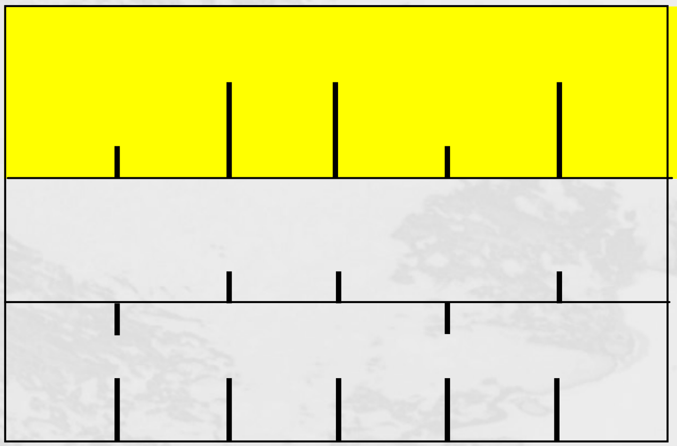
X-ray diffuse scattering in 3D

from atomic to mesoscopic scale

A. Bosak (ESRF), D. Chernyshov (SNBL)

What is diffuse scattering?



f_i

$= f_i - f_{ave} \longrightarrow$ Diffuse scattering

$+ \; f_{ave} \longrightarrow$ Bragg scattering

$$I_{diff}(\mathbf{Q}) = I_{tot}(\mathbf{Q}) - I_{Bragg}(\mathbf{Q})$$

$$I_{tot}(\mathbf{Q}) = \sum_i \sum_j f_i(\mathbf{Q}) f_j^*(\mathbf{Q}) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

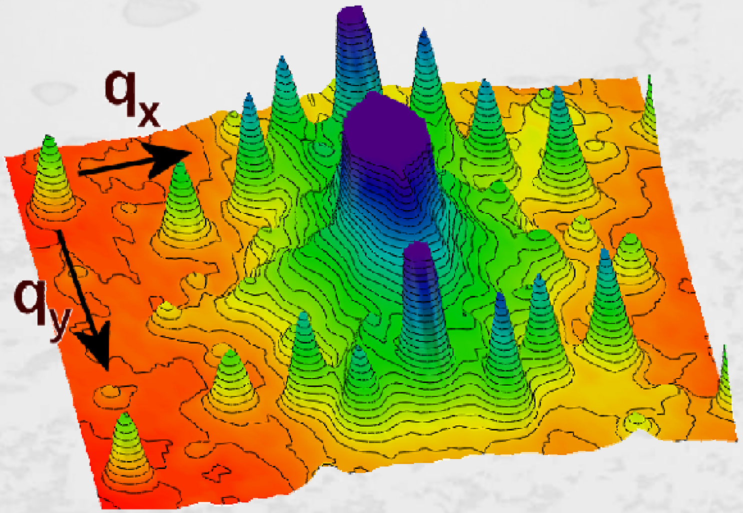
$$I_{Bragg}(\mathbf{Q}) = \sum_i \sum_j f_{ave}(\mathbf{Q}) f_{ave}^*(\mathbf{Q}) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

$$I_{diff}(\mathbf{Q}) \approx \sum_i \sum_j \left(f_{ave}(\mathbf{Q}) - f_i(\mathbf{Q})\right)\left(f_{ave}^*(\mathbf{Q}) - f_j^*(\mathbf{Q})\right) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

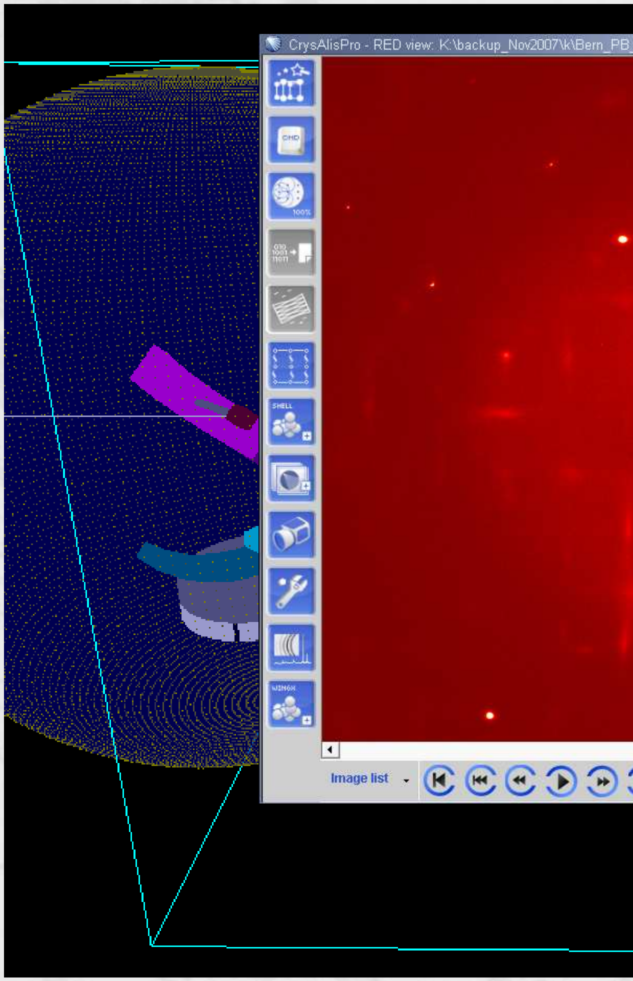
Why do we study diffuse scattering?

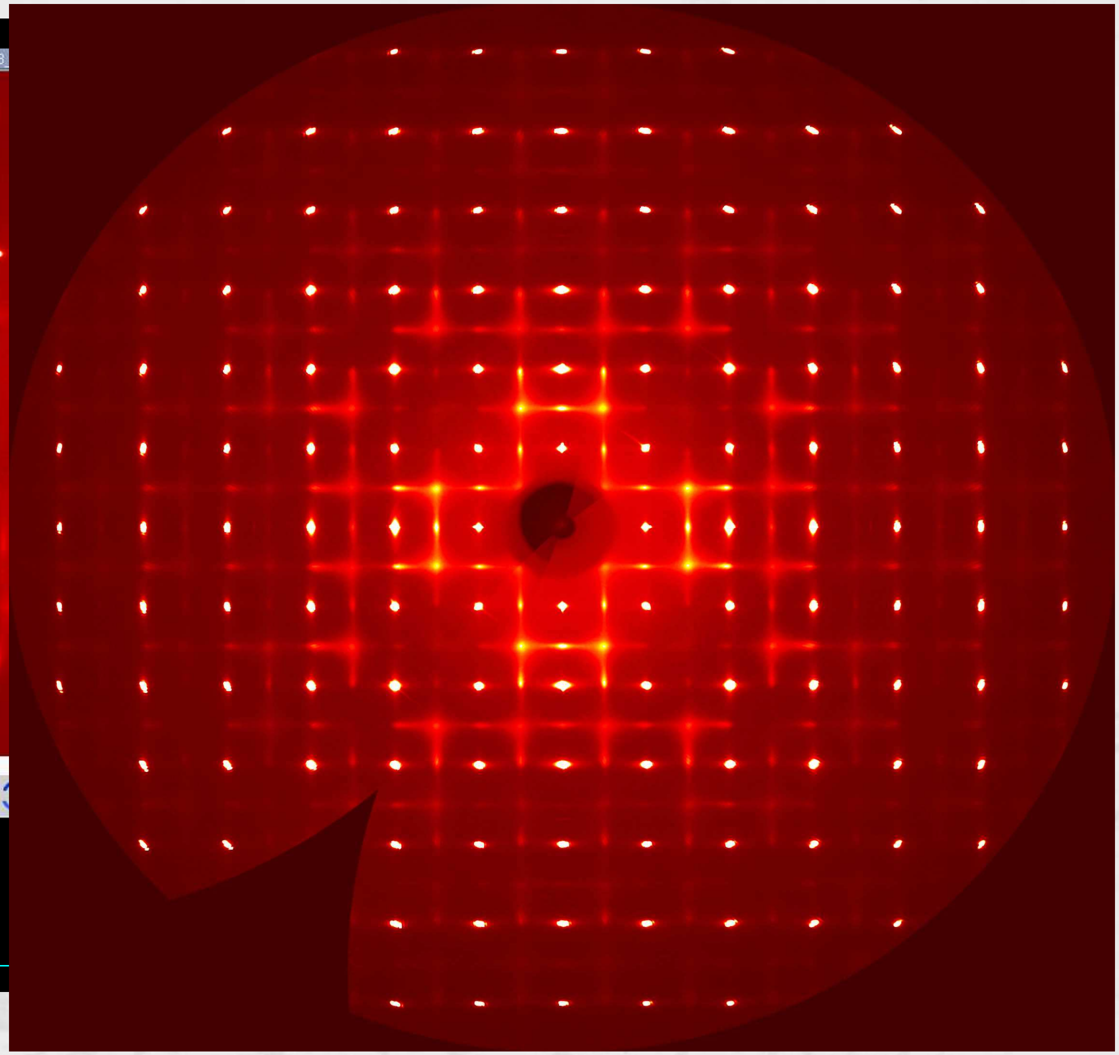
Structure defines properties… but what is the structure?

• Many mechanical, magnetic, electronic and optical properties depend not only on the average crystal structure, but also on correlated disorder .
• Diffuse intensities are usually much weaker than Bragg scattering and one needs a bright source of radiation to see the diffuse signal.
• At variance with Bragg scattering, there is still no unique protocol allowing to routinely characterize disorder from diffuse scattering data.



How do we study diffuse scattering?





Perspectives

phenomena | **analysis** | **experiment**

phenomena

- ***New scattering phenomena, like dynamic diffuse scattering***
- ***Thermal diffuse scattering for lattice dynamics***
- ***Multi-site correlations***

Bosak, A., Chernyshov, D. *Model-free reconstruction of lattice dynamics from thermal diffuse scattering,* Acta Cryst. A, 64, 598-600, 2008

analysis

- ***A protocol for analysis of diffuse intensities for disordered structures***
- ***A protocol for lattice dynamics calculations***
- ***Fast and reliable 3D reconstruction of reciprocal space***

Schaub, P.; Weber, T.; Steurer, W. *Exploring local disorder in single crystals by means of the three-dimensional pair distribution function* , Philos. Mag. 87 2781-2787, 2007

experiment

- ***Fast detector with large dynamic range and energy discrimination***
- ***Flexible geometry of the goniostat for an optimal coverage of requested reciprocal volumes***

Brönnimann *et al.*, *The Pilatus 1M Detector.* J. Synchrotron Rad., **13**, 120-130. 2007

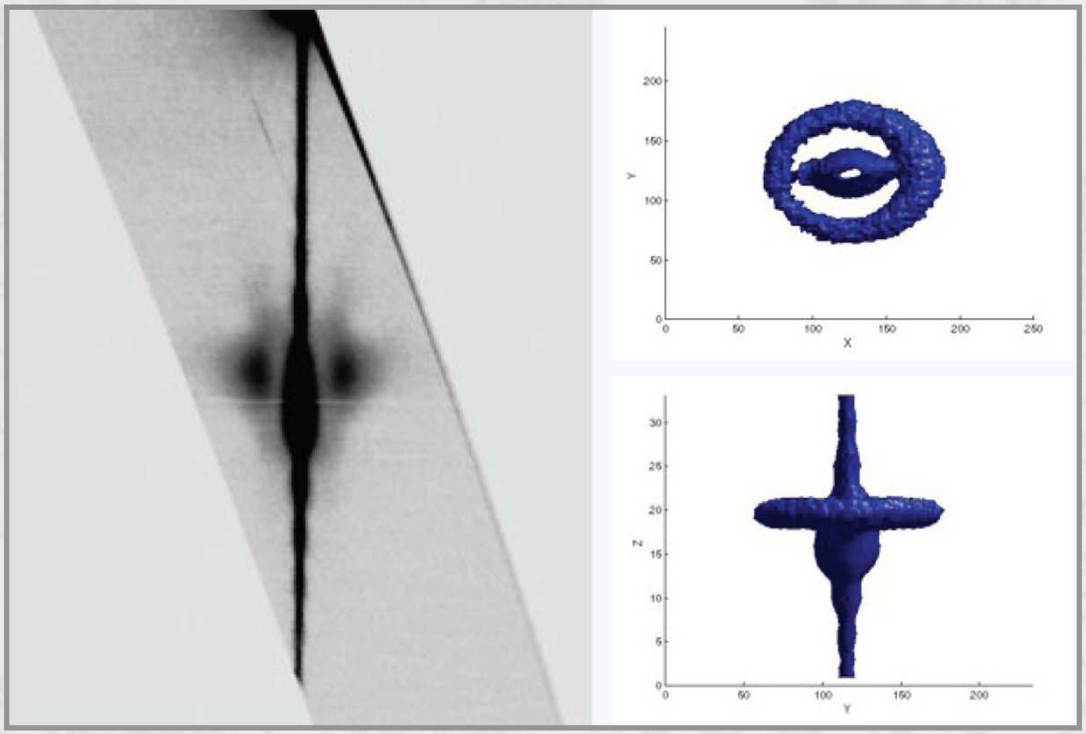
“Dream” mode

- Recover RS during experiment
- Indexing-free mode
- Ability to visualize entire RS and necessary slices
- Forget nightmare of converting different image formats
- Friendly interface
- License free = can be given to our users

Domain walls in $PbTiO_3$ thin films

Collaboration:
F. Mo, L.S. Thoresen, D.W. Breiby,
T. Tybell (*NTNU, Trondheim, Norway)*
D. Chernyshov (*SNBL)*

MAPLE script:
3D visualisation from MAR CCD files



50 unit cells $PbTiO_3$ / $SrTiO_3$
(103) Reflection

field **<u>off</u>**

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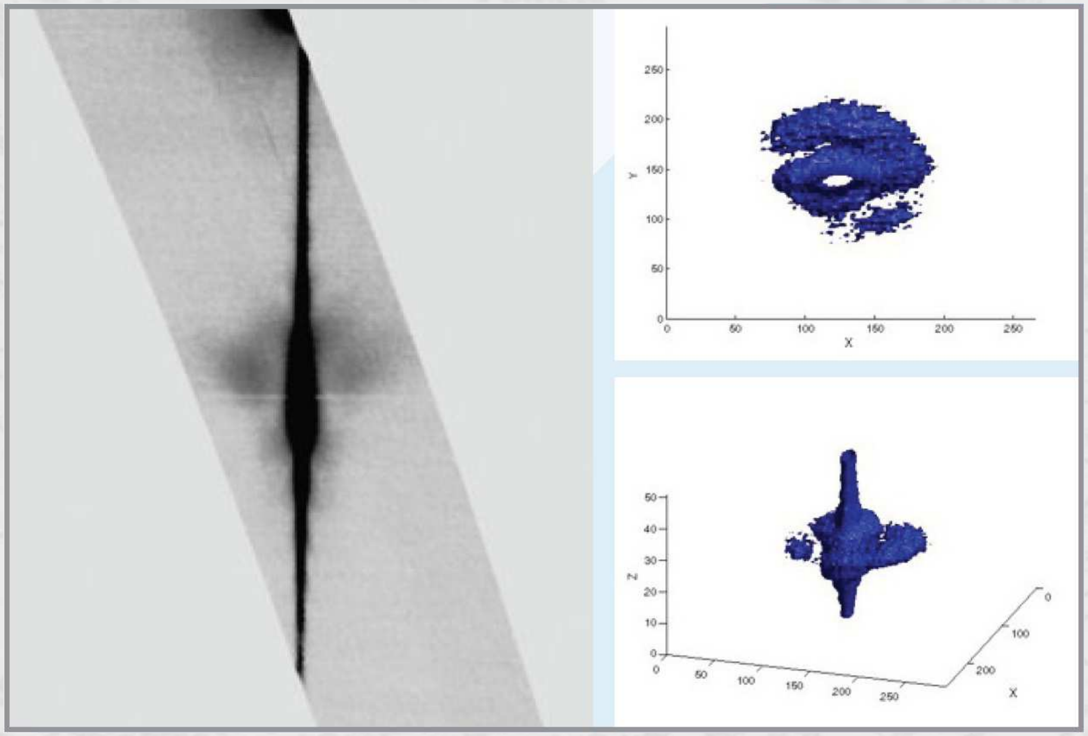

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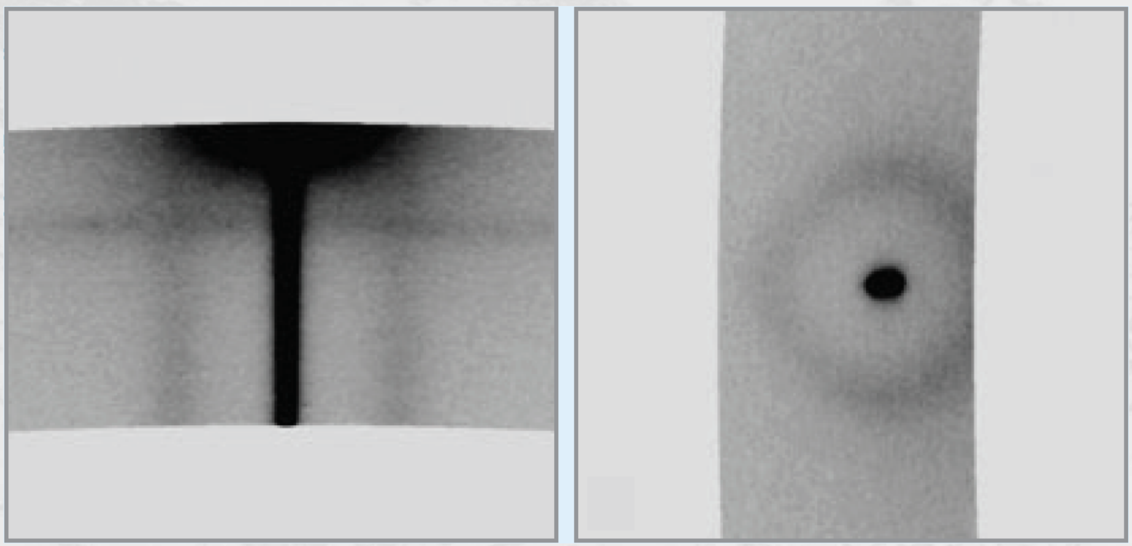
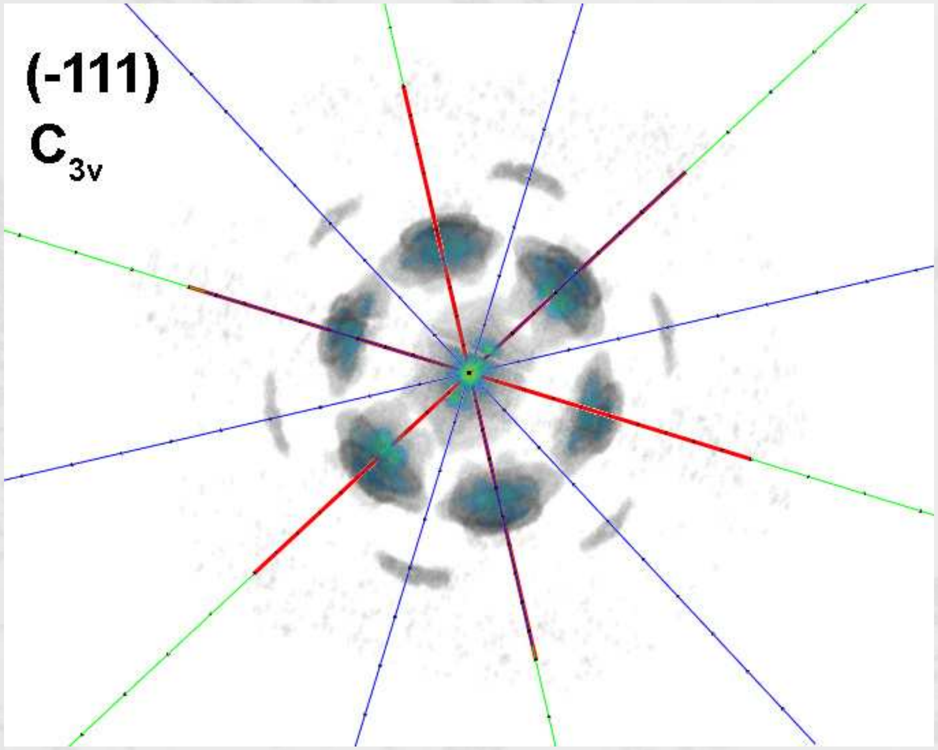
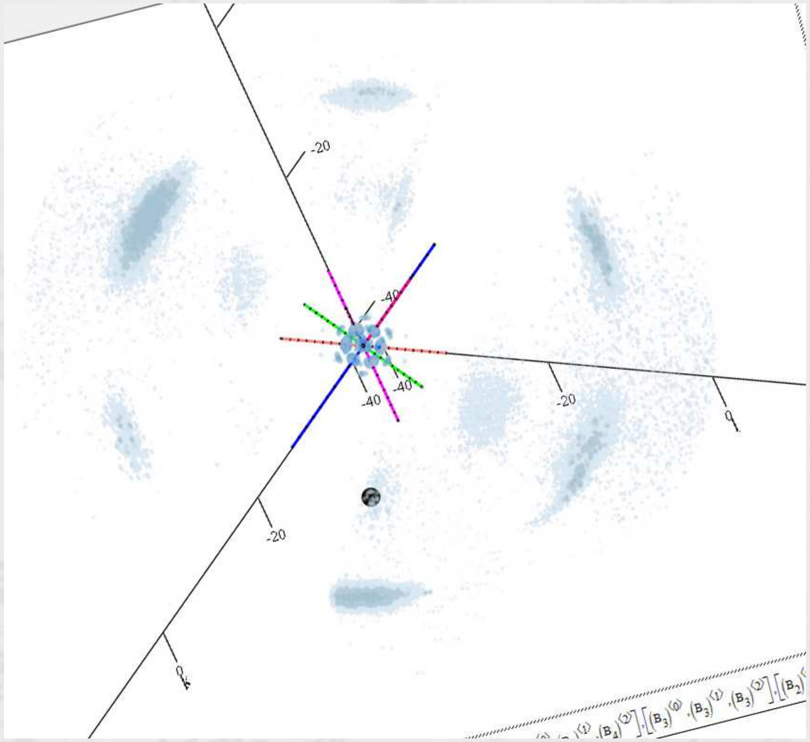


6 unit cells $PbTiO_3$ / $SrTiO_3$
(103) reflection

field **off**

Self-assembly of CdSe nanoparticles





Moscow State University: Mathcad (SAXS -> 3D)

Where is the periodicity?

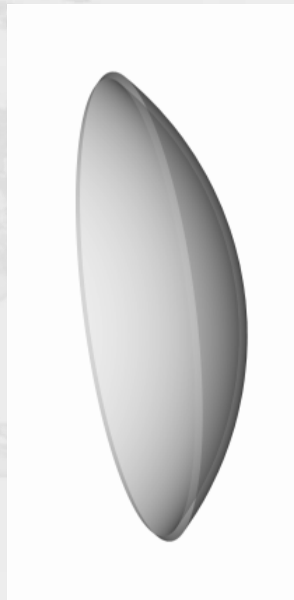
Swiss Norwegian Beam Lines / MAR Image Plate / MAR output

Towards 3D representation

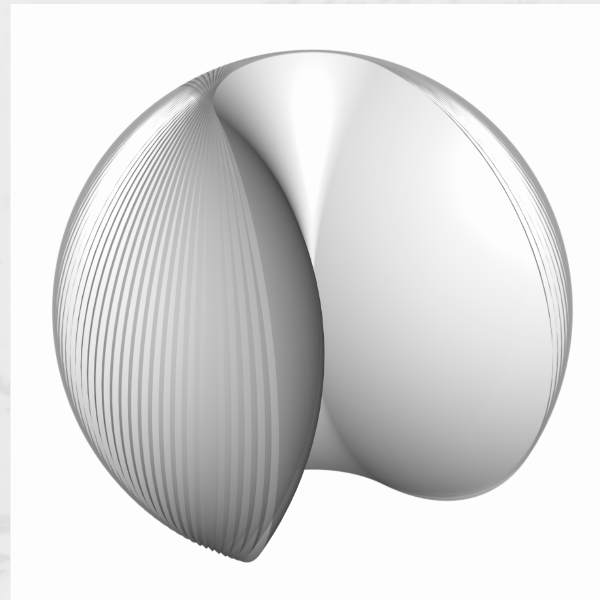
flat image
CBF
MAR
EDF
BSL
...

masking, corrections, UB matrix retrieval, application of symmetry elements, etc.

sphere



space filling

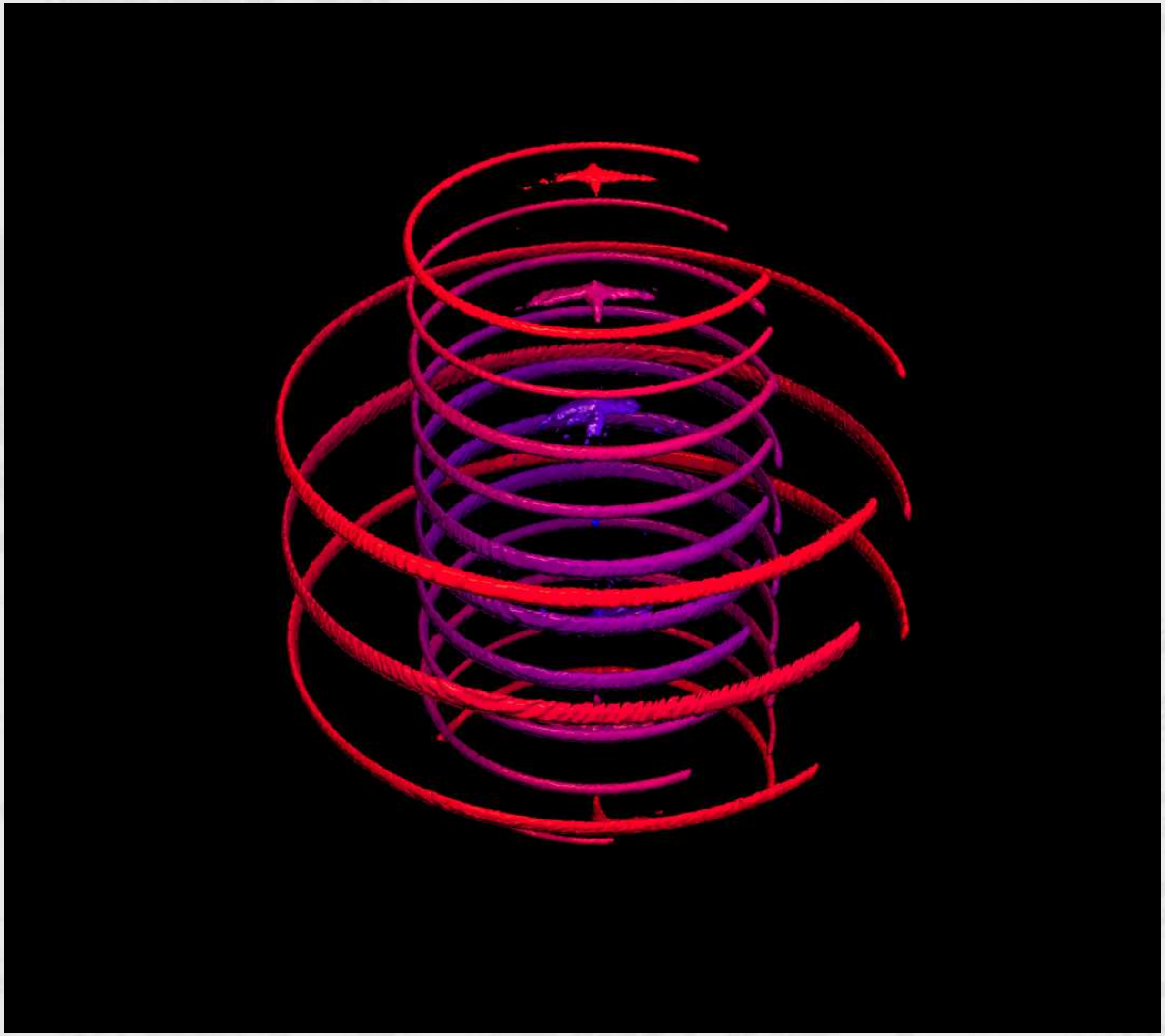


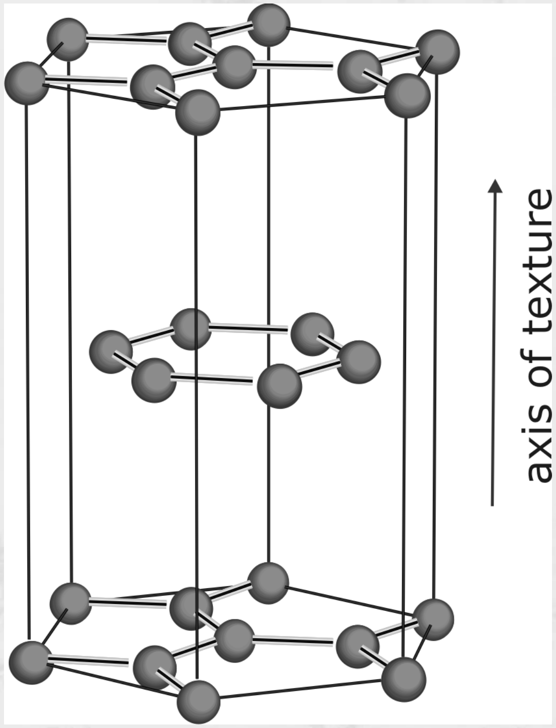
CCP4 map format

UCSF Chimera

VRML
X3D
POV-Ray
...

Pyrolytic graphite: fiber texture

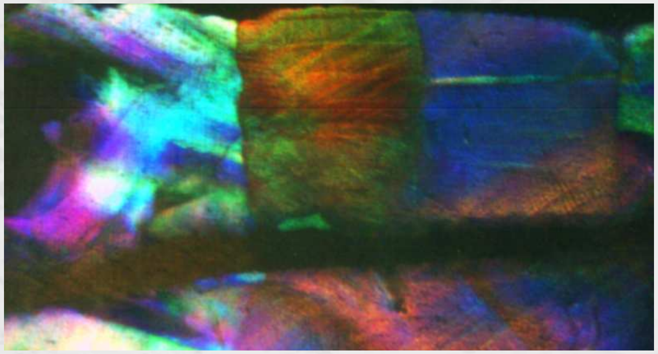




What is the structure of precious opal?

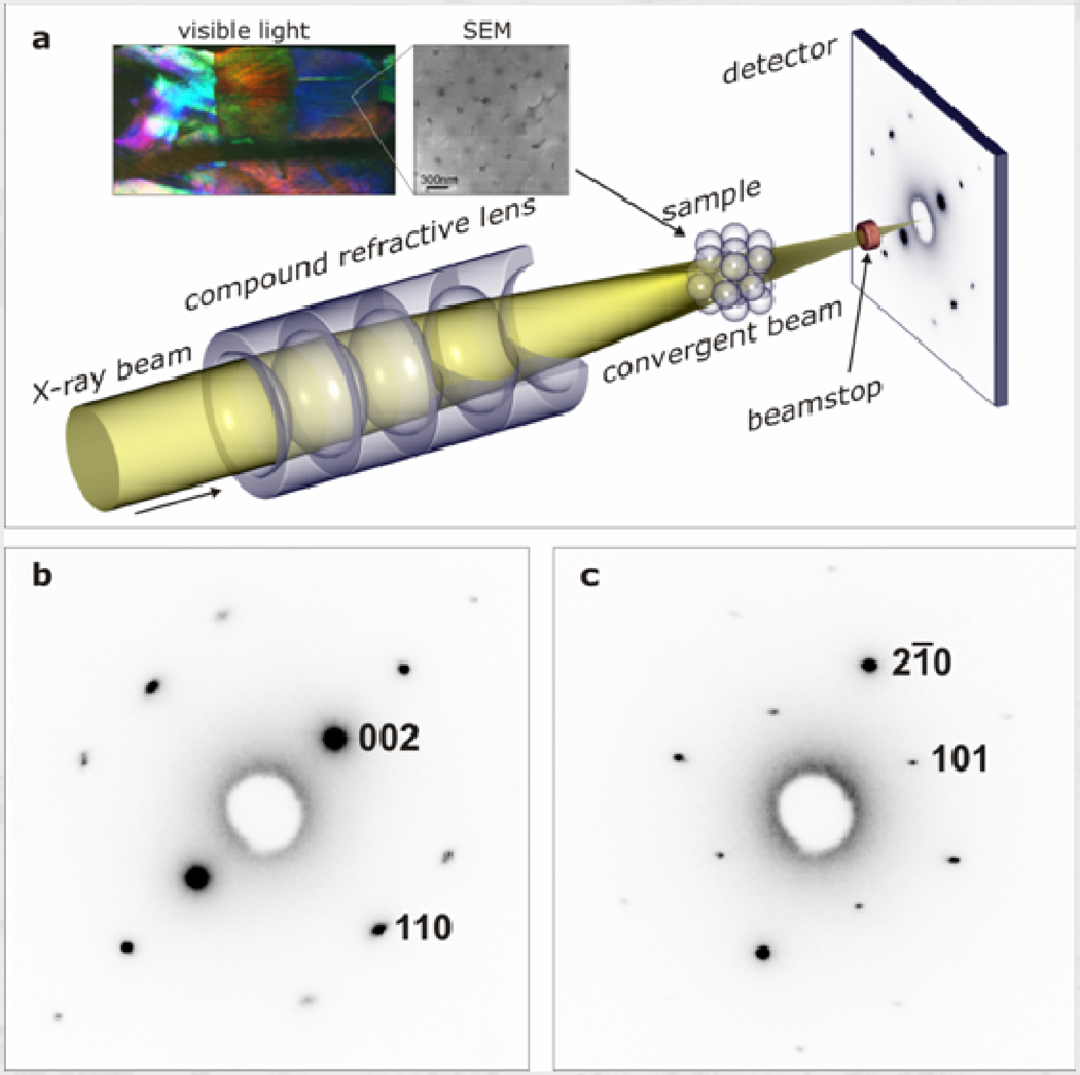
Collaboration: A. Bosak (ESRF), A. Snigirev (ESRF), K. Napolsky (MSU)

Compound refractive lens based setup: ID06 / CCD

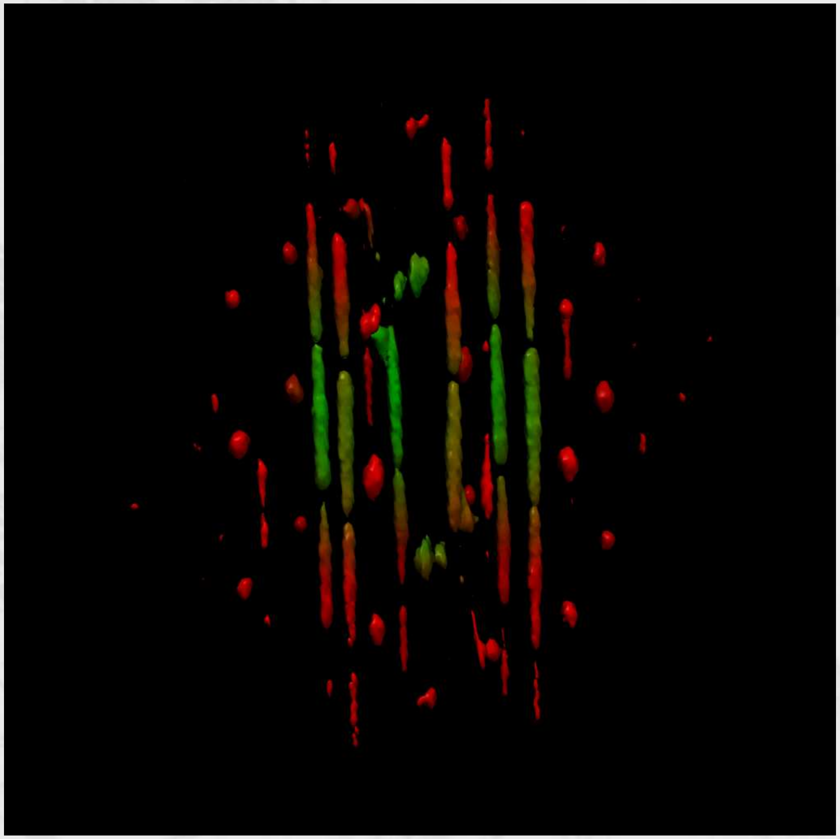


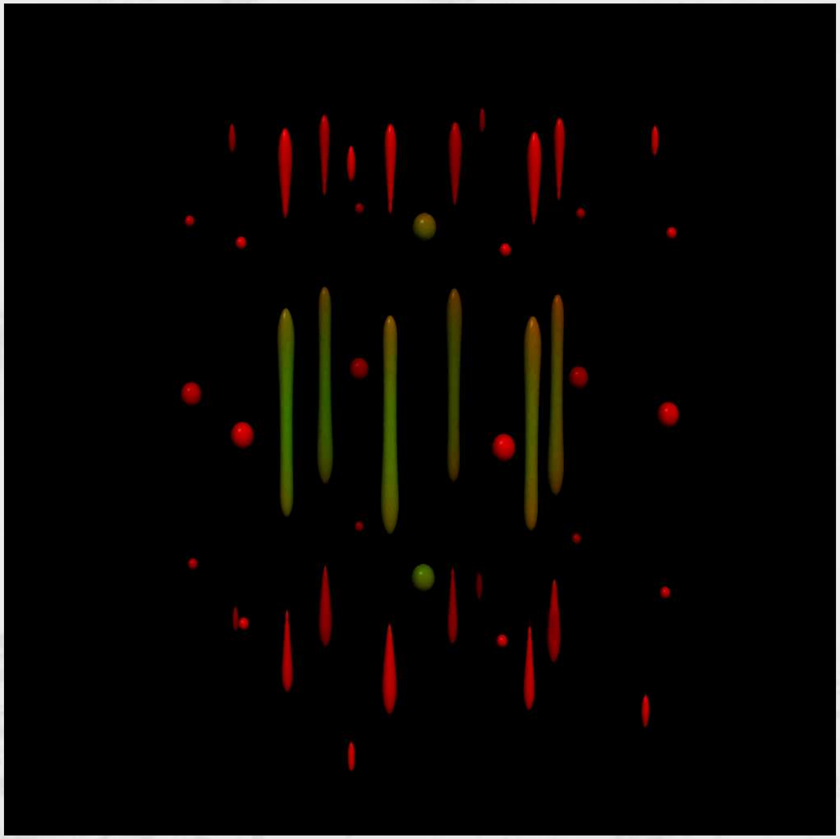
Australian opal

any opal: stacking of hexagonal dense layers



Hexagonal stacking: not fully random





AB and BA sequences have different probabilities!

Diffuse scattering in « prussian blue »

Crystalline, Mixed-Valence Manganese Analogue of Prussian Blue: Magnetic, Spectroscopic, X-ray and Neutron Diffraction Studies

Patrick Franz,† Christina Ambrus,† Andreas Hauser,‡ Dmitry Chernyshov,†,§ Marc Hostettler,† Jürg Hauser,† Lukas Keller,‖ Karl Krämer,† Helen Stoeckli-Evans,# Philip Pattison,⊥ Hans-Beat Bürgi,† and Silvio Decurtins†,*

Contribution from the Departement für Chemie und Biochemie und Laboratorium für Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

J. AM. CHEM. SOC. 2004, *126*, 16472–16477

$Mn(II)[Mn(III)(CN)_6]_{2/3}{\cdot}(6H_2O)_{1/3}{\cdot}yH_2O$

2D

1D

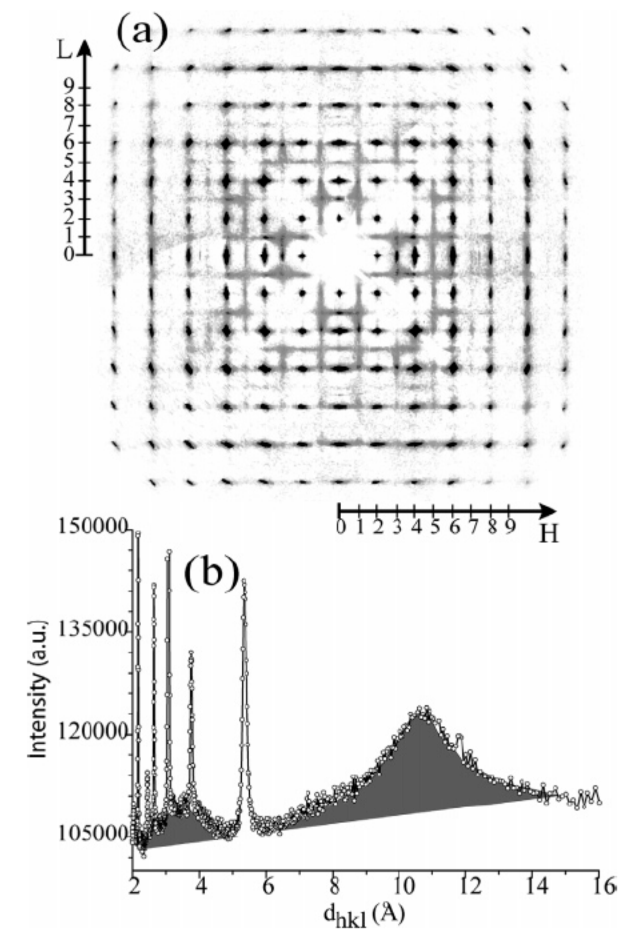


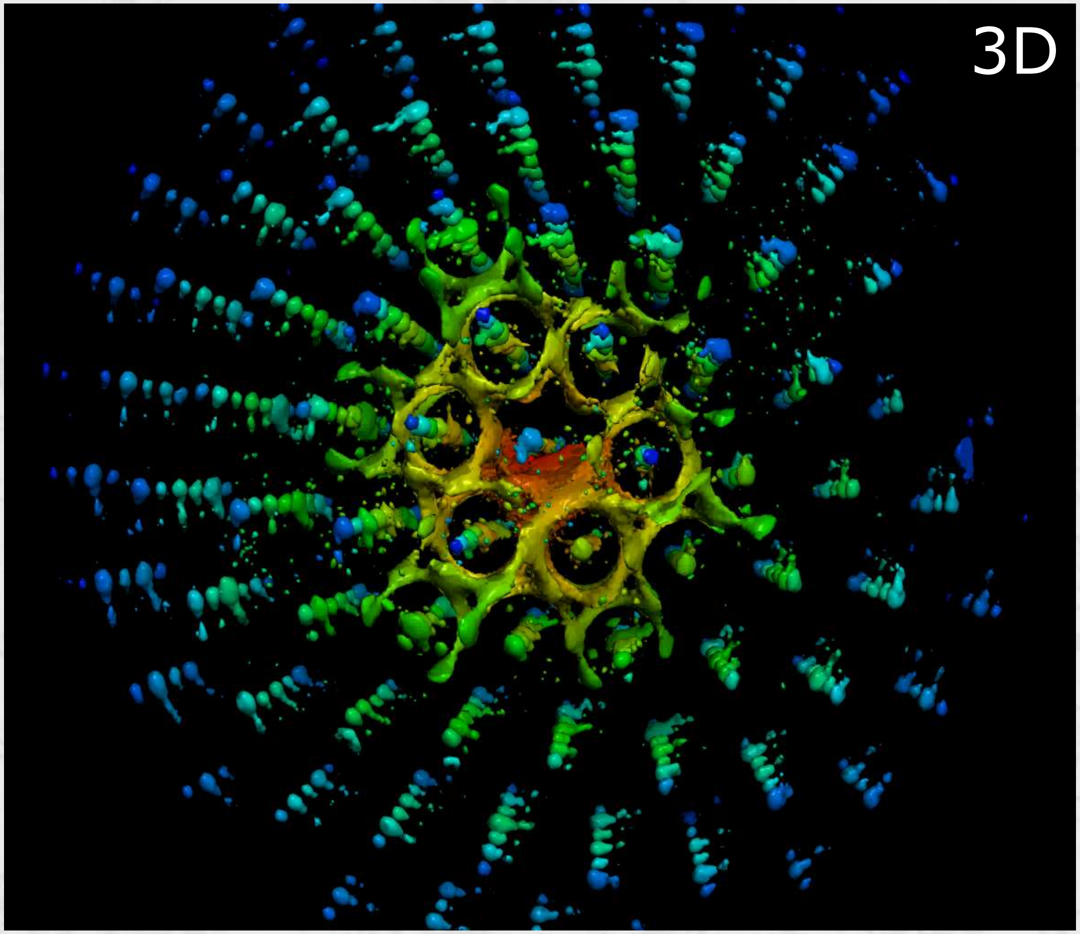
Figure 8. (a) Diffuse scattering of **1** obtained from a) single-crystal X-ray diffraction (H0L-layer, $T = 293$ K), (b) neutron powder diffraction (153 K). The gray areas in the powder diagram indicate diffuse contributions and correspond to the blurred features seen in a).

Swiss Norwegian Beam Lines / MAR Image Plate / MAR output

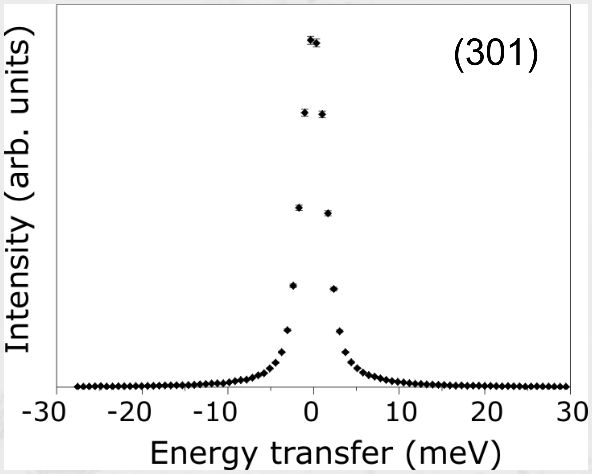
Pure disorder: no phonon contribution

$Mn(II)[Mn(III)(CN)_6]_{2/3} \cdot (6H_2O)_{1/3} \cdot yH_2O$

replacement of $[Mn(CN)_6)]$ by $[6H_2O]$



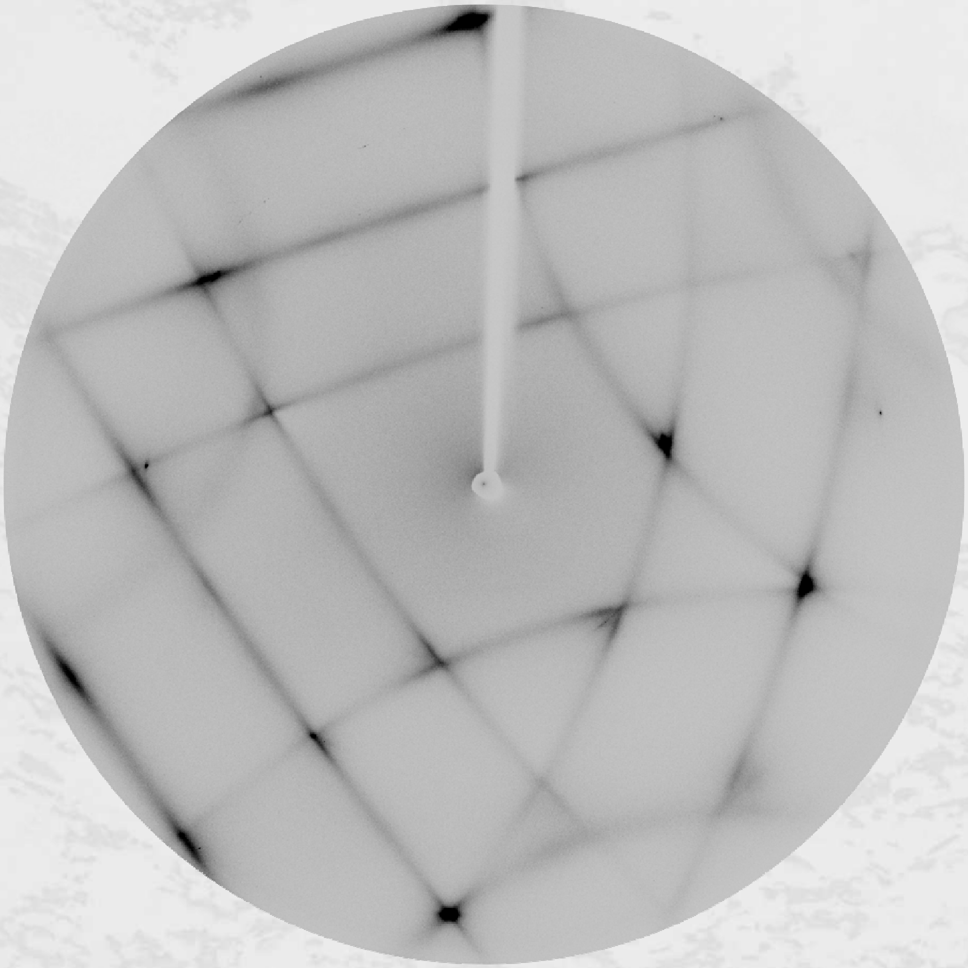
elastic or inelastic?
IXS @ ID28!



inelastic contribution to the strong diffuse features is negligible

Diffuse scattering in perovskite

Piezoelectrics $Li_x(K_{0.5}Na_{0.5})_{1-x}NbO_3$



Collaboration:
A. Bosak
ESRF
D. Chernyshov
SNBL
D. Damjanovic
EPFL, Lausanne
M. Korablev-Dyson
SpbGPU, St. Petersburg
S.Vakhrushev
A.F. Ioffe PTI, St. Petersburg

High temperature:
cubic phase, three families of diffuse planes normal to <100>, <010>, <001>

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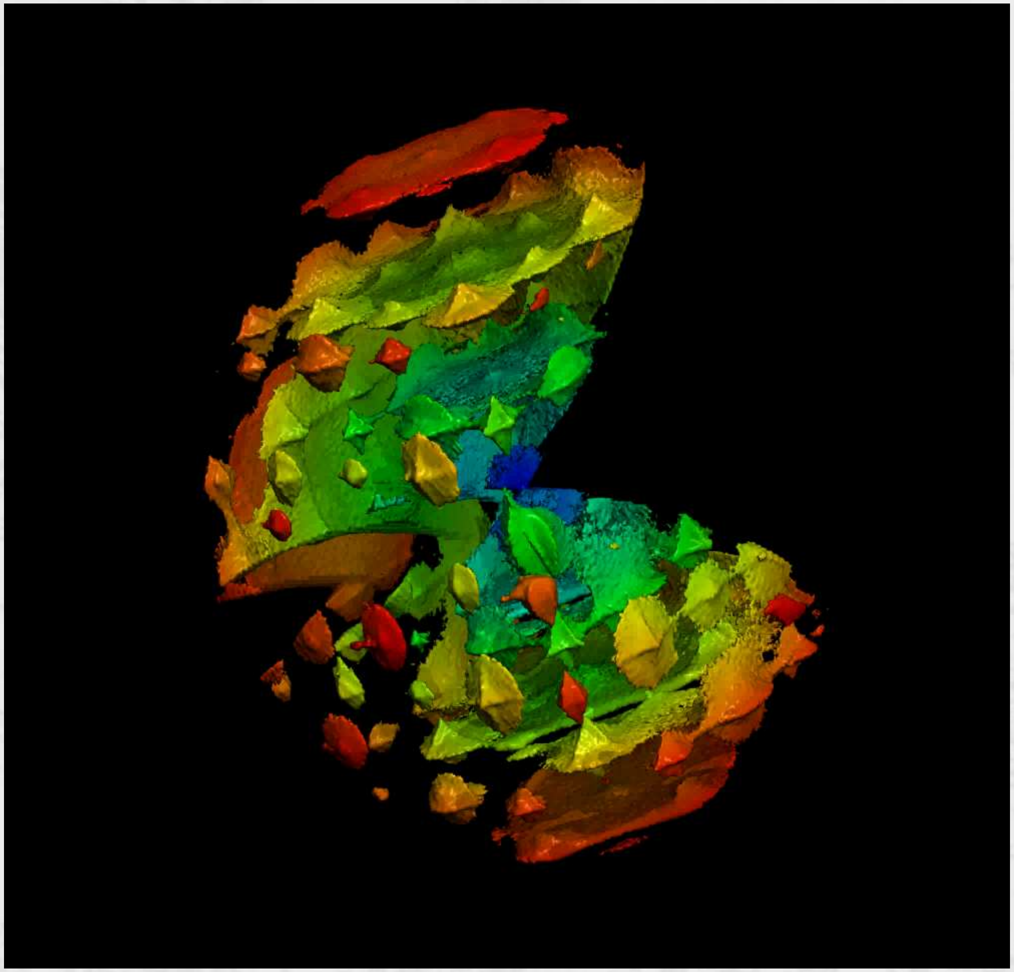

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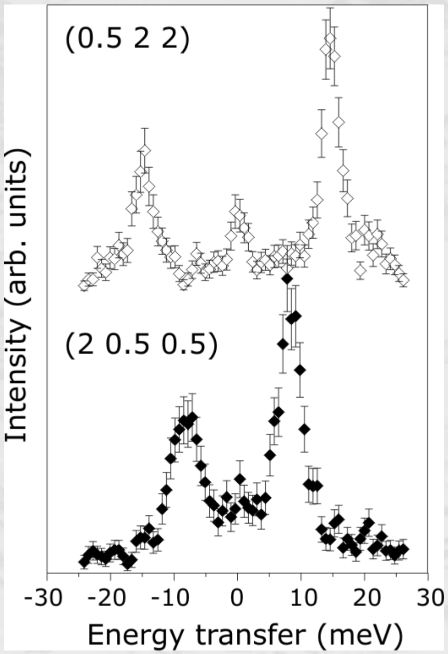
High temperature:
cubic phase, three families of diffuse planes normal to <100>, <010>, <001>

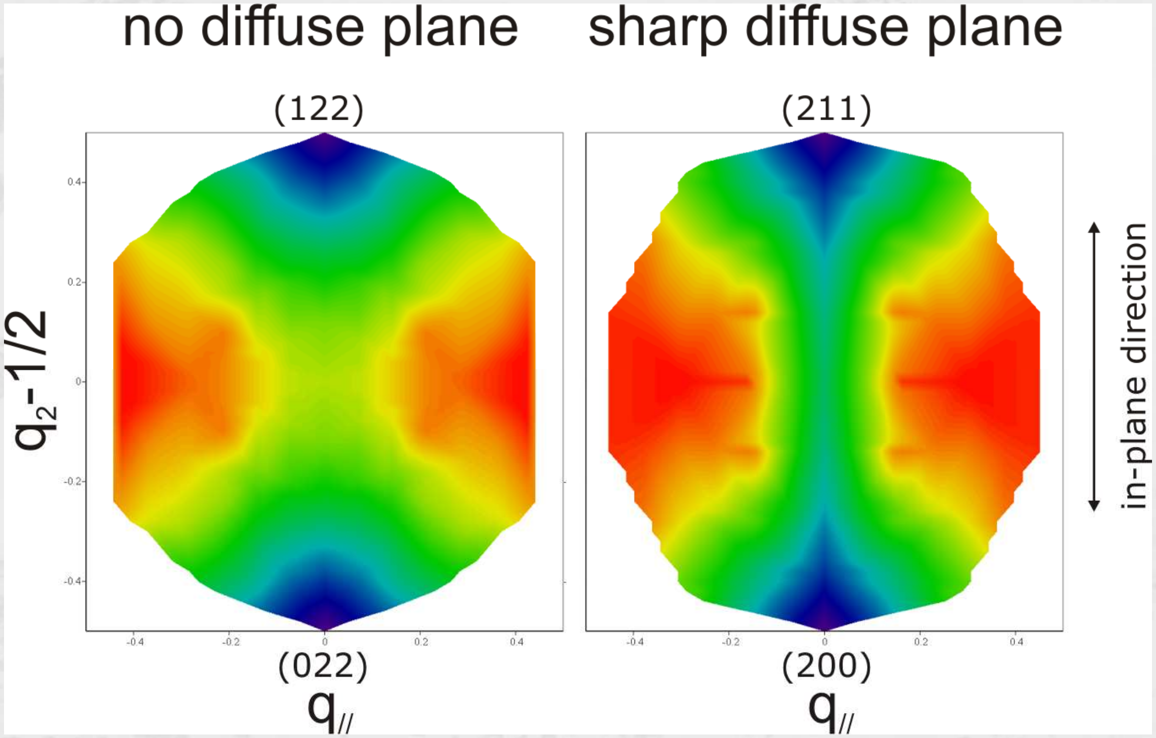
Phonons only: no static disorder

Ambient temperature:

orthorhombic phase, only one family of diffuse planes normal to <001> survives

elastic or inelastic?
IXS @ ID28!



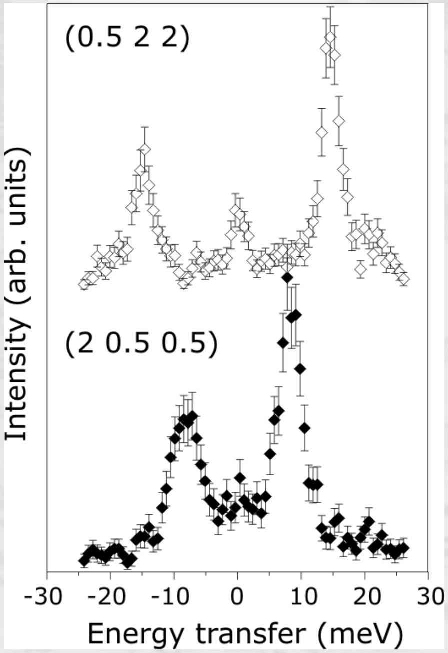


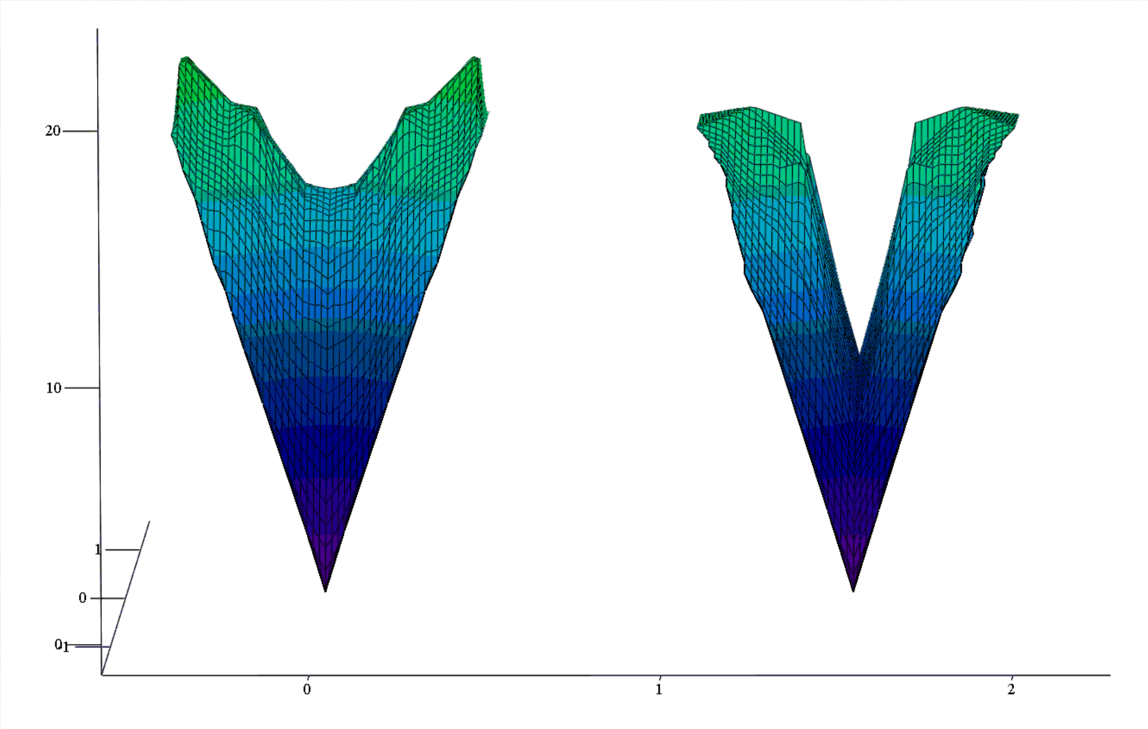
sharp diffuse features correspond to strong phonon softening

Phonons only: no static disorder

Ambient temperature:
orthorhombic phase, only one family of diffuse planes normal to <100> survives

elastic or inelastic?
IXS @ ID28!





sharp diffuse features correspond to strong phonon softening

Where we are now

- RS recovery during experiment
- Indexing-free mode
- Ability to see entire RS and necessary slices
- Forget nightmare of converting different image formats
- Friendly interface
- License free = can be given to our users

- ➢ possible for a slow detector
- ➢ yes, but not for integration
- ➢ done
- ➢ works for MAR, EDF, BSL, CBF (PILATUS)
- ➢ simple interface
- ➢ yes

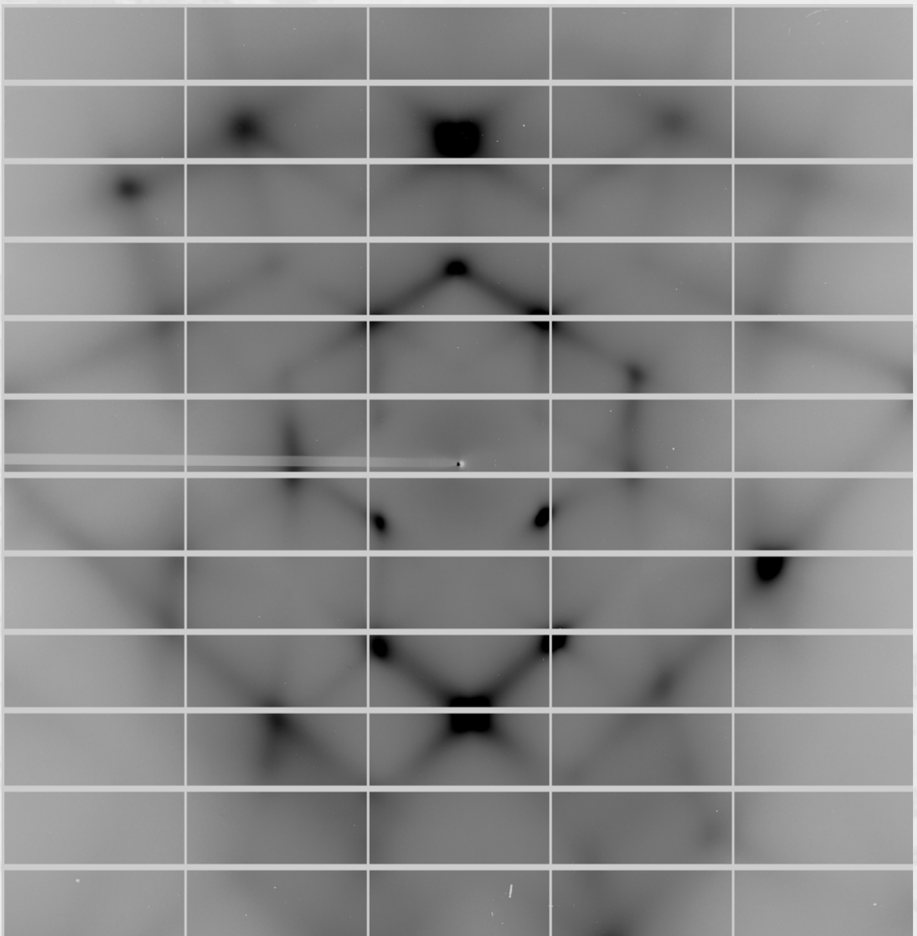
NTNU, Trondheim, Norway: MAPLE (MAR CCD -> 3D)
Moscow State University: Mathcad (SAXS -> 3D)
EPFL, Lausanne, Switzerland: home-developed code (Crysalis reconstructions -> CCP4 maps)

Additional options

- Choice of 3D mesh resolution
- High resolution slicing
- Arbitrary detector position
- Lorentz and polarization corrections
- External orientation matrix
- Laue averaging

What do we gain with pixel detector?

Thermal diffuse scattering in silicon



raw image taken with
PILATUS 6M detector

area detectors -> revival of TDS since 1999

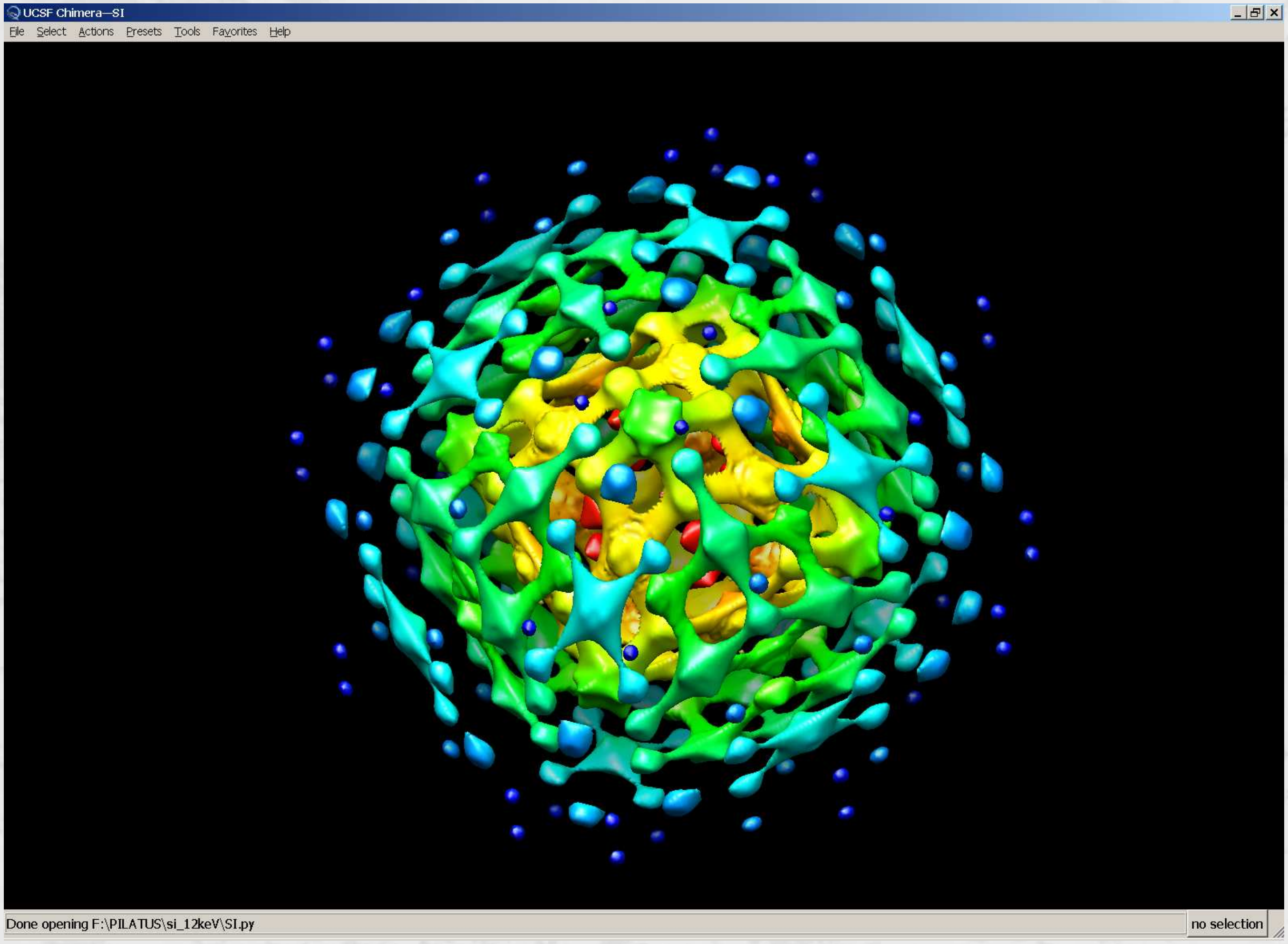
M. Holt, Z. Wu, H. Hong, P. Zschack, P. Jemian, J. Tischler, H. Chen, T.-C. Chiang
Phys. Rev. Lett. ***83****, 3317 (1999)*

fitting of single images with lattice dynamics model

new age with pixel detectors?

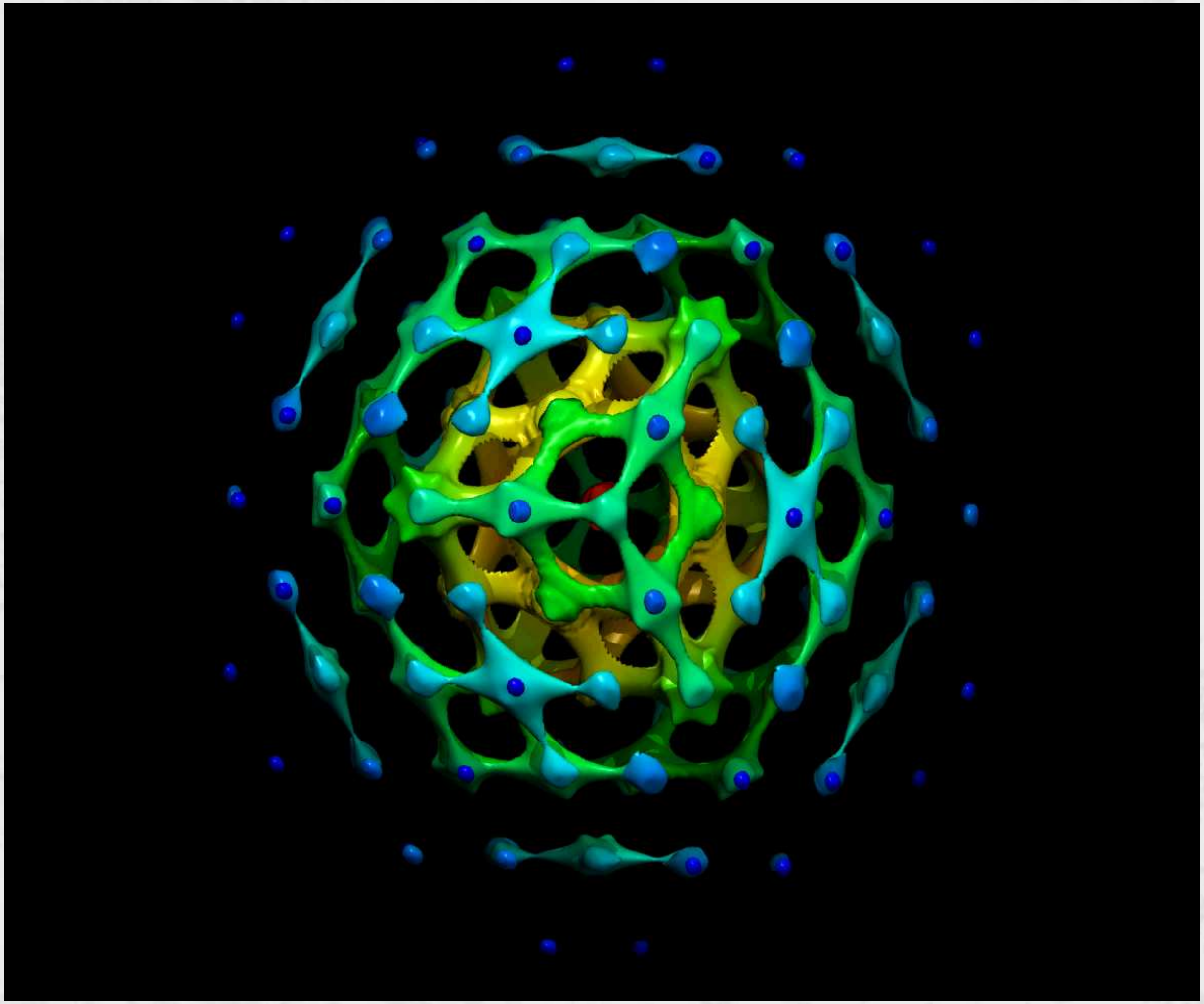
FULL reciprocal space can be explored in few minutes

3D TDS mapping in silicon



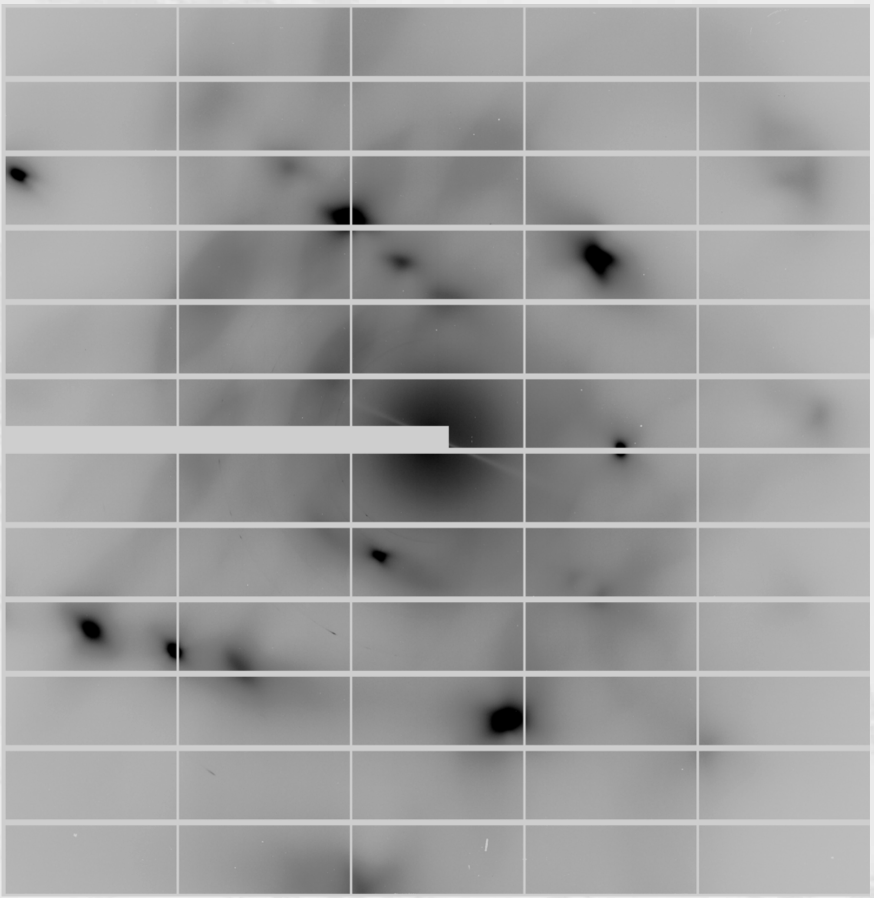
constant TDS intensity surface – phonon contribution only

3D TDS mapping in silicon

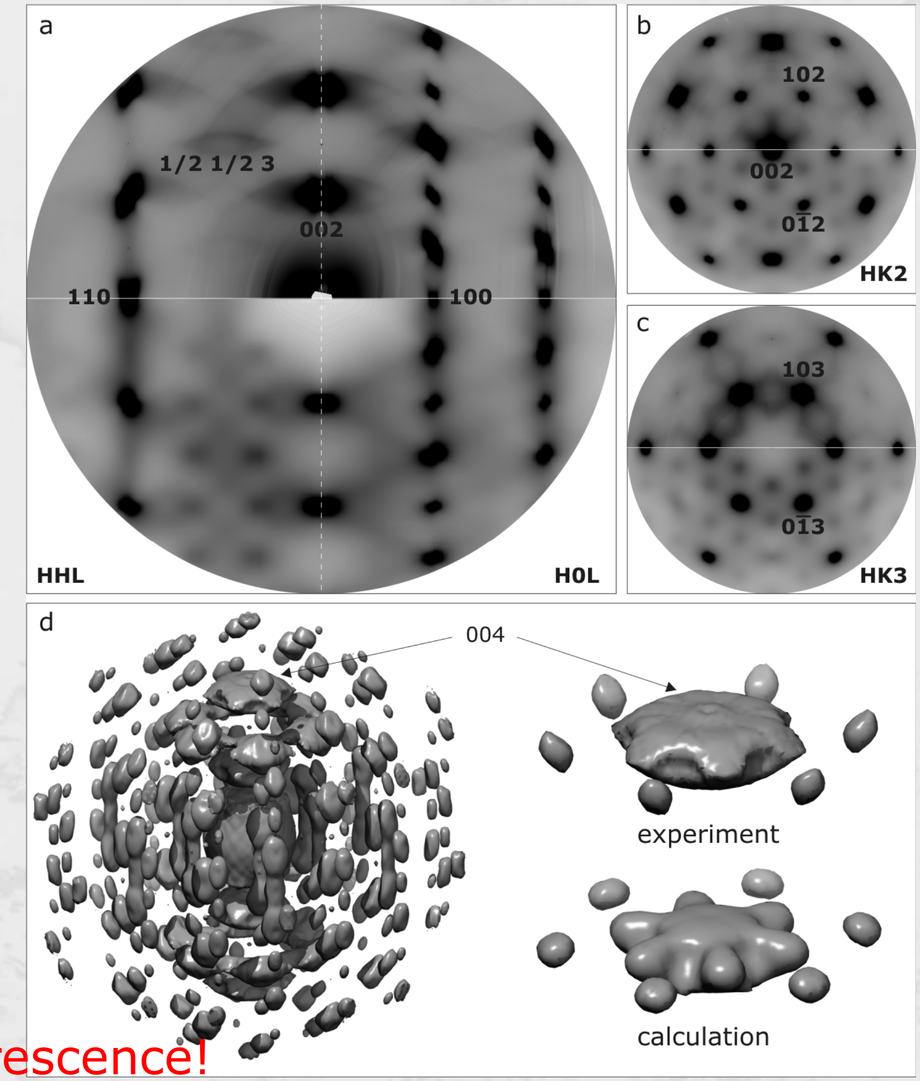


rendering performed
with POV-Ray software

Kohn surface visualization in zinc metal

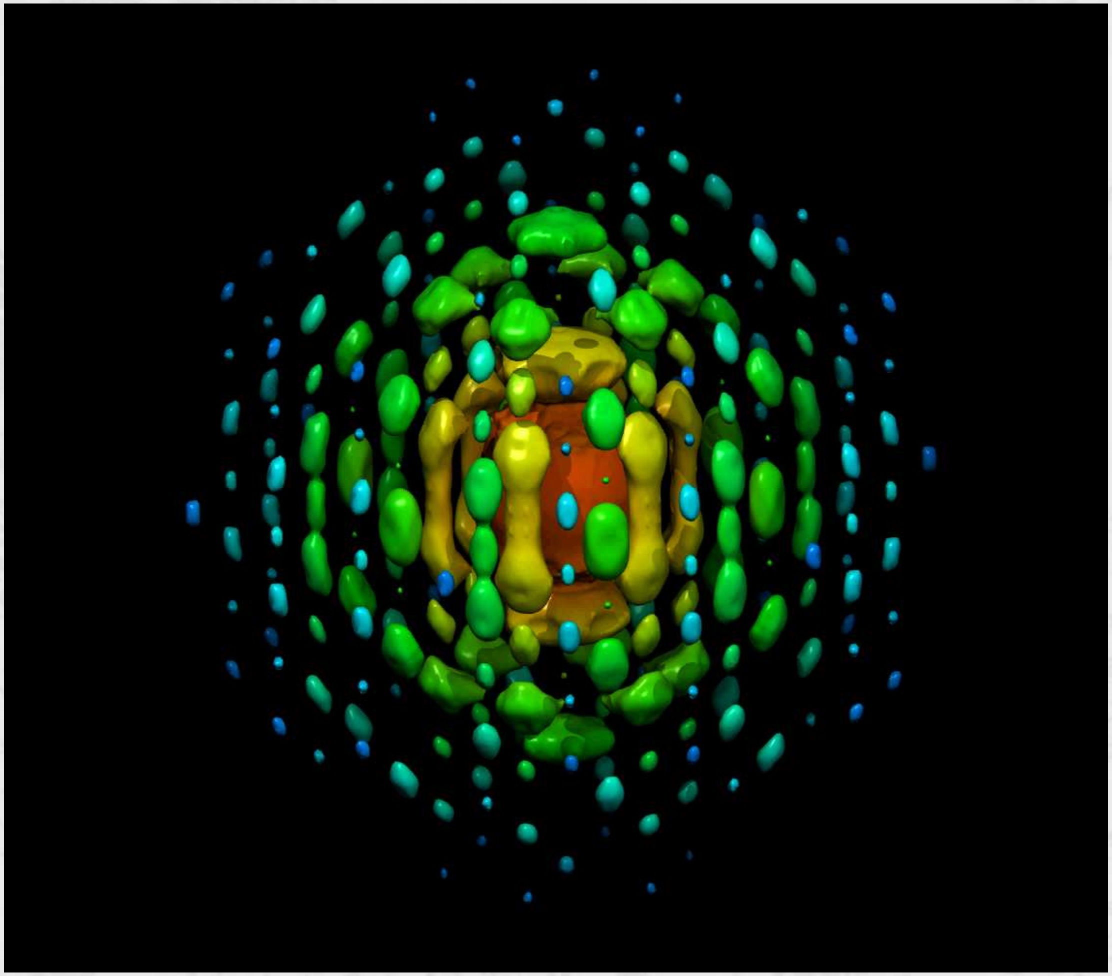


raw image



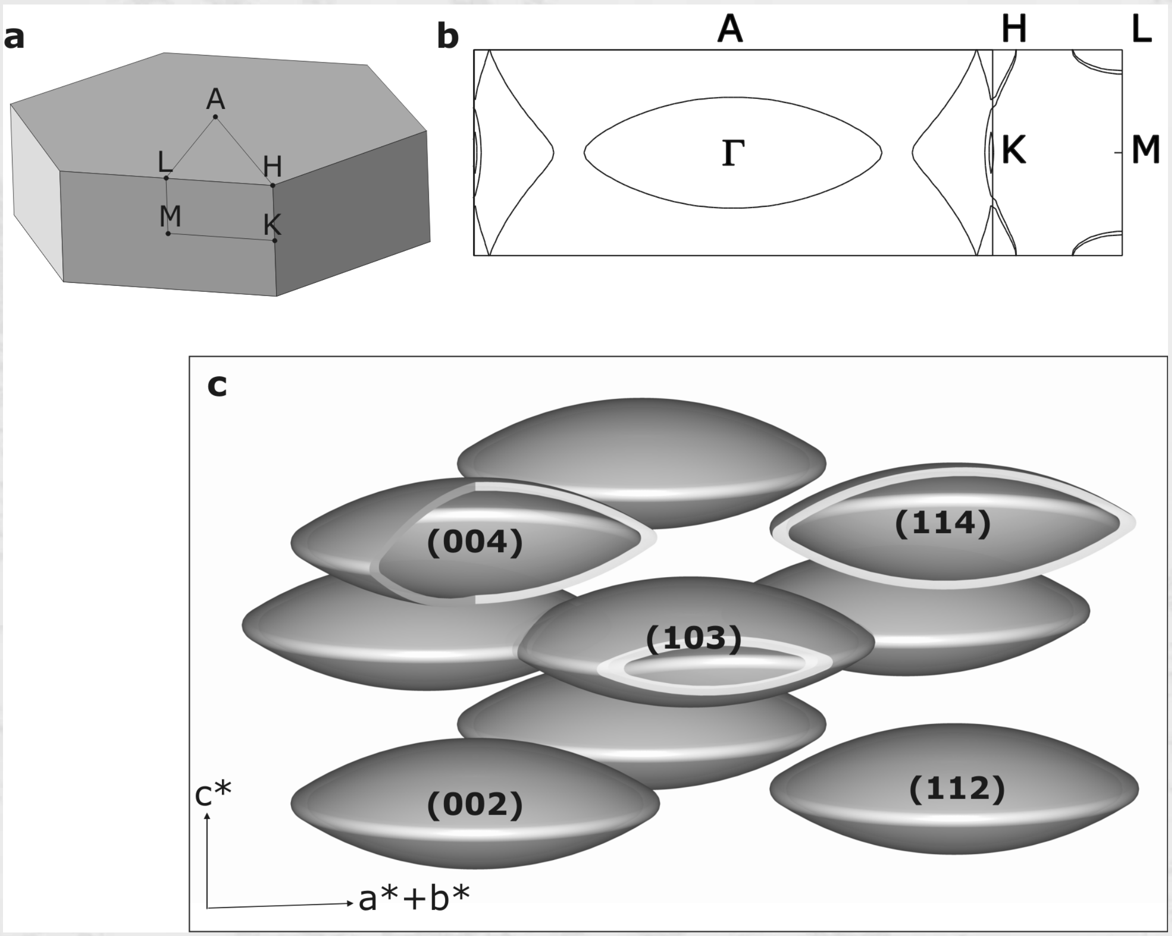
PILATUS: strong suppression of fluorescence!

… and 3D TDS representation



elastic contribution can be neglected (proven by IXS)

Nearly free electron model



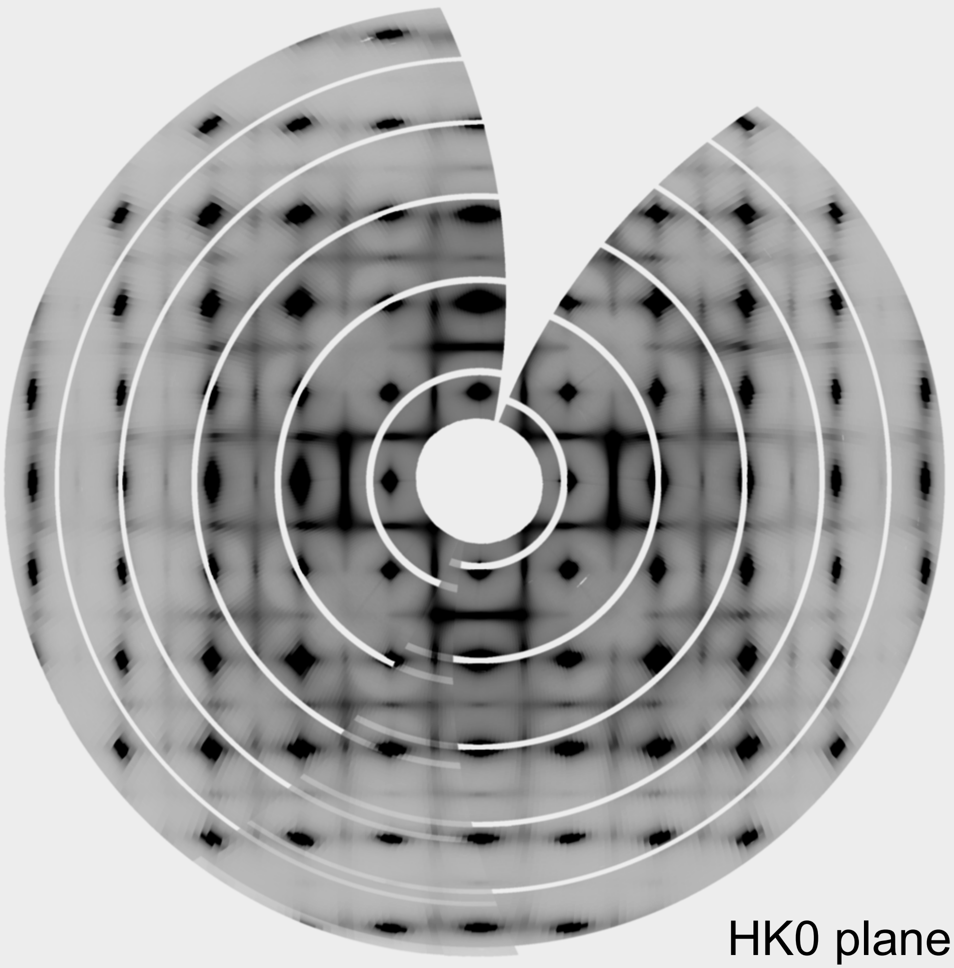
$k_f \sim 1.57$ Å^{-1}

measured on the images

$k_f \sim 1.573$ Å^{-1}

free electron model with 2 electrons per Zn atom

Prussian blue again



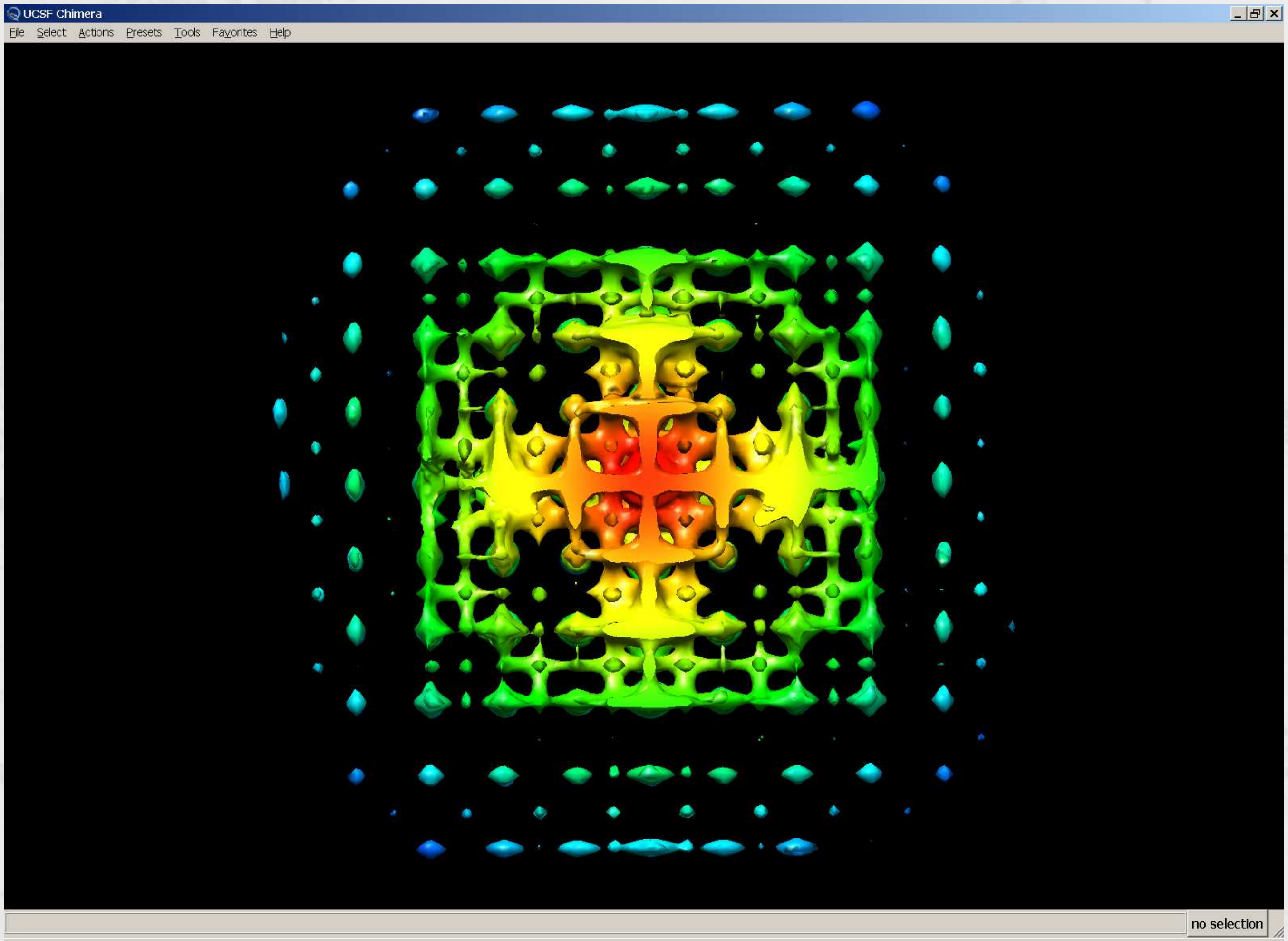
$Mn(II)[Mn(III)(CN)_6]_{2/3} \cdot (6H_2O)_{1/3} \cdot yH_2O$

replacement of $[Mn(CN)_6)]$ by $[6H_2O]$

not fully random!

inelastic contribution to the strong diffuse features is negligible

Step towards 3D pair distribution function?



Pioneering work:

P. Schaub, T. Weber, W. Steurer
Phil. Mag. **87**, 18 (2007)

Concluding remarks

- Protocol for diffuse scattering experiment

  (mapping of reciprocal space, inspection in 3D, inelastic probes)

- Variety of examples illustrating mesoscopic correlations in 3D still waits for a theoretical interpretation

  (prussian blue analogues, ferroelectric perovskites, photonic crystals)

- A combination of bright X rays (ID) with fast detector (PILATUS) would give <u>fast</u> access to high-quality data on reciprocal space

  (kinetic of disorder fluctuations in 3D, mapping in real and reciprocal space (distribution of correlated disorder in a bulk sample)…)