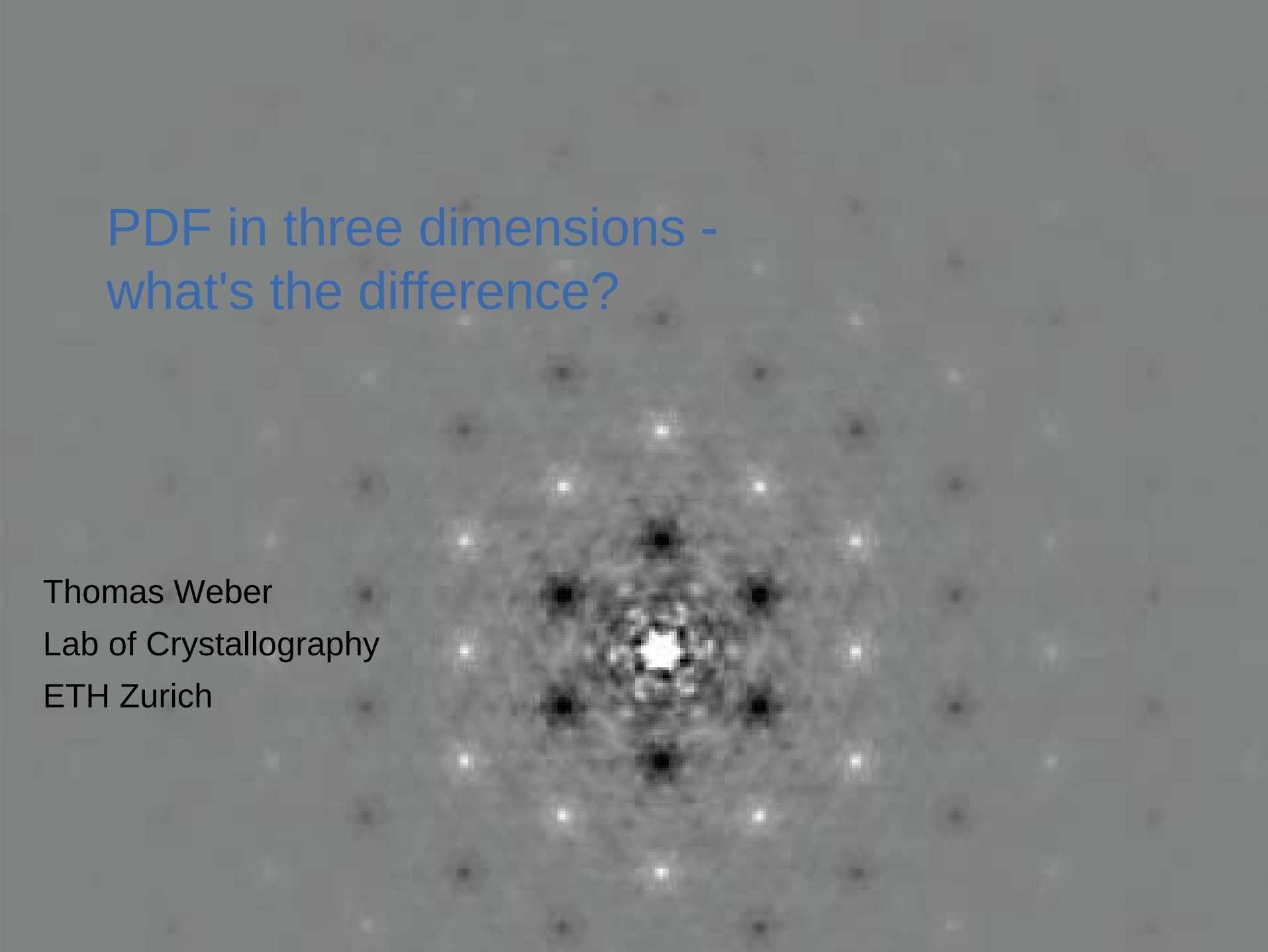
PDF in three dimensions - what's the difference?



Thomas Weber

Lab of Crystallography

ETH Zurich

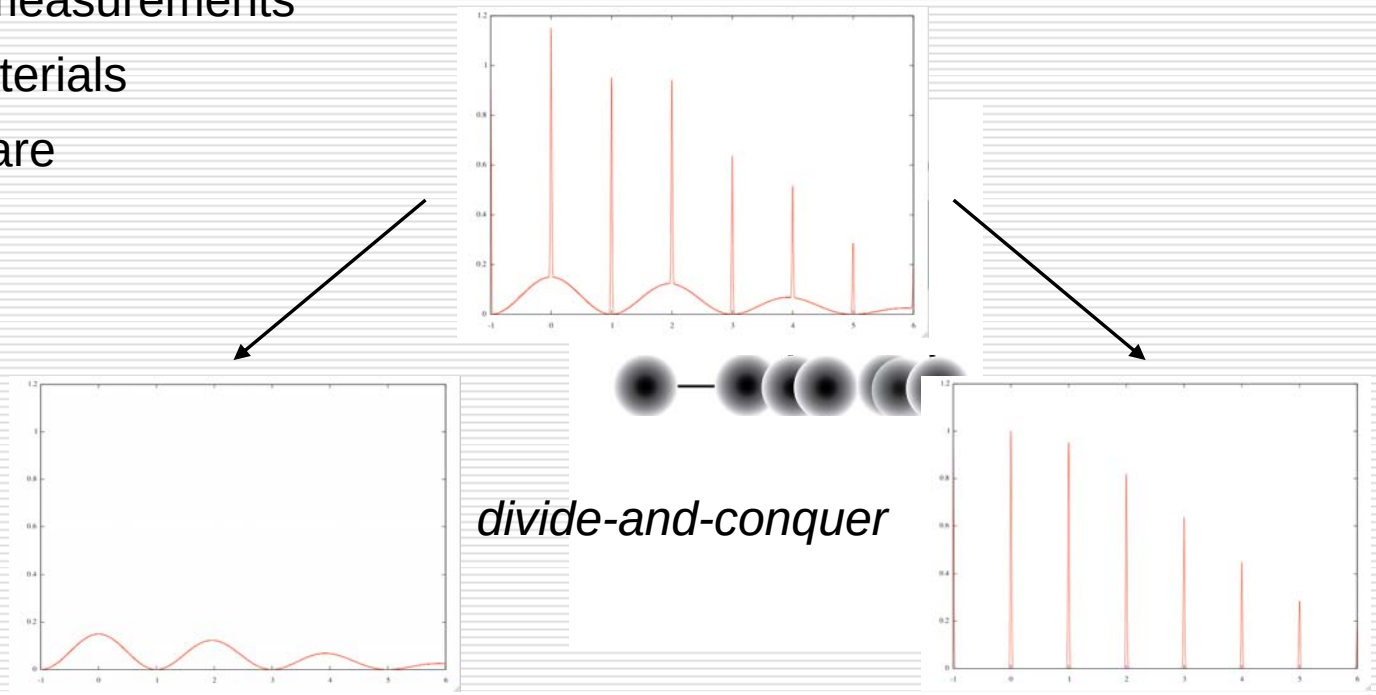
Why 3D-PDF?

1D-PDF is very successful

- nano-crystals
- measurement of high-resolution data
- non-ambient conditions
- time resolved measurements
- amorphous materials
- powerful software
- ...

3D-PDF from single crystals

- provides information about direction of inter-atomic vectors
- allows separation of different classes of diffraction phenomena



divide-and-conquer

Outline

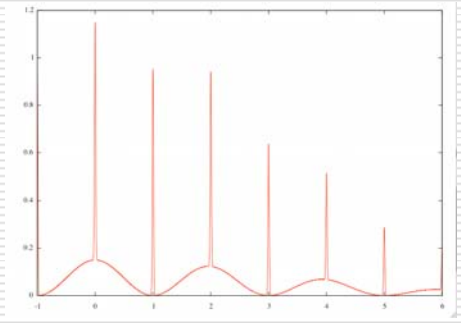
- Theory
- Examples
  - Disorder in a 3D periodic disordered crystal
  - Disorder in quasicrystals
- Outlook

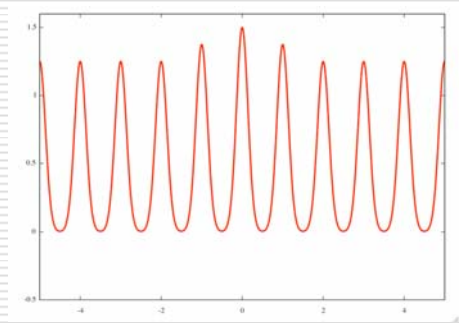
Theory

Fundamental relations

$FT\ [\ I_{total}(\mathrm{hkl})\ ] = P_{total}(\mathrm{xyz})$

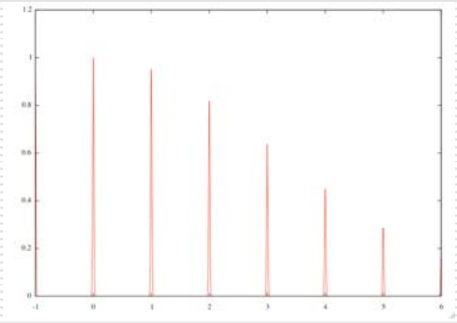
auto-correlation of the real structure

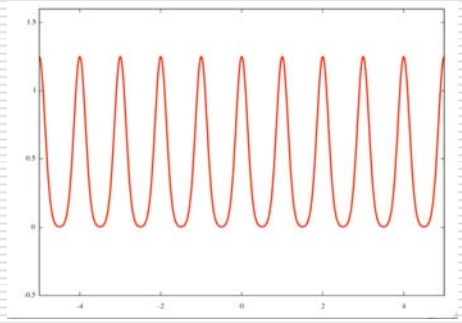




$FT\ [\ I_{Bragg}(\mathrm{hkl})\ ] = P_{aver}(\mathrm{xyz})$

classical Patterson function

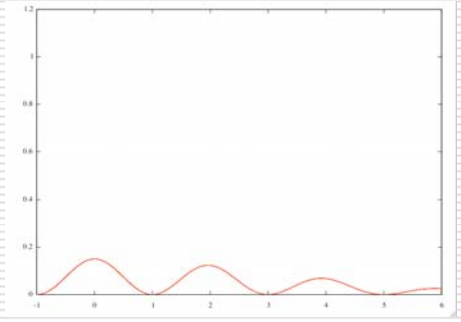


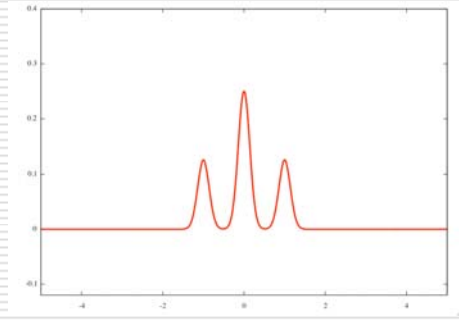


$FT\ [\ I_{diffuse}(\mathrm{hkl})\ ] = FT\ [\ I_{total}(\mathrm{hkl}) - I_{Bragg}(\mathrm{hkl})\ ] =$

$P_{total}(xyz) - P_{aver}(xyz) = \Delta P(xyz)$

auto-correlation of deviations from the average structure



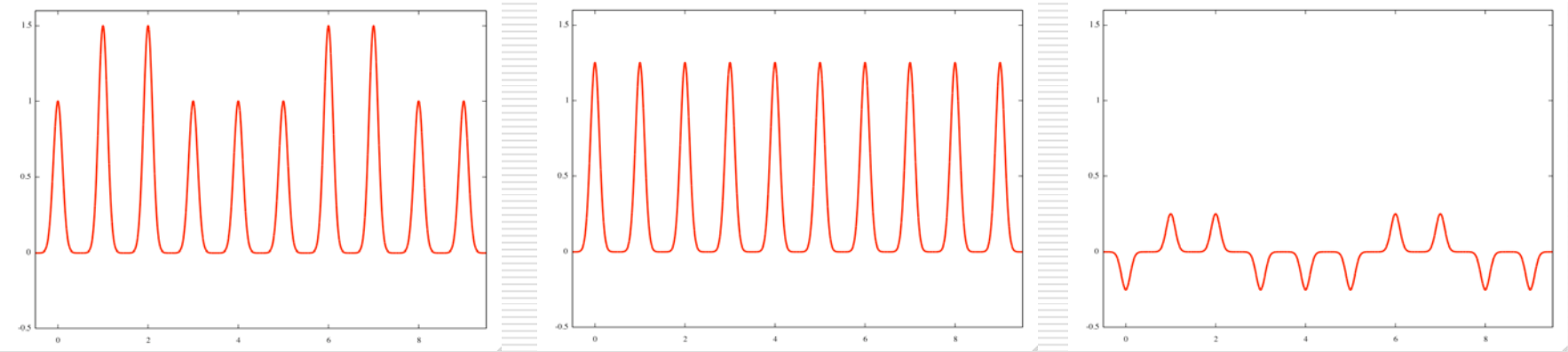


Theory

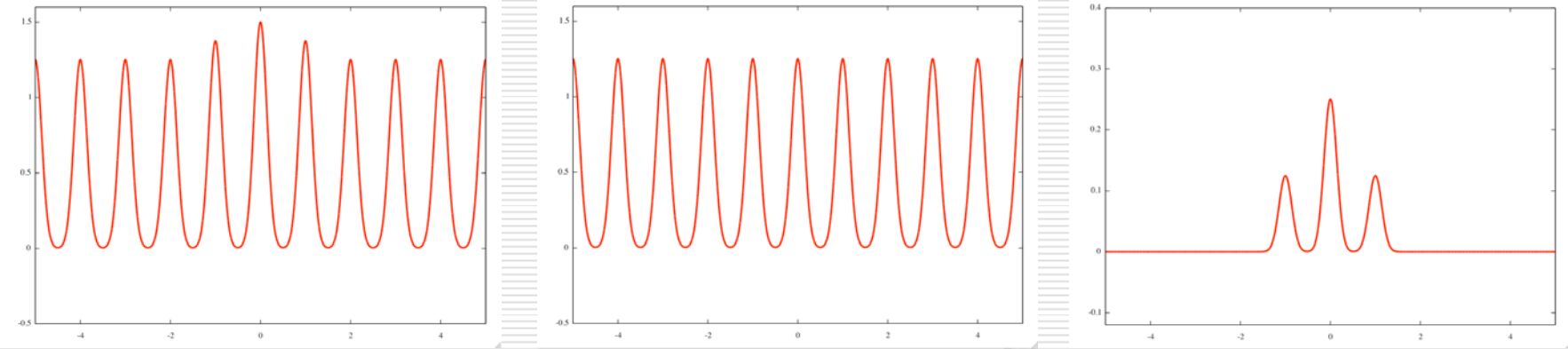
Example: single crystal with positive correlation

real structure - average structure = difference structure

physical space



PDF

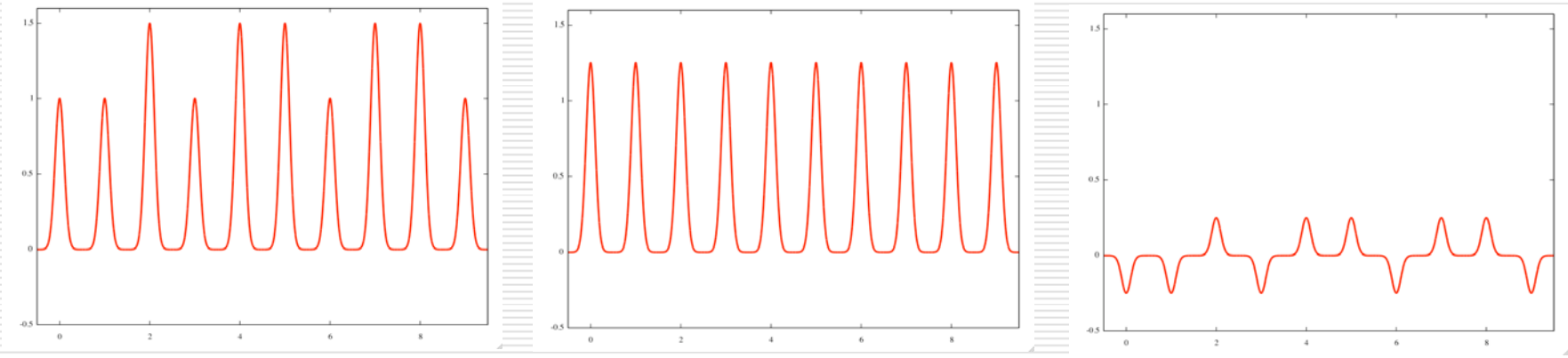


Theory

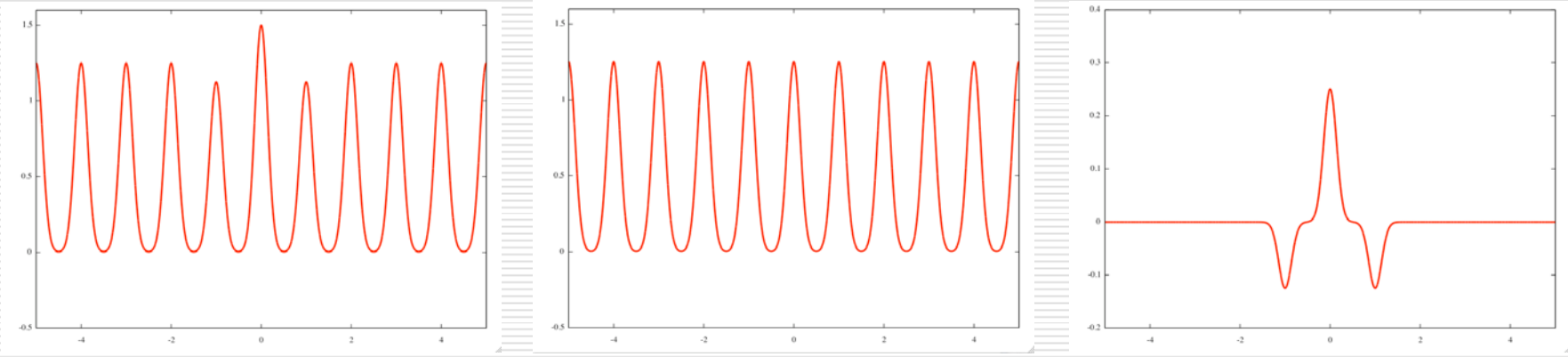
Example: single crystal with negative correlation

real structure - average structure = difference structure

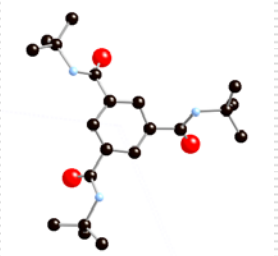
physical space



PDF

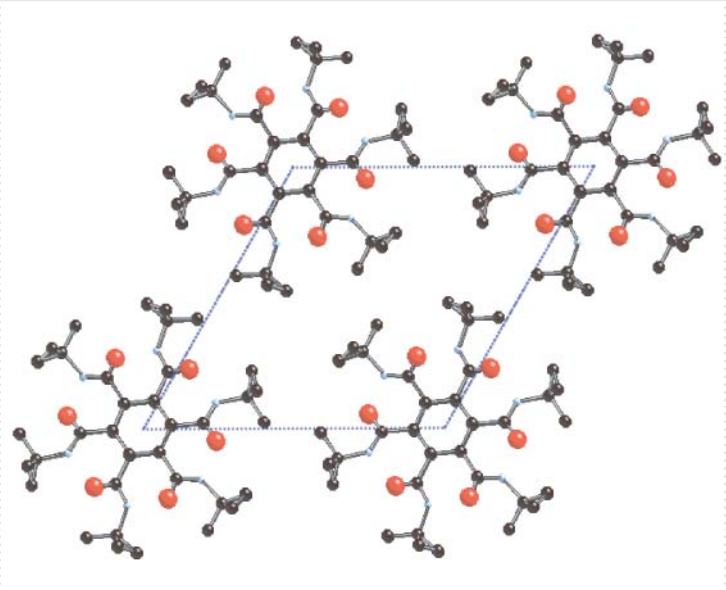


Disorder in N,N',N"–tris–*t*–butyl–1,3,5–benzenetricarboxamide



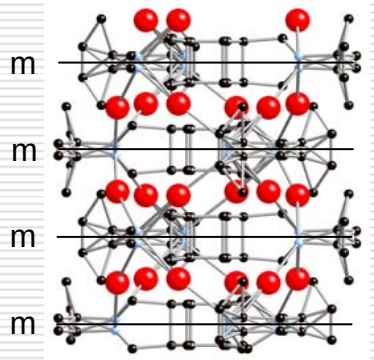
top view

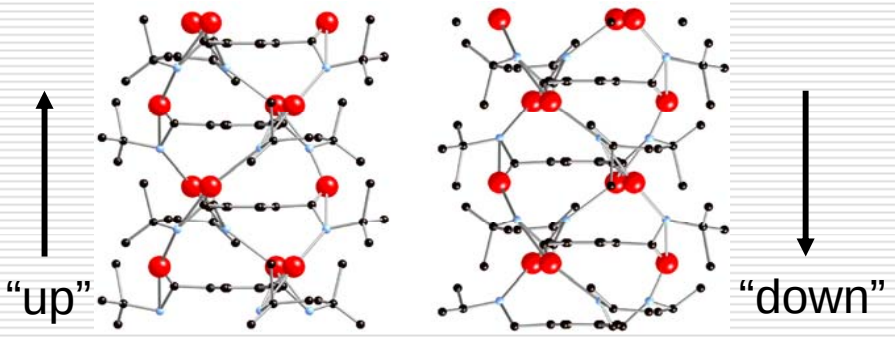
average structure = real structure



side view

average structure





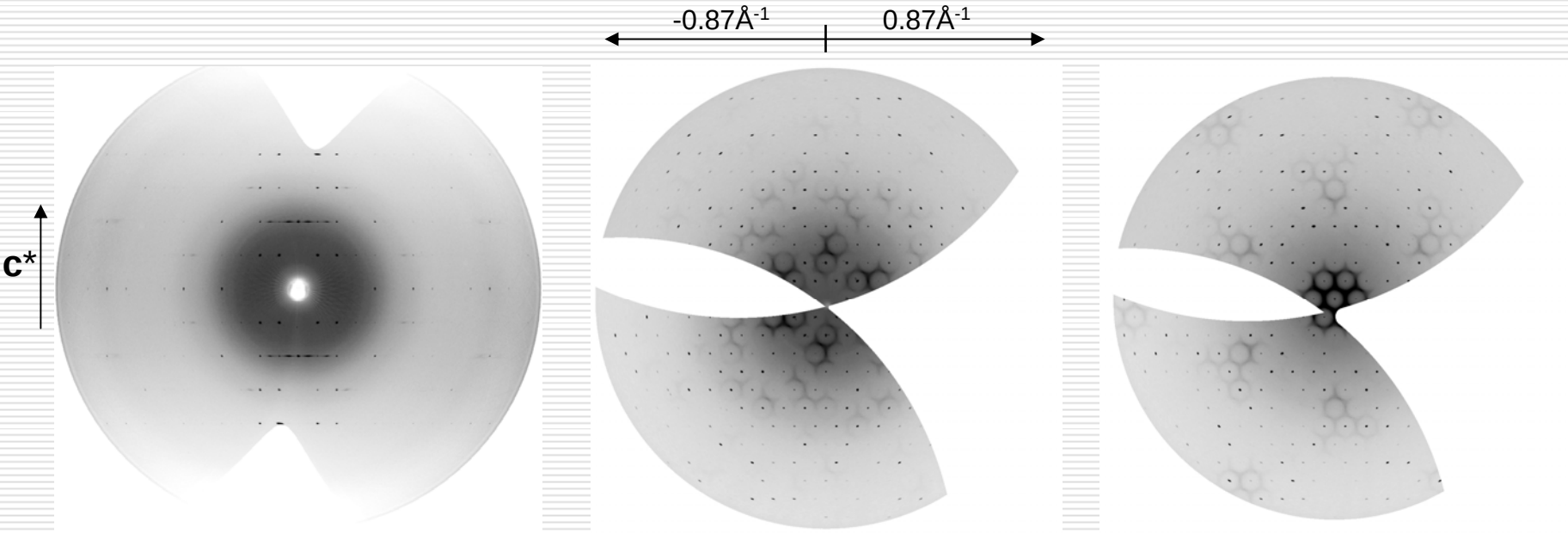
real structure

$P6_3/m$
a=14.100 Å
c=6.930Å

what's the distribution of up and down columns?

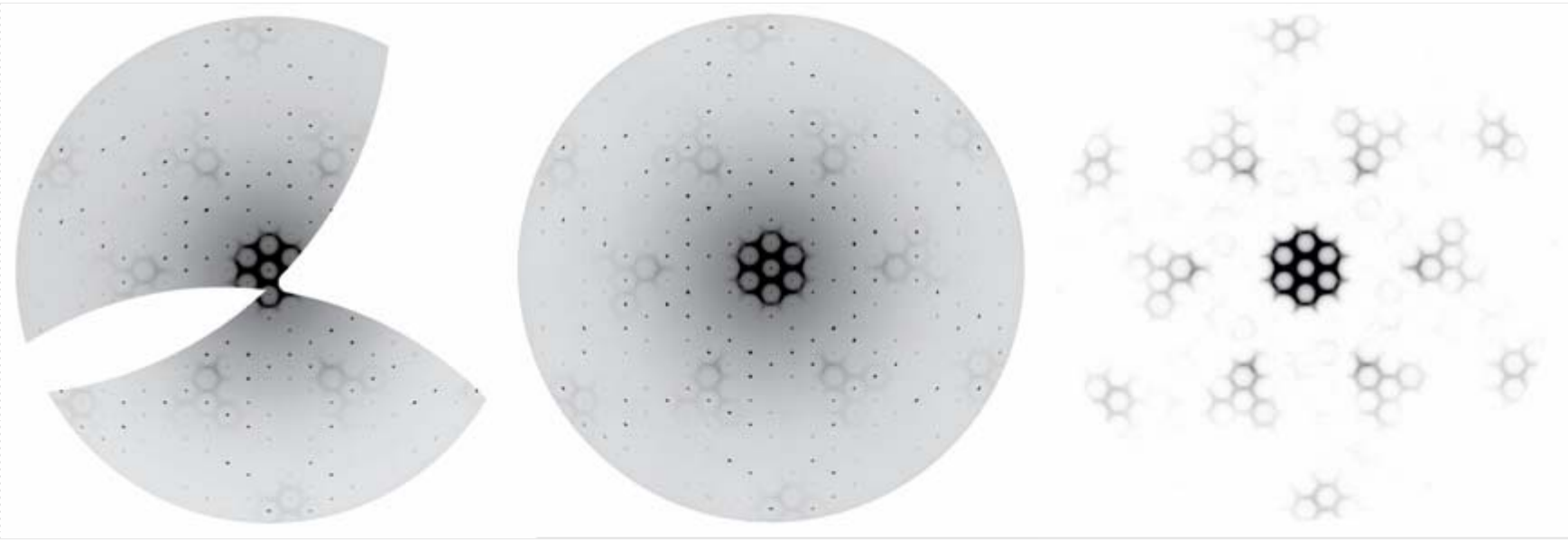
Example: Disorder in N,N',N"–tris–*t*–butyl–1,3,5–benzenetricarboxamide

diffraction patterns (measured at SNBL@ESRF)



h0l hk1 hk2

Data processing



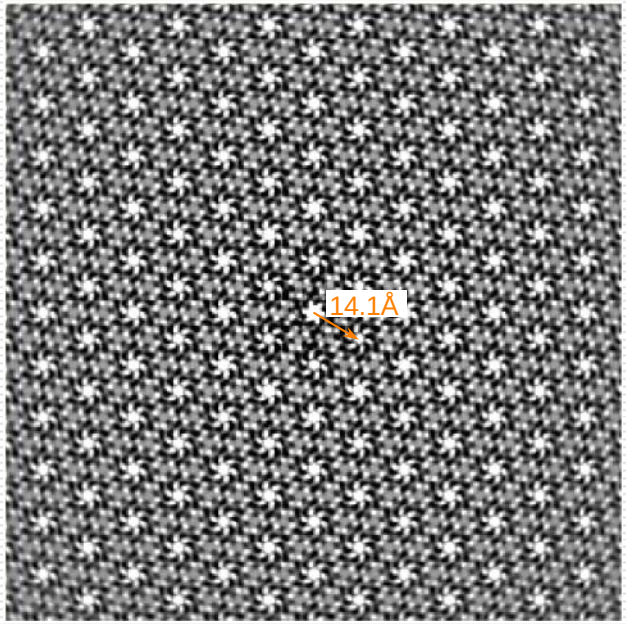
reconstruction of reciprocal space (XCAVATE)

symmetry averaging

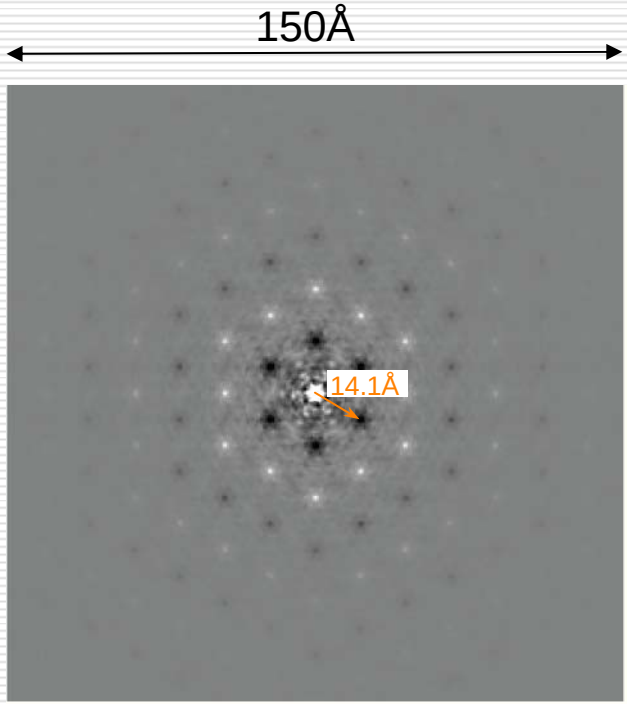
elimination of Bragg reflections and background scattering

Result

zero layer PDF (z = 0)



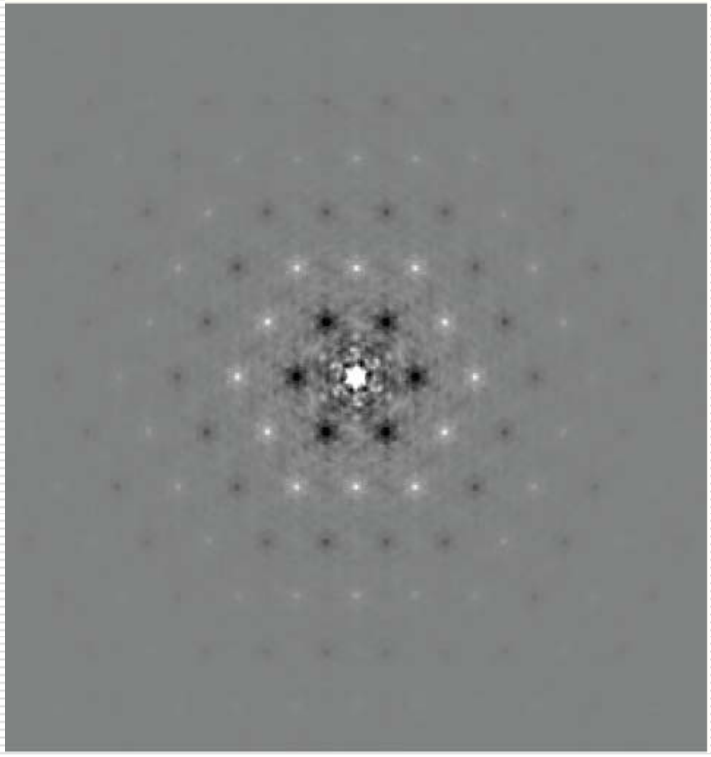
from Bragg + diffuse scattering



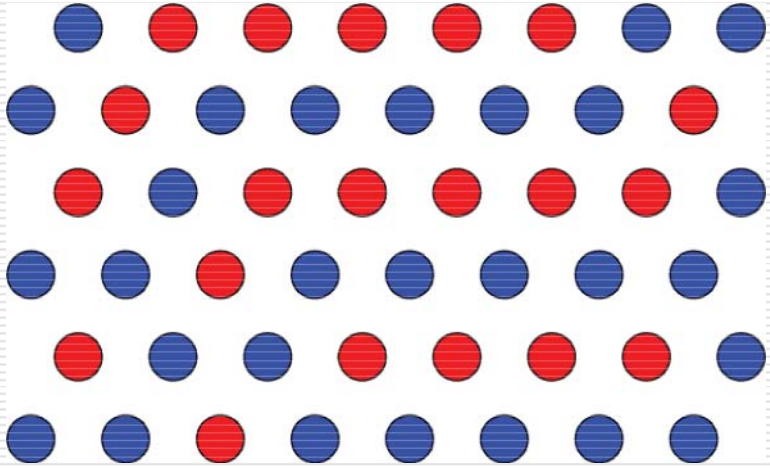
from diffuse intensities alone

Result

structure model

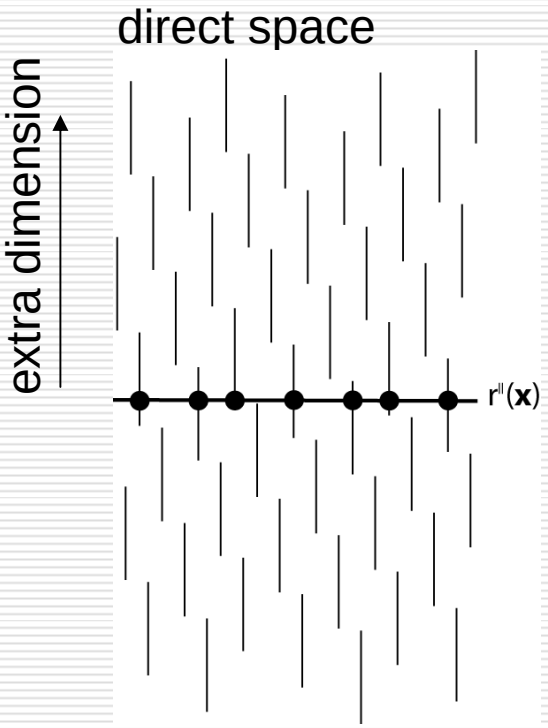


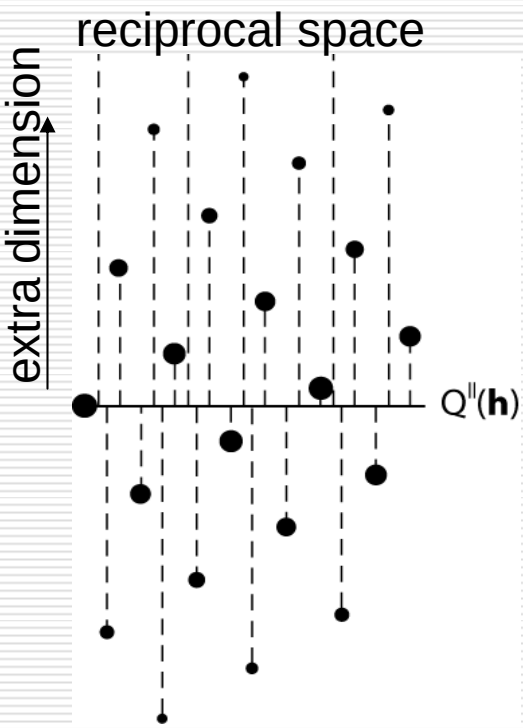
preference for negative next neighbour correlations



Order and disorder in quasicrystals

higher dimensional periodic description of quasicrystals:





but disorder reflects local properties, which are best described in physical space

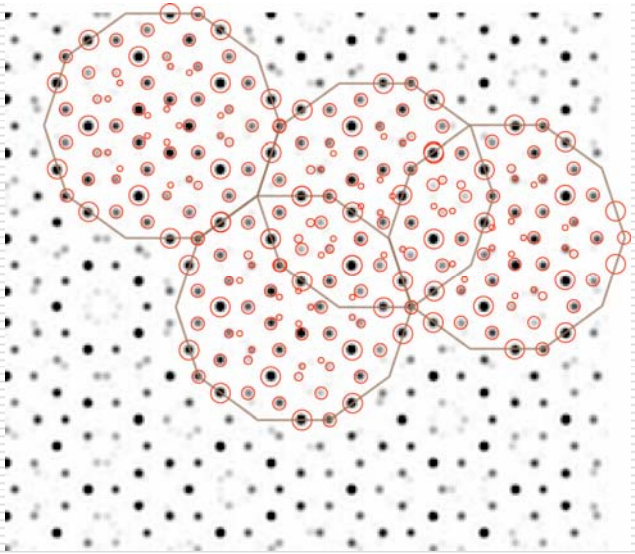
⇒ higher-dimensional description is not helpful for understanding disorder

⇒ 3D-PDF analysis is a ‘natural’ approach for understanding the local structure

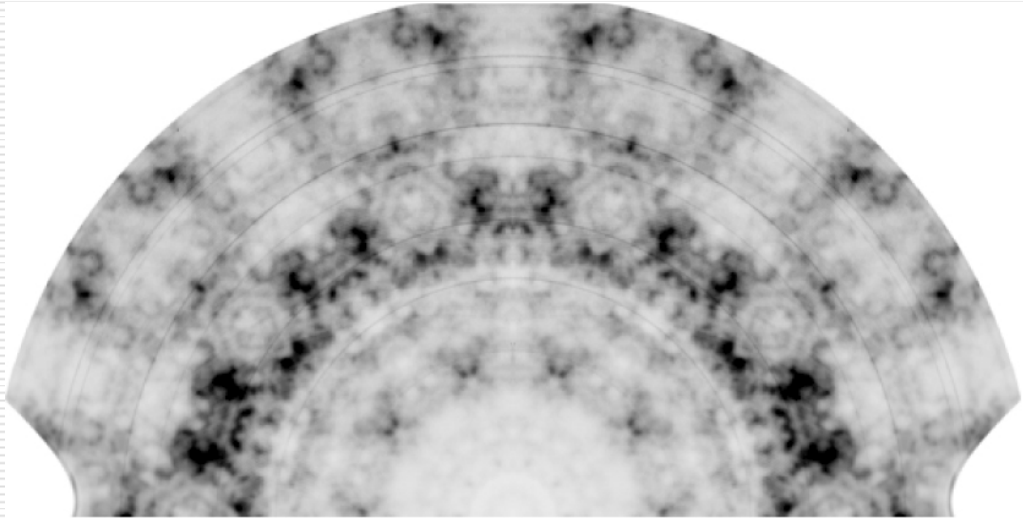
Disorder in quasicrystals

problems

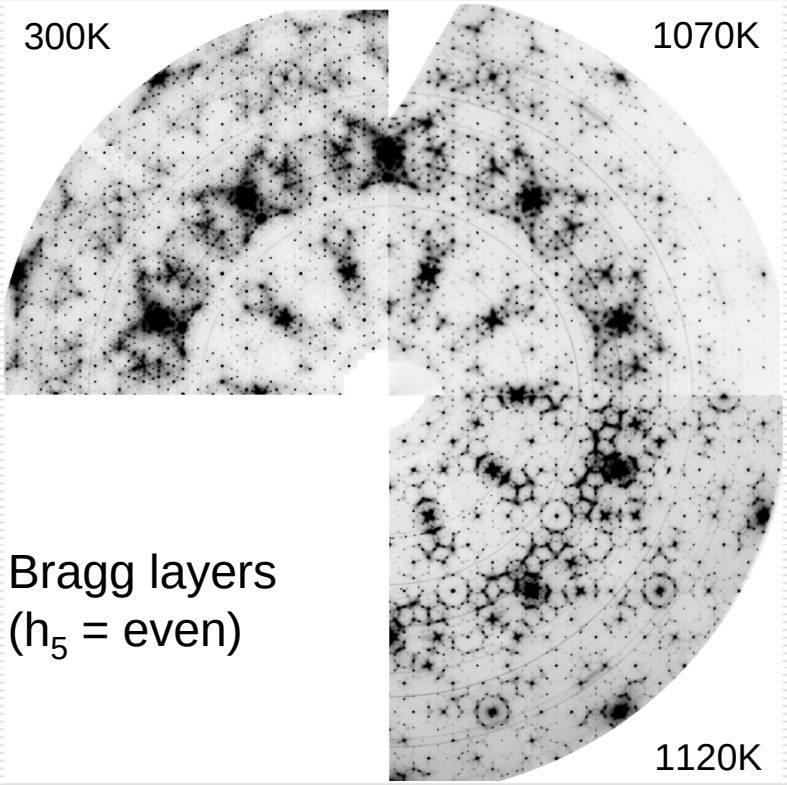
- Bragg structure is usually not as accurately known as in the case of periodic crystals



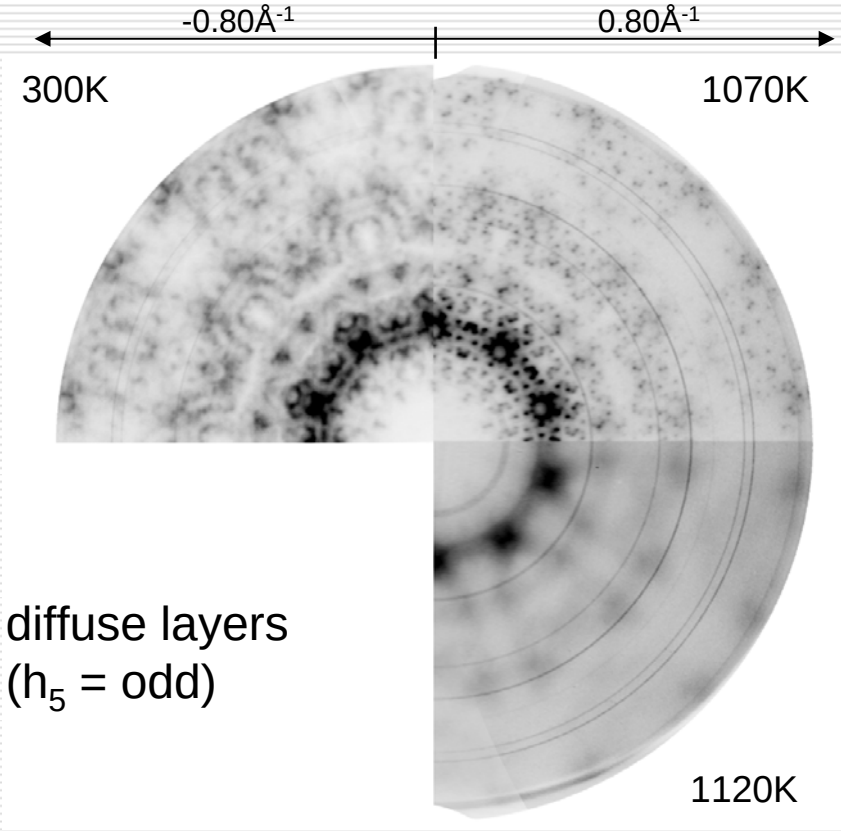
- diffuse diffraction patterns may be extremely complicated



Diffraction patterns of *d*-AlCoNi



Bragg layers
(h_5 = even)

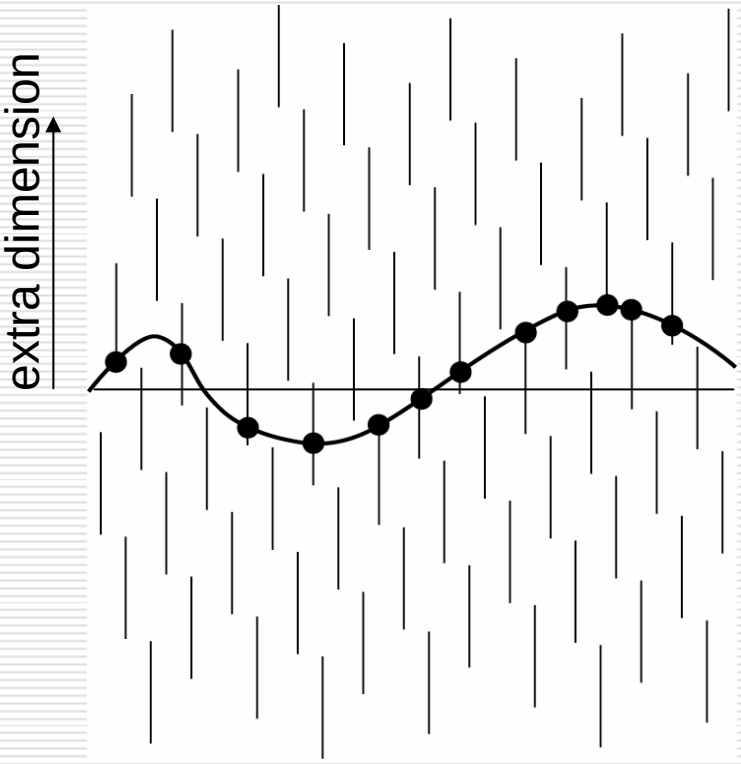


diffuse layers
(h_5 = odd)

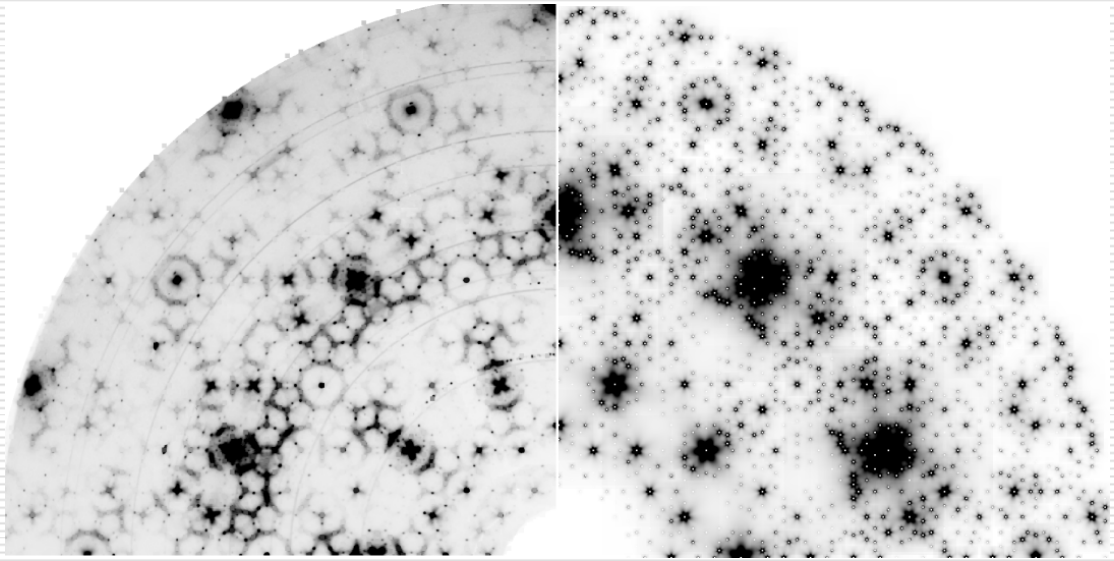
⇒ three different diffraction features (Bragg scattering, diffuse scattering in Bragg layers, diffuse scattering in interlayers) that can be analyzed independently

Diffuse scattering in Bragg layers
Modelling as phasonic diffuse scattering

appearance of diffuse scattering is typical for phasonic disorder



calculated phason diffuse scattering (PDS) (hydrodynamic theory, based on Bragg intensities + elastic constants)



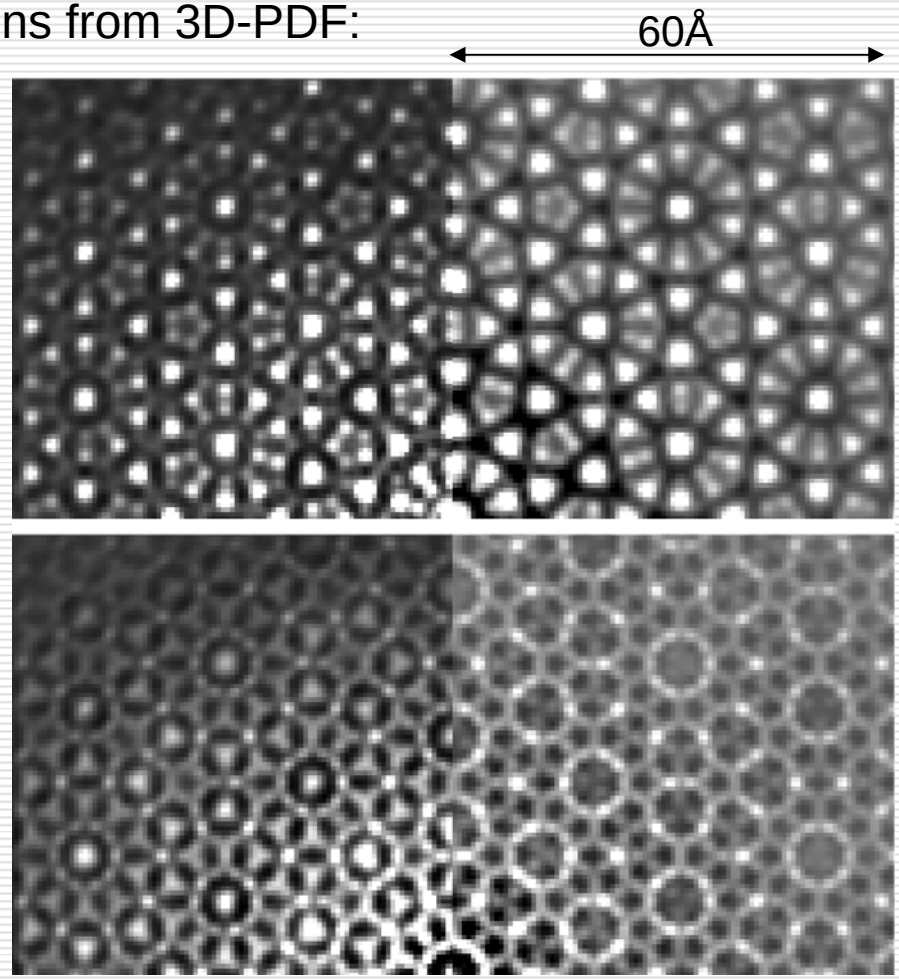
observed

calculated

Diffuse scattering in Bragg layers

Interpretation by PDFs

sections from 3D-PDF:



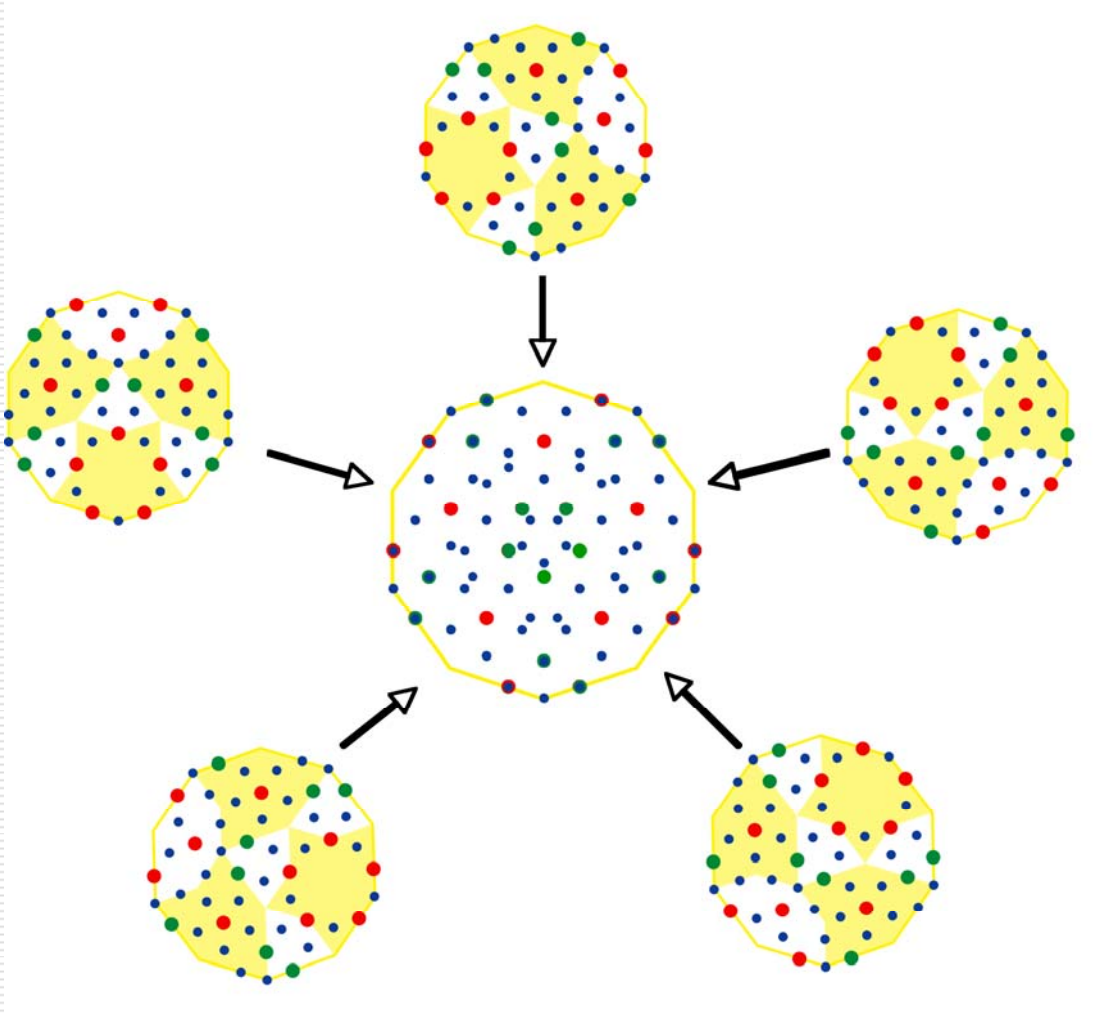
conclusions:

- diffuse scattering can be described as phasonic diffuse scattering

- good agreement between observed and calculated PDF densities for small (< 30Å) inter-atomic vectors

what's the atomistic interpretation?

Atomistic interpretation of phasonic disorder in *d*-AlCoNi



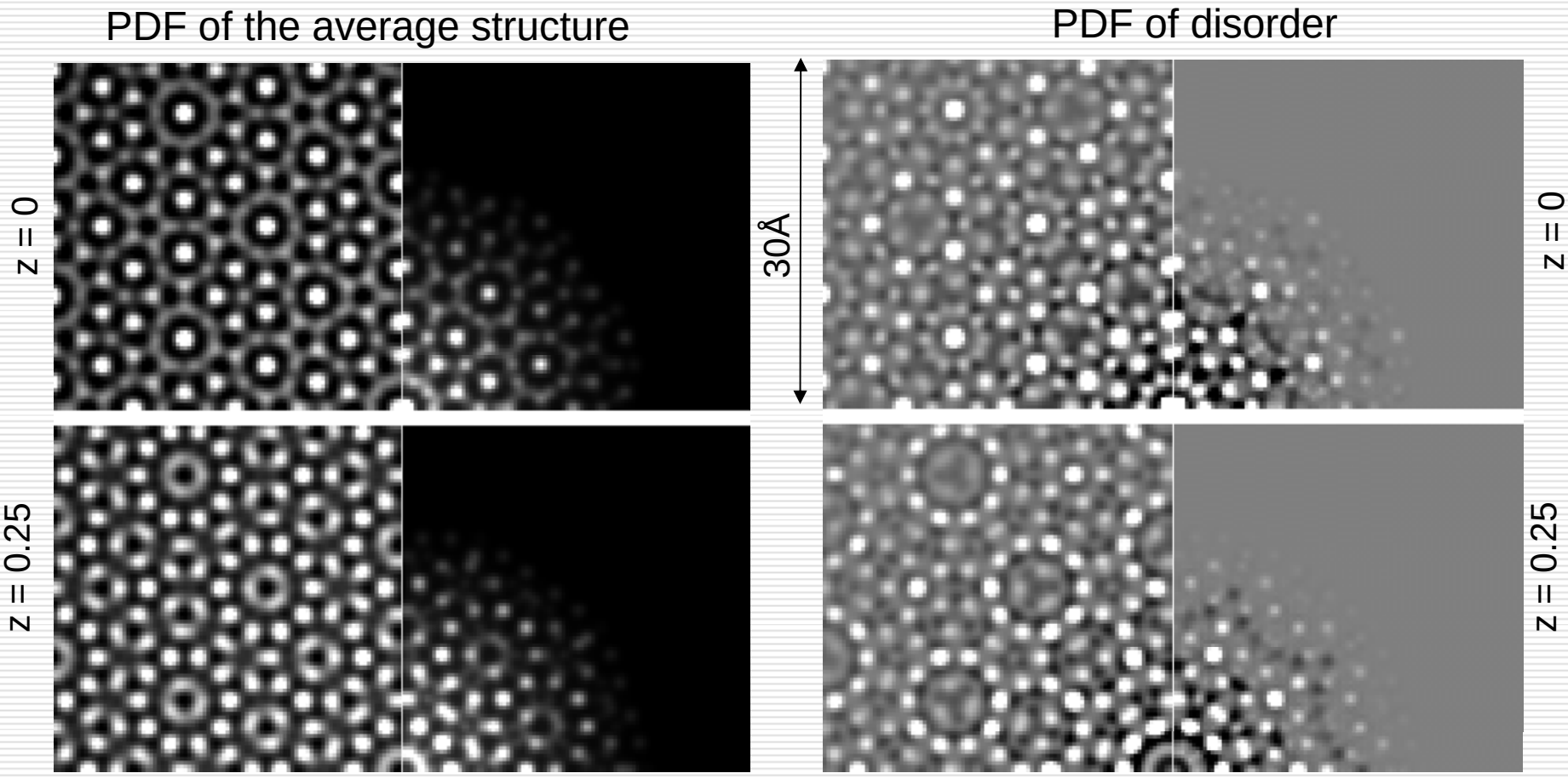
proposed disorder model

‘Abe-cluster’ known from electron microscopy is the structure building component and shows five-fold orientational disorder

model is restricted to one cluster only; correlations beyond one one cluster are ignored

$\Rightarrow$ no information about the spatial distribution of the cluster is needed

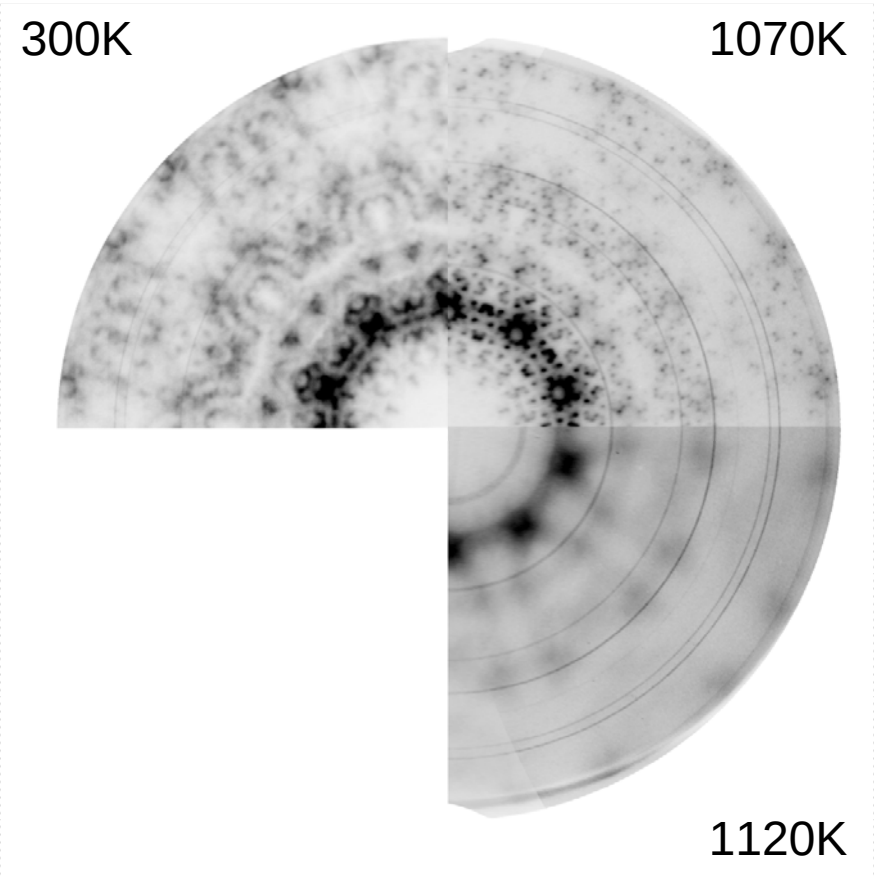
Atomistic model

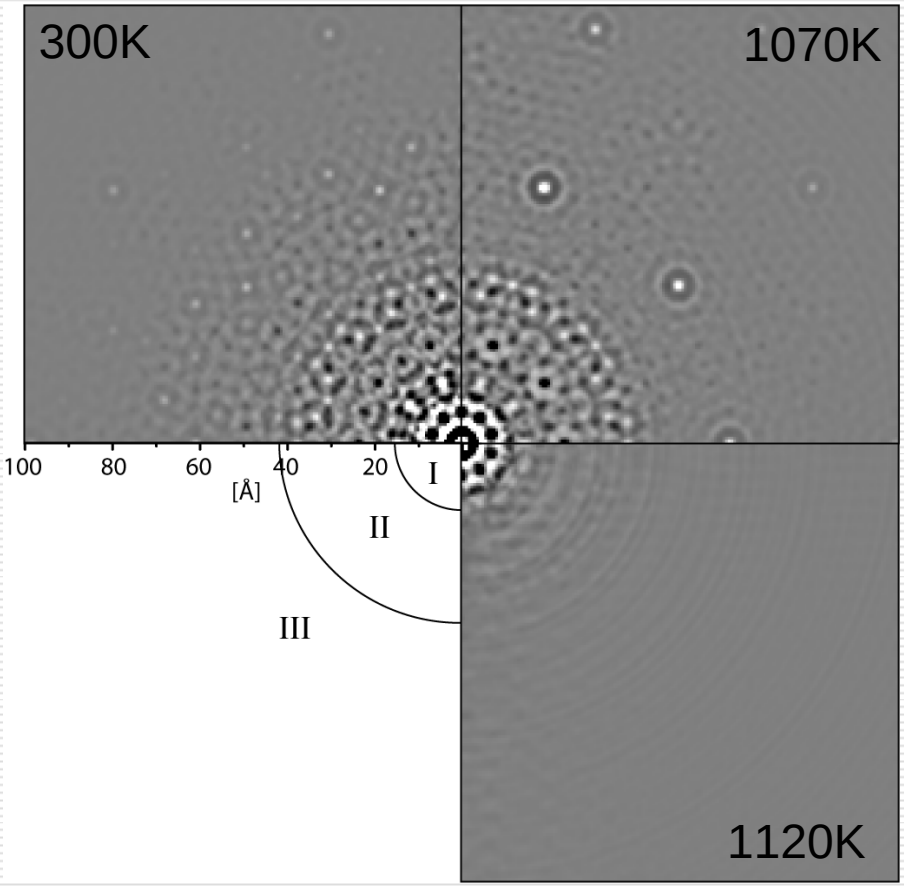


PDF from Bragg reflections average cluster from diffuse scattering ‘difference’ cluster

=> **atomistic model for phasonic disorder could be identified**

PDF analysis of diffuse scattering in inter-layers





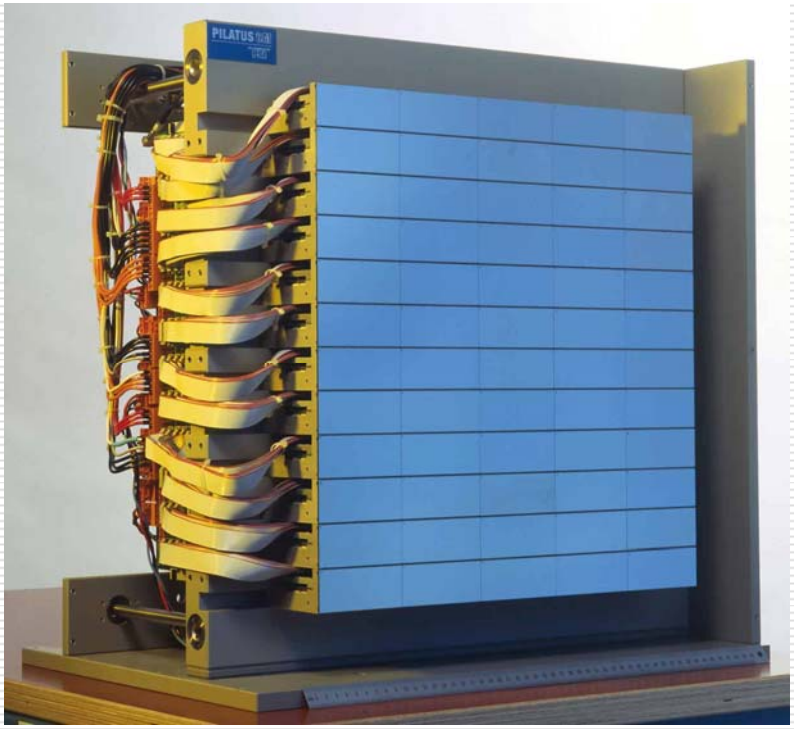
=> further details in Philippe Schaub's talk

Outlook

current bottle-necks

- missing user friendly software for
  - data reduction
  - calculation of 3D-PDF
  - quantitative modelling disorder with PDF data
  - visualisation
- quality of current x-ray area detectors (image plates, CCDs)
  - high intrinsic background
  - low read-out frequency (1Hz - 0.01Hz)
  - limited dynamic range (<18bit)
  - no energy discrimination
  - blooming effects (CCDs)
  - non-erasable pixels, if heavily overexposed (IPs)

Pilatus 6M Detector



developed at Swiss-Light-Source

characteristics

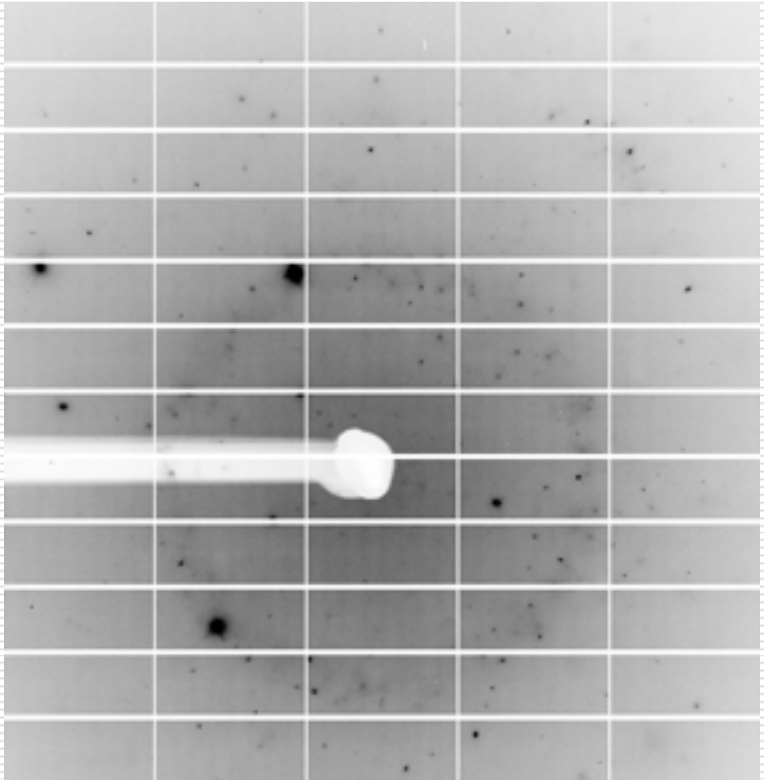
- large area detector (2463 x 2527 pixels, total active area of 424 x 435 mm^2)
- absence of intrinsic noise allows background-free measurements
- read-out frequency of 10 Hz allows fast measurements of complete data sets (e.g. 180° scan, 0.1°/frame in 3 minutes)
- dynamic range: 20 bit (soon 32 bit)
- pixel size 172 µm x 172µm
- energy discrimination

Fluorescence scattering suppression

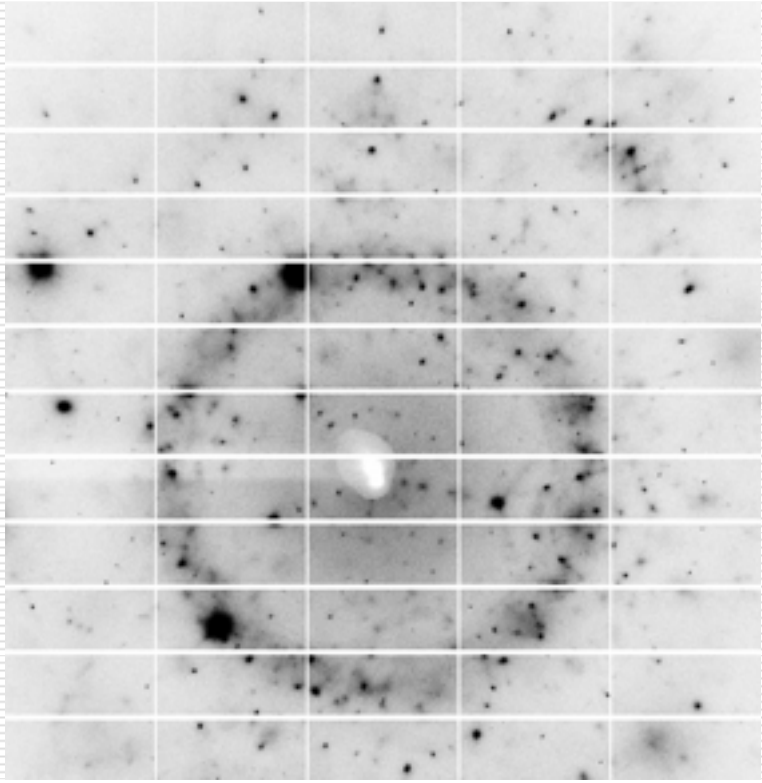
Example: *i*-AlCuFe - a ‘perfect’ quasicrystal

beam energy: 16keV; fluorescence edge (Cu) ~8.5keV

energy threshold: 8keV



energy threshold: 10keV



=> opens possibility to see disorder that was never seen before

Summary

- 3D-PDF allows investigation of disorder in extremely complex systems
- 3D-PDF is an ab-initio method for understanding disorder
- *divide-and-conquer* method allows reduction of complexity by
  - selective Fourier transformation
  - selective interpretation of PDF (talk by Philippe Schaub)
- even low resolution data can be interpreted successfully if supra-molecular or long-range order properties are of interest
- new experimental possibilities allow
  - high quality single crystal measurements
  - fast experiments (non-ambient and time-resolved investigations)

Acknowledgement

Philippe Schaub (N,N',N"–tris–*t*–butyl–1,3,5–benzenetricarboxamide)

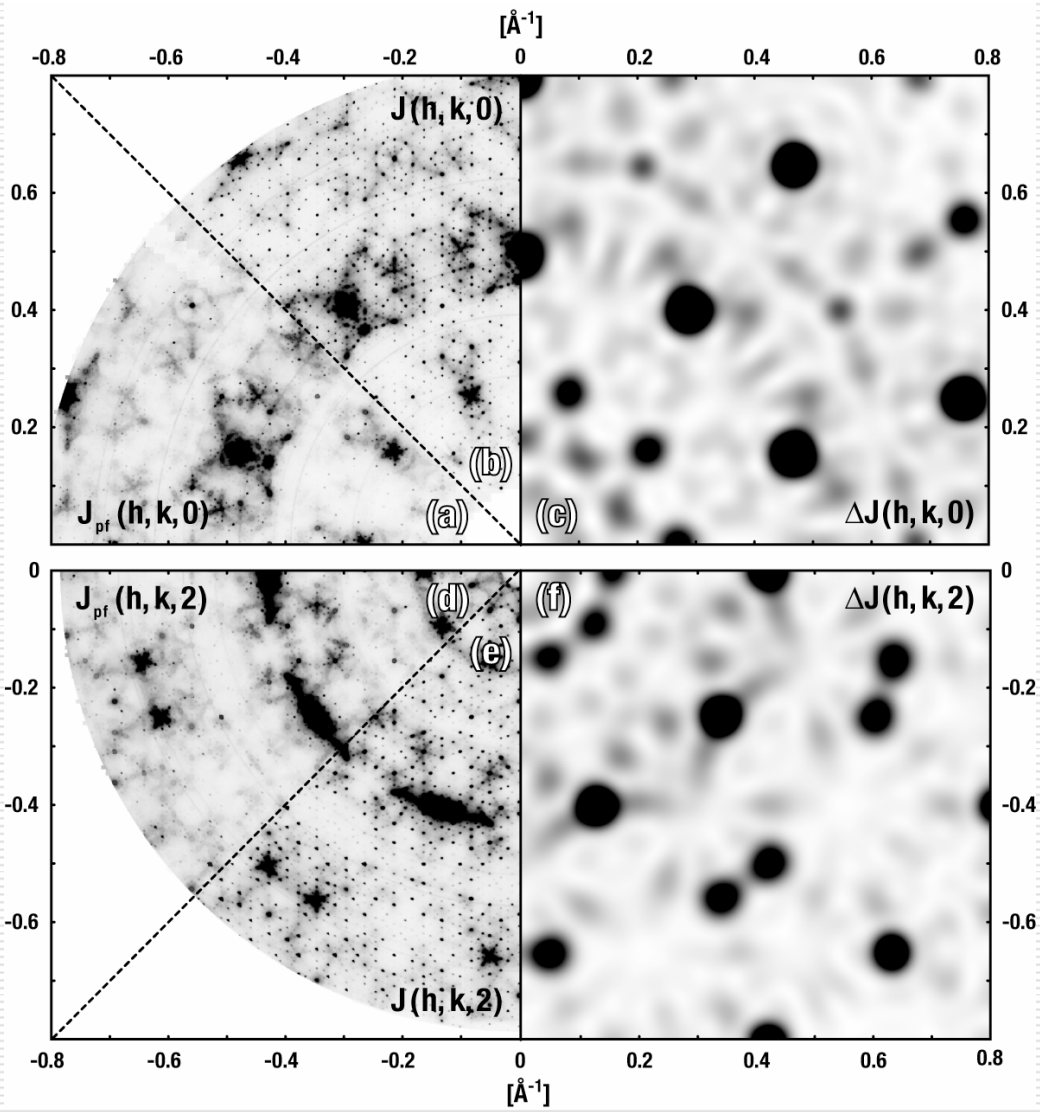
Miroslav Kobas (AlCoNi)

SNBL team at ESRF for experimental support

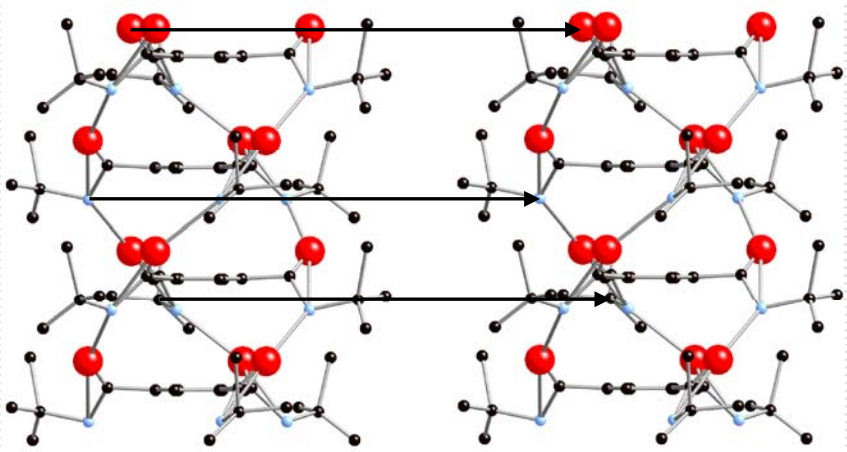
SLS detector group

Prof. Walter Steurer

Swiss National Foundation for funding this work

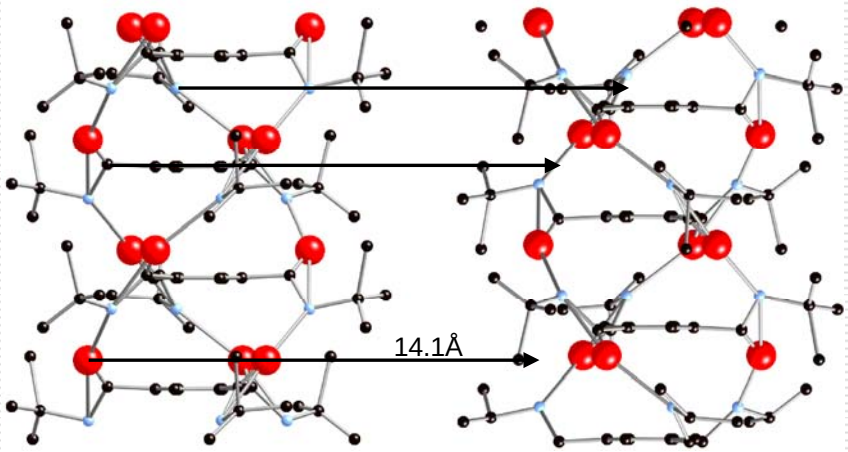

[Å^{-1}]
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
J(h, k, 0)
J$_{pf}$(h, k, 0)
(a)
(b)
(c)
ΔJ(h, k, 0)
J$_{pf}$(h, k, 2)
(d)
(e)
(f)
ΔJ(h, k, 2)
J(h, k, 2)

Interpretation of the PDF



parallel arrangement:

translation vectors connect equivalent atoms of the real structure
=> positive contribution to PDF

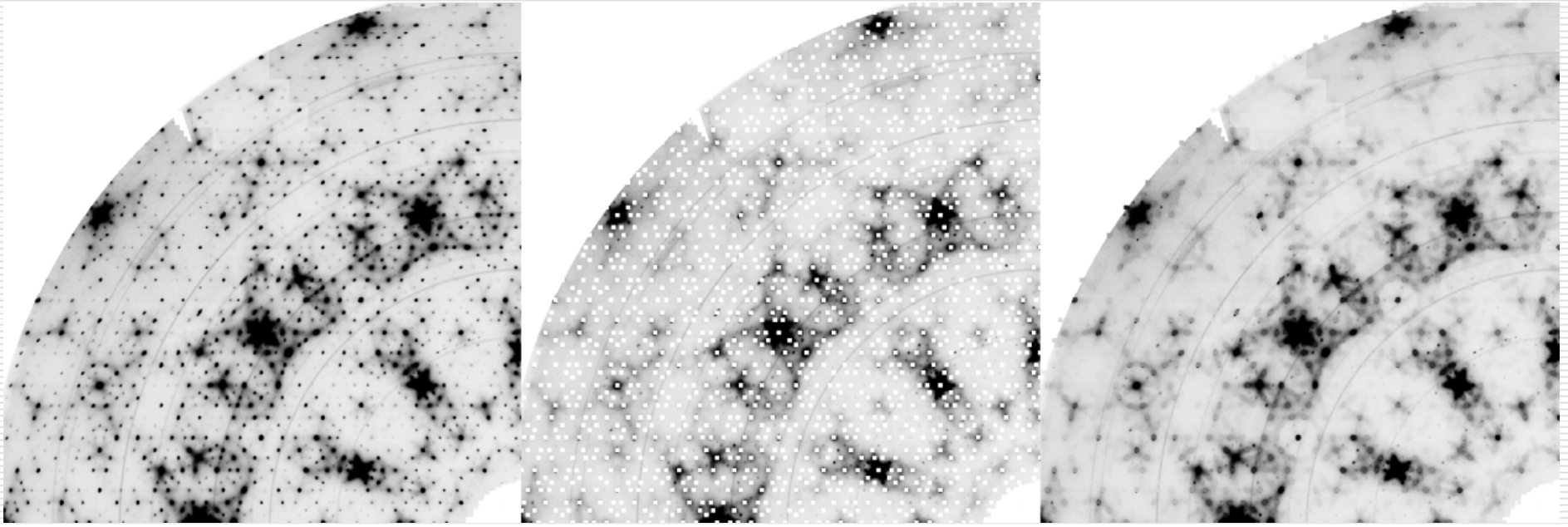


anti-parallel arrangement:

translation vectors do not connect atoms of the real structure
=> negative contribution to PDF

Diffuse scattering in Bragg layers
Data processing

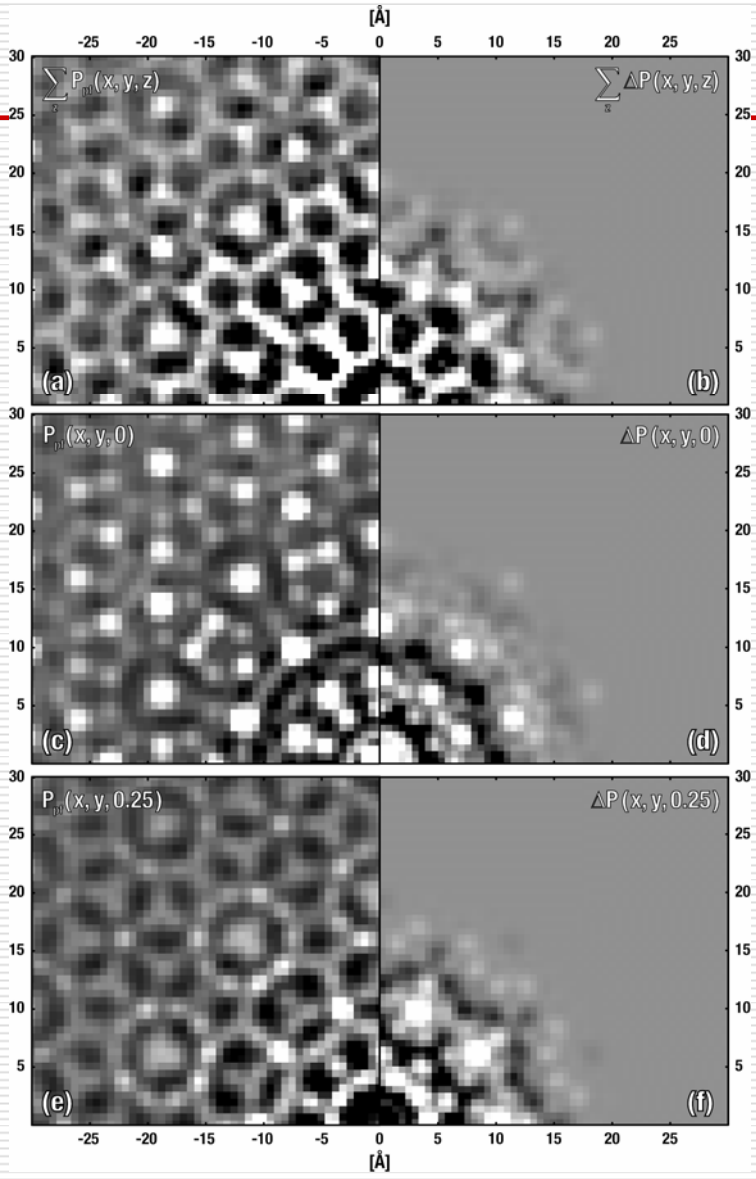
punch-and-fill method



original

punched

filled


[Å]
-25 -20 -15 -10 -5 0 5 10 15 20 25
30 25 20 15 10 5
$\sum_{\alpha} P_{\mu\nu}(x, y, z)$
$\sum_{\alpha} \Delta P(x, y, z)$
(a)
(b)
$P_{\mu\nu}(x, y, 0)$
$\Delta P(x, y, 0)$
(c)
(d)
$P_{\mu\nu}(x, y, 0.25)$
$\Delta P(x, y, 0.25)$
(e)
(f)
[Å]