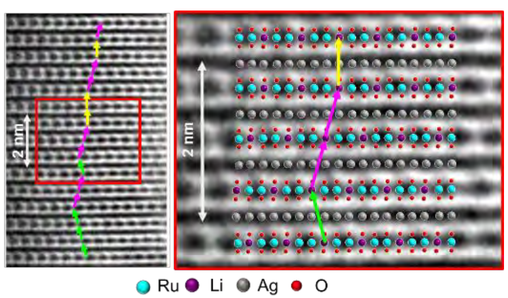
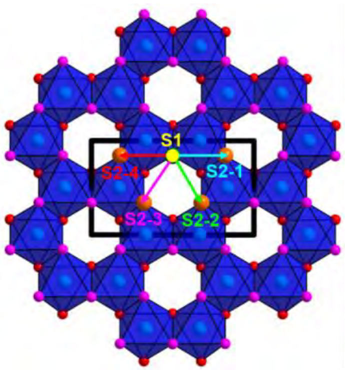
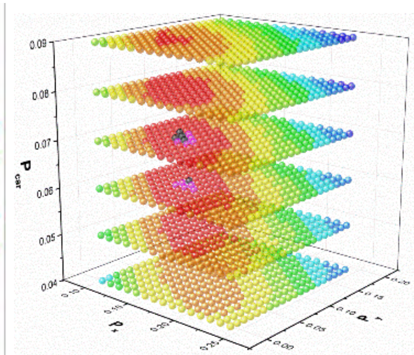
Max-Planck-Institute
for Solid State Research

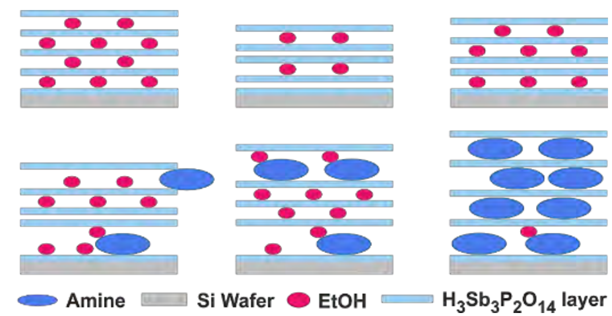
Scientific Facility
X-ray Diffraction

Refinement of disordered inorganics









S. Bette, B. Hinrichsen, M. Däntl, M.A. Plass, B.V. Lotsch, T. Takayama, H. Takagi, R.E. Dinnebier

Naneed Workshop, December 6th – December 8th 2022 • Mainz (Germany)

***ideal* single crystal:**

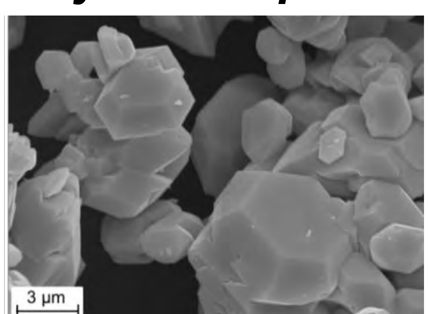
Definition of crystal: a solid composed of atoms, ions, or molecules arranged in a pattern that is periodic in three dimensions.

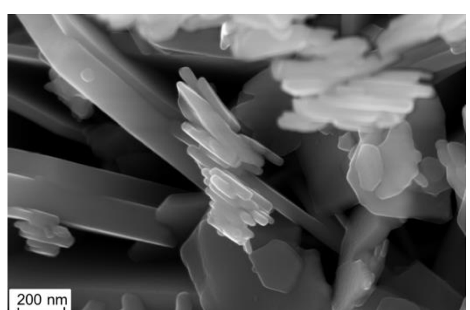
***real* single crystals:**

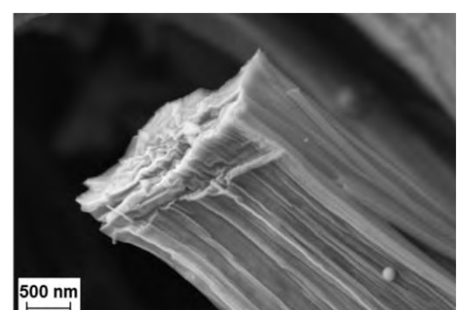
mosaic spread

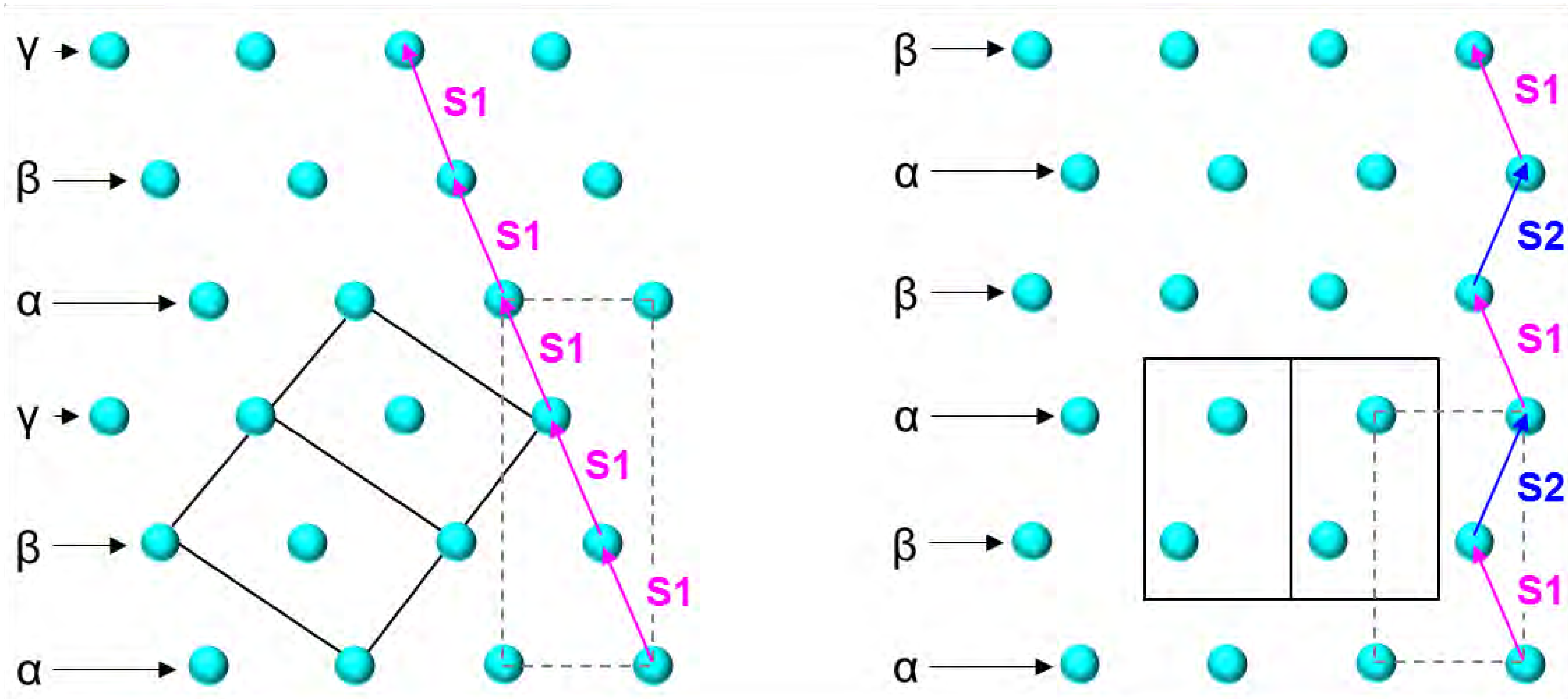
twinning

***crystalline powder*:**









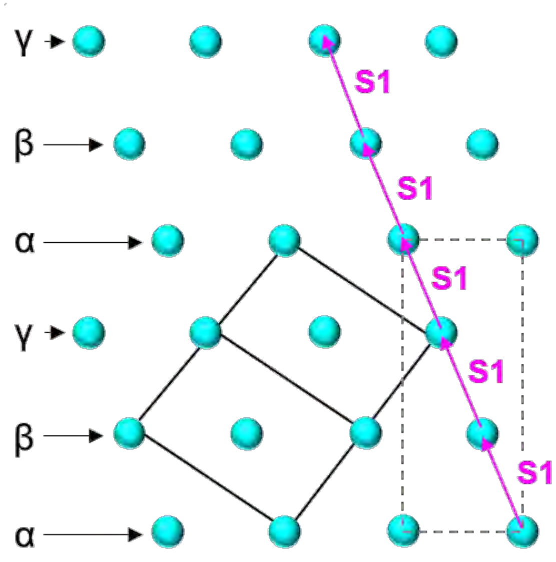
ccp-stacking of metal ions
e.g. copper

hcp-stacking of metal ions
e.g. magnesium

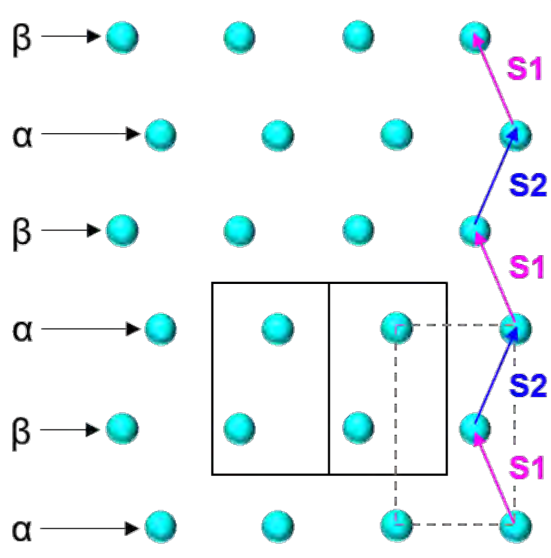
S. Bette, R.E. Dinnebier *Chapter 2: Understanding stacking disorder in layered functional materials using powder diffraction*, Crystallography in Material Science, DeGruyter (Berlin), 1st edition (2021), 55-92.

How Stacking Faults effect Powder Diffraction Patterns

Stacking Orders in closed packed Structures



ccp-stacking of metal ions
e.g. copper



hcp-stacking of metal ions
e.g. magnesium

unit cell transformation:

$a, b, c, \alpha, \beta, \gamma$

↓

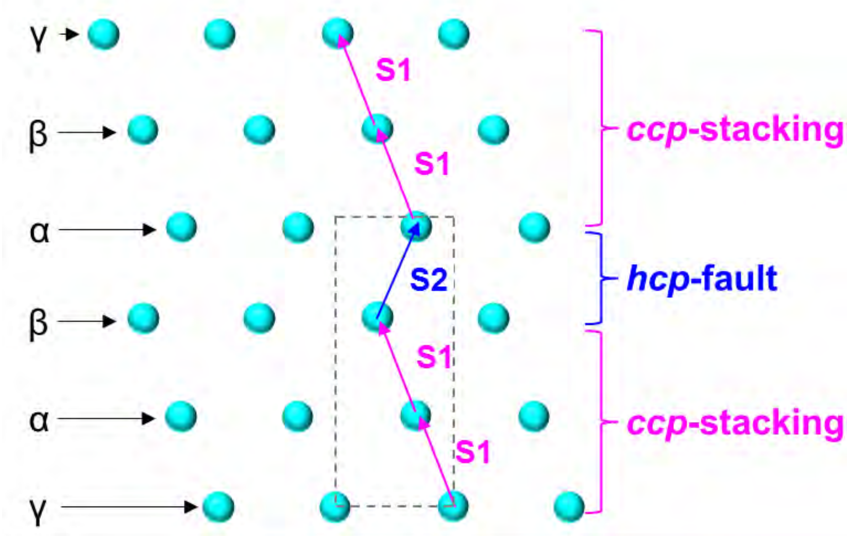
$a', b', c',$
$\alpha' = 90°, \beta' = 90°,$
$\gamma' = 90°$ or $120°$

$$\mathbf{Si} = \begin{pmatrix} s_{xi} \\ s_{yi} \\ s_{zi} \end{pmatrix}$$

ccp: $$\mathbf{S1} = \begin{pmatrix} 1/3 \\ -1/3 \\ 1/3 \end{pmatrix}$$

hcp: $$\mathbf{S1} = \begin{pmatrix} 1/3 \\ -1/3 \\ 1/2 \end{pmatrix} \quad \mathbf{S2} = \begin{pmatrix} -1/3 \\ 1/3 \\ 1/2 \end{pmatrix}$$

Example: *hcp*-faults in *ccp* Cu



Frequency of faults is described by a *transition probability* matrix:

transition from↓/ to→	S1	S2
S1	P_{11}	P_{12}
S2	P_{21}	P_{22}

global constraint: $$\sum_{j=1}^{j=n} P_{ij}=1$$

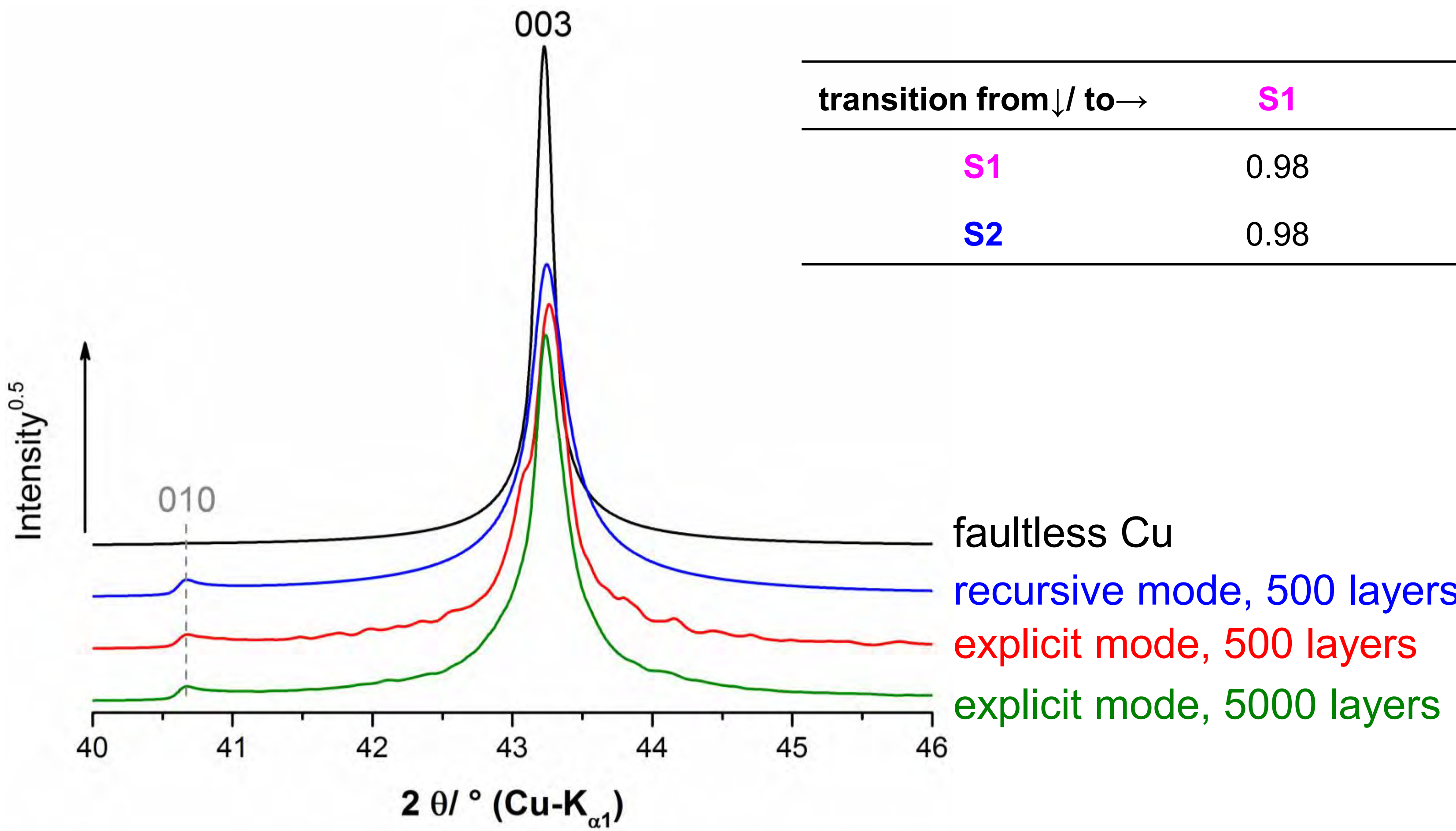
Fundamental Modes of *DIFFaX*

explicit: a XRPD pattern from *one* pre-defined or random sequence of layers and stacking vectors is simulated

recursive: a averaged diffraction pattern is calculated from *all* possible stacking sequences with *transition probability matrix* used as a weighting scheme.

M. M. J. Treacy, J. M. Newsam, M. W. Deem *Proc. R. Soc. London Ser. A* **1991**, *433*, 499-520.

Example: 2 % *hcp*-faults in *ccp* Cu

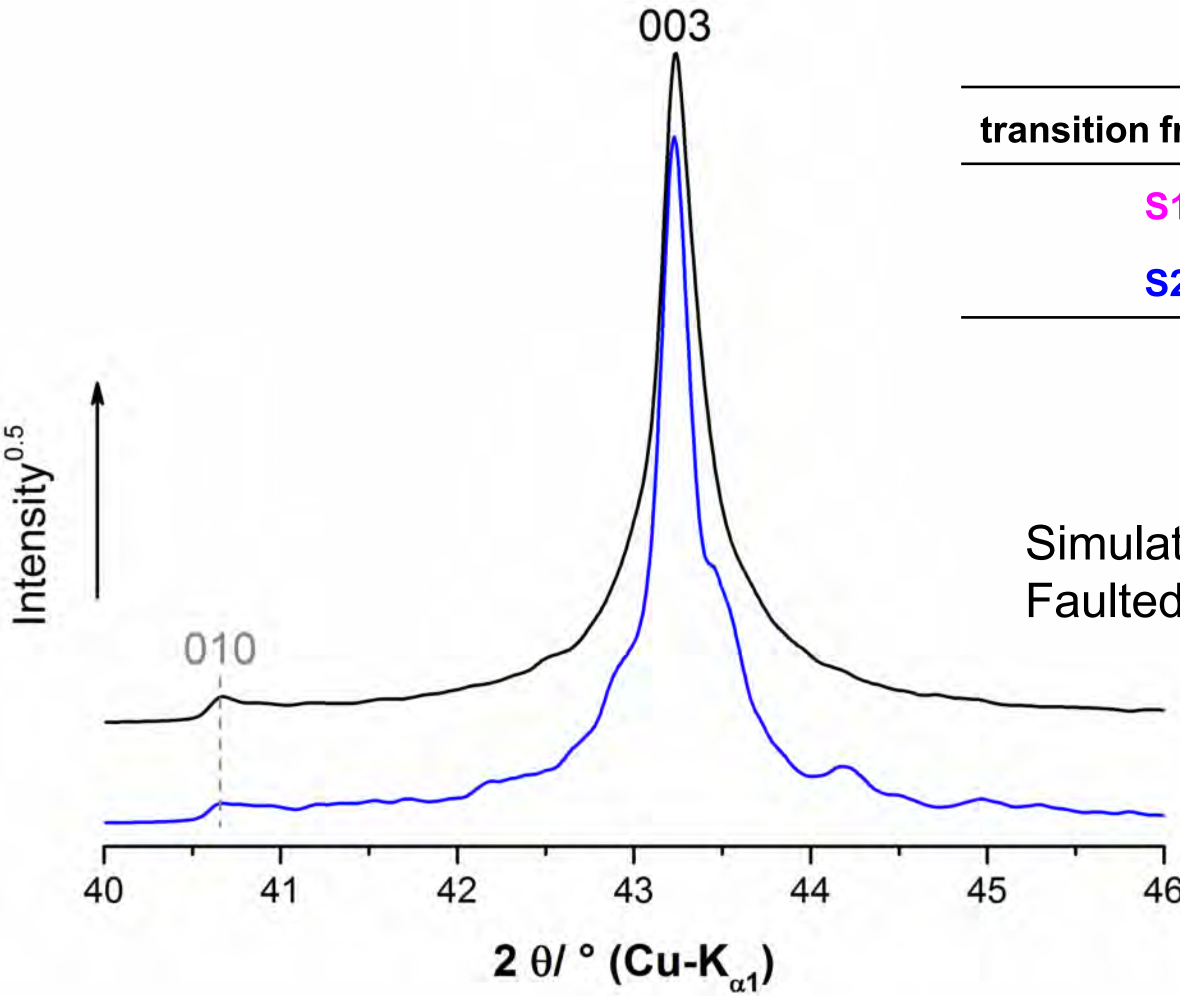


transition from↓/ to→	S1	S2
S1	0.98	0.02
S2	0.98	0.02

- for a large number of layers, the explicit mode creates similar results as the recursive mode!

M. M. J. Treacy, J. M. Newsam, M. W. Deem *Proc. R. Soc. London Ser. A* **1991**, *433*, 499-520.

Example: 2 % *hcp*-faults in *ccp* Cu



transition from↓/ to→	S1	S2
S1	0.98	0.02
S2	0.98	0.02

Simulation of a stacking
Faulted supercell with TOPAS:

- Identical to the explicit mode in *DIFFaX*

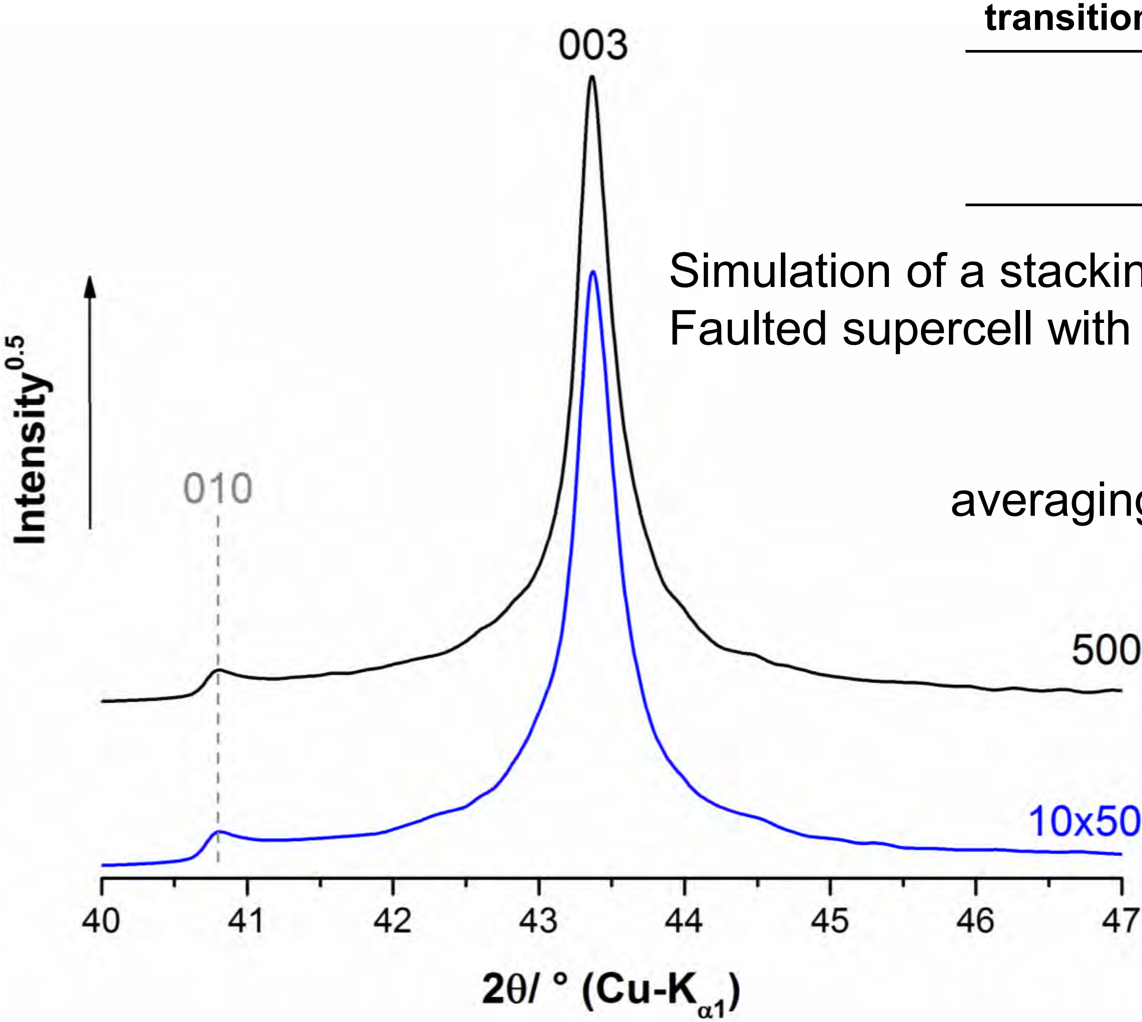
A. A. Coelho, J. S. O. Evans, J. W. Lewis, *J. Appl. Cryst.* **2016**, *49*, 1740-1749.

Example: 2 % *hcp*-faults in *ccp* Cu

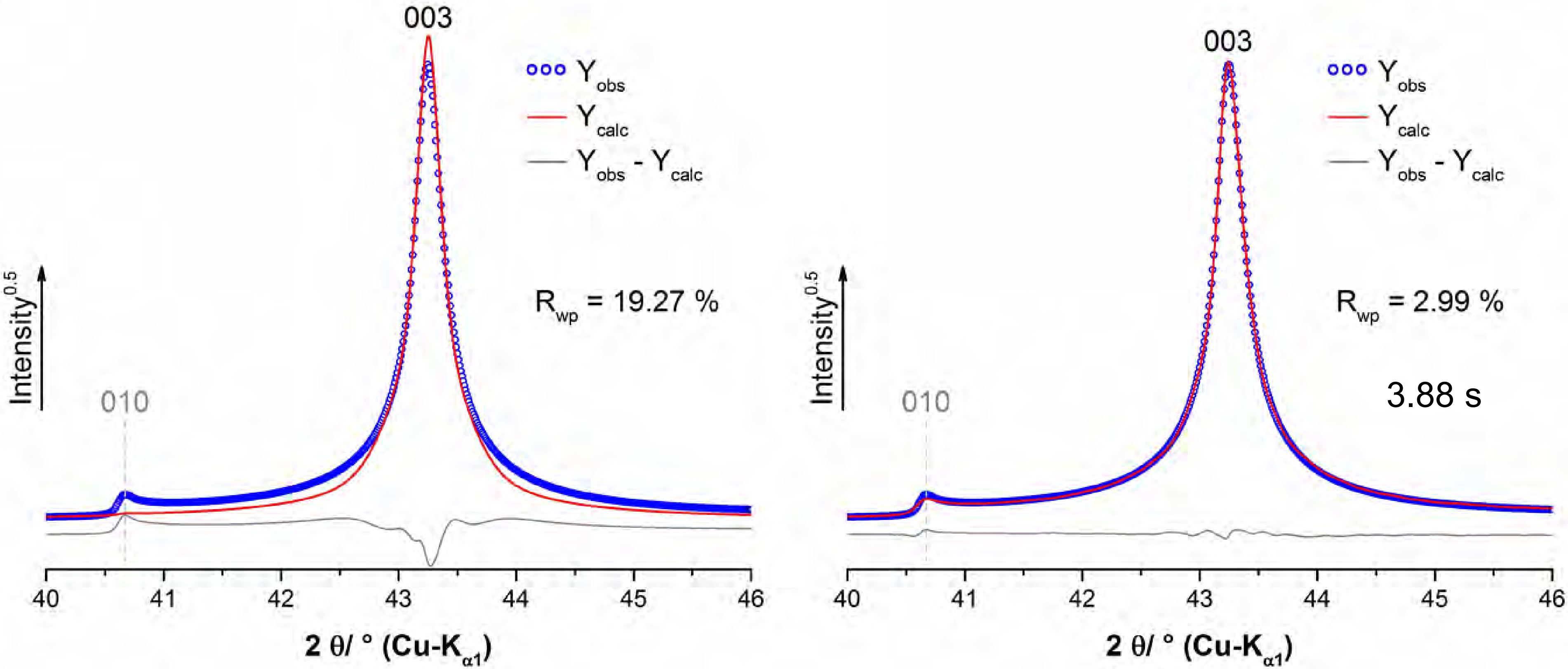
transition from↓/ to→	S1	S2
S1	0.98	0.02
S2	0.98	0.02

Simulation of a stacking
Faulted supercell with TOPAS:

averaging simulations: $I = \frac{\sum_{i=1}^{N} I_i}{N}$



A. A. Coelho, J. S. O. Evans, J. W. Lewis, *J. Appl. Cryst.* **2016**, *49*, 1740-1749.



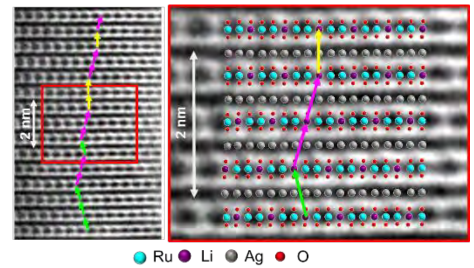
1 out of 100 Rietveld refinements using the faultless structure (left) and a 5000 layer supercell (2 % fault probability)

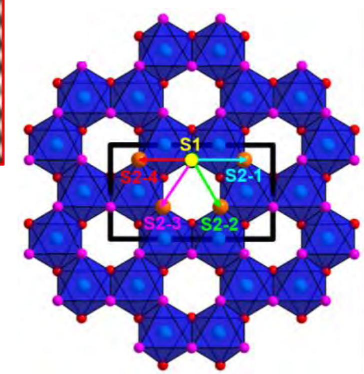
A. A. Coelho, J. S. O. Evans, J. W. Lewis, *J. Appl. Cryst.* **2016**, *49*, 1740-1749.
C. M. Ainsworth, J. W. Lewis, C.-H. Wang, A. A. Coelho, H. E. Johnston, H. E. A. Brand, J. S. O. Evans, *Chemistry of Materials* **2016**, *28*, 3184-3195.

Outline

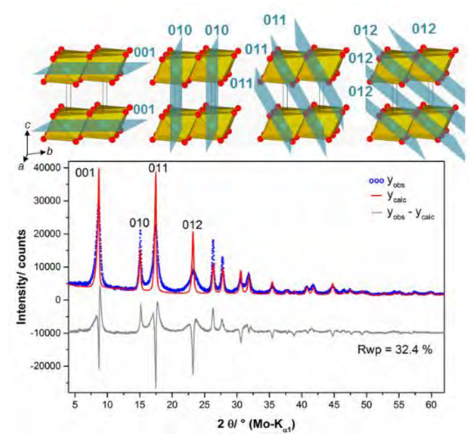
How can we utilize these software features for getting a better understanding of our materials?

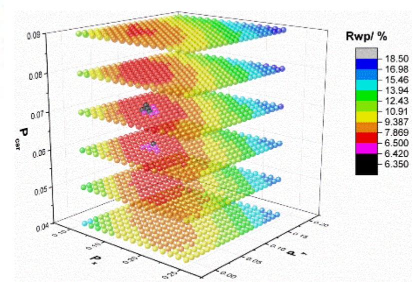
1. Honeycomb Compounds
   a) $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$
      – derivation of the layer constitution
   b) $Li_3HoBr_{6-x}I_x$ – intra- vs. interlayer disorder



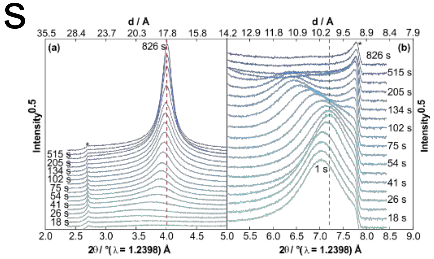


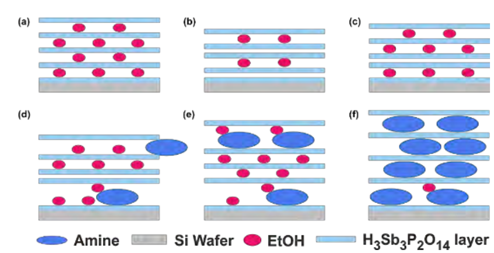
2. Brucite-type materials
   a) NCA precursors – optimization of multiple parameters





3. Excursus into thin films
   a) spin coated $H_3Sb_3P_3O_{14}$ thin films



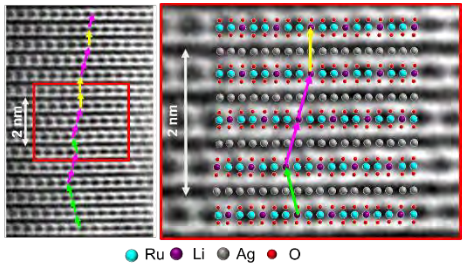


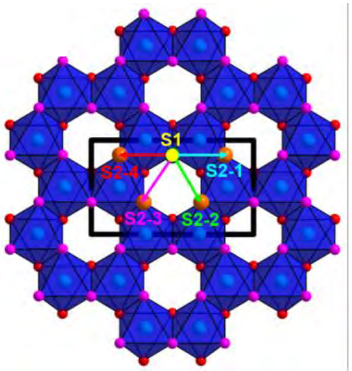
4. Conclusions and Outlook

Outline

How can we utilize these software features for getting a better understanding of our materials?

1. Honeycomb Compounds
   a) $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$ – derivation of the layer constitution
   b) $Li_3HoBr_{6-x}I_x$ – intra- vs. interlayer disorder





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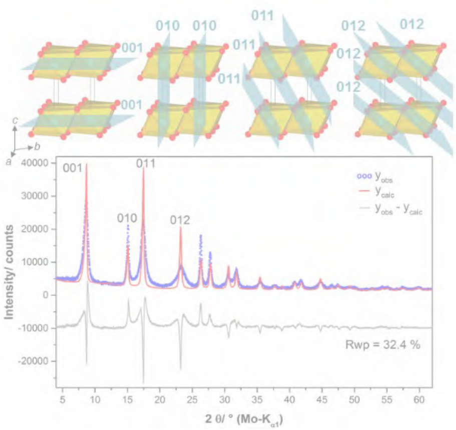

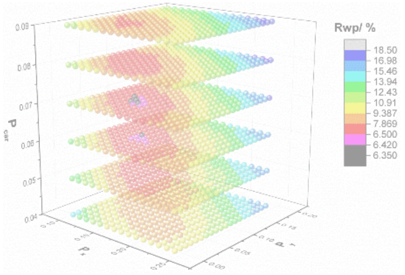

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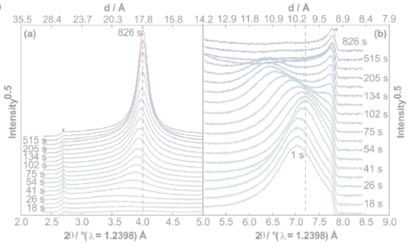
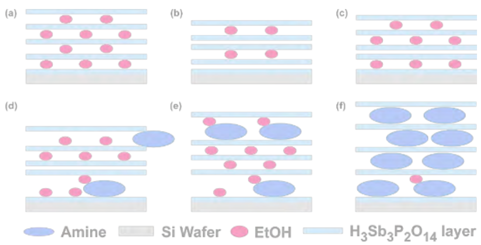


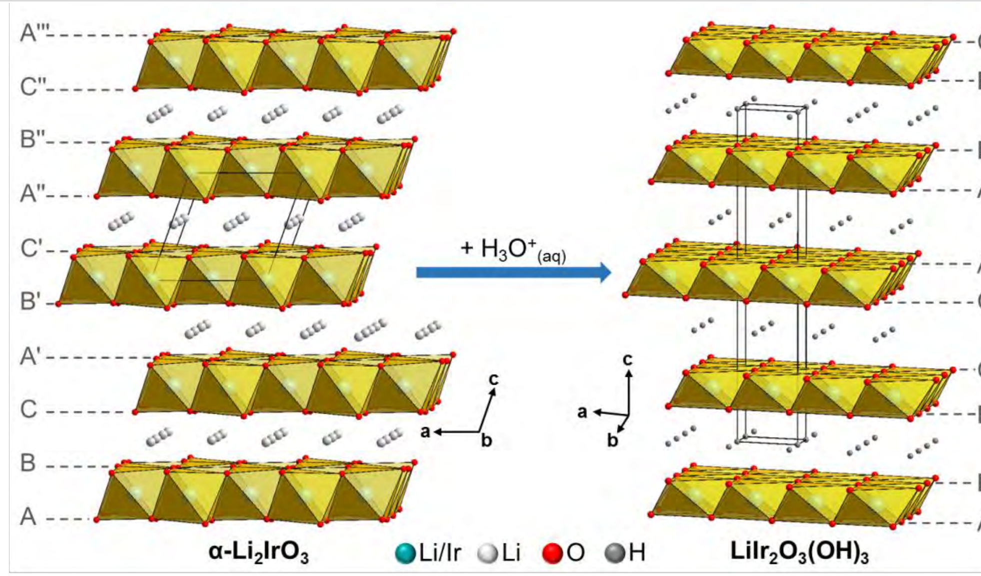


4. Conclusions and Outlook

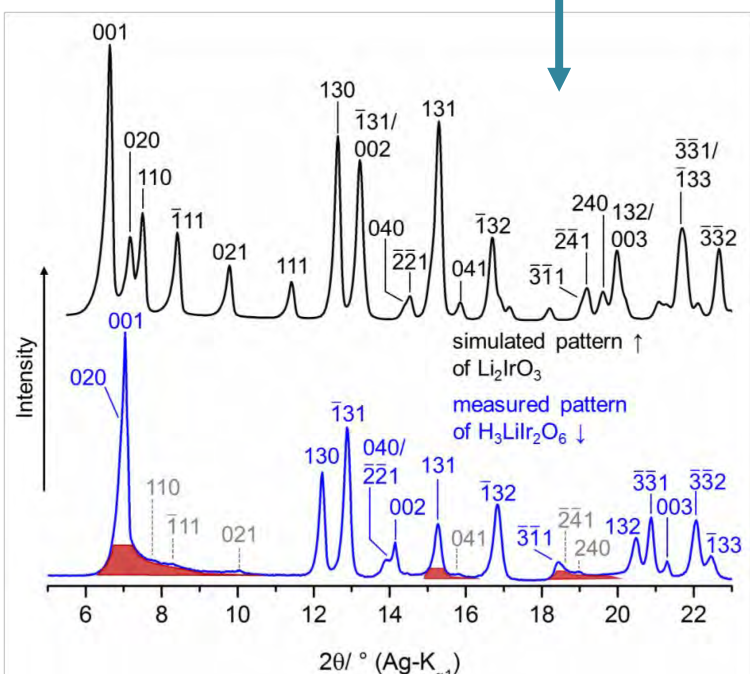
Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

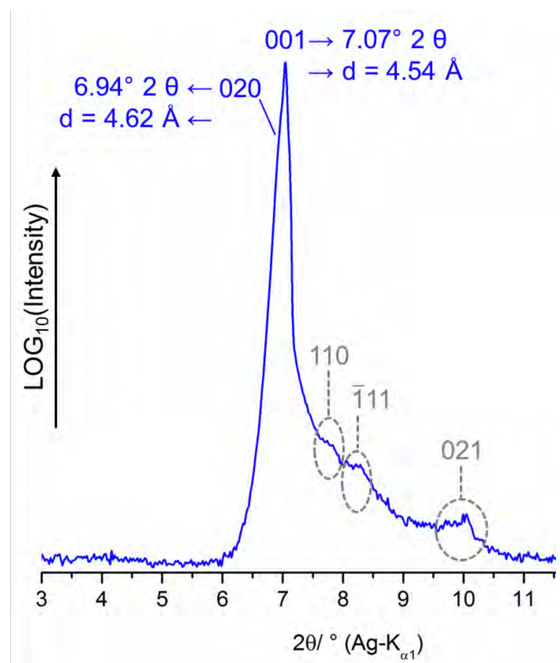
Derivation of the layer constitution

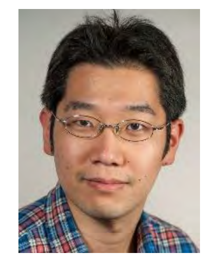
- synthesis by cation exchange via *soft chemistry* →



- heavy stacking faulting of the sheets indicated by anisotropic peak broadening in the XRPD pattern





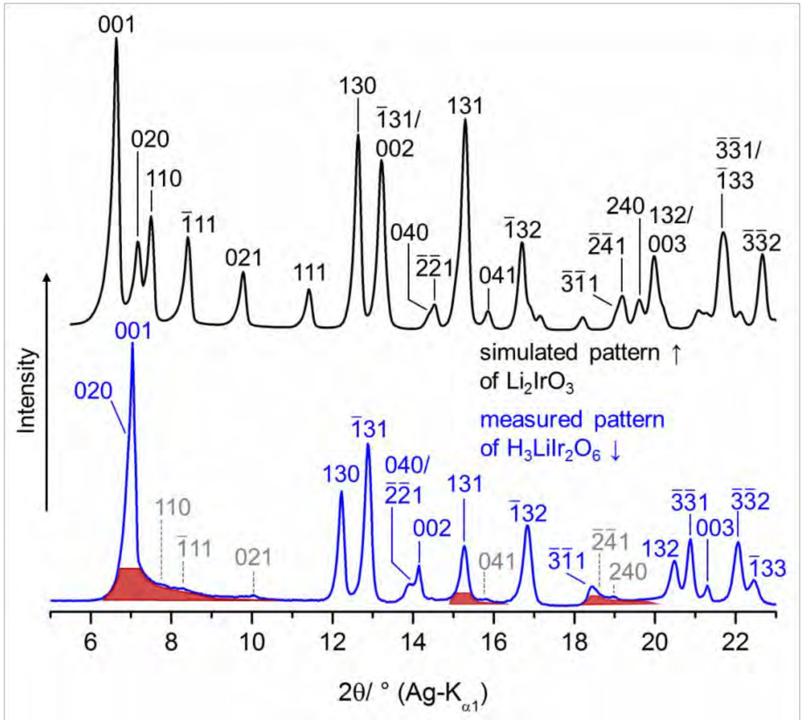


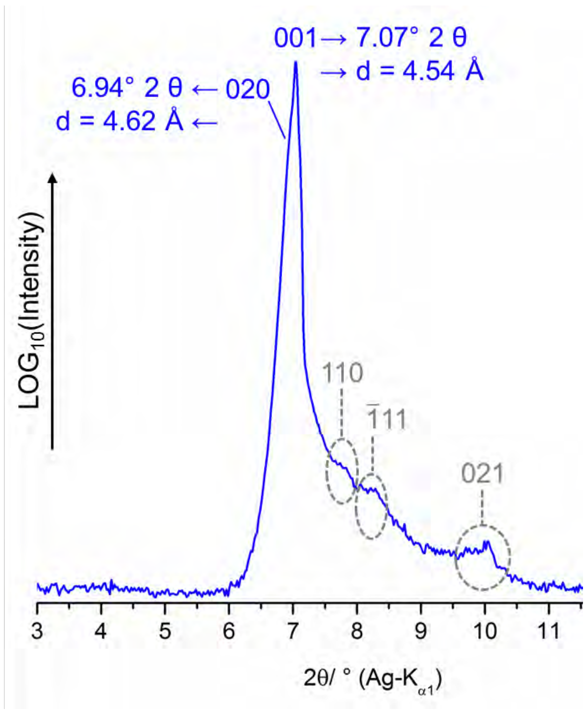
T. Takayama

H. Takagi

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Derivation of the layer constitution





anisotropic peak broadening

↓

approaches like Stephens model failed

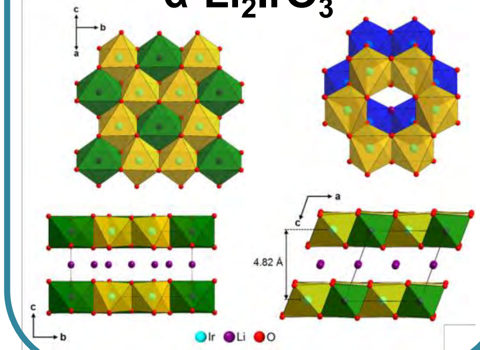
↓

~~*ab-inito* methods~~

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

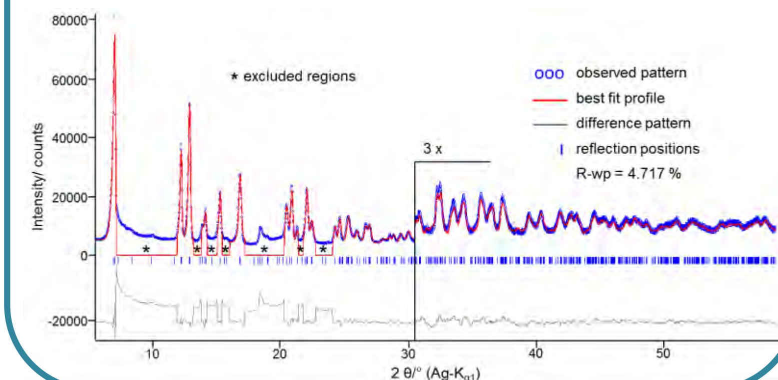
Derivation of the layer constitution

crystal structure of α-Li_2IrO_3



layer constitution
starting model

Rietveld refinement
exclusion of broadened regions



highly unstable refinement

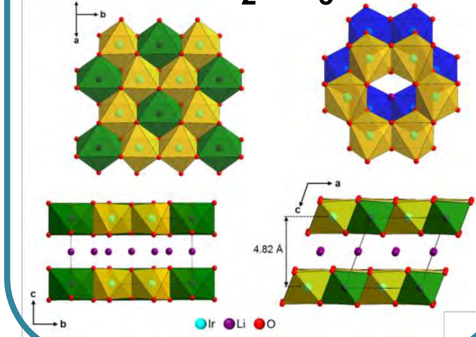
stacking order

indexing

	α-Li_2IrO_3	$H_3LiIr_2O_6$
Space Group	*C*2/*m*	*C*2/*m*
***a*/ Å**	5.1633(2)	5.3489(8)
***b*/ Å**	8.9294(3)	9.2431(14)
***c*/ Å**	5.1219(2)	4.8734(6)
***β*/ °**	109.759(3)	111.440(12)
***V*/ Å³**	222.24(1)	224.27(6)

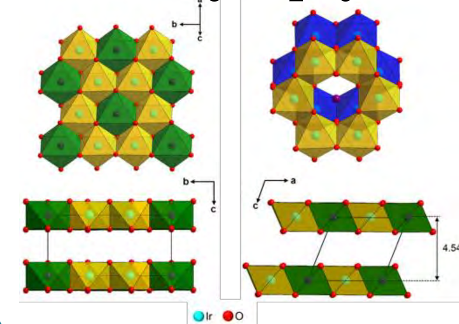
Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$
Derivation of the layer constitution

crystal structure of α-Li_2IrO_3

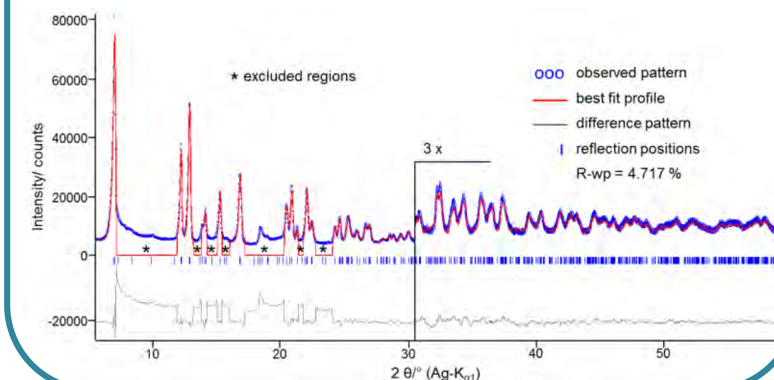


layer constitution
starting model

ideal crystal of $H_3LiIr_2O_6$



Rietveld refinement
exclusion of broadened regions



stacking order

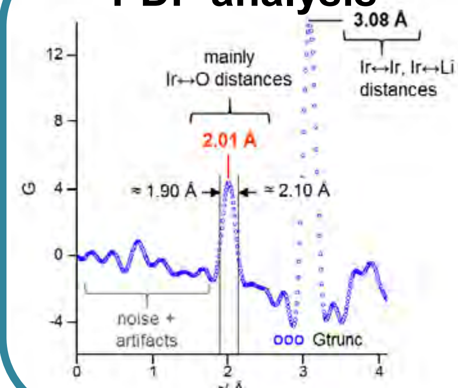
robust, reproducible results

bond lengths
restraints

indexing

	α-Li_2IrO_3	$H_3LiIr_2O_6$
Space Group	*C2/m*	*C2/m*
***a*/ Å**	5.1633(2)	5.3489(8)
***b*/ Å**	8.9294(3)	9.2431(14)
***c*/ Å**	5.1219(2)	4.8734(6)
***β*/ °**	109.759(3)	111.440(12)
***V*/ Å³**	222.24(1)	224.27(6)

PDF-analysis

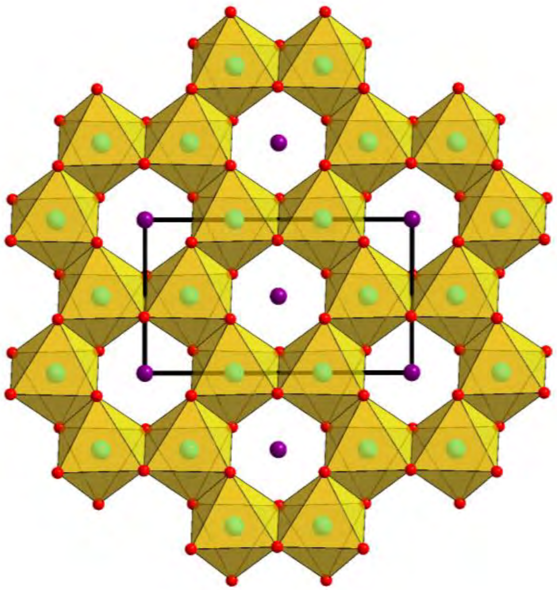


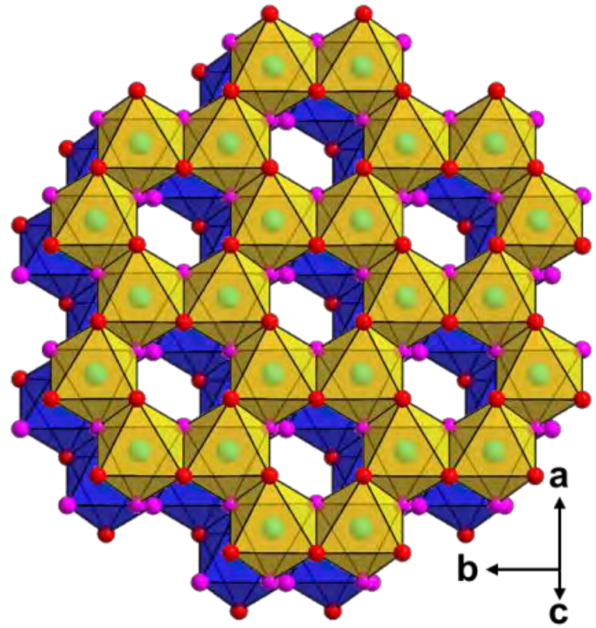
Microstructural refinements using TOPAS

Tackling Problems: Derivation of the layer constitution

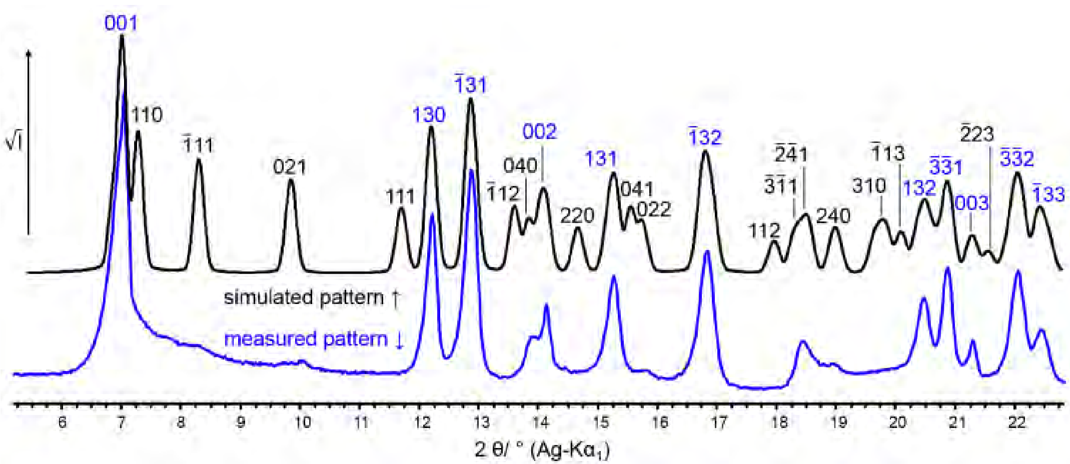
- layer constitution of the ideal structure:

  honeycomb layer

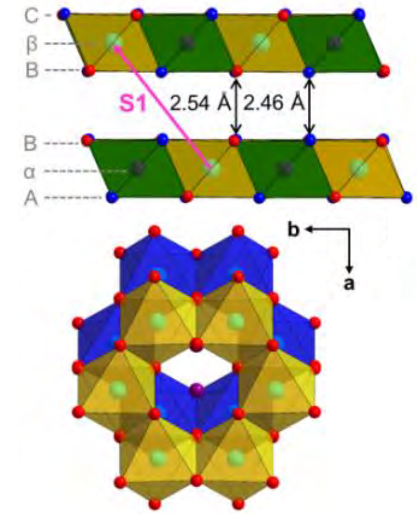




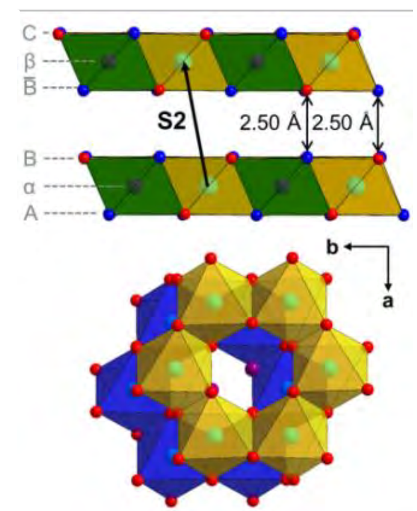
Ir Li O



- stacking order of the ideal structure:

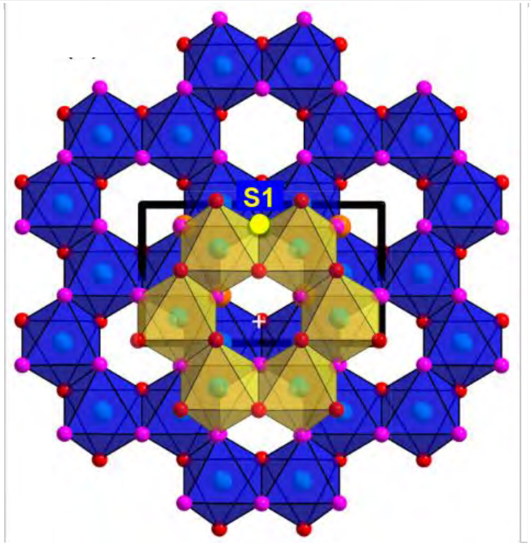


- alternative stacking order of the ideal structure:



Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Derivation of the of the stacking vectors

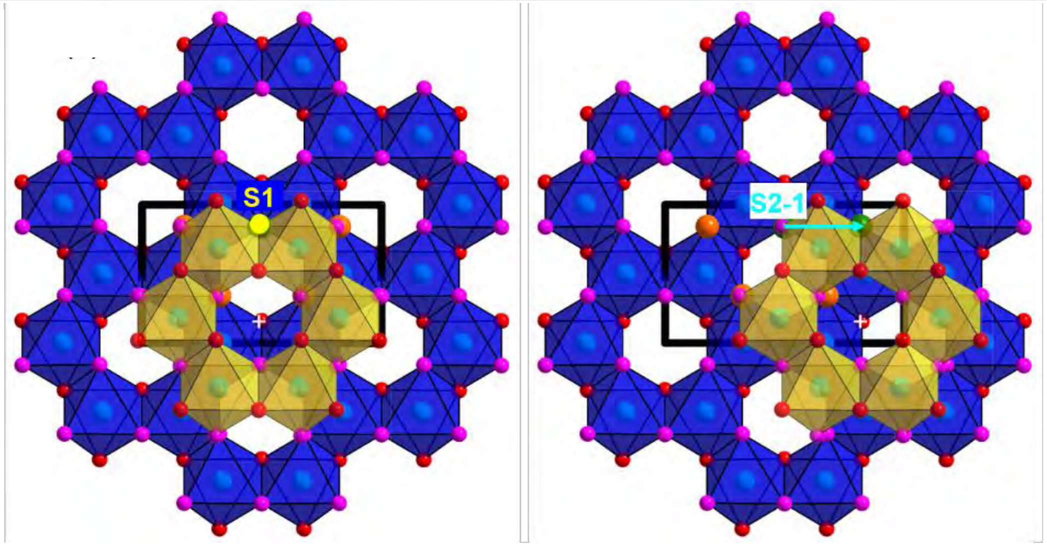


Ir/Ru ● bottom layer: bottom side O; top layer: top side O ● O1 sites indicating the stacking vectors

● bottom layer: top side O; top layer: bottom side O ● O2 sites indicating the alternative stacking vectors

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

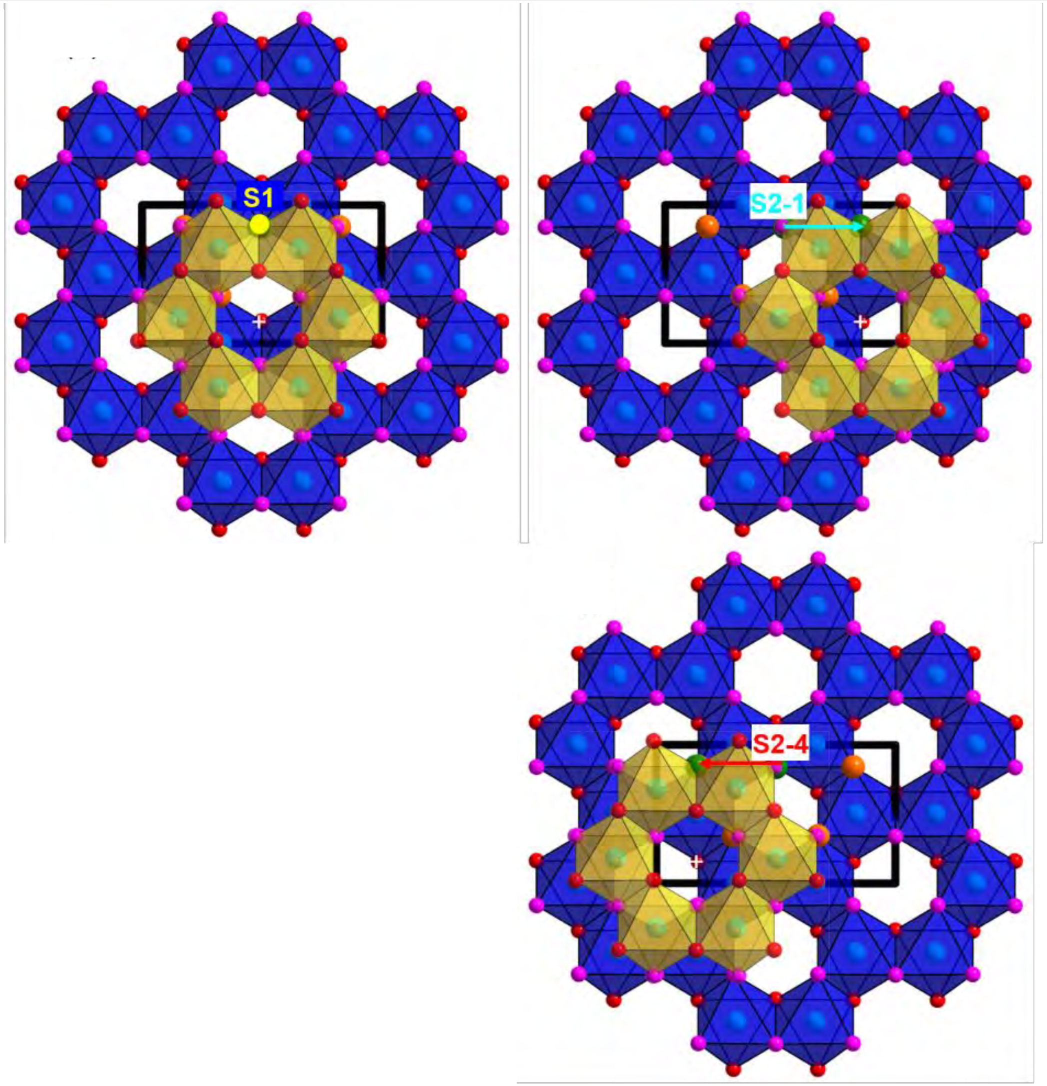
Derivation of the of the stacking vectors



Ir/Ru
bottom layer: bottom side O; top layer: top side O
bottom layer: top side O; top layer: bottom side O
O1 sites indicating the stacking vectors
O2 sites indicating the alternative stacking vectors

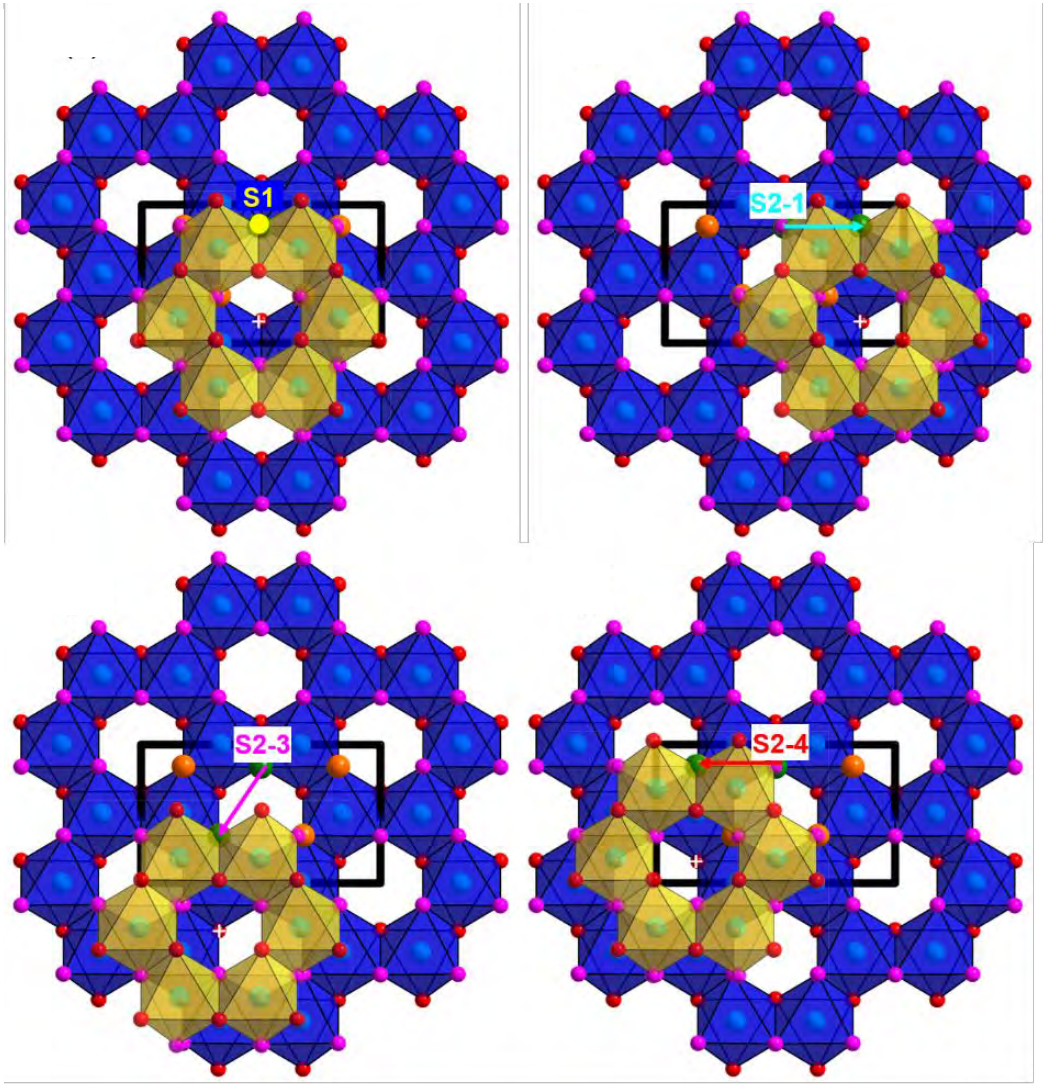
Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Derivation of the of the stacking vectors



Ir/Ru bottom layer: bottom side O; top layer: top side O O1 sites indicating the stacking vectors

bottom layer: top side O; top layer: bottom side O O2 sites indicating the alternative stacking vectors

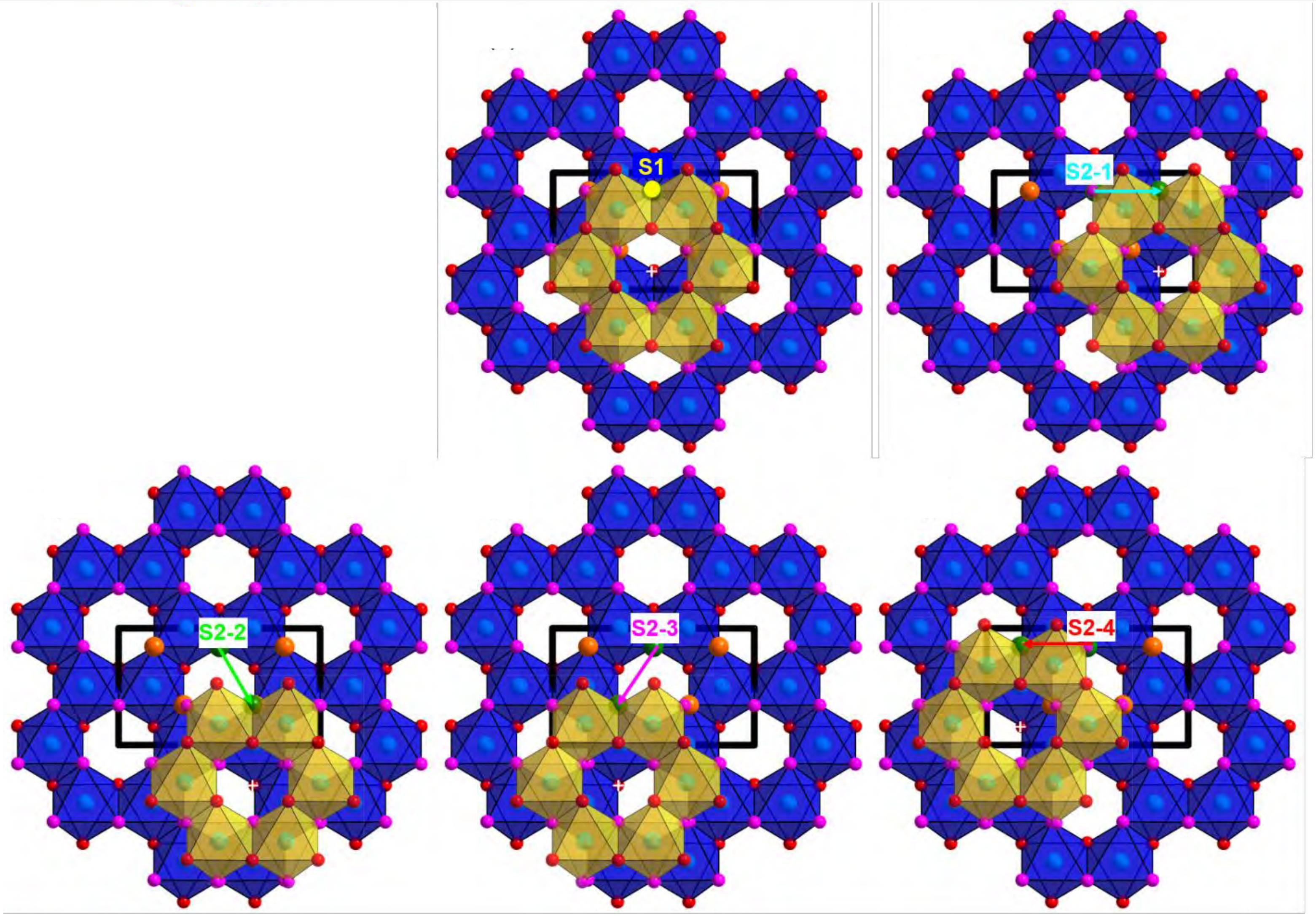


Ir/Ru · bottom layer: bottom side O; top layer: top side O · O1 sites indicating the stacking vectors

bottom layer: top side O; top layer: bottom side O · O2 sites indicating the alternative stacking vectors

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

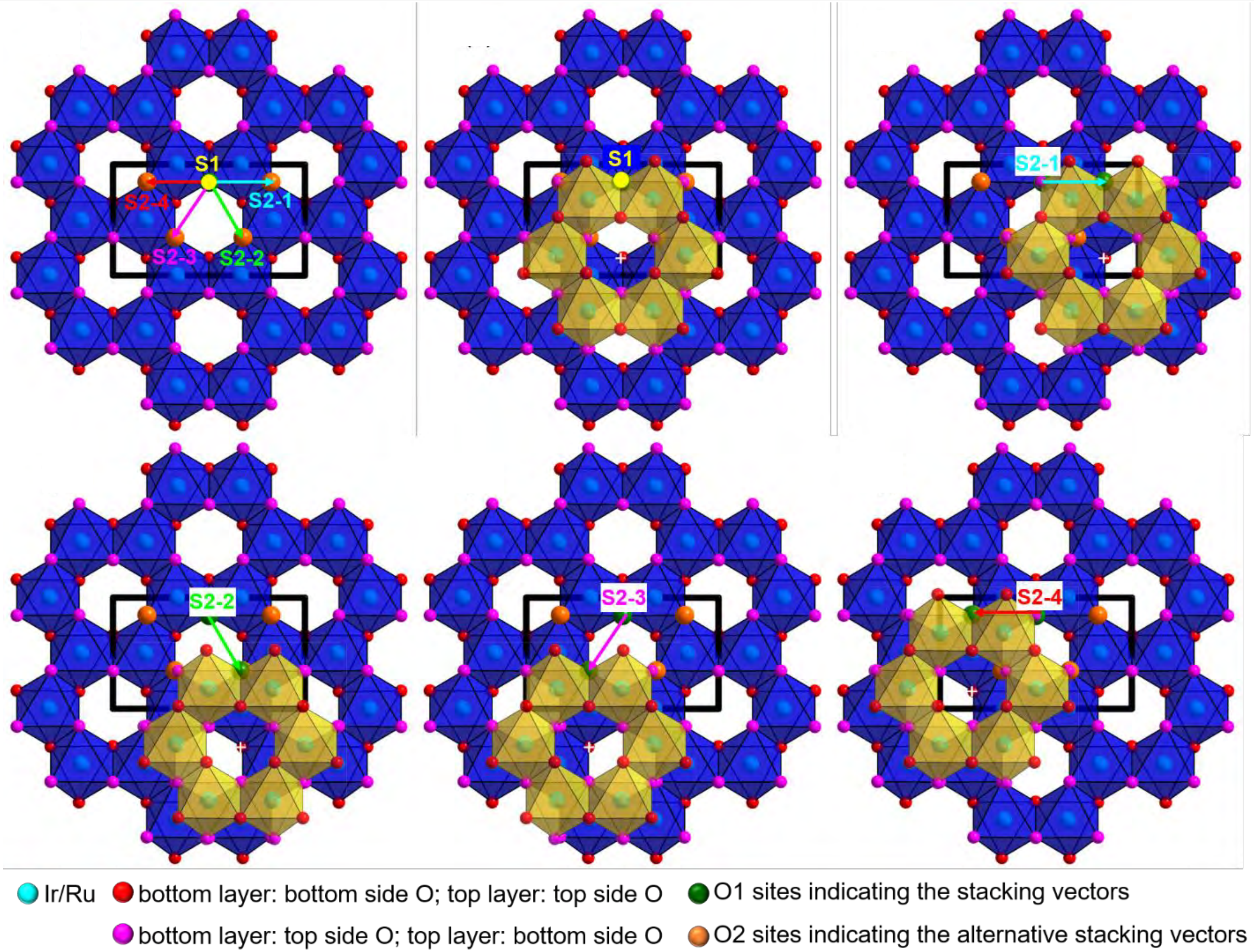
Derivation of the of the stacking vectors

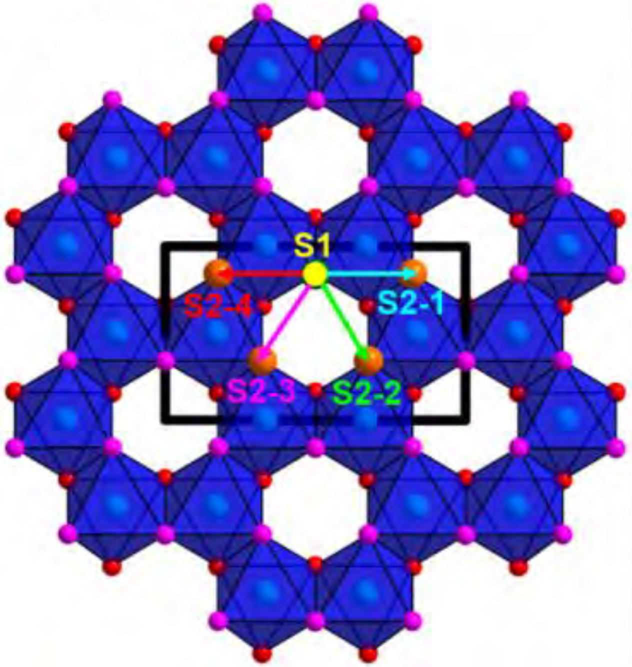


Ir/Ru bottom layer: bottom side O; top layer: top side O
O1 sites indicating the stacking vectors
bottom layer: top side O; top layer: bottom side O
O2 sites indicating the alternative stacking vectors

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Derivation of the of the stacking vectors



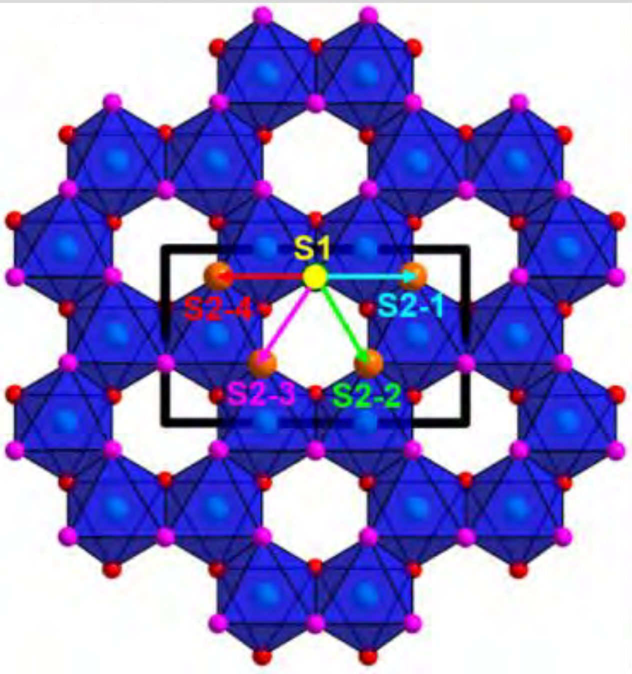


from↓/ to→	O1-H-O1 Contact	O1-H-O2 contact-1	O1-H-O2 contact-2	O1-H-O2 contact-3	O1-H-O2 contact-4
O1-H-O1 contact	P_{11}, S1	P_{12}, S2-1	P_{13}, S2-2	P_{14}, S2-3	P_{15}, S2-4
O1-H-O2 contact-1	P_{21}, S1	P_{22}, S2-1	P_{23}, S2-2	P_{24}, S2-3	P_{25}, S2-4
O1-H-O2 contact-2	P_{31}, S1	P_{32}, S2-1	P_{33}, S2-2	P_{34}, S2-3	P_{35}, S2-4
O1-H-O2 contact-3	P_{41}, S1	P_{42}, S2-1	P_{43}, S2-2	P_{44}, S2-3	P_{45}, S2-4
O1-H-O2 contact-4	P_{51}, S1	P_{52}, S2-1	P_{53}, S2-2	P_{54}, S2-3	P_{55}, S2-4

assumption:
all alternative
stacking orders
are equally
favorable

↓

global
fault probability:
P_x

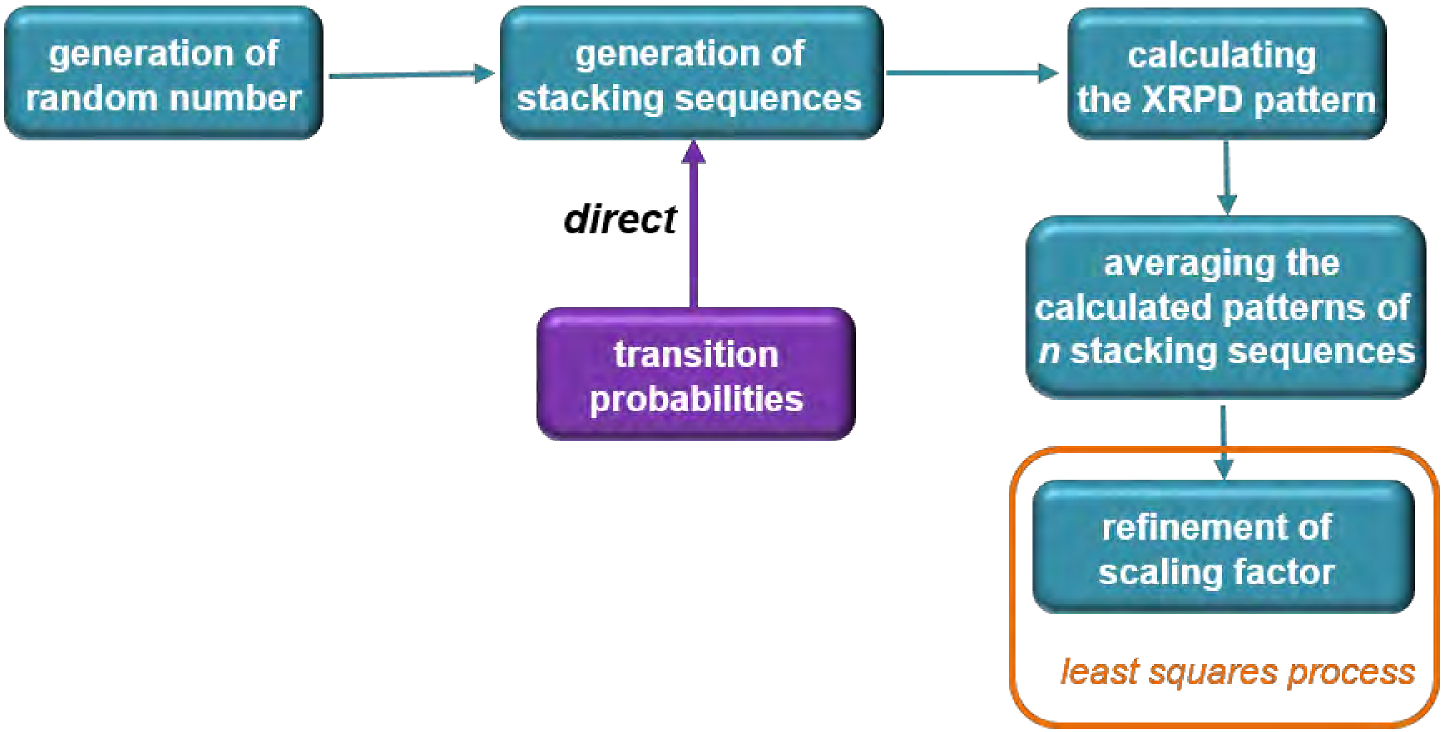


from↓/ to→	O1-H-O1 Contact	O1-H-O2 contact-1	O1-H-O2 contact-2	O1-H-O2 contact-3	O1-H-O2 contact-4
O1-H-O1 contact	$1\text{-}P_x$, S1	$0.25\cdot P_x$, S2-1	$0.25\cdot P_x$, S2-2	$0.25\cdot P_x$, S2-3	$0.25\cdot P_x$, S2-4
O1-H-O2 contact-1	$1\text{-}P_x$, S1	$0.25\cdot P_x$, S2-1	$0.25\cdot P_x$, S2-2	$0.25\cdot P_x$, S2-3	$0.25\cdot P_x$, S2-4
O1-H-O2 contact-2	$1\text{-}P_x$, S1	$0.25\cdot P_x$, S2-1	$0.25\cdot P_x$, S2-2	$0.25\cdot P_x$, S2-3	$0.25\cdot P_x$, S2-4
O1-H-O2 contact-3	$1\text{-}P_x$, S1	$0.25\cdot P_x$, S2-1	$0.25\cdot P_x$, S2-2	$0.25\cdot P_x$, S2-3	$0.25\cdot P_x$, S2-4
O1-H-O2 contact-4	$1\text{-}P_x$, S1	$0.25\cdot P_x$, S2-1	$0.25\cdot P_x$, S2-2	$0.25\cdot P_x$, S2-3	$0.25\cdot P_x$, S2-4

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Parameter opitmization

Problem: optimization of the microstructural parameters i.e. the transition probabilities



Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Parameter opitmization

Problem: optimization of the microstructural parameters i.e. the transition probabilities

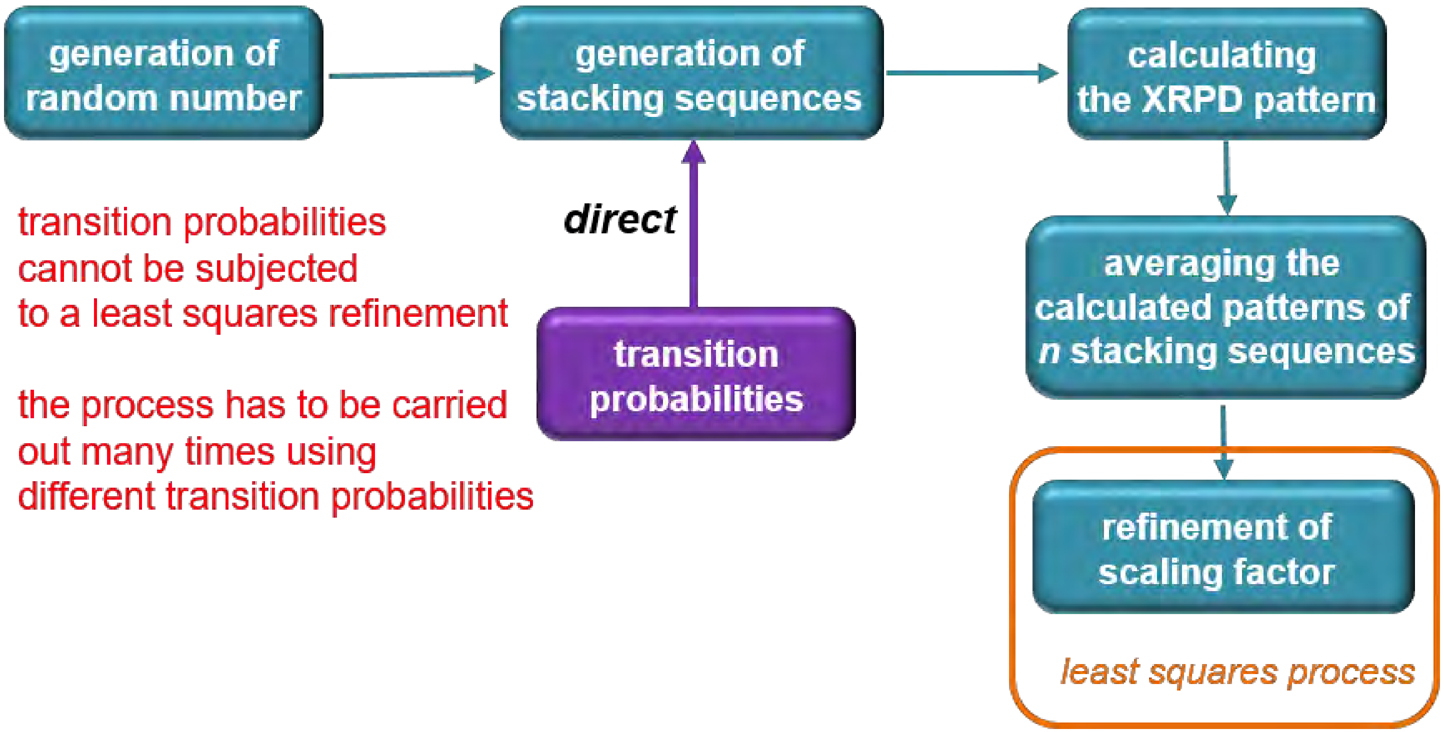
generation of random number → generation of stacking sequences → calculating the XRPD pattern → averaging the calculated patterns of *n* stacking sequences → refinement of scaling factor

transition probabilities → *direct* → generation of stacking sequences

least squares process

- transition probabilities cannot be subjected to a least squares refinement

Problem: optimization of the microstructural parameters i.e. the transition probabilities



- transition probabilities cannot be subjected to a least squares refinement
- the process has to be carried out many times using different transition probabilities

Problem: optimization of the microstructural parameters i.e. the transition probabilities

generation of random number → generation of stacking sequences → calculating the XRPD pattern → averaging the calculated patterns of *n* stacking sequences → refinement of scaling factor

transition probabilities → (*direct*) → generation of stacking sequences

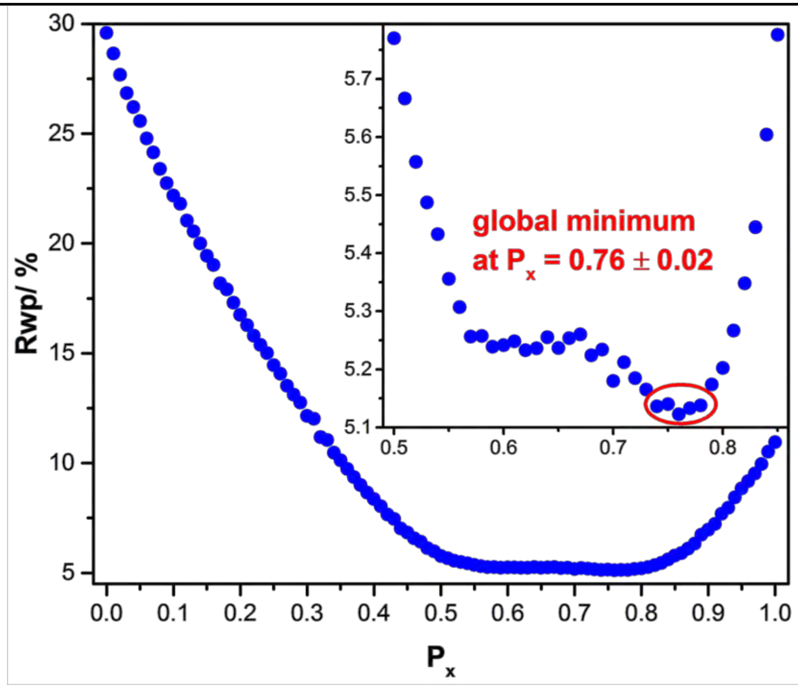
least squares process (refinement of scaling factor)

- transition probabilities cannot be subjected to a least squares refinement
- the process has to be carried out many times using different transition probabilities
  - grid search optimization

Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

Parameter opitmization

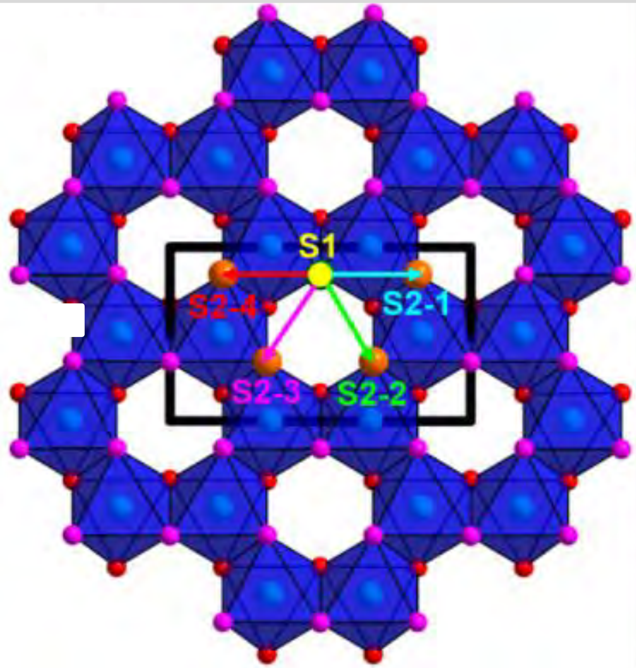
from↓/ to→	O1-H-O1 Contact	O1-H-O2 contact-1	O1-H-O2 contact-2	O1-H-O2 contact-3	O1-H-O2 contact-4
O1-H-O1 contact	1-P_x, S1	0.25· P_x, S2-1	0.25· P_x, S2-2	0.25· P_x, S2-3	0.25· P_x, S2-4
O1-H-O2 contact-1	1-P_x, S1	0.25· P_x, S2-1	0.25· P_x, S2-2	0.25· P_x, S2-3	0.25· P_x, S2-4
O1-H-O2 contact-2	1-P_x, S1	0.25· P_x, S2-1	0.25· P_x, S2-2	0.25· P_x, S2-3	0.25· P_x, S2-4
O1-H-O2 contact-3	1-P_x, S1	0.25· P_x, S2-1	0.25· P_x, S2-2	0.25· P_x, S2-3	0.25· P_x, S2-4
O1-H-O2 contact-4	1-P_x, S1	0.25· P_x, S2-1	0.25· P_x, S2-2	0.25· P_x, S2-3	0.25· P_x, S2-4



Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

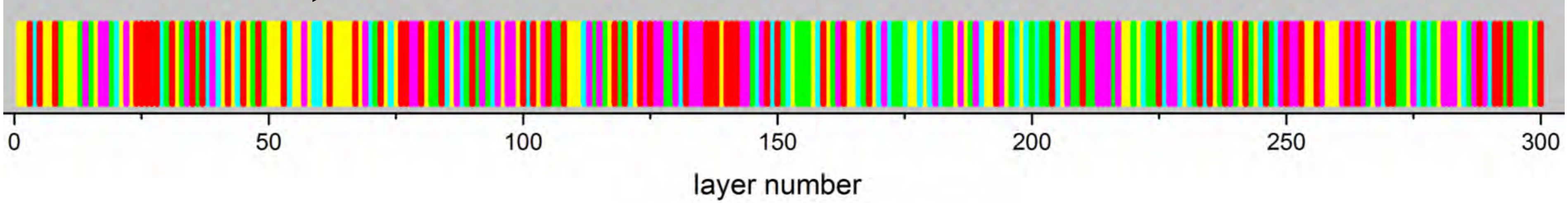
Interpretation of the result

from↓/ to→	O1-H-O1 Contact	O1-H-O2 contact-1	O1-H-O2 contact-2	O1-H-O2 contact-3	O1-H-O2 contact-4
O1-H-O1 contact	**0.24**, S1	**0.19**, S2-1	**0.19**, S2-2	**0.19**, S2-3	**0.19**, S2-4
O1-H-O2 contact-1	**0.24**, S1	**0.19**, S2-1	**0.19**, S2-2	**0.19**, S2-3	**0.19**, S2-4
O1-H-O2 contact-2	**0.24**, S1	**0.19**, S2-1	**0.19**, S2-2	**0.19**, S2-3	**0.19**, S2-4
O1-H-O2 contact-3	**0.24**, S1	**0.19**, S2-1	**0.19**, S2-2	**0.19**, S2-3	**0.19**, S2-4
O1-H-O2 contact-4	**0.24**, S1	**0.19**, S2-1	**0.19**, S2-2	**0.19**, S2-3	**0.19**, S2-4



| S1 | S2-1 | S2-2 | S2-3 | S2-4

stacking order
c-direction



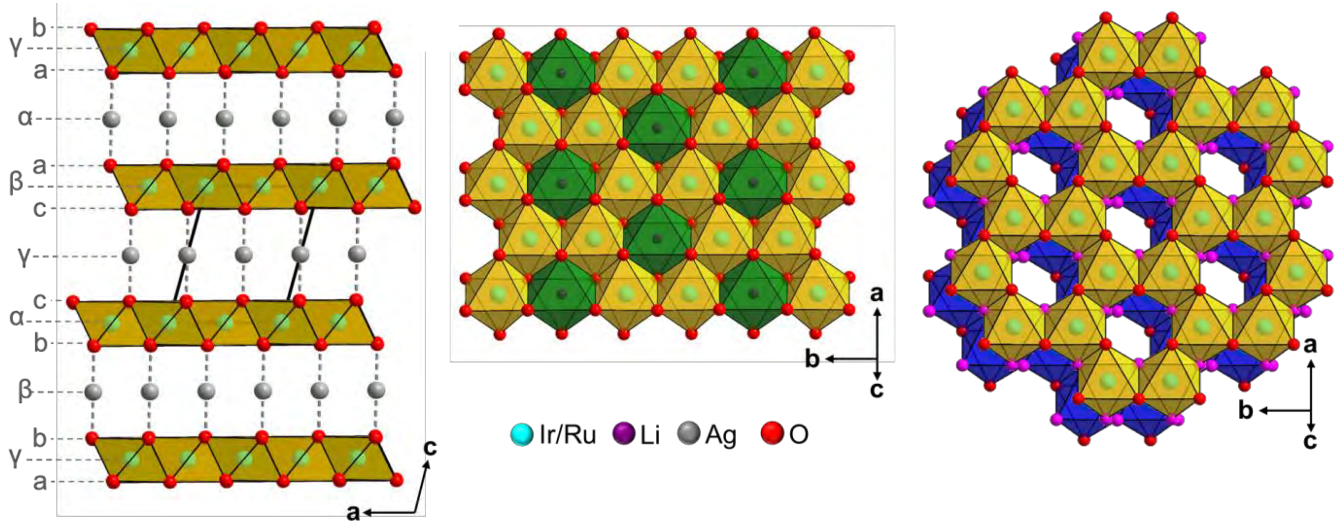
- extension of the coherently stacked sections ≤ 2.4 nm in *c*-direction!

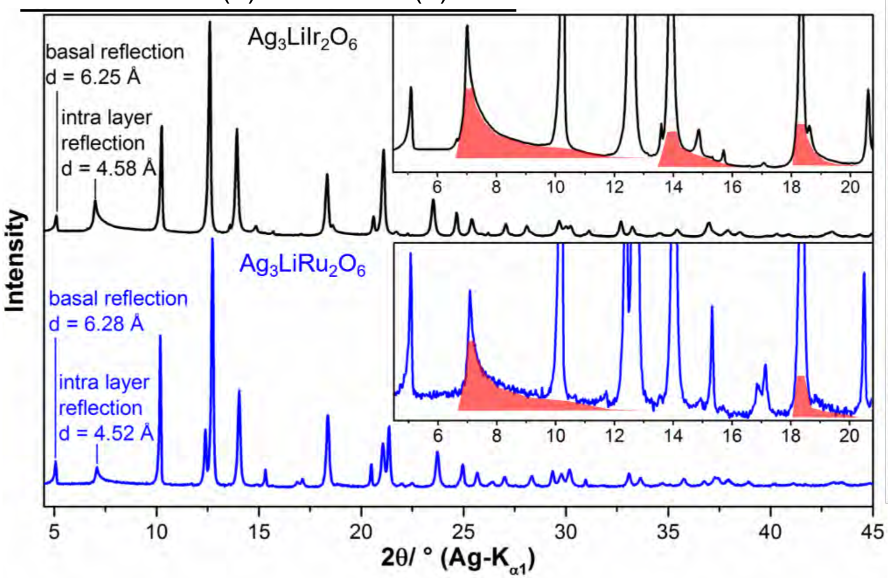
Honeycomb Compounds - $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$

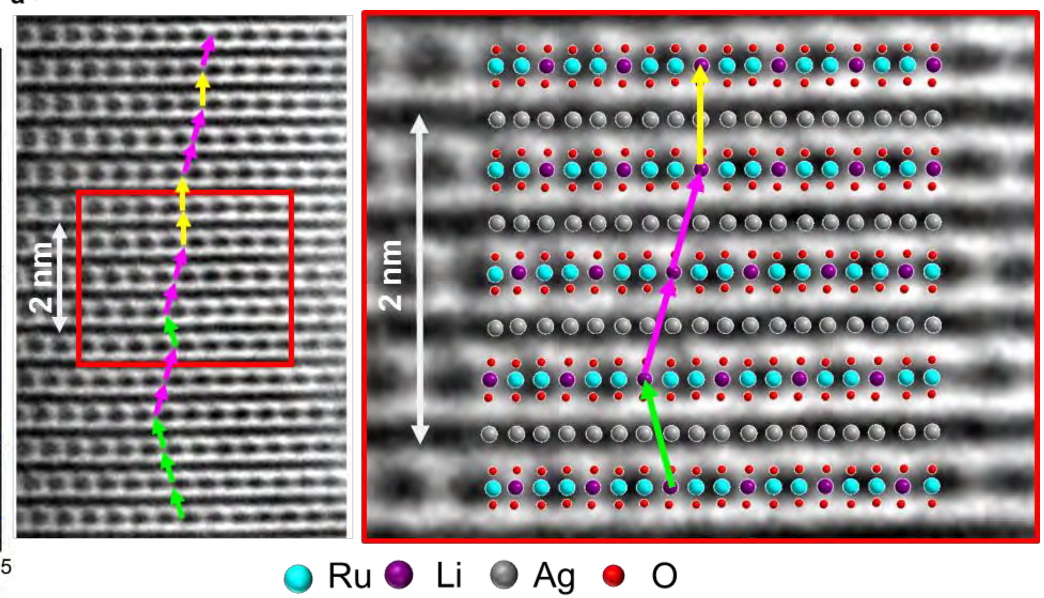
Transfer to related systems

$Ag_3LiIr_2O_6$ / $Ag_3LiRu_2O_6$

	$Ag_3LiIr_2O_6$	$Ag_3LiRu_2O_6$
	*C*2/*m* (12)	*C*2/*m* (12)
Z	2	2
a **/Å**	5.287(1)	5.226(1)
b **/Å**	9.151(2)	9.036(1)
c **/Å**	6.503(1)	6.527(1)
α **/°**	90	90
β **/°**	106.1(1)	105.7(1)
γ **/°**	90	90
V **/Å³**	302.32(9)	296.66(6)







Bette, S., Takayama, T., Duppel, V., Poulain, A., Takagi, H, Dinnebier, R.E. *Dalton Trans.* **2019**, 48, 9250 – 9259.

More Honeycomb Compounds - $Li_3HoBr_{6-x}I_x$

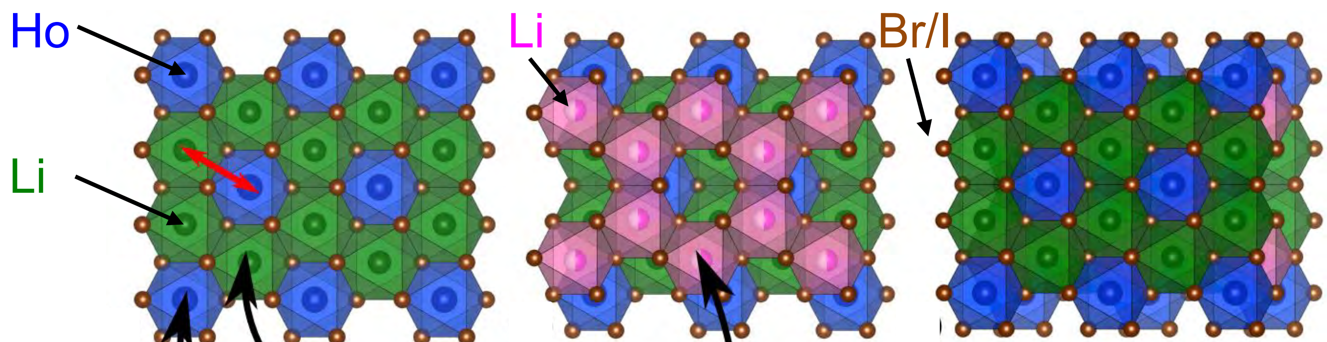
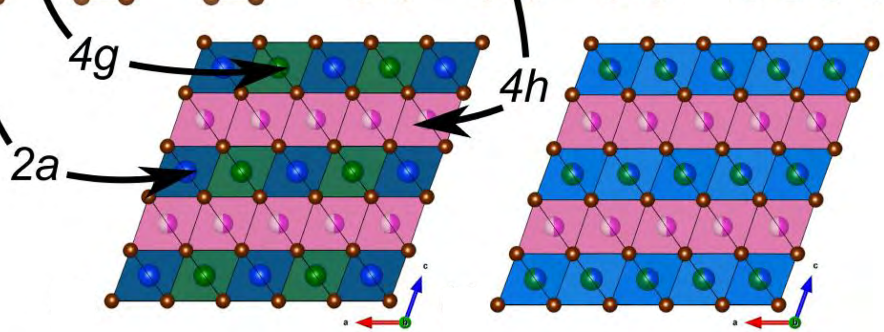
intra- vs. interlayer disorder

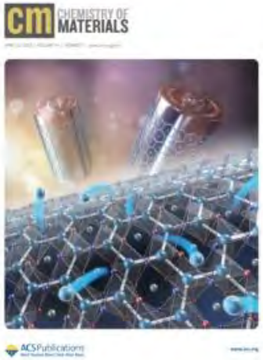
$$HoBr_3 + 3\text{-}x\ LiBr + x\ LiI \xrightarrow{1000\ °C} Li_3HoBr_{6-x}I_x\ (x \leq 3)$$

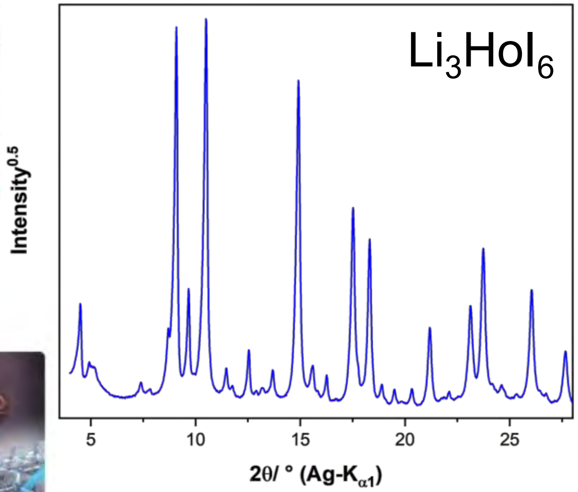
$$HoI_3 + 3\text{-}0.5x\ LiBr + 0.5x\ LiI \xrightarrow{1000\ °C} Li_3HoBr_{6-x}I_x$$

M.A. Plass

B.V. Lotsch

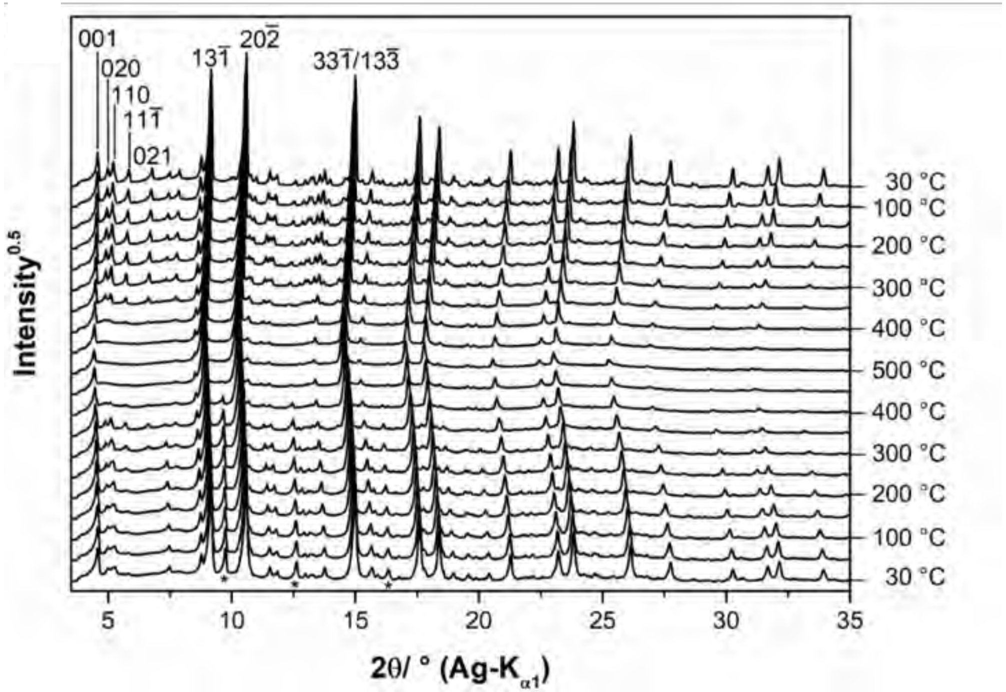







Plass, M.A., Bette, S., Dinnebier, R.E., Lotsch, B. *Chem. Mater.* **2022**, 34, 3227-3235.

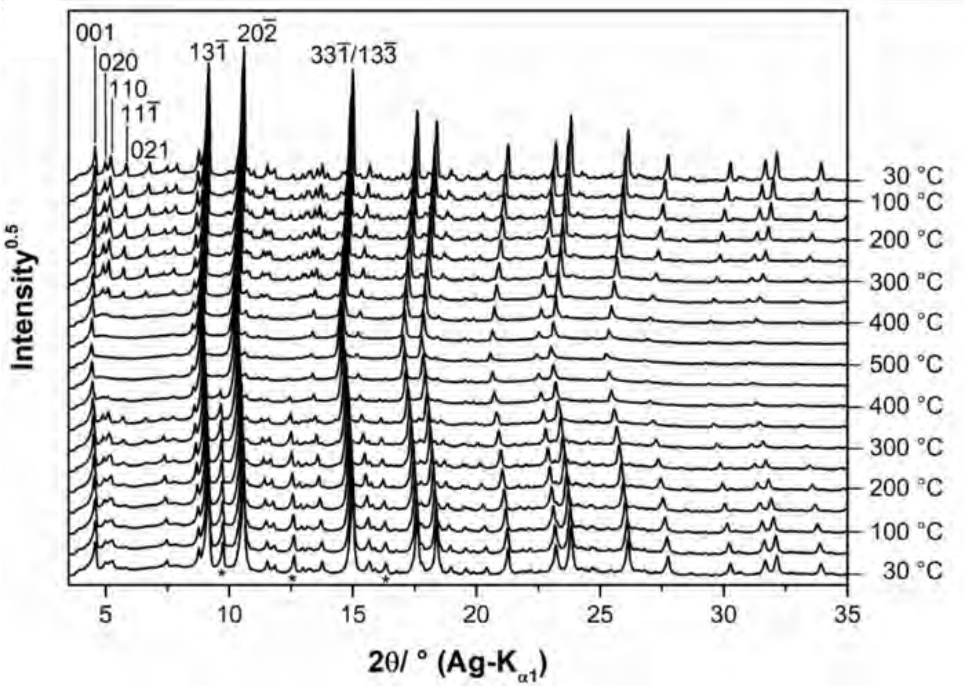
Heating of Li_3HoI_6:

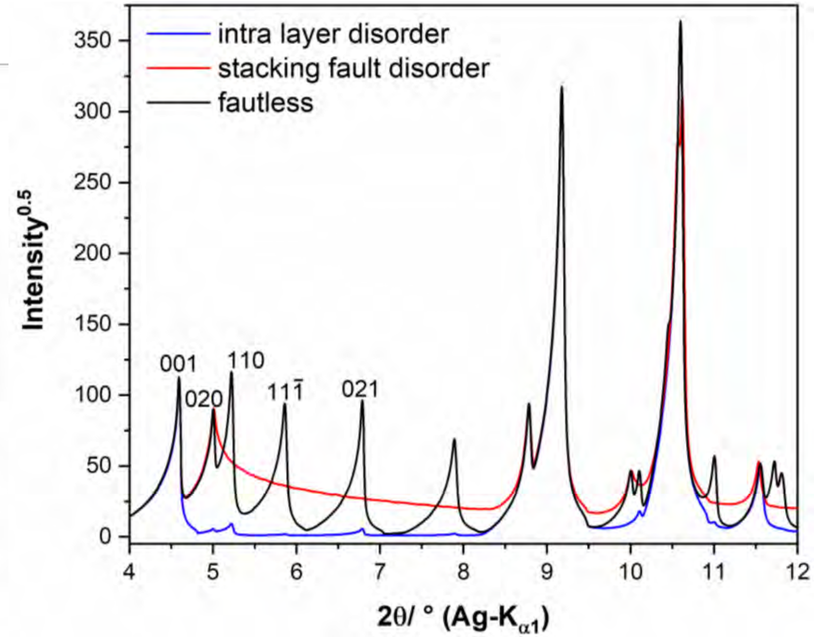


- considerable thermal expansion
- by heating 110, 11$\bar{1}$, 021 appear from diffuse scattering
- further heating leads a reduction of the intensity of the 020, 110, 11$\bar{1}$ and 021 reflection

Honeycomb Compounds - $Li_3HoBr_{6-x}I_x$
intra- vs. interlayer disorder

Heating of Li_3HoI_6:





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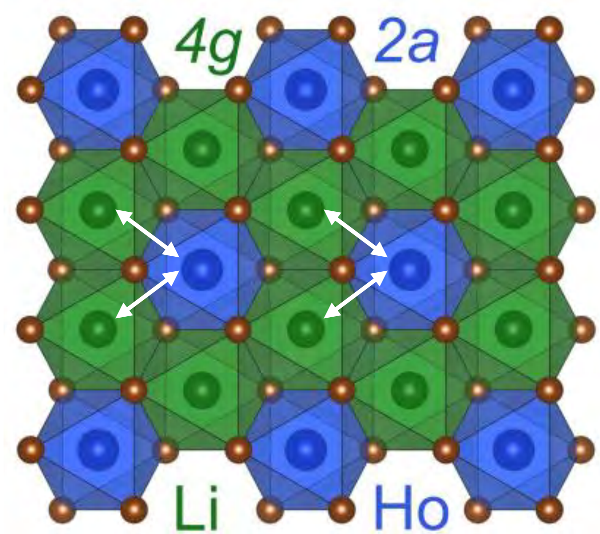
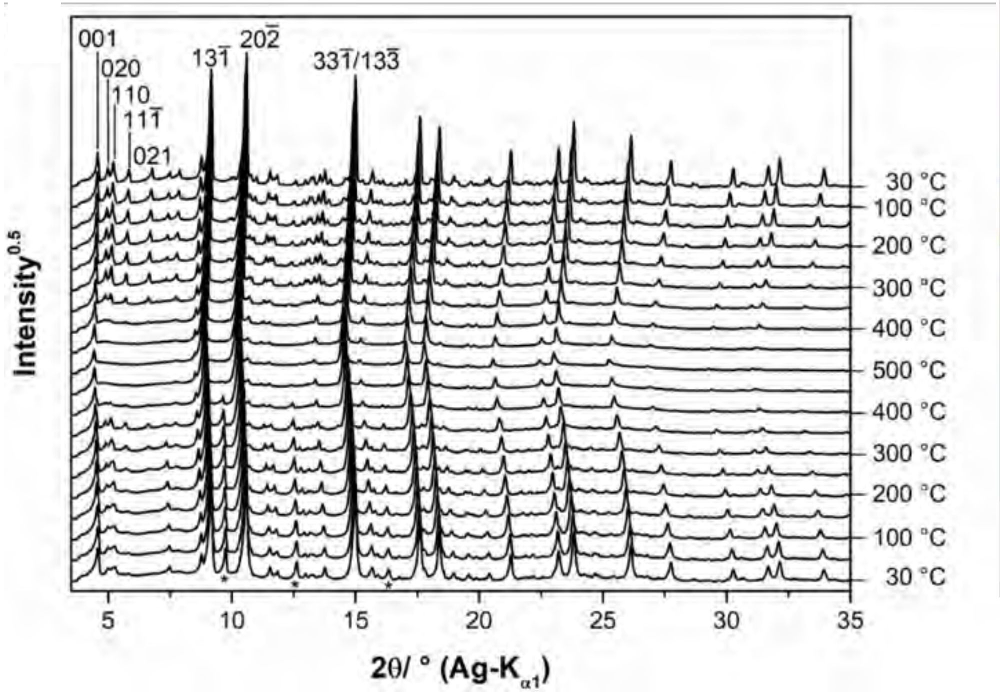
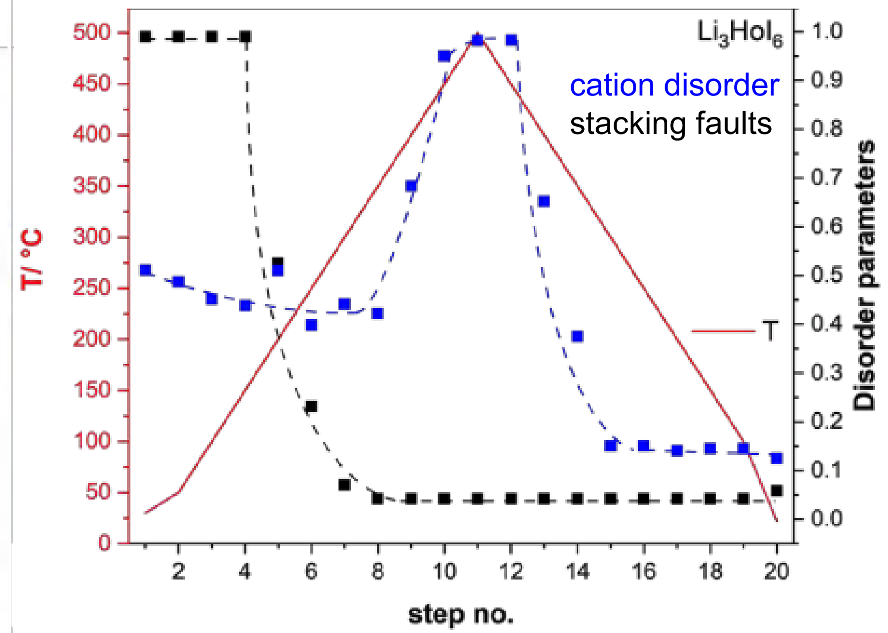


Honeycomb Compounds - $Li_3HoBr_{6-x}I_x$

intra- vs. interlayer disorder

Heating of Li_3HoI_6:





- considerable thermal expansion
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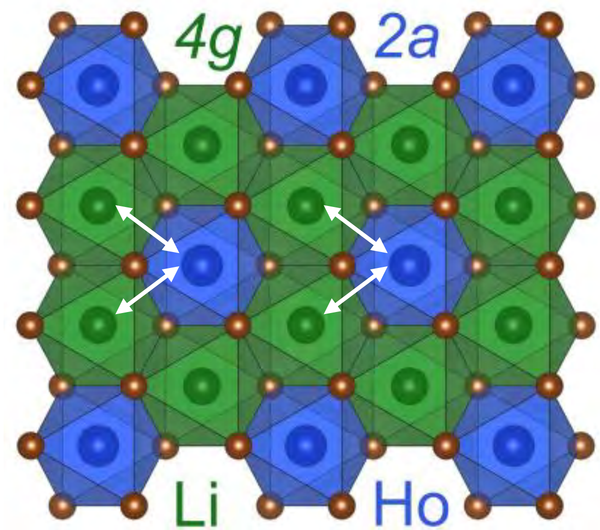
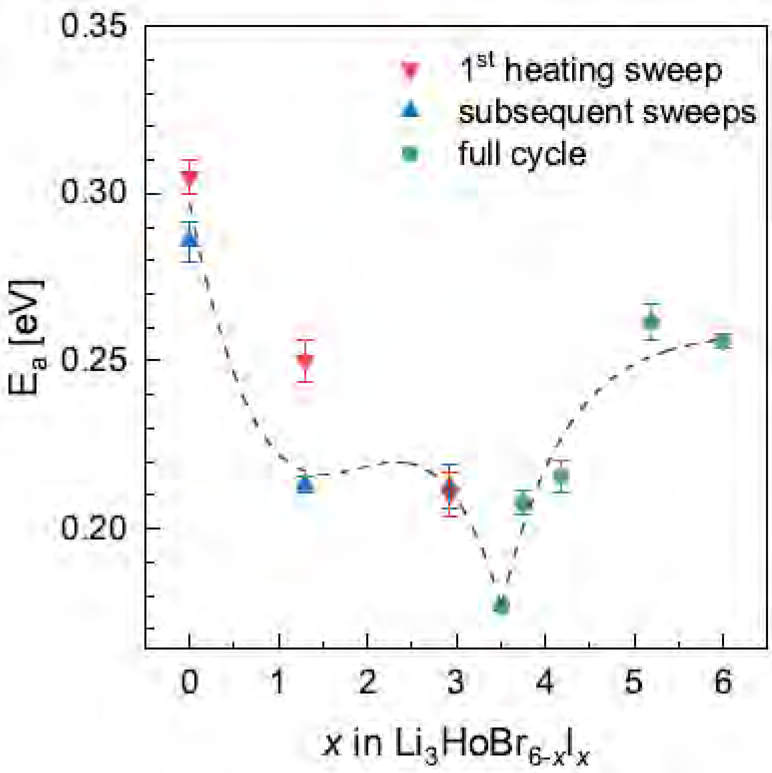
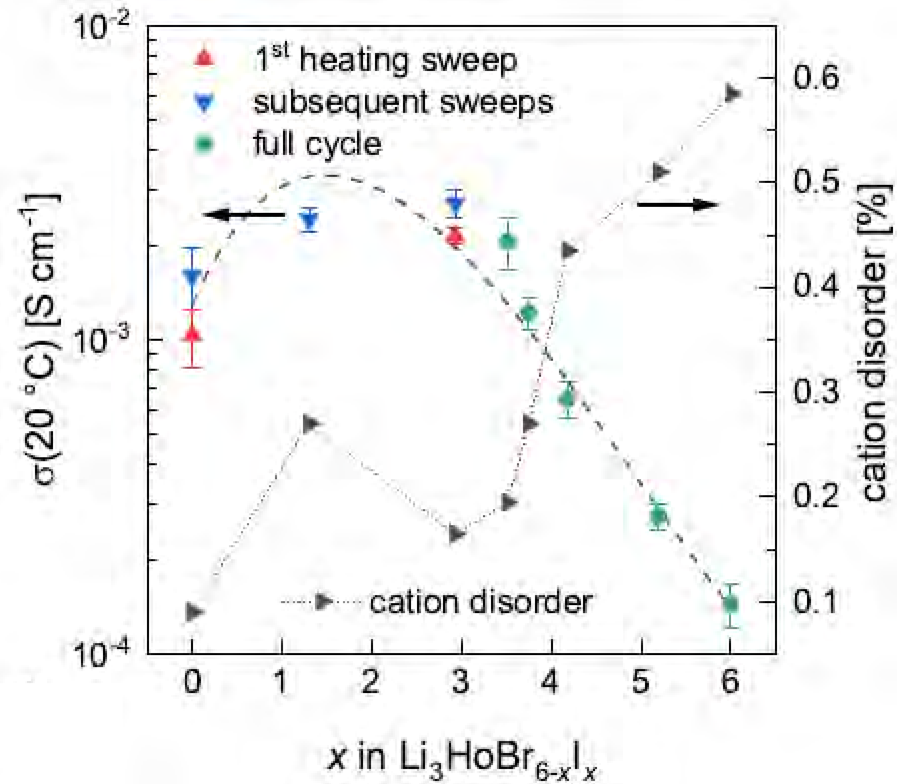


Honeycomb Compounds - $Li_3HoBr_{6-x}I_x$
intra- vs. interlayer disorder

The impact of disorder on ion conductivity:





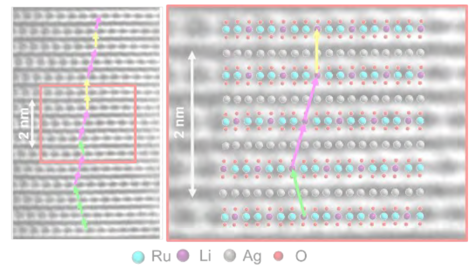
- intralayer cation disorder rather impacts ion conductivity than interlayer stacking fault disorder

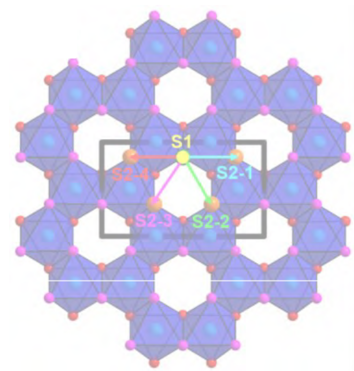
Plass, M.A., Bette, S., Dinnebier, R.E., Lotsch, B. *Chem. Mater.* **2022**, in press.

Outline

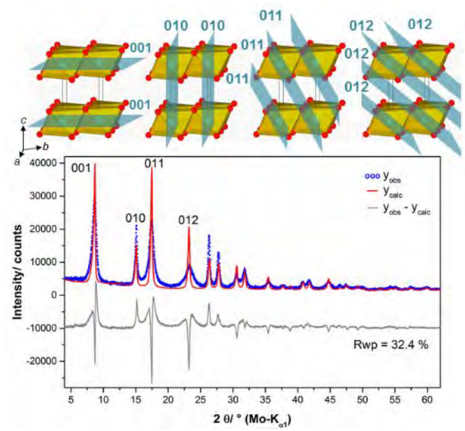
How can we utilize these software features for getting a better understanding of our materials?

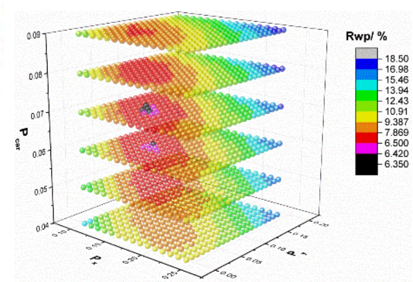
1. Honeycomb Compounds
   a) $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$ – derivation of the layer constitution
   b) $Li_3HoBr_{6-x}I_x$ – intra- vs. Interlayer disorder



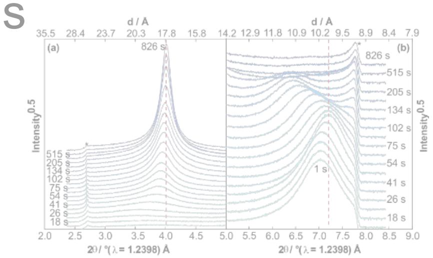


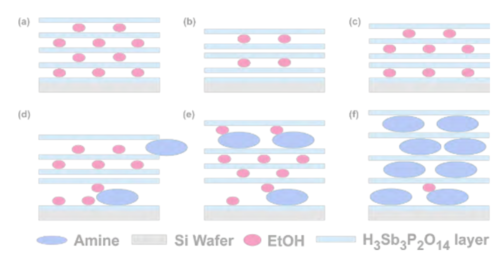
2. Brucite-type materials
   a) NCA precursors – optimization of multiple parameters





3. Excursus into thin films
   a) spin coated $H_3Sb_3P_3O_{14}$ thin films



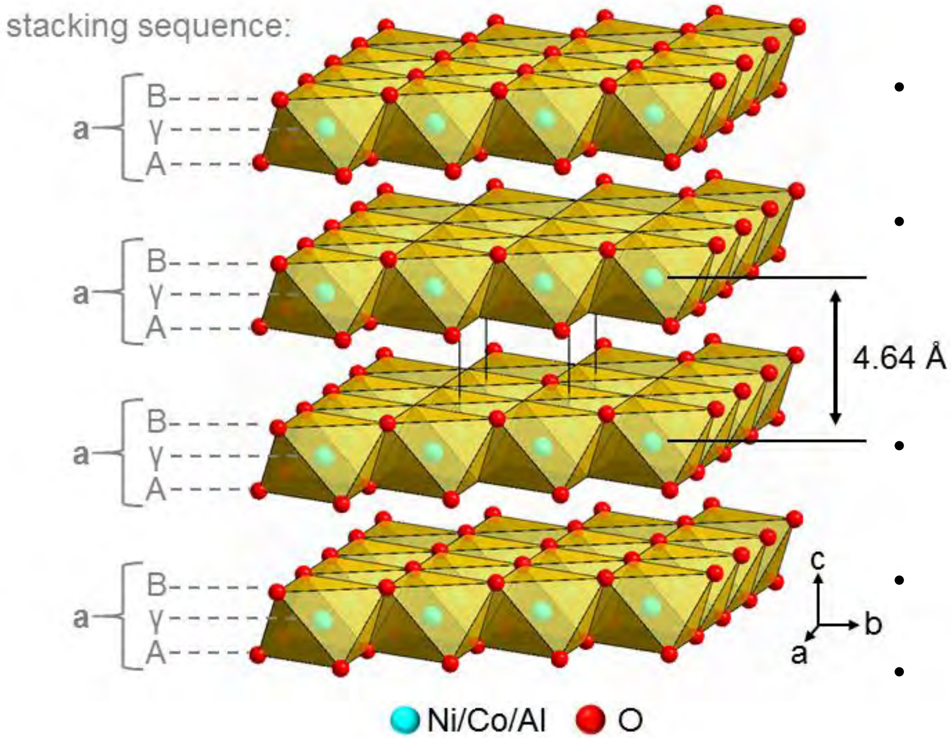


4. Conclusions and Outlook

Brucite-type materials
NCA precursors – optimization of multiple parameters

NCA and NCM Battery material precursor

- “(Ni, Co, Al/Mn)$(OH)_2$ compounds”



- layered double hydroxide (LDH) phase
- cation sublattice (NCA): 90 % Ni, 5 % Co, 5 % Al
- cation sublattice (NCM): 85 % Ni, 10 % Co, 5 % Mn
- brucite-type lattice
- space group $P\bar{3}m1$

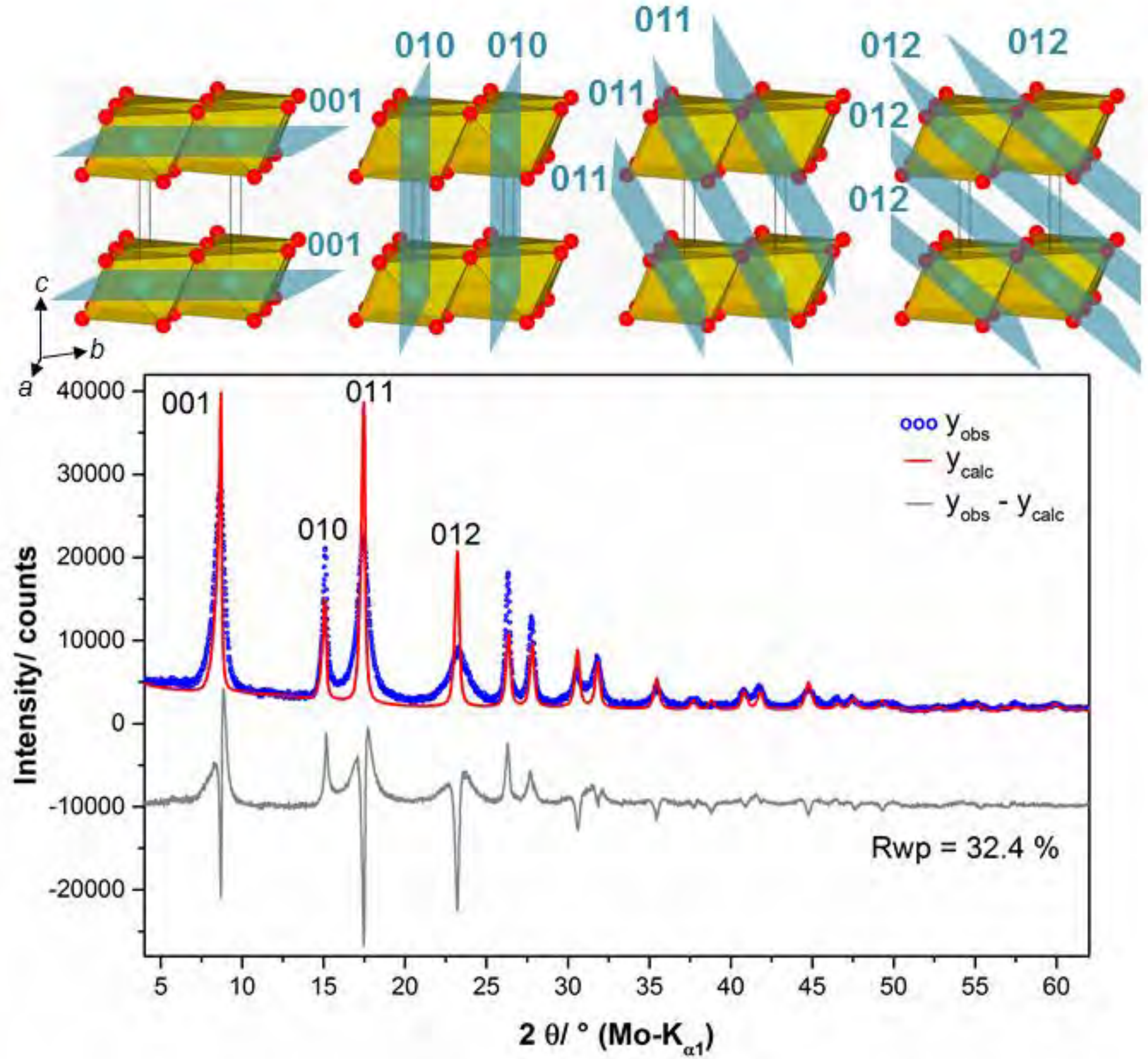
BASF
We create chemistry

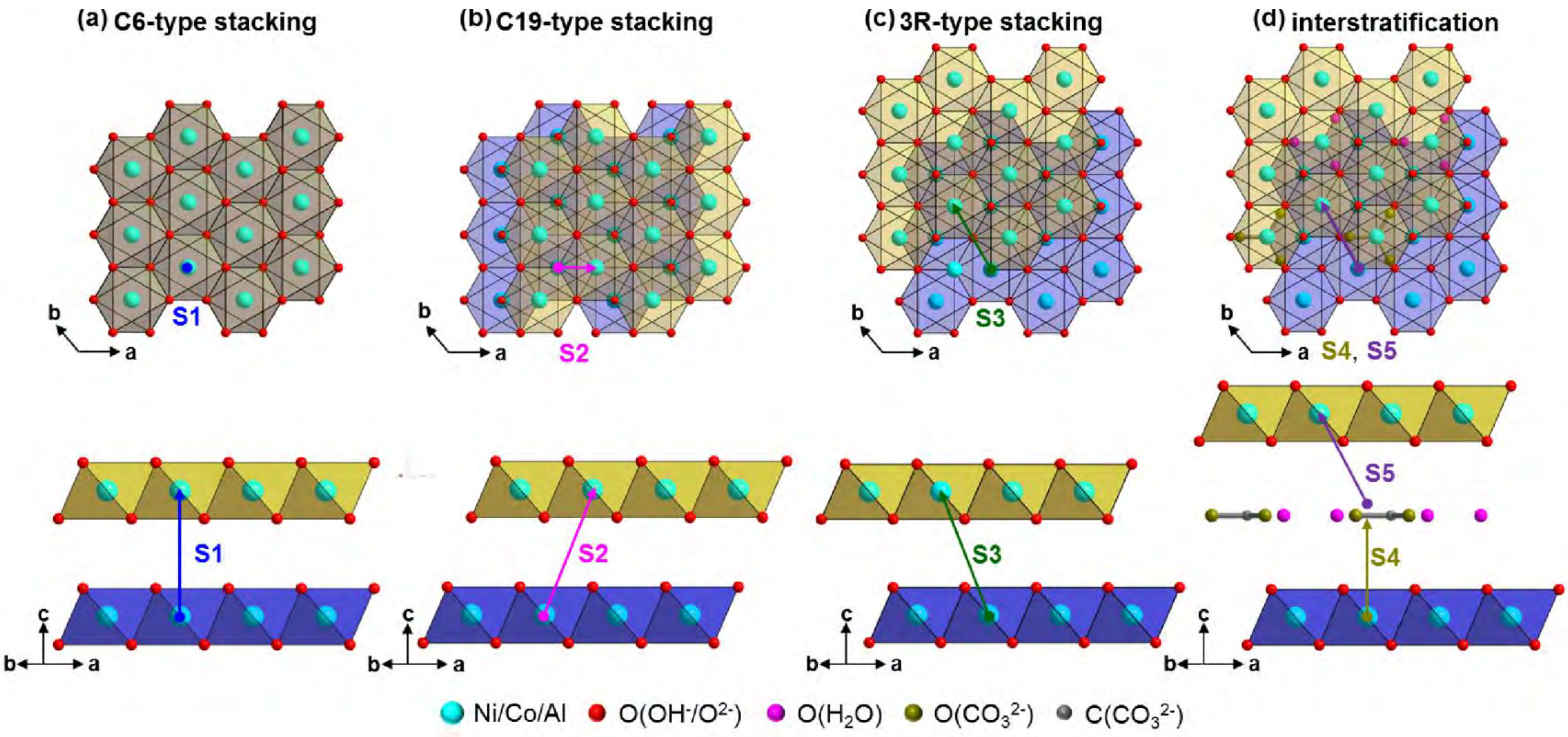
B. Hinrichsen

Bette, S., Hinrichsen, B., Pfister, D., Dinnebier, R.E. *J. Appl. Cryst.* **2020**, 53, 76-87.

Brucite-type materials

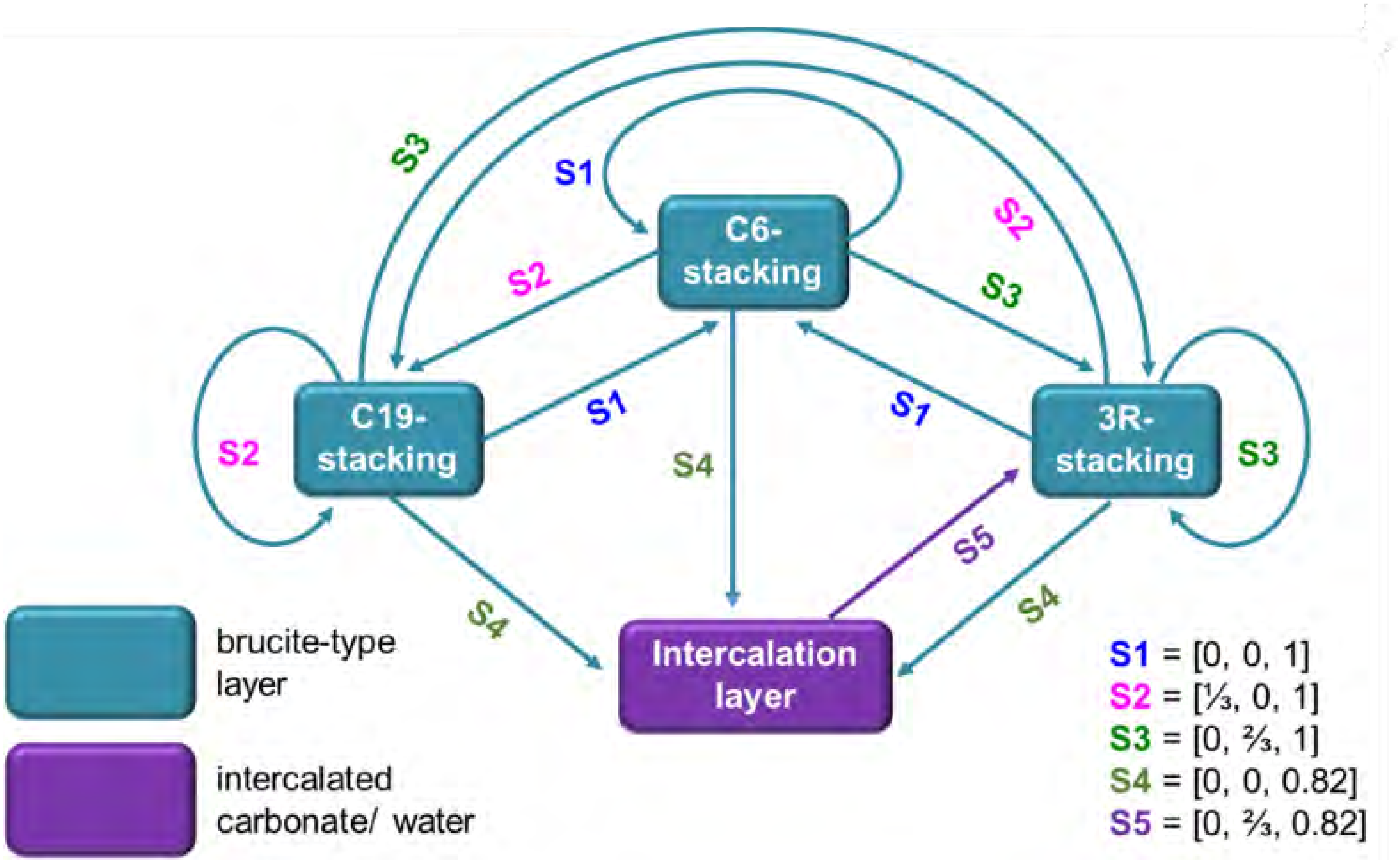
NCA precursors – optimization of multiple parameters





Bette, S., Hinrichsen, B., Pfister, D., Dinnebier, R.E. *J. Appl. Cryst.* **2020**, 53, 76-87.

Defining possible transitions



Bette, S., Hinrichsen, B., Pfister, D., Dinnebier, R.E. *J. Appl. Cryst.* **2020**, 53, 76-87.

Building a microstructural model

to→ /from↓	C6-stacking	C19-stacking	3R-stacking	Inter-calation
C6-stacking	$1-P_x-P_y-P_{car}$ S1	P_x, S2	P_y, S3	P_{car}, S4
C19-stacking	$1-P_x-P_y-P_{car}$ S1	P_x, S2	P_y, S3	P_{car}, S4
3R-stacking	$1-P_x-P_y-P_{car}$ S1	P_x, S2	P_y, S3	P_{car}, S4
Inter-calation	0	0	0	1, S5

Brucite-type materials

NCA precursors – optimization of multiple parameters

Problem 2: optimization of the transition probabilities

```
num_runs 1000300
seed
…
str
…
prm px = …;

prm py = …;

prm pcar =…;

   generate stack sequences
     {
…
```

- When P_x, P_y and P_{car} should be varied 0.00 to 1.00 in 0.01 increments

↓

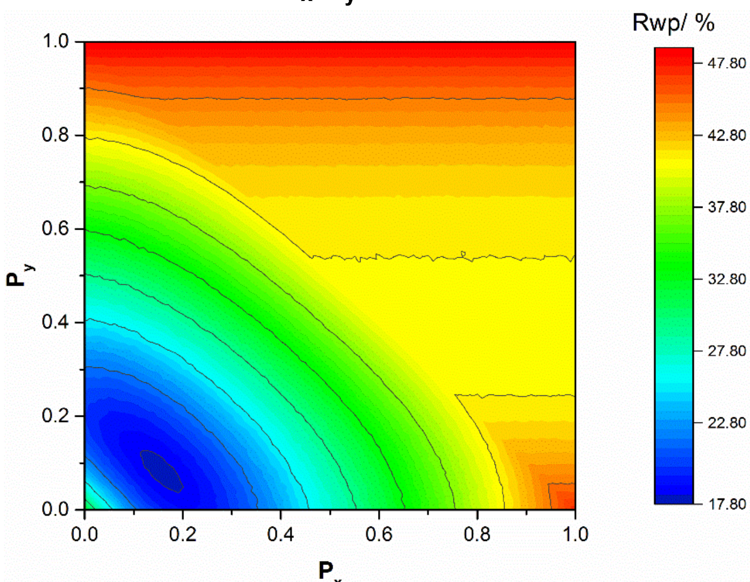
- ≈ 10,000,300 Rietveld refinements

➢ **≈ 58 days!**

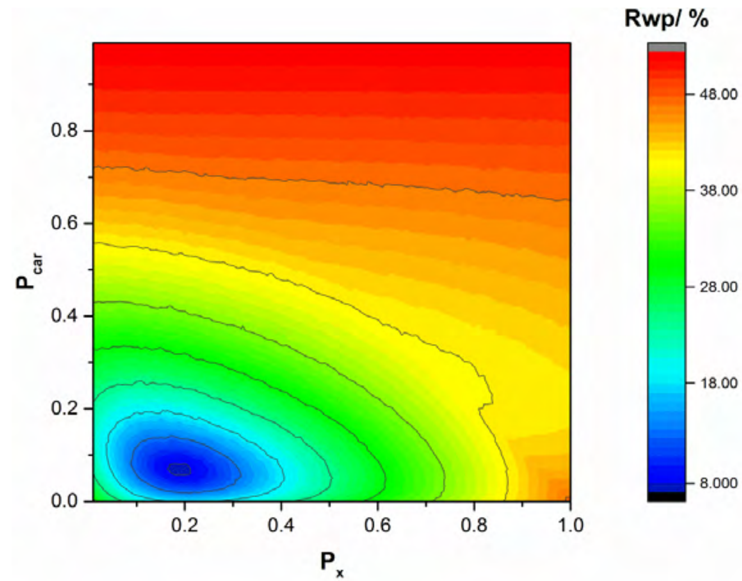
Coelho, A.A. *J. Appl. Cryst.* **2018**, 51, 210.I Bette, S. et al. *Dalton Trans.* **2019**, 48, 9250.I
Bette, S. et al. *J. Appl. Cryst.* **2020**, 53, 76-87.

Problem 2: optimization of the transition probabilities

P_x-P_y-surface



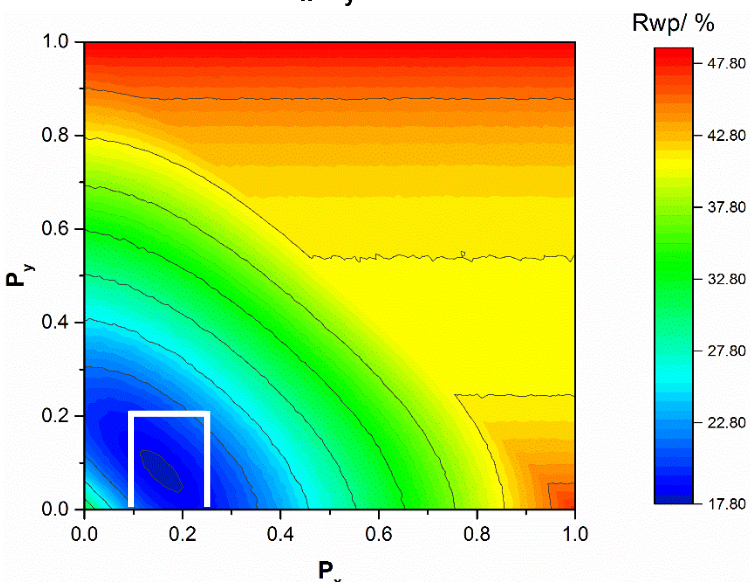
P_x-P_{car}-surface



Coelho, A.A. *J. Appl. Cryst.* **2018**, 51, 210.I Bette, S. et al. *Dalton Trans.* **2019**, 48, 9250.I Bette, S. et al. *J. Appl. Cryst.* **2020**, 53, 76-87.

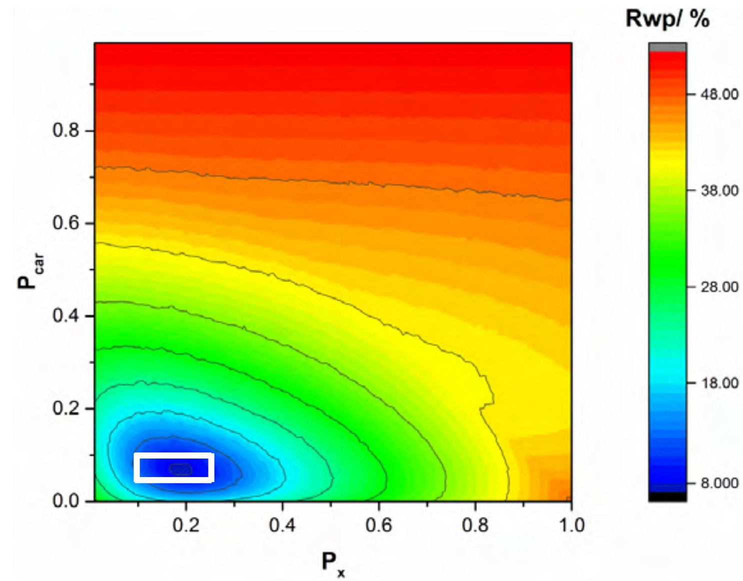
Problem 2: optimization of the transition probabilities

P_x-P_y-surface



global minimum within 0.10 ≤ P_x ≤ 0.24 ∪ 0.00 ≤ P_y ≤ 0.19

P_x-P_{car}-surface

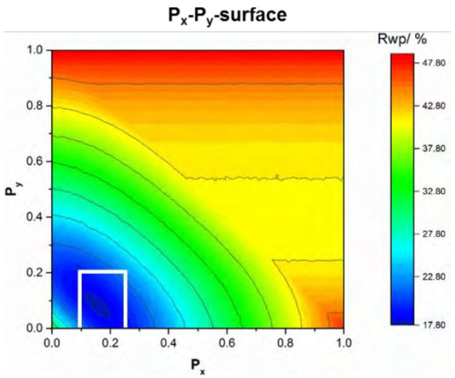


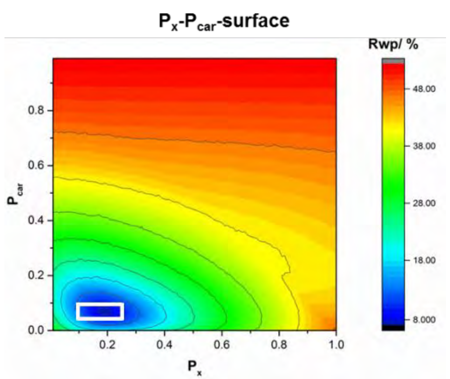
global minimum within 0.10 ≤ P_x ≤ 0.24 ∪ 0.04 ≤ P_{car} ≤ 0.09

Coelho, A.A. *J. Appl. Cryst.* **2018**, 51, 210.I Bette, S. et al. *Dalton Trans.* **2019**, 48, 9250.I
Bette, S. et al. *J. Appl. Cryst.* **2020**, 53, 76-87.

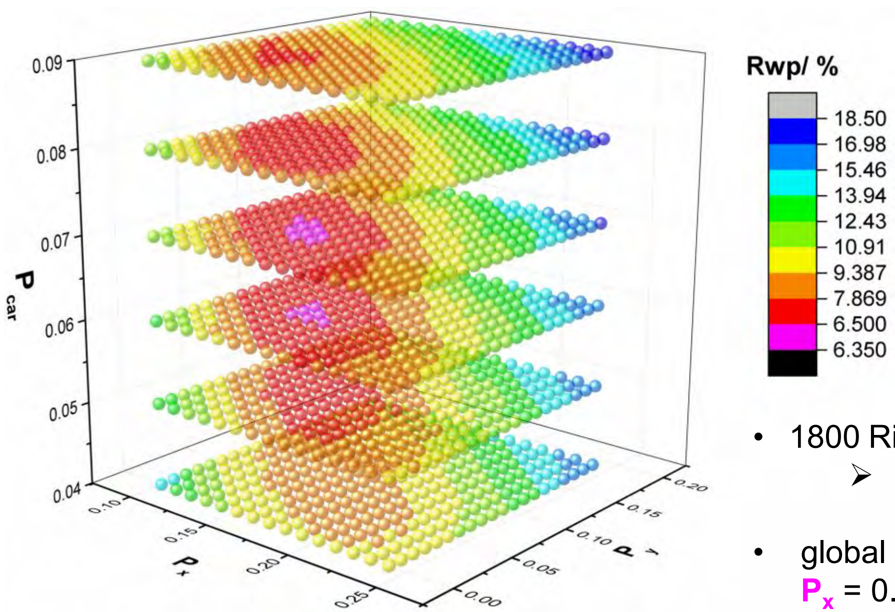
Brucite-type materials
NCA precursors – optimization of multiple parameters

Problem 2: optimization of the transition probabilities





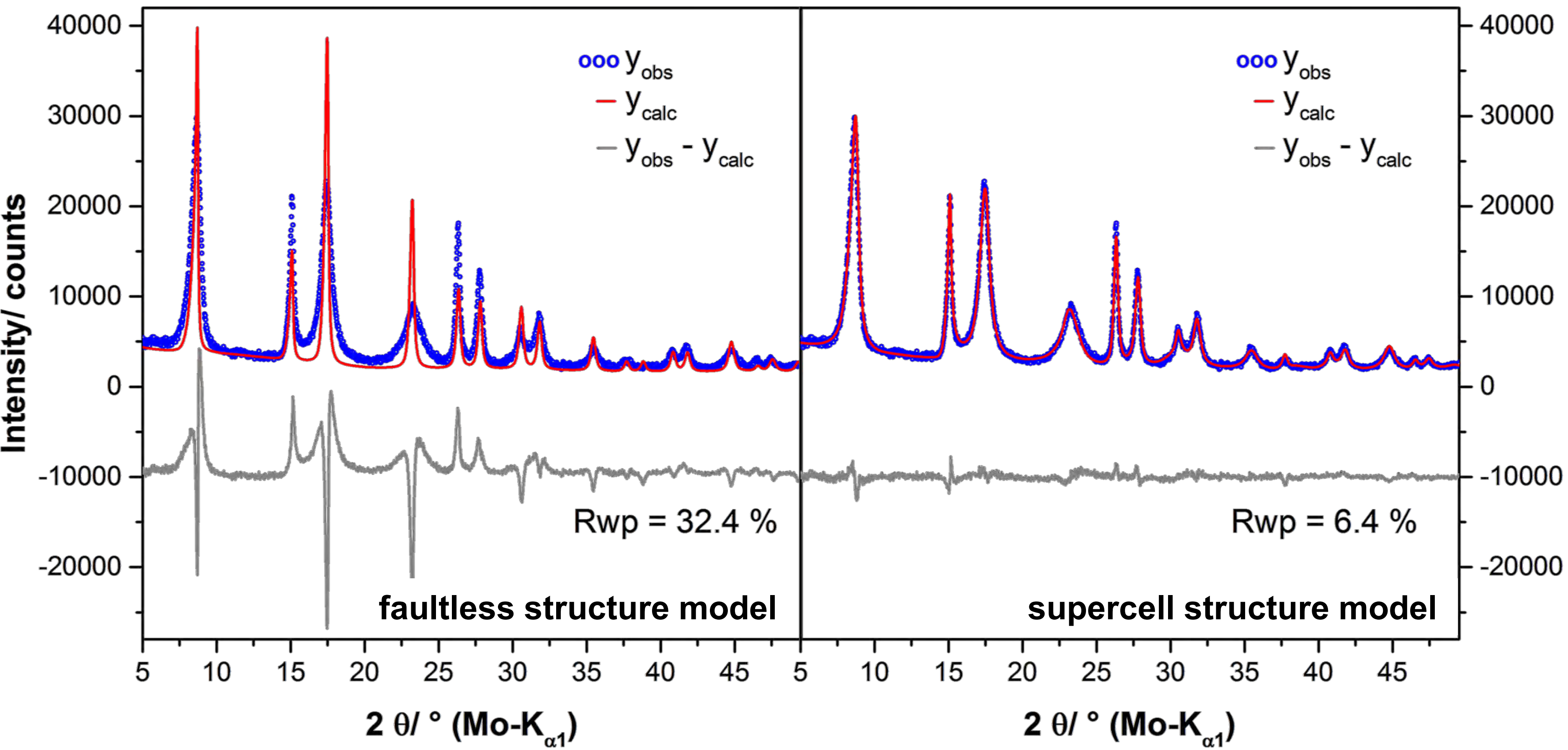
- Narrowing down the 3-dimensional grid to:
  $0.10 \leq P_x \leq 0.24 \cup 0.00 \leq P_y \leq 0.19 \cup 0.04 \leq P_{car} \leq 0.09$ → 1800 grid points



- 1800 Rietveld refinements
  - ≈ 2.5 h
- global minimum at:
  $P_x = 0.15$, $P_y = 0.06$, $P_{car} = 0.07$

Coelho, A.A. *J. Appl. Cryst.* **2018**, 51, 210.l Bette, S. et al. *Dalton Trans.* **2019**, 48, 9250.l
Bette, S. et al. *J. Appl. Cryst.* **2020**, 53, 76-87.

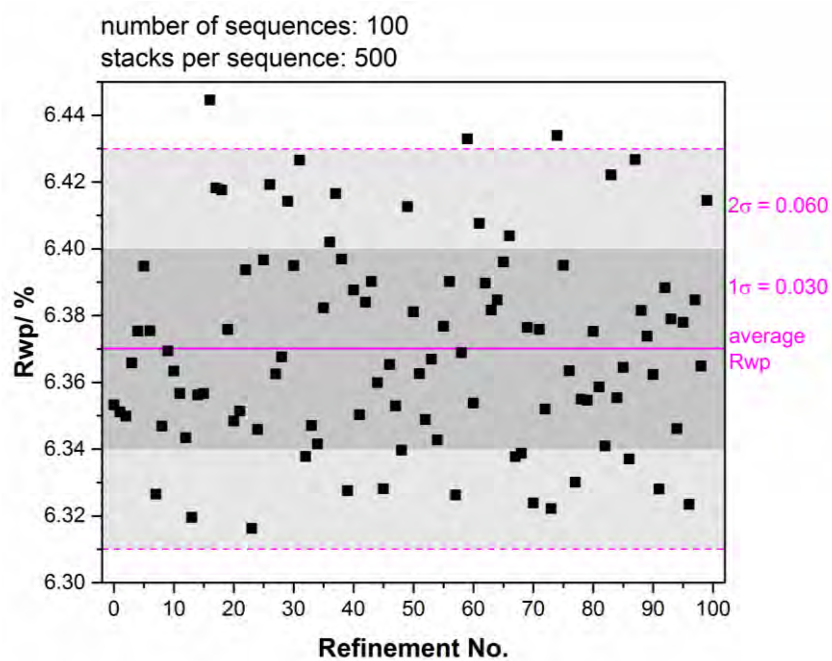
Problem 2: optimization of the transition probabilities

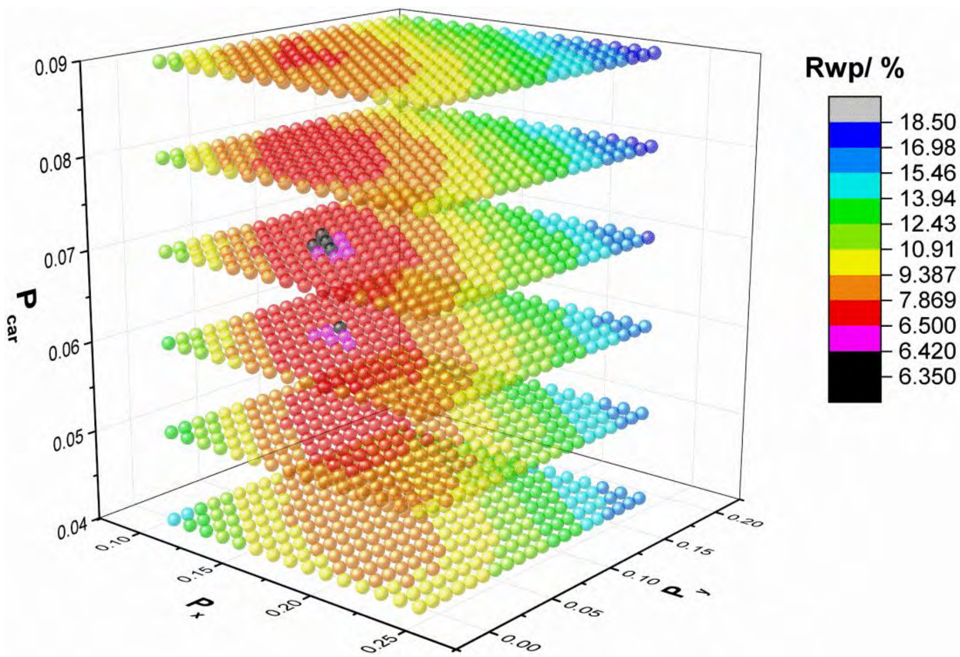


Bette, S., Hinrichsen, B., Pfister, D., Dinnebier, R.E. *J. Appl. Cryst.* **2020**, 53, 76-87.

Problem 2: optimization of the transition probabilities

Scattering of the results





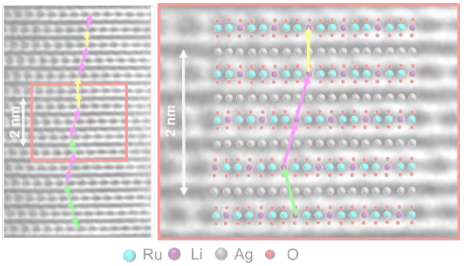
- Minimum at: P_x = 0.15(1), P_y = 0.06(1), P_{car} = 0.07(1), Rwp = 6.4 %

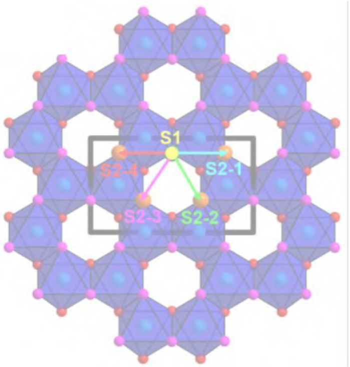
Bette, S., Hinrichsen, B., Pfister, D., Dinnebier, R.E. *J. Appl. Cryst.* **2020**, 53, 76-87.

Outline

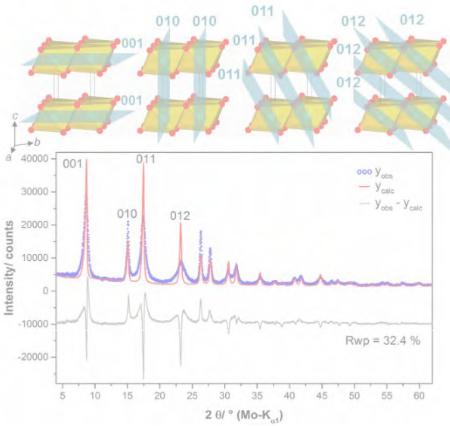
How can we utilize these software features for getting a better understanding of our materials?

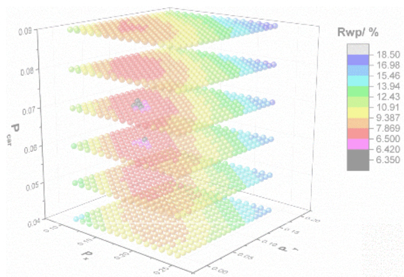
1. Honeycomb Compounds
   a) $H_3LiIr_2O_6$, $Ag_3Li(Ir/Ru)_2O_6$ – derivation of the layer constitution
   b) $Li_3HoBr_{6-x}I_x$ – intra- vs. Interlayer disorder



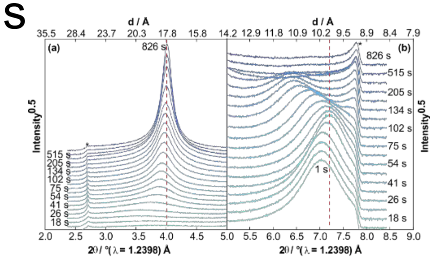


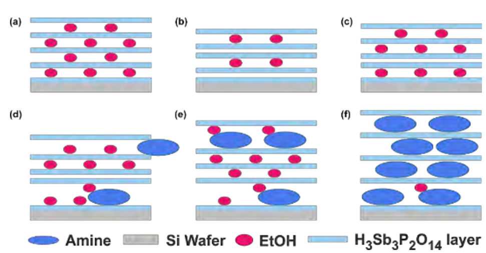
2. Brucite-type materials
   a) NCA precursors – optimization of multiple parameters





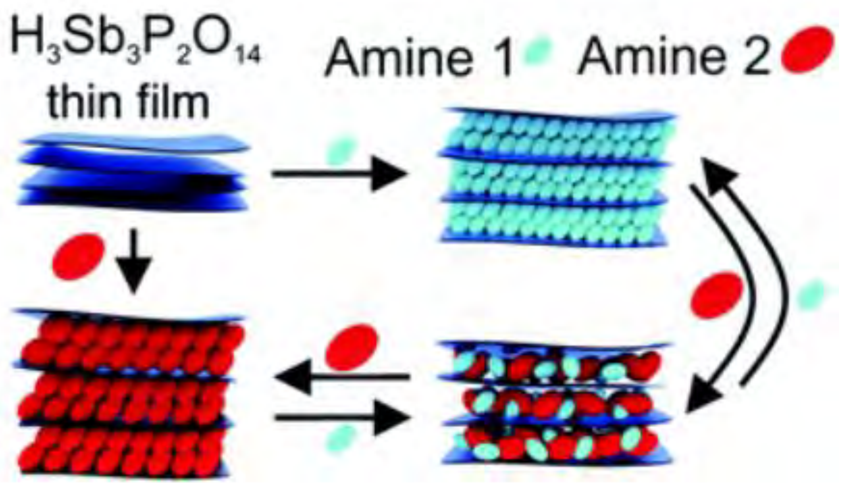
3. Excursus into thin films
   a) spin coated $H_3Sb_3P_3O_{14}$ thin films





4. Conclusions and Outlook

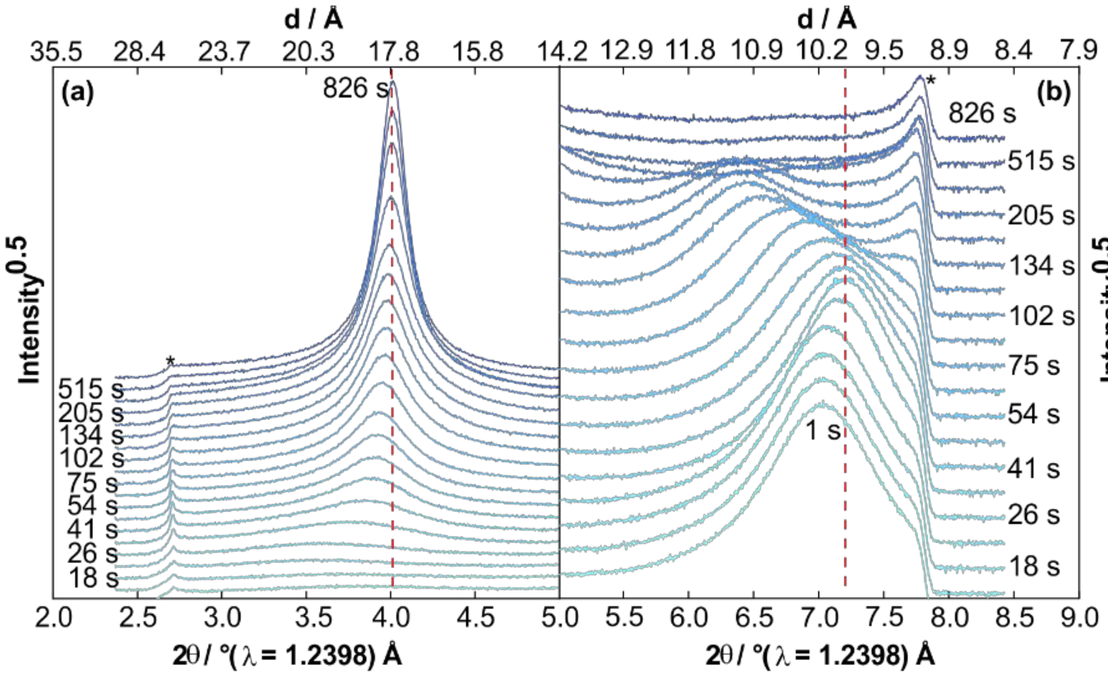
spin coated $H_3Sb_3P_3O_{14}$ thin films

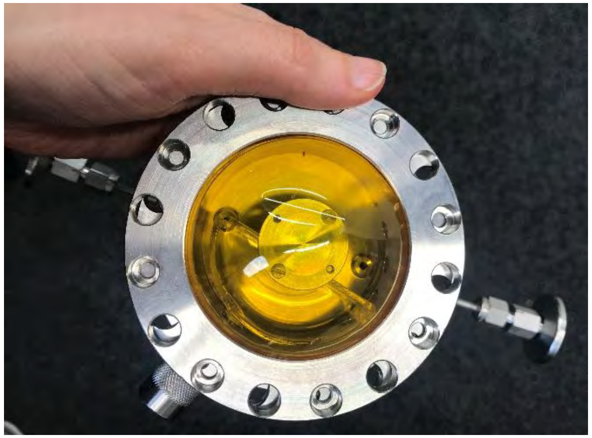


M. Däntl

B.V. Lotsch

- *in situ* monitoring of amin intercalation



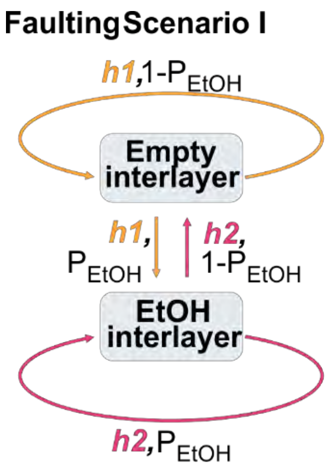


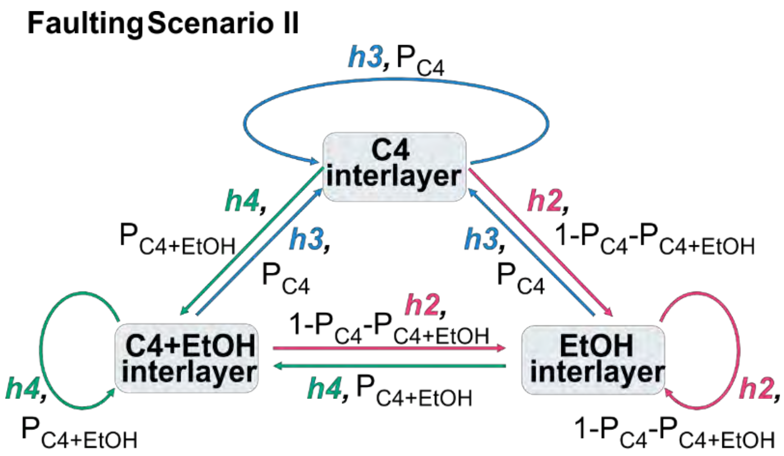
- home built cell, amine dissolved in **EtOH**, intercalation via gas transport

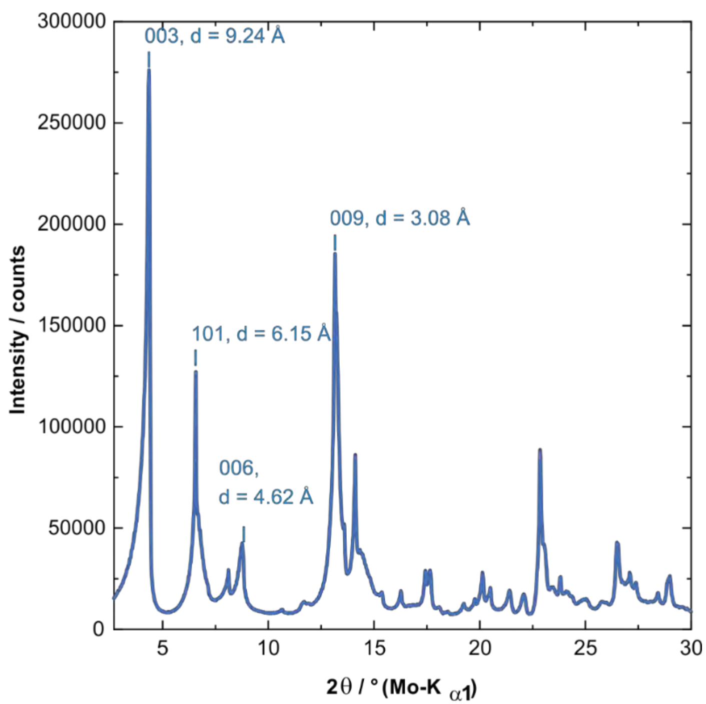
3D-networks and thin films

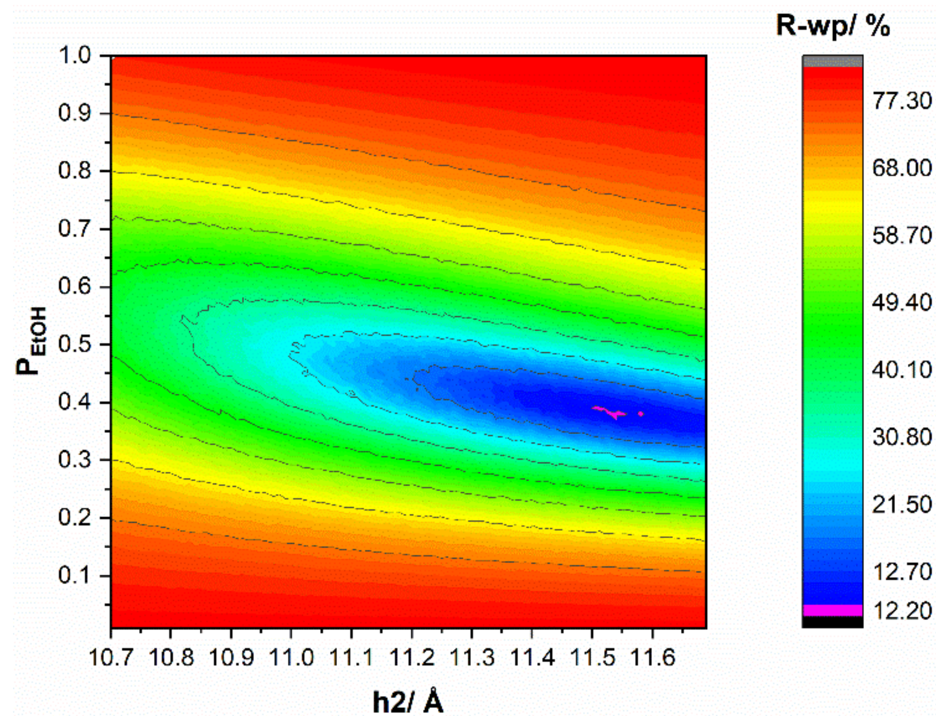
spin coated $H_3Sb_3P_3O_{14}$ thin films

- intercalation of EtOH, amin or of both EtOH and amin possible
- only the interlayer distance of the prestine amin (h1) was known





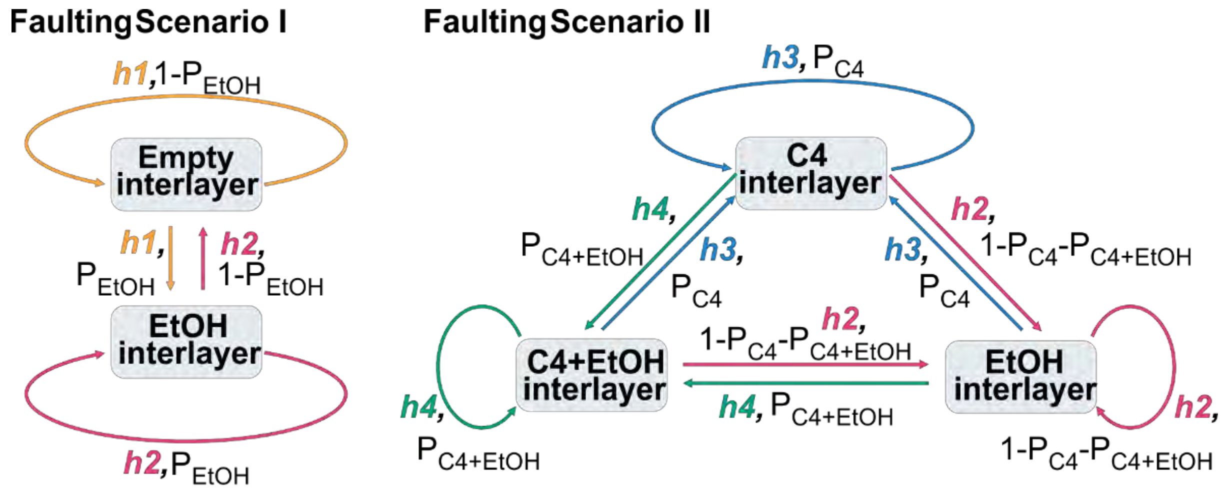


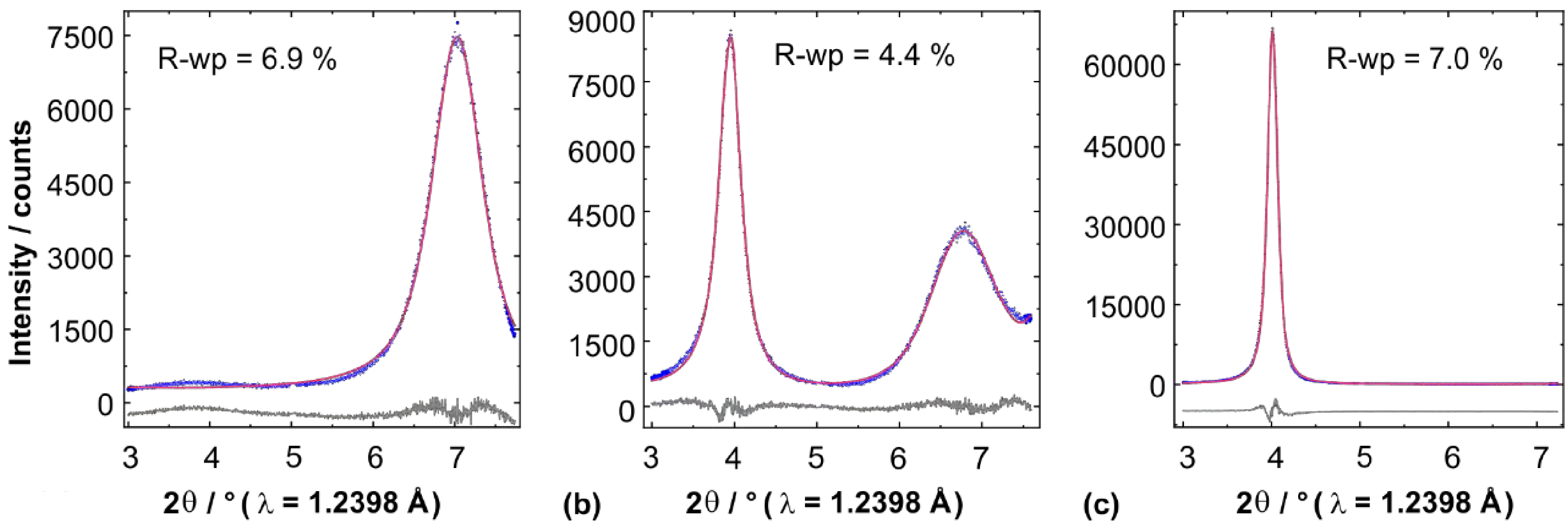


3D-networks and thin films

spin coated $H_3Sb_3P_3O_{14}$ thin films

- after derivation of the interlayer distances all patterns were refined using a two phase model

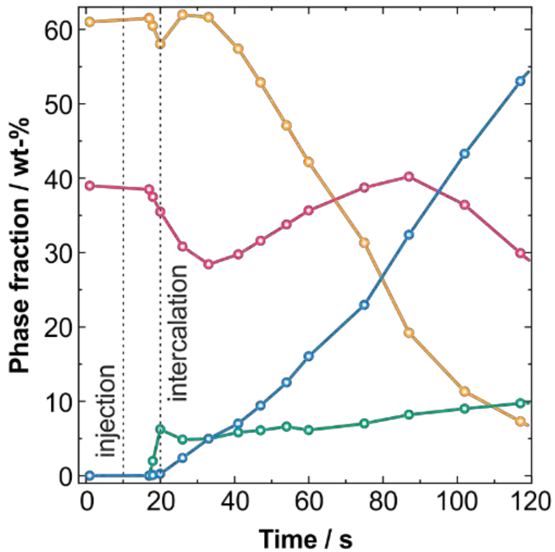


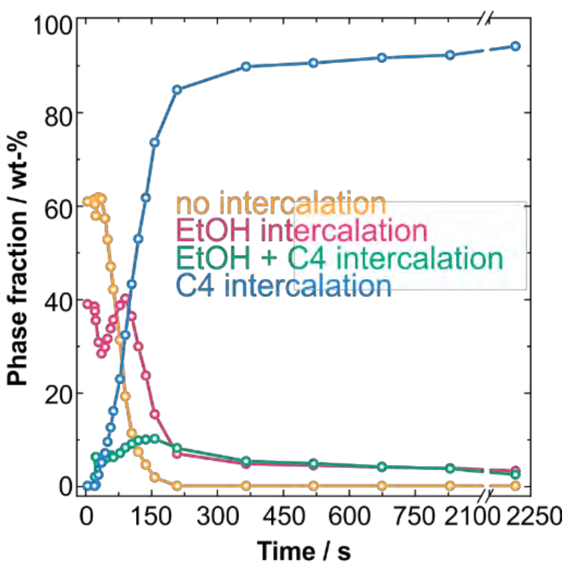


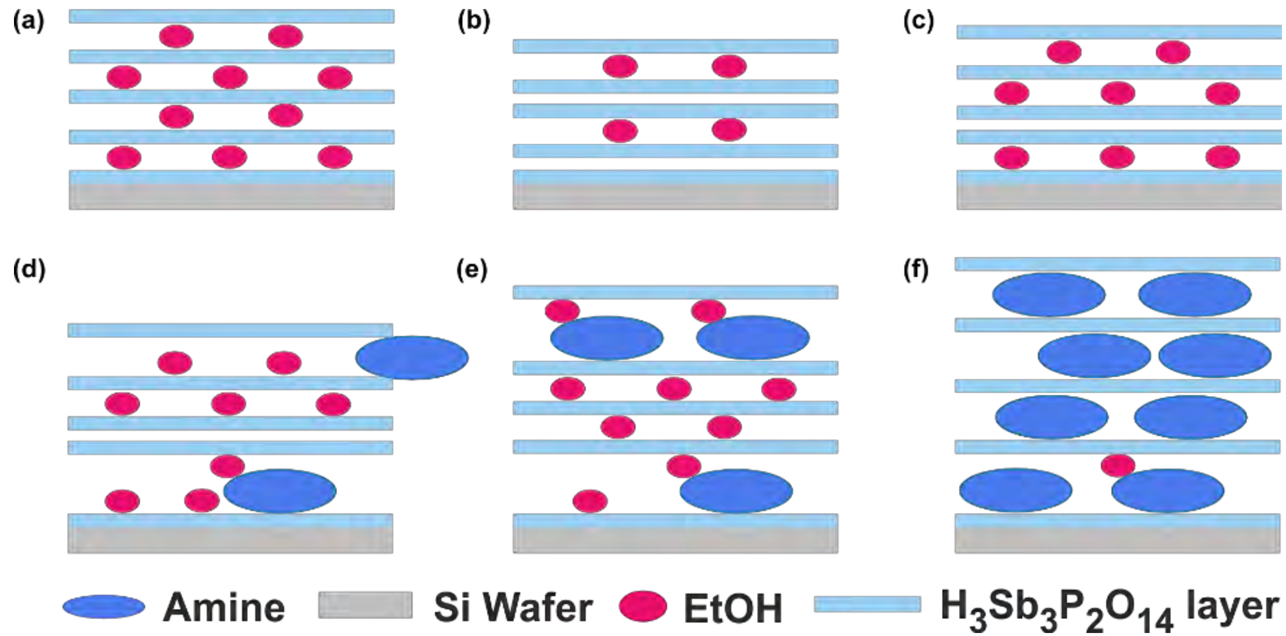
Däntl, M., Maschita, J., Wochner, P., Jiménez-Solano, A.m Vignolo-Gonzalez, H., Putzky, D., Dinnebier, R, E., Bette, S., Lotsch, B.V. *in preparation*

3D-networks and thin films

spin coated $H_3Sb_3P_3O_{14}$ thin films





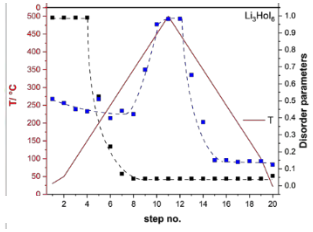


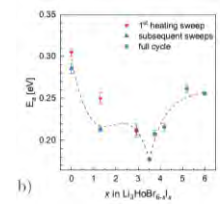
a) initally EtOH is present from spin coating
b) deintercalation of EtOH by evaporation (EtOH)
c) injection amin solution (in EtOH) → EtOH saturation of the atmosphere → EtOH reinterclation
d) intercalation of amin in EtOH intercalated layers
e) extrusion of EtOH from double intercalated layers
f) final state

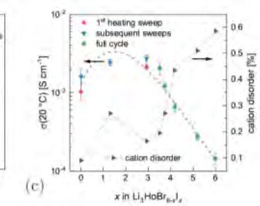
Däntl, M., Maschita, J., Wochner, P., Jiménez-Solano, A.m Vignolo-Gonzalez, H., Putzky, D., Dinnebier, R, E., Bette, S., Lotsch, B.V. *in preparation*

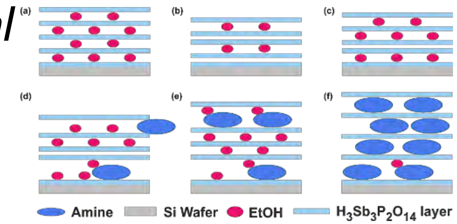
Conclusions and Outlook

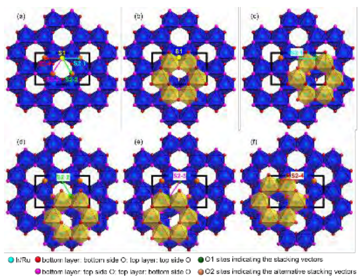
- qualitative and quantitative information on disorder like stacking faults become more and more important to understand *crystal structures, properties* and *chemical processes*











Conclusions and Outlook

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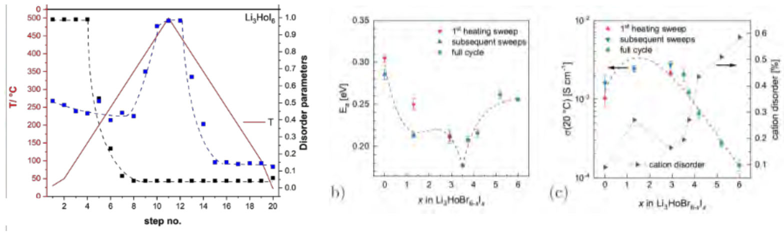
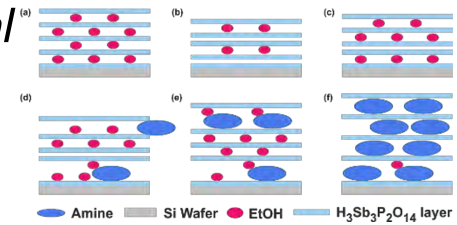
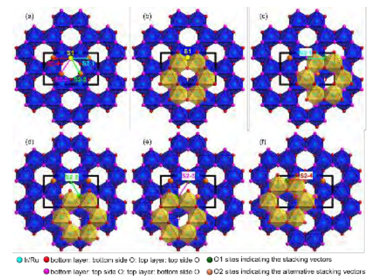
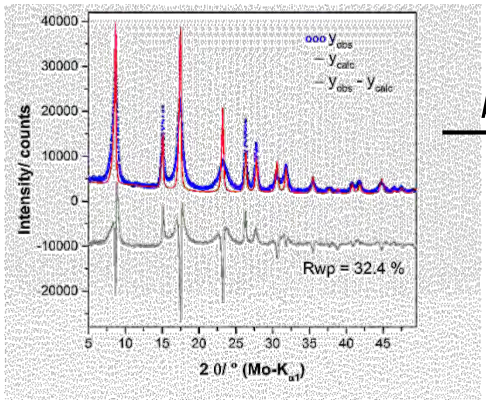






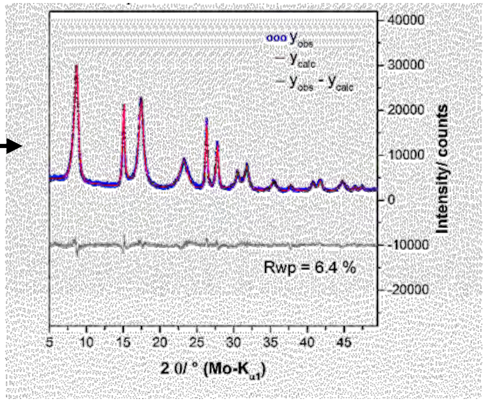
- in an ideal world:



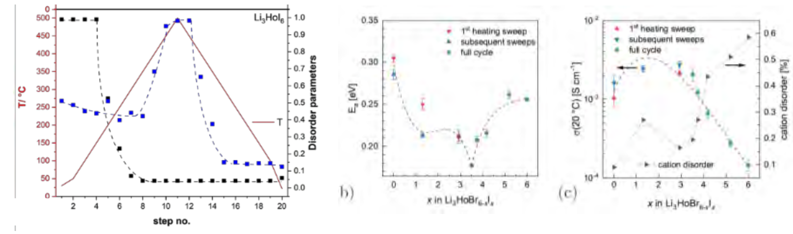
press button

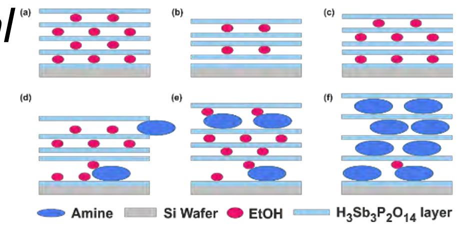
the magic black box

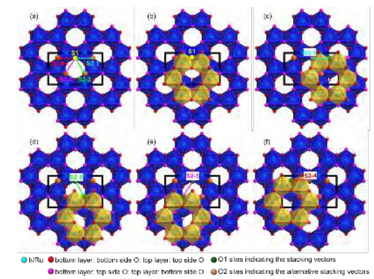
output



Conclusions and Outlook

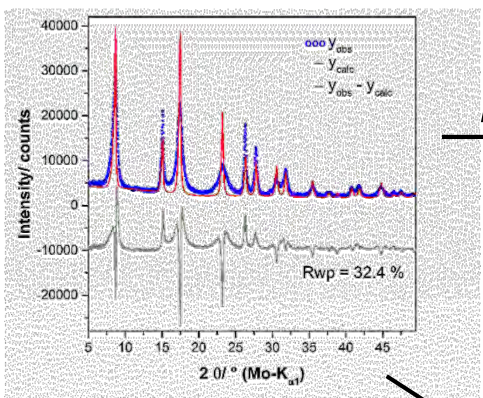






- qualitative and quantitative information on disorder like stacking faults become more and more important to understand *crystal structures, properties* and *chemical processes*

- in an ideal world:



press button

the magic black box

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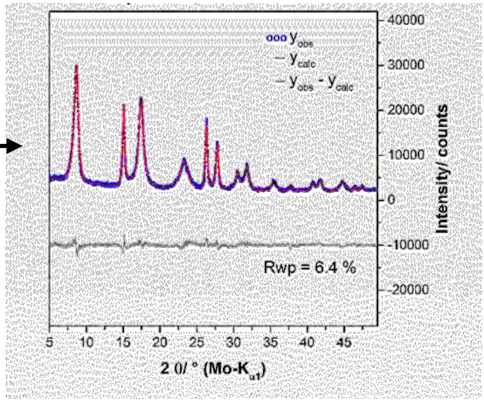
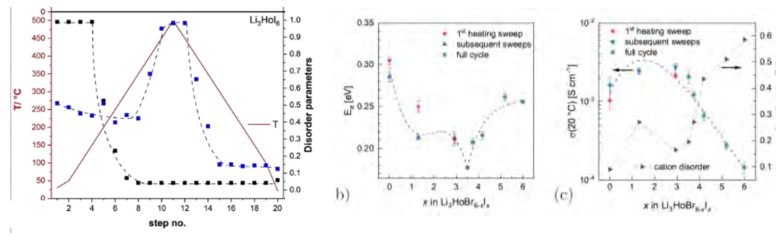


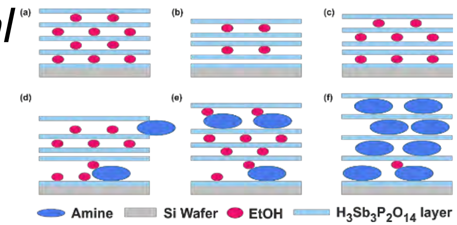
- the real world:

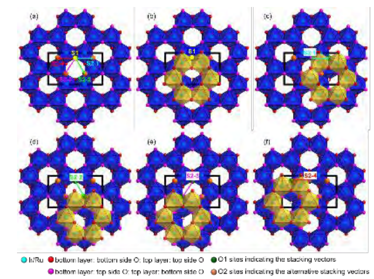
derive layer constitution, stacking vectors, …

Conclusions and Outlook

- qualitative and quantitative information on disorder like stacking faults become more and more important to understand *crystal structures, properties* and *chemical processes*

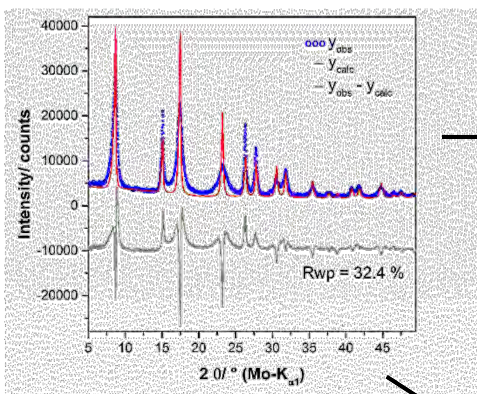






- in an ideal world:

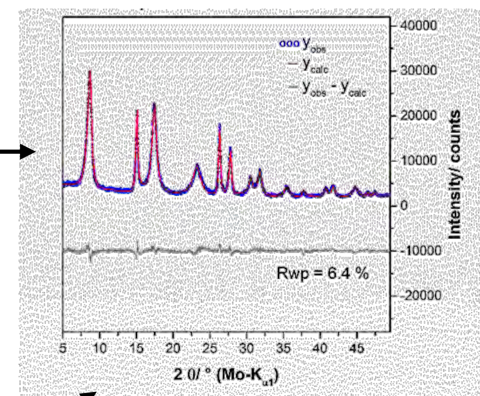
We are getting closer!



press button

the magic black box

output



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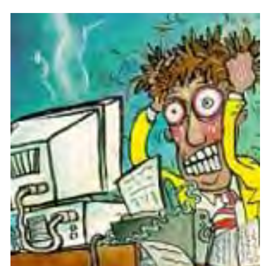
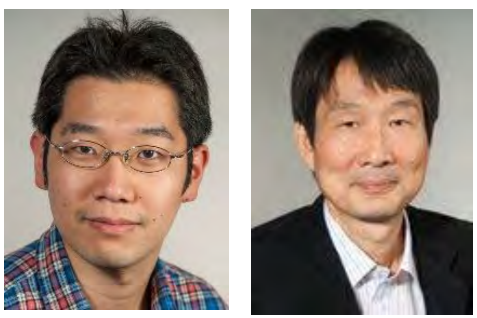


adapt already known routines

Acknowledgement

Max-Planck-Institute
for Solid State Research



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BASF
We create chemistry

A.A. Coelho

Thank you for your attention!