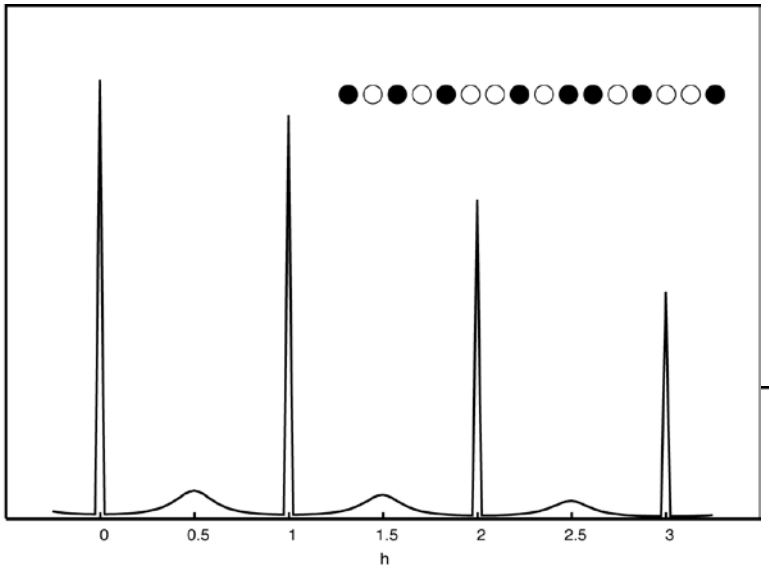
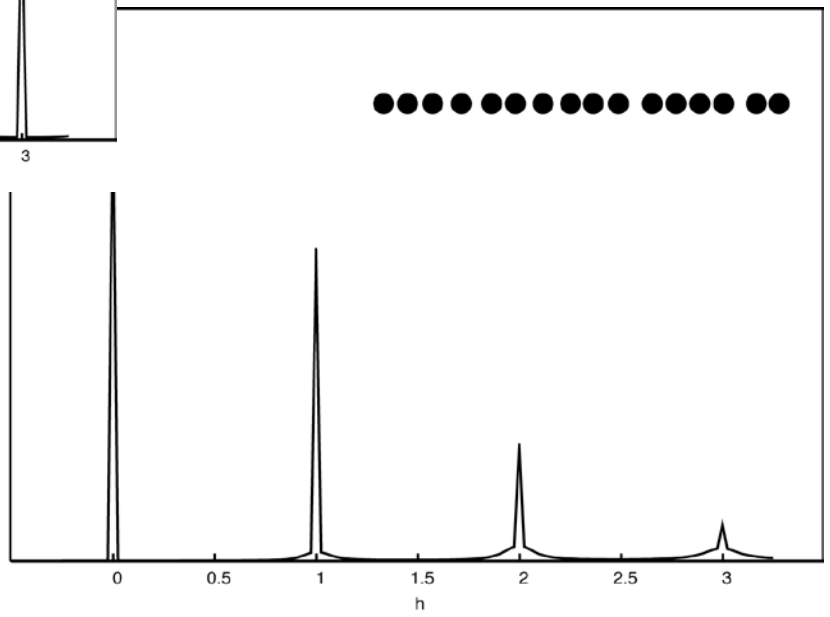
Bragg diffraction and diffuse scattering



Occupational disorder

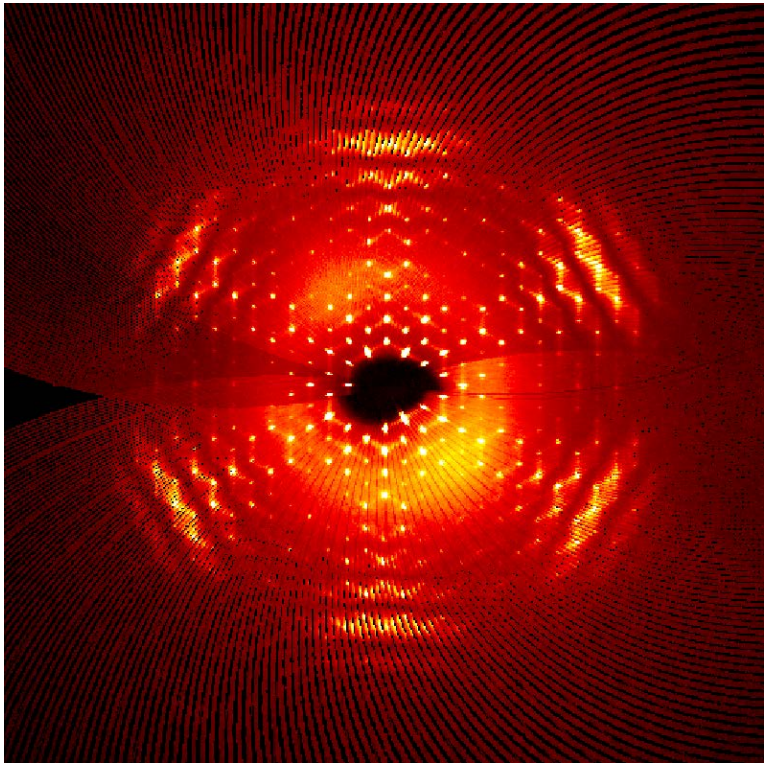


Positional disorder

Loss of translation –
Lost in translation

UNIVERSITÄT BERN

Universität Zürich[UZH]



CAL, May 2015

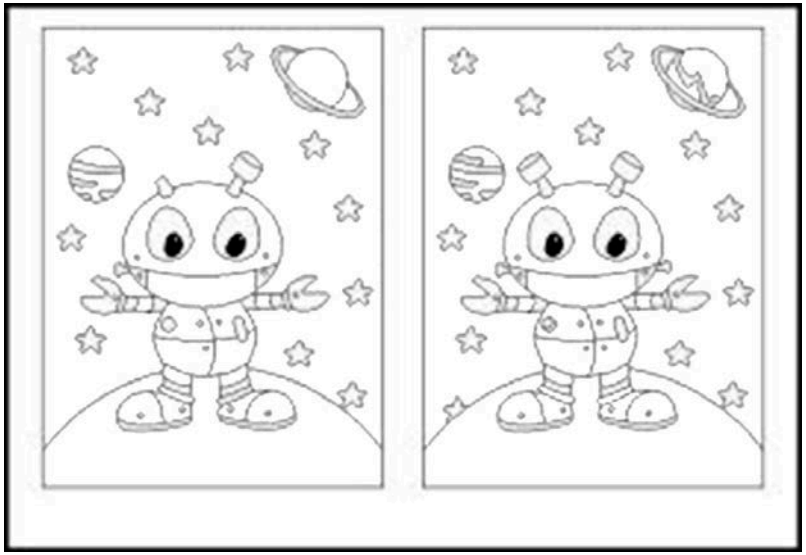
Overview

- Single crystal structure analysis, potential and limitations
- Why study diffuse scattering?
- Classifying disorder with some examples of disordered materials, pictures of their diffuse scattering and some simple rules
- An outline of a real-life case study:
  Qualitative consideration
  3D-Difference Pair Distribution Function
  Monte Carlo crystal builder
  Parameter opt. by differential evolution
  Some results

Single crystal structure analysis

CSD:
>750‘000
structures
in Jan. 2015

(~20%
disordered)



Disorder implies that not all unit cells are the same

Challenge: find the differences between them

Why study disorder diffuse scattering?

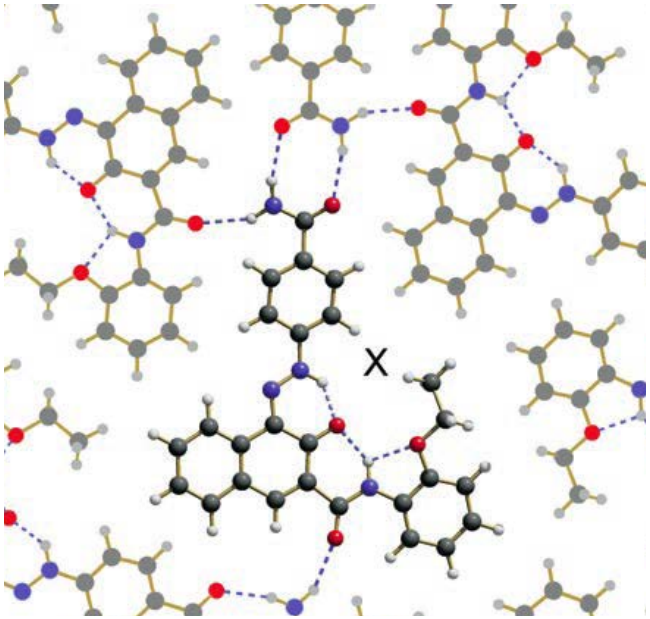
- Many materials owe whatever (interesting) properties they have to disordered arrangements of atoms and molecules
- Some materials are intentionally synthesized with disorder; verify their structure
- Disorder diffuse scattering tends to be weak compared to Bragg scattering. With synchrotron radiation, intense neutron beams and pixel detectors it can now be measured reliably
- No general protocol for determining disordered structures
- Interpretation of diffuse scattering is computationally intensive. With today's computing power this is no longer a major problem

Some simple rules for classifying disorder

Reciprocal space		Direct space
1) Sharp Bragg reflections only	→	3D-periodic structure, ideal, no defects
2) Sharp diffuse streaks	→	2D-periodic perpendicular to the streaks, disordered in streak directions
3) Sharp diffuse planes	→	1D-periodic perpendicular to the planes, disordered in directions within the plane
4) Diffuse clouds	→	0D-periodic, no fully ordered direction

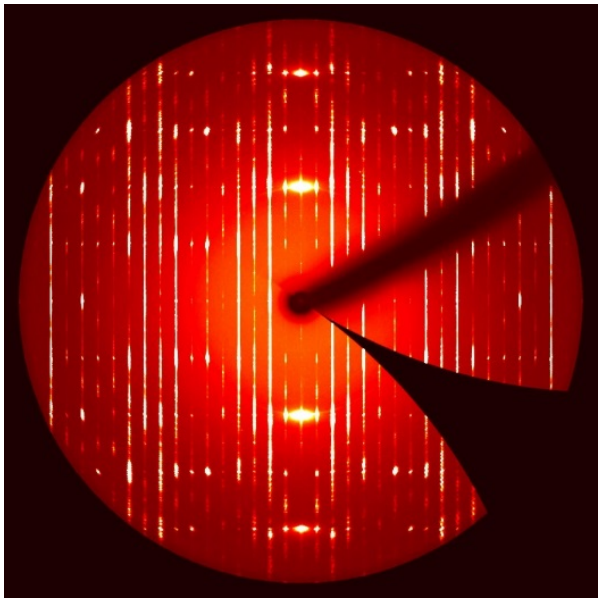
Example I of disordered materials:
Pigment Red 170

Constituent of spray paint,
used in the car industry,



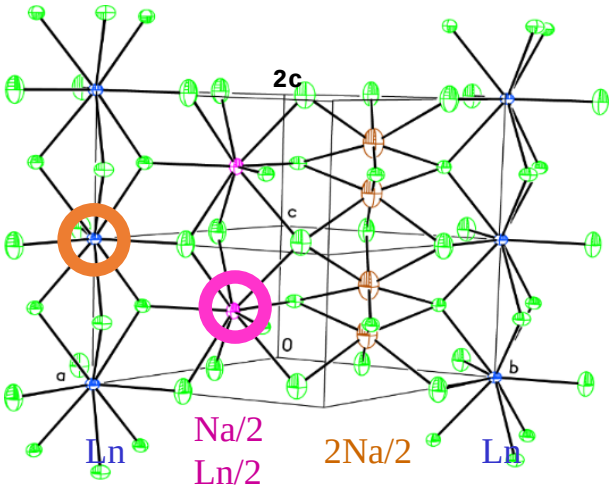
M. U. Schmidt, D. W. M. Hofmann,
C. Buchsbaum, Angew. Chem. Int. Ed.
2006, 45, 1313 –1317

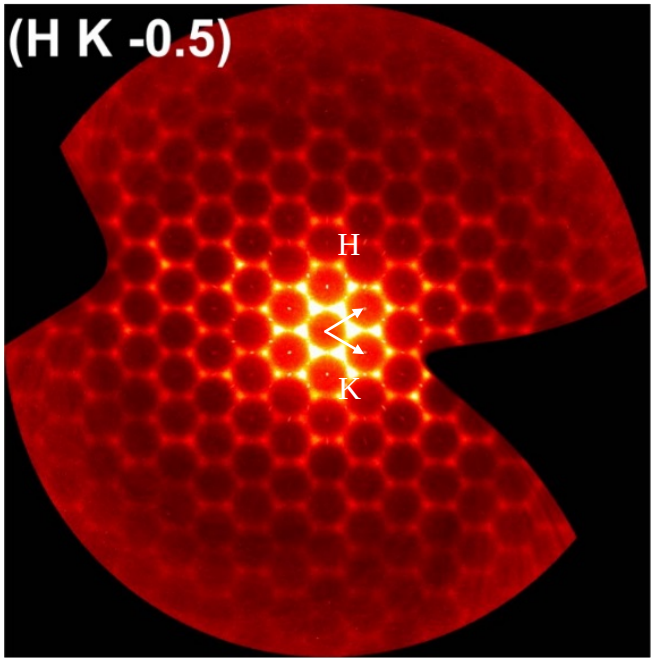
engineering problem:
Light-fastness



diffuse lines

Example II of disordered materials: light up-conversion ($NaLnF_4$, doped)



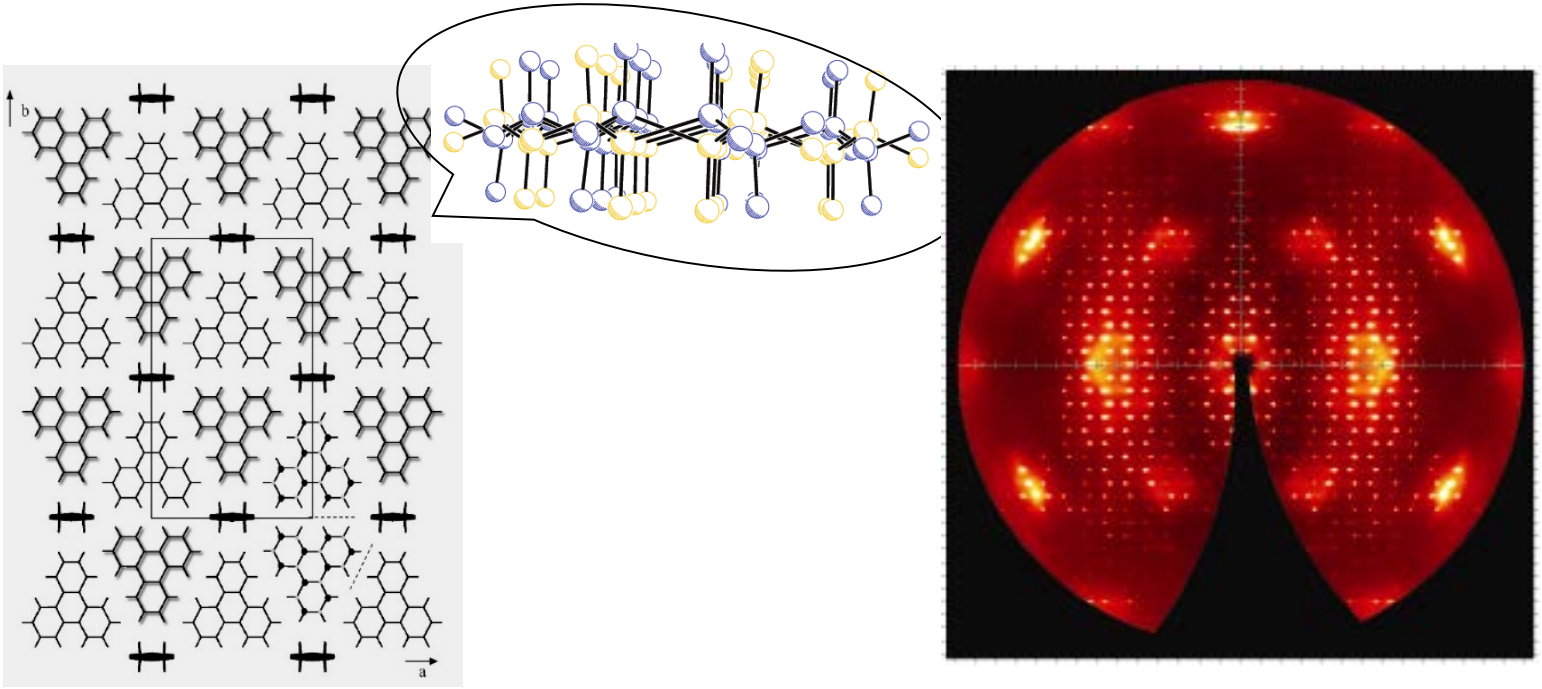


- *Single crystal X-ray structure:*
  two Ln-sites, both C_3-symmetric

- *UV/VIS spectroscopy:*
  two Ln-sites, one C_3-, one C_1-symmetric

Na Ln F_4

Example III of disordered materials: host-guest inclusion compound, SHG active



- Superposition [R-PHTP+S-PHTP]/2
- 5-fold positional disorder of NPP

Perhydrotriphenylene$_2$ * 1-(4-Nitrophenyl)piperazine$_5$

More simple rules

Substitutional disorder, where is the information?

In direct space:

– Two or more different atoms, ions or molecules occupy the same site in the unit cell

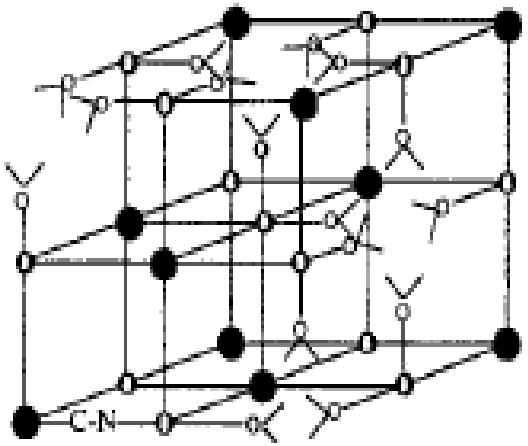
In reciprocal space:

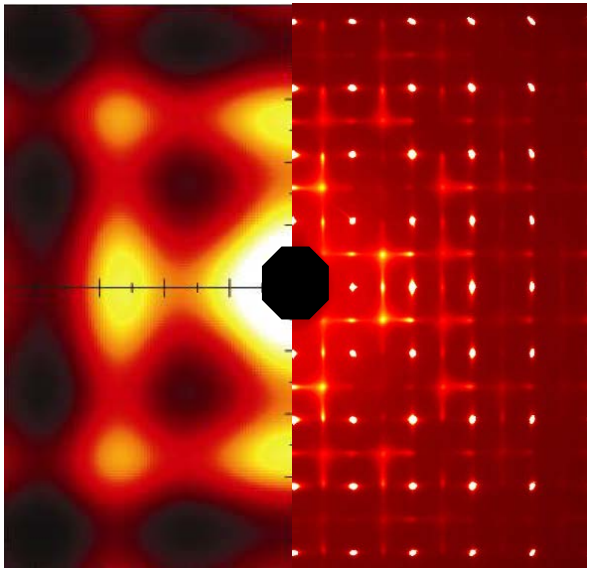
- Intensity governed by difference of atomic ionic or molecular form
  factors.
- Modulation of diffuse intensity indicates correlations between disordered sites

Example IV of disordered materials: Prussian blue analog of Mn, $Mn_3[Mn(CN)_6]_2(H_2O)_6$,

(mixed-valence and magnetic properties)

- $(H_2O)_6$
- $\underline{2\{Mn^{3+}(CN)_6\}}$
- $3\{Mn^{2+}\}$

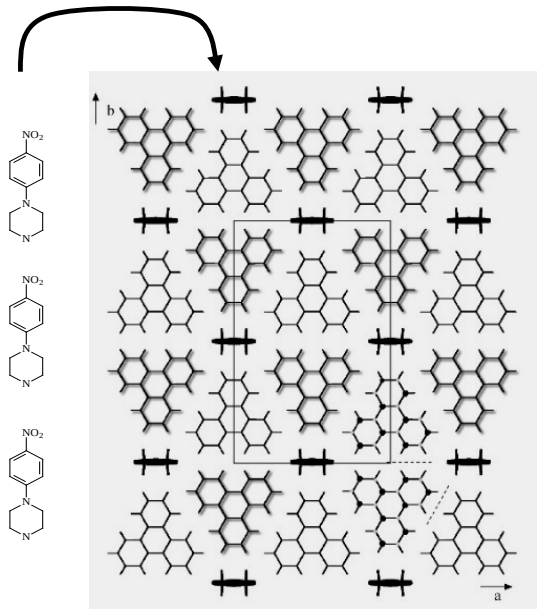


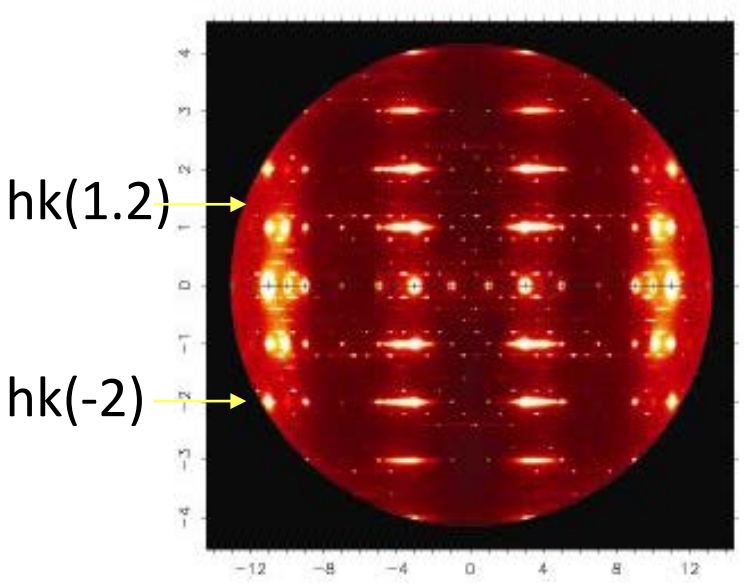


-NaCl lattice: 3 Mn^{2+} occupy edges, $\underline{2\{Mn^{3+}(CN^-)_6\}}$ and $(H_2O)_6$ clusters occupy corners and face centres of cube.

Difference form factor $\Delta f^2 = |f[Mn(CN)_6] - f[(H2O)_6|^2$ and observed scattering in hk0-layer

1-(4-Nitrophenyl) piperazine included in perhydrotriphenylene (PHTP) shows SHG



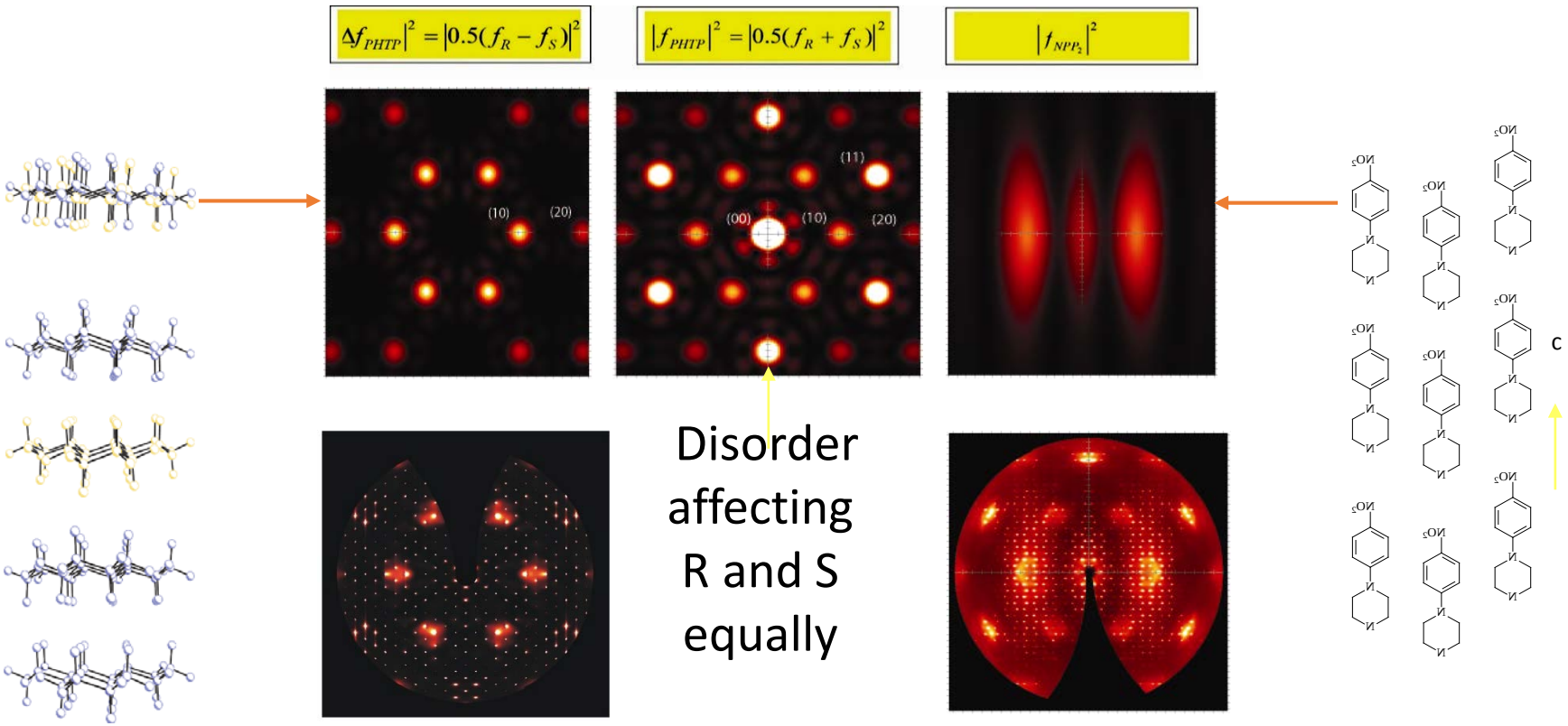


Average structure:

- Racemic disorder of the PHTP host (Spgr Cmcm)
- Positional disorder of the guest along the tunnel (Spgr $Cmc2_1$)

O. König, H.B.Bürgi, T. Armbruster, J. Hulliger, Th. Weber, *JACS*, **119** (1997) 10632

Assignment of diffuse scattering to host and guest and to different kinds of disorder



T. Weber, M. Estermann, H.B. Bürgi, *Acta Cryst.*, **B57** (2001) 579

Beyond simple rules

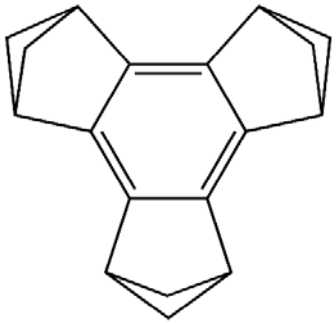
- Layer stacking
  Different layer sequences ↔ different energies

- Loss of translation
  Difference 3D Pair Distriution function, 3D-ΔPDF

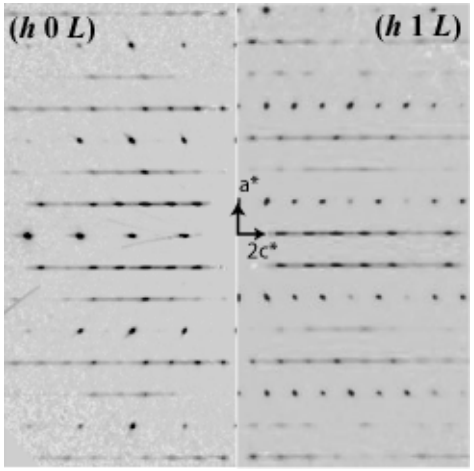
- Monte Carlo simulations of disordered model crystals

- optimization of model parameters
  global optimization methods (differential evolution, genetic algorithms, swarm optimization)

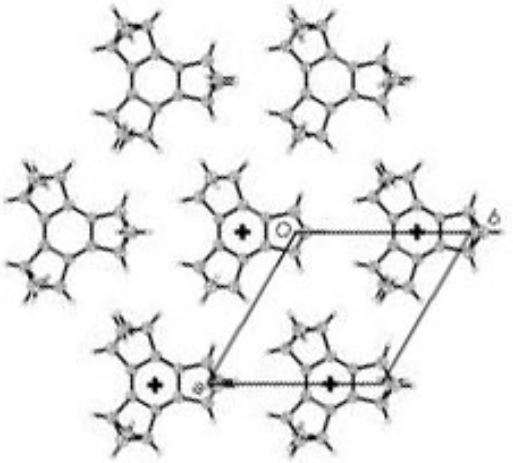
Bond alternation in benzenoid structures



Tris(bicyclo-[2.1.1]hexeno)-benzene

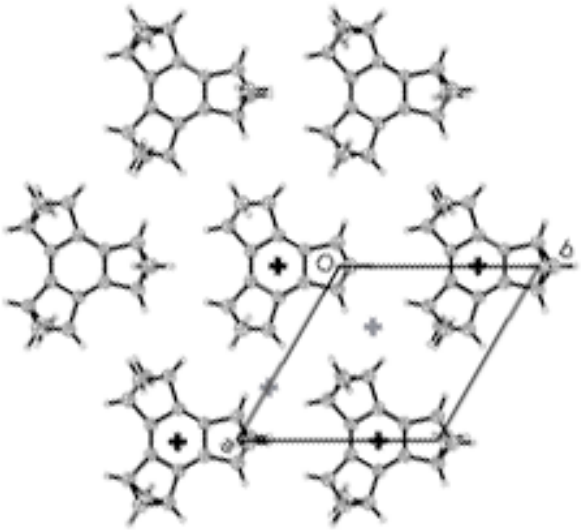


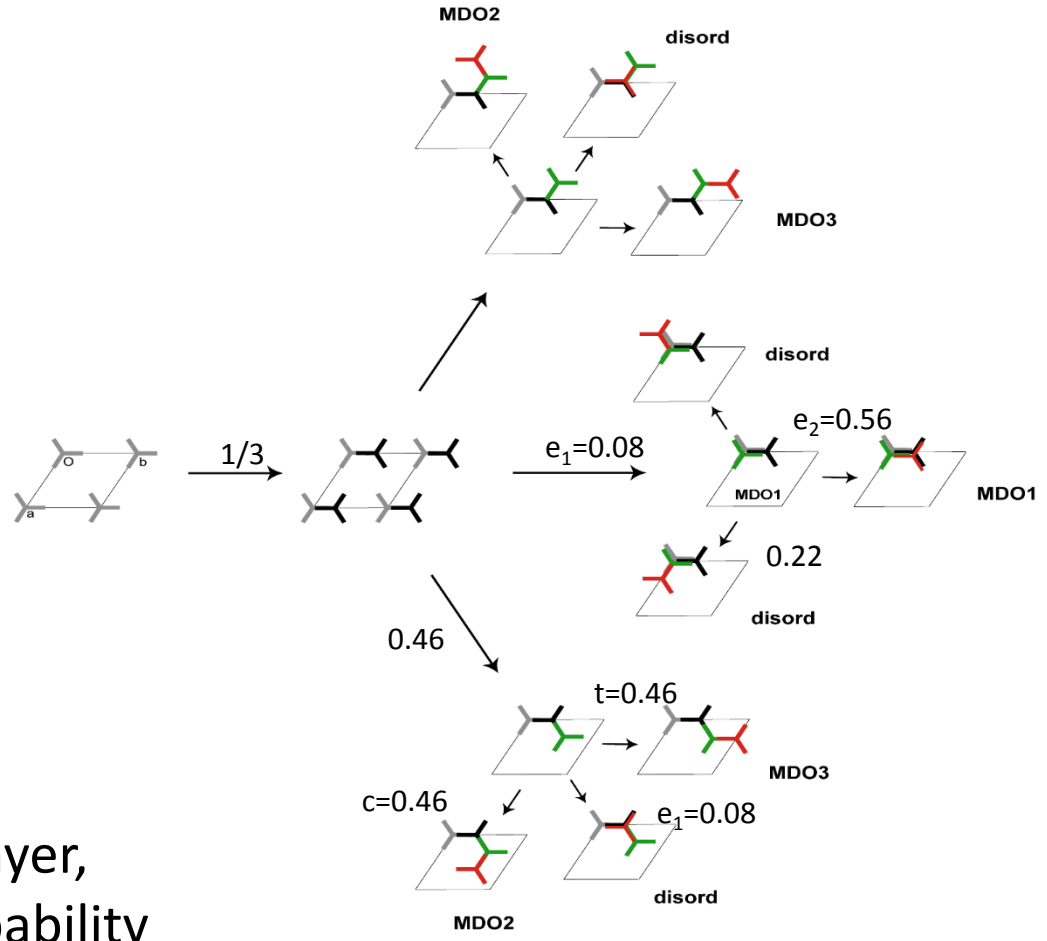
- Structure solved in subcell from Bragg reflections only (arrows)
- Pronounced bond alternation of about 0.09 Å (R1 ~ 0.03)
- Disordered stacking of ordered molecular layers



H.-B. Bürgi, K.K. Baldridge, K.Hardcastle, N.L. Frank, P. Gantzel, J.S. Siegel, J. Ziller.
Angew. Chem. Int. Ed. 34 (1995) 1454-1456.

Stacking disorder of C_{18} H_{18}

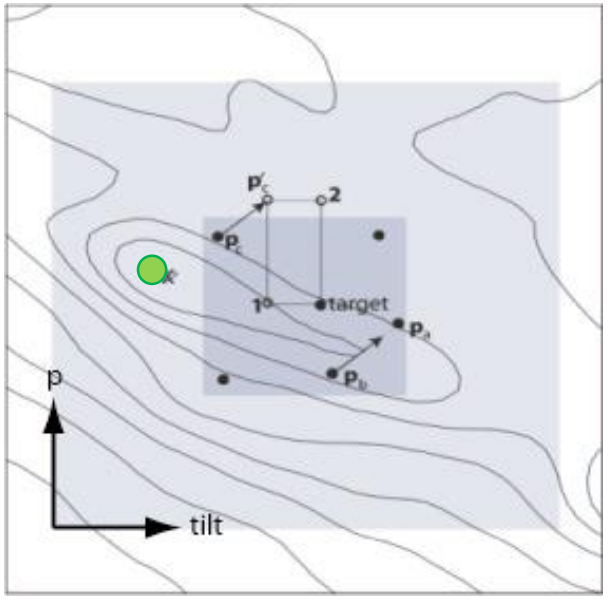


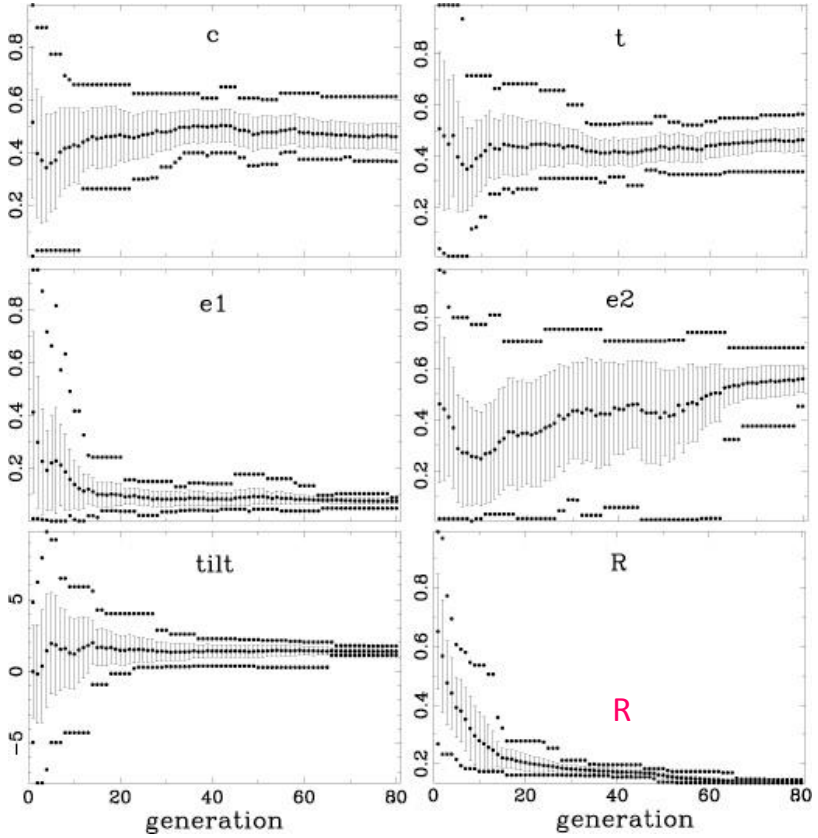


Three ways to stack any layer,
each with a different probability

H.-B. Bürgi, M. Hostettler, H. Birkedal, D. Schwarzenbach, Z. Krist., 220 (2005) 1066-1075

Genetic algorithm for optimisation of model parameters

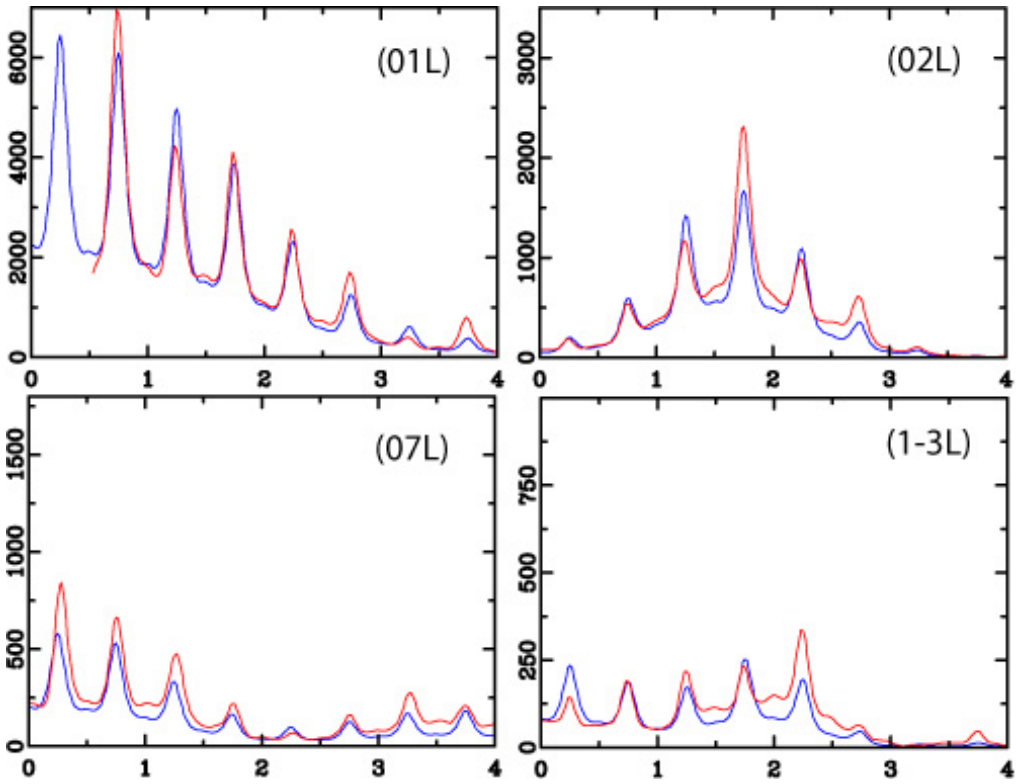




Parameter optimization: finding lowest minimum on Fitness surface by Differential evolution (schematic)

Th. Weber, H.-B. Bürgi, Acta Crystallogr. A58 (2002) 526-540.
H.-B. Bürgi, J. Hauser, Th. Weber, R.B. Neder, Crystal Growth & Design 5 (2005) 2073-2083

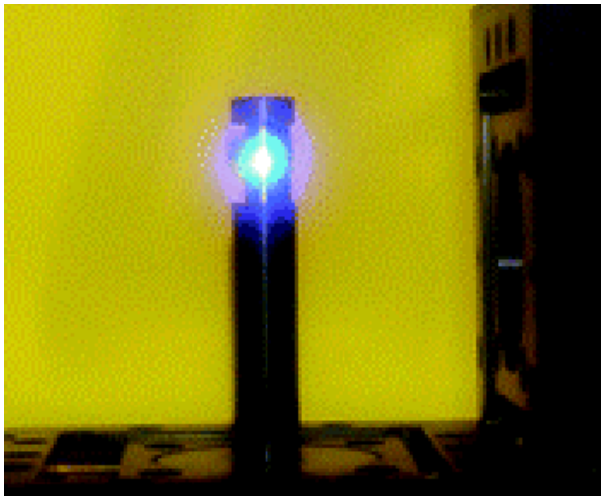
Building the model: four layers



	dif. evol.	analytical
c	0.46(5)	0.46
t	0.47(6)	0.46
e1	0.075(8)	0.08
e2	0.54(5)	0.56

Model	**Mean R (%)**
2 layers	43.0(4)
3 layers	19.2(2)
4 layers	18.3(2)

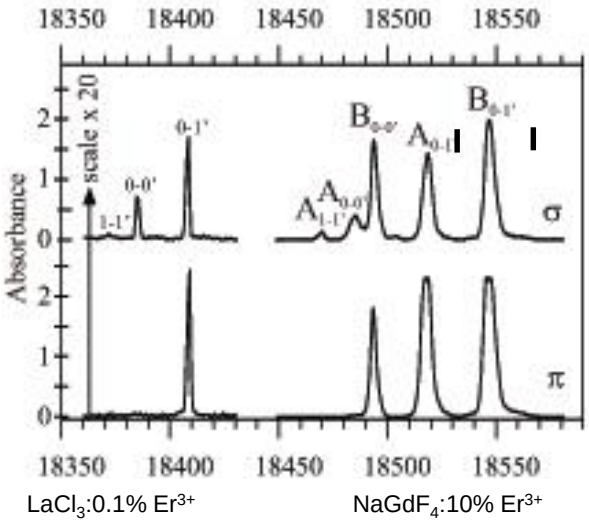
Case study: Upconversion phosphors



$NaLaF_4 : Yb^{3+}$, Er^{3+} and

$NaGdF_4 : Yb^{3+}$, Er^{3+}

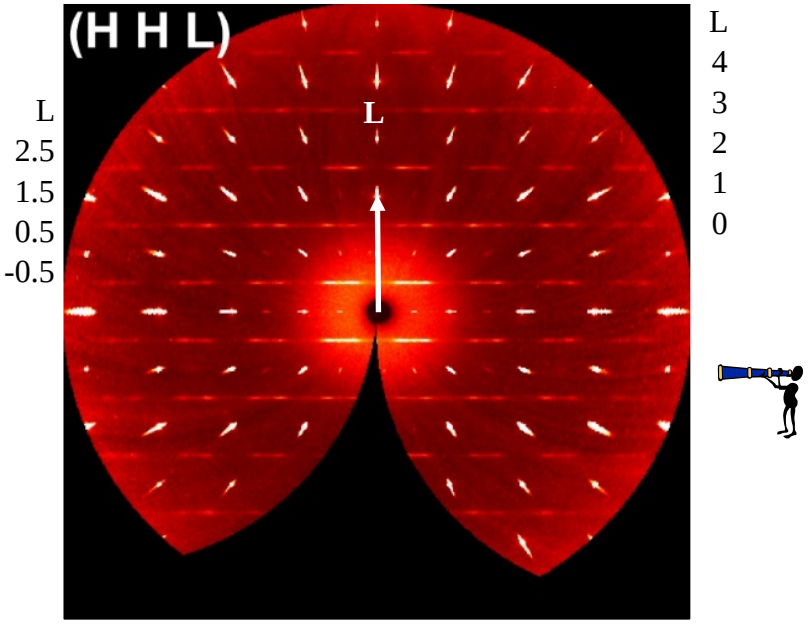
Among best materials for NIR → VIS, green → blue conversion



$LaCl_3$:0.1% Er^{3+} $NaGdF_4$:10% Er^{3+}

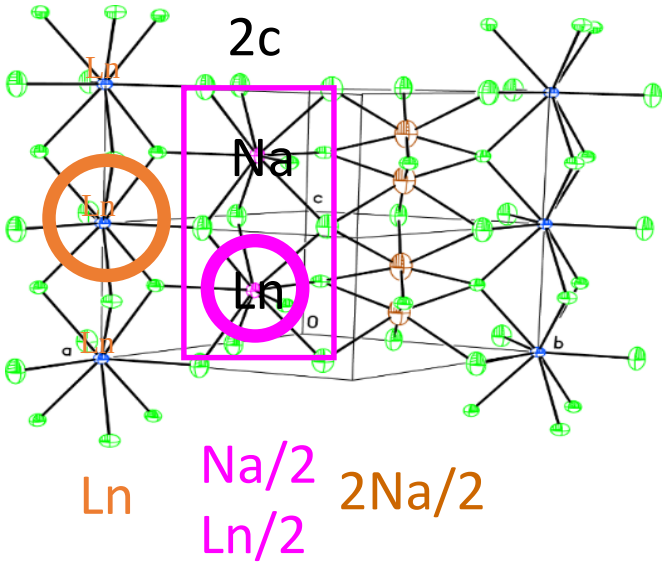
Polarized absorption spectra

- $NaGdF_4$:10% Er^{3+} (right): two sites: A (C_{3h}), B (C_1)
- $LaCl_3$:0.1% Er^{3+} (left): one site (C_{3h})



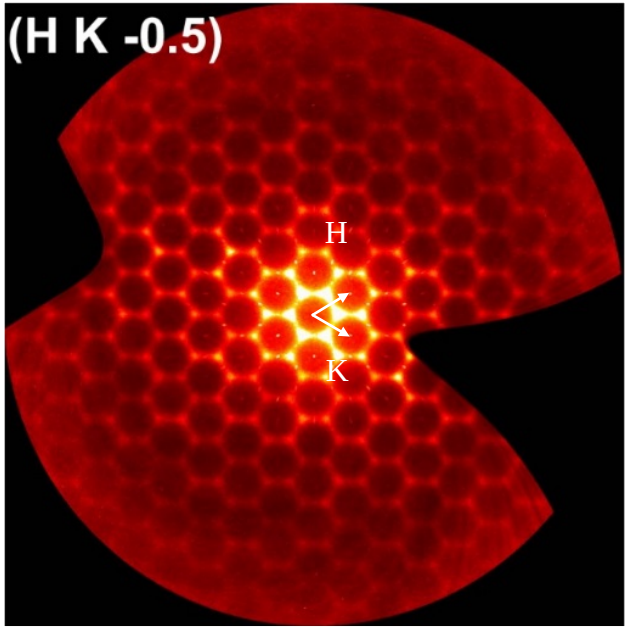
$NaLnF_4$, diffuse scattering I

- Regular array of Bragg peaks
- in addition: sharp, horizontal lines at half-integer L

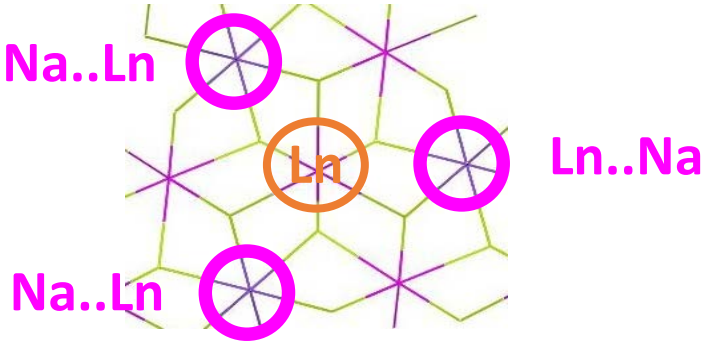


- translational period along c doubled
- Columns with Ln…Na…Ln…Na
- strictly alternating along c

$NaLnF_4$, diffuse scattering II



- honeycomb pattern of diffuse scattering
- Ordered surrounded by disordered columns



Ln	|	|	|
|	Ln	Ln	Na
Ln	|	|	|
|	Na	Na	Ln
Ln	|	|	|
|	Ln	Ln	Na
Ln	|	|	|

- Coulomb frustration

Quantitative approach I: 3D-ΔPDF

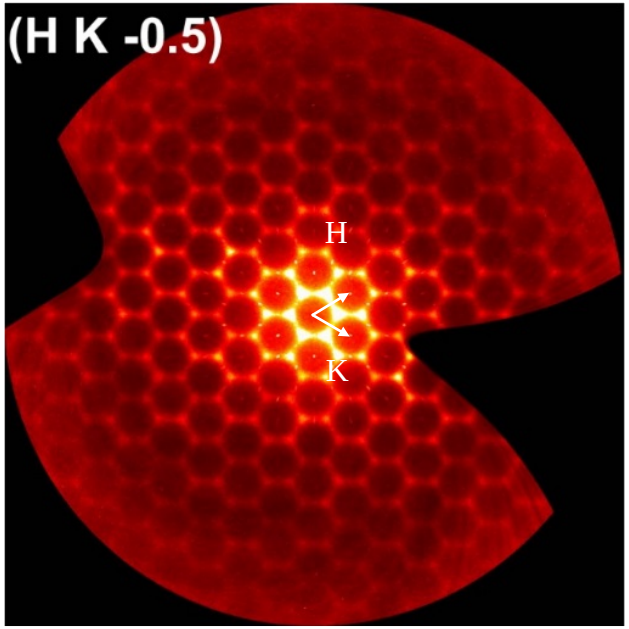
- The 3D Pair Distribution Function (3D-ΔPDF) is the FT of the total scattered intensity:

$$\text{3D-PDF}(u\ v\ w) = \int (I_{Bragg} + I_{diff}) \exp[2\pi i(hu+kv+lw)]\ dh\ dk\ dl$$
$$= P(u\ v\ w) + \text{3D-}\Delta\text{PDF}$$

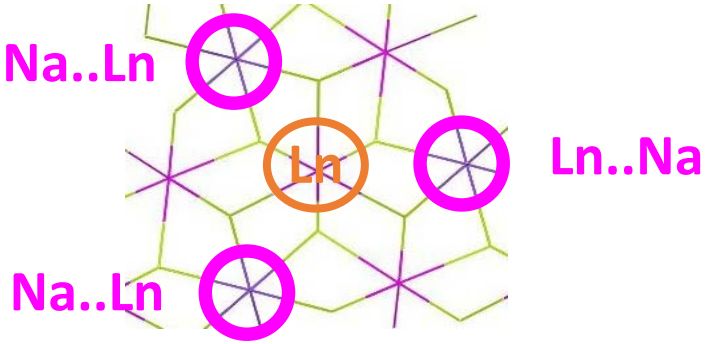
- The 3D-ΔPDF(u v w)is the difference between the non-periodic 3D-PDF of the disordered, non-periodic crystal and the Patterson function P(u v w) of the periodic average structure

- 3D-ΔPDF(u v w) = 3D-PDF(u v w) – P(u v w)

$NaLnF_4$, diffuse scattering II

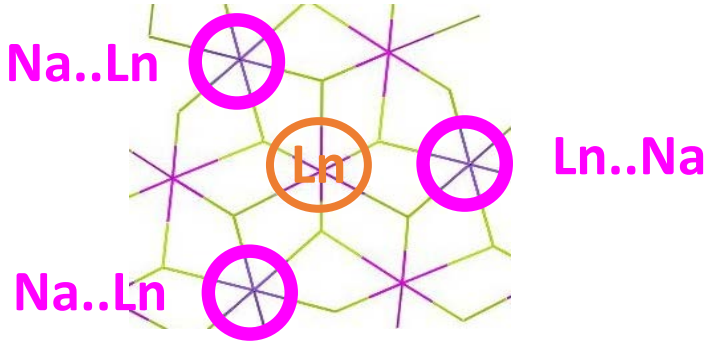


- honeycomb pattern of diffuse scattering
- Ordered surrounded by disordered columns



Ln	|	|	|
|	Ln	Ln	Na
Ln	|	|	|
|	Na	Na	Ln
Ln	|	|	|
|	Ln	Ln	Na
Ln	|	|	|

- Coulomb frustration



Example: Na/La translation vector (a, 0, 0)

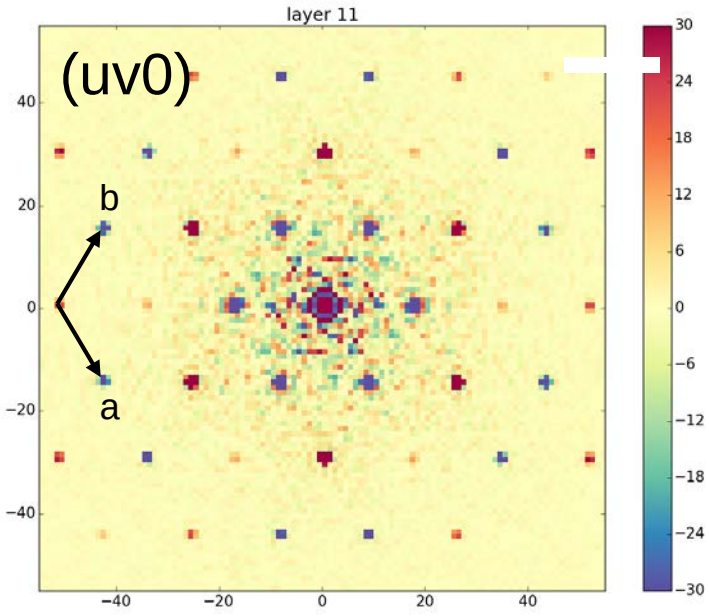
Vectors between the mixed Na/La columns one **a**-translation apart

$Z_{La} = 57$, $Z_{Na} = 11$, $c_{La} = c_{Na} = 0.5$ $p_{Na\ldots La(100)} = 0.6$

Na…Na(100)	$[c_{Na}\cdot p_{Na\ldots Na(100)} - c_{Na}\cdot c_{Na}]\cdot Z_{Na}\cdot Z_{Na}$ =	-6.1
Na…La(100)	$[c_{Na}\cdot p_{Na\ldots La(100)} - c_{Na}\cdot c_{La}]\cdot Z_{Na}\cdot Z_{La}$ =	31.4
La….Na(100)	$[c_{La}\cdot p_{La\ldots Na(100)} - c_{La}\cdot c_{Na}]\cdot Z_{La}\cdot Z_{Na}$ =	31.4
La….La(100)	$[c_{La}\cdot p_{La\ldots La(100)} - c_{La}\cdot c_{La}]\cdot Z_{La}\cdot Z_{la}$ =	-162.5
	SUM =	-105.8

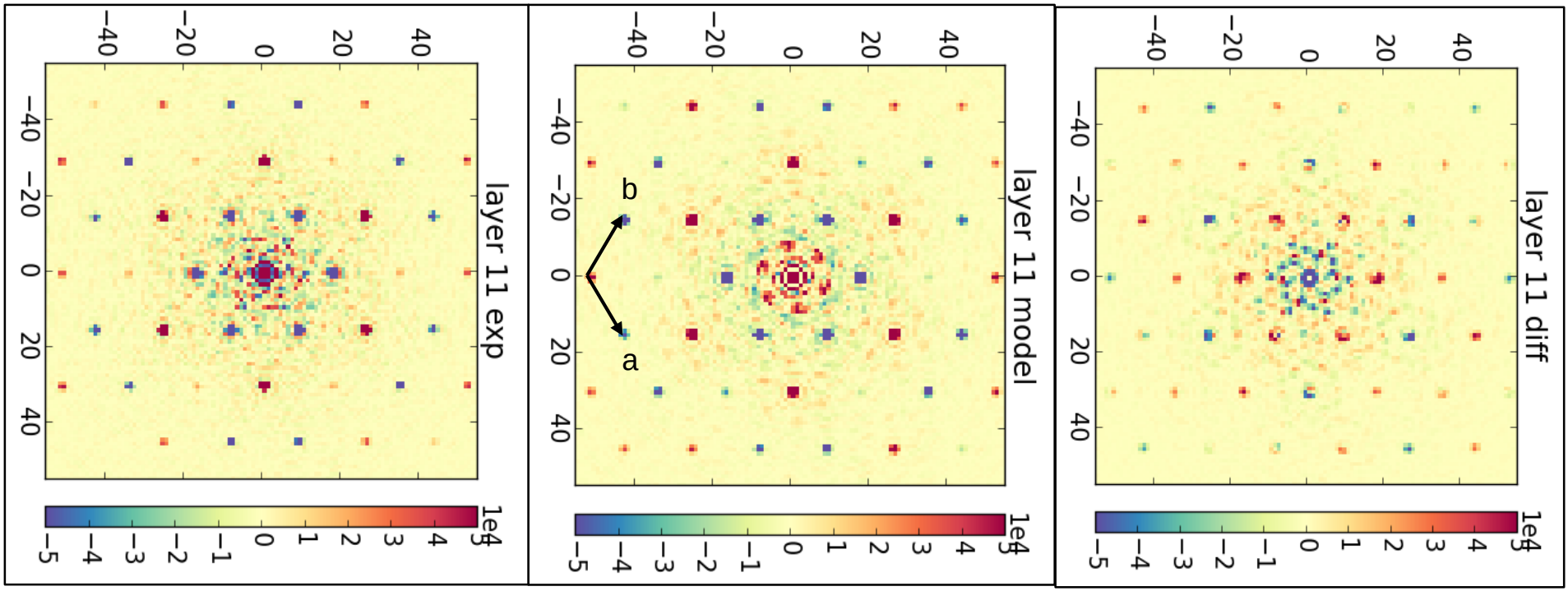
Conclusion: If La prefers a Na neighbor at a distance of (a 0 0), the peak at 3D-ΔPDF (1 0 0) should be negative.

Example of a 3D-ΔPDF for NaLnF4



- Origin in center, a and b indicated on the left
- Note the positive (red) and negative (blue) peaks
- 3D-ΔPDF can be parametrized in terms of interatomic vectors
- $r_{mn}(uvw)$ between
- atoms m and n which are uvw unit cells apart and their probability of occurence which is the difference between those in the disordered and average structures: $p_{mn}(uvw) - c_m c_n$.

Comparison experiment – model - difference



Quantitative approach II: Monte Carlo crystal simulation

- Model parameters: (Ising parameters), geometrical parameters (atomic or molecular displacements), Atomic Displacement Parameters

- Probabilistic crystal builder

- Simultaneous construction of up to MANY individual CRYSTALS from MANY different parameters sets (= genes), each with 10^3 – 10^6 unit cells, calculation of intensities

- Optimization of parameters by differential evolution. Fitness selection against experimental intensities (R)

Quantitative approach II: MC simulations

- Monte Carlo crystal builder

- Model parameters: interaction between Na…La ‘up‘ and ‘down‘ columns, displacements of atoms from average positions

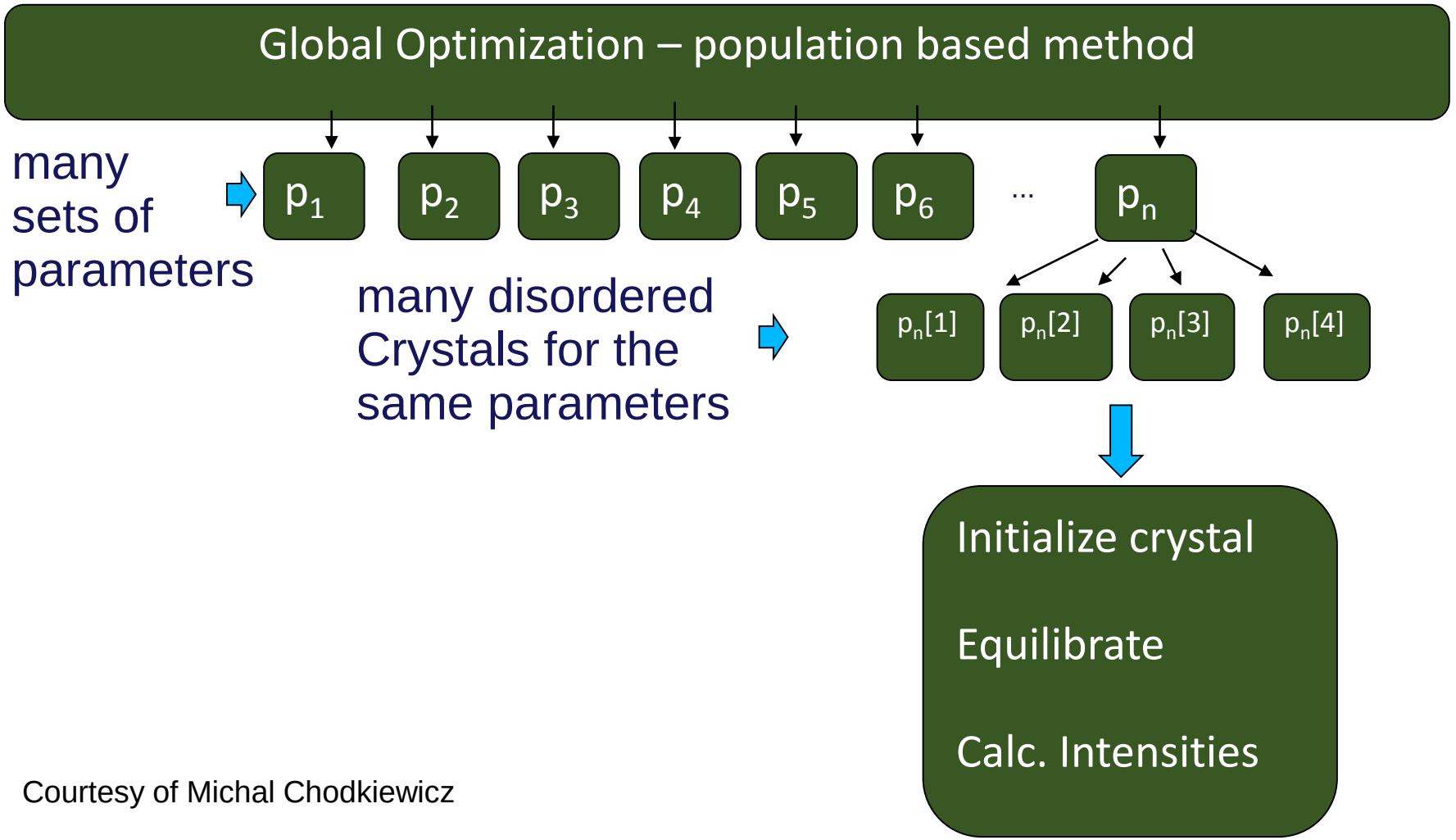
- Simultaneous construction – unit cell by unit cell – of *N* random crystals (phenotypes) from *N* different parameter sets (= genes), each with thousands of Na…La-columns

- ‘Energy minimization’

- Calculation of intensities, comparison with experiment

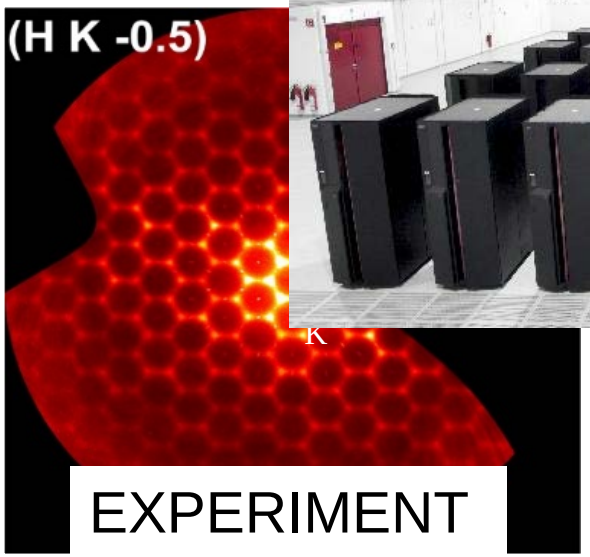
- Optimization of parameters by differential evolution. Fitness selection against experimental intensities (R)

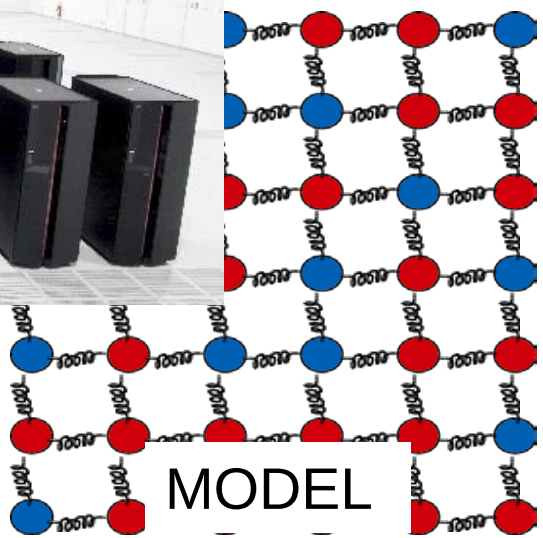
Parallelization of parameter optimization



Courtesy of Michal Chodkiewicz

ZODS
Zürich – Oak Ridge Disorder Simulations

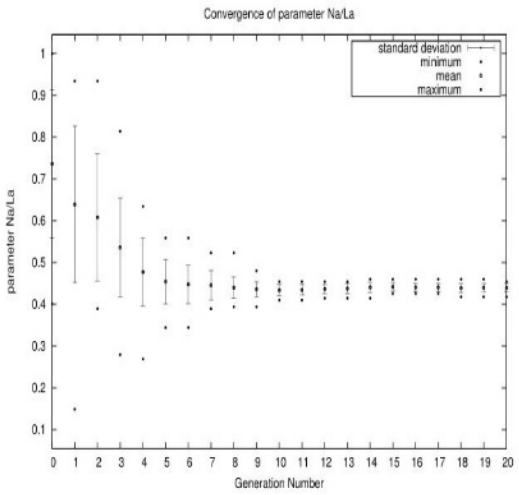


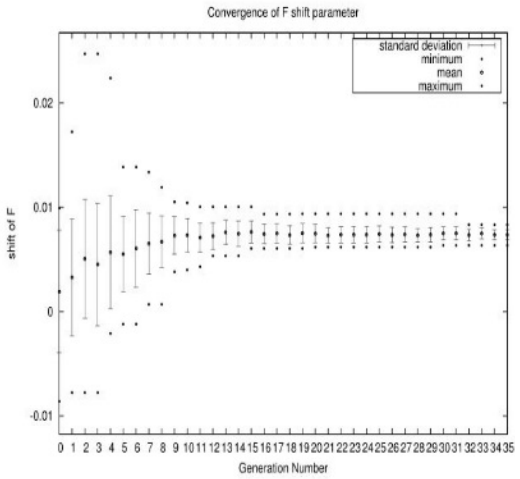


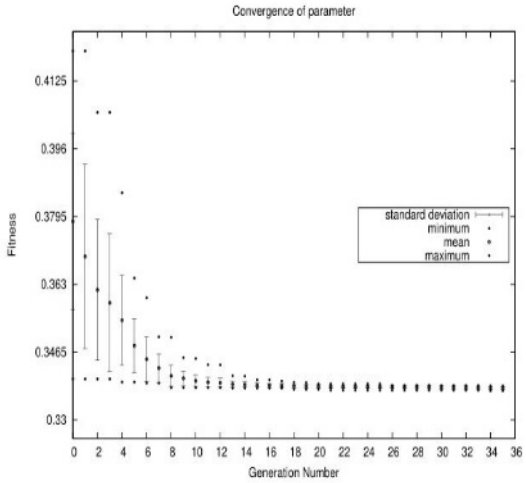
Courtesy of Michal Chodkiewicz

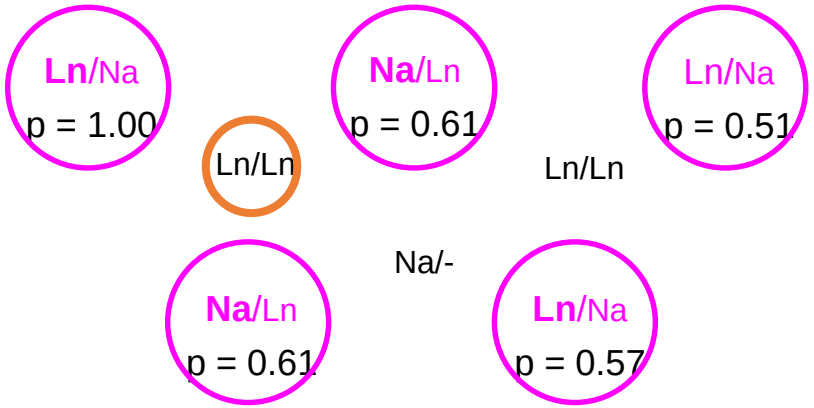
Some Results

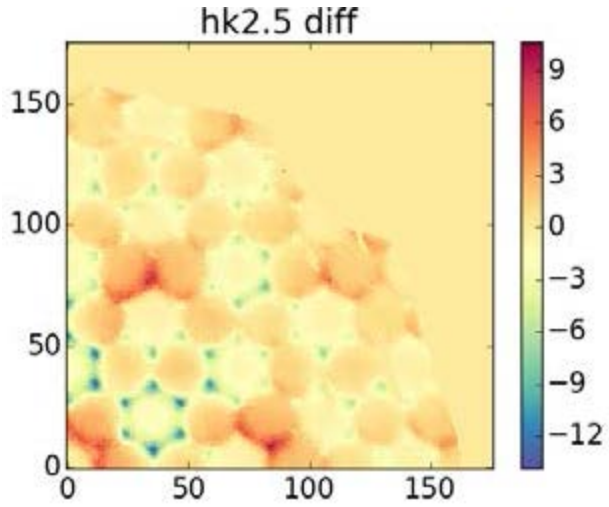
Progress of refinement, Correlations between columns, I_{obs}-I_{model},



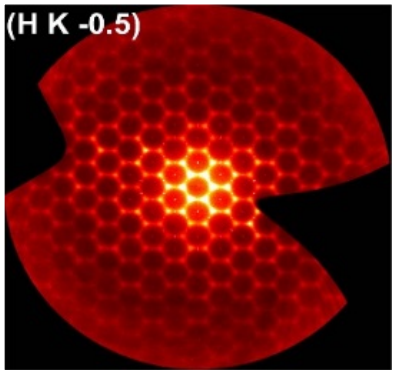








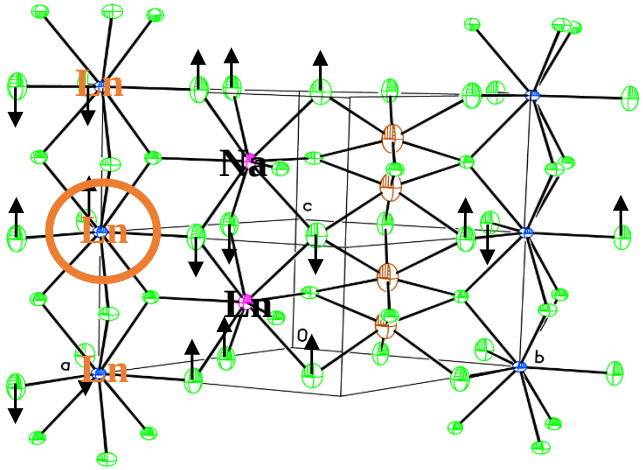
$NaLnF_4$, diffuse scattering III



- F^- will not want to be midway between Ln^{3+} and Na^+, shifted towards Ln^{3+} !

- disordered Ln^{3+} : local C_{3h} symmetry

- Ln^{3+} in ordered column: C_1 symmetry!

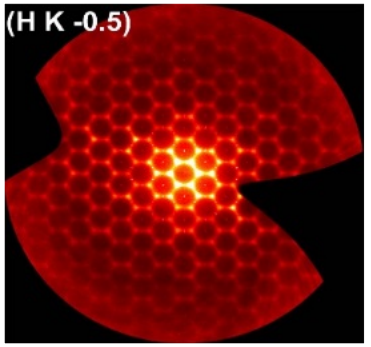


- Explains spectroscopic observation, provides a basis for modeling the high efficiency of upconversion

A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, Th. Weber, H. U. Güdel, H.-B. Bürgi, Angew. Chemie Int. Ed. **45** (2006) 2802

A summary

1) Do the best experiment possible, both on Bragg AND diffuse scattering
   - high intensity primary beam (Synchrotrons)
   - low(no)-noise detector (Pilatus)

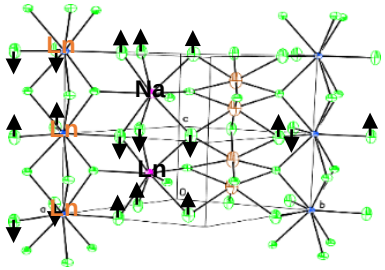


2) Find best average structure and scrutinize for features that contradict the principles of chemistry and physics

---

3) Qualitative interpretation of diffuse scattering with simple (analytical) models ($NaLnF_4$)

4) Quantitative model of disorder and parameter optimization by numerical methods



5) Evaluate local structure