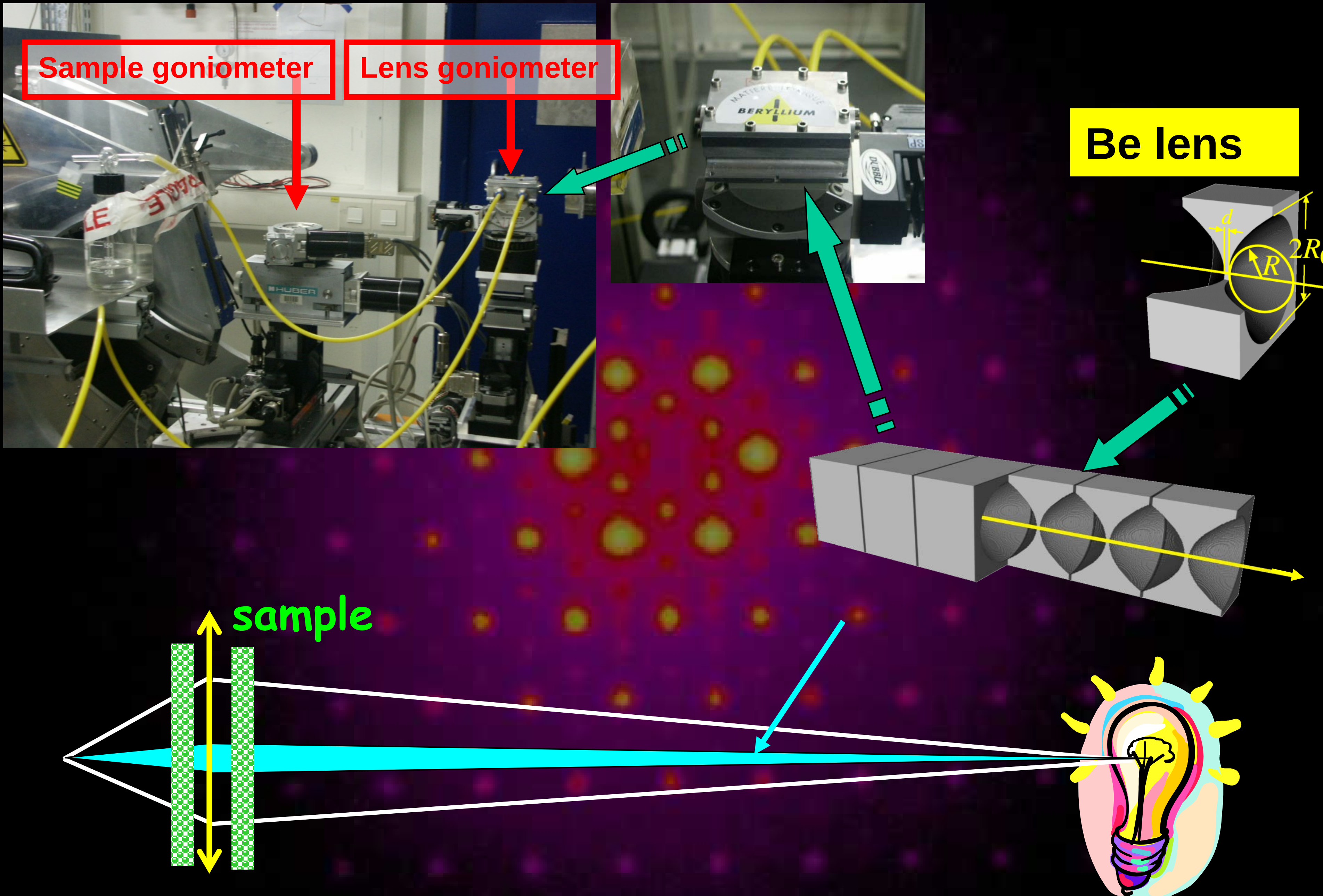
Scattering experiment



High angular resolution is needed
How do we get it?

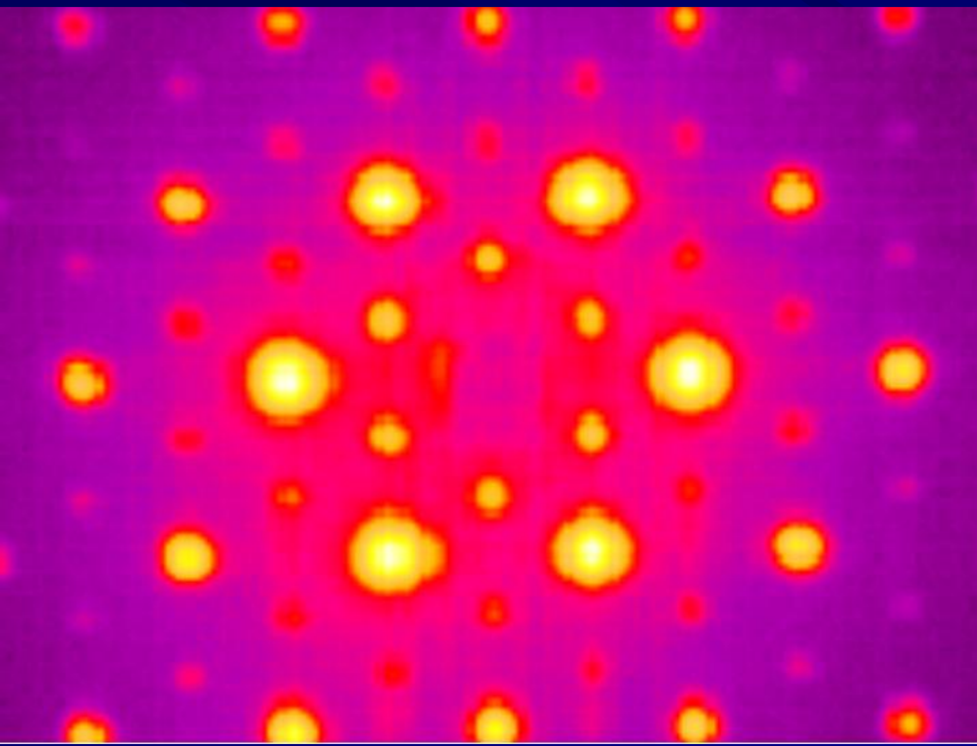
- parallel beam?
- pencil beam?

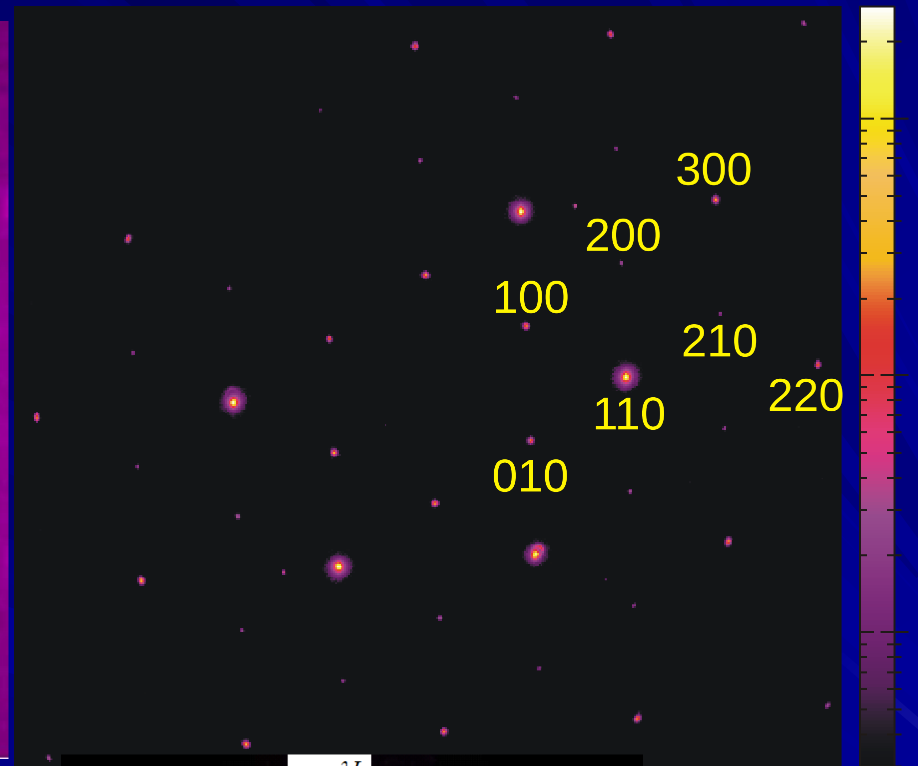

$$l_{tr} = \frac{\lambda L}{d}$$
A coherent patch
sample
Up to a mega-Ångstrom!
1
sample
2
sample
3



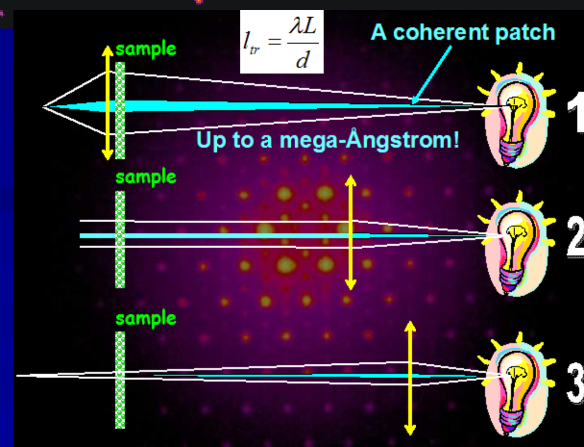
A. Snigirev, V. Kohn, V, I. Snigireva, B. Lengeler, B, Nature, 1996

Microradian diffraction



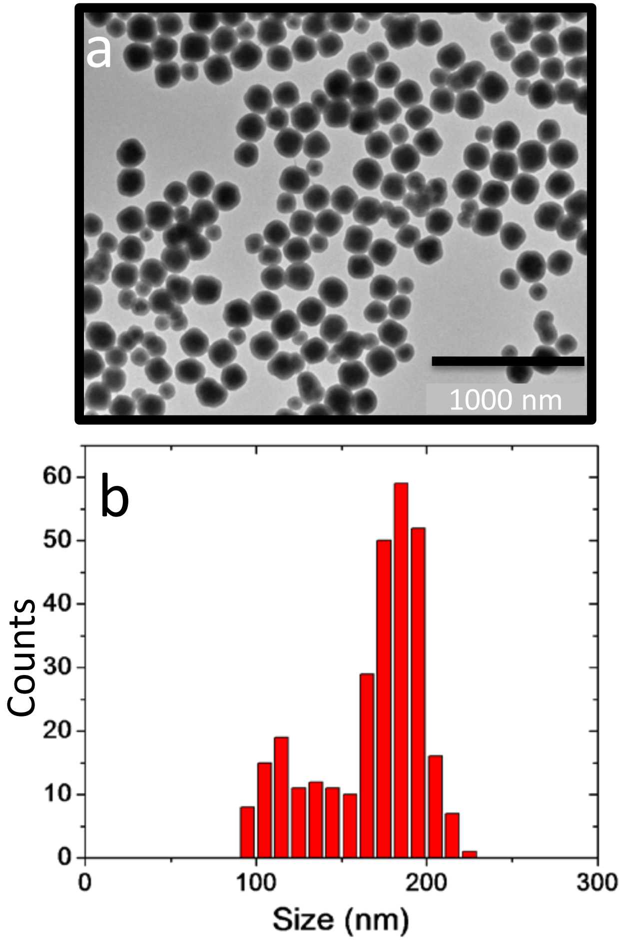


- Peak width: Long-range order
- Peak tails: fluctuations



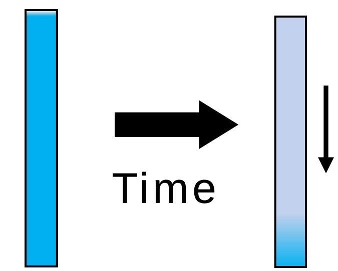
Route 1: *Magnetic dipolar spheres*

System under study : Silica coated magnetite spheres

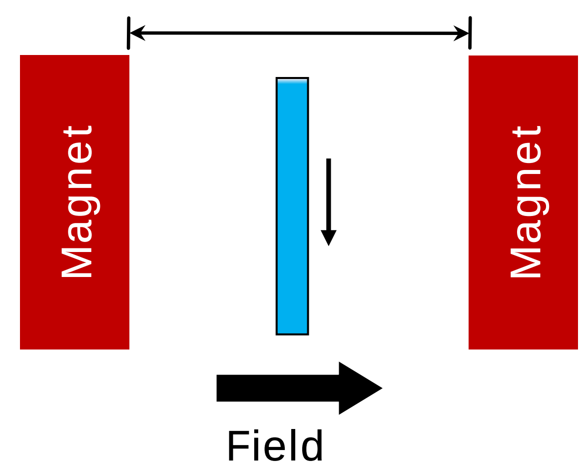


Sedimentation Conditions

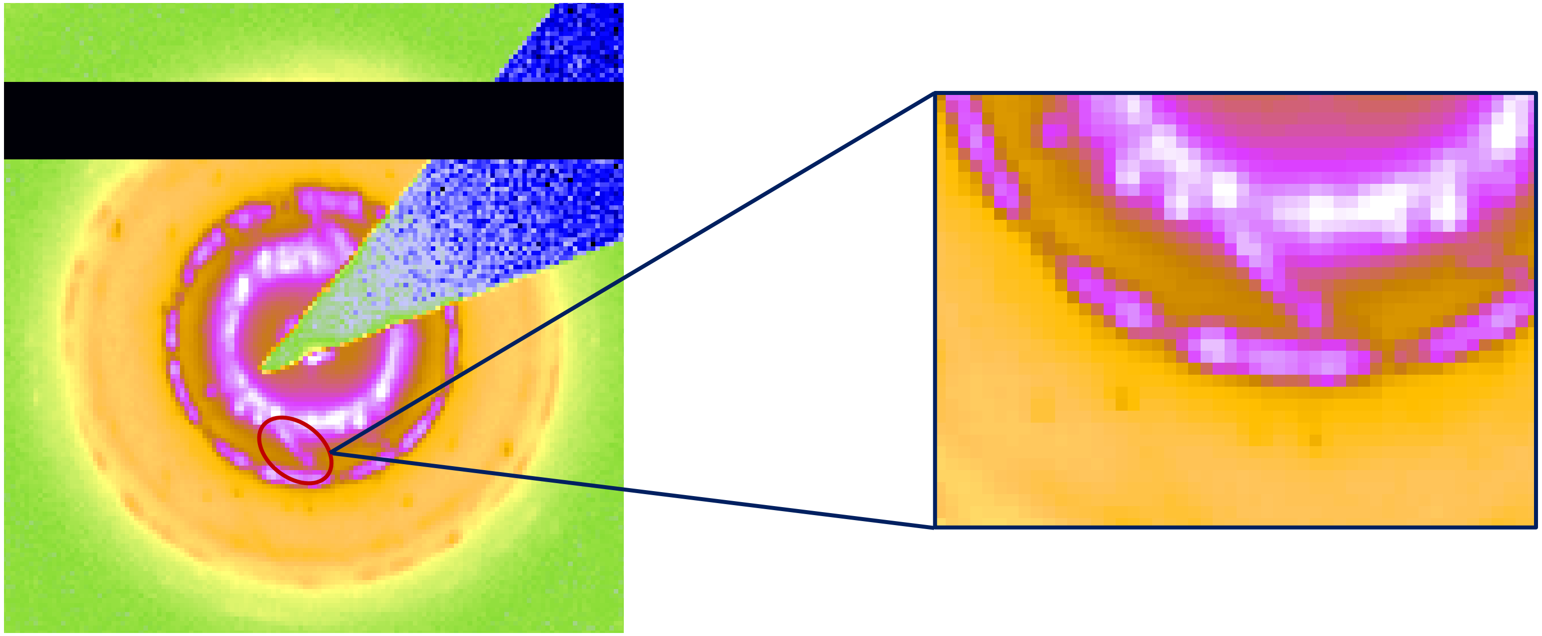
- Gravity



- Magnetic Field

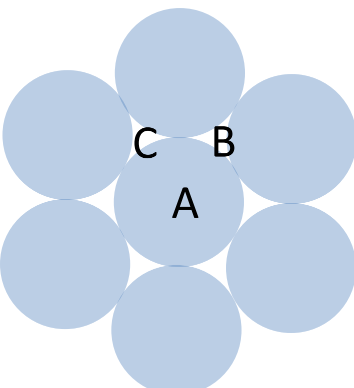


Structures in the absence of magnetic field

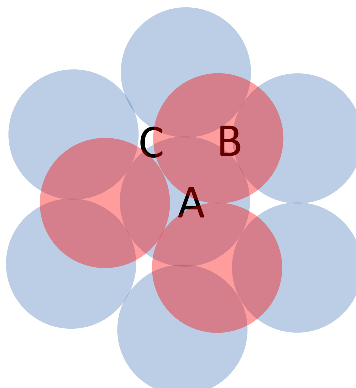


Extended features (Bragg scattering rods) characteristic for RHCP crystals

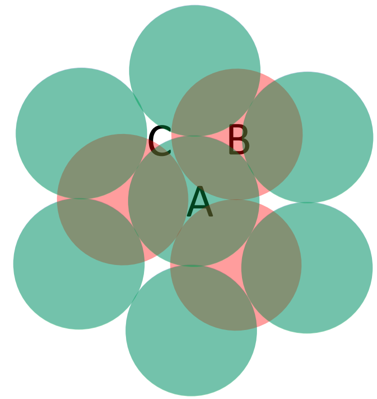
Arrangements of colloids in FCC and HCP stacking



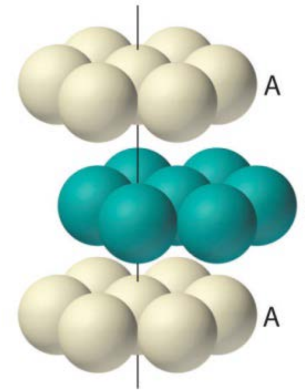
A



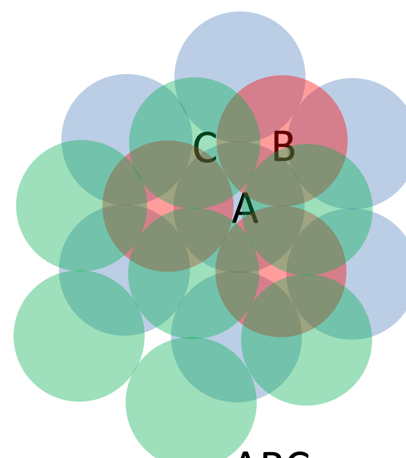
A B



ABA



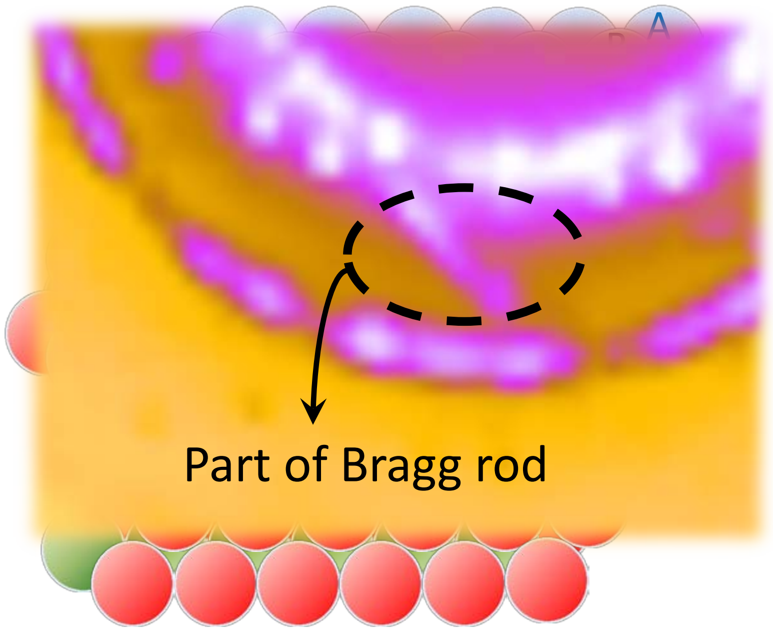
Hexagonal close packed (HCP)



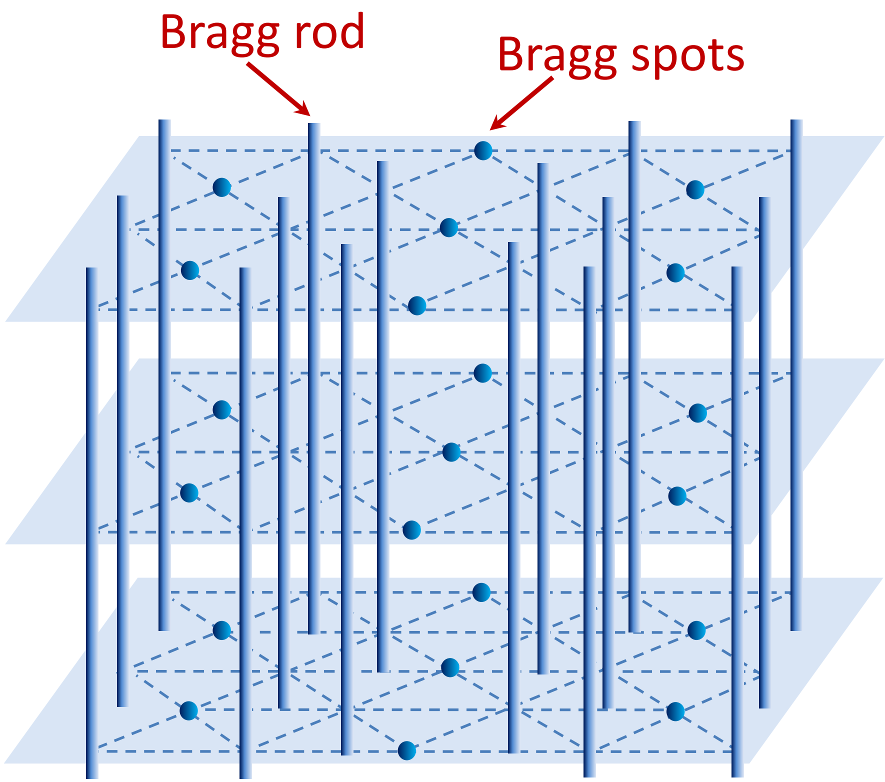
ABC

Face centered cubic (FCC)

Random Hexagonal Close Packed (RHCP) stacking

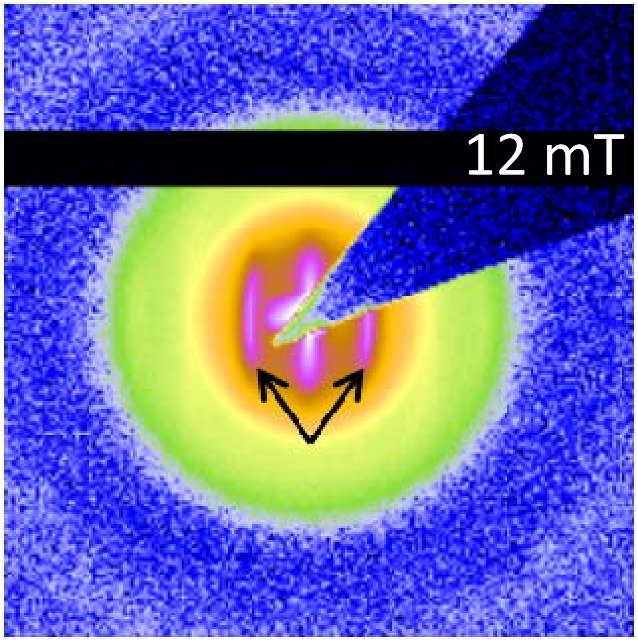


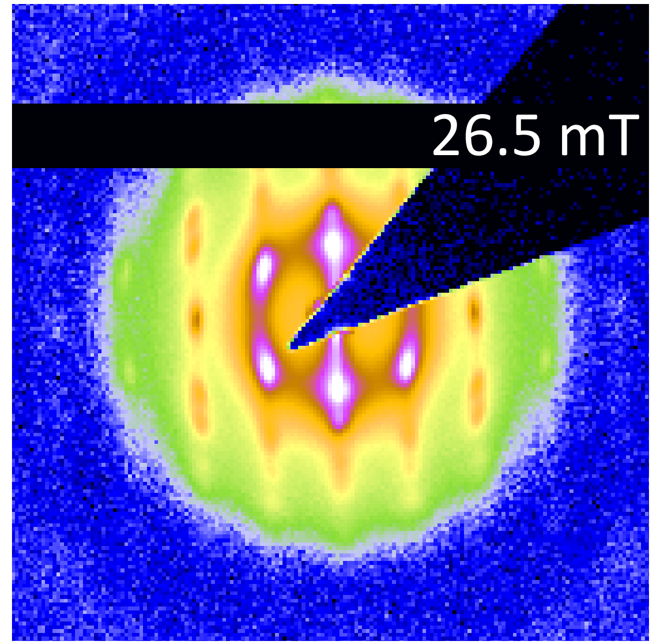
Real space RHCP structure

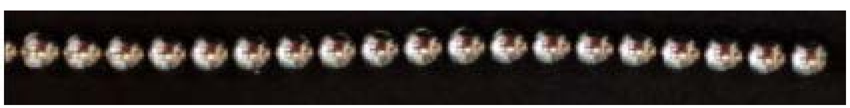


Reciprocal lattice of RHCP structure

Structures observed at different magnetic field

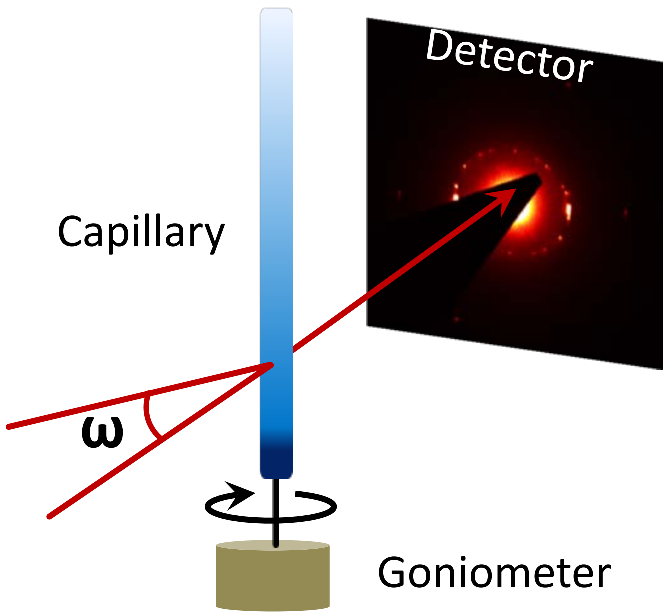


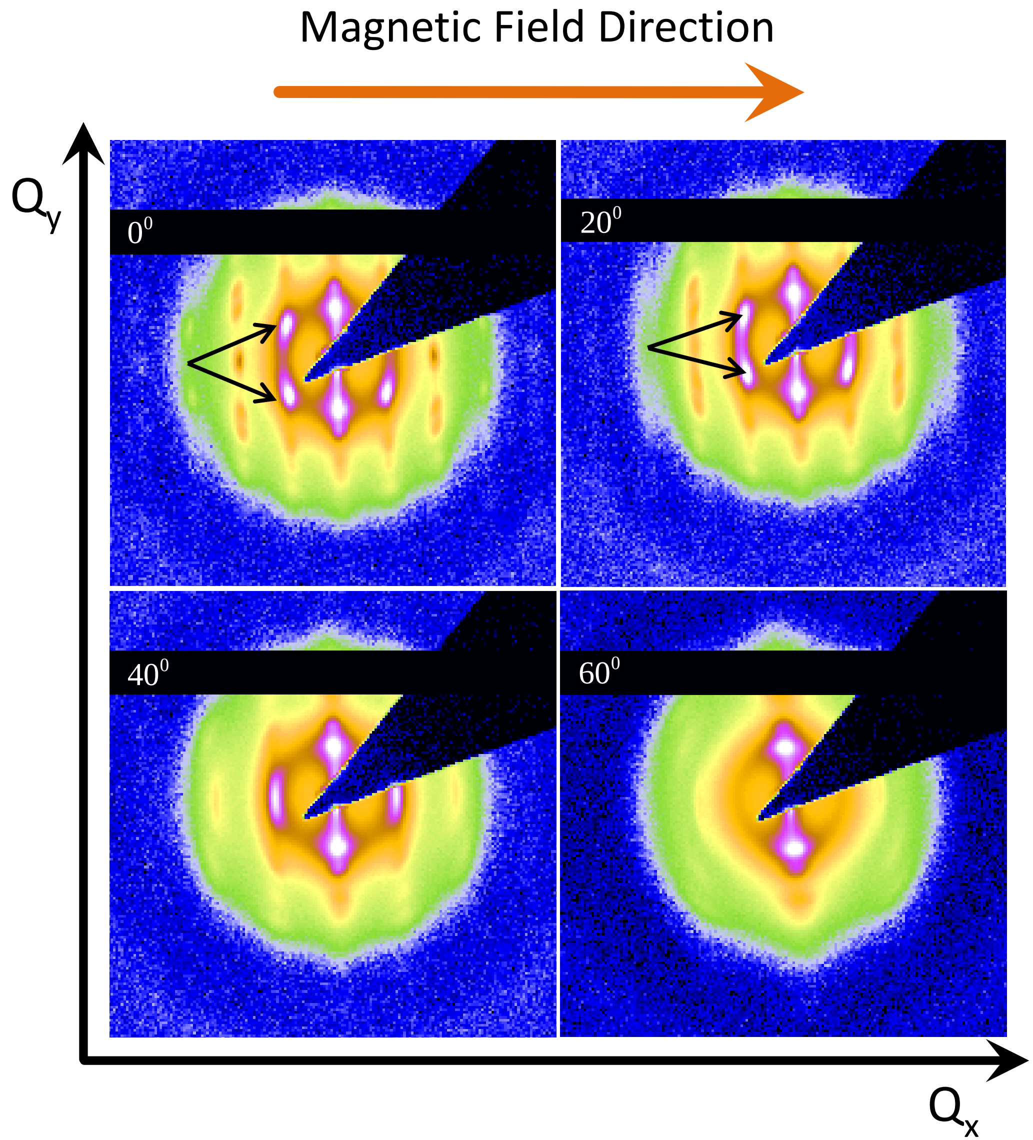




Structure ?

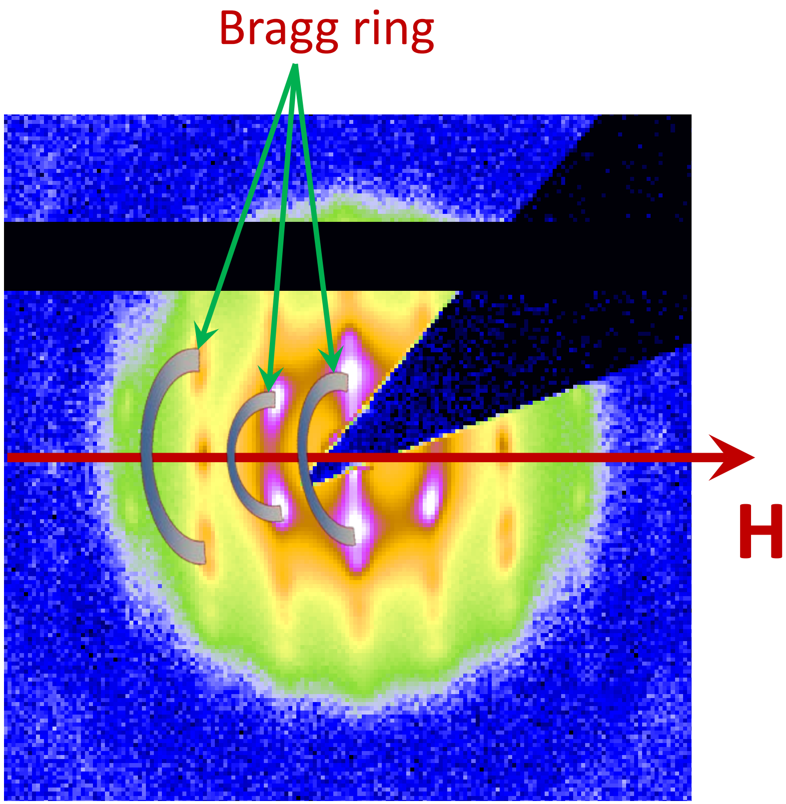
Rotation Scan





Point to note:

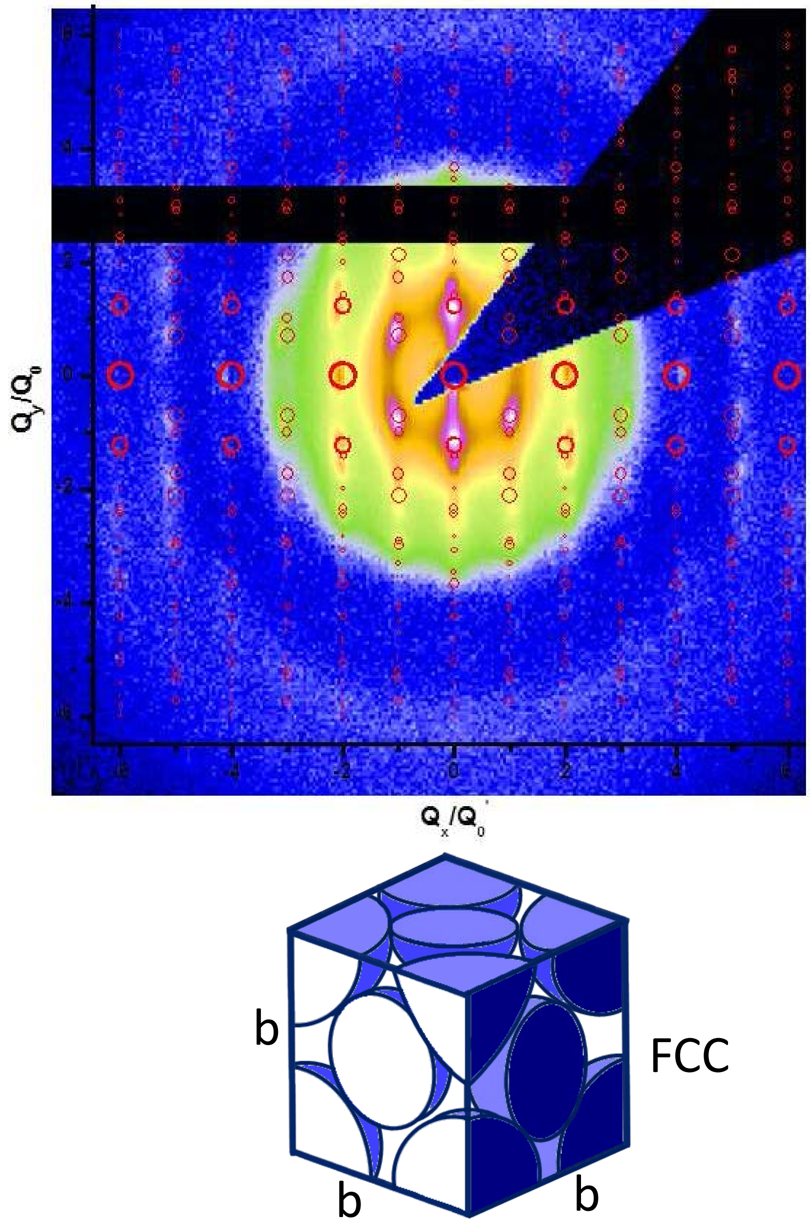
As we rotate the crystal Peaks are moving towards increasing Q_x and decreasing Q_y.

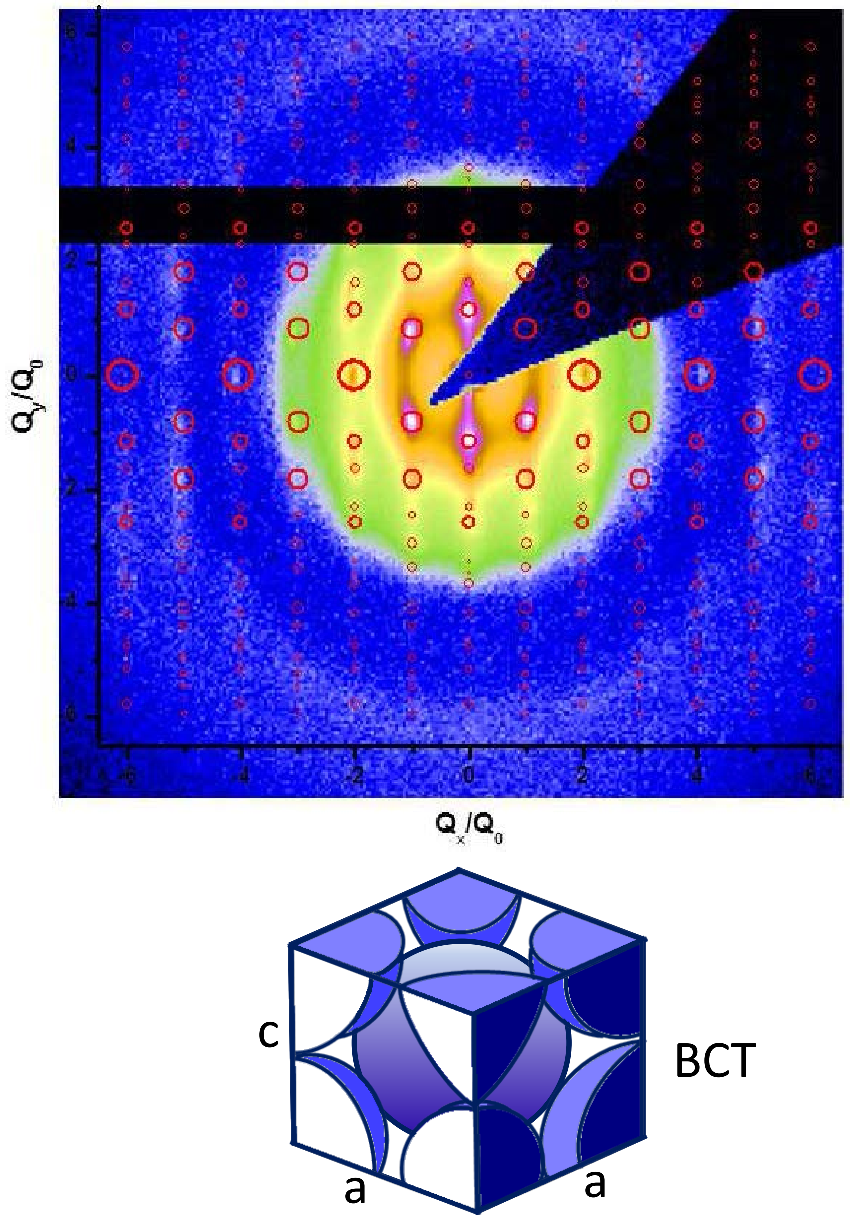


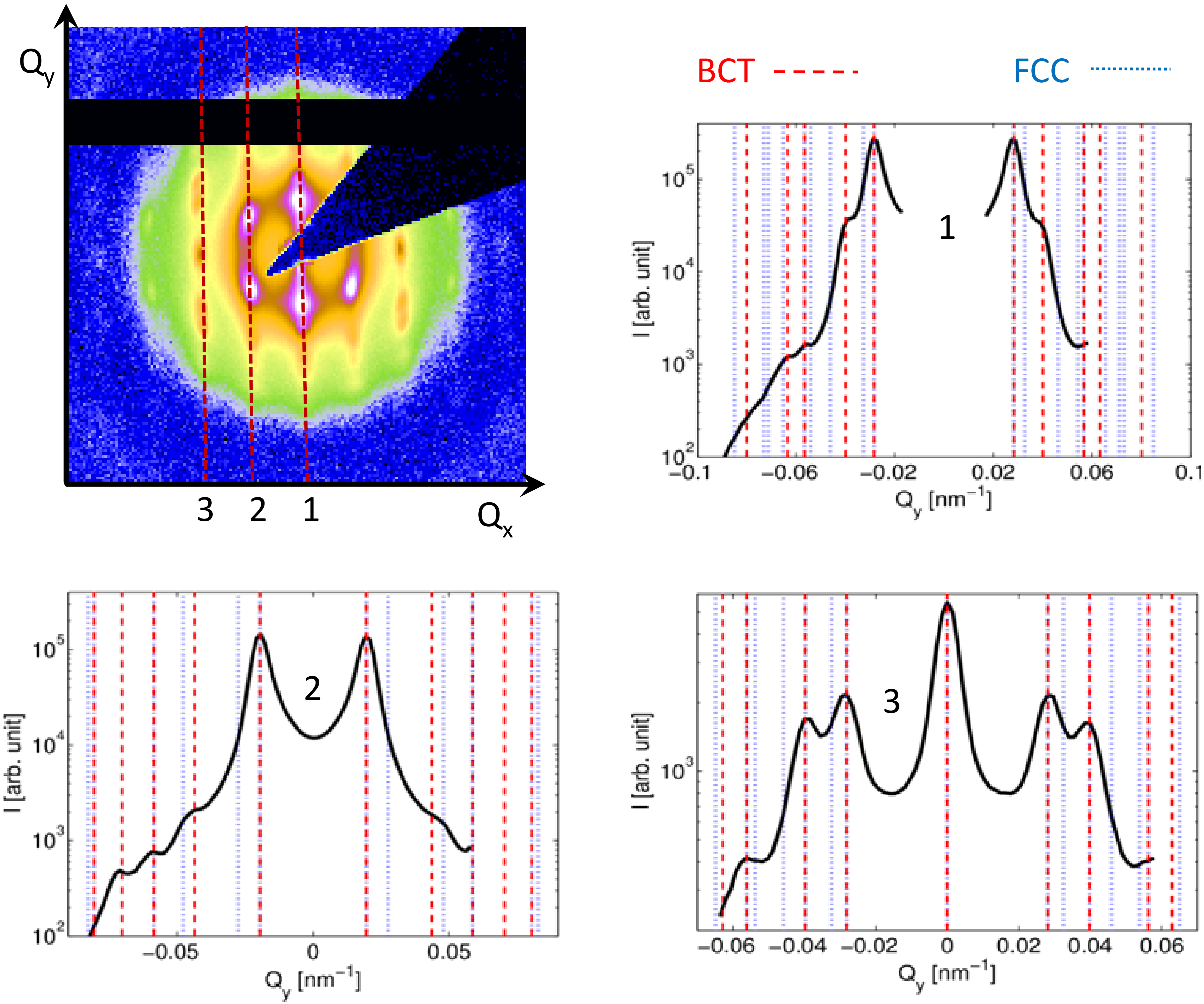
It's not a single crystal
but
a texture

Effectively the diffraction pattern at normal incidence ($\omega = 0^0$) contains all the information

Modelling the structure



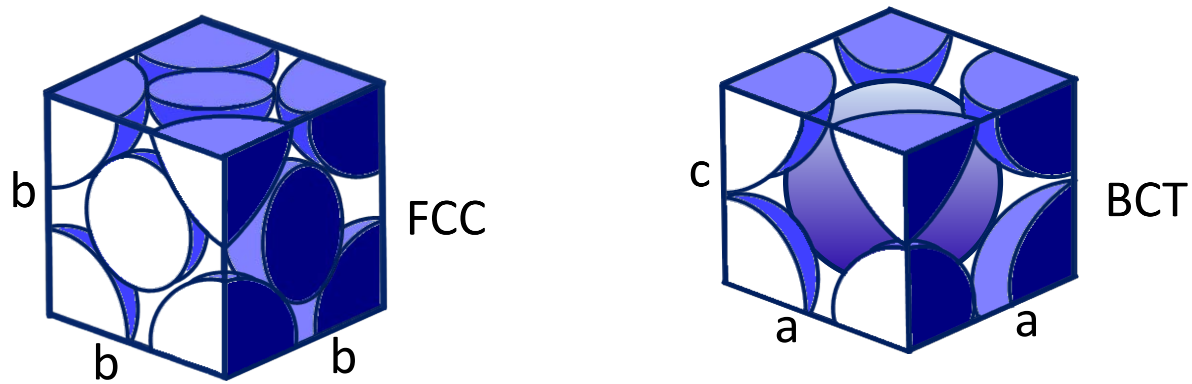




Q_y
Q_x
3
2
1
BCT
FCC
I [arb. unit]
Q_y [nm^-1]

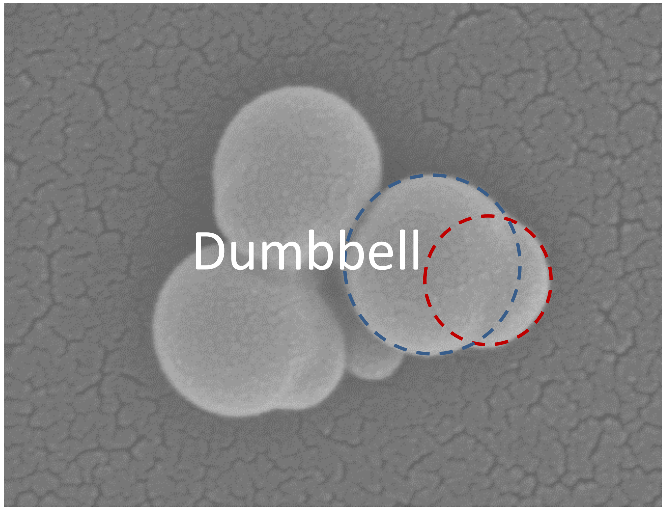
Conclusion 1

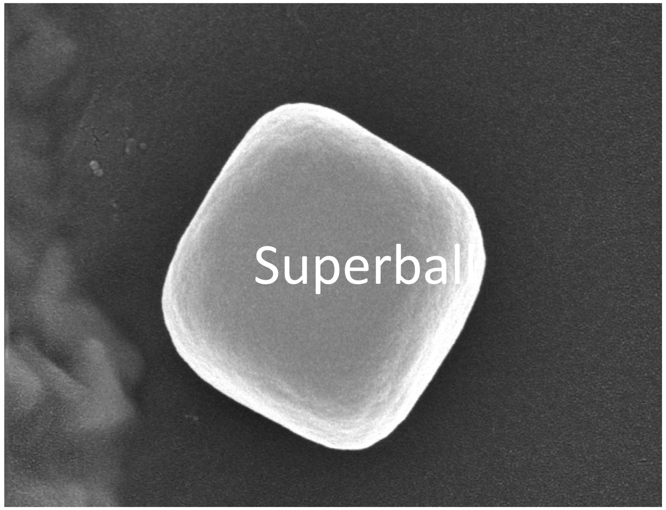
- Magnetic dipole-dipole interactions allow to manipulate colloidal self-organized architecture
- Without magnetic field the crystal structure is RHCP
- In the presence of magnetic field it is BCT
- The *c/a* ratio deviates by 15% from the value expected for touching hard spheres



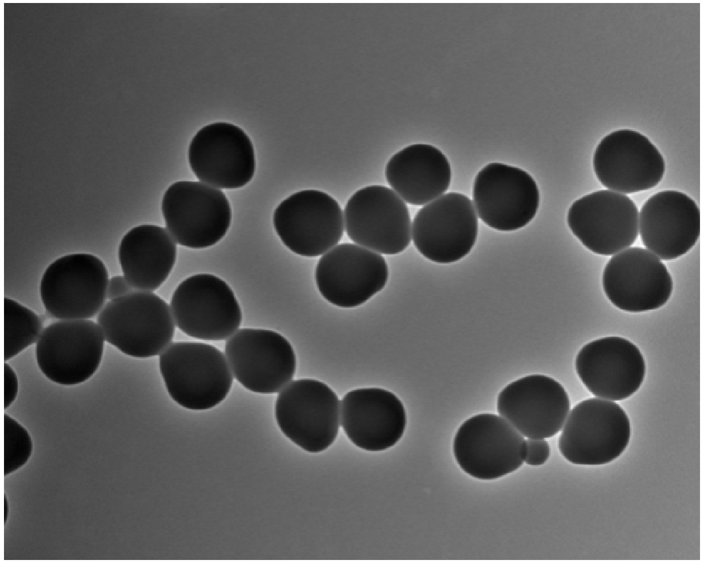
Antara Pal, Vikash Malik, Le He, Ben H. Erné, Yadong Yin, Willem K. Kegel, Andrei V. Petukhov, Angew. Chem. Int Ed. 54, 1803, 2015.

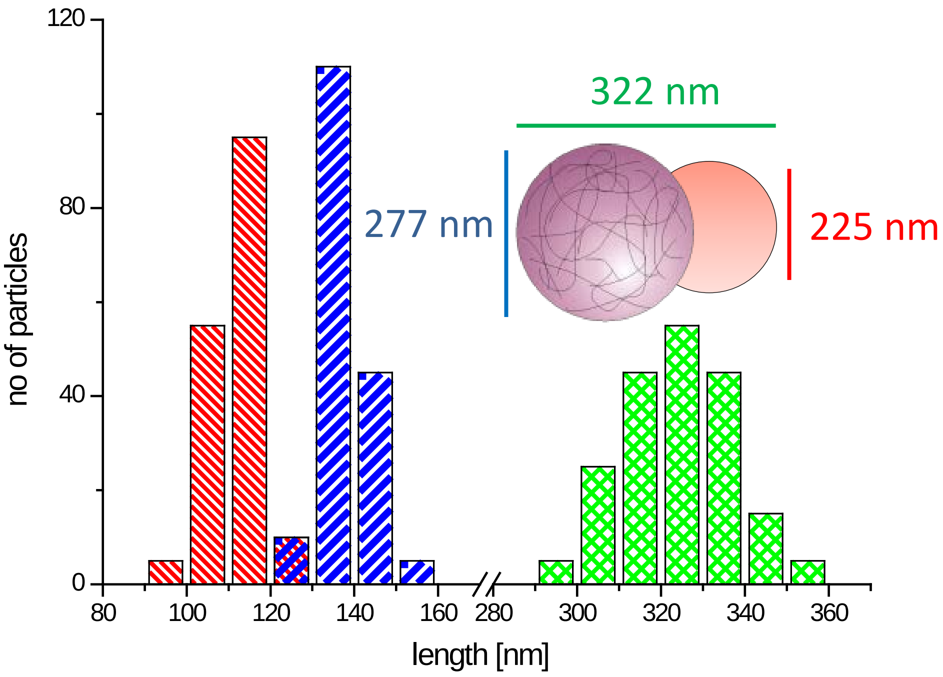
Route 2: *Introducing Shape Anisotropy*



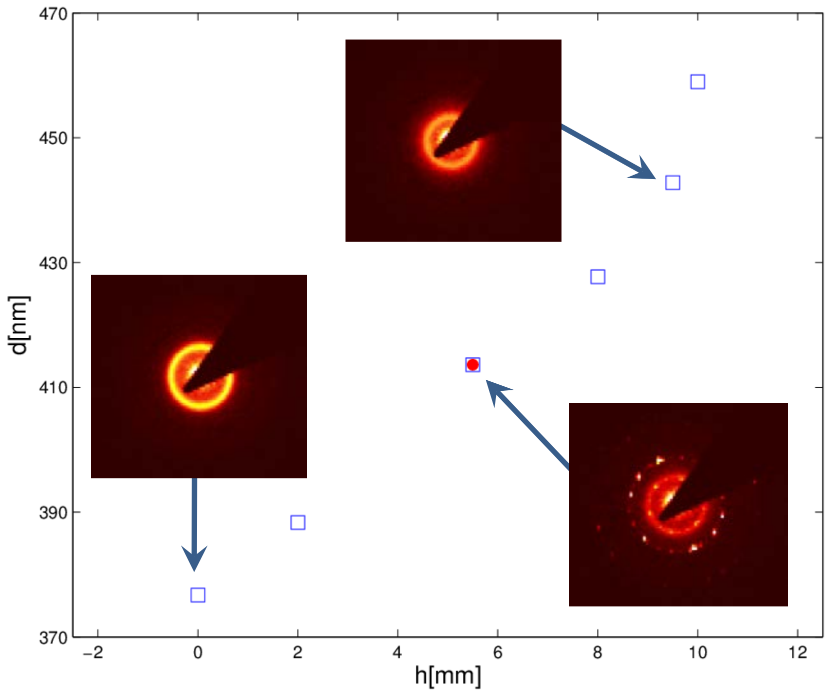


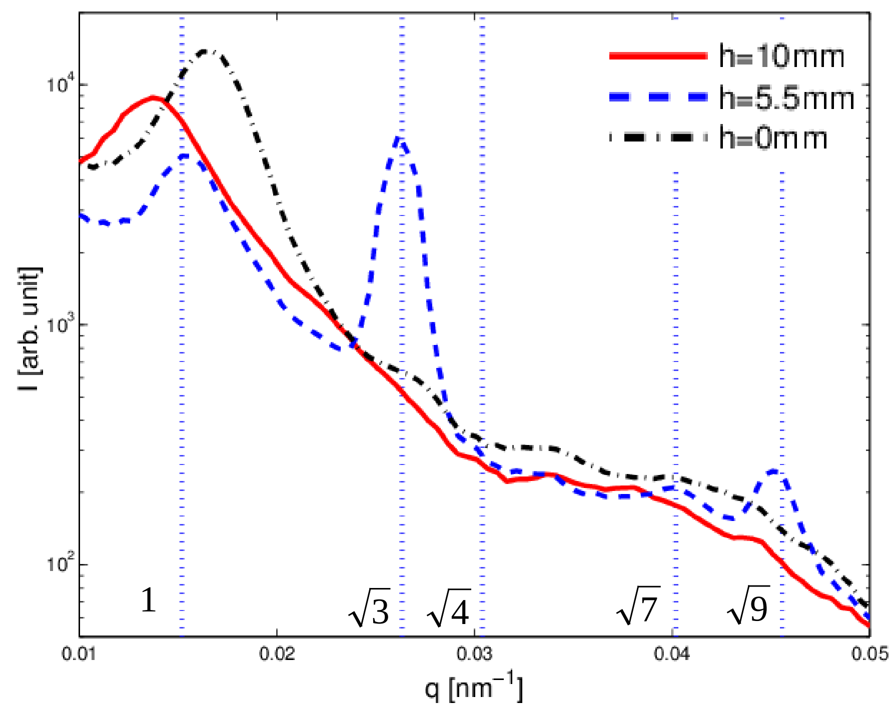
Colloidal Dumbbell





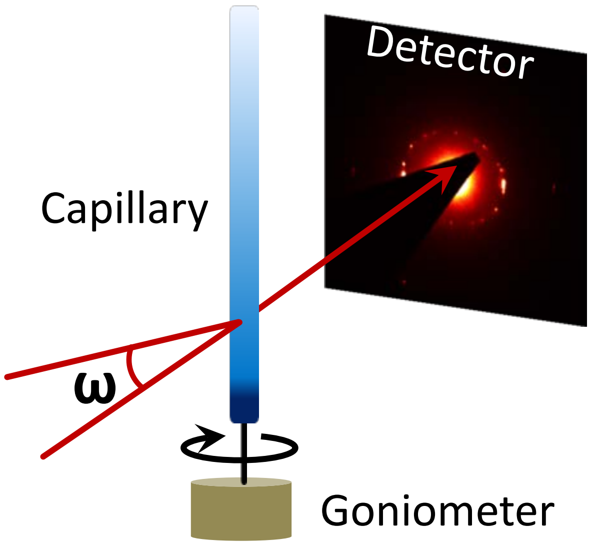
Scan along the length of the capillary

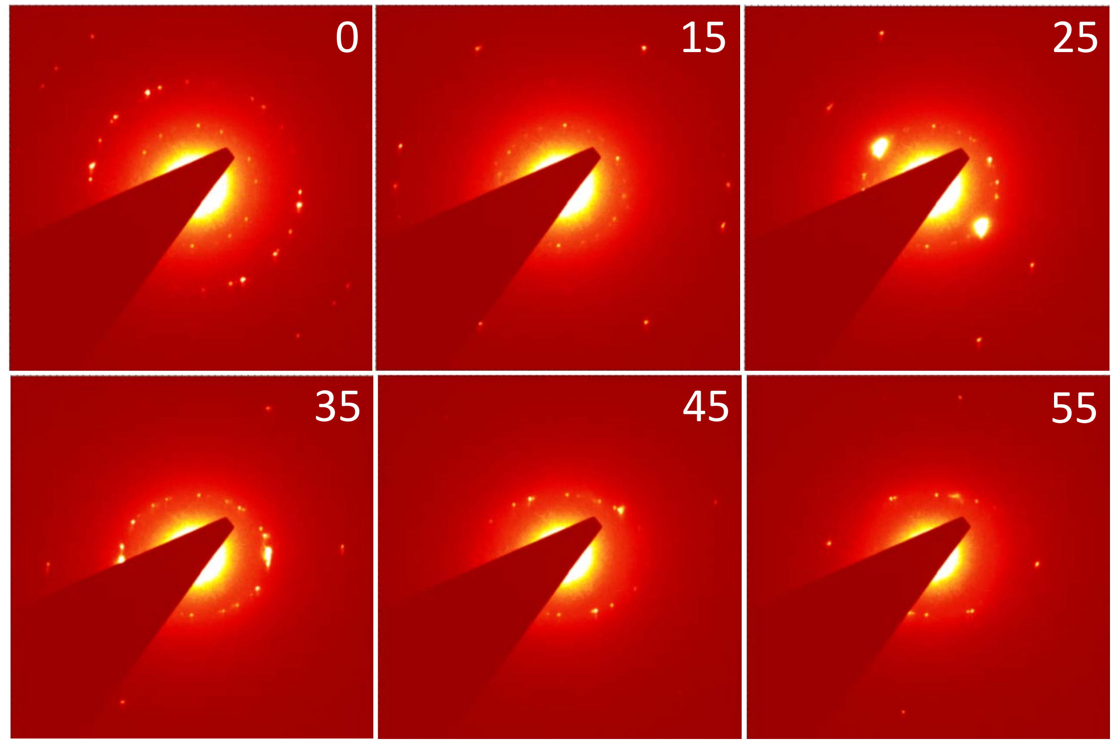




1. Isotropic ⟶ Crystal ⟶ Glass
2. Crystal is multi domain and made up of hexagonally packed layers.

What is the crystal structure?





Points to note:

1. Peaks in the first-order ring **DO NOT** vanish as we rotate the crystal

   Not Bragg spots but the intensity is distributed along Bragg rods

2. Very strong diffraction peaks at specific angles (e.g., @ 25^o)

   Which correspond to FCC structure

Conclusion 2

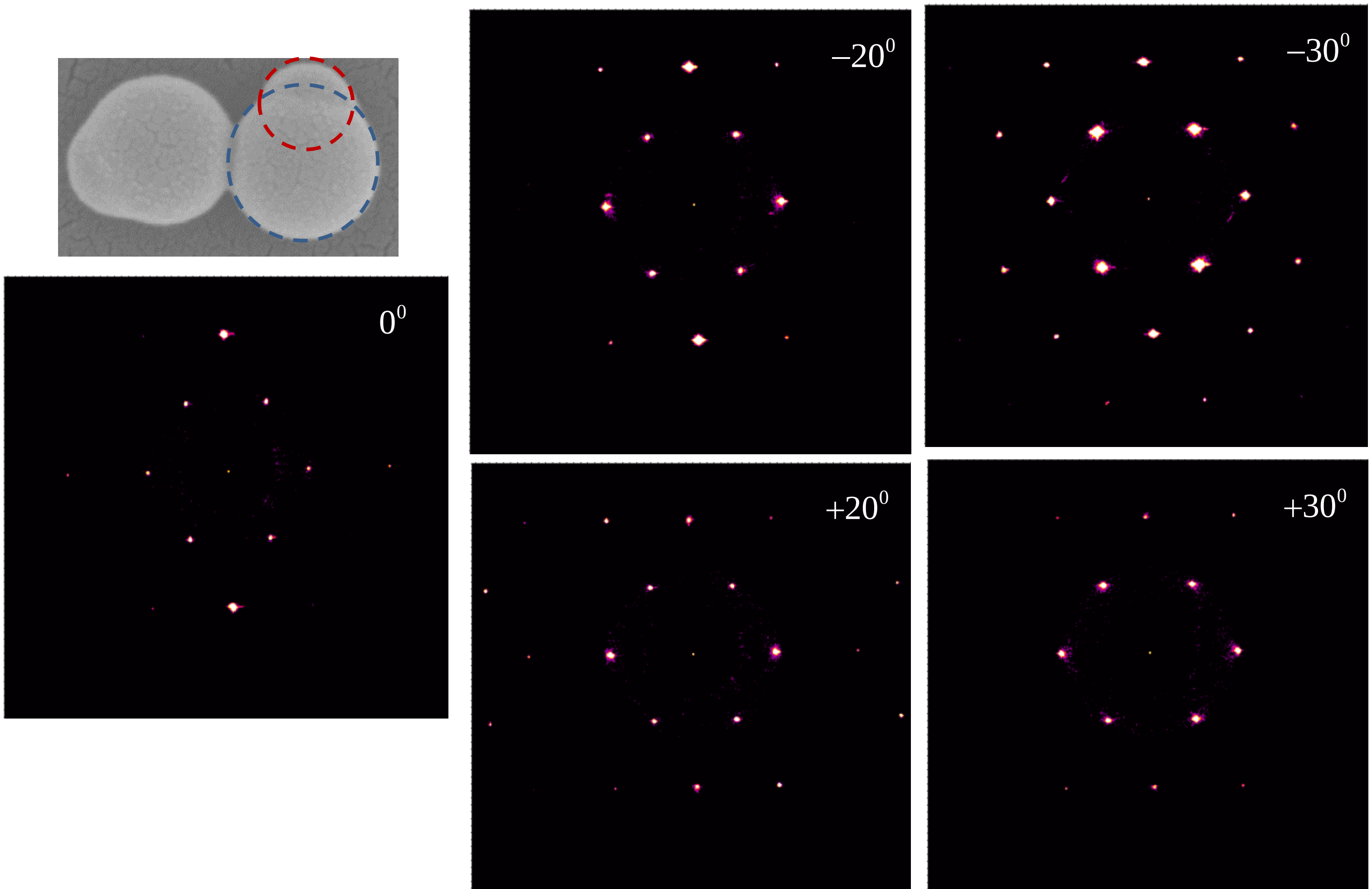
- Overall FCC structure with a small amount of stacking fault which leads to the formation of Bragg rods.

- We DO NOT see any effect of anisotropy.
  - Effective shape of the particles become spherical due to large Debye length.
    → Plastic crystals

Antara Pal, Janne-Mieke Meijer, Joost R. Wolters, Willem K. Kegel and Andrei V. Petukhov, *J. Appl. Cryst., 48, 238, 2015.*

Outlook

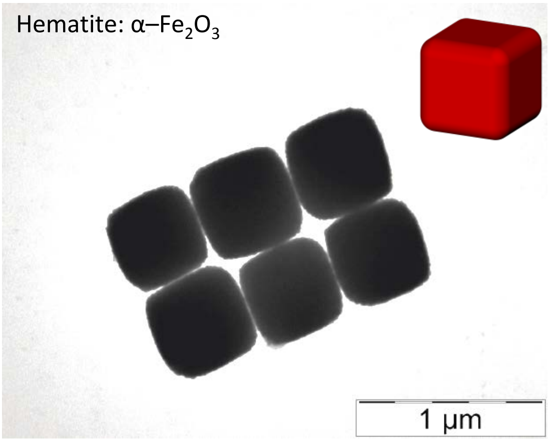
- Recently: Probed the effect of salt concentration on the crystal structure.



ID-02, ESRF

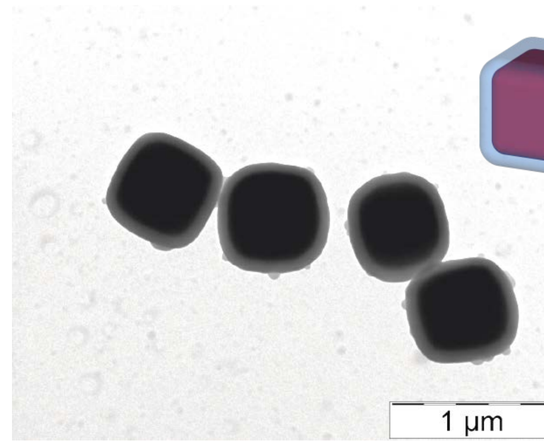
System – Hollow Silica Cubes

Sol-gel method: 2M $FeCl_3$ + 5,4 M NaOH @ 100 °C for 8 days



Sugimoto *et al*. Colloidal Surfaces A 1993

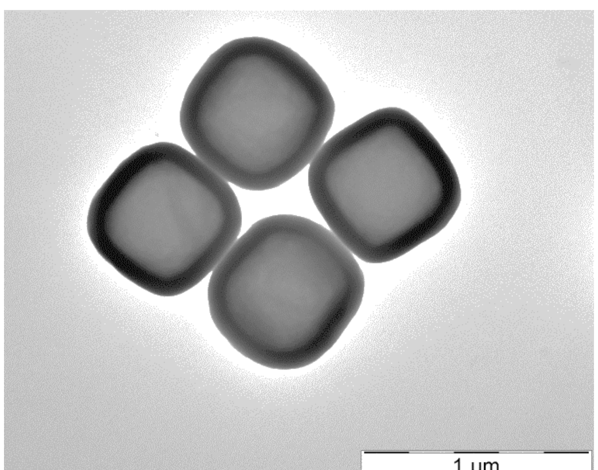
Silica coating: adapted Stöber method



Graf *et al.* Langmuir 2003,

Two step method
1. Fluorescent dye-ITC + APS +TEOS
2. TEOS

Dissolve hematite core: Conc. HCl

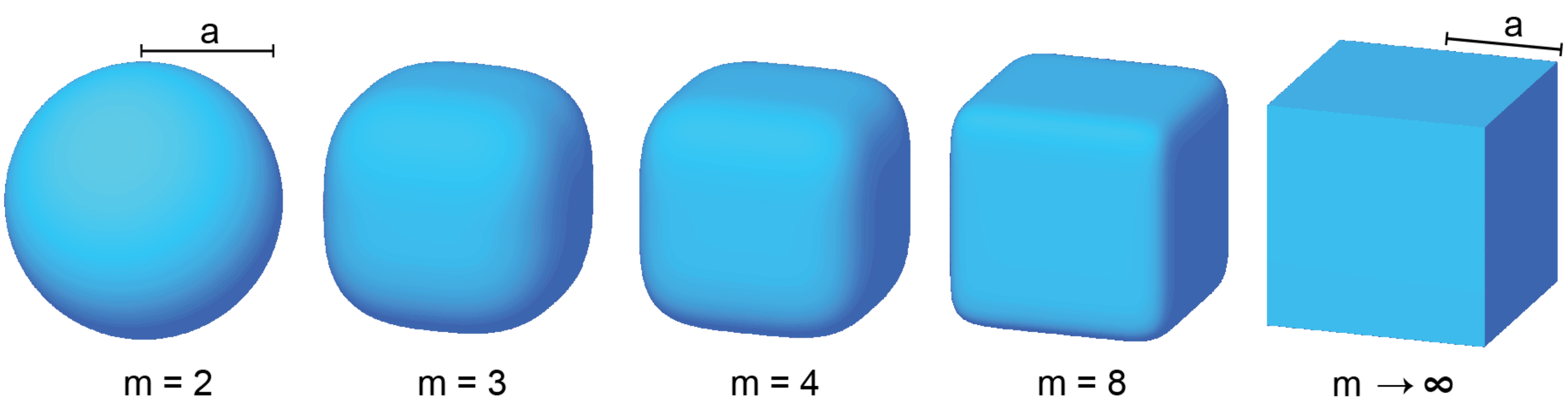


L. Rossi *et al.* Soft Matter 2011

Superball Colloids

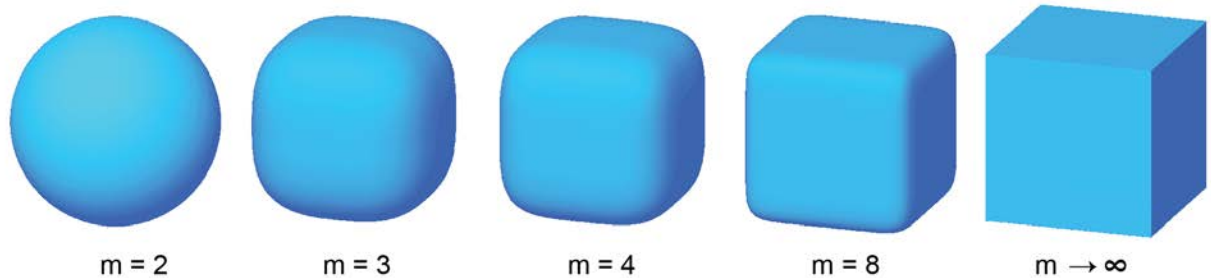
- Superball shape:

$$\left|\frac{x}{a}\right|^m + \left|\frac{y}{b}\right|^m + \left|\frac{z}{c}\right|^m = 1$$



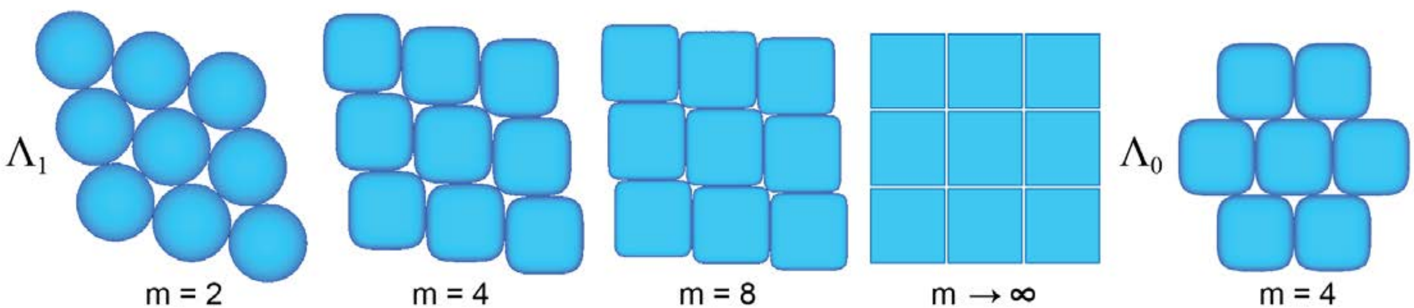
Packing of Superballs

$$\left|\frac{x}{a}\right|^m + \left|\frac{y}{b}\right|^m + \left|\frac{z}{c}\right|^m = 1$$

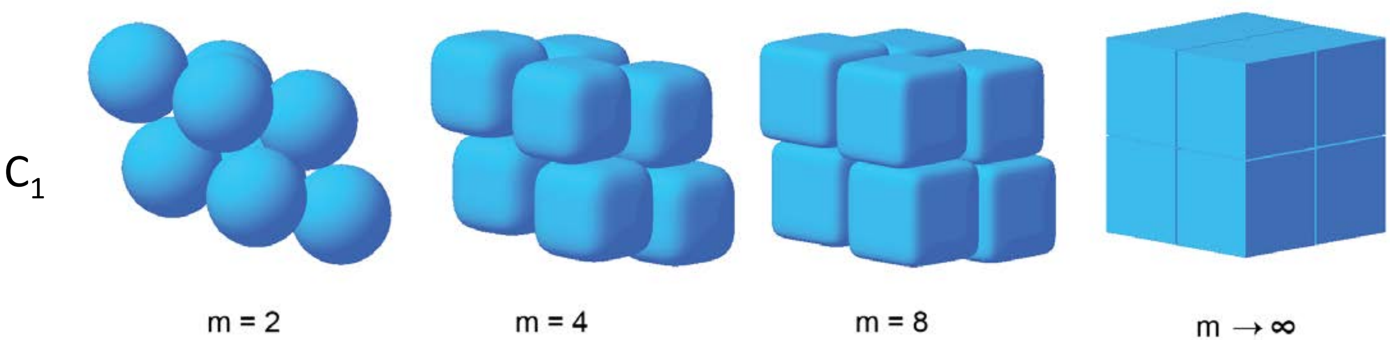


Optimal packings

2D



3D



Batten, R.D.; Stillinger, F.H.; Torquato, S. Phys. Rev. E (2010)

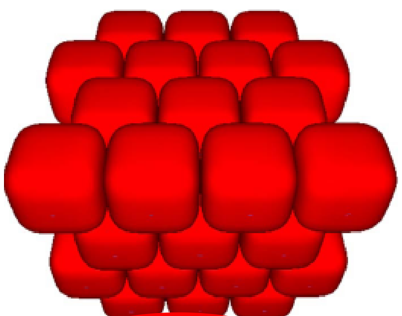
Simulations of Superball Structures

Jioa *et al.*

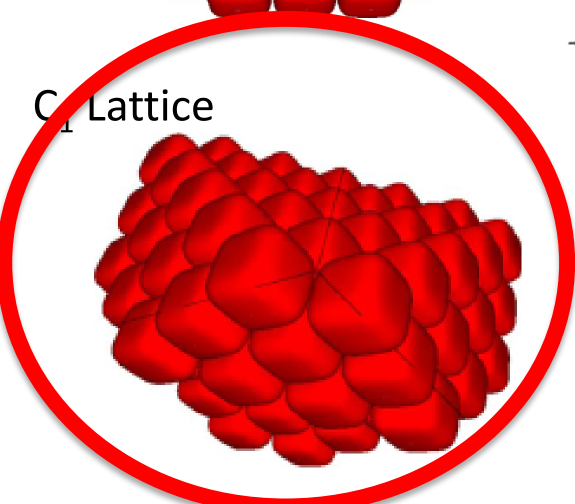
Densest packings of superballs

C_0 lattice

p (= m/2)



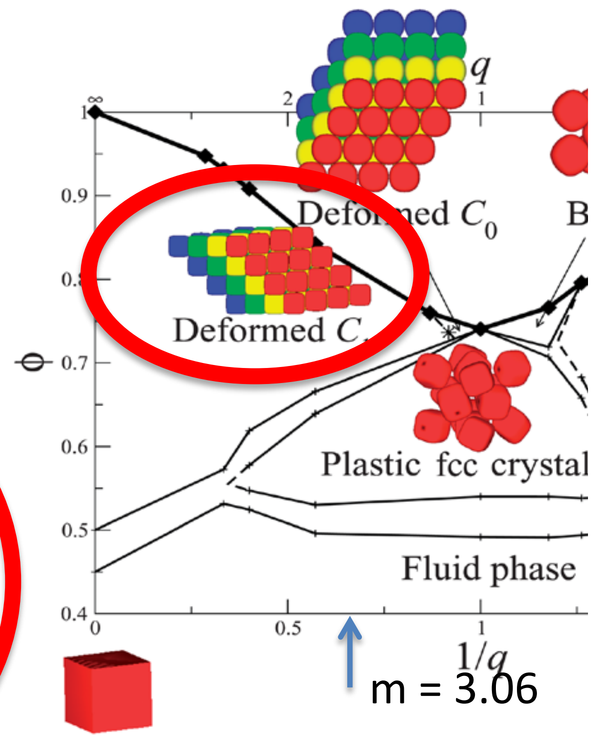
C_1 Lattice



Ran *et al.*

Phase behavior of superballs

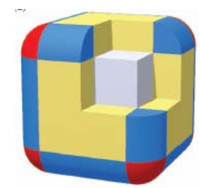
1/q (= 2/m)

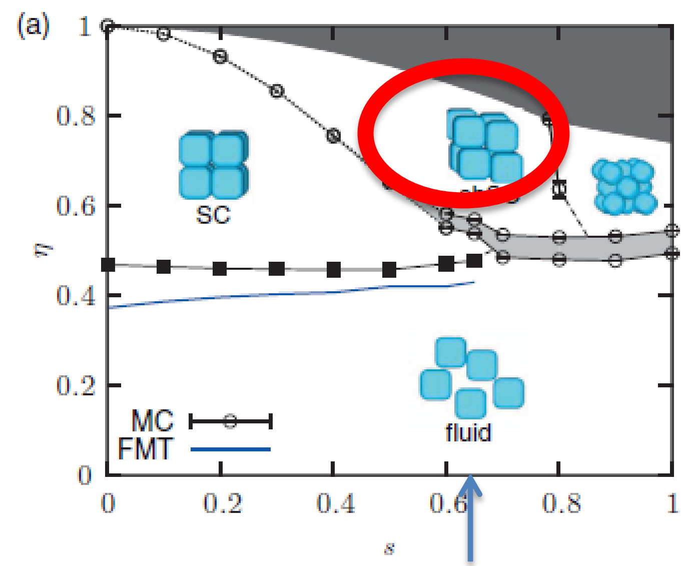


Marechal *et al.*

Phase behavior of parallel rounded cubes

s= 1/q (= 2/m)



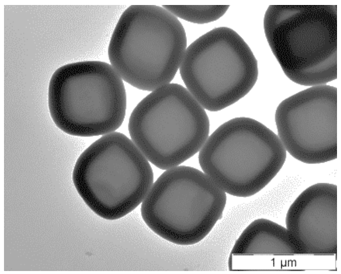


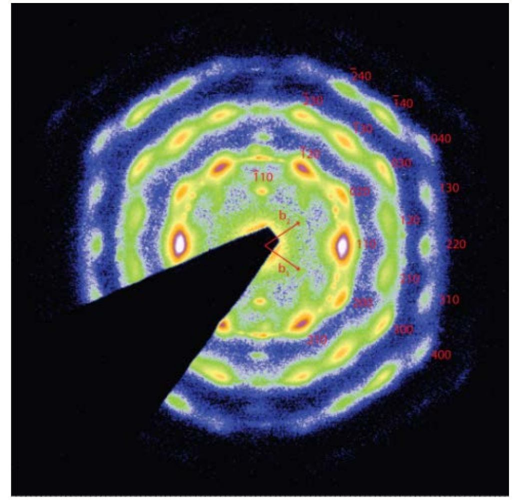
Jiao *et al.* Phys Rev, 2009; Ni *et al.* Soft Matter, 2012; Marechal *et al,* J. Chem. Phys., 2012

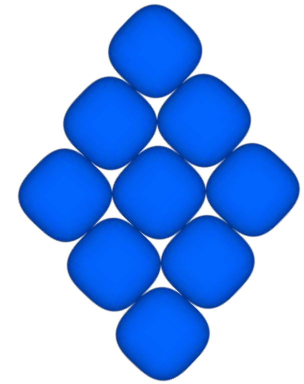
Structure formed by Superballs

- Colloidal hollow silica cubes:

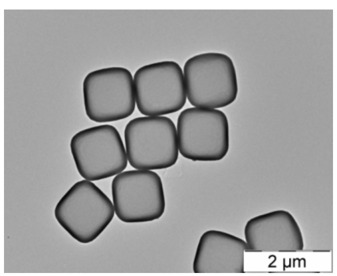
m = 2.9

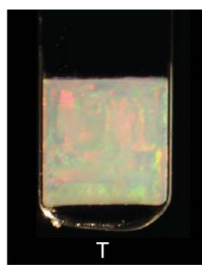


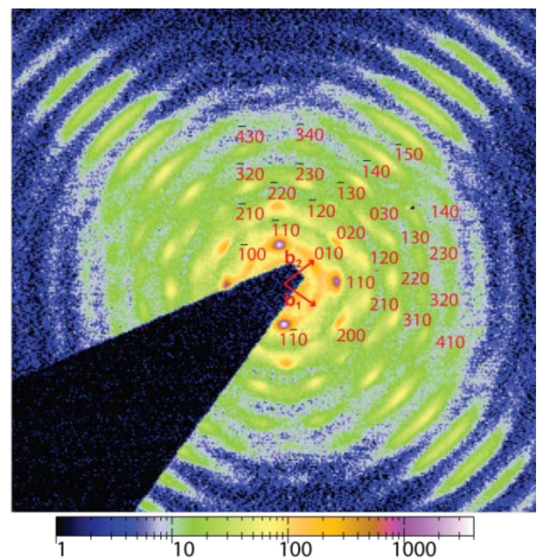


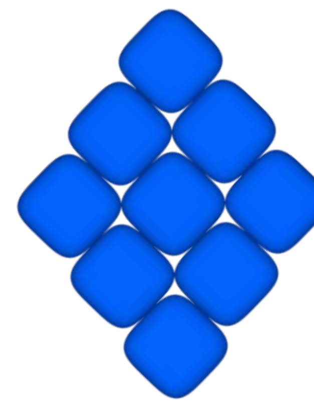


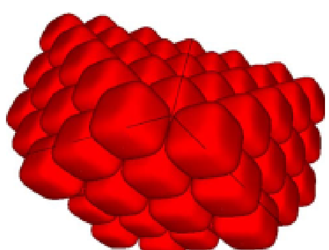
m = 3.6



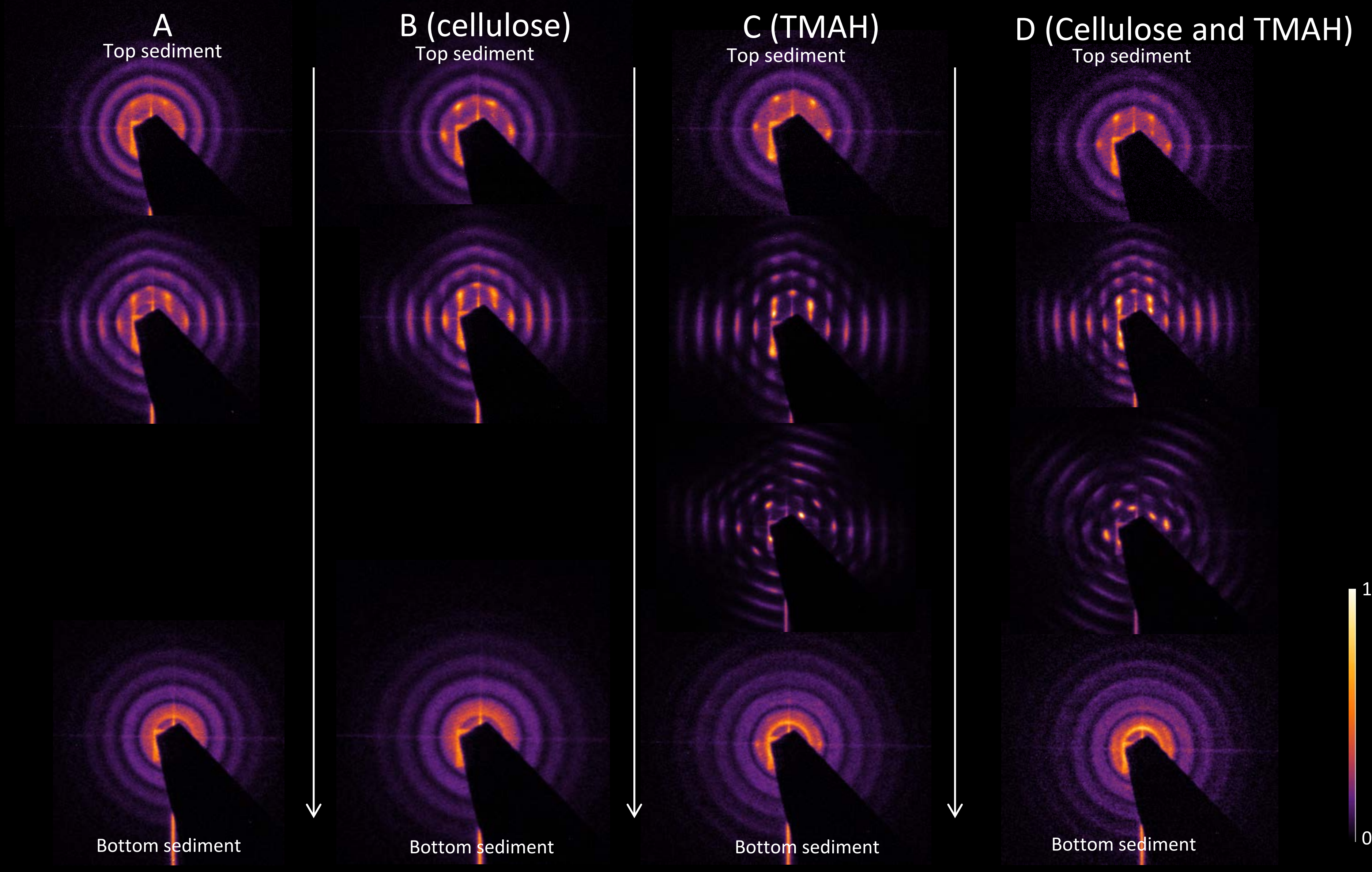




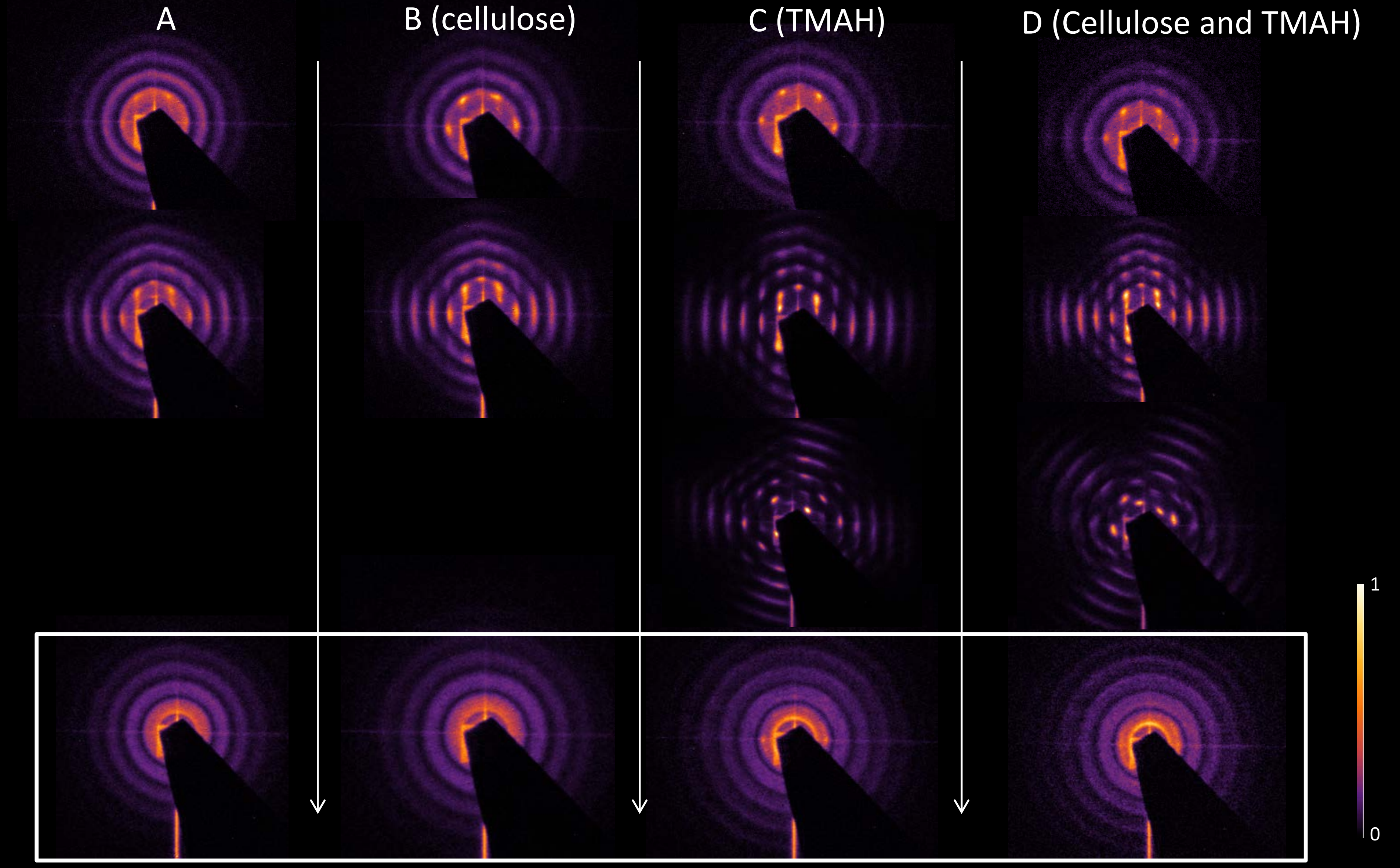




Part B: **Results: overview**



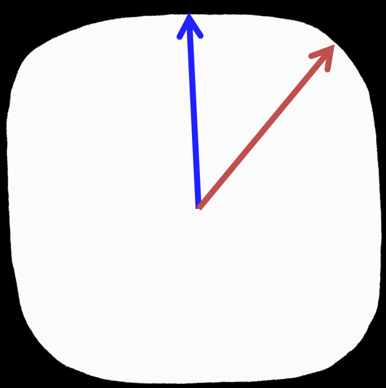
Part B: **Results: No order**

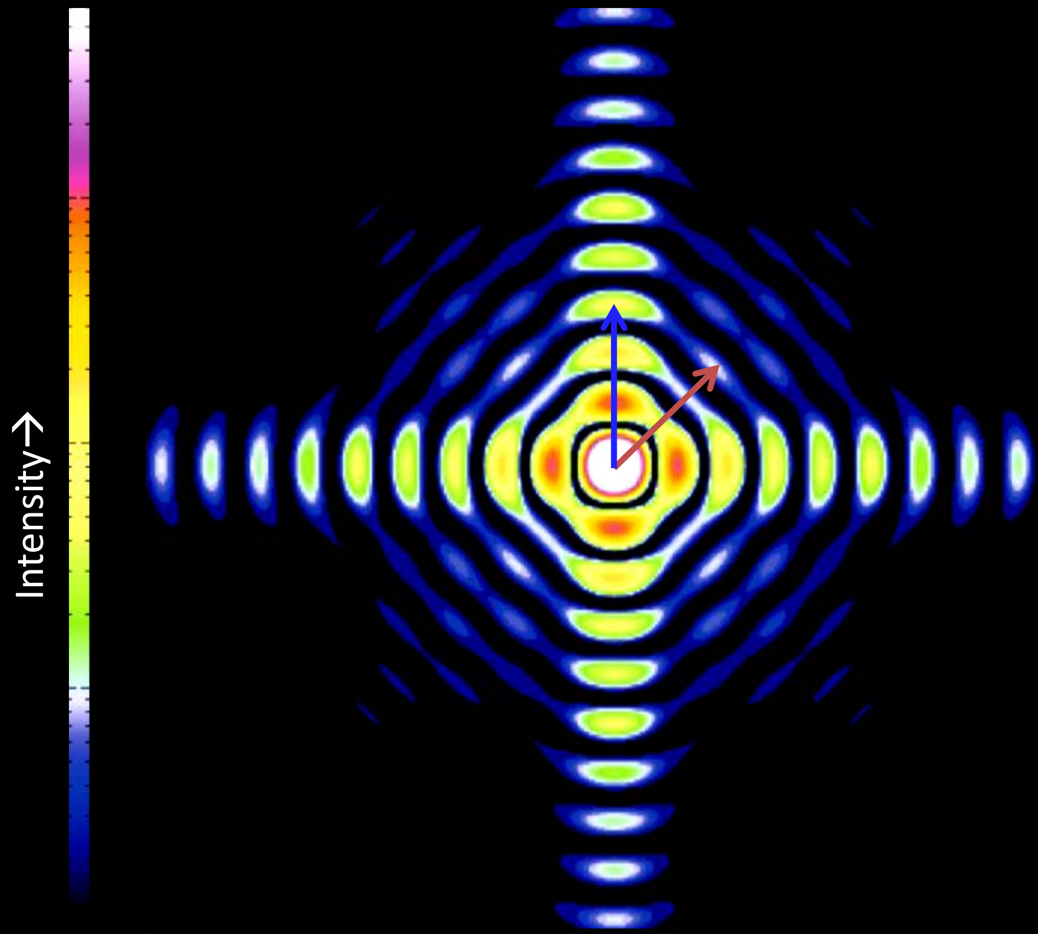


Part B: **Form factor of a superball**

1. Flat faces

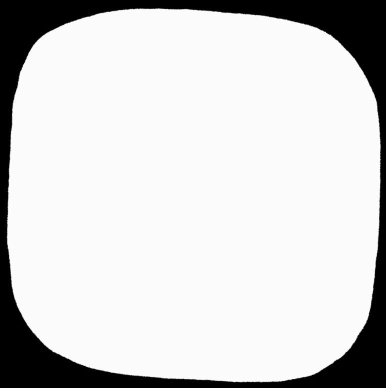
2. What is short in real space…

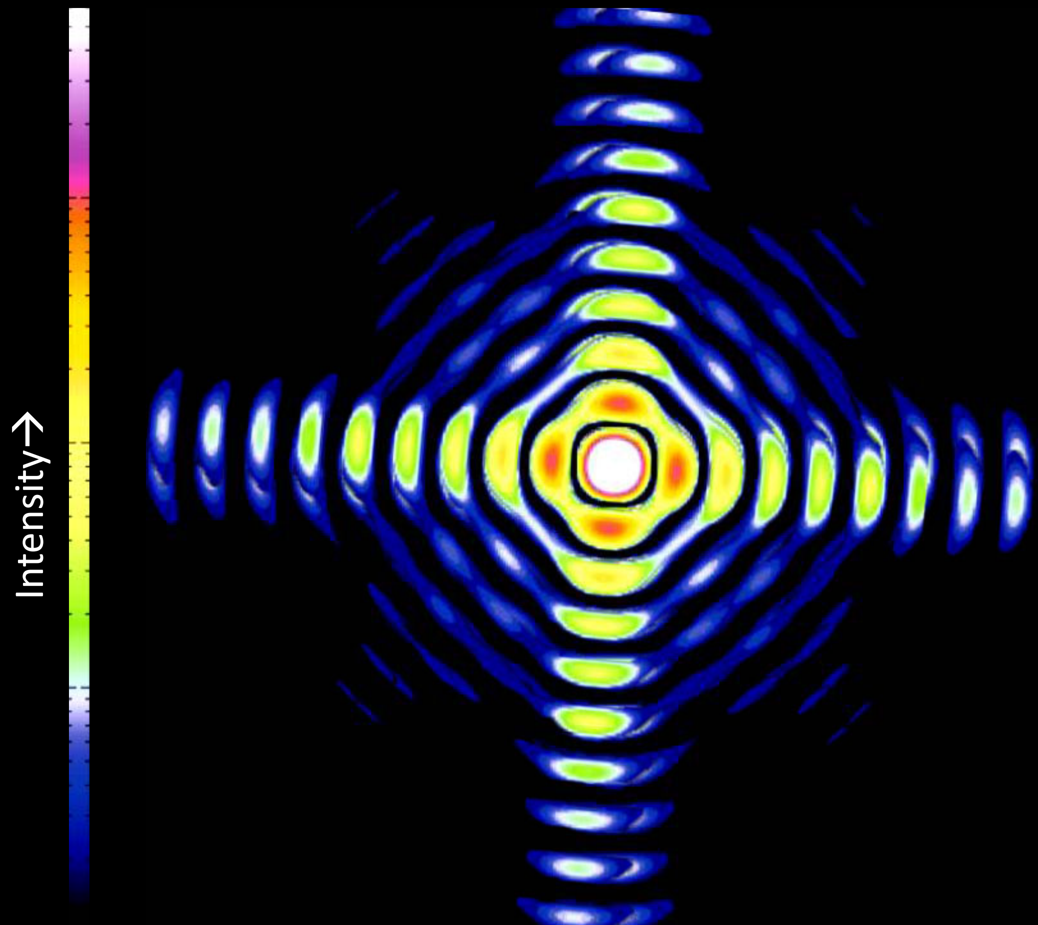




2D form factor of a superball with m = 3.6
Calculated by Janne-Mieke

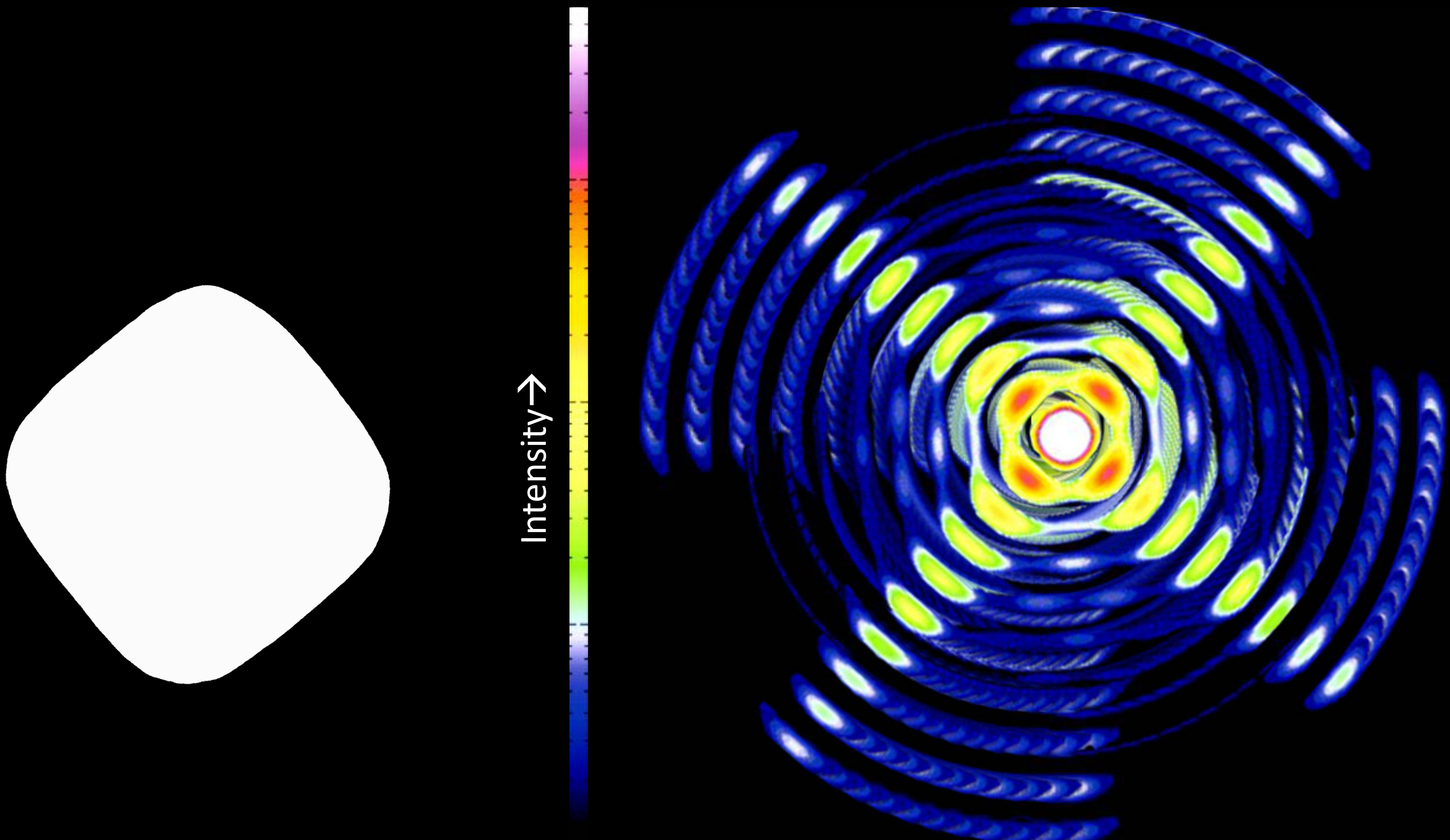
Part B: **Form factor of a superball**





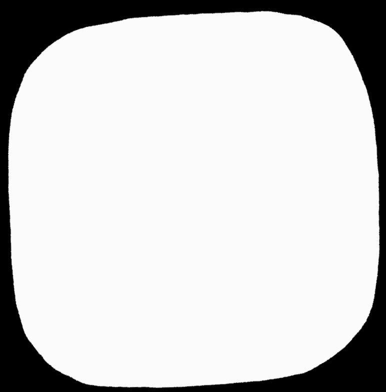
2D form factor of a superball with m = 3.6
Calculated by Janne-Mieke

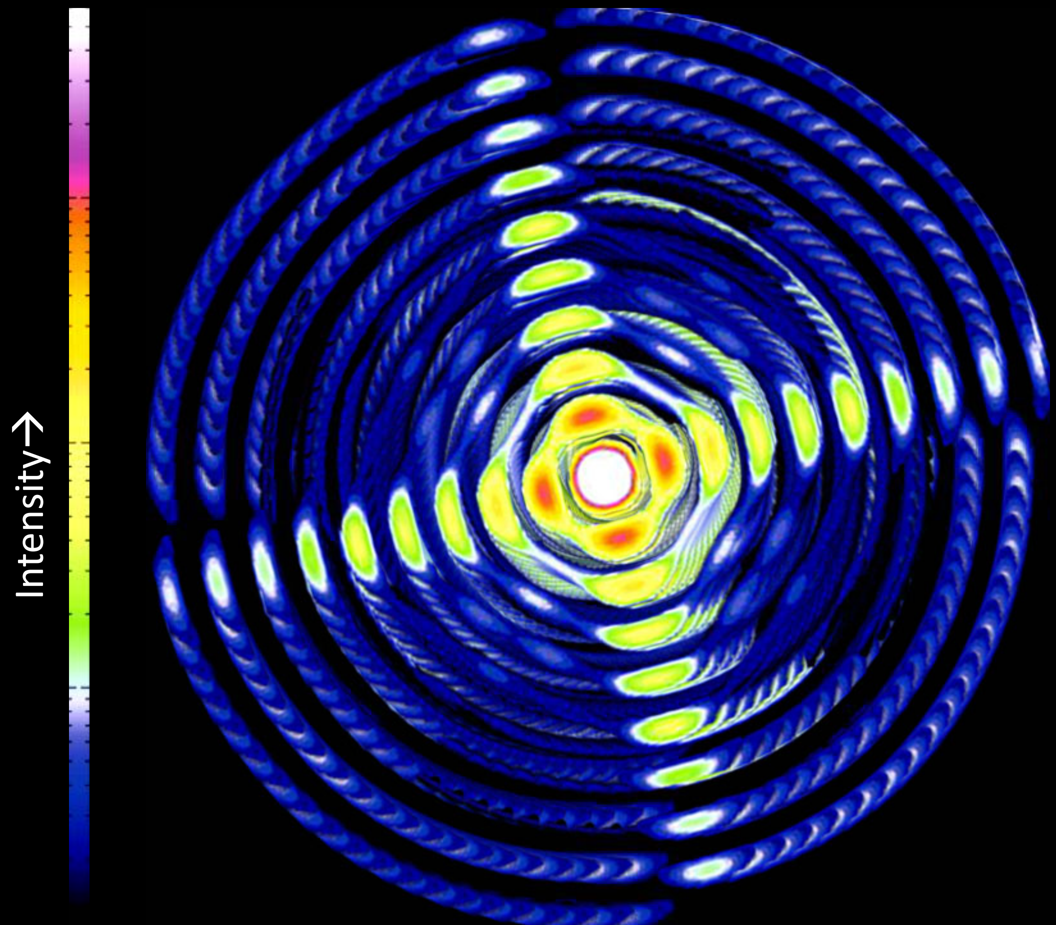
Part B: **Form factor of a superball**



2D form factor of a superball with m = 3.6
Calculated by Janne-Mieke

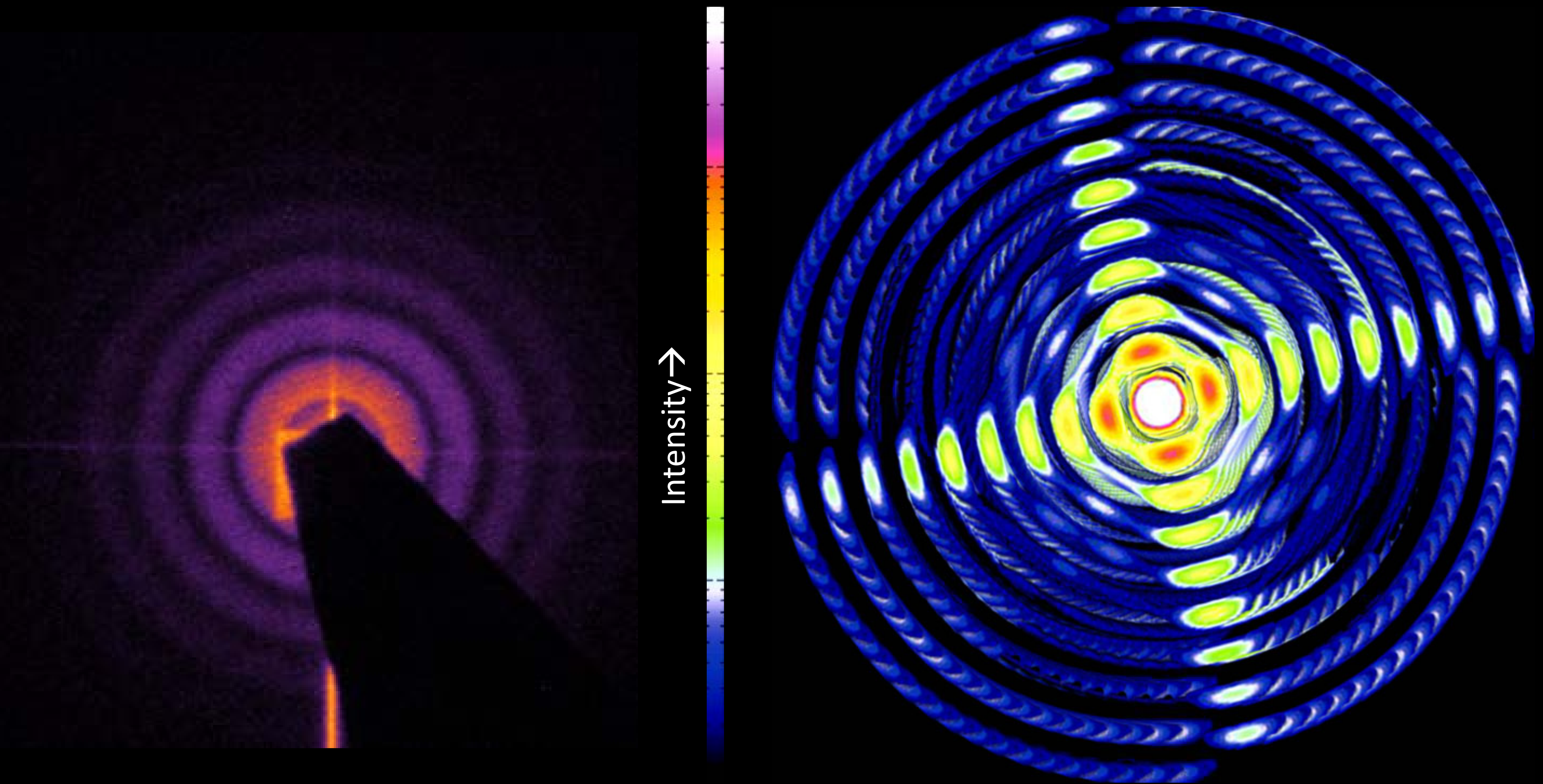
Part B: **Form factor of a superball**





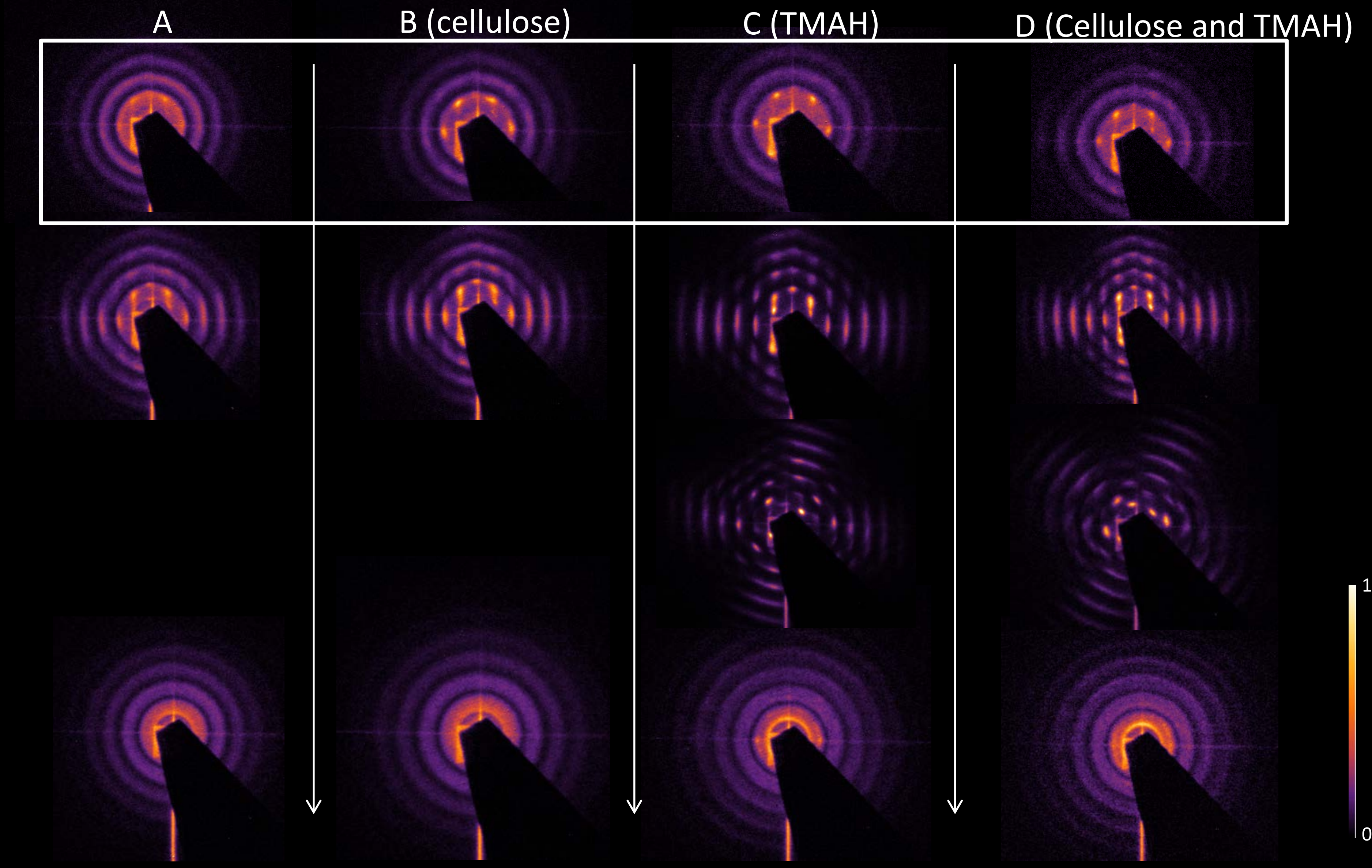
2D form factor of a superball with m = 3.6
Calculated by Janne-Mieke

Part B: **Form factor of a superball**

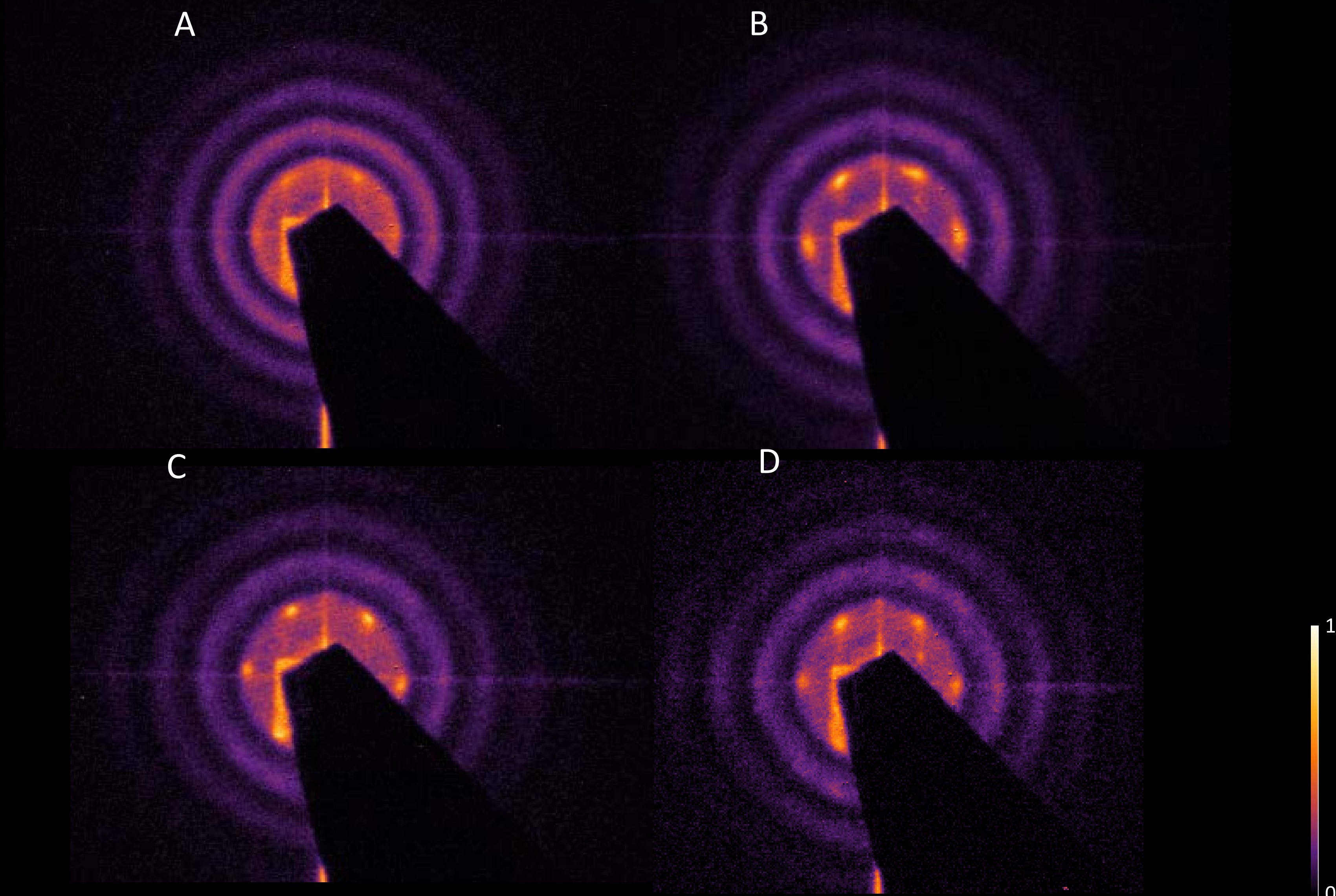


2D form factor of a superball with m = 3.6
Calculated by Janne-Mieke

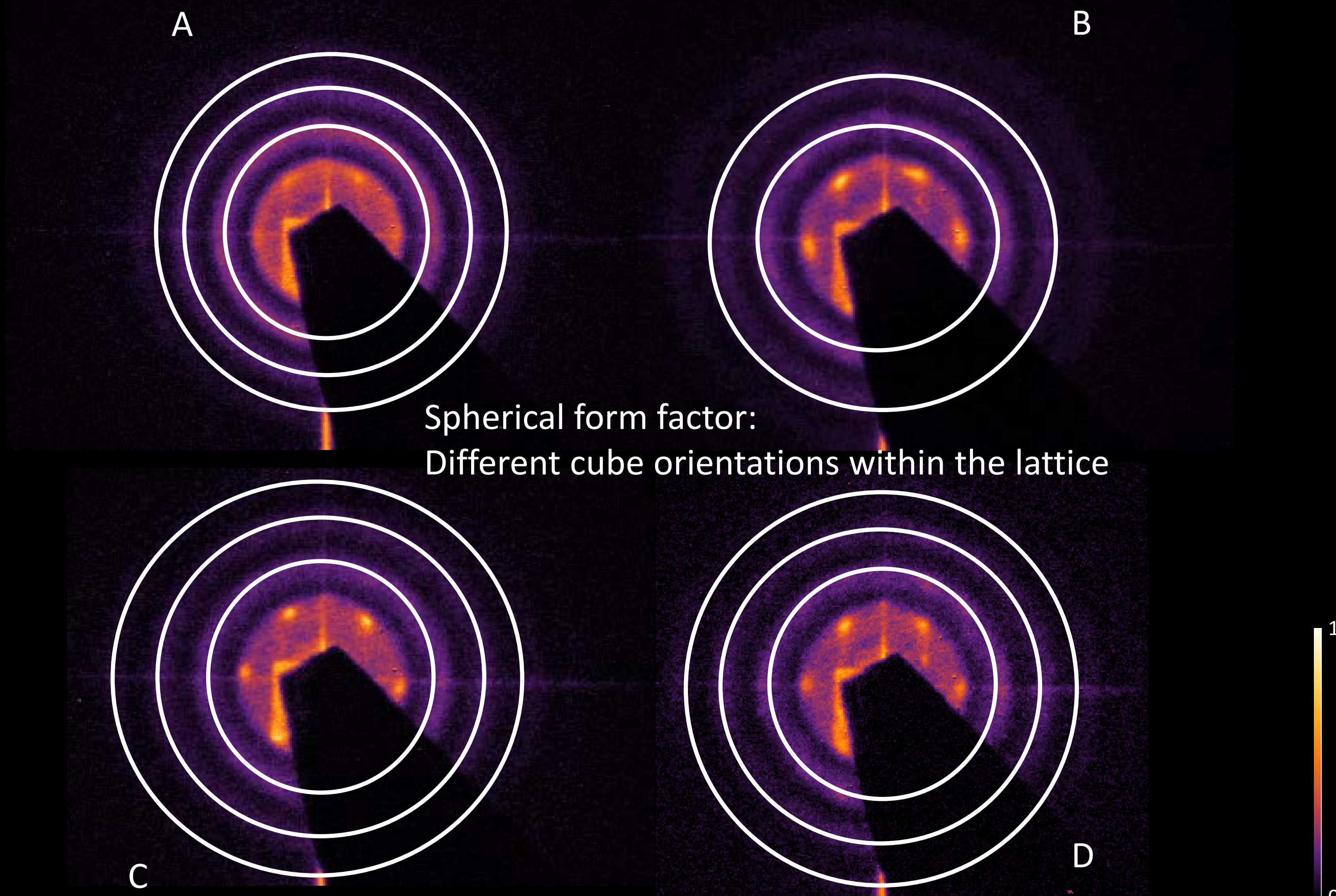
Part B: **Results: Rotator hexagonal**



Part B: **Results: Rotator hexagonal**

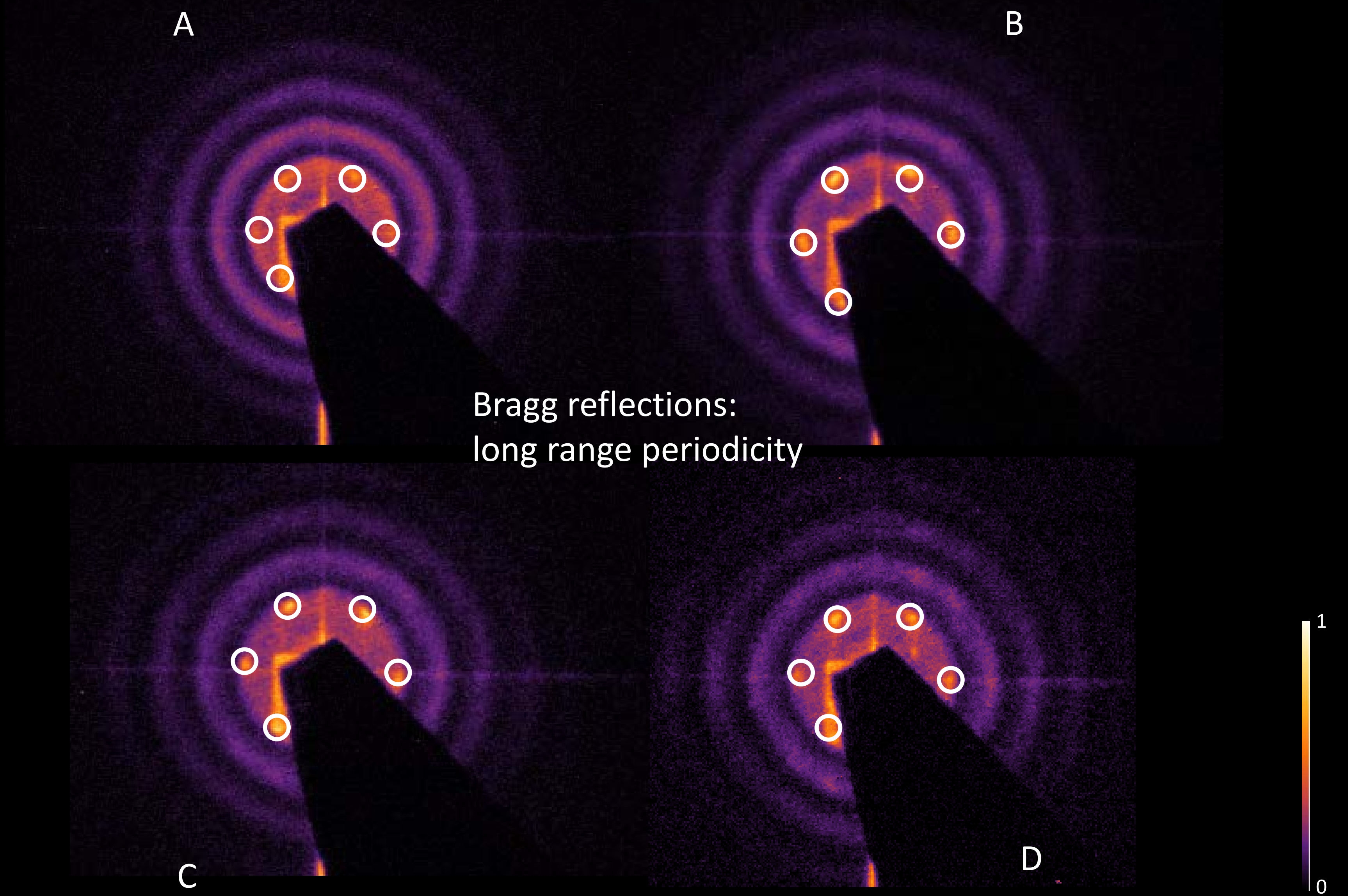


Part B: **Results: Rotator hexagonal**

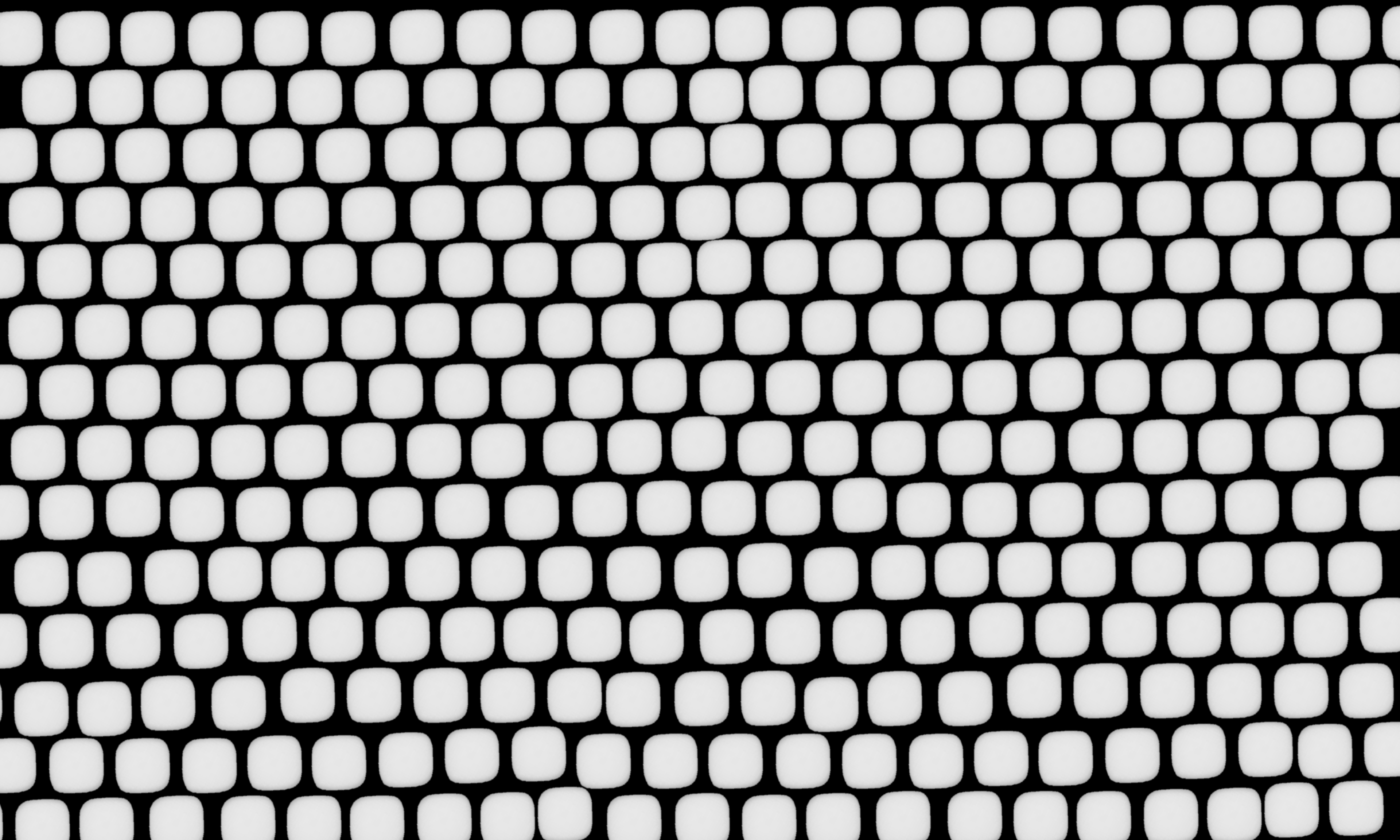


Spherical form factor:
Different cube orientations within the lattice

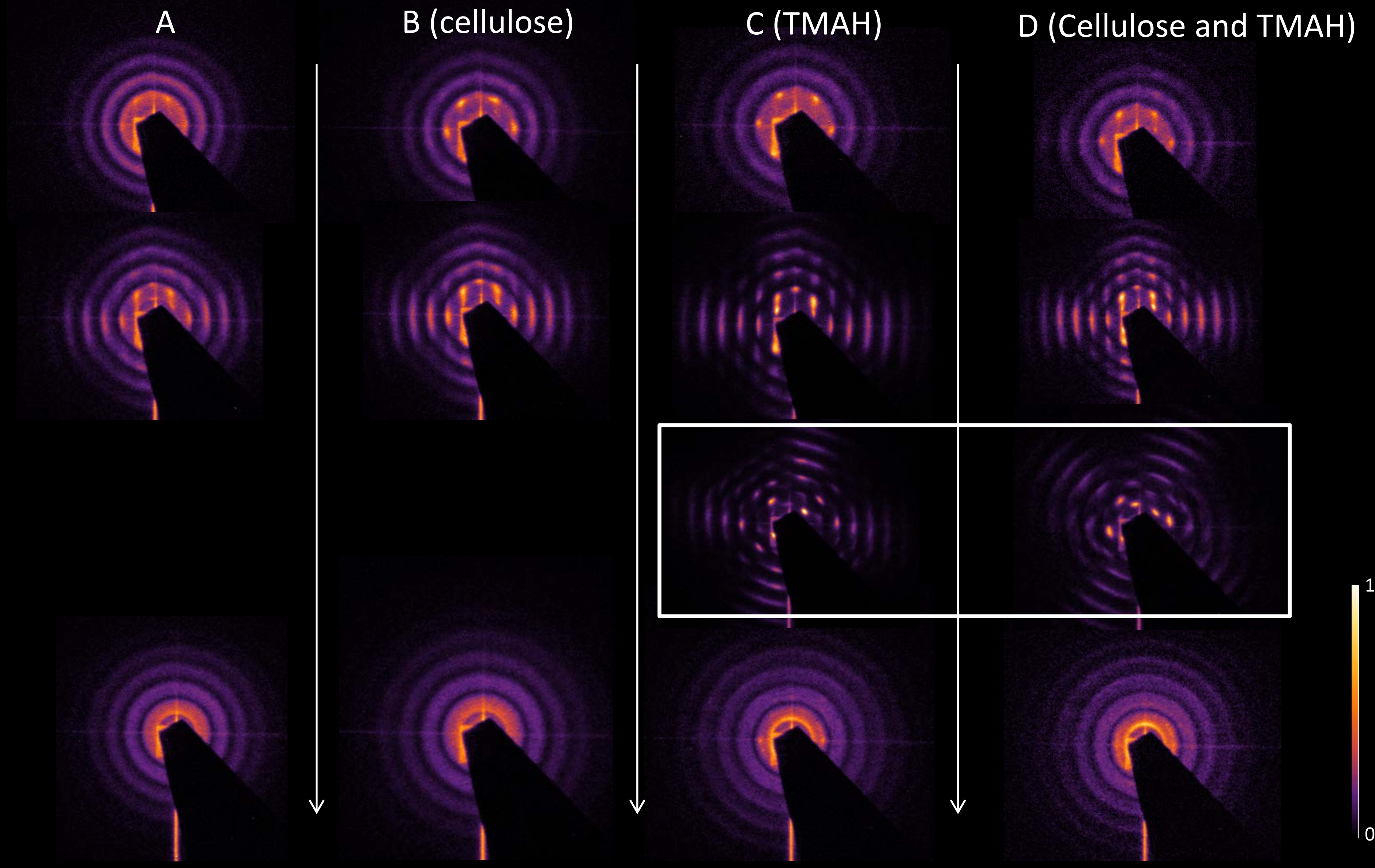
Part B: **Results: Rotator hexagonal**



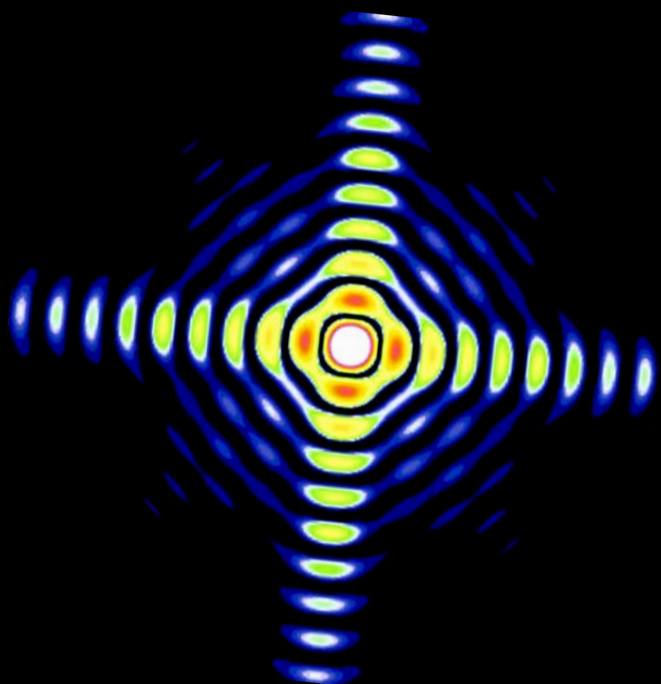
Part B: **Rotator hexagonal**



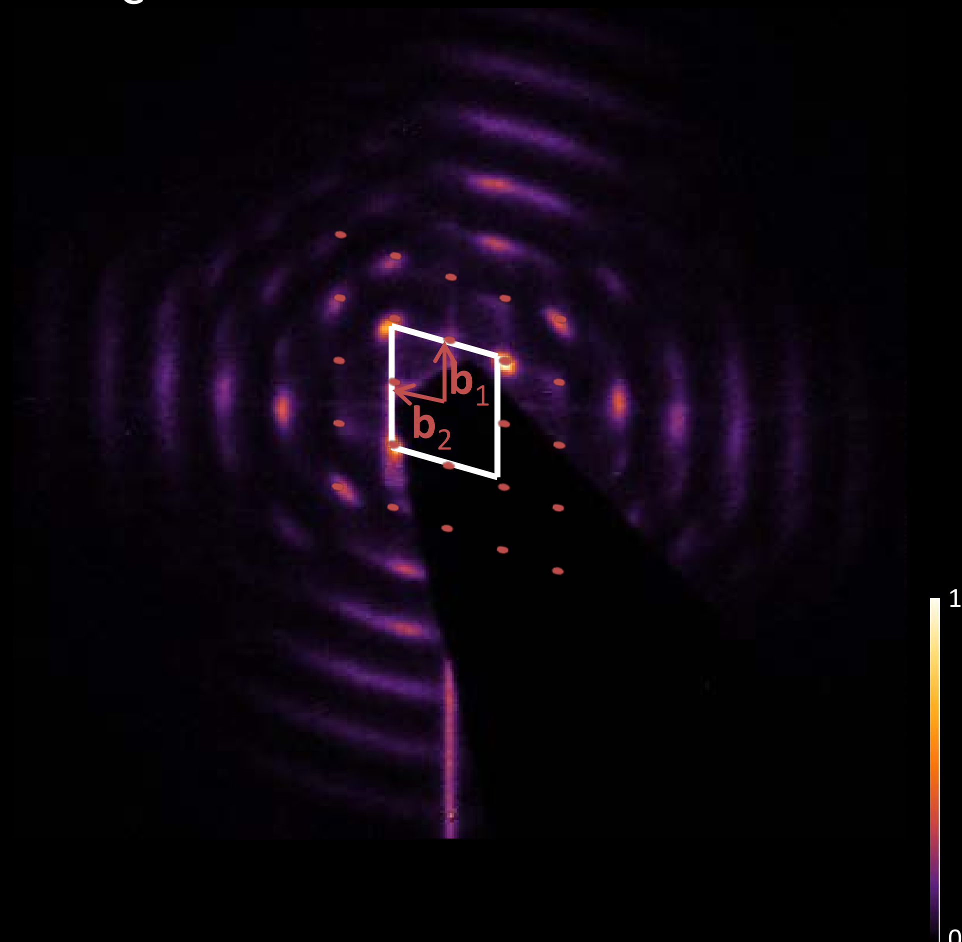
Part B: **Results: Rhombic**



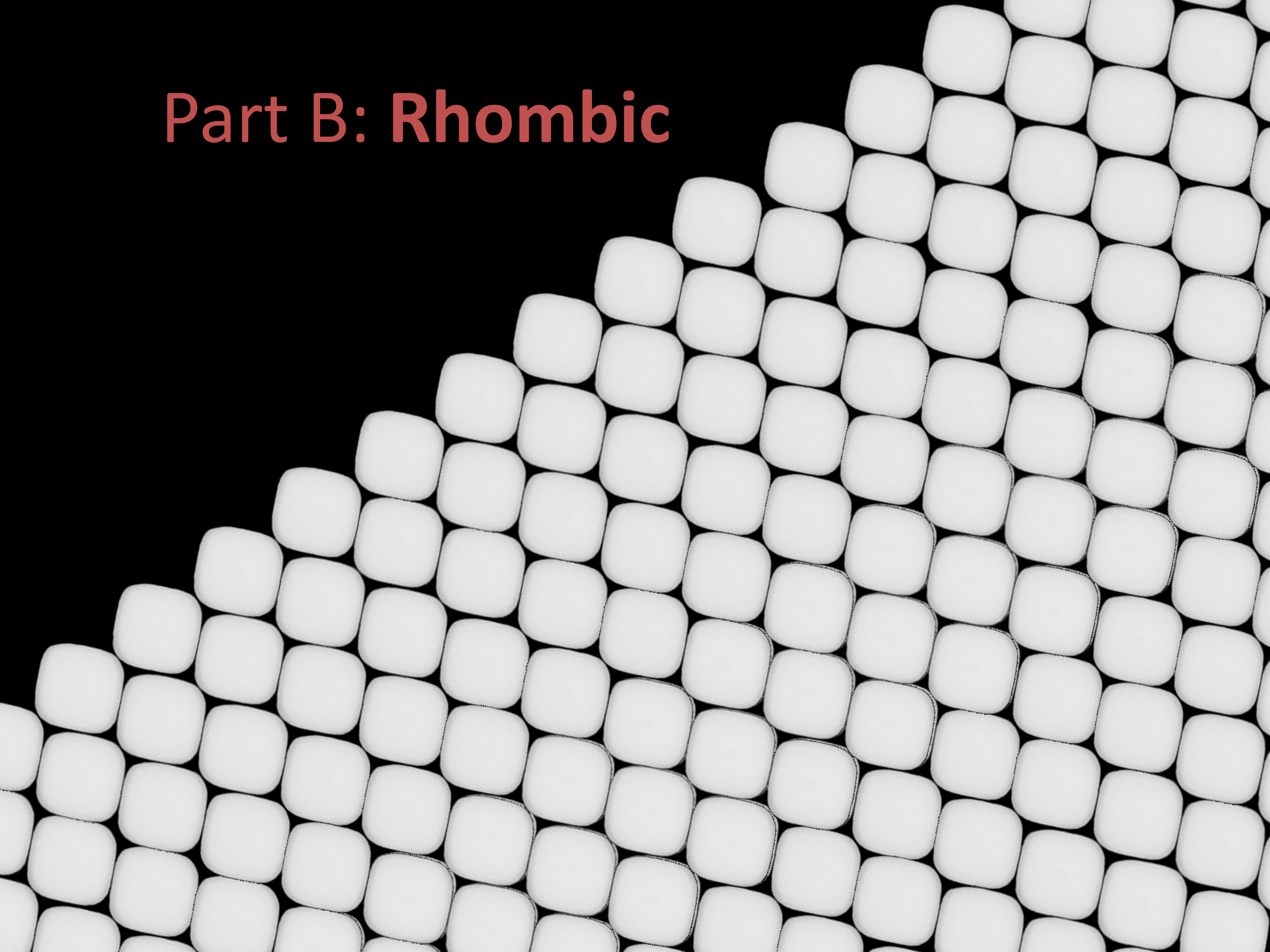
Part B: **Results: Rhombic**



C

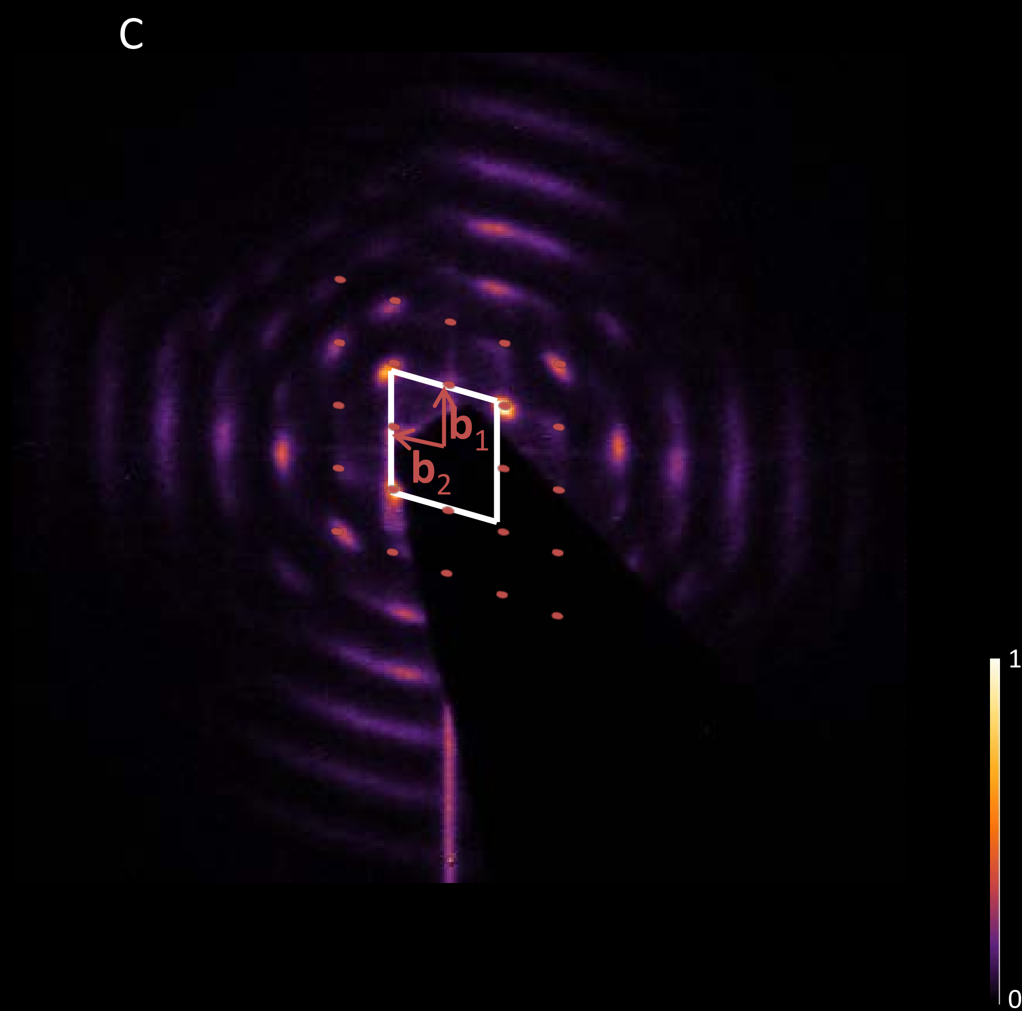


Part B: **Rhombic**

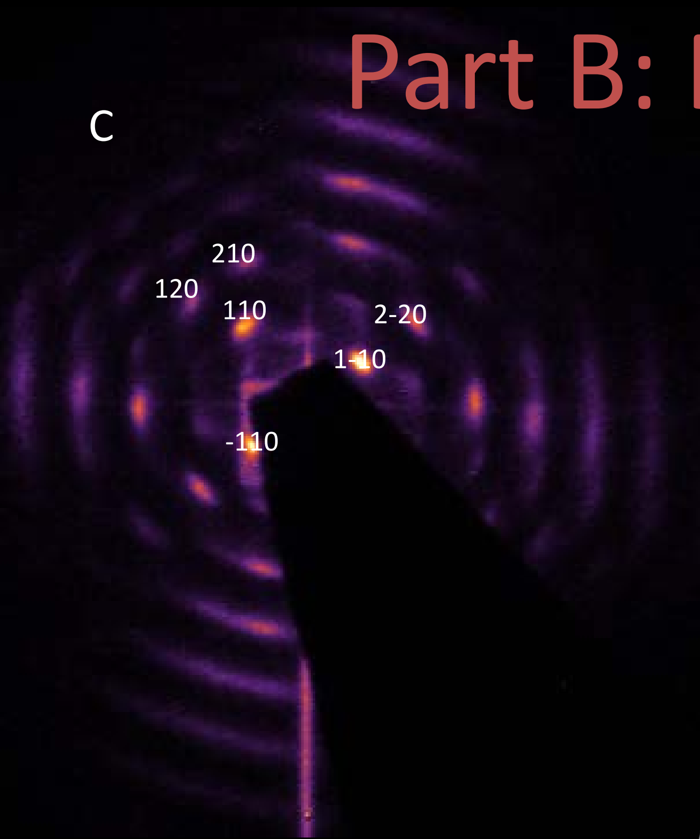


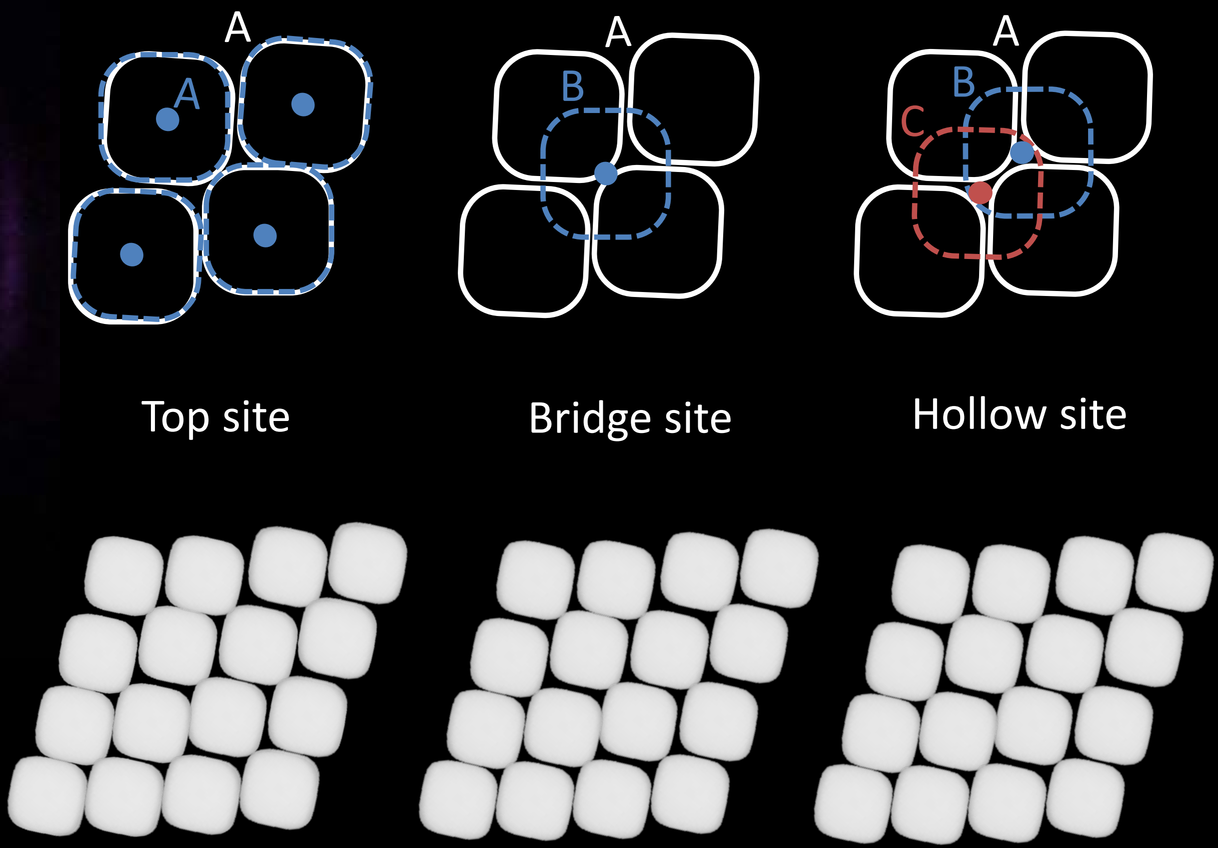
Part B: **Rhombic: Stacking**

Intensities:
Some peaks are
hardly visible.
Why?

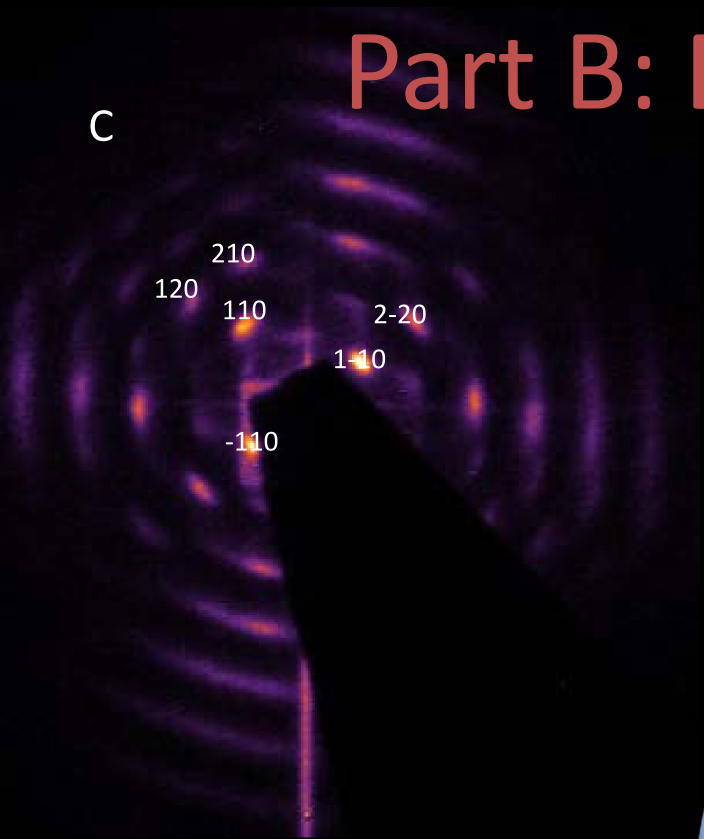


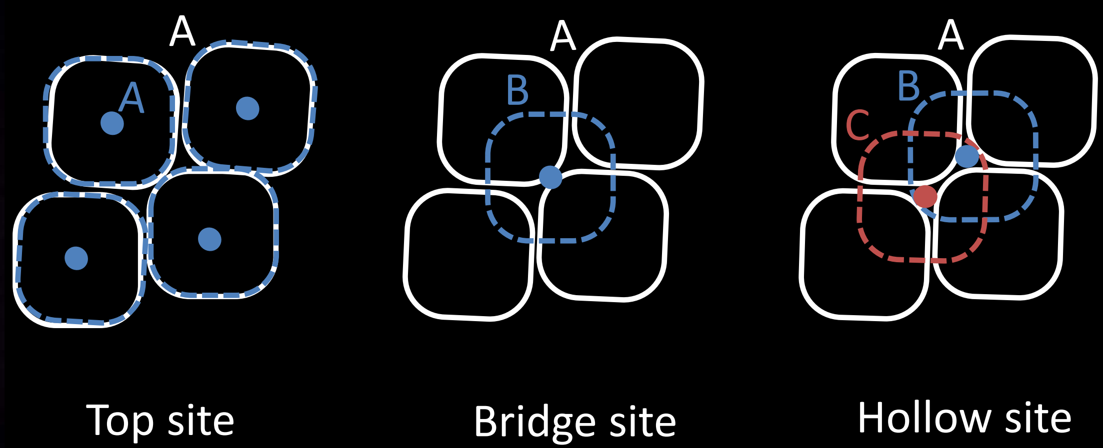
Part B: **Rhombic: Stacking**

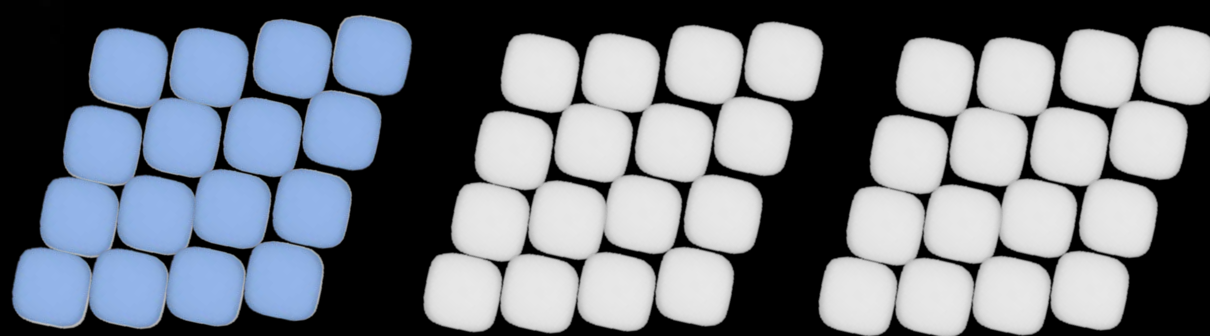




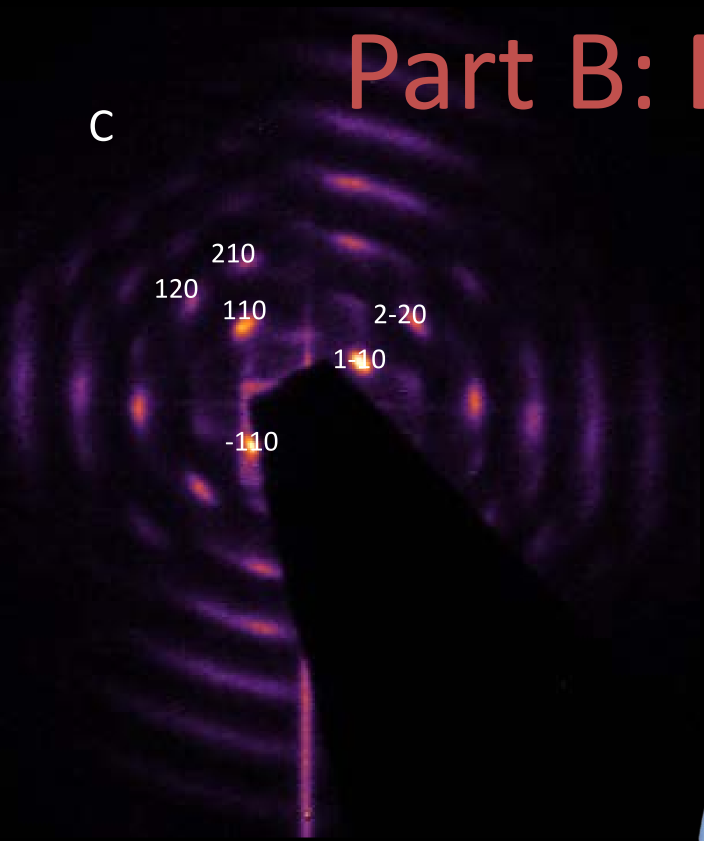
Part B: **Rhombic: Stacking**

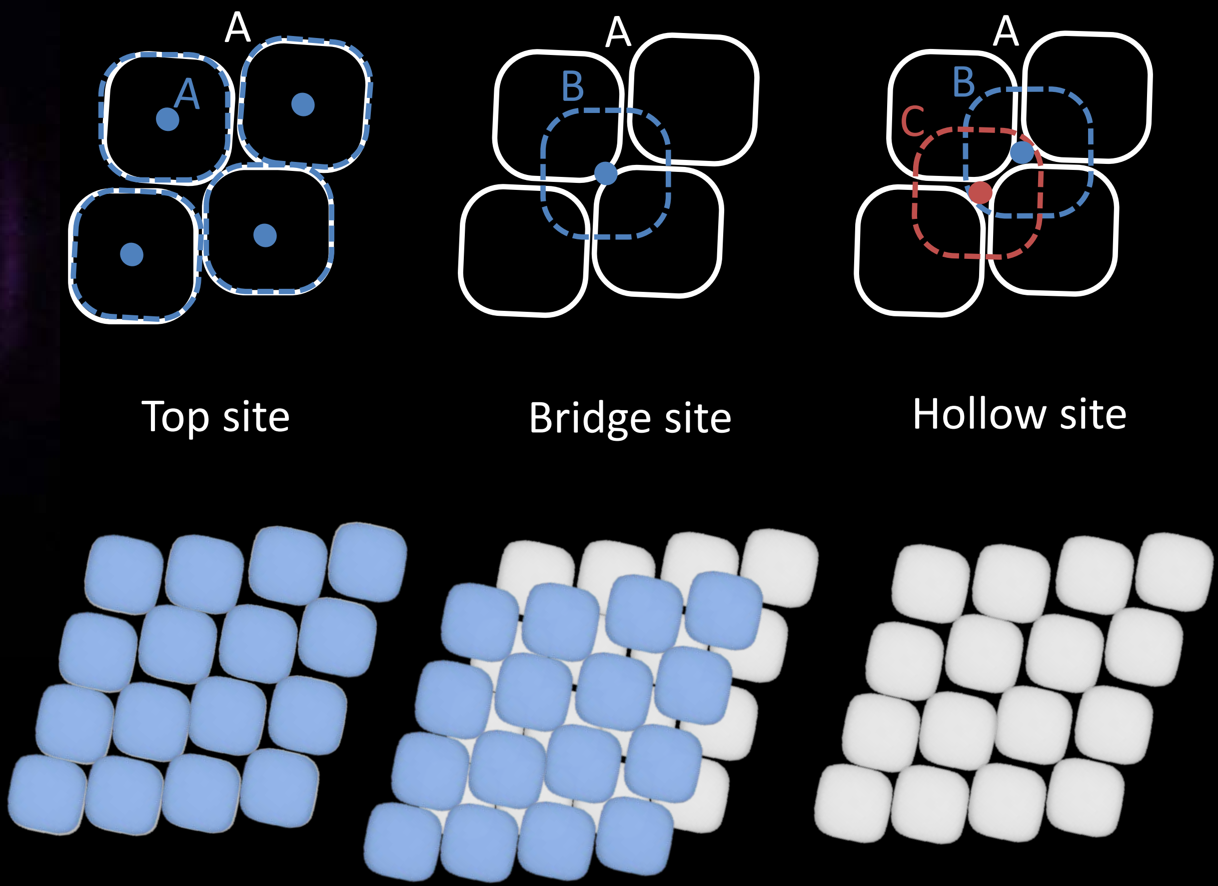




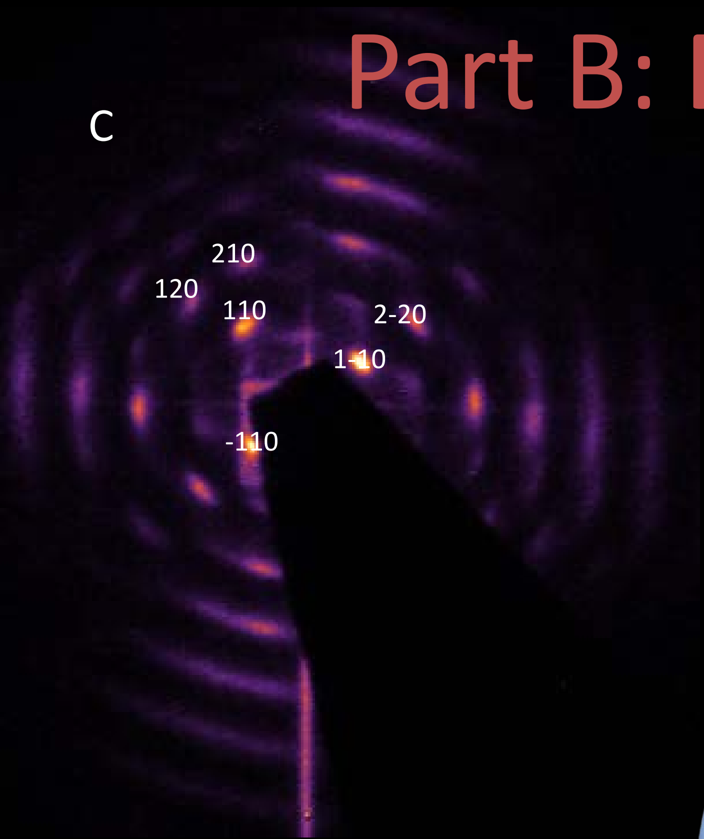


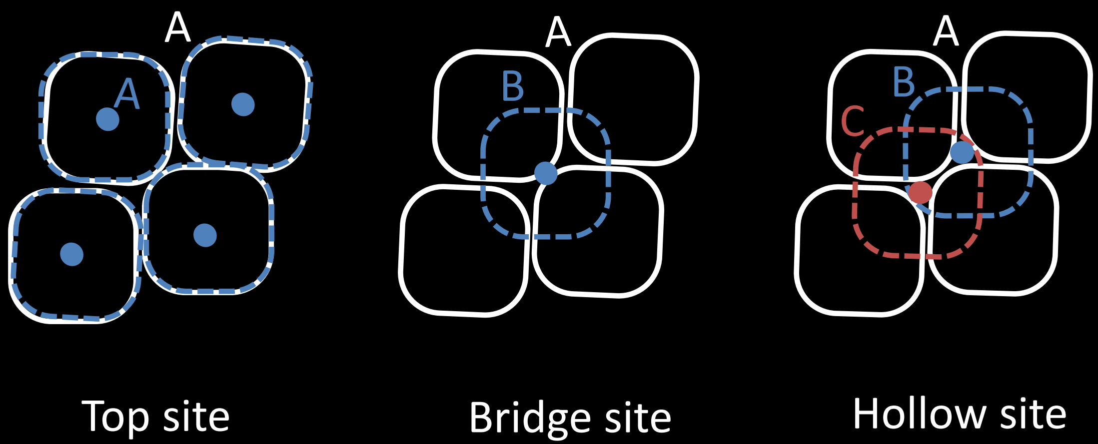
Part B: **Rhombic: Stacking**

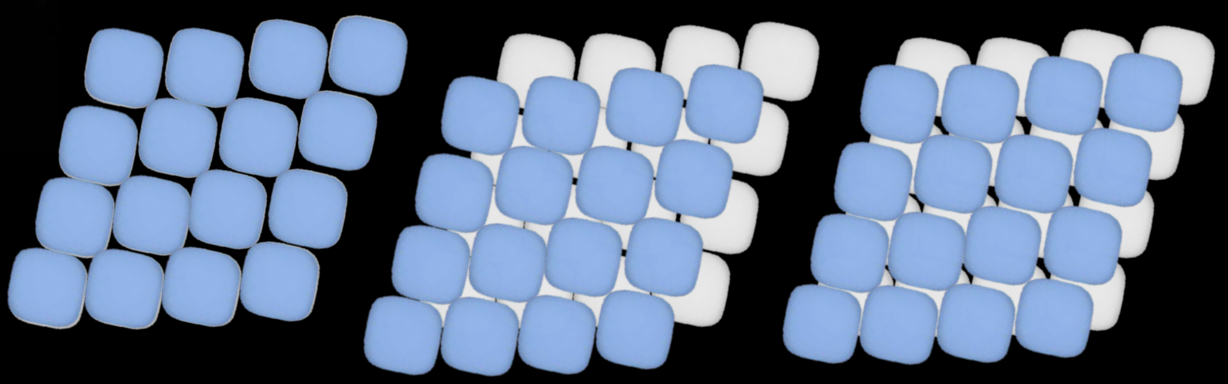




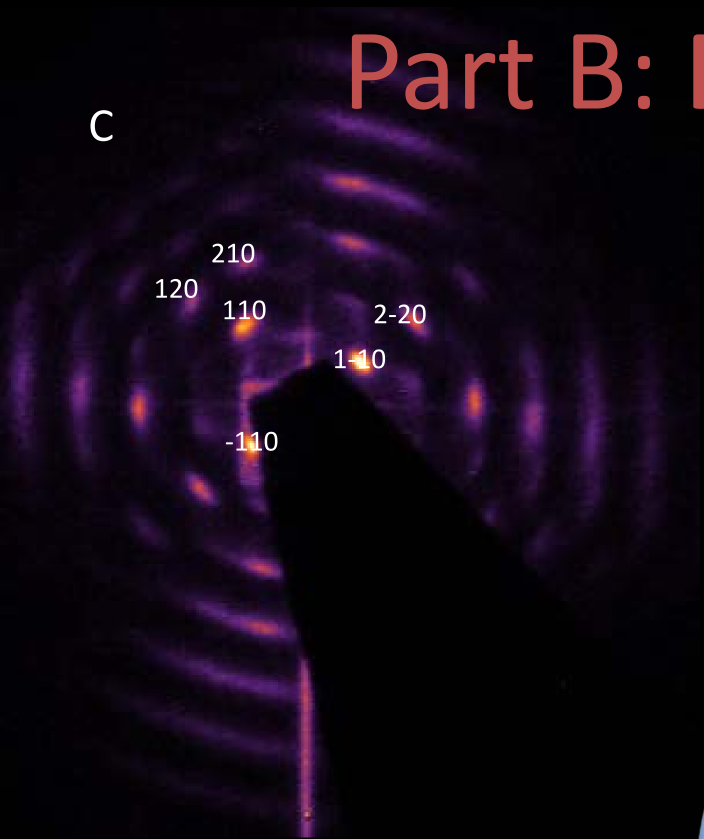
Part B: **Rhombic: Stacking**

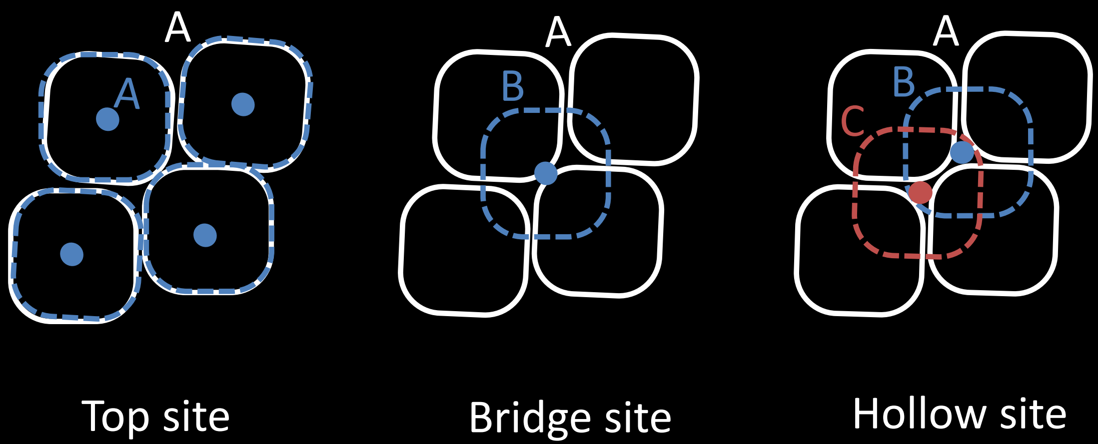


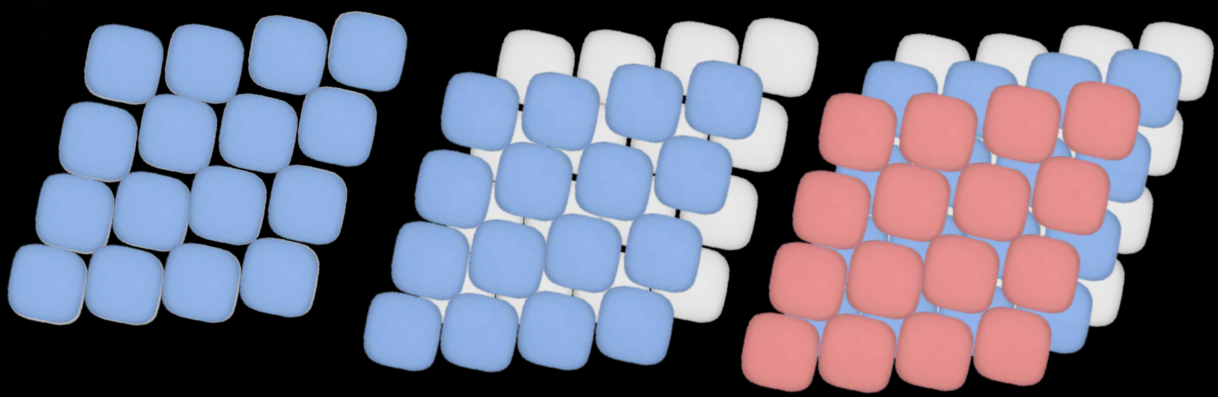




Part B: **Rhombic: Stacking**

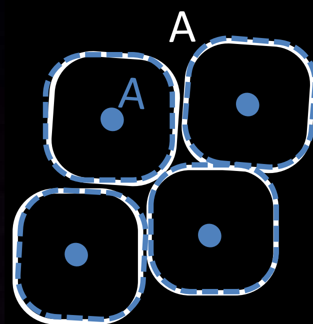




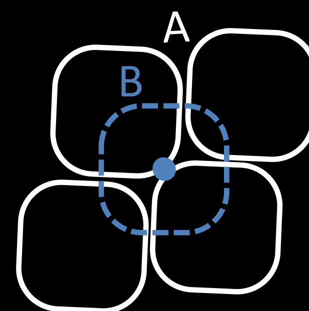


Part B: **Rhombic: Stacking**

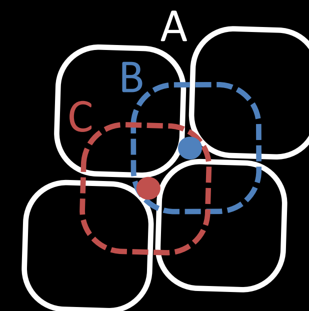
100?



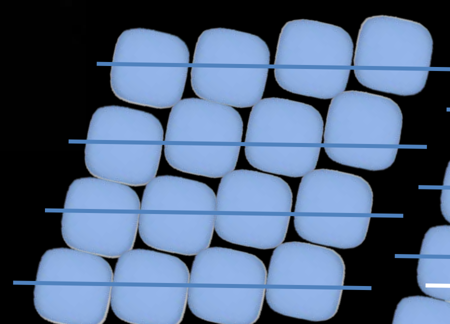
Top site



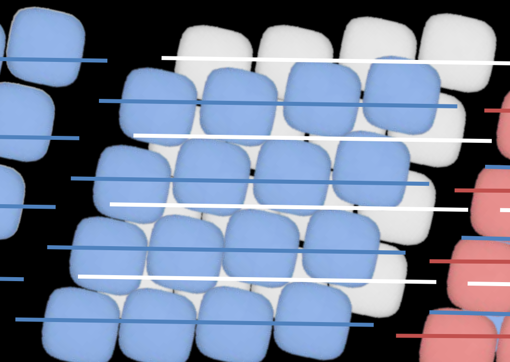
Bridge site



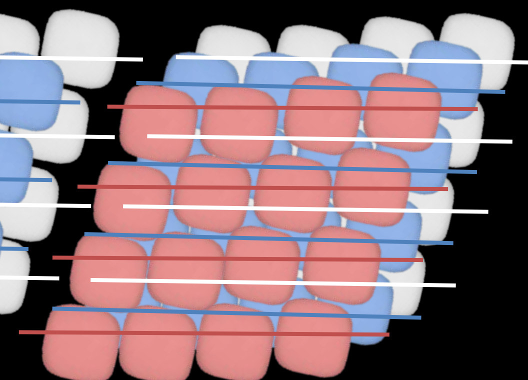
Hollow site



100 peak

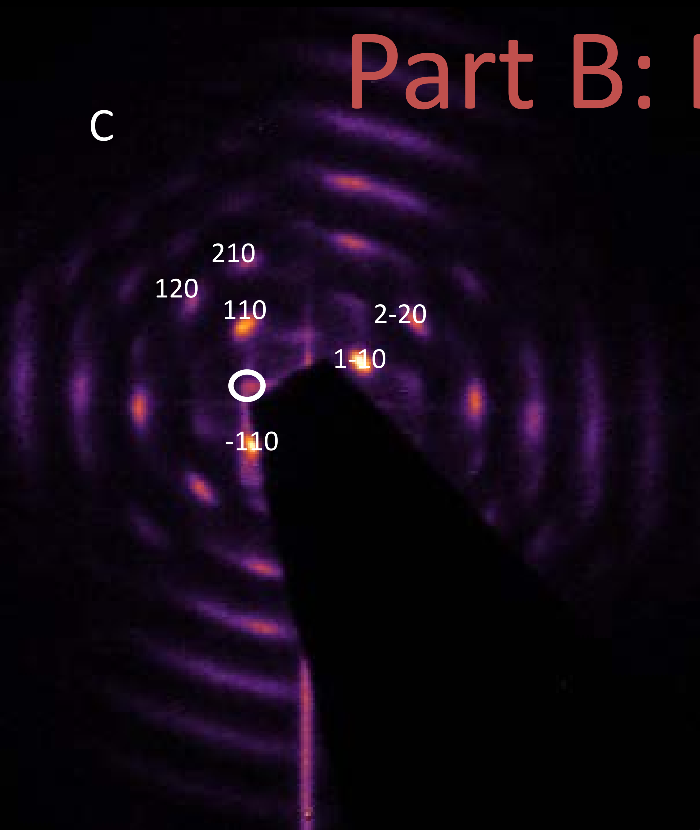


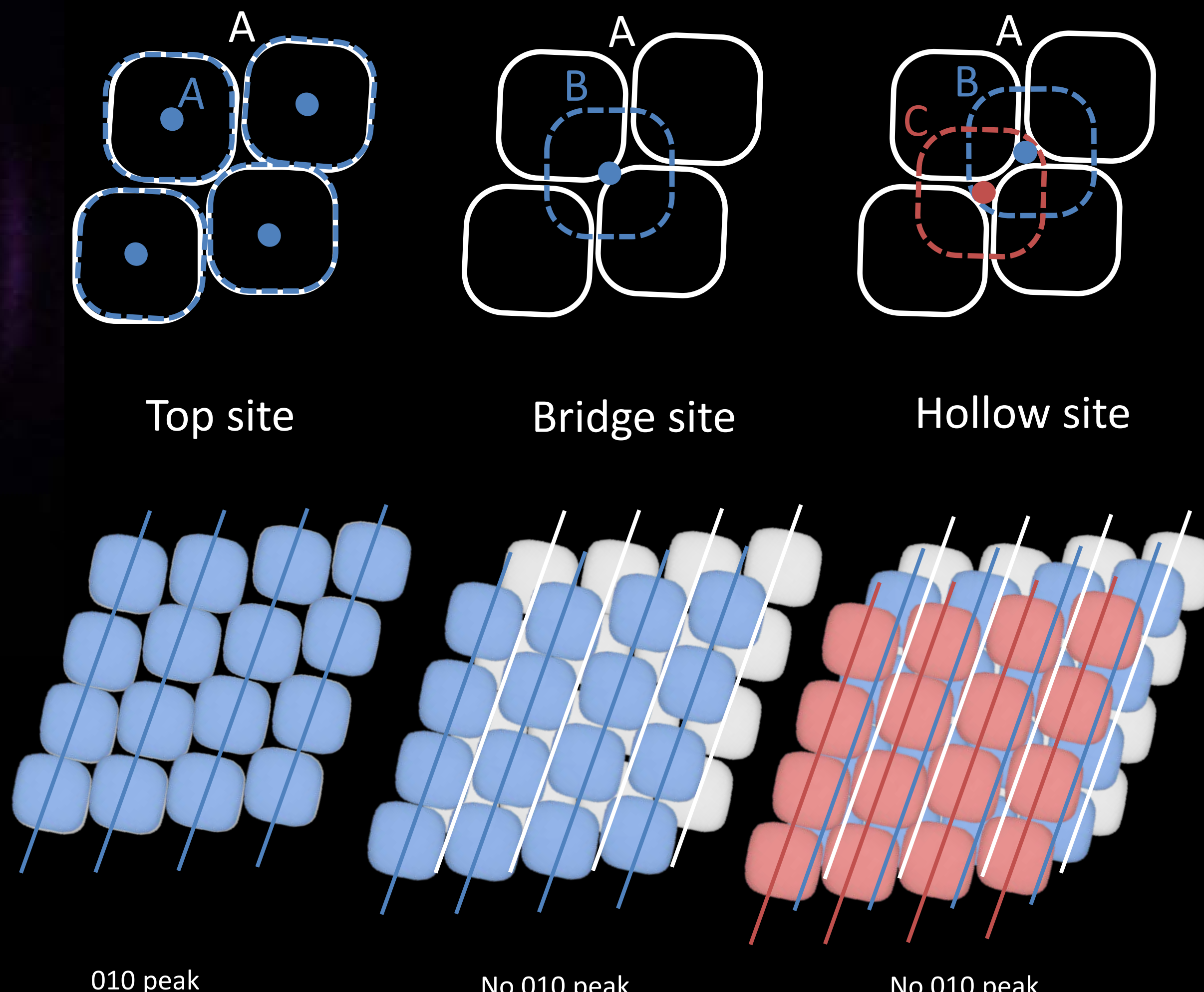
No 100 peak



No 100 peak

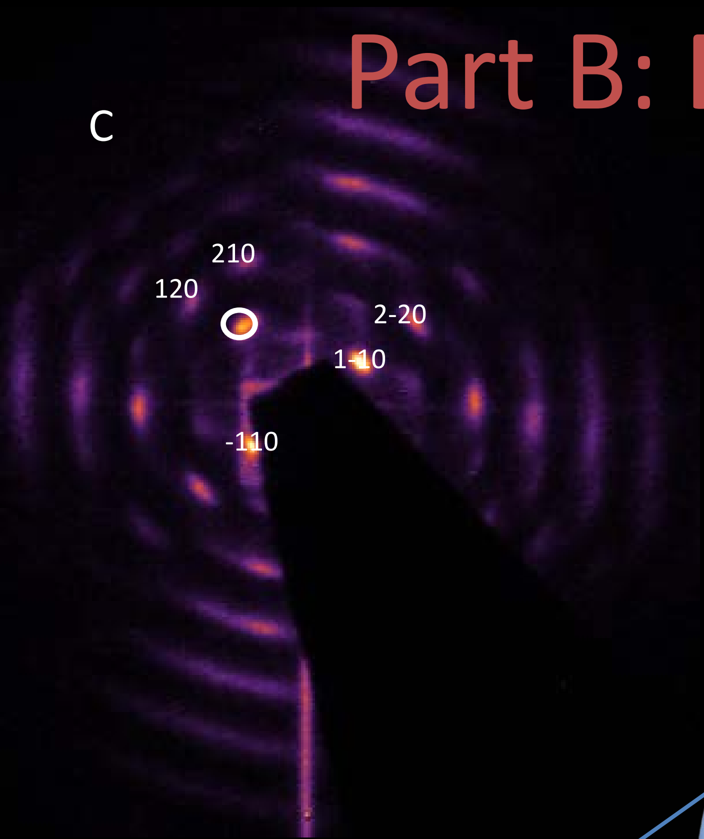
Part B: **Rhombic: Stacking**



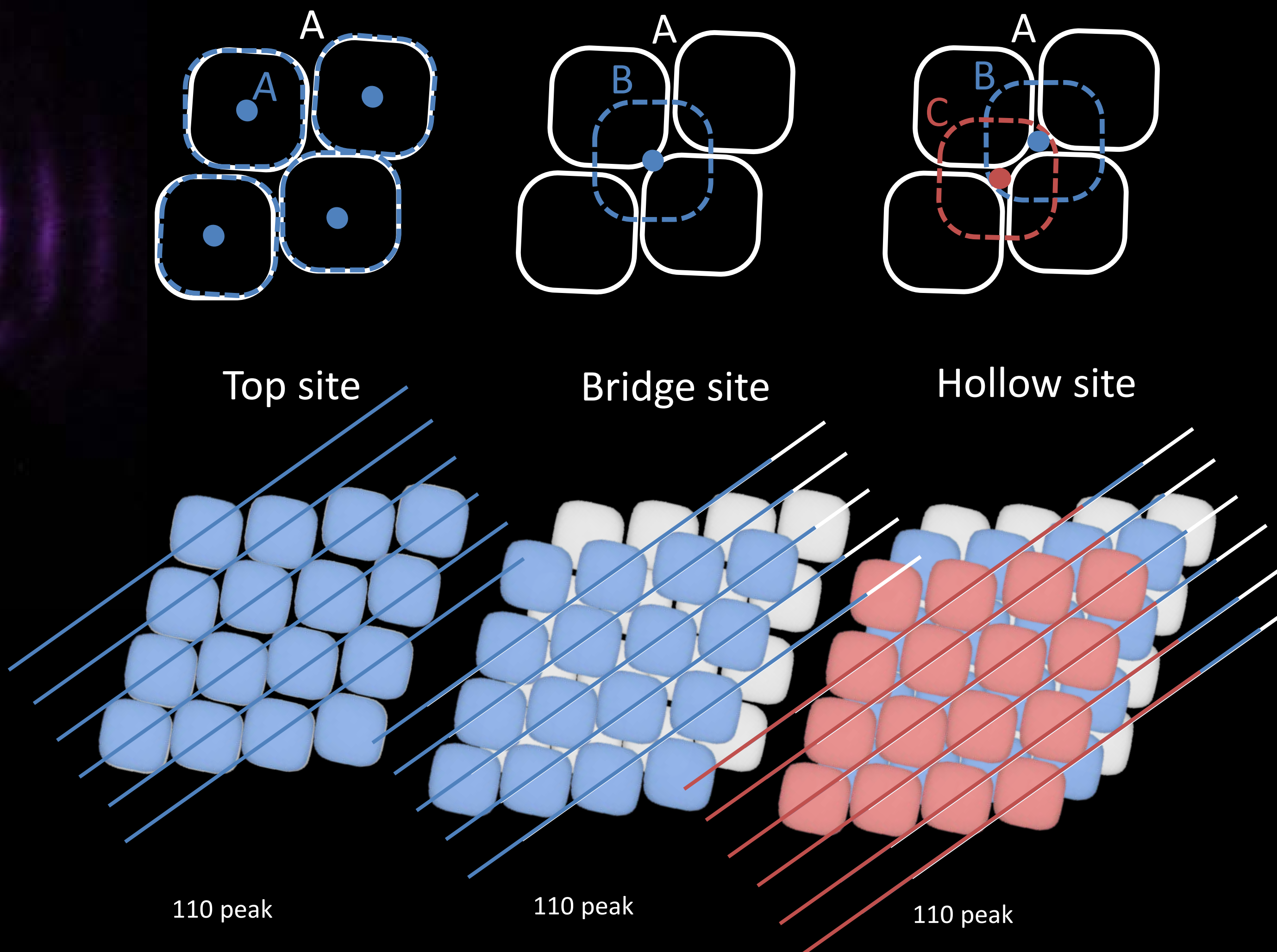


010?

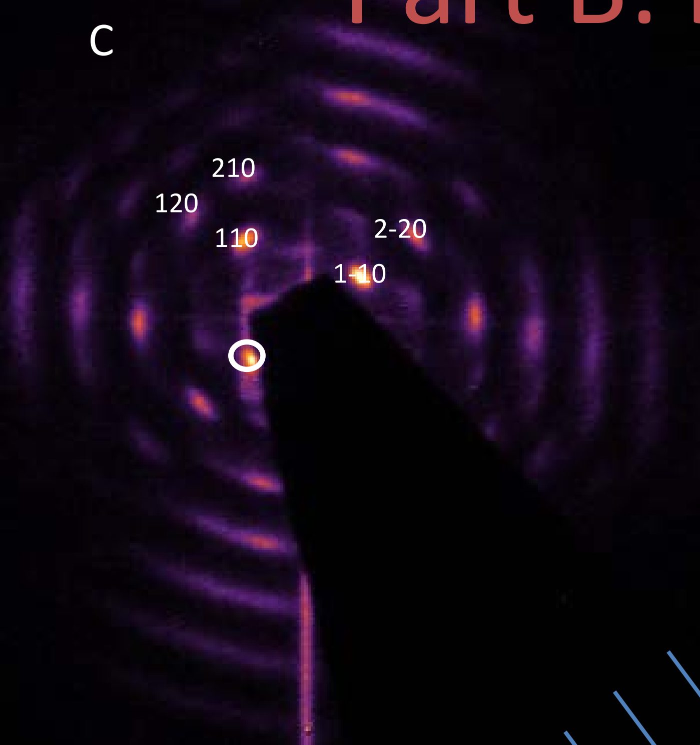
Part B: Rhombic: Stacking



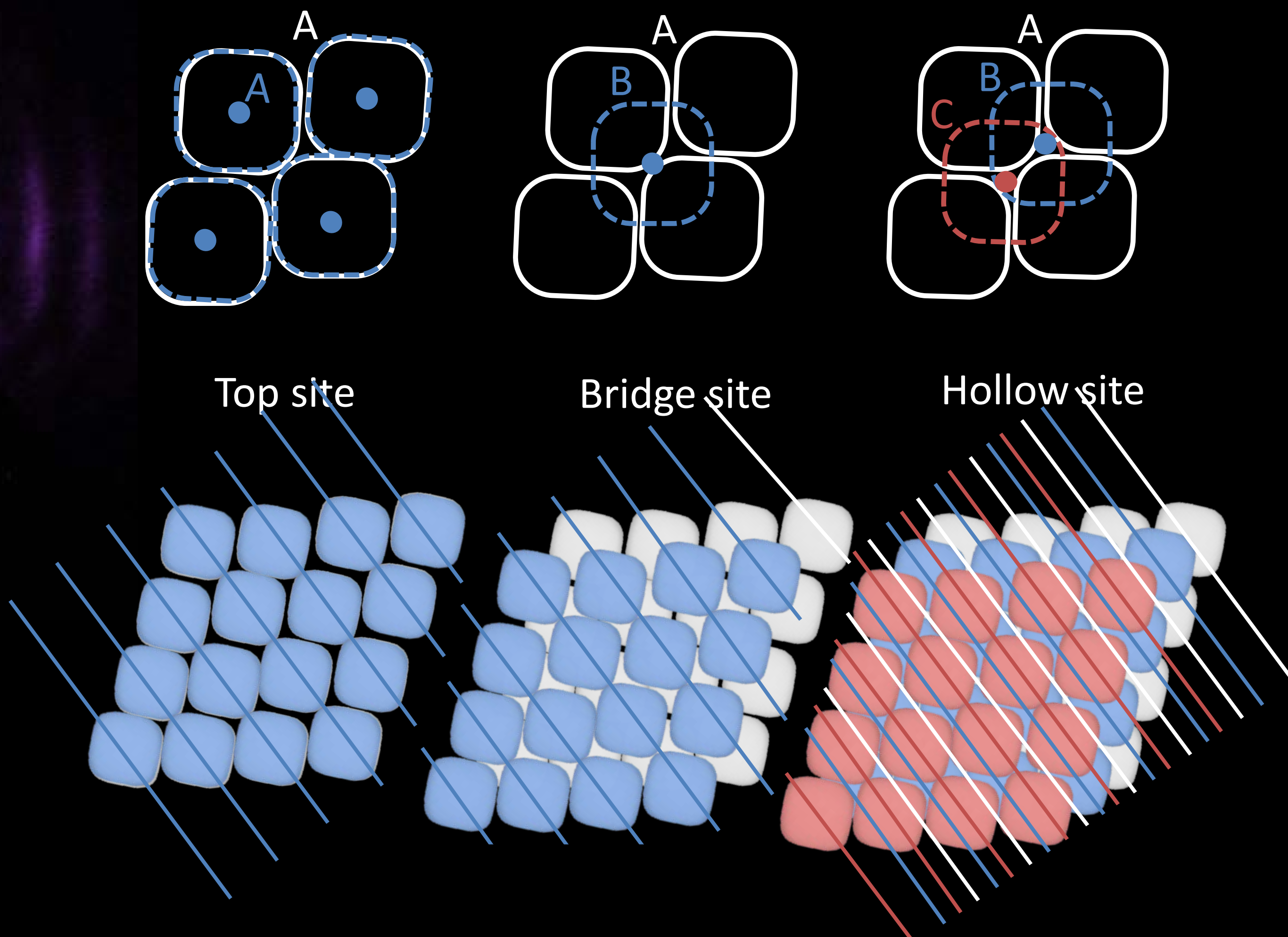
110?



Part B: **Rhombic: Stacking**



-110?

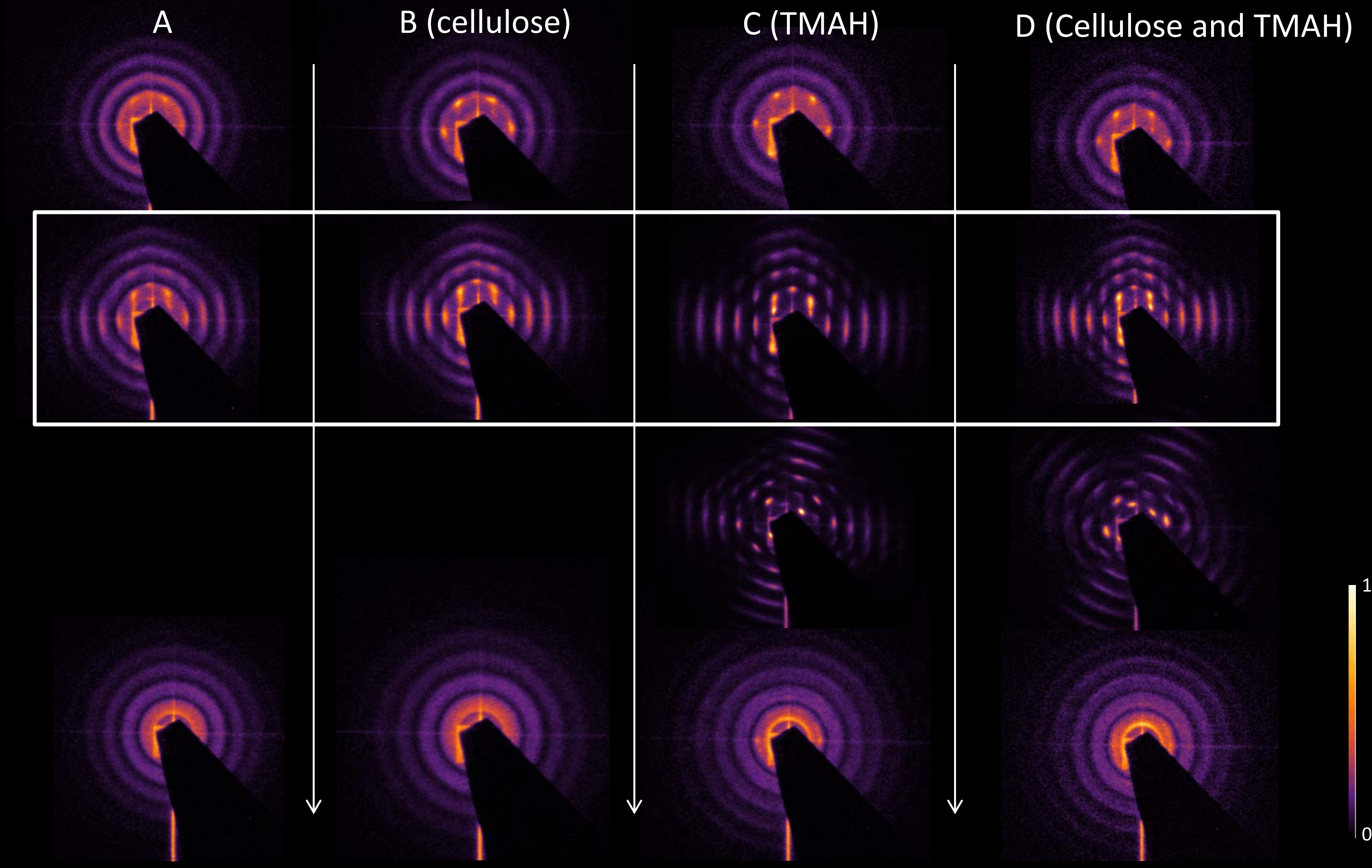


-110 peak

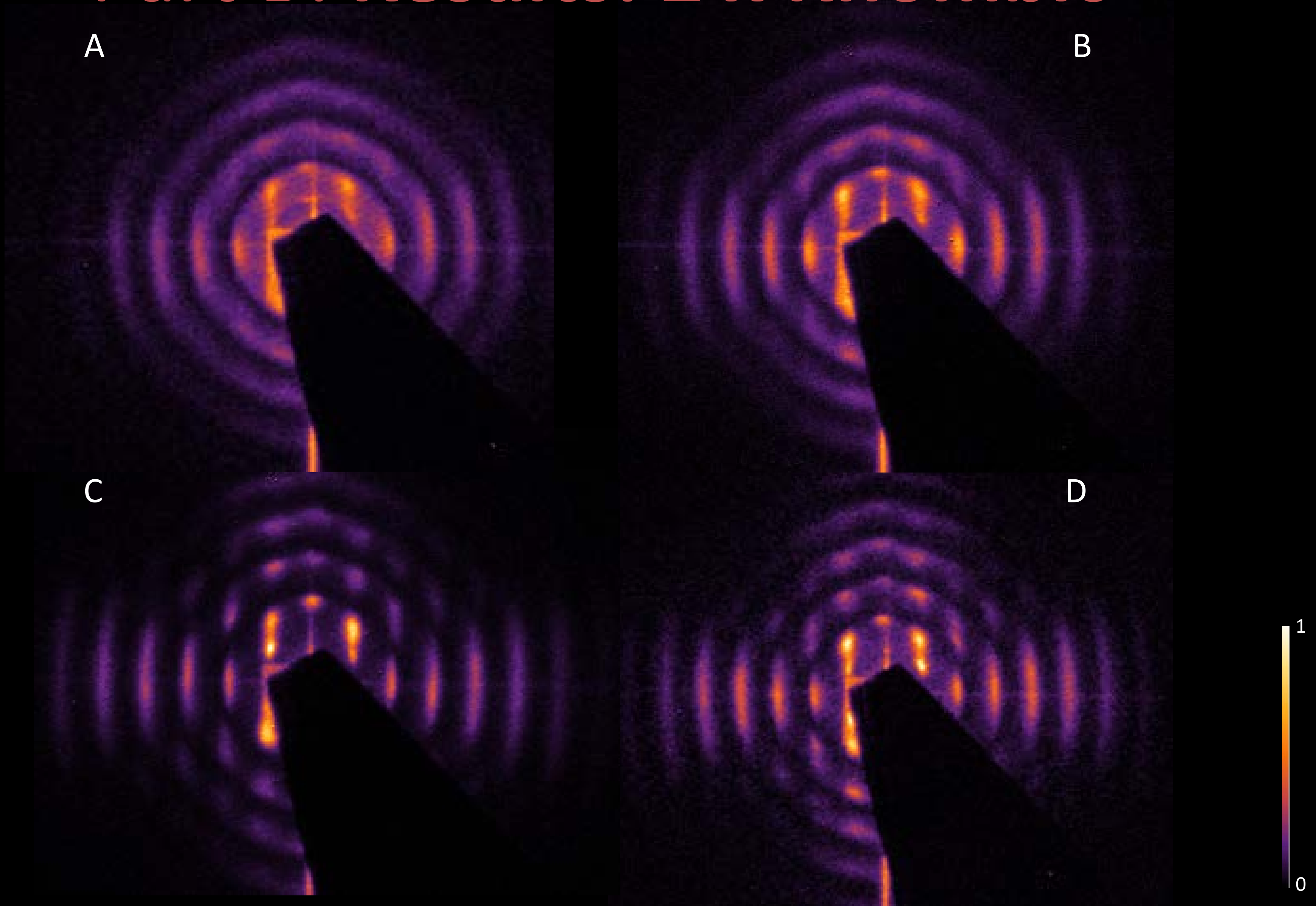
-110 peak

No -110 peak

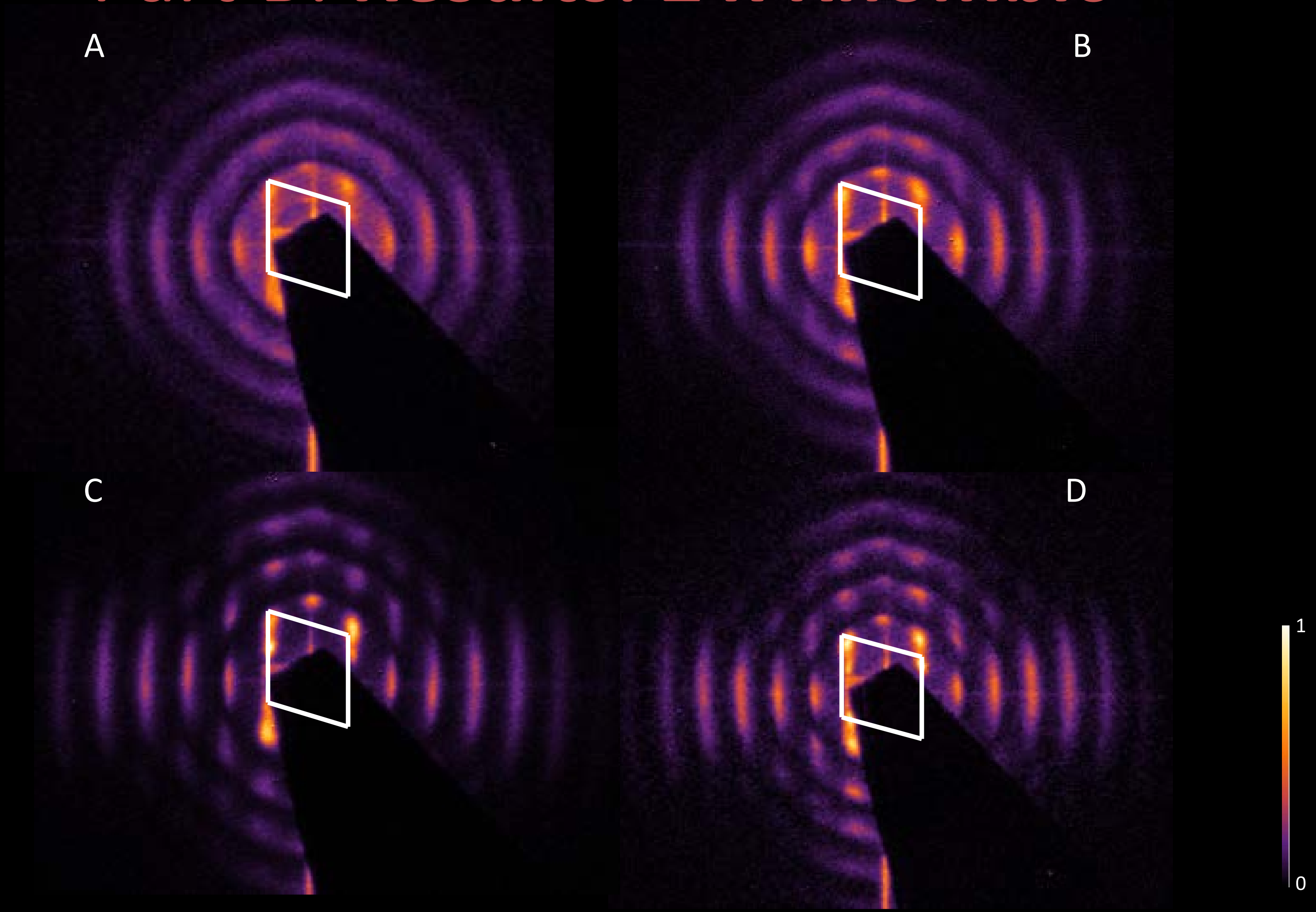
Part B: **Results: 2 x Rhombic**



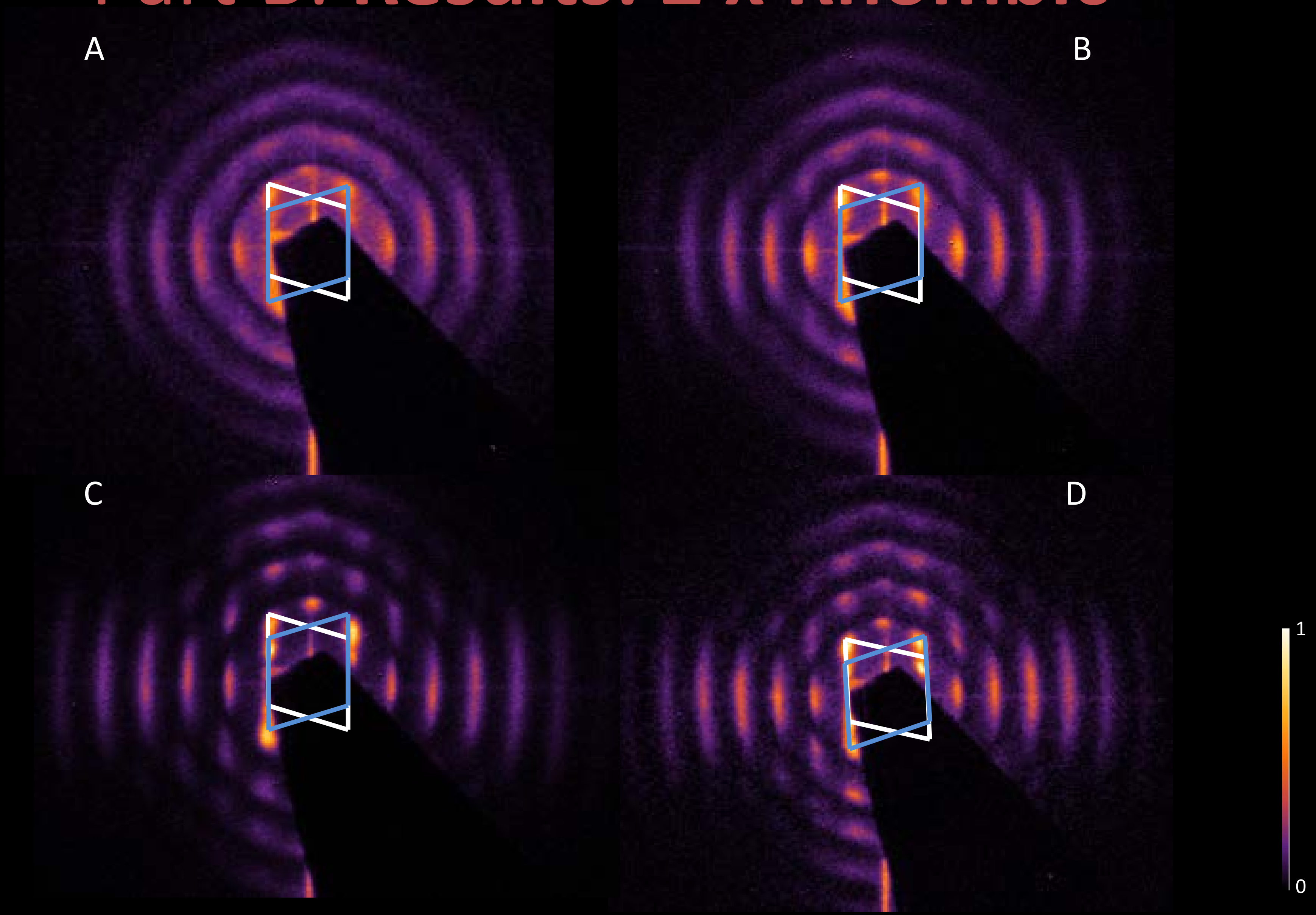
Part B: **Results: 2 x Rhombic**



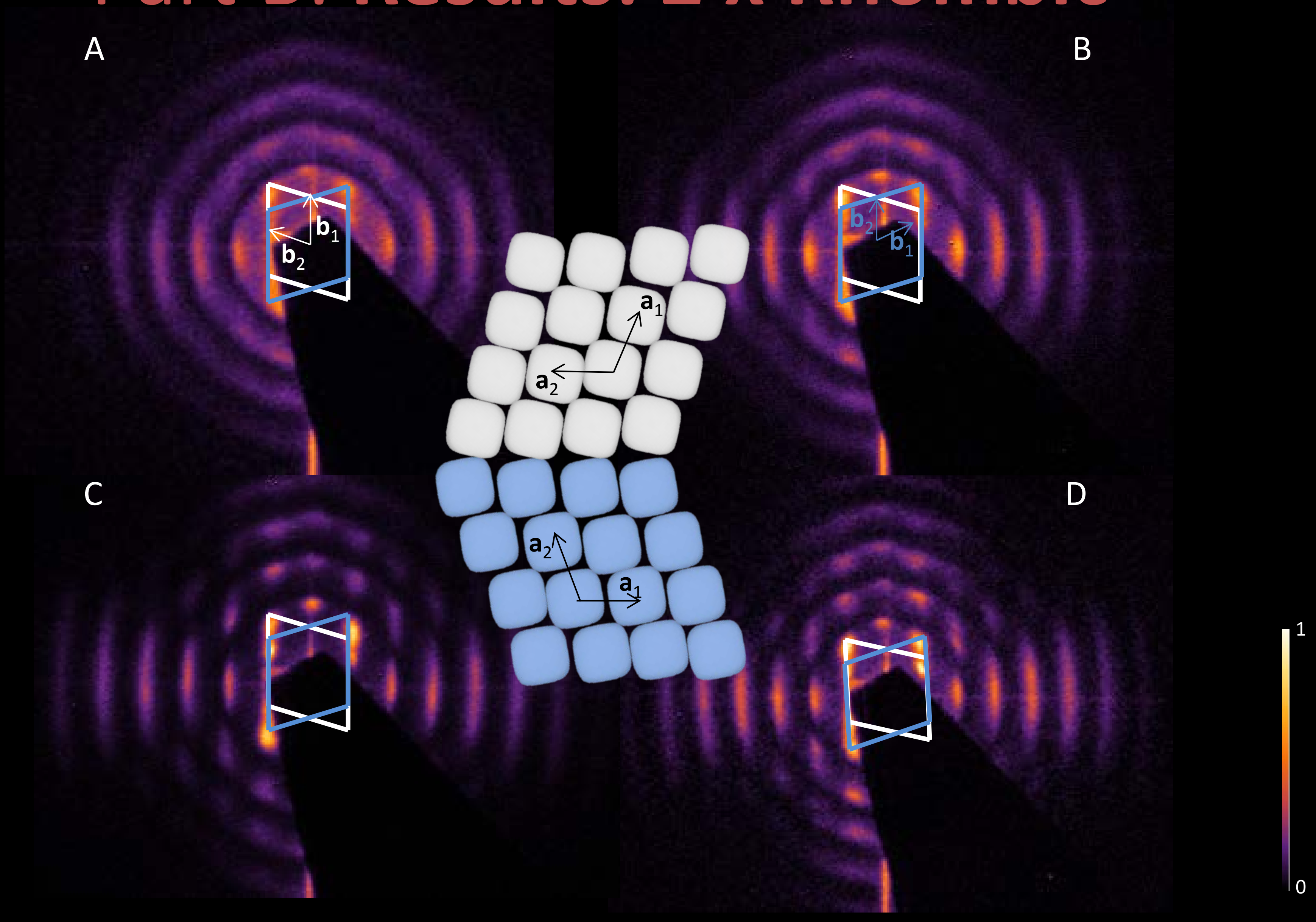
Part B: **Results: 2 x Rhombic**



Part B: **Results: 2 x Rhombic**



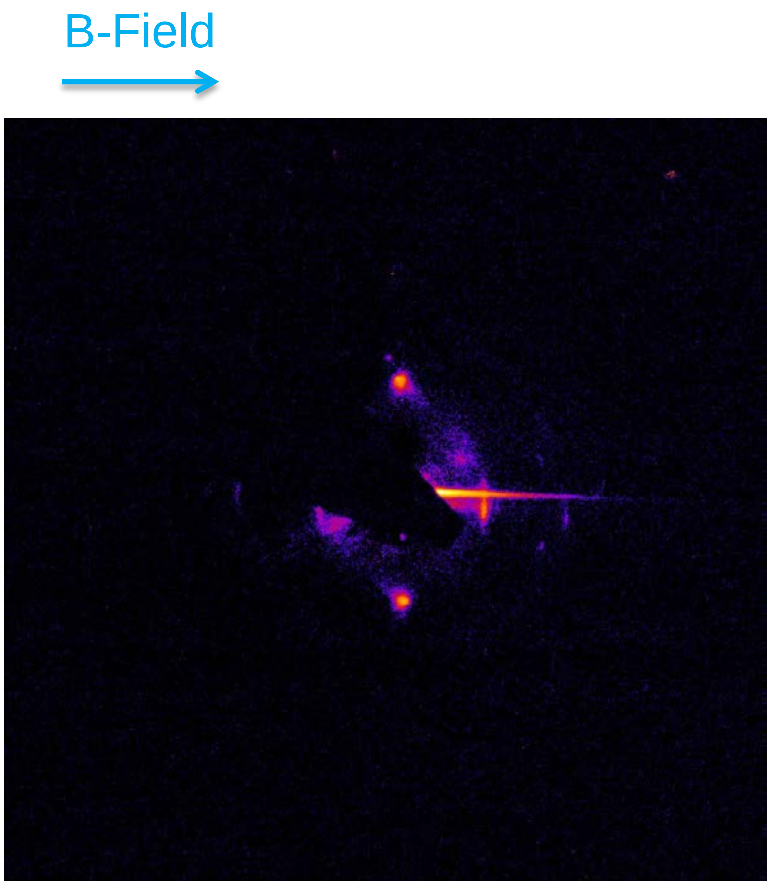
Part B: **Results: 2 x Rhombic**



Conclusion 3

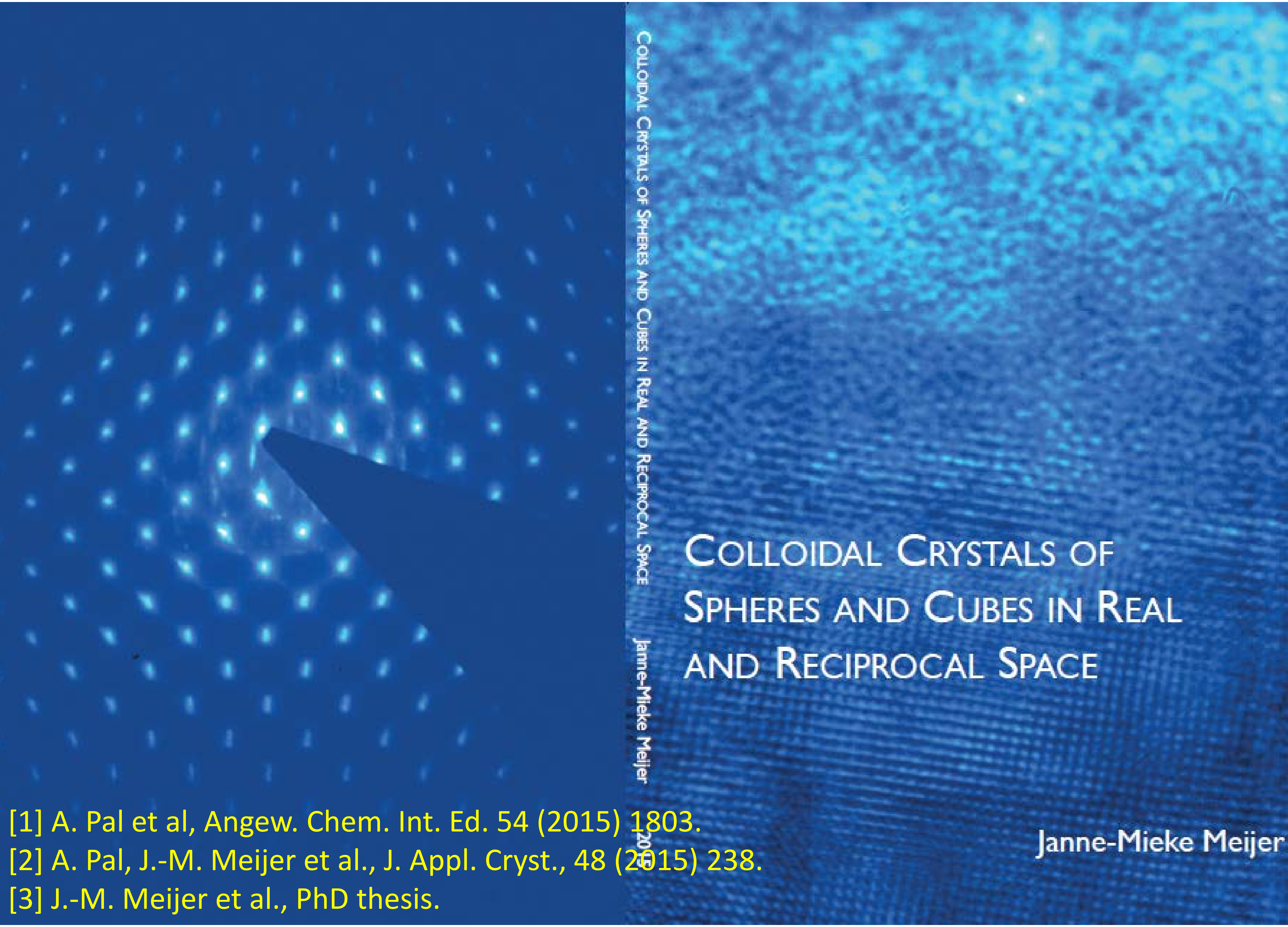
- Plastic and rhombic crystals are formed due to the effect of the particle shape depending on the osmotic pressure/concentration.

- Manipulation of the colloidal assemblies by shape is achieved.



J. Meijer, D. V. Byelov, L. Rossi, A. Snigirev, I. Snigireva, A. P. Philipse, and A. V. Petukhov,, Soft Matter 9, 10729 (2013)

Janne-Mieke Meijer, PhD thesis;
J.-M. Meijer, A. Pal, V. Meester, , H.N.W. Lekkerkerker, A.P. Philipse and A.V. Petukhov, *in preparation.*
K.-A. van der Zon, BSc thesis, July 2015.



[1] A. Pal et al, Angew. Chem. Int. Ed. 54 (2015) 1803.
[2] A. Pal, J.-M. Meijer et al., J. Appl. Cryst., 48 (2015) 238.
[3] J.-M. Meijer et al., PhD thesis.

Acknowledgements

Van 't Hoff Lab

- Antara Pal
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- Henk Lekkerkerker
- Wilem Kegel
- Albert Philipse

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- Guiseppe Portale

Team at the ID02 Beamline

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- S. Prevost

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- Vikash Malik
- Le He
- Yadong Yin

NWO Nederlandse Organisatie voor Wetenschappelijk Onderzoek

Thank you for your attention!