Single Crystal Diffuse Scattering

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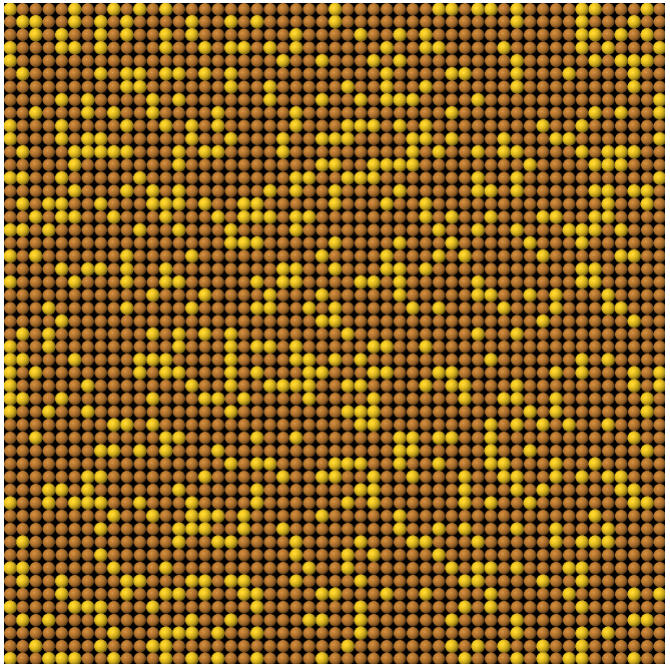
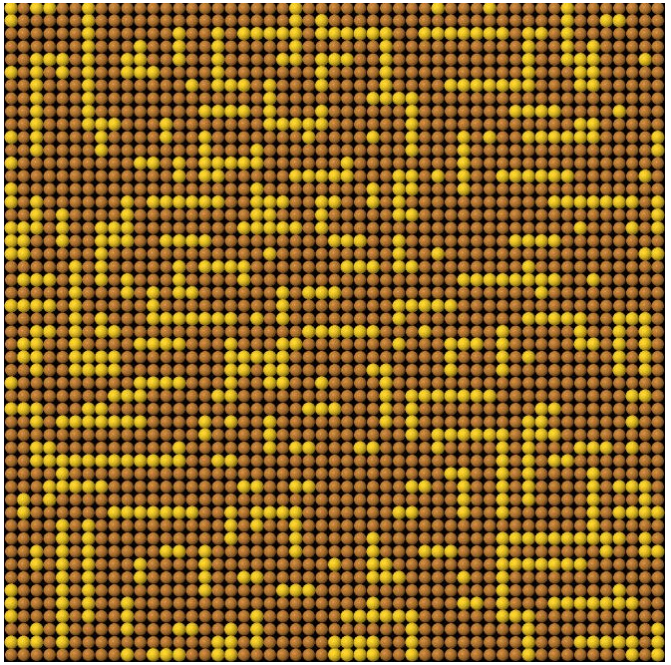
Disordered Structures

Partial cross section of 200x200 unit cell model crystals
Composition 75% A 25% B



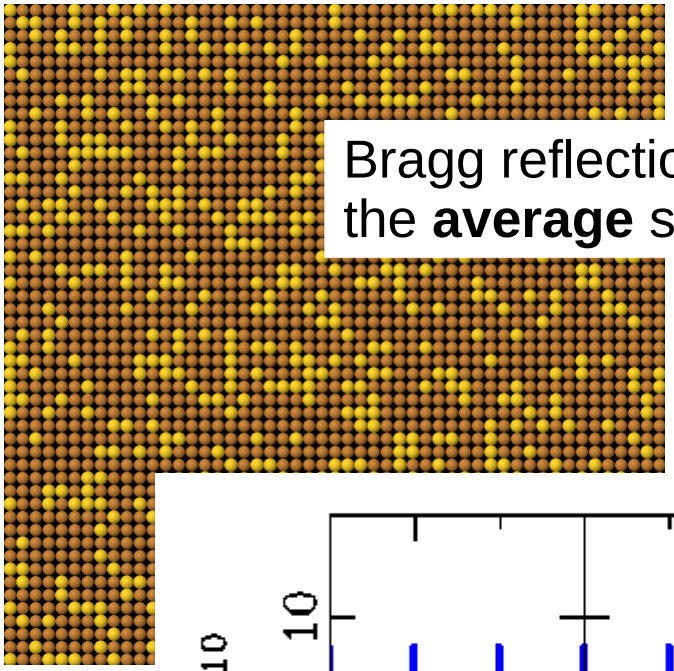
Random position of A B atoms



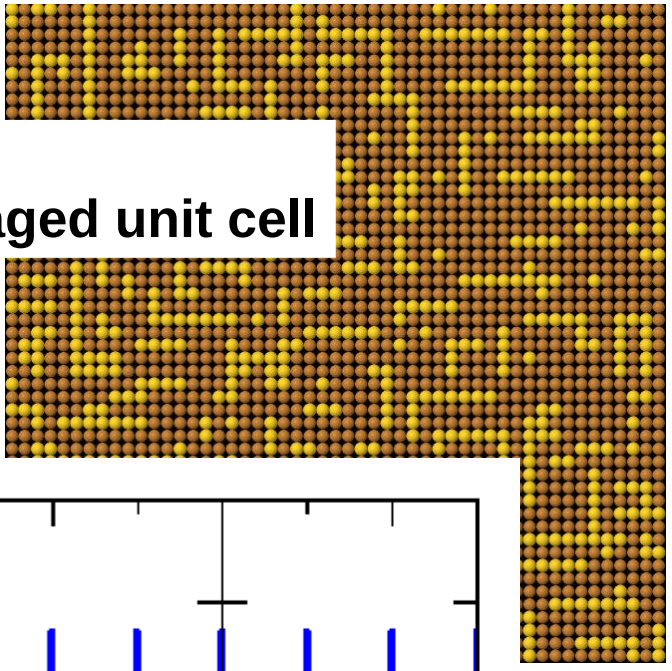
Non-random position of A B atoms

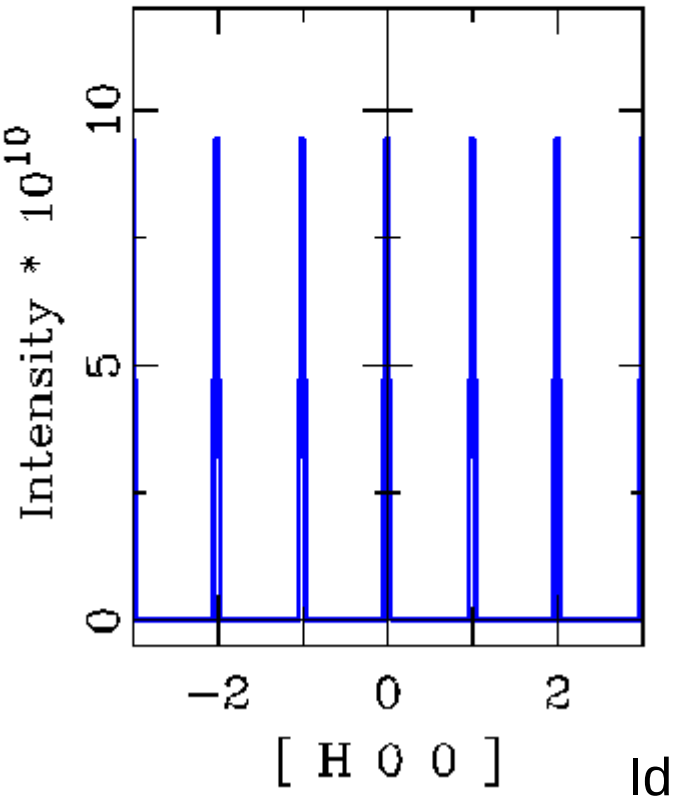
Properties of the two crystals will differ

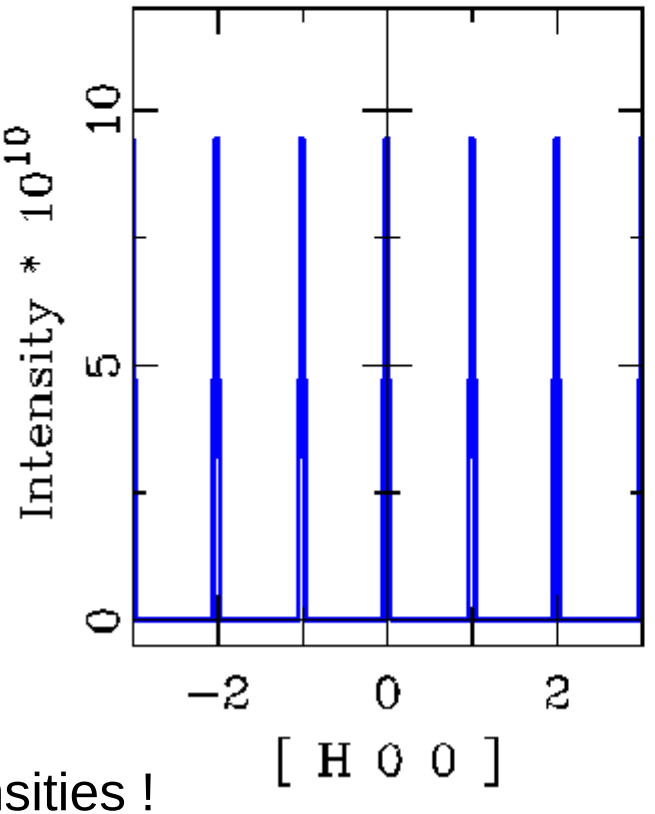
Effect on Bragg Reflections



Bragg reflections *see* the global picture,
the **average** structure, i.e. just **one averaged unit cell**



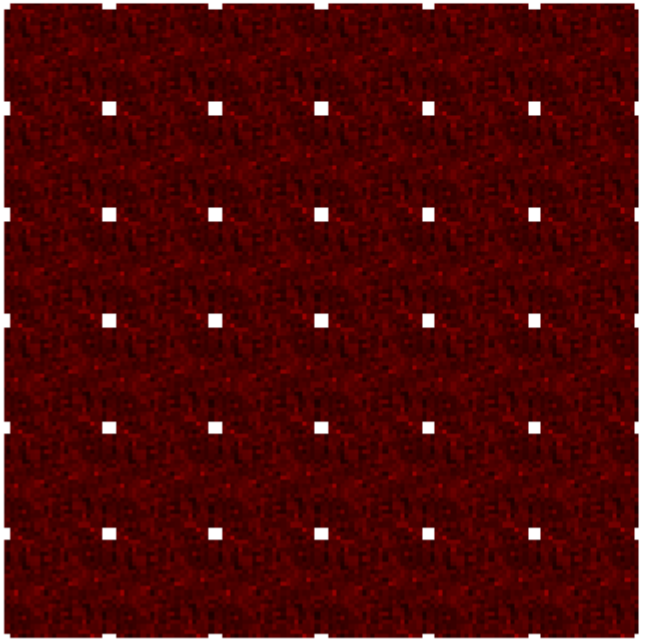




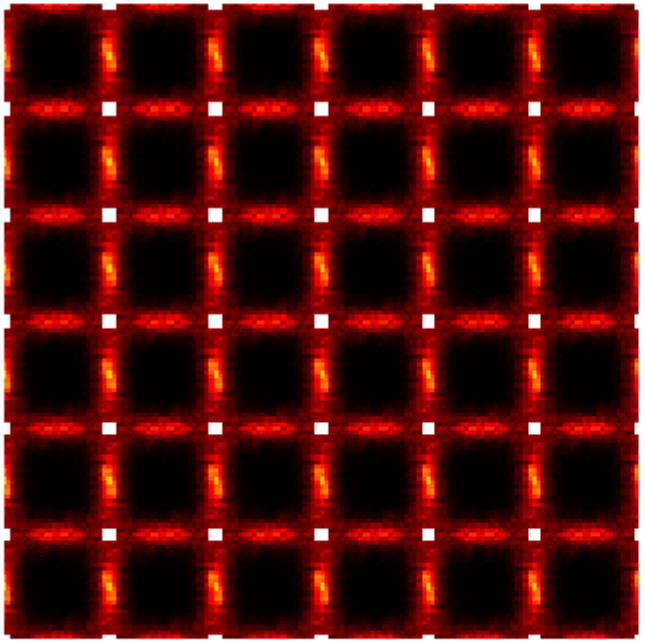
Identical intensities !

Diffuse scattering to the rescue ...

Diffuse scattering *sees* the local picture,
the **deviations** from the average structure,
the local (approximate) periodicity on a short scale



Continuous unstructured scattering



Modulated diffuse scattering

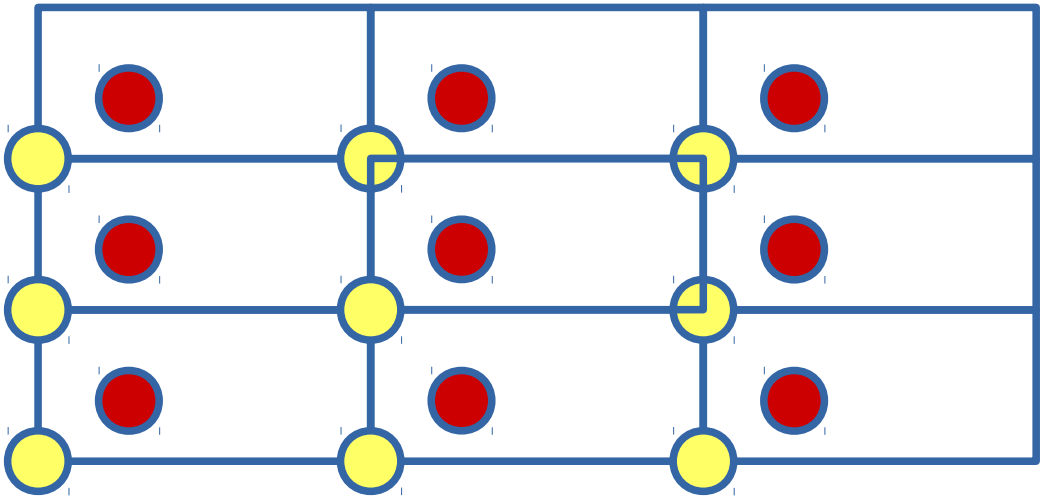
Structure factor

$$F(hkl) = \sum_{j=1}^{N} f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$ Sum over all N atoms in one unit cell

In the experiment this is really:

$$F(hkl) = \sum_{R_a=-\infty}^{\infty} \sum_{R_b=-\infty}^{\infty} \sum_{R_c=-\infty}^{\infty} \sum_{j(abc)=1}^{N} f_j e^{2\pi i(hx_j + ky_j + lz_j + hR_a + kR_b + lR_c)}$$

Sum over all N atoms in all unit cells R_a, R_b, R_c



If all unit cells are identical and strictly periodic to ± ∞ :

F(hkl) = 0 unless hkl are whole numbers
Bragg reflections only

J. Cowley: Diffraction Physics

Structure factor

$$F(hkl) = \sum_{R_a=-\infty}^{\infty} \sum_{R_b=-\infty}^{\infty} \sum_{R_c=-\infty}^{\infty} \sum_{j(abc)=1}^{N} f_j e^{2\pi i (h x_j + k y_j + l z_j + h R_a + k R_b + l R_c)}$$

Sum over all N atoms in all unit cells R_a, R_b, R_c

If all unit cells are identical and strictly periodic to ± ∞ :

F(hkl) = 0 unless hkl are whole numbers

Diffuse scattering is oberved if:

- **crystal is truncated by surfaces**

  truncation rod surface diffraction, surface crystallography, LEED, RHEED

- **atoms move within the crystal**

  Vibrations: Thermal diffuse scattering
  Diffusion: Quasielastic neutron scattering

- **individual unit cells differ throughout the crystal**

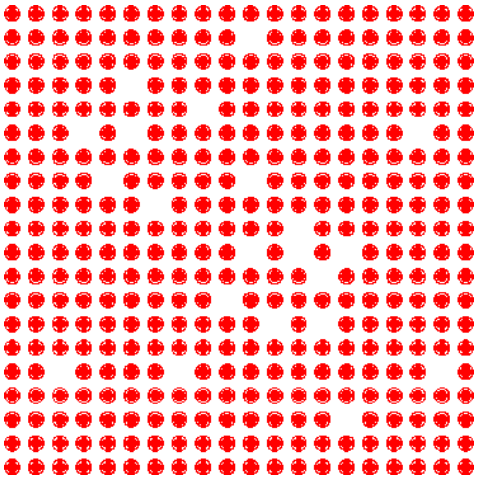
  Disorder: diffuse scattering between Bragg reflections
  ==> This talk; W. Paulus, P. Welch, N. Roth
  ==> E.M. Schmidt
  Real structures: diffuse scattering predominantly close to Bragg reflections

Defect types

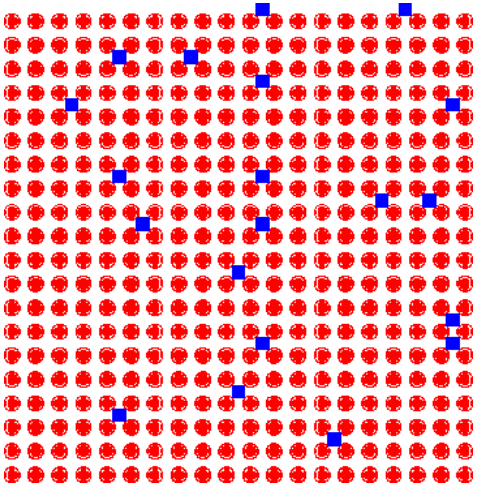
Point defects

individual missing, wrong, additional atoms
small clusters

missing atoms

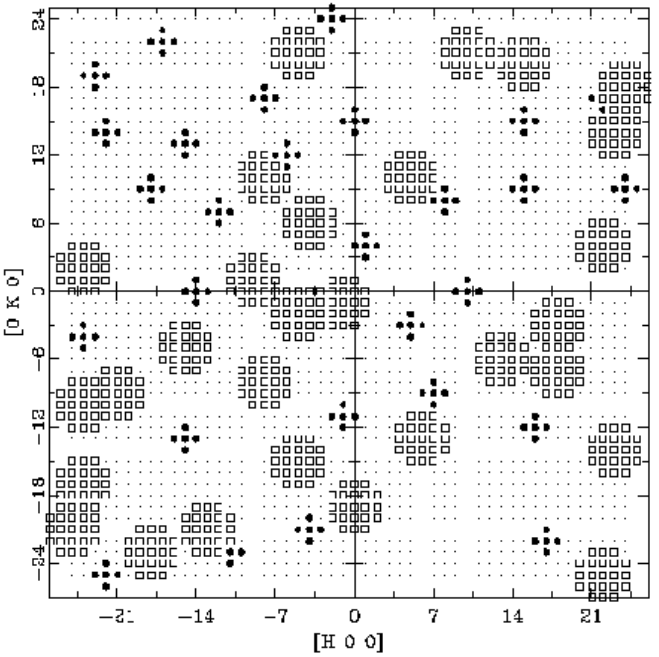


Interstitials



with overall
charge neutrality

small clusters



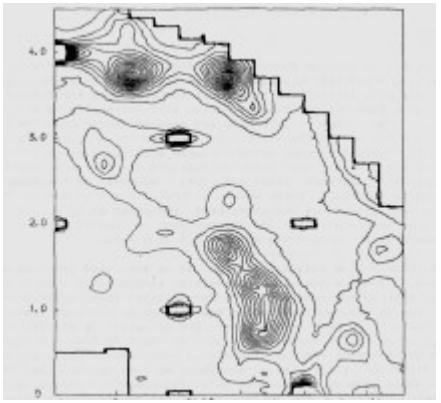
Predominantly in inorganic materials

Metal Alloys, non-stiochiometric oxides and halides

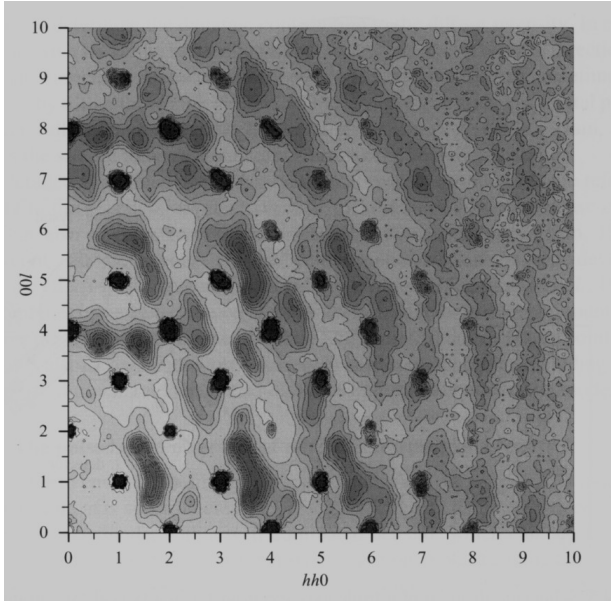
Defect types

Point defects

individual missing, wrong, additional atoms
small clusters



(Ca, Y, Zr) O_2



Predominantly in inorganic materials

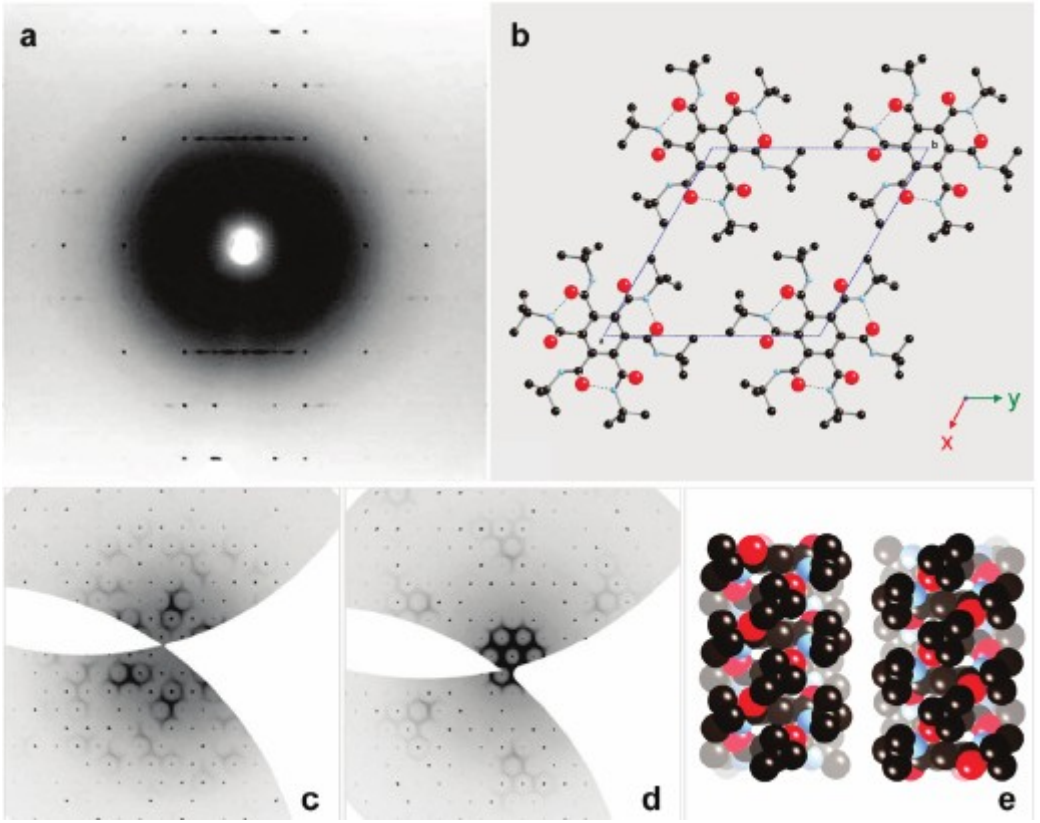
Metal Alloys, non-stiochiometric oxides and halides

Neder, PhD Munich 1990

Defect types

Point defects

individual missing, wrong, additional atoms
small clusters
Different molecular conformations



Perfect structure model

Disorder:
Rotate molecule around [100]

Stacks with perfect periodicity along c
Either *up* or *down*

Diffuse scattering in Trisamides
Kristiansen et al. Cryst. Growth & Design (2009), **9**, 2556

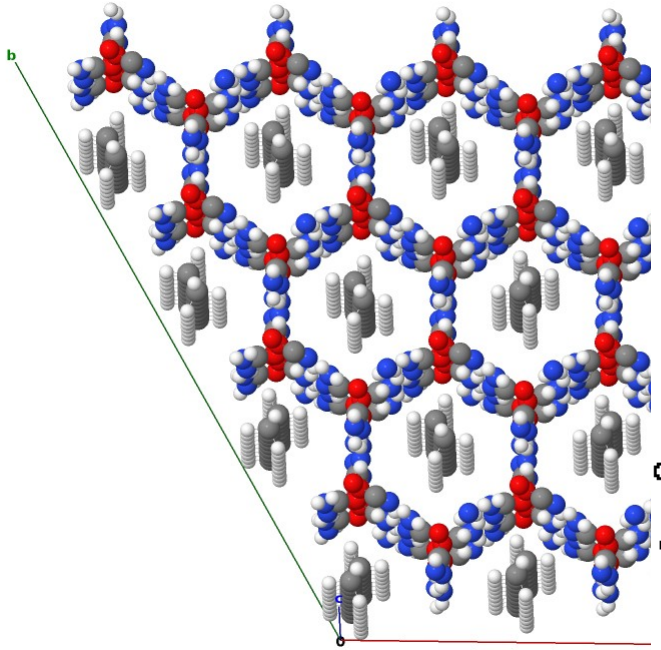
Defect types

Point defects

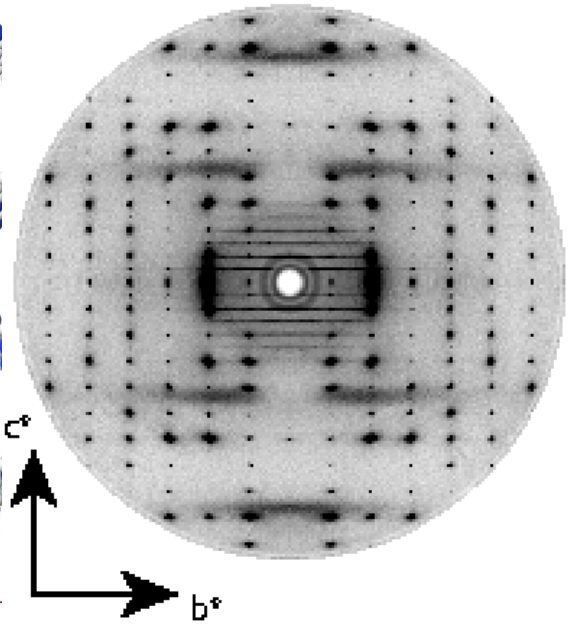
individual missing, wrong, additional atoms
small clusters

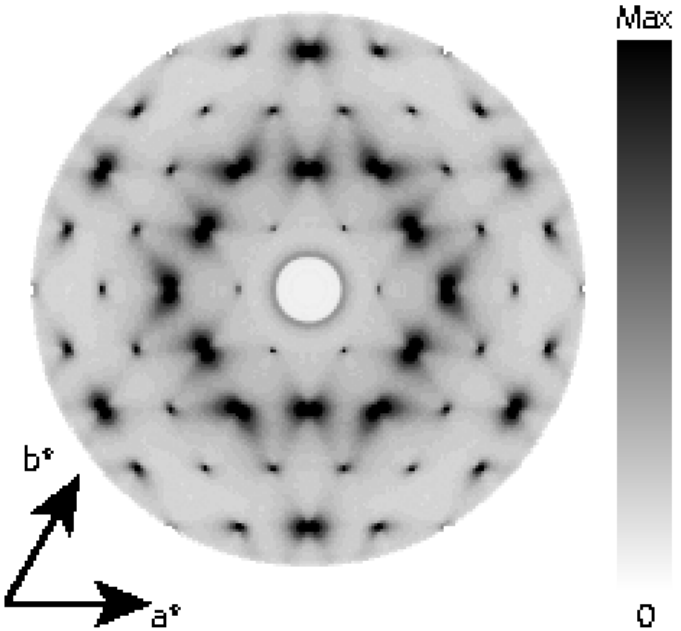
Linear defects

embedded molecules in channels of host strucure



Alcane chains in Urea





Th Weber PhD München 1994

Welberry & Mayo J. Appl. Cryst 29, 1996

Defect types

Point defects

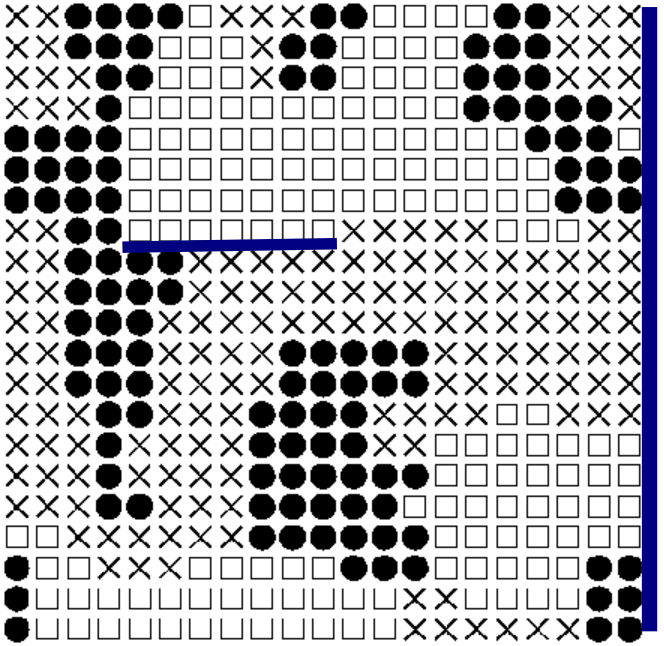
individual missing, wrong, additional atoms
small clusters

Linear defects

embedded molecules in channels of host strucure

Planar defects

stacking faults, wrong layer types, missing layers
surfaces, boundaries, dislocations



Predominantly in layered materials

Clays, mica, closed packed structures (Co, Cu, ZnS, SiC)

Defect types

Point defects

individual missing, wrong, additional atoms
small clusters

Linear defects

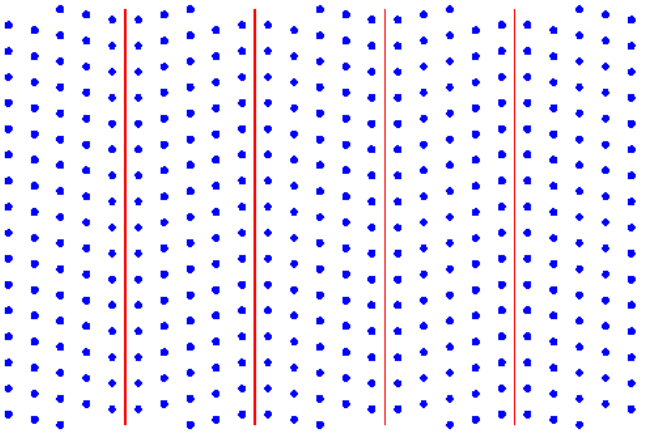
embedded molecules in channels of host strucure

Planar defects

stacking faults, wrong layer types, missing layers
surfaces, boundaries, dislocations

3-D defects

dissolutions, twins, anti phase domains
surfaces, boundaries



Defect types

Point defects

individual missing, wrong, additional atoms
small clusters

Linear defects

embedded molecules in channels of host strucure

Planar defects

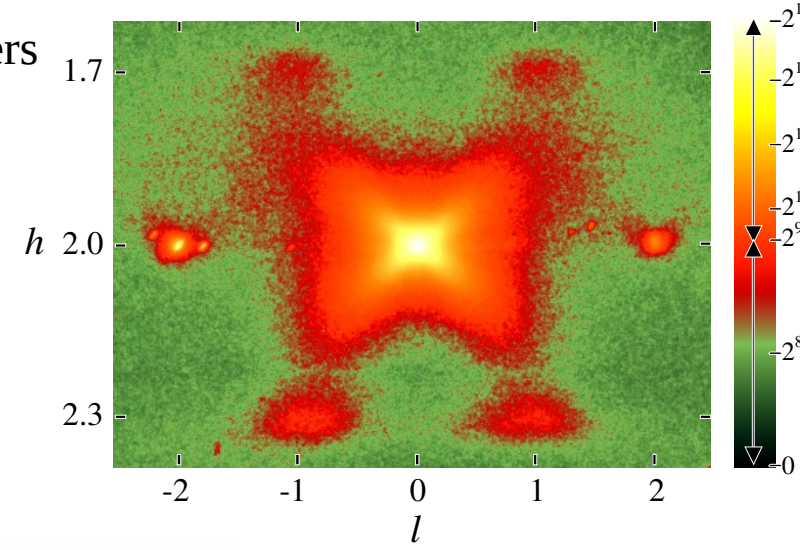
stacking faults, wrong layer types, missing layers
surfaces, boundaries, dislocations

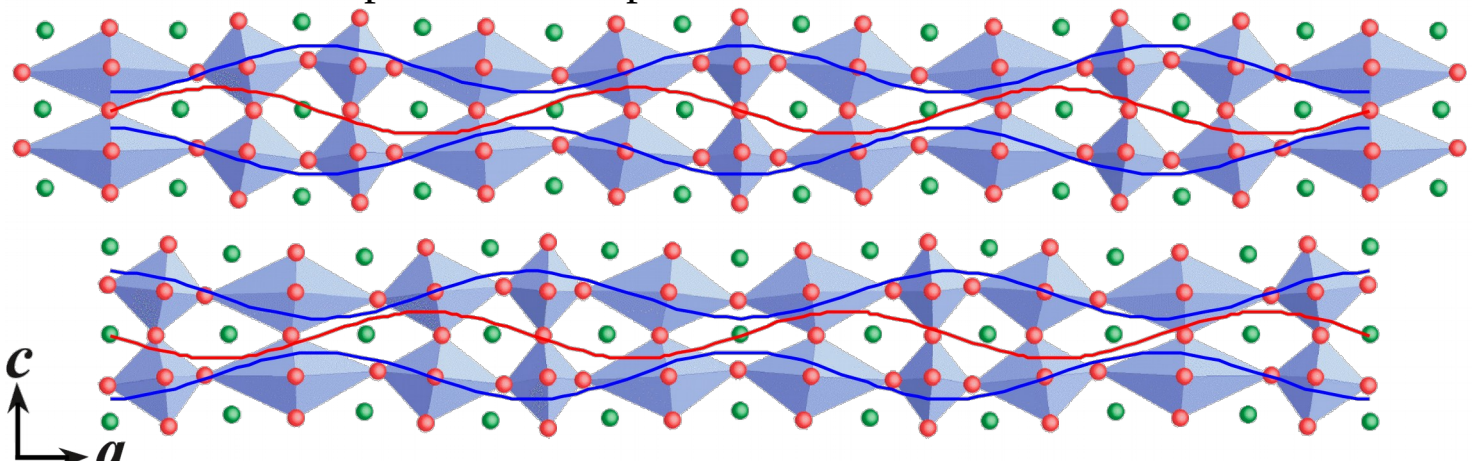
3-D defects

dissolutions, twins, anti phase domains
surfaces, boundaries

Waves

periodic modifications of the crystal
position, composition, valence





$La_{1.2}\ Sr_{1.8}\ Mn_2\ O_7$

R. Osborn et al.

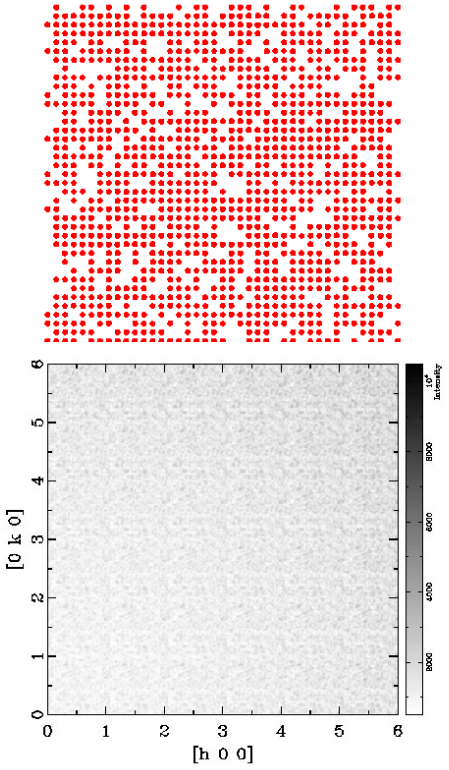
Defect correlations

uncorrelated defects

Location of individual defects
is independent of each other

randomly distributed point defects

diffuse scattering shows no features

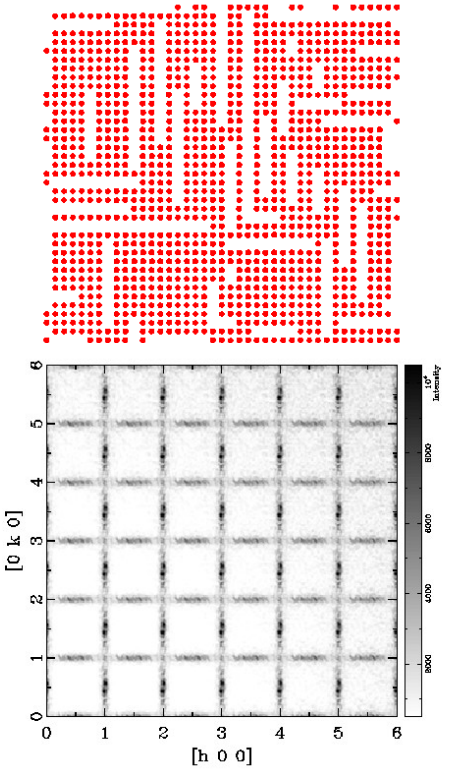


correlated defects

Location of a defect influences the location
of defects in the immediate vicinity

point defects along rows

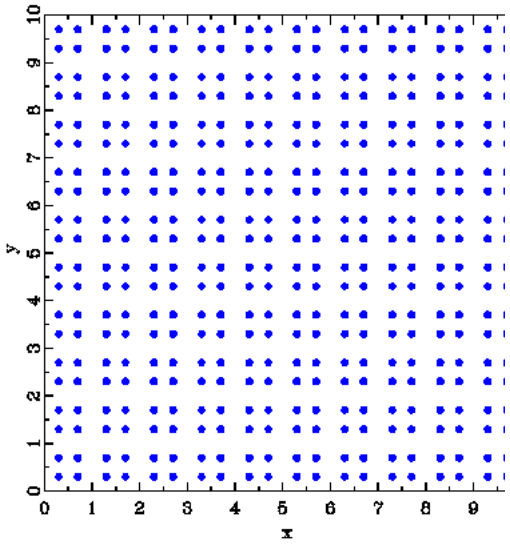
diffuse scattering in planes normal
to the lines



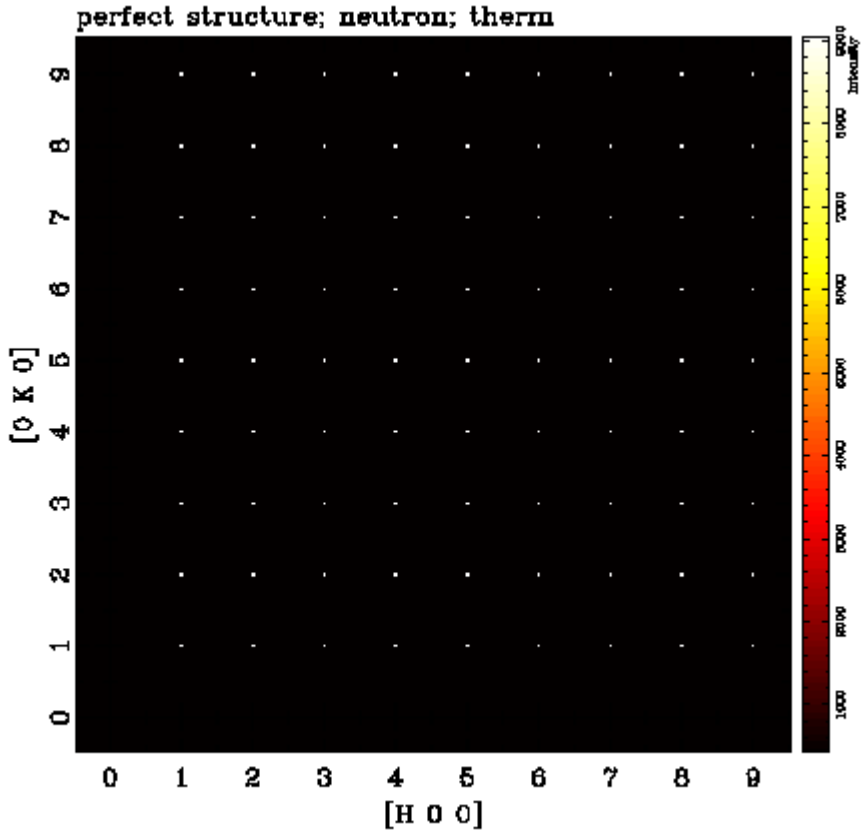
Concentration of defects
is identical,
average structure is identical !
Bragg reflections are identical !

Disorder versus Diffraction

perfect crystal structure



Neutron scattering



rigid molecules in P4mm

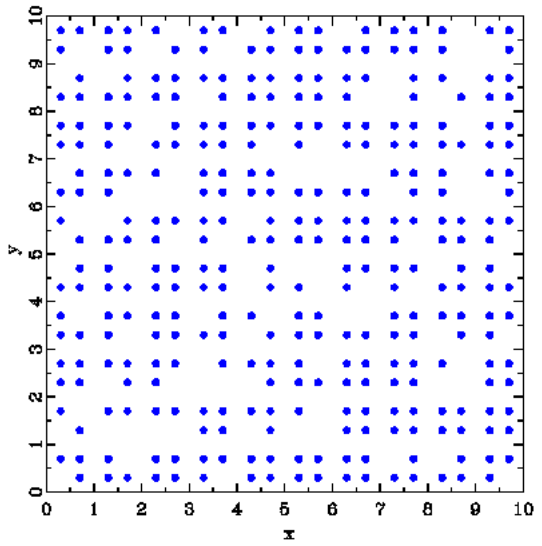
Intensity at Bragg reflections only

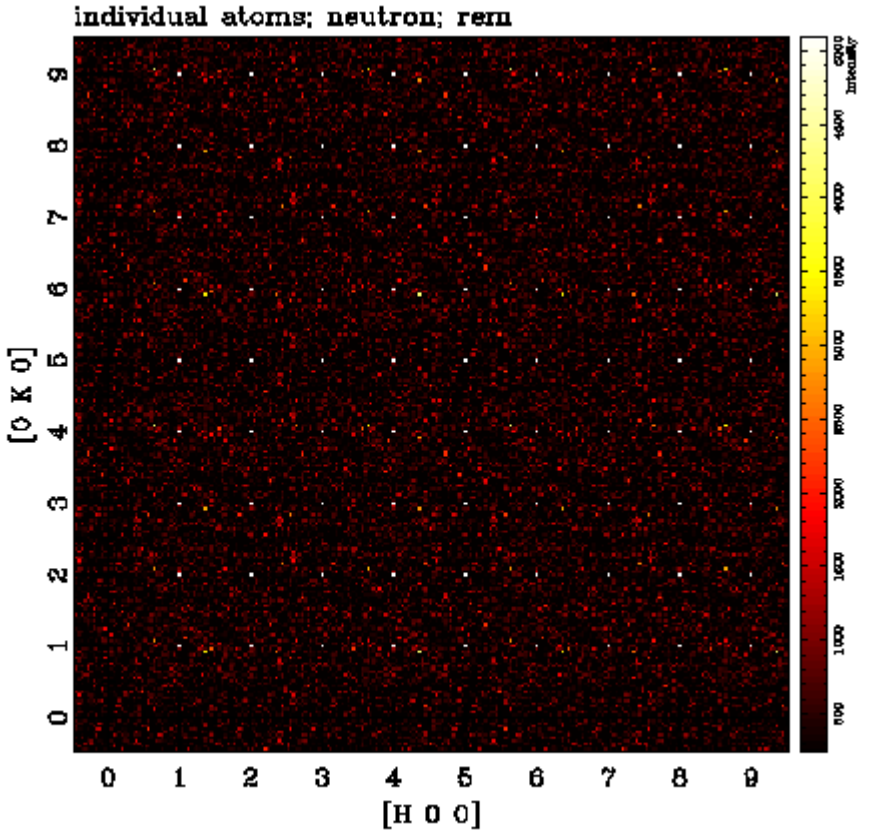
Intensity varies with structure factor

Disorder versus Diffraction

Individual atoms removed, no correlations

Neutron scattering





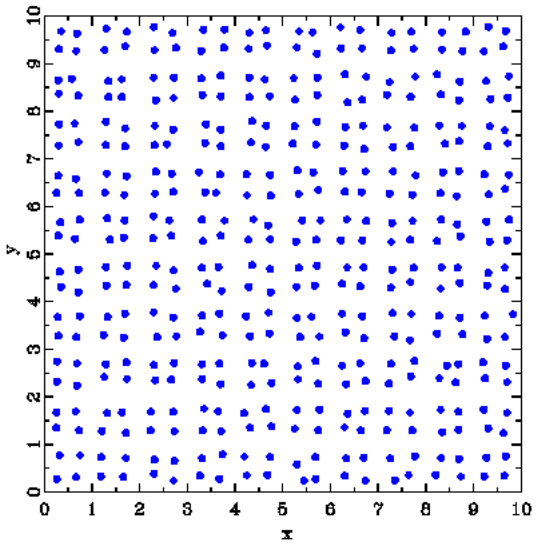
rigid molecules in P4mm
Bonds destroyed

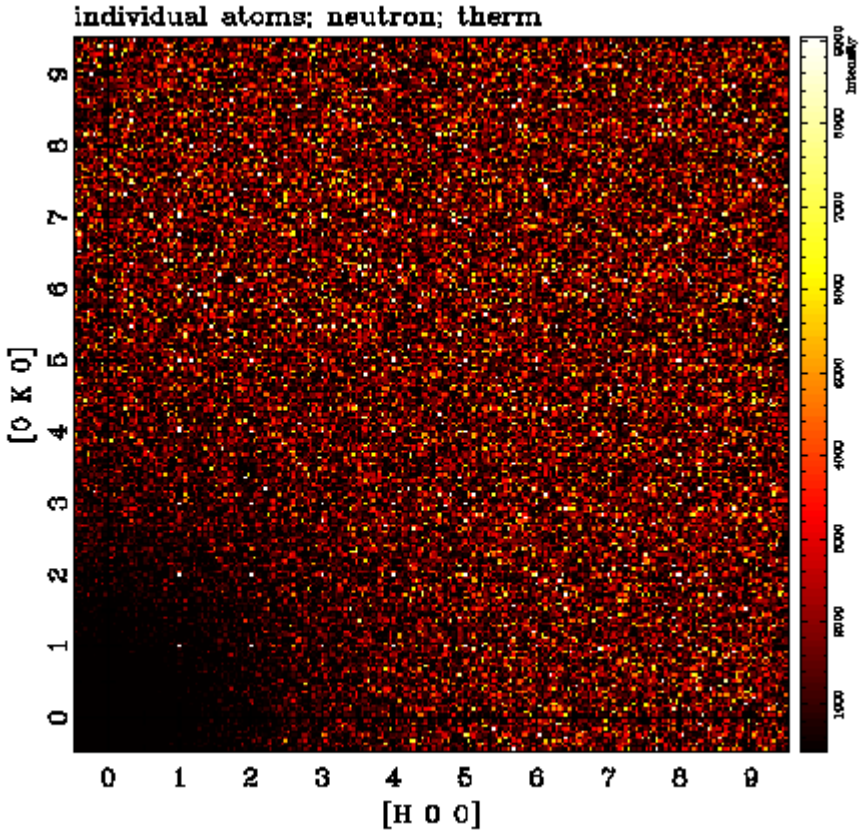
→ Intensity at Bragg reflections
and monotonic diffuse Laue scattering
no special structure

Disorder versus Diffraction

all atoms shifted randomly, thermal displacement

Neutron scattering





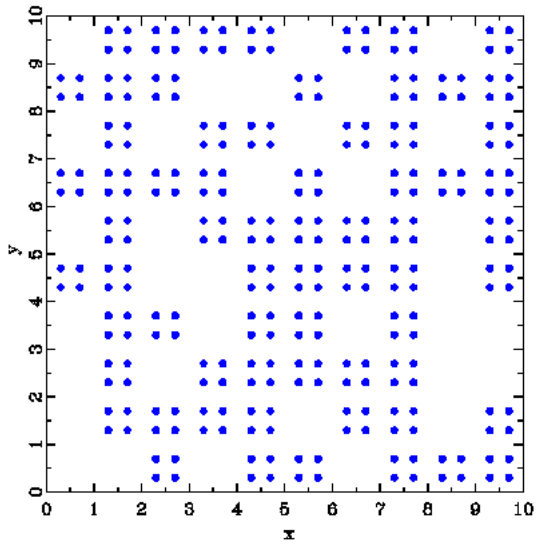
rigid molecules in P4mm
bonds destroyed

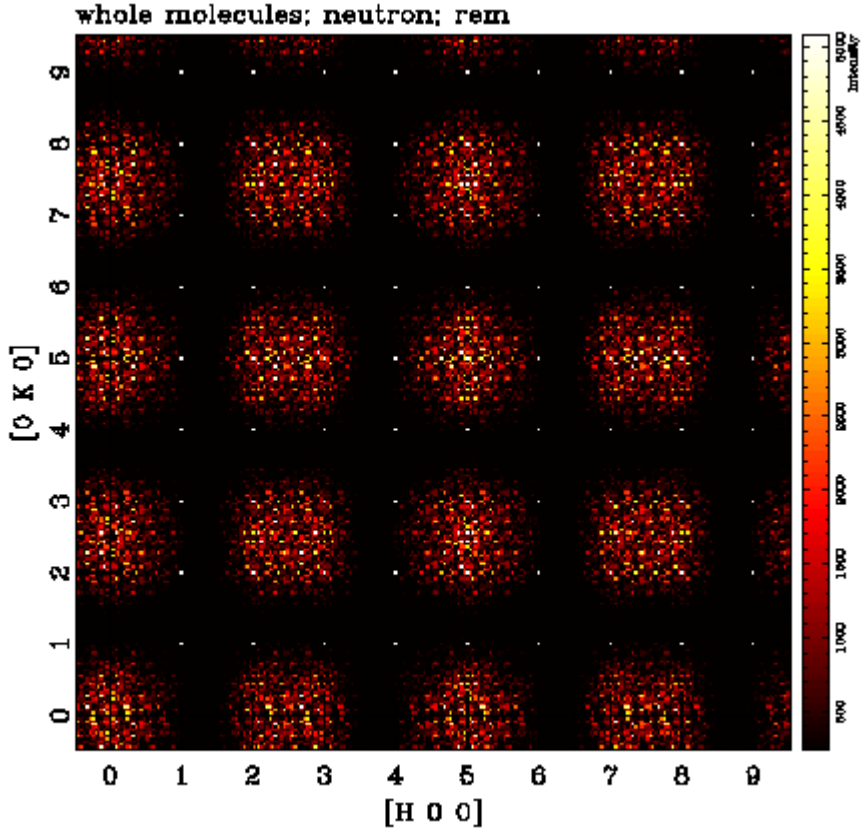
→ Intensity at Bragg reflections and
isotropic diffuse scattering
weak close to reciprocal origin

Disorder versus Diffraction

25 % of all molecules removed, no correlations

Neutron scattering



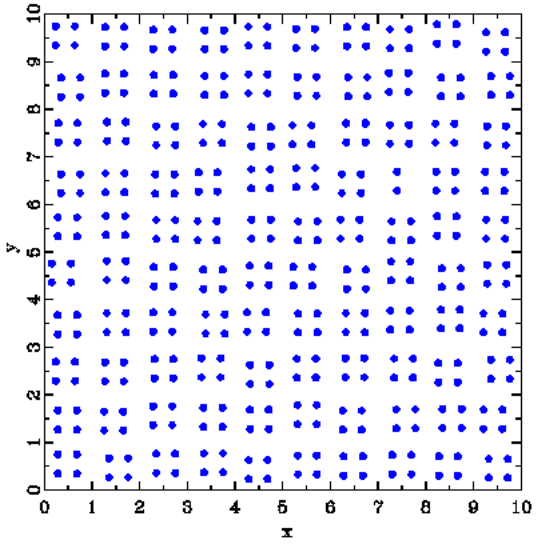


rigid molecules in P4mm

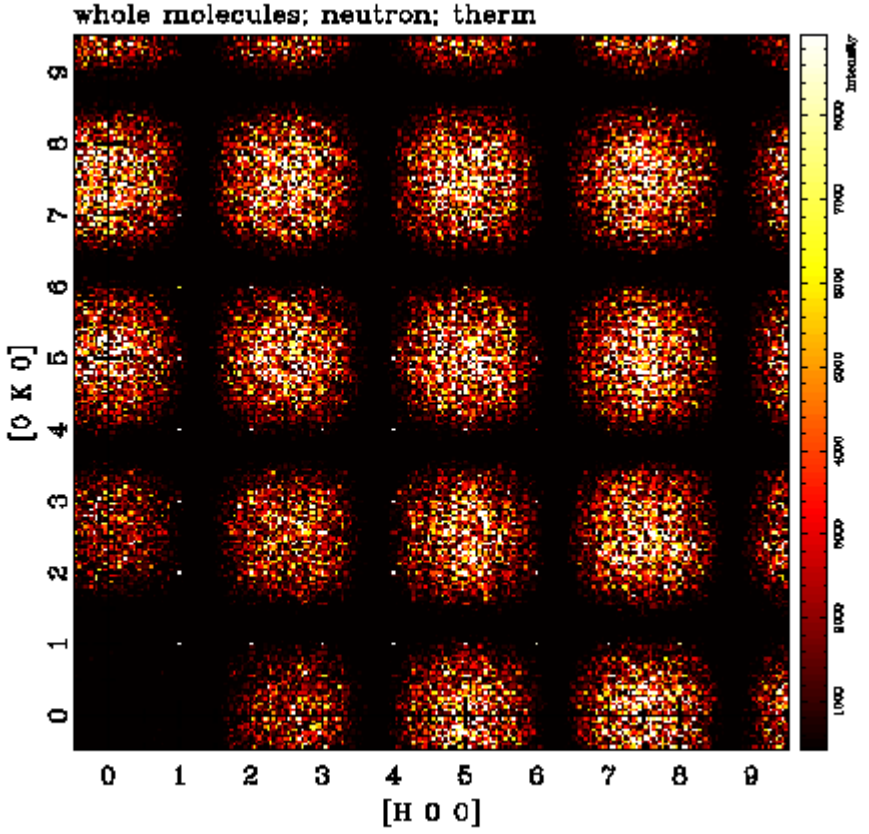
isotropic diffuse intensity
modulated by molecular structure factor

Disorder versus Diffraction

all molecules shifted randomly



Neutron scattering



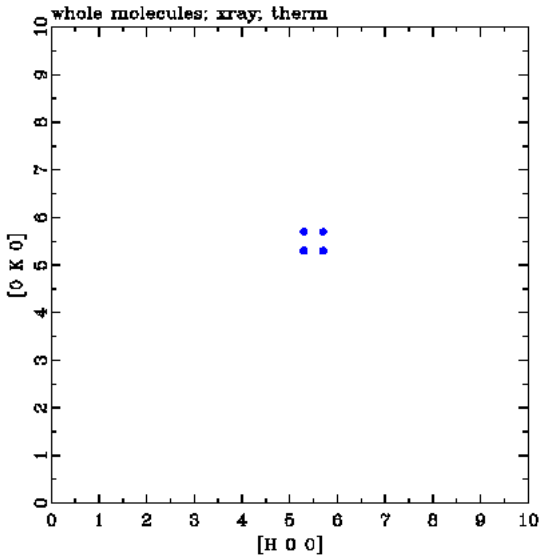
rigid molecules in P4mm

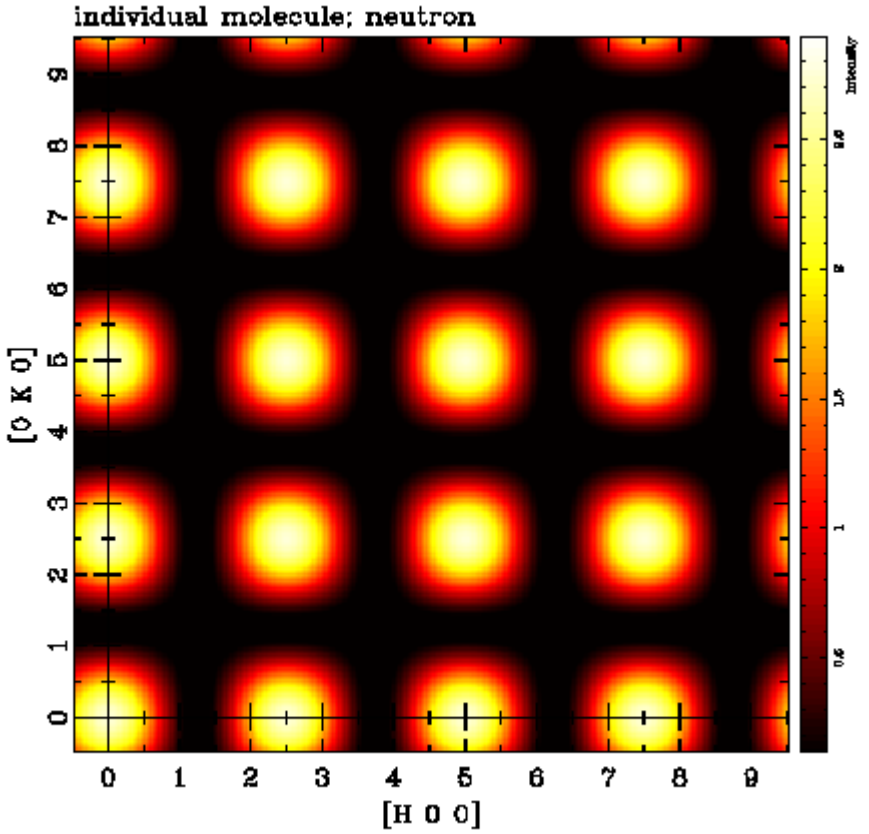
→ isotropic diffuse intensity
modulated by molecular structure factor
weak close to reciprocal origin

Disorder versus Diffraction

diffraction pattern of a single molecule

Neutron scattering



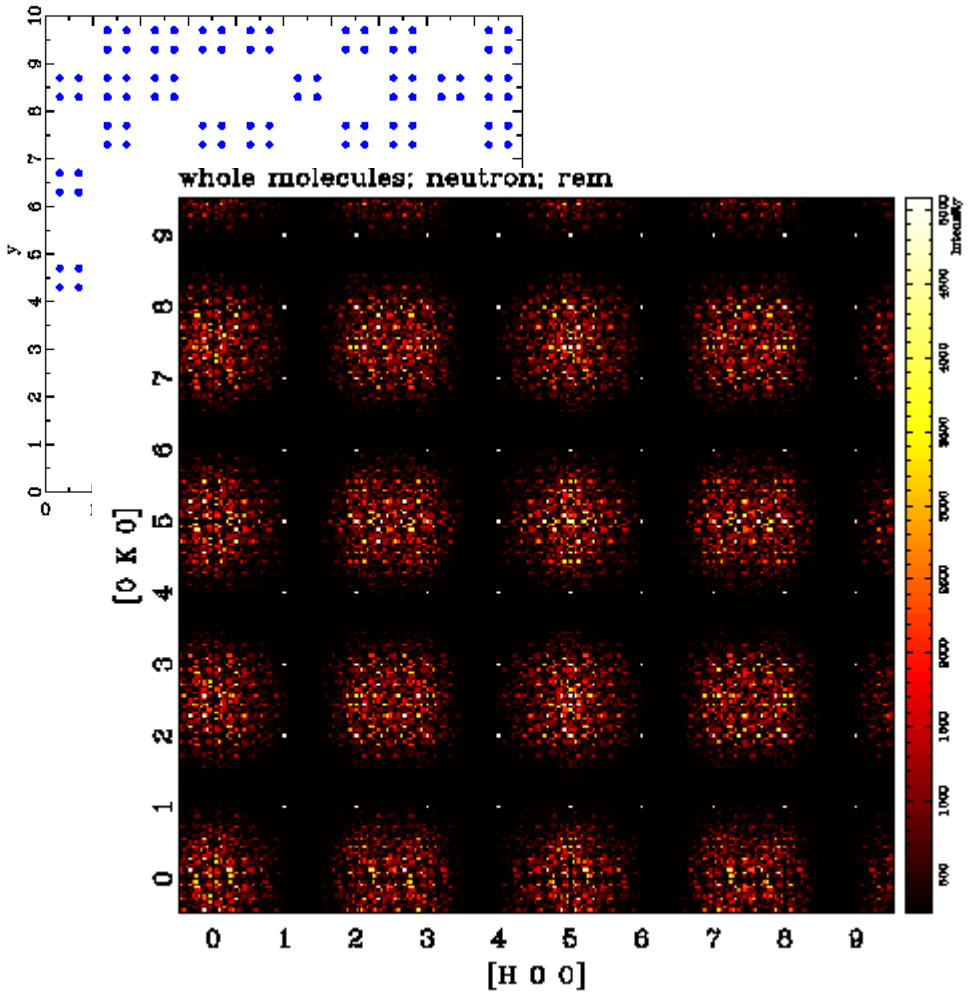


rigid molecules in P4mm

intensity modulated by molecular structure factor

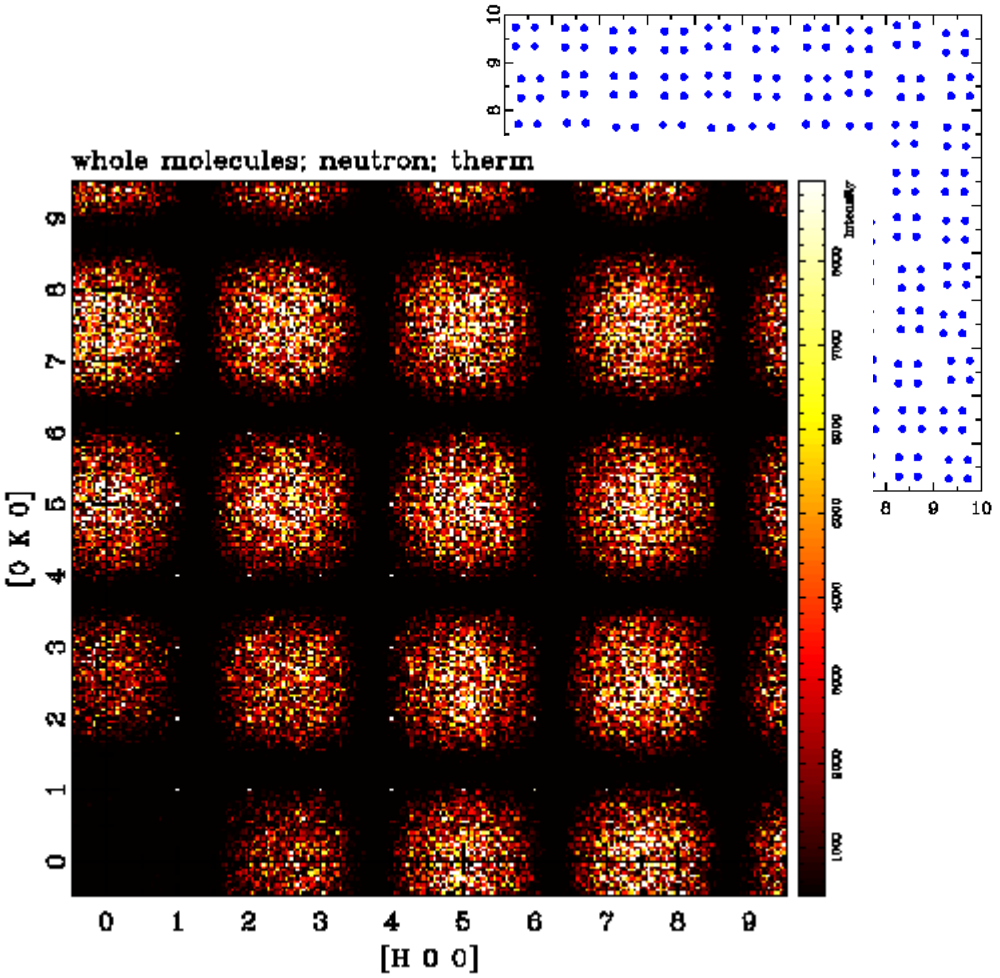
Disorder versus Diffraction

Substitutional disorder



Intensity is homogeneous
througout reciprocal space

Displacement disorder



Intensity is weak
near reciprocal origin

Disorder versus Diffraction

$$F(hkl) = \sum_{j=1}^{M} f_j e^{2\pi i (h x_j + k y_j + l z_j)} \qquad F(\vec{h}) = \sum_{j=1}^{M} f_j e^{2\pi i \, \vec{h}\vec{r}_j}$$

$f \rightarrow \langle f \rangle + \Delta f$ Form factor as average form factor plus local deviation

$\vec{r} \rightarrow \langle \vec{r} \rangle + \Delta \vec{r}$ Position as average position plus local deviation

$$F(\vec{h}) = \sum_{j=1}^{M} \left(\langle f_j \rangle + \Delta f_j \right) e^{2\pi i \, \vec{h}\left(\langle \vec{r}_j \rangle + \Delta \vec{r}_j \right)}$$

Pure substitutional disorder $\Delta \vec{r} = 0$

$$F(\vec{h}) = \sum_{j=1}^{M} \left(\langle f_j \rangle + \Delta f_j \right) e^{2\pi i \, \vec{h}\langle \vec{r}_j \rangle}$$

$$= \sum_{j=1}^{M} \langle f_j \rangle e^{2\pi i \, \vec{h}\langle \vec{r}_j \rangle} +$$

Identical to perfect structure

$$\sum_{j=1}^{M} \Delta f_j e^{2\pi i \, \vec{h}\langle \vec{r}_j \rangle}$$

For neutrons independent of $|\vec{h}|$

For X-ray, e^- dependent on $|\vec{h}|$

Disorder versus Diffraction

$$F(hkl) = \sum_{j=1}^{M} f_j e^{2\pi i (h x_j + k y_j + l z_j)} \qquad F(\vec{h}) = \sum_{j=1}^{M} f_j e^{2\pi i \, \vec{h} \vec{r}_j}$$

$f \rightarrow \langle f \rangle + \Delta f$ Form factor as average form factor plus local deviation

$\vec{r} \rightarrow \langle \vec{r} \rangle + \Delta \vec{r}$ Position as average position plus local deviation

$$F(\vec{h}) = \sum_{j=1}^{M} \left(\langle f_j \rangle + \Delta f_j \right) e^{2\pi i \, \vec{h} \left(\langle \vec{r}_j \rangle + \Delta \vec{r}_j \right)}$$

Pure displacement disorder $\Delta f = 0$

$$F(\vec{h}) = \sum_{j=1}^{M} \langle f_j \rangle \; e^{2\pi i \, \vec{h} \left(\langle \vec{r}_j \rangle + \Delta \vec{r}_j \right)}$$

$$= \sum_{j=1}^{M} \langle f_j \rangle \; e^{2\pi i \, \vec{h} \langle \vec{r}_j \rangle} \; e^{2\pi i \, \vec{h} \Delta \vec{r}_j}$$

If: $\vec{h} \Delta \vec{r} = 0$ ⇒ Sum identical to perfect crystal

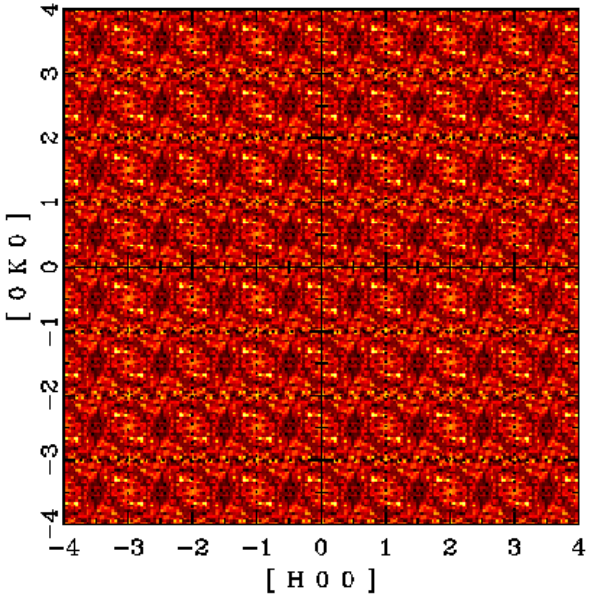
- $|\vec{h}|$ small ==> diffuse scattering weak near reciprocal origin
- All $\Delta \vec{r}$ similar ==> extinction rules for diffuse scattering

Short range order versus Diffraction

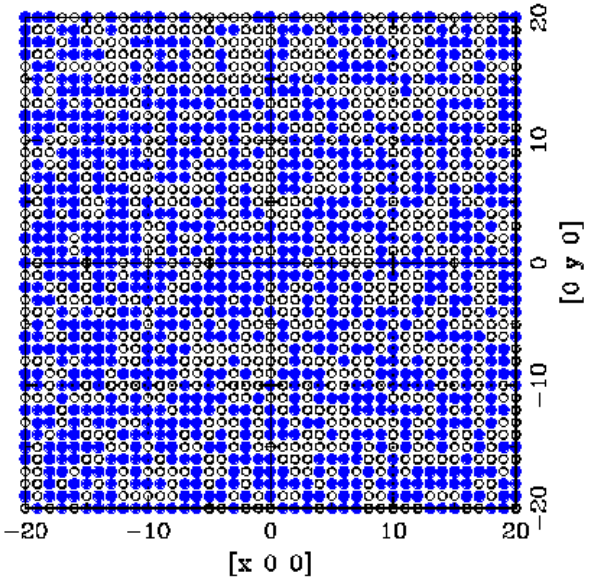
Short Range Order SRO

local structure shows tendency to prefered neighbors like AAAAA or ABABAB

often just the immediate or next few neighbors



unstructured
diffuse scattering



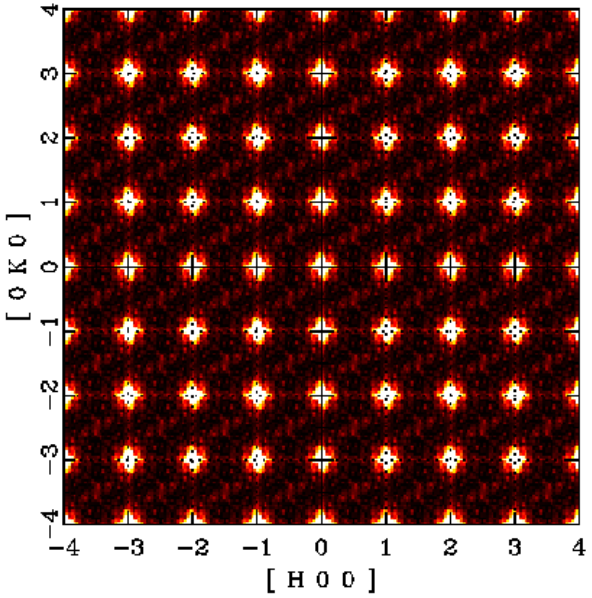
random position

Short range order versus Diffraction

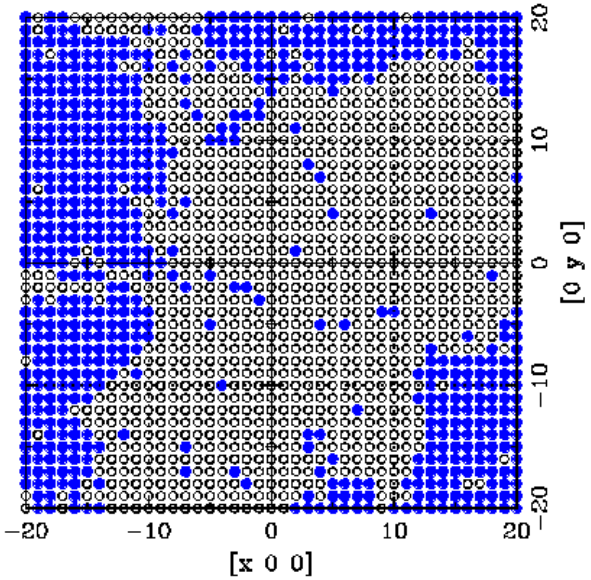
Short Range Order SRO

local structure shows tendency to prefered neighbors like AAAAA or ABABAB

often just the immediate or next few neighbors



diffuse scattering
below Bragg reflections
width indicates SRO range



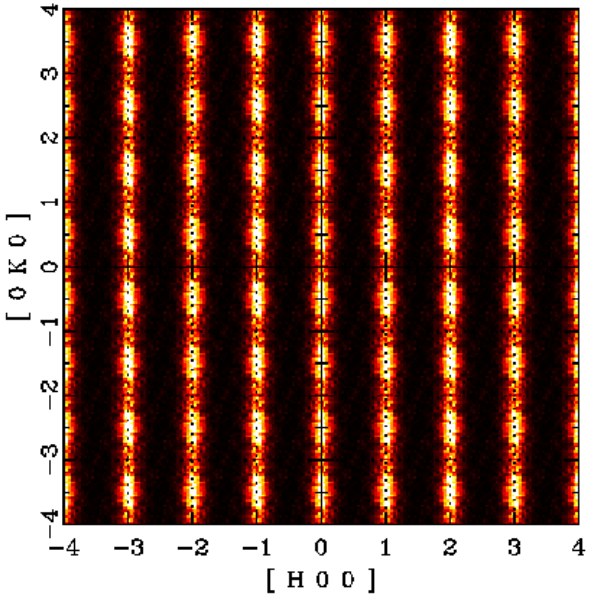
tendency to **equal**
next neighbors

Short range order versus Diffraction

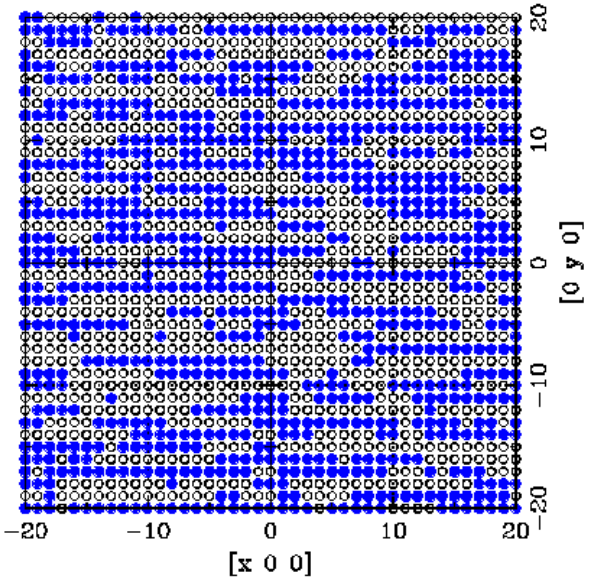
Short Range Order SRO

local structure shows tendency to prefered neighbors like AAAAA or ABABAB

often just the immediate or next few neighbors



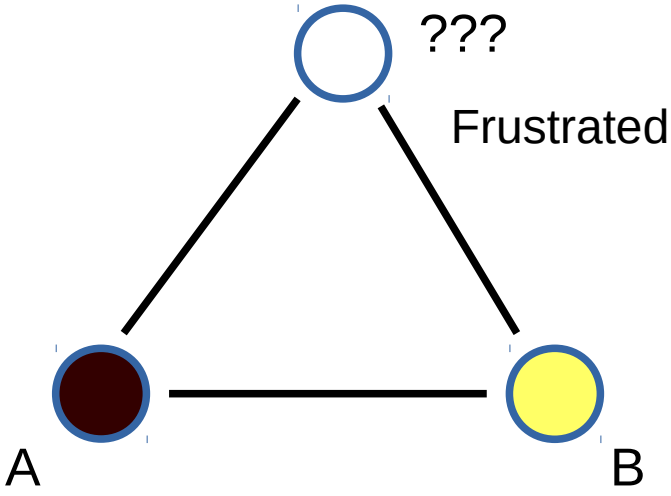
diffuse scattering planes
at Bragg reflections
normal to [100]
width indicates SRO range

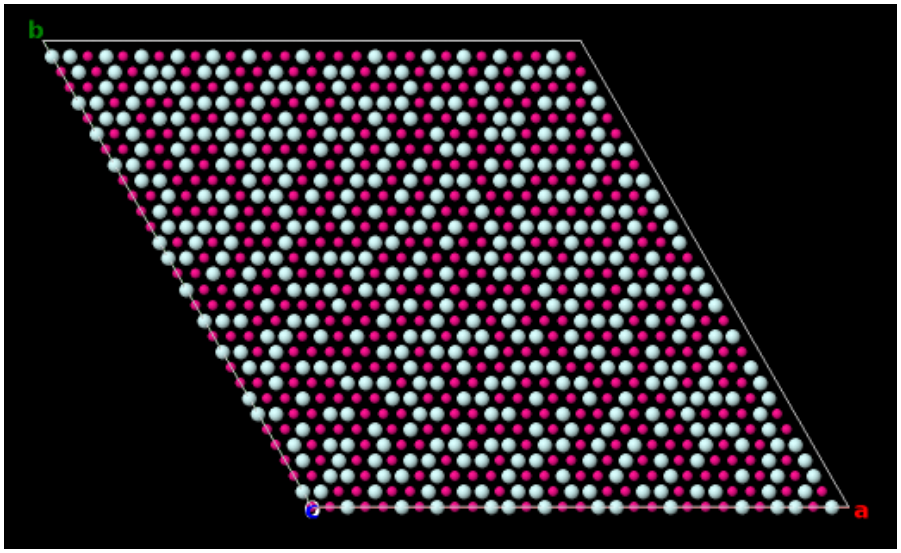


[100] **equal** neighbors
[010] **random** neighbors

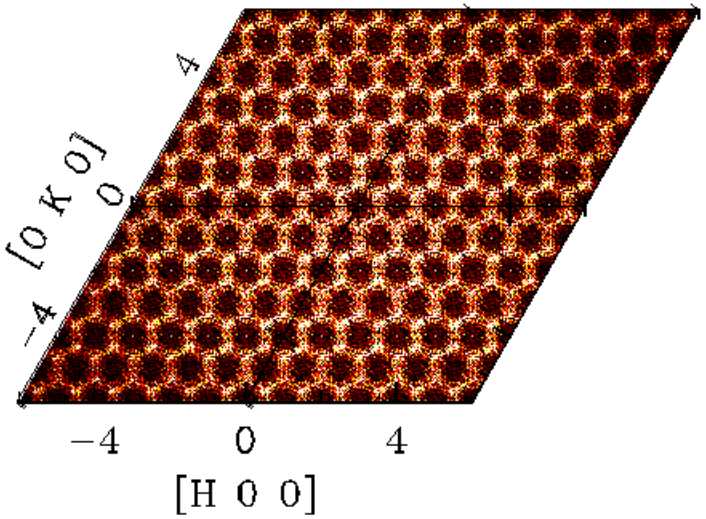
Short range order versus Diffraction

Negative correlations in hexagonal structures

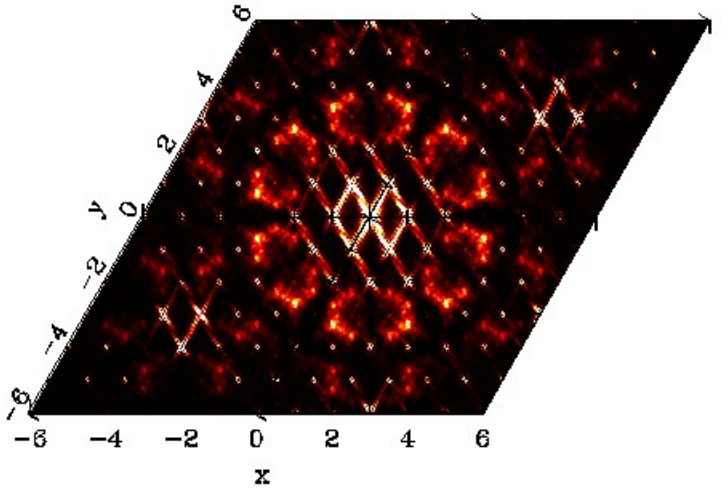




negative correlation cannot be realized perfectly!!!



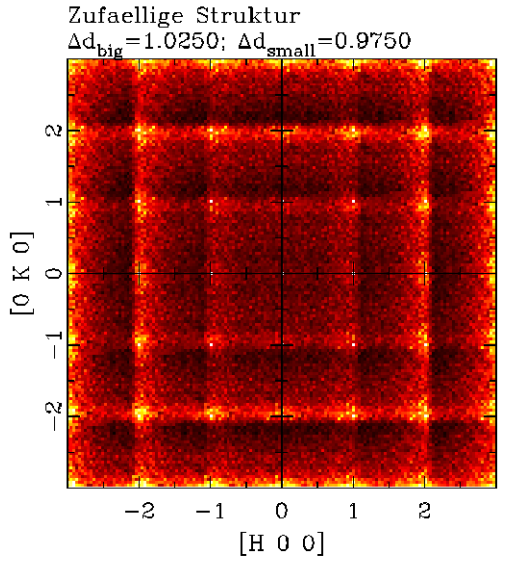
Diffuse scattering *ring* like around Bragg

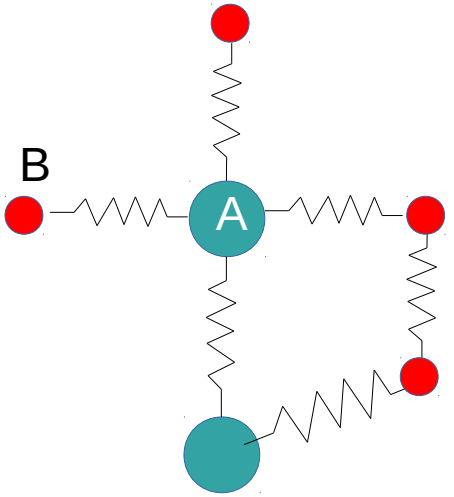


Diffuse scattering with molecules

Size effect versus Diffraction

Radii: $r_A > r_B$





[100]

[010]

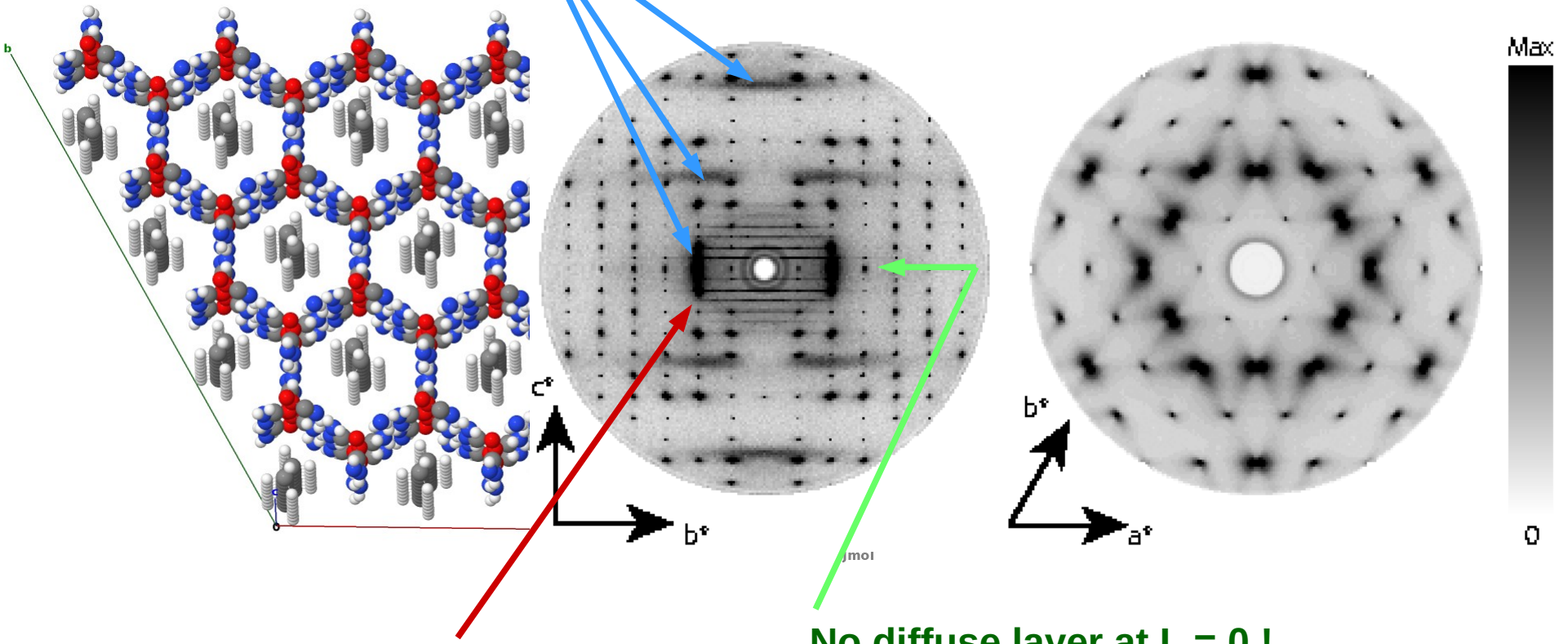
Form factors $f_A > f_B$

Asymmetrically shaped diffuse scattering
Higher intensity at smaller values of h
“size effect”

Initial interpretation / Model building

Very broad diffuse scattering,
no regularity in reciprocal space

Scattering by single molecule



No diffuse layer at L = 0 !

$$F(hk0) = \sum_{j=1}^{M} f_j e^{2\pi i(h x_j + k y_j + 0 z_j)}$$

Independent of z coordinates
==> hk0 *sees* projected structure

No diffuse: projected structure is periodic

Diffuse layers fade away from
Reciprocal origin

Predominantly substitutional
disorder: Orientation in channels

Th Weber PhD München 1994

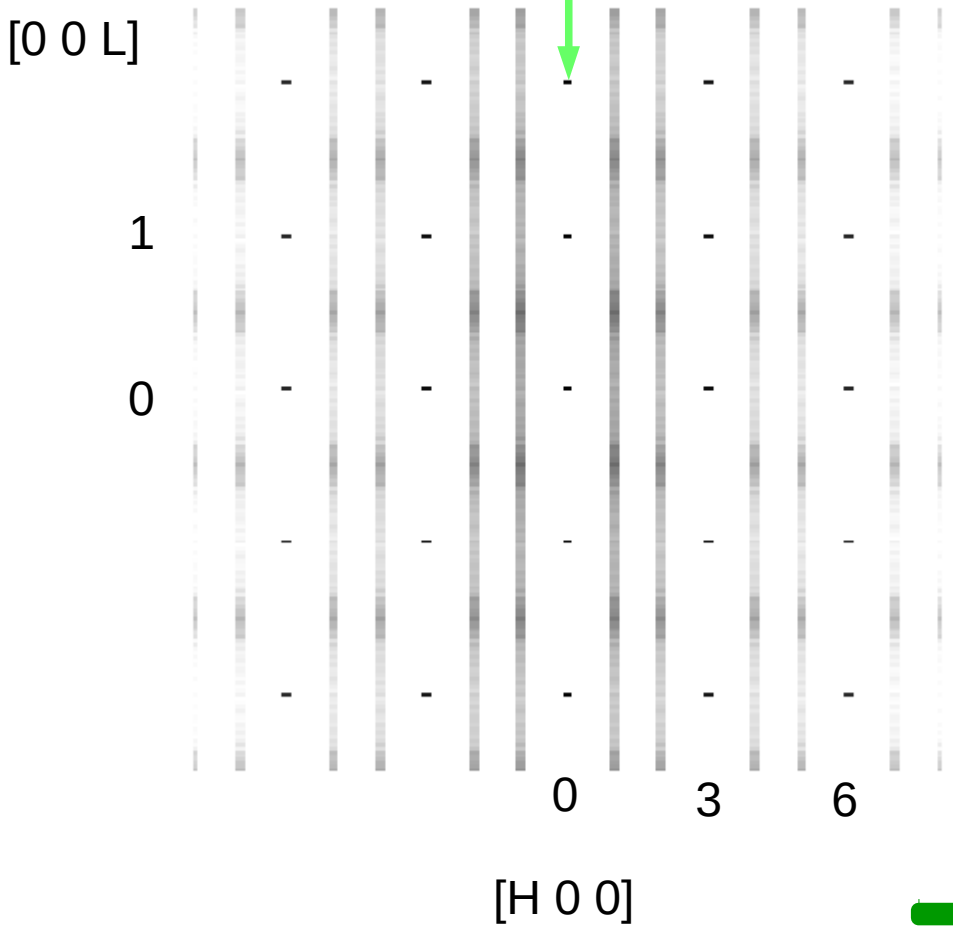
Welberry & Mayo J. Appl. Cryst 29, 1996

Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflecions

No diffuse rod at H = 0 !



$$F(00l) = \sum_{j=1}^{M} f_j e^{2\pi i(0x_j + 0y_j + lz_j)}$$

Independent of x,y coordinates
==> 00L *sees* projected structure

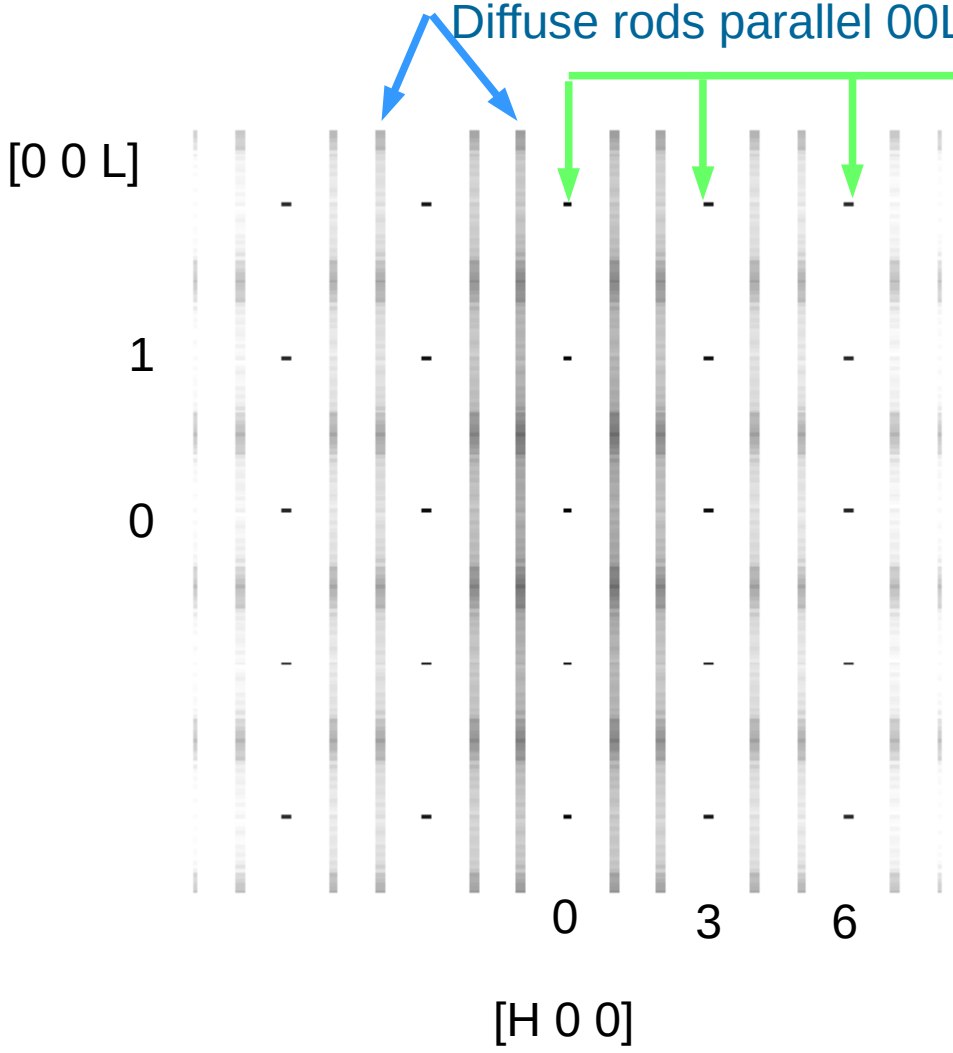
No diffuse: projected structure is periodic along c all layers are identical

Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflecions

No diffuse rod at H = 3n !



$$F(30l) = \sum_{j=1}^{M} f_j e^{2\pi i(3(x_j + \Delta x_j) + 0\,y_j + l\,z_j)}$$

$$F(30l) = \sum_{j=1}^{M} f_j e^{2\pi i(3x_j + 0\,y_j + l\,z_j)} \cdot e^{2\pi i\,3\Delta x_j}$$

If 3Δx = n, exponential factor is equal to 1

==> structure factor is equal to that of perfect structure

No diffuse: Δx = 1/3

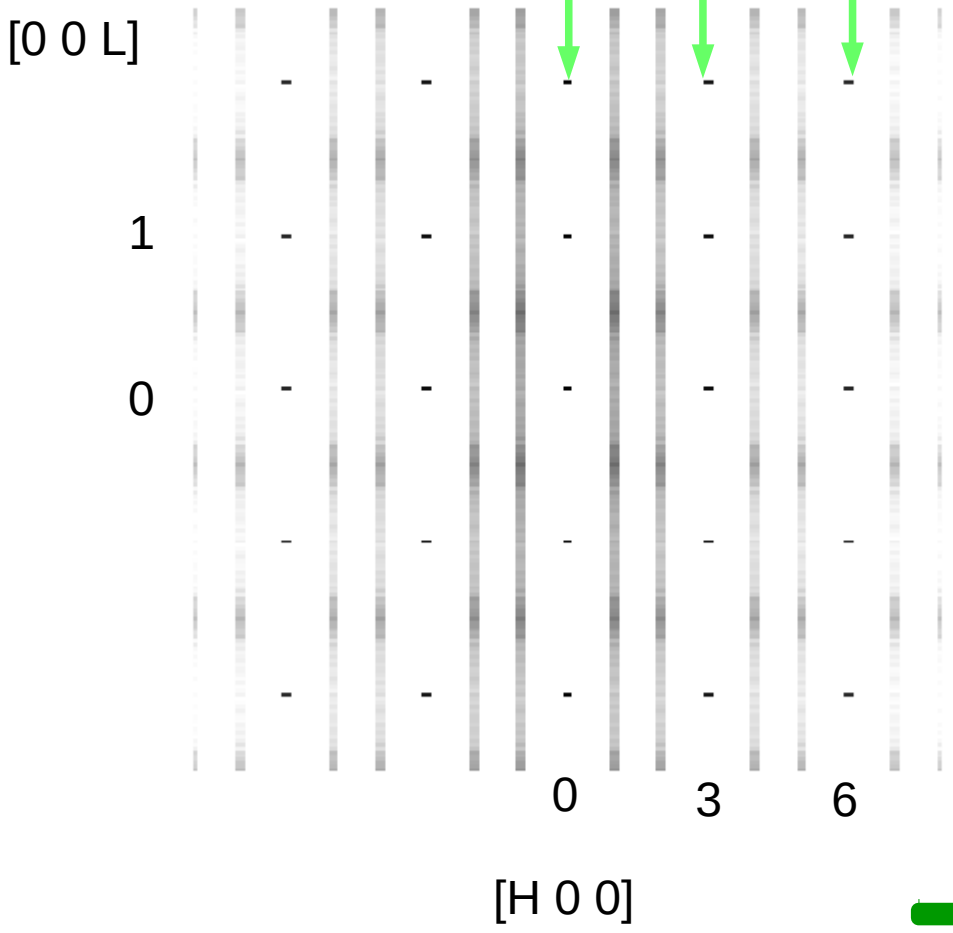
Layers are shifted by 1/3!

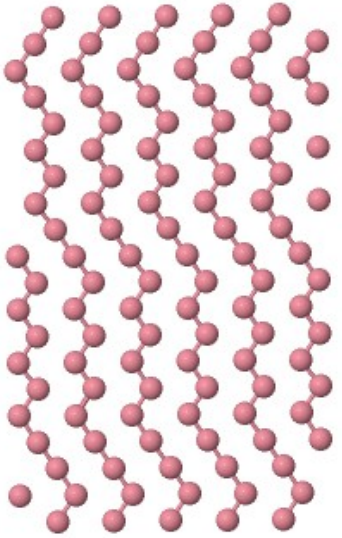
Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflecions

No diffuse rod at H = 3n !





No diffuse: Δx = 1/3

Layers are shifted by 1/3!

***Diffuse* extinction rules give insight into shifts in the structure**

Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

} independent of each other !

no unified theory of diffuse scattering

Generally:	Dimension direct space <==>	3 – dimension reciprocal space
	0-D point defects	3D (unstructured) diffuse scattering
	1-D linear defects	2D planes normal to lines in direct
	2-D planar defects	1-D rods normal to planes in direct
	3-D defects	0-D maxima / satellites

Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

} independent of each other !

no unified theory of diffuse scattering

No periodicity:	Dimension direct space <==>	3 – dimension reciprocal space
All 3 directions	0-D point defects	3D (unstructured) diffuse scattering
2 directions	1-D linear defects	2D planes normal to lines in direct
1 direction	2-D planar defects	1-D rods normal to planes in direct
0 directions	3-D defects	0-D maxima / satellites

Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

} independent of each other !

no unified theory of diffuse scattering

Generally:	substitutional defects	<==>	neutron: no systematic trend X-ray: diffuse scattering stronger close to origin
	displacement defects		diffuse scattering weaker close to origin
	No diffuse scattering defects in layer of plane through reciprocal origin	<==>	Projected structure is periodic on average: 1D channels alike Stack of identical layers
	diffuse extinction rules	<==>	Restrict shifts with structure
	diffuse scattering defects consists of:	<==>	Distribution of defects multiplied by molecular form factor

Literature

Welberry & Weber, Review of Crystallography (2015)
100 Years of Diffuse Scattering
Review of diffuse scattering and disordered structures

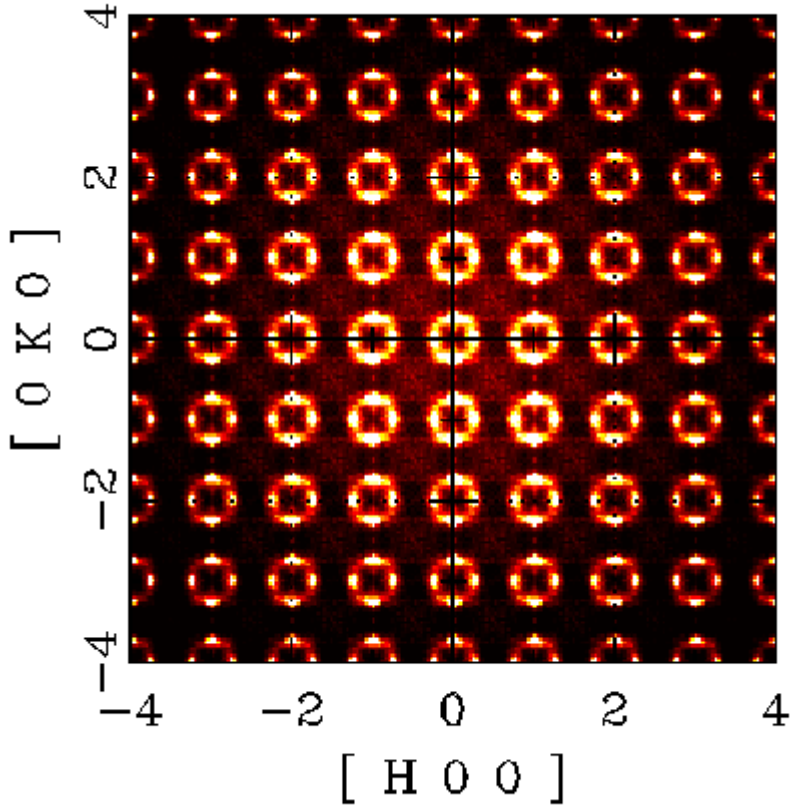
Neder & Proffen, (Oxford, 2008)
Diffuse Scattering and Defect Structure Simulation
Simulation and refinement of disordered structures, cook book

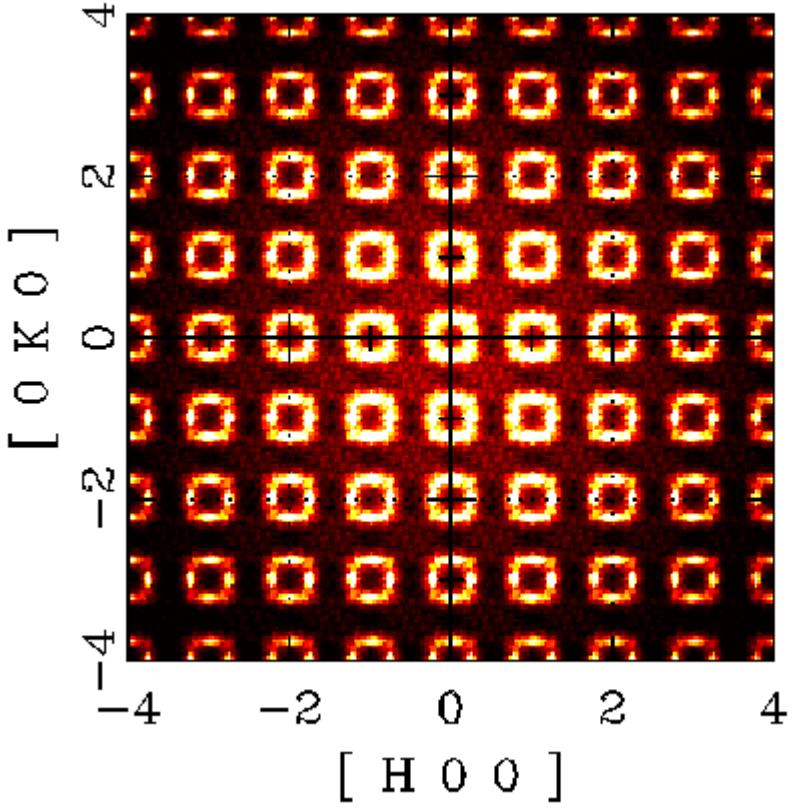
T.R. Welberry (Oxford,2004)
Diffuse X-ray Scattering and Models of Disorder
Limited to X-ray diffraction, short experimental part,
otherwise extensive theory, many examples

V.M. Nield & D.A. Keen (Oxford, 2001)
Diffuse Neutron Scattering from Crystalline Materials
Limited to neutronen diffraction, otherwise extensive theory,
experimental methodse, some simulations, many examples

A word of caution

Essentially identical diffuse scattering





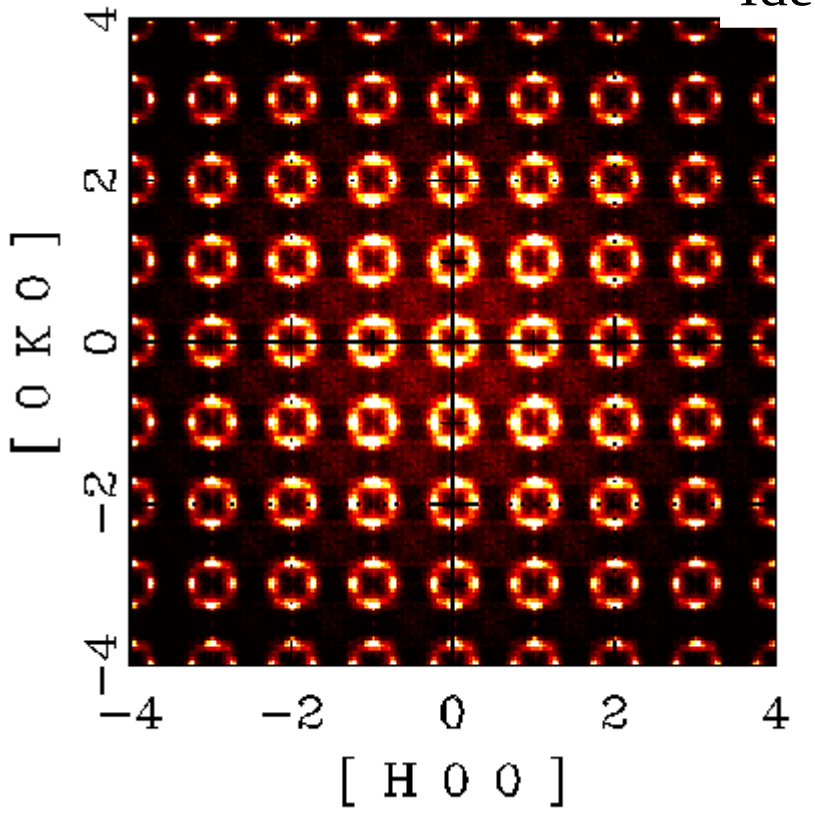
A:B = 1:1

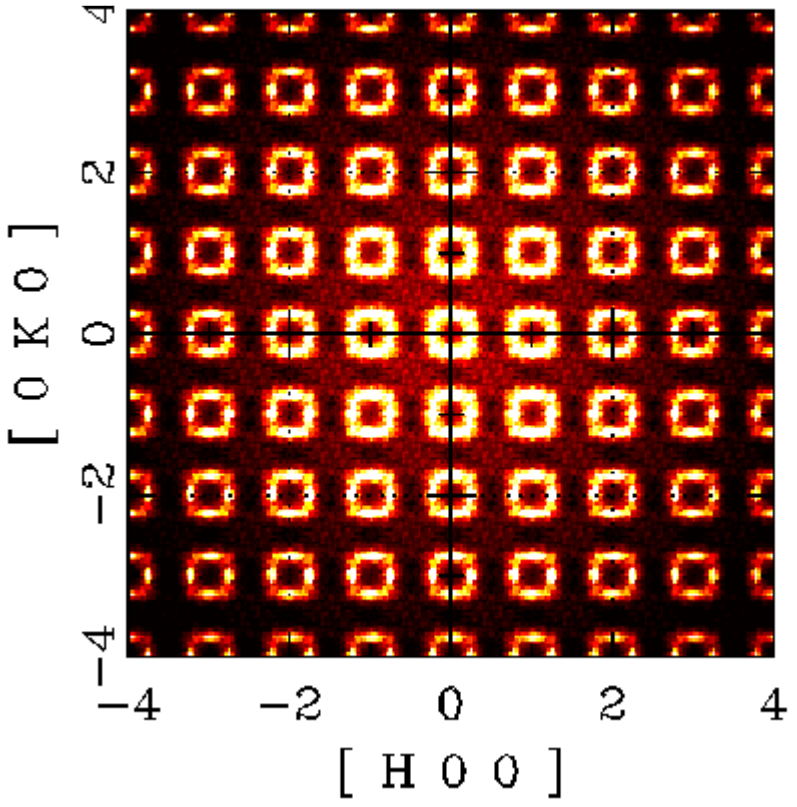
A word of caution

A:B = 3:1

Analyze single crystal refinement
Obtain complementary information:
HRTEM, SAXS, SANS, PDF, Chemistry
Spectroscopy (NMR, EXAFS, ...)
Helps to define correct starting model

Identical Correlations





What is a single crystal ? Kaolinite 1 x 2 x 0,2 µm

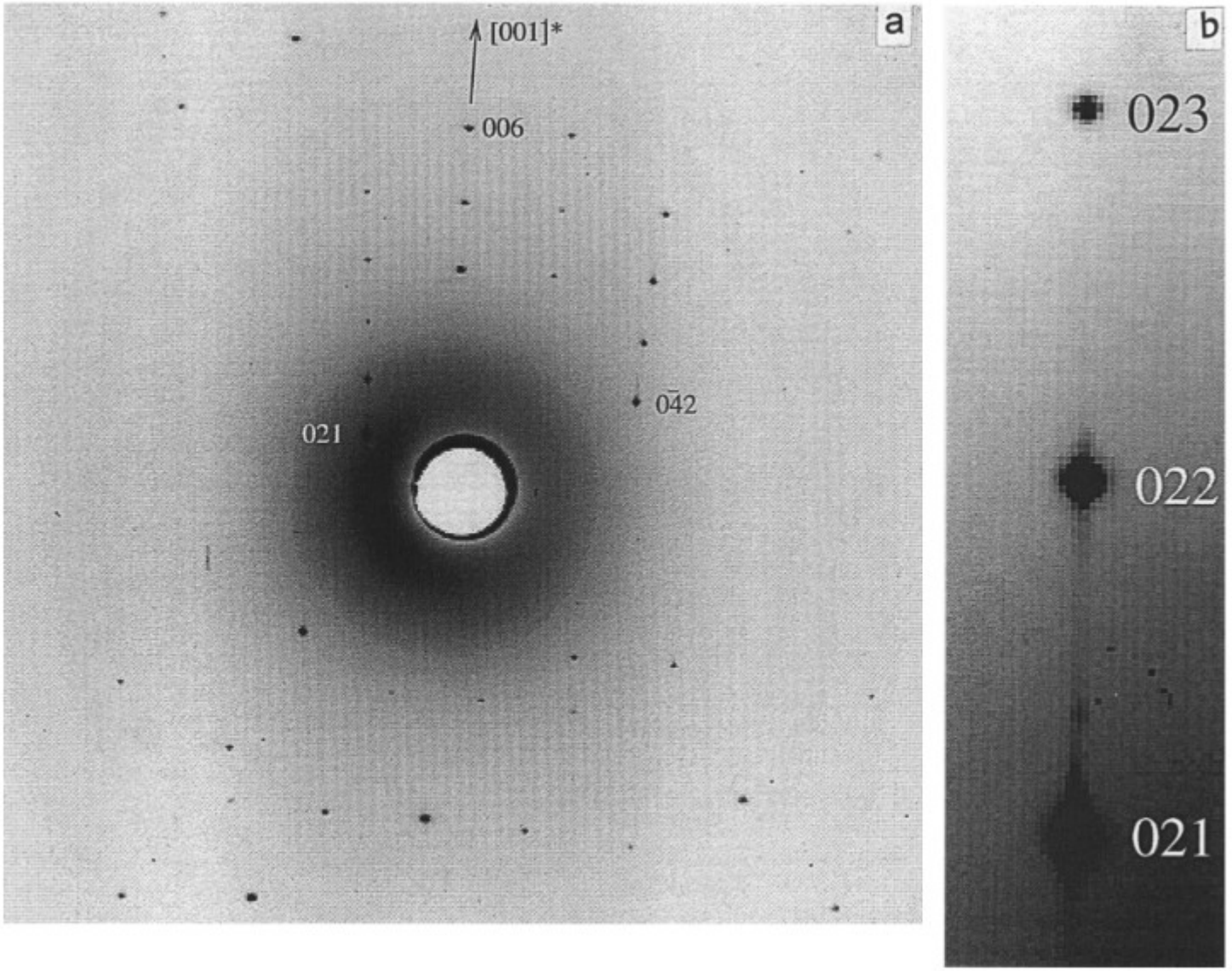
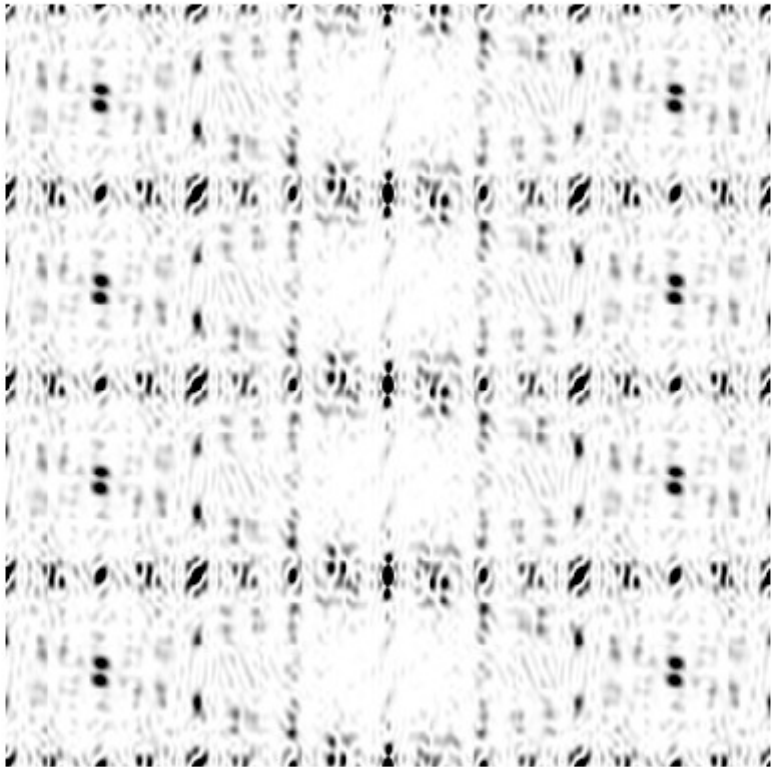


Figure 1. Section of the diffraction pattern of the 8 µm³ crystal. (a) The enlarged section shows the diffuse scattering parallel to [001]* through the 02*l* reflections. (b) The reflection at the bottom of this enlargement is the 021.

Clays and Clay Minerals, (1999), 47, 487

And finally



$\mathcal{F}^{-1}$