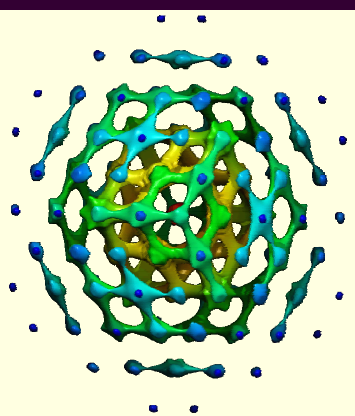
3D Mapping of Reciprocal Space with Synchrotron Light.



Dmitry Chernyshov

Swiss-Norwegian Beam Lines
at ESRF

Фонд Дмитрия Зимина
Династия

outlook

- Bragg and diffuse scattering, Order and disorder.
- Examples of diffuse scattering experiments
- How we do it, and how we are going to do.

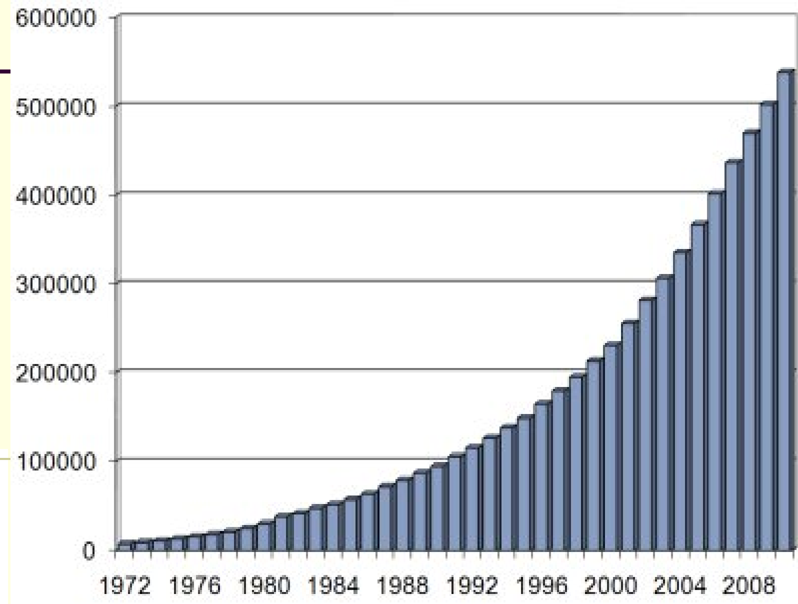
«The effect of the thermal motion on an x-ray beam traversing the crystal has been compared with the effect of the agitated surface of the sea on the image of the setting sun. There is no sharp reflection, but a diffuse ribbon of light stretching towards the observer. This diffusion is obviously produced by the innumerable waves of various length and direction.»

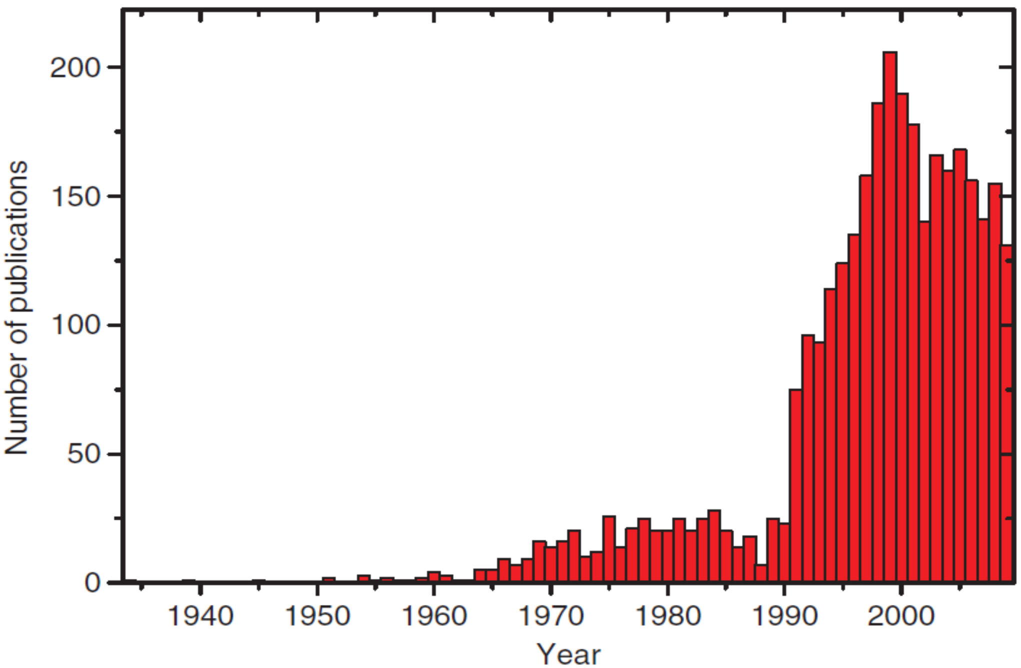
Rep. Prog. Phys. **9**, (1942)

Max Born

X-ray diffraction measuring order … and disorder

Heavy-atom structures	Patterson method	1930‘s
Equal-atom structures	Direct methods	1950‘s
Triclinic structures	4-circle diffractom.	1960‘s
Incommensurate and Quasicrystal structures	Higher dimensional crystallography	1980‘s



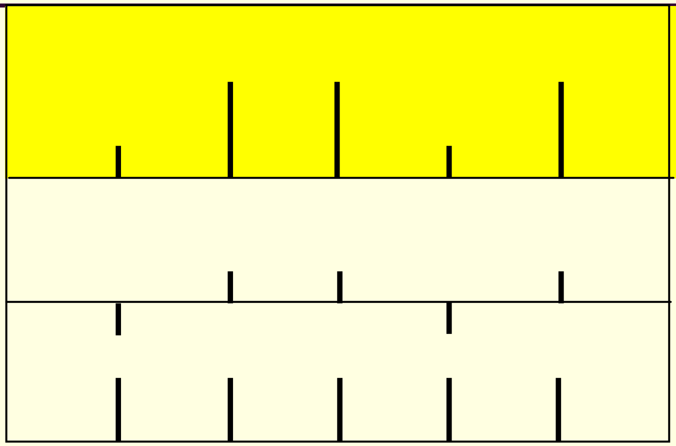


The development of the field of diffuse scattering in terms of publications.

Disordered structures:
Diffuse scattering

D.Chernyshov, A. Bosak Phase Transitions **83**, 77 (2010)

What is diffuse scattering?



f_i

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

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

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

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

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

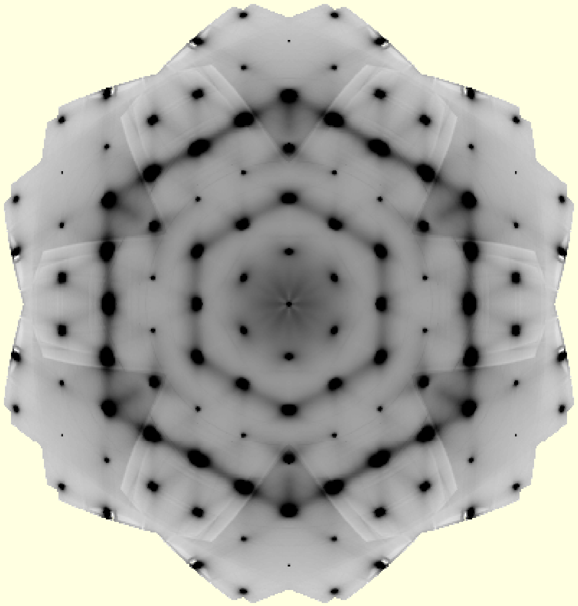
$$I_{diff}(\mathbf{Q}) \approx \sum_i \sum_j \left(f_{ave}(\mathbf{Q}) - f_i(\mathbf{Q})\right)\left(f_{ave}^*(\mathbf{Q}) - f_j^*(\mathbf{Q})\right) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

disorder and diffuse scattering

- Compositional fluctuations
  (solid solutions, alloys….)

- Static displacements
  lattice relaxation near a defect…

- Phonons
  Thermal diffuse scattering…

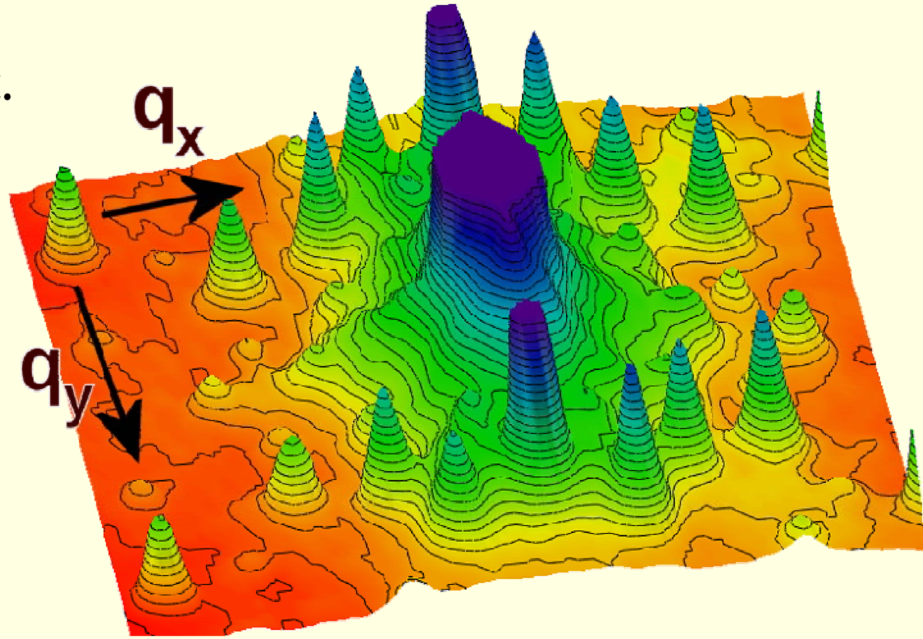


At variance with Bragg scattering

- very weak diffraction intensity
- signal is not well localized in the reciprocal space

Mapping Reciprocal Space – what do we expect to see?

- Superstructure reflections – long range order, commensurate or not.
- Diffuse scattering due to fluctuations of composition
- Thermal diffuse scattering - phonons
- Lattice deformations near defects, local strains, fluctuations of static displacements
- Domains and domain walls
- Effects of electron-phonon coupling



From history of diffuse scattering

Diffuse rods in diamonds

C.V. Raman and P. Nilakantan, 'Specular Reflection of X-rays by High Frequency Sound Waves', *Nature*, 145 (1940) 667.

Raman: we see effect of waves generated by X-rays

K. Lonsdale and I.E. Knaggs et al., 'Diffuse Reflection of X-rays by Single Crystals,' *Nature*, 146 (1940) 332-333.

Lonsdale and Born: we see effect of elastic waves

Schrodinger writes to Born

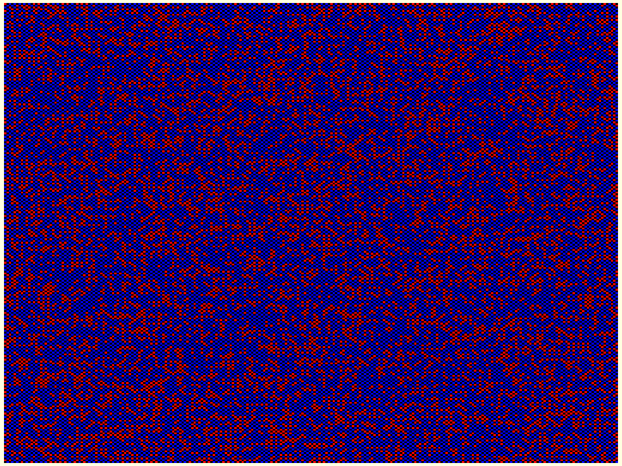
"Either you or Mrs. Lonsdale, in a future publication, should give a simple derivation of Raman's funny formula that fits quantitatively with his experiments! For if you don't, people with or no clear insight into theory will believe that his formula can only be derived in his lunatic way and, since it is so well supported by experiment, they will take that to be a confirmation of this lunatic way of thinking"[90].

M. Born, K. Lonsdale and H. Smith, 'Quantum Theory and Diffuse X-ray Reflexions', *Nature* 149 (1942) 402-40.

Modern lattice dynamics has started..

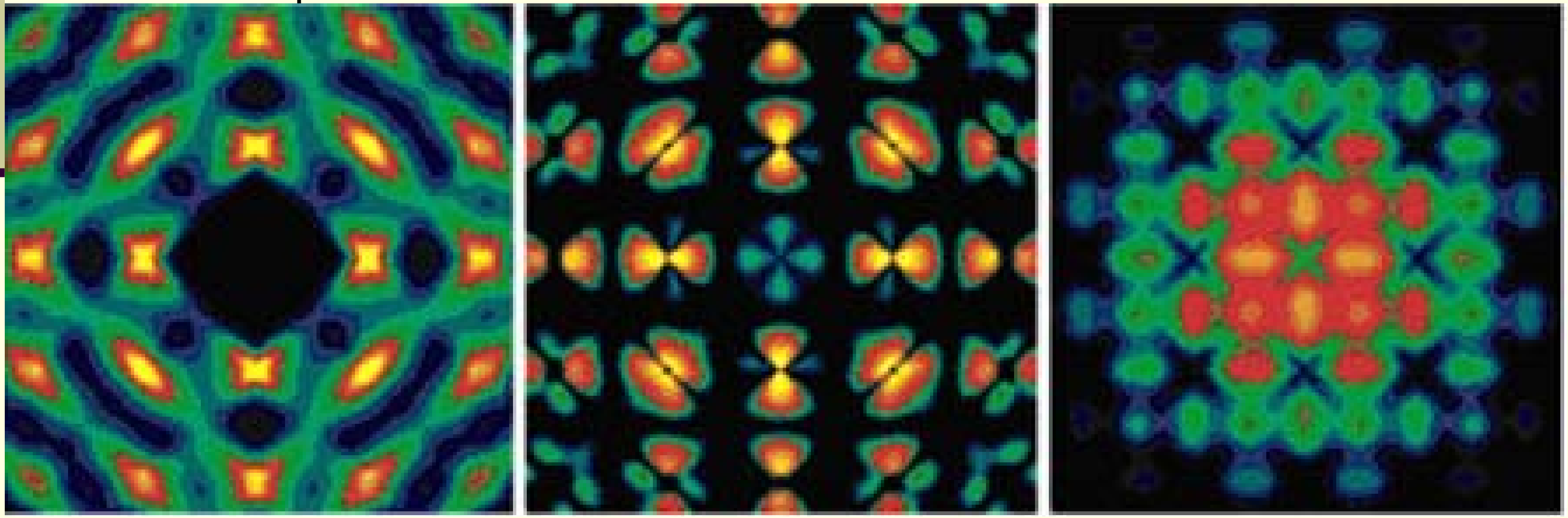
Modeling diffuse scattering

- TDS and phonons
- Huang scattering and elastic modules
- Short-range order and correlation coefficients



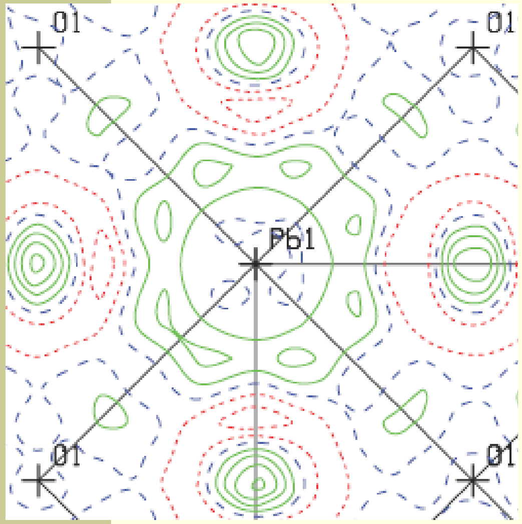
$$I_{\mathbf{q}} = N\left\langle \left|c_{\mathbf{q}}\right|^2 \right\rangle \left[\left(f_{\mathbf{q}}^A - f_{\mathbf{q}}^B\right) - \mathbf{q}A_{\mathbf{q}}\right]^2 + TDS$$

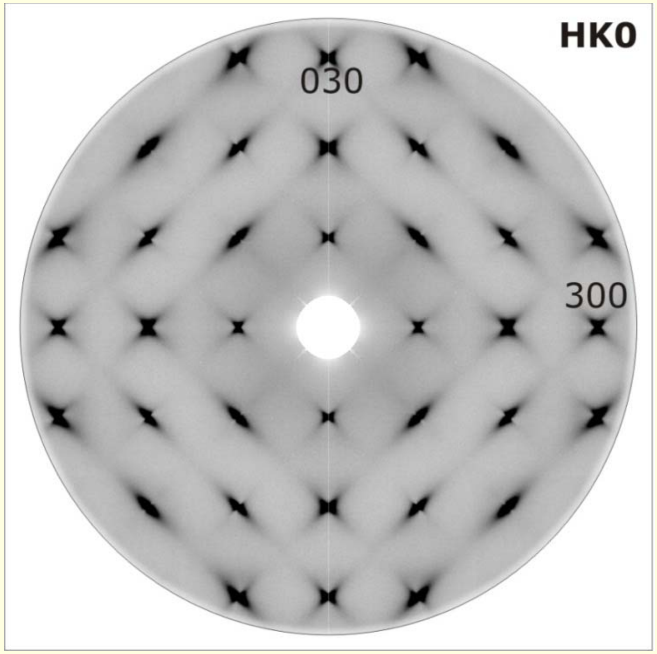
- Real space disordered models

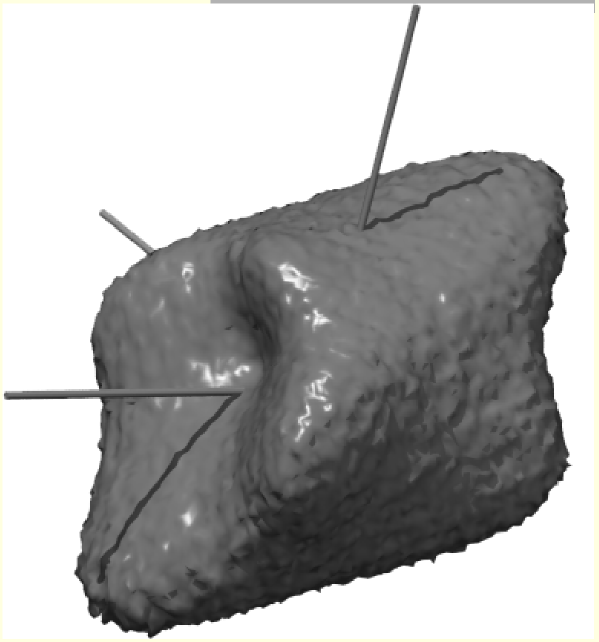


Mezger M., Reichert H., Ramsteiner I.B., Udyansky A., Shchyglo O., Bugaev V.N., Dosch H., Honkimäki V. Phys. Rev., B 73, (2006)

Example I: Relaxor ferroelectics - correlated displacements





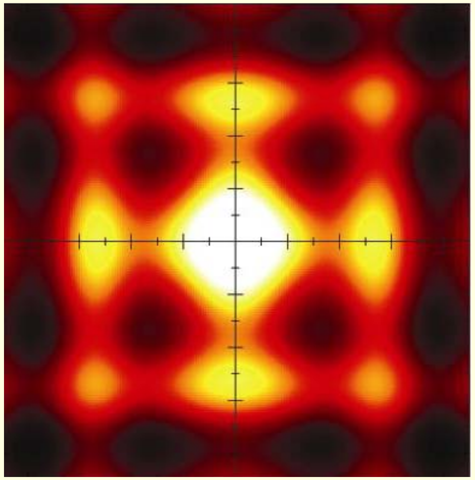


http://lanl.arxiv.org/abs/1101.0490

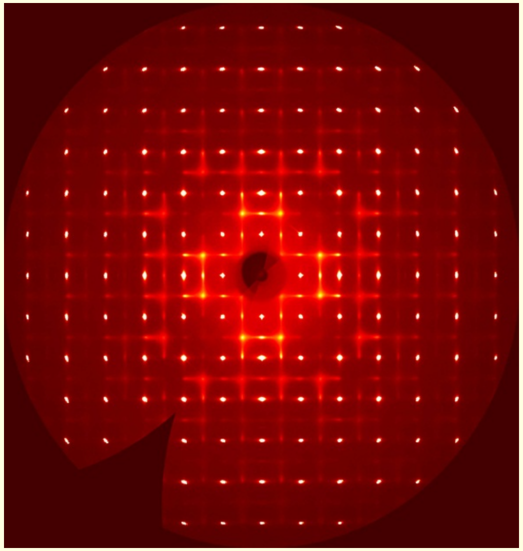
Experimental protocol

- Collect data for the average structure
- Collect diffuse data in a large volume of RS, inspect reciprocal layers
- Collect diffuse data in neighborhood of selected Bragg nodes or specific location in RS.

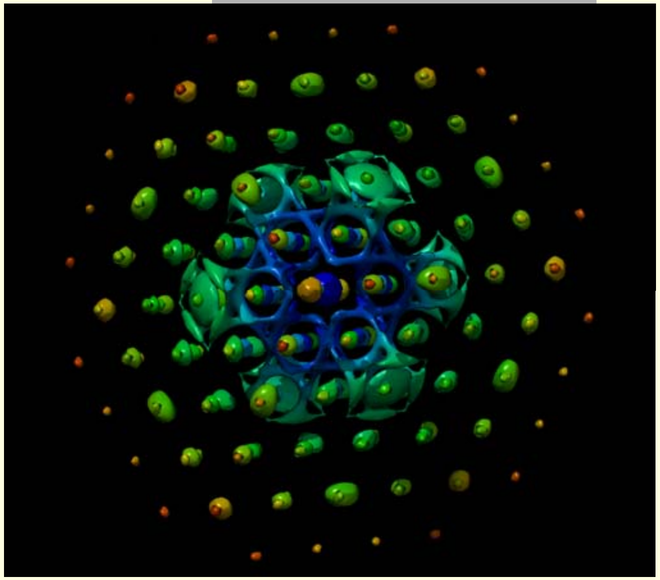
Example II: Prussian Blue Analogue – correlated chemical disorder



$F(\mathbf{q}) = (f_{6H_2O} - f_{Mn(CN)_6})^2$



$I(\mathbf{q}) \propto F(\mathbf{q}) \cdot S(\mathbf{q})$

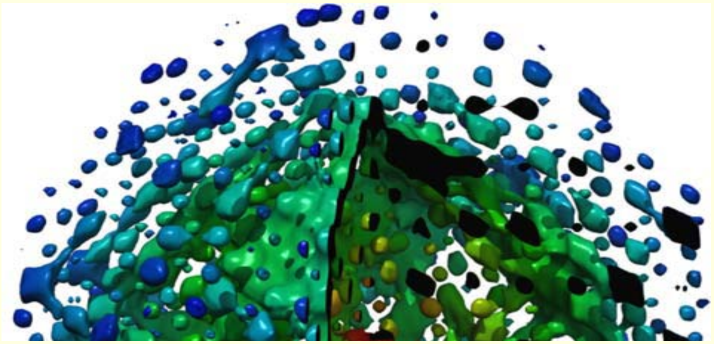


Chernyshov, D., Bosak, A. Phase Transitions, 2010

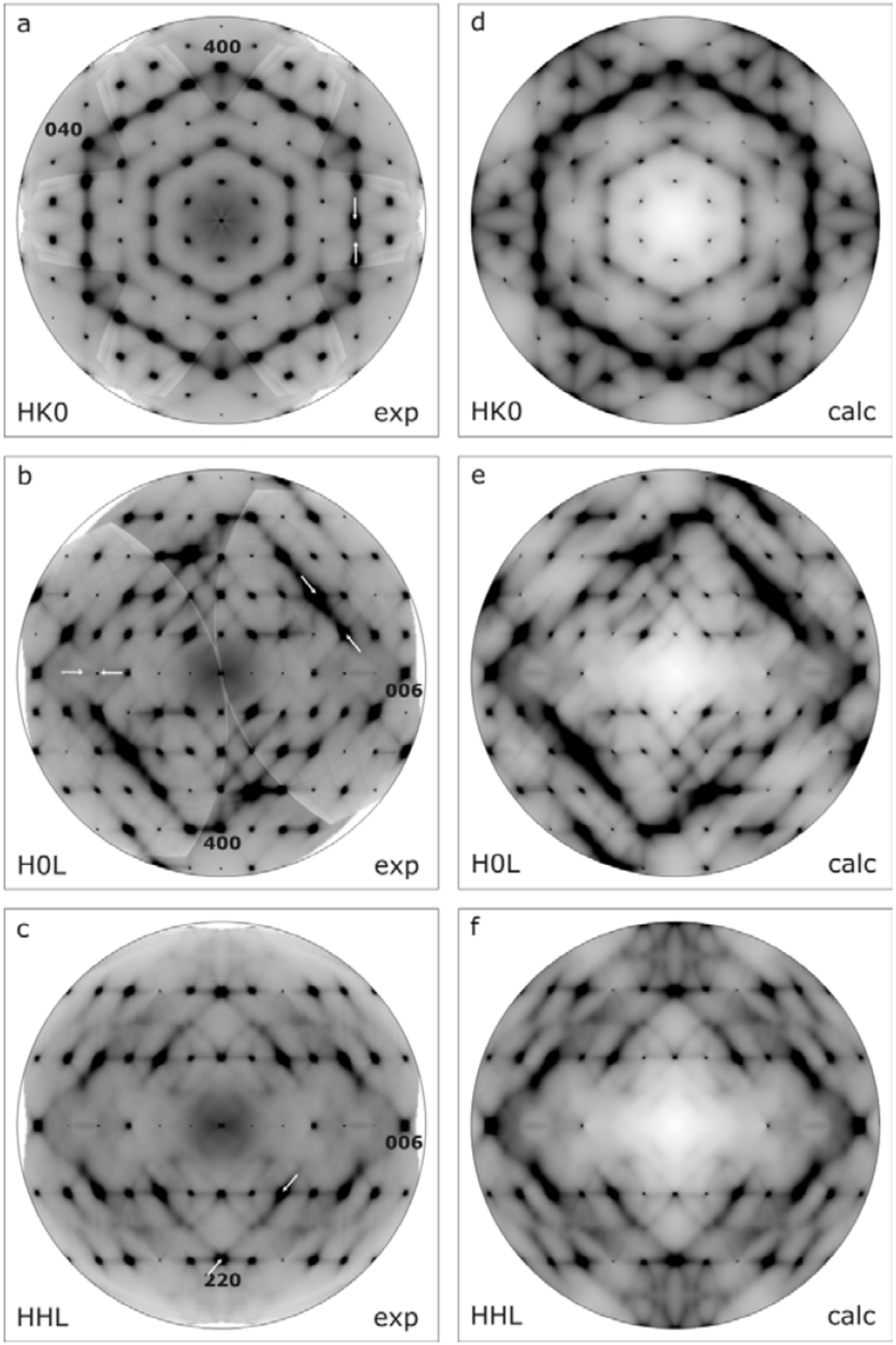
Notes on analysis

- Analyze average structure first to find what is disordered
- Calculate difference form-factor to see modulation of diffuse scattering
- Correct for this modulation to see genuine correlation pattern

Example III: TDS in Quartz – only phonons

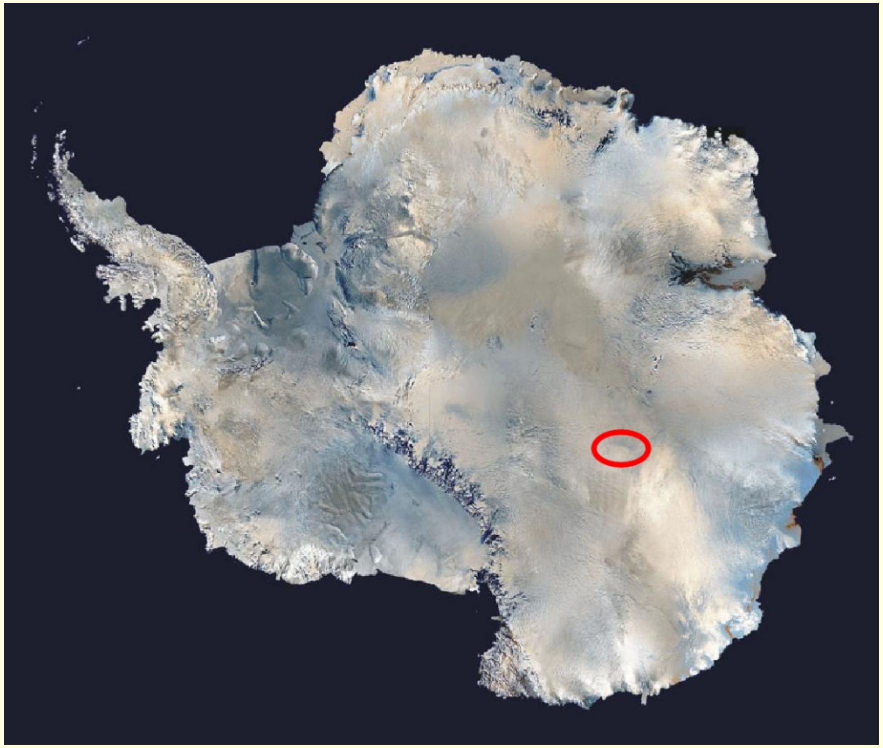


A. Bosak et al,
Zeitschrift für Kristallographie 2011



- The softest phonons are not located along high symmetry directions
- Certain features in the phonon density of states are not related to phonon dispersions in high-symmetry direction

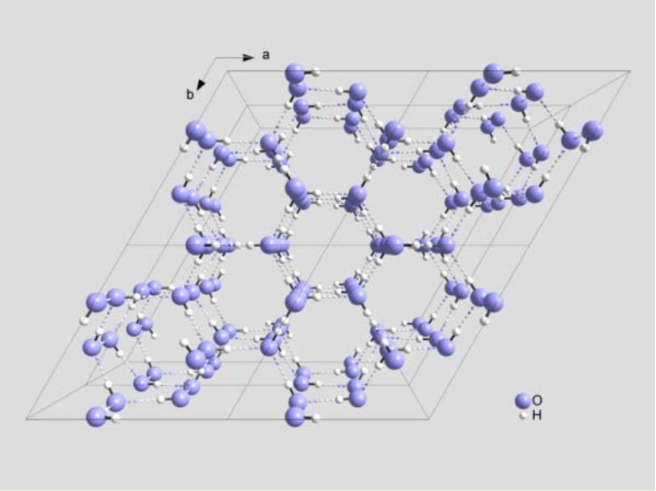
Example IV: normal Ice - something inelastic?



H_2O: not accessible for INS
D_2O: not the same as H_2O
($m_D = 2m_H$)

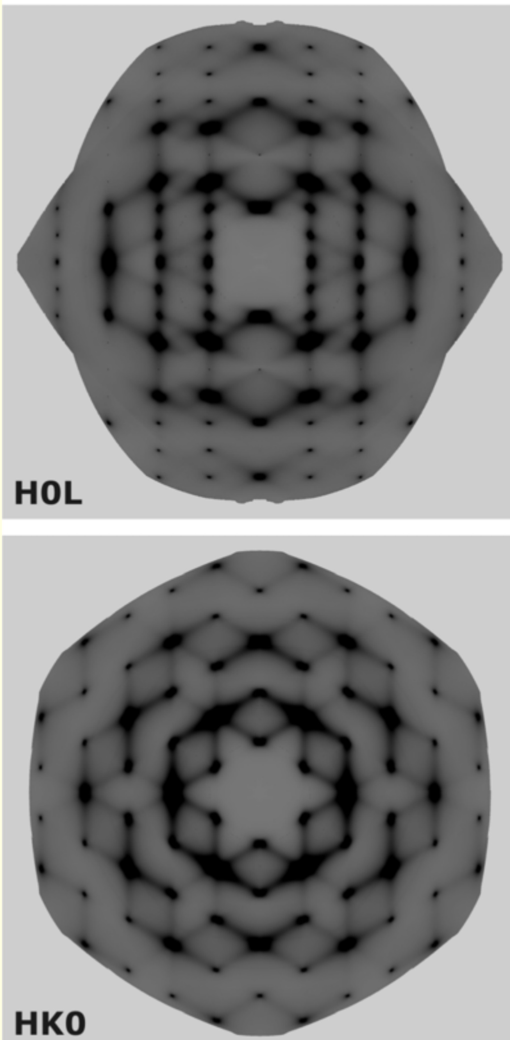
IXS: never done on single crystals

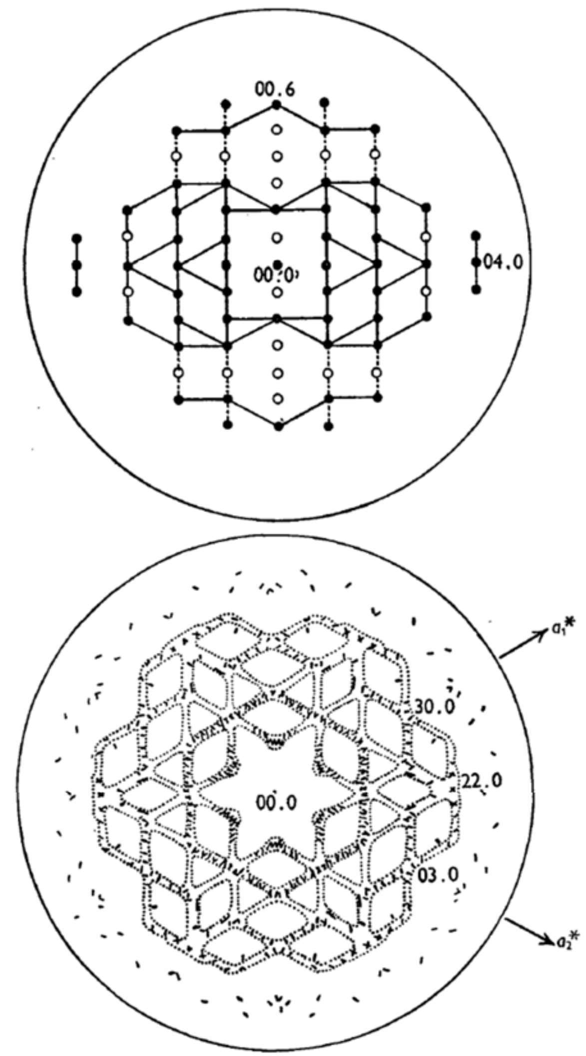
diffuse x-ray scattering:
the first and the last experiment in 1949 [*Acta Cryst. 2, 222-228 (1949) P. G. Owston*]



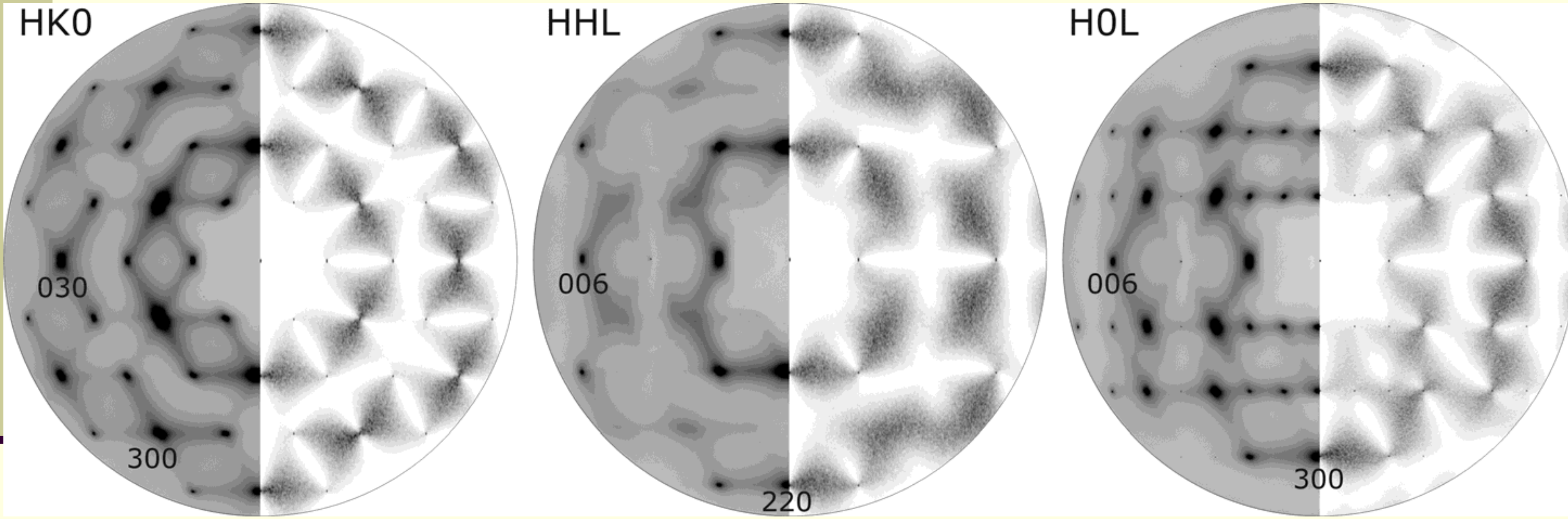
natural single crystals
from Vostok station
depth: 3500 m
typical size: 1 m

2011 1949



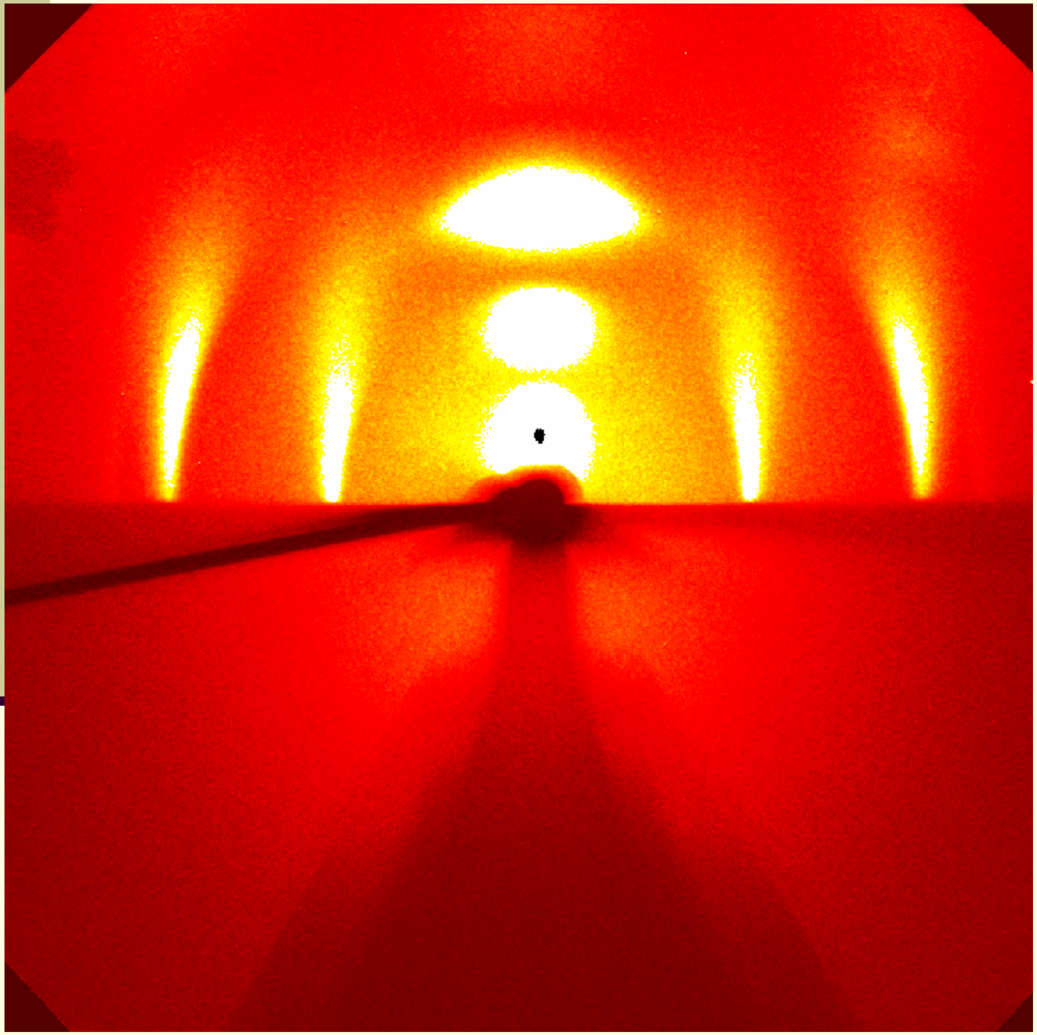


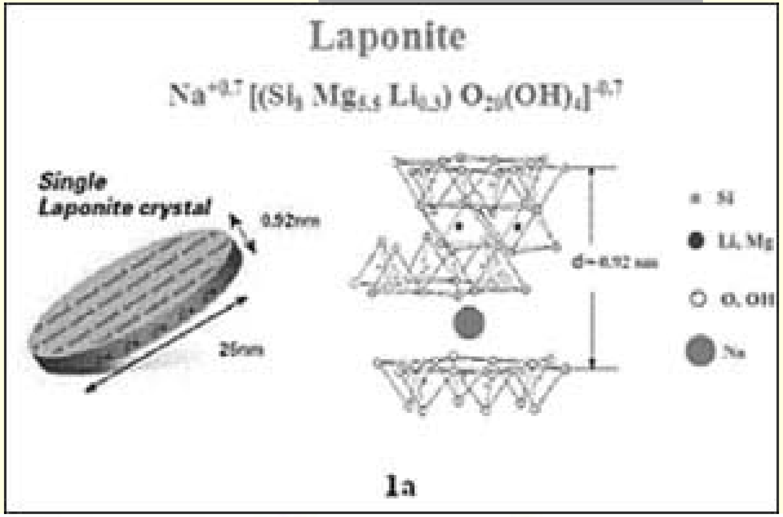
Static or Dynamic?



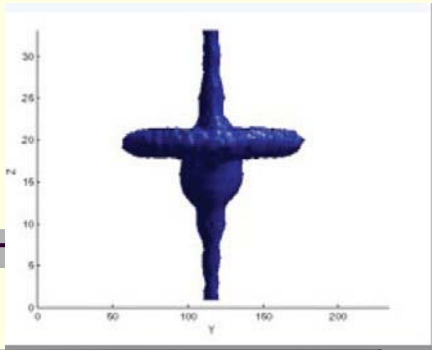
- Diffuse scattering generated with "ice rules" shows a similarity but it is much more smeared comparing with experiment (i.e. much less correlated)
- IXS shows that most of scattering is inelastic

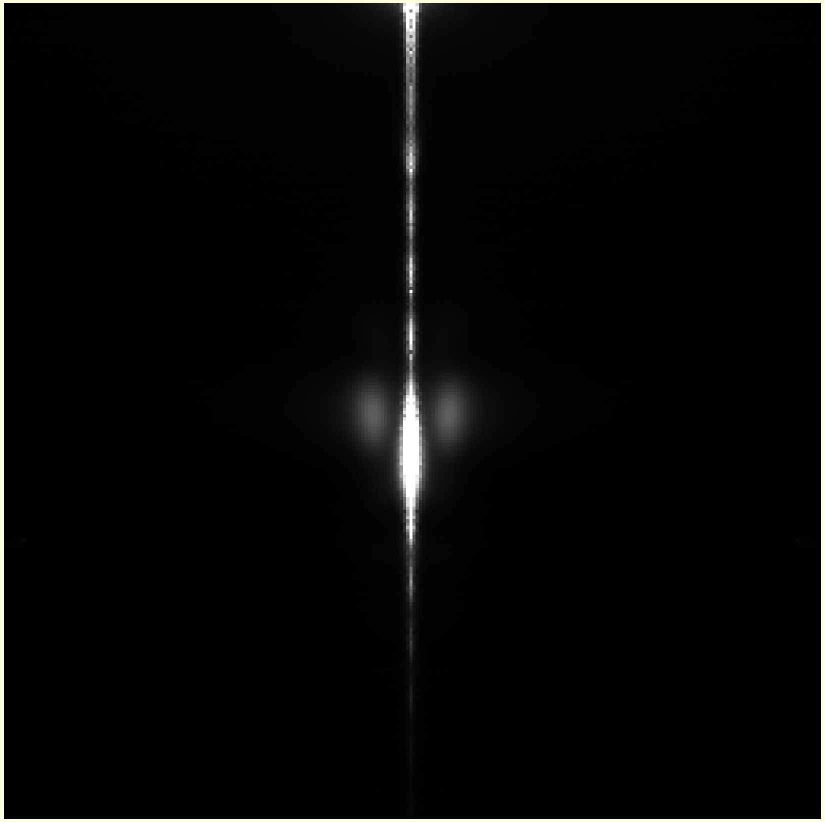
Example V: thin films

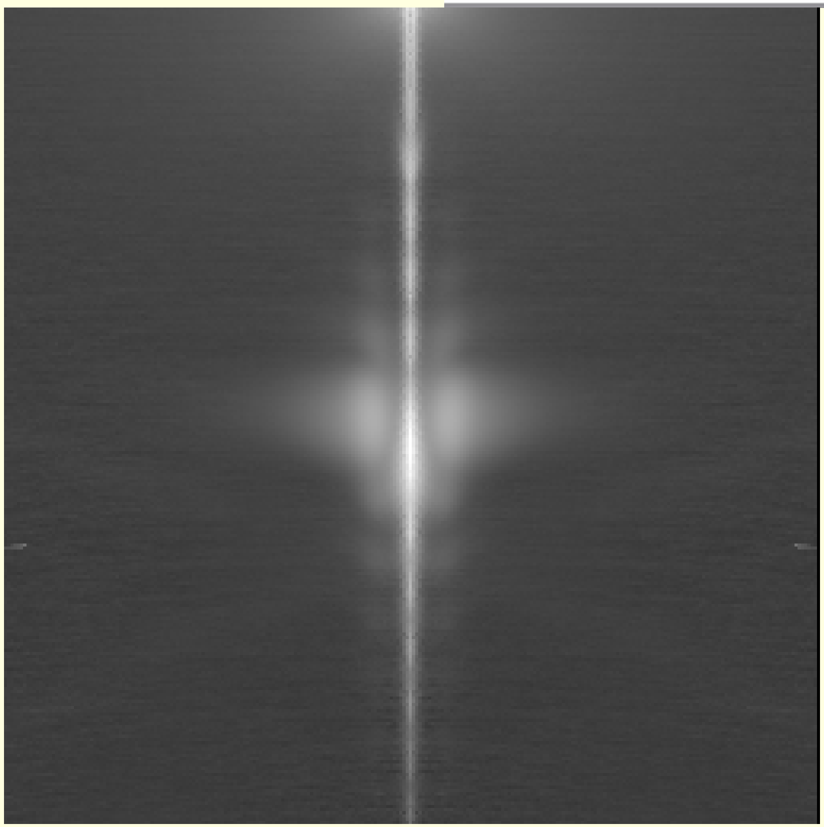




$PbTiO_3$ thin film



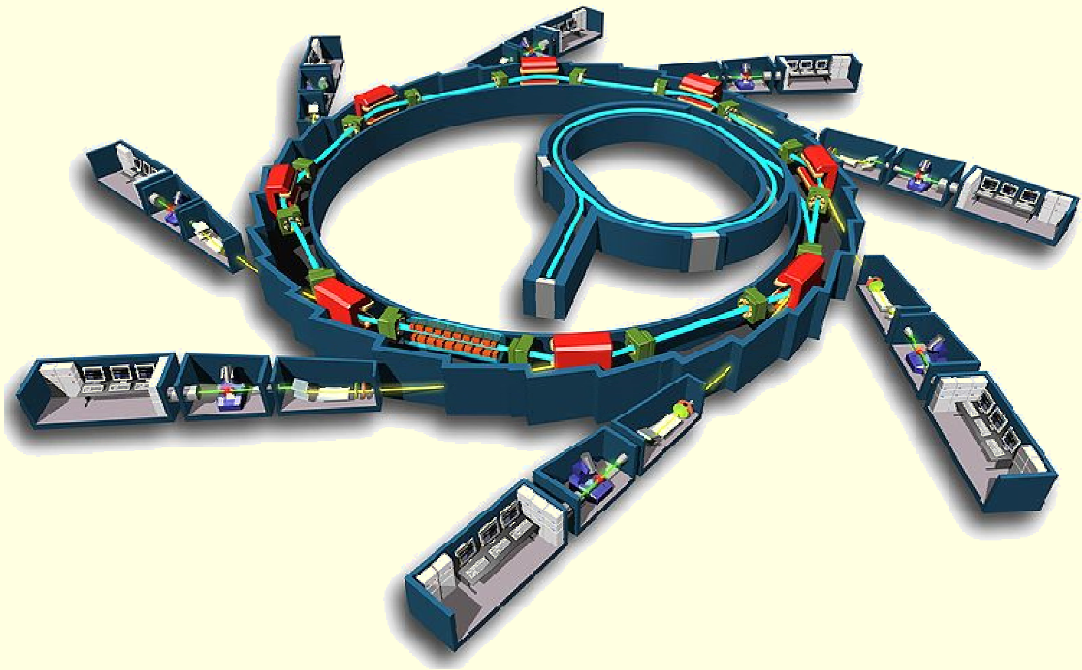




PTO (50 u.c.)/STO, T. Tubelle, Norway

Bragg and Diffuse scattering with synchrotron radiation

- High brightness of radiation and accurate detection of scattered photons
- Fast collection of complete and redundant scattering data
- Evolution of scattered pattern with temperature, pressure, external field, time..
- Possibility to combine elastic and inelastic scattering experiments, small and wide angle scattering, imaging and many other options.



www.esrf.eu

data collection modes for diffuse scattering

- 1D scans –point detector or area detector data.
- 2D scans – reconstructed layers of reciprocal space
- 3D data –diffuse scattering in a large volume or locally near a Bragg node.
- Diffuse scattering as a function of external stimuli.

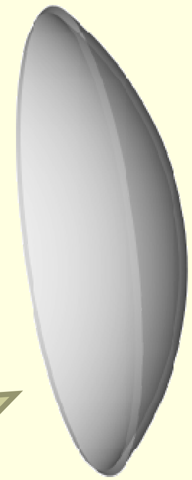
MAR345 – large maps of reciprocal space, tolerates overexposure. Slow

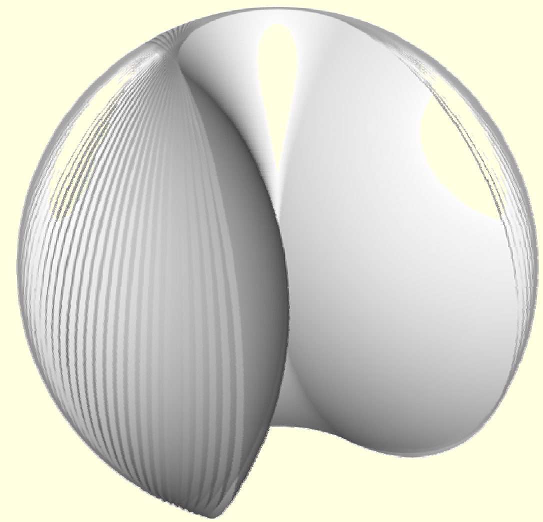
TITAN CCD (KUMA6) – local maps, does not like overexposure. Relatively fast

Completeness and redundancy (use different orientations, scan in different directions), accurate intensities, accurate Bragg data, well calibrated parameters of a diffractometer….

From area detector images to 3D data

flat image
MAR
EDF
CBF
...





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

CCP4 map format

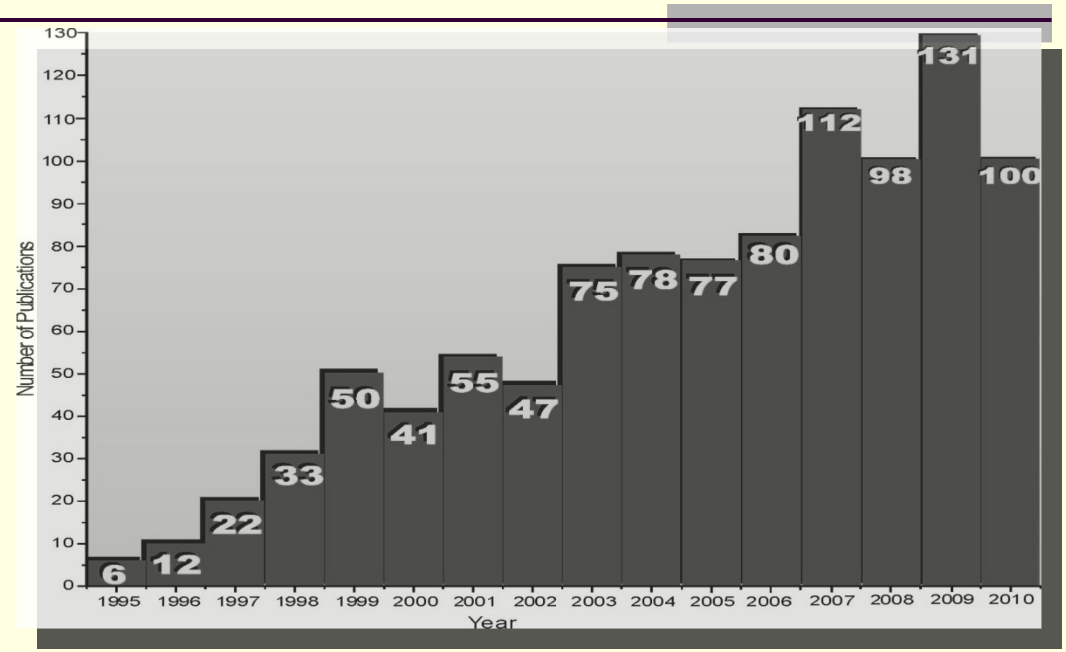
UCSF Chimera

VRML
X3D
POV-Ray
...

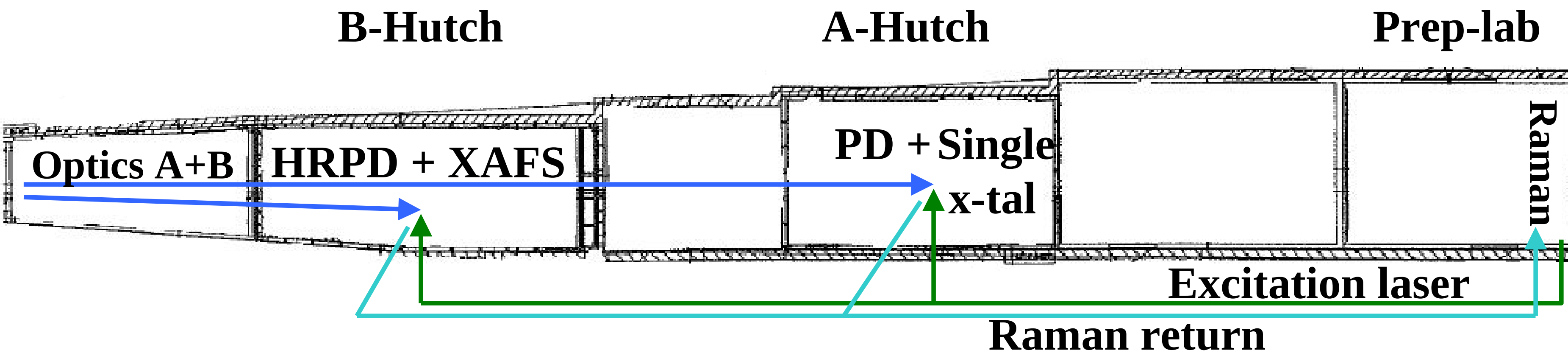
Swiss-Norwegian Beam Lines

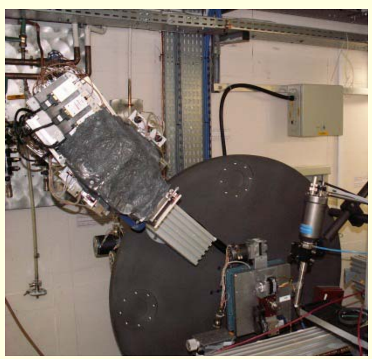
A joint project funded by the Norwegian Research Council and the Swiss State Secretariat for Education and Research in Switzerland

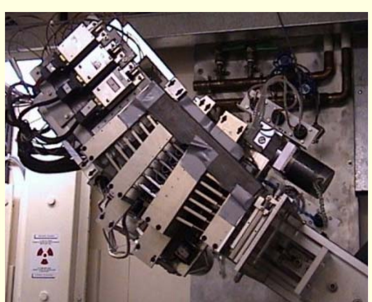
Open for users since autumn '94

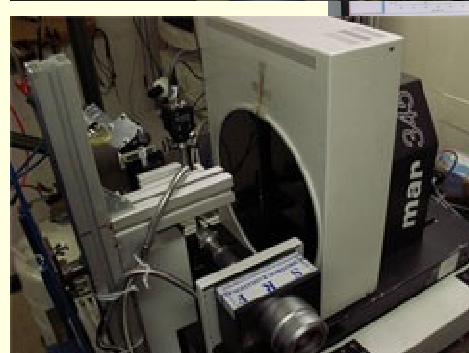


Swiss-Norwegian Beam Lines





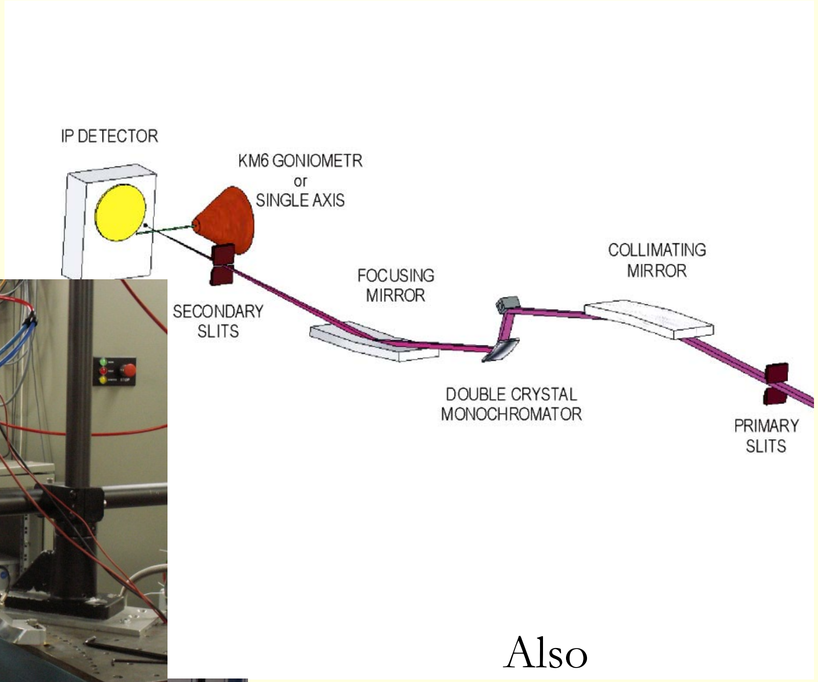


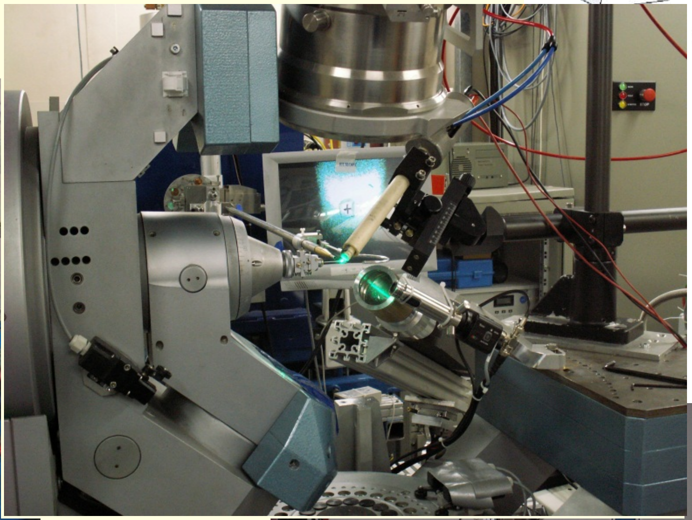


A-line

<u>First Branch (A-Line) is dedicated to</u>:

- **Single Crystal Diffraction**
- **Powder Diffraction**
- **High Pressure Experiments**





Also

- Photocrystallography
- Thin films
- Ordered nanoarrays

and

Diffuse scattering

Bragg and diffuse scattering – a dream mode

- Fast – to follow kinetics with SC data
- Suppress background contributions – to see weak features
- Experimental pre-sets - smart scans and tested strategies of data collection
- Friendly software to collect, represent and analyze the data

A Complete Set = Bragg + Diffuse

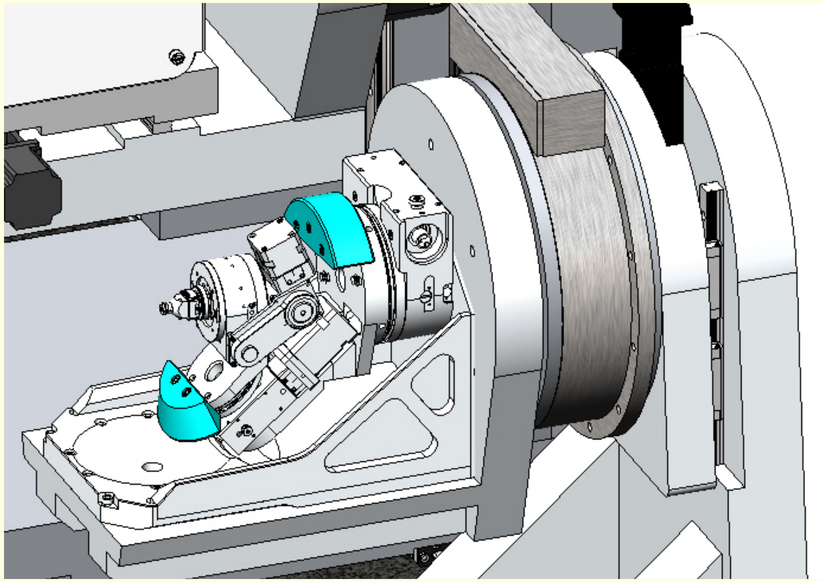
❈Collect Bragg data structure

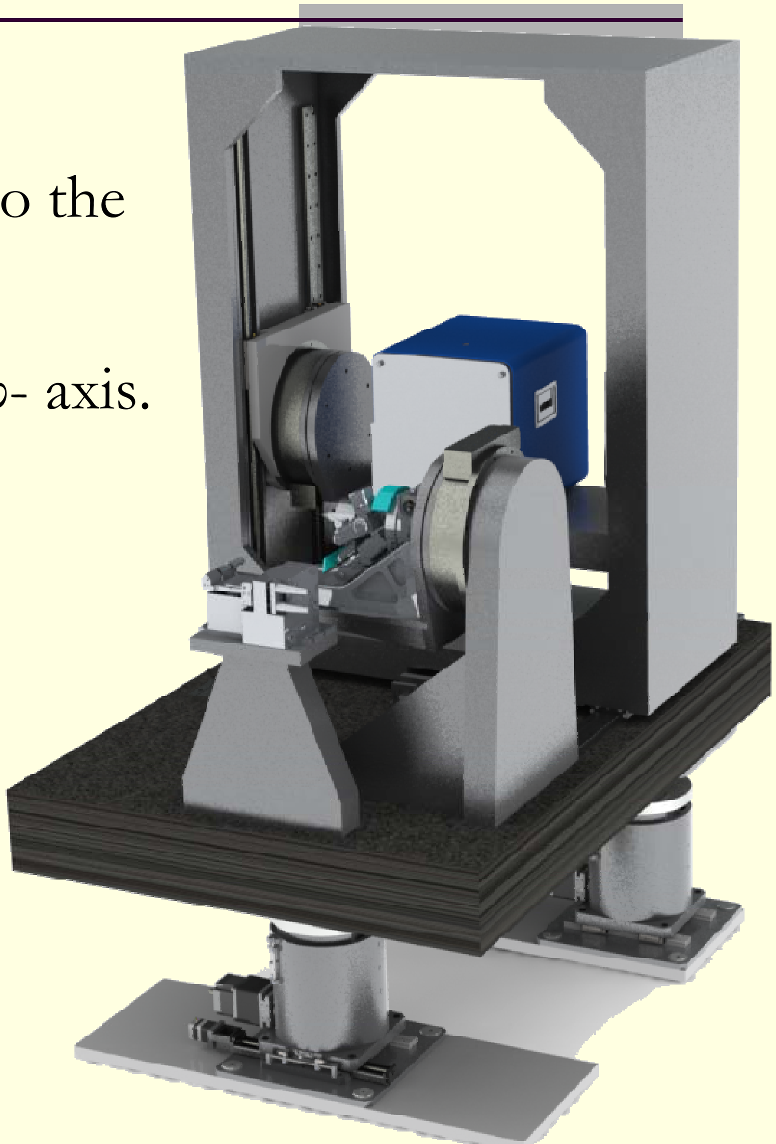
❈Collect diffuse scattering data in a large volume of RS

❈Collect diffuse scattering data near selected Bragg nodes of specific locations in RS.

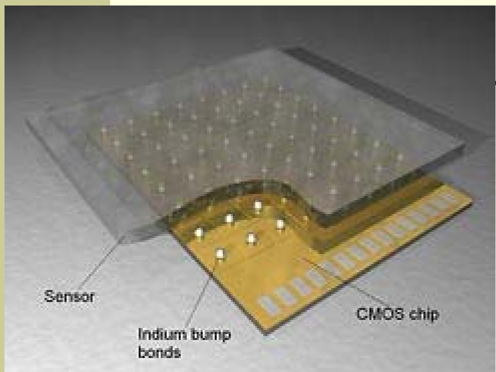
New Diffractometer for Mapping of Reciprocal Space

- PILATUS 2M – shutter free mode
- Detector movements along and normal to the beam, tilting option.
- Huber 3-axis goniometer or heavy-load φ- axis.
- Collimation and alignment tools.





The detector



Number of modules 3 × 8 = 24

Reverse-biased silicon diode array

Sensor thickness 450 µm

Pixel size 172 × 172 µm2

Format 1475 × 1679 = 2,476,525 pixels

Area 254 × 289 mm2

Dynamic range 20 bits

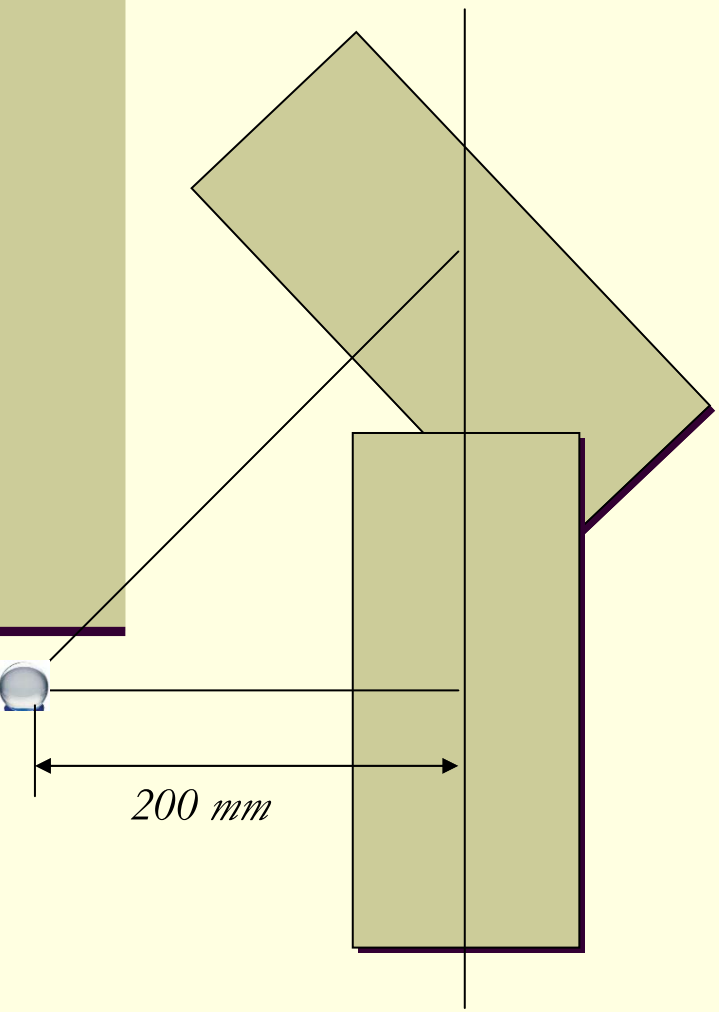
Counting rate per pixel > 2 x 106 X-ray/s

Framing rate 30 Hz

Key features

- Direct detection of X-rays in single-photon-counting mode
- Radiation-tolerant design
- High dynamic range
- Short readout time
- High frame rates
- High counting rates
- No dark current or readout noise
- Adjustable threshold to suppress fluorescence
- Excellent point-spread function
- Electronically gateable
- Shutterless operation

Up to high angles – for good crystals and high-quality Bragg data



Strategy

$2\Theta_{max}$~72°, for λ=0.65 A → d_{hkl}=0.55 A

2 detector positions **X** 3 omega runs ~full sphere

- Structure solution
- Temperature evolution of crystal structure
- Atomic Displacement Parameters
- Kinetics – on scale of minutes for full data, seconds for partial datasets
- Low-resolution maps of large volumes in Reciprocal Space

With high angular resolution…

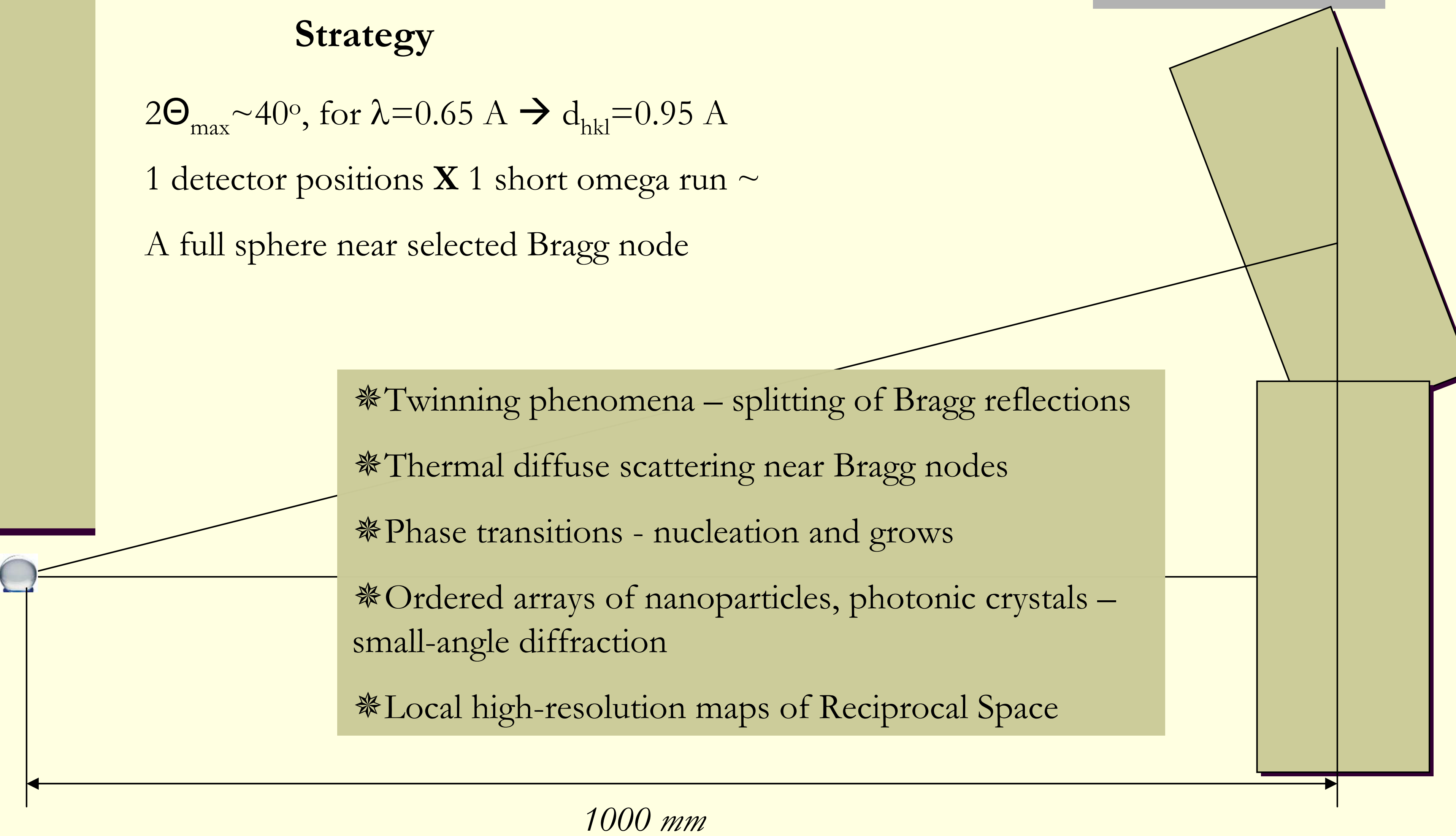
Strategy

$2\Theta_{max} \sim 40^o$, for $\lambda = 0.65$ A → $d_{hkl} = 0.95$ A

1 detector positions **X** 1 short omega run ~

A full sphere near selected Bragg node

- Twinning phenomena – splitting of Bragg reflections
- Thermal diffuse scattering near Bragg nodes
- Phase transitions - nucleation and grows
- Ordered arrays of nanoparticles, photonic crystals – small-angle diffraction
- Local high-resolution maps of Reciprocal Space



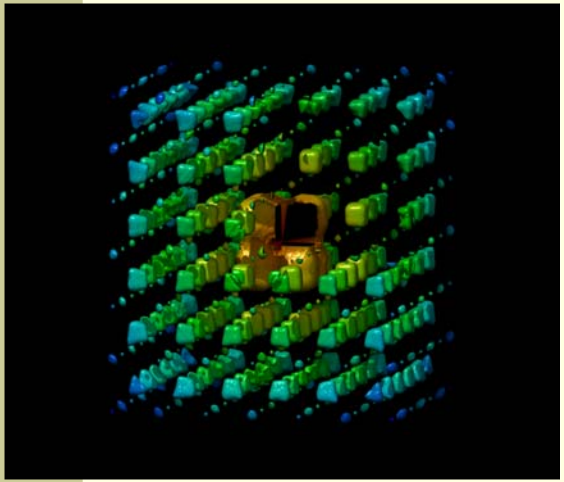
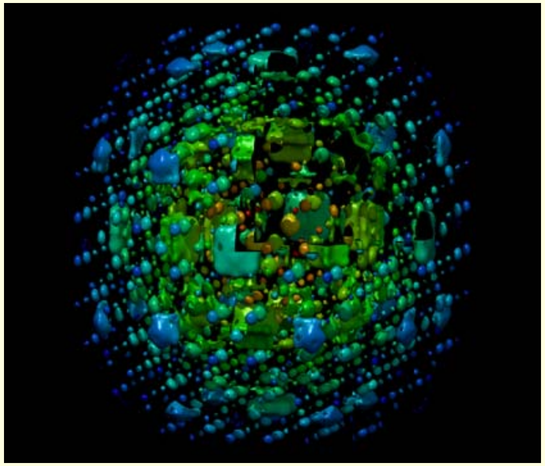
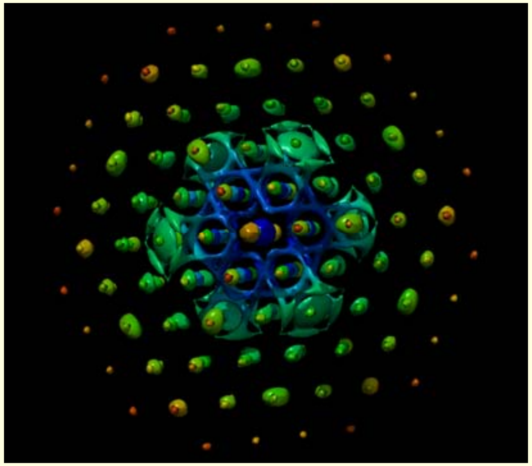
Summary – how to collect good data with synchrotron light

- Start from good Bragg data

(classic diffraction experiment but may need high Q to resolve a disorder, or to get high quality ADPs)

- Collect large volume diffuse map
- Collect HR local maps
- Parameterize a disorder with correlation pattern and Huang and TDS with elastic moduli
- Does not work? Inspect your maps with IXS/INS.
- Repeat as a function of external field…..

Thank you for your attention!

Thanks to

Alexeï Bosak (ESRF), Sergey Vakhrushev (PTI),
Michael Krisch (ESRF), Phil Pattison (SNBL),
Moritz Hoesch (Diamond), Björn Winkler (Goethe-Universität)
Staff and users of SNBL

"Physics is like sex: sure, it may give some practical results, but that's not why we do it."

Richard P. Feynman