H2020-MSCA ITN
Grant n. 956099

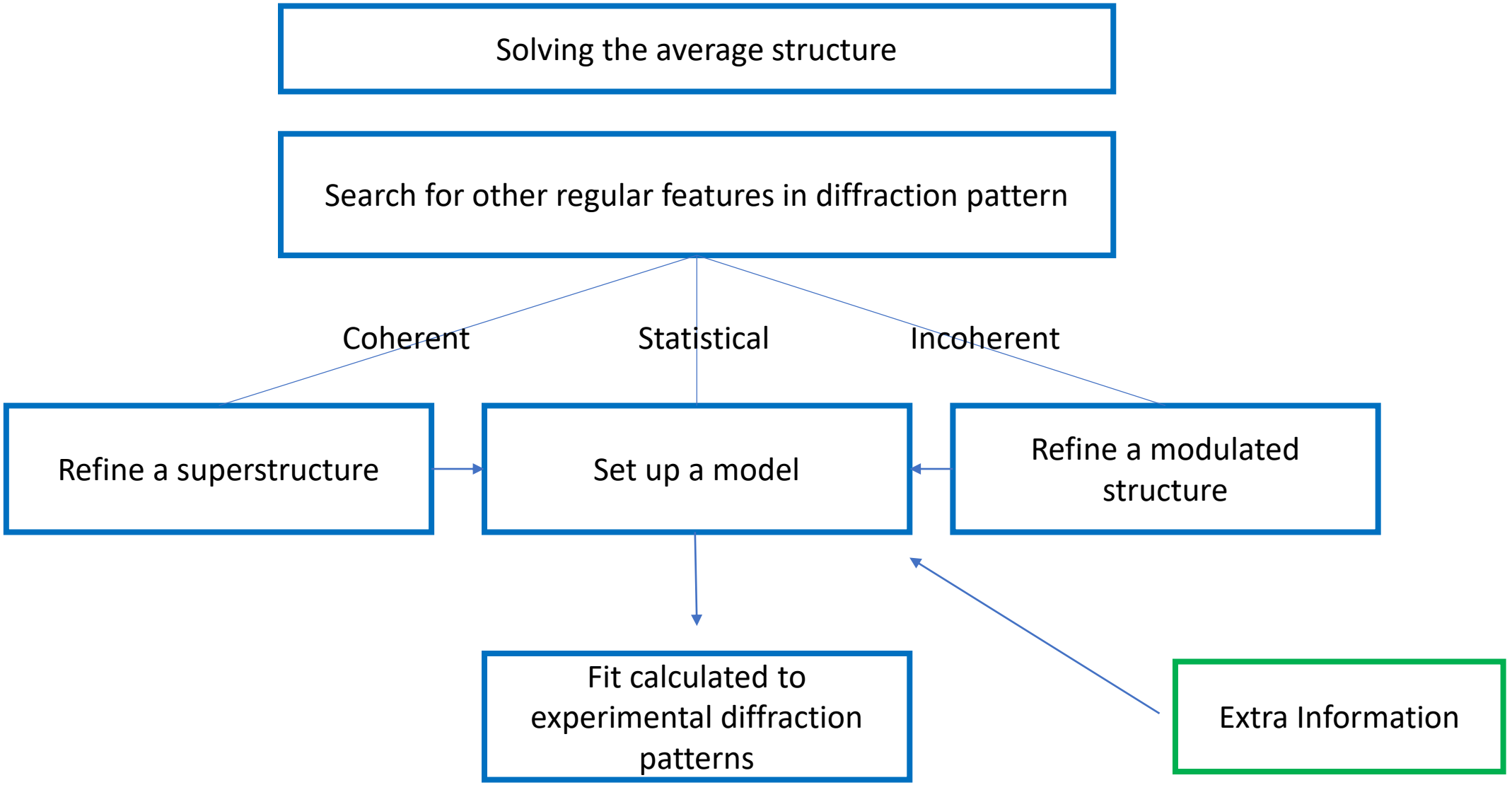
JOHANNES GUTENBERG UNIVERSITÄT MAINZ

Electron Microscopy Centre Mainz EMC-M

3D ED on defect structures

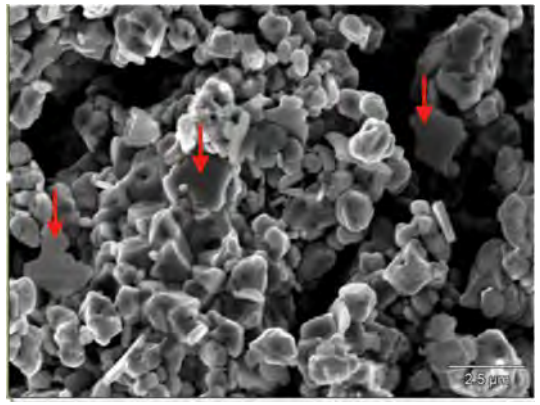
Ute Kolb – University Mainz, Germany

Diffuse scattering – a general path



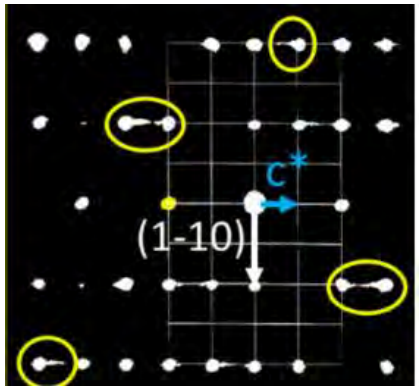
High pressure oxynitride $SnGe_4N_4O_4$

Philipp Gollé Leidreiter in Cooperation with Prof. Riedel Darmstadt

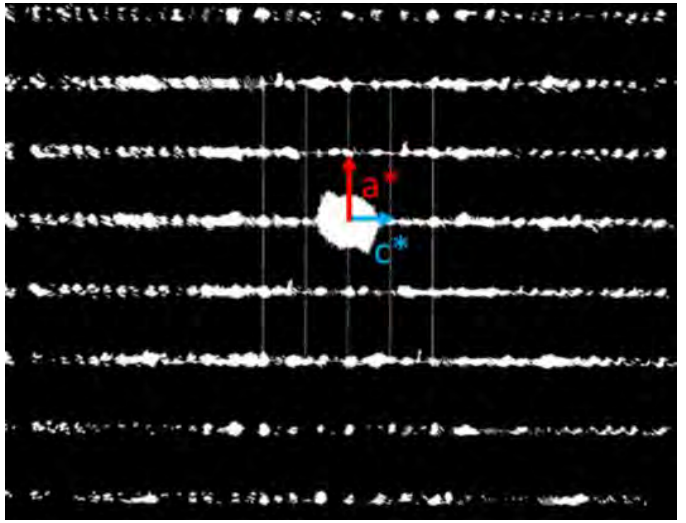


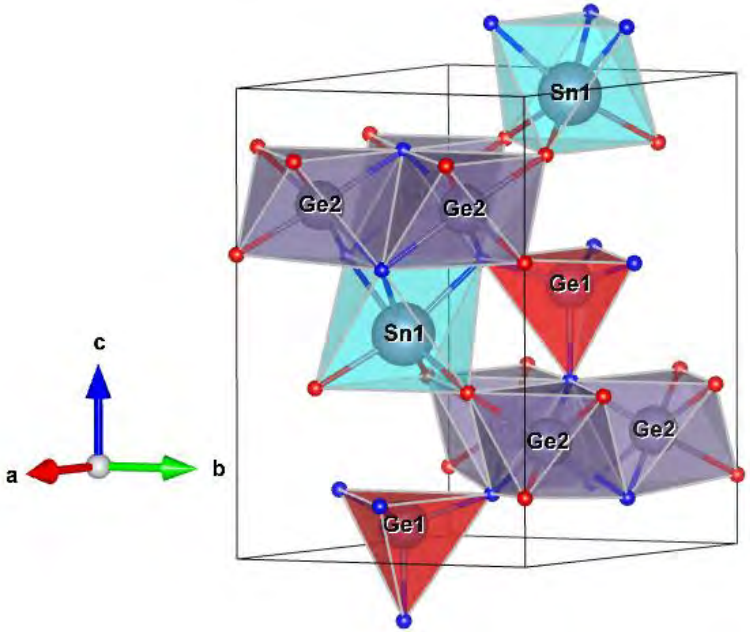
Ge rich crystals selected by EDXS

Sample HH228



Sample HH266

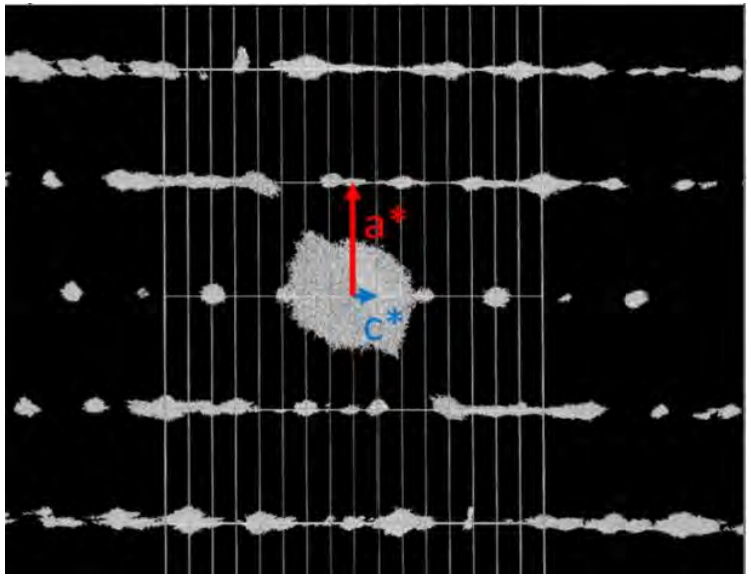




Space group: $P6_3cm$
Structure type: Nolanite
Sequence: ABAC

Rhombohedral phase

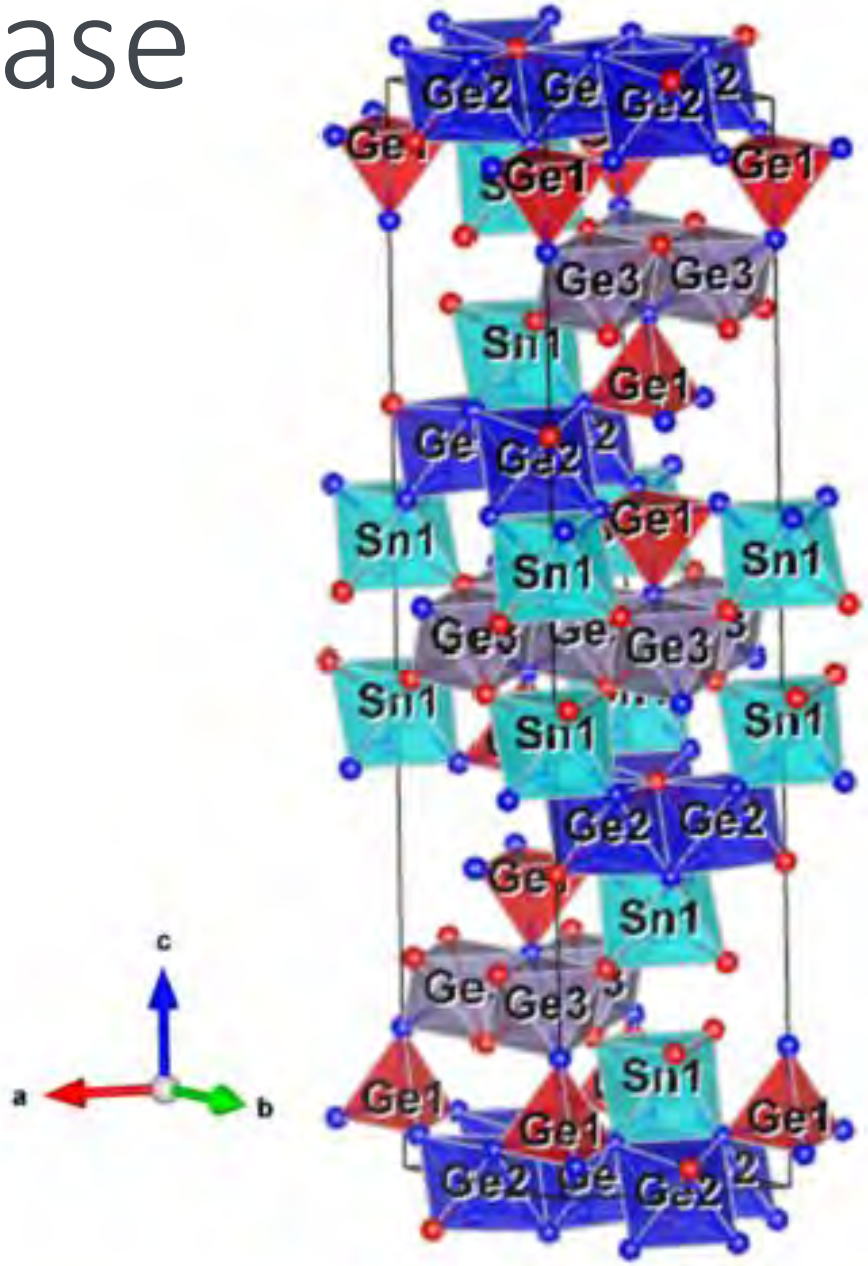
Sample HH266



3*c, a and b sligthly smaller

Space group R -3m

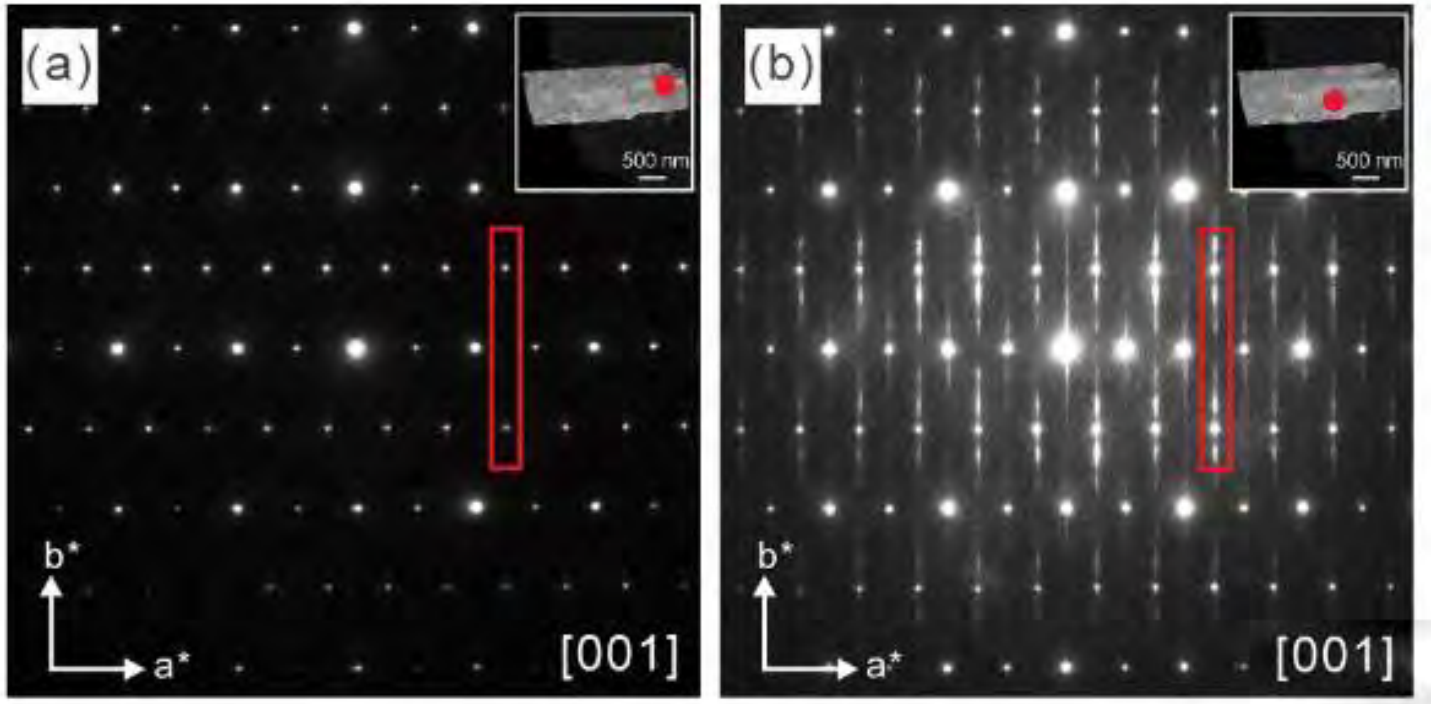
6R polytype of Nolanite structure

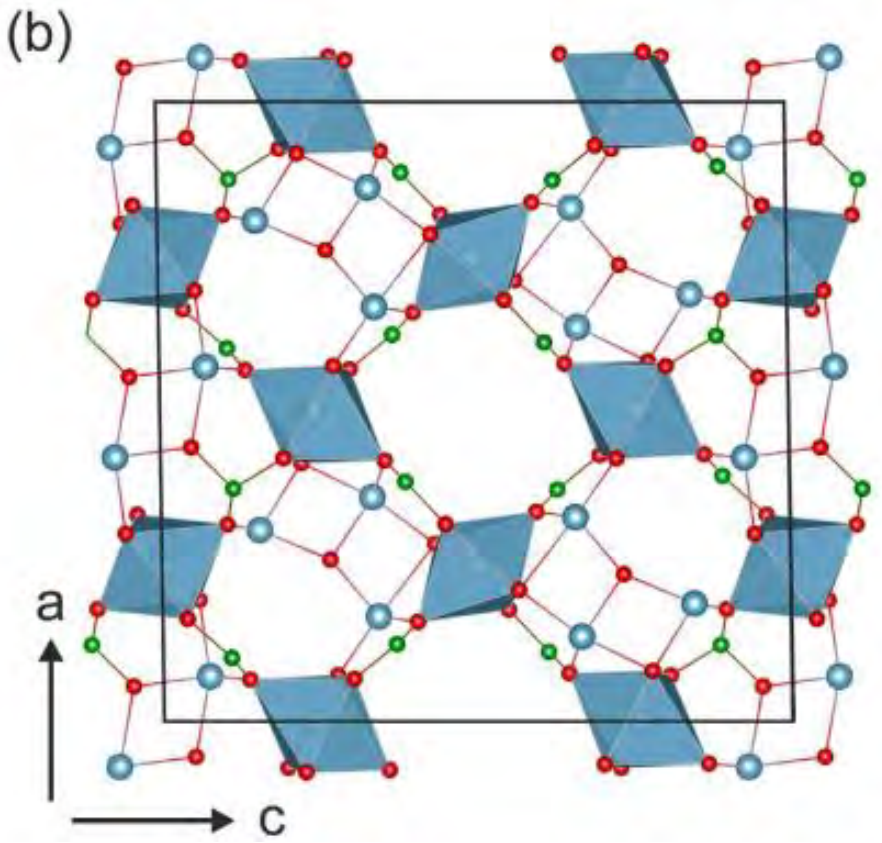


2 Layers of Nolanite
1 Layer of Spinel

Stacking sequence:
AB-ABC-AC-ABC-BC

Solving the average crystal structure of $Al_4B_2O_9$

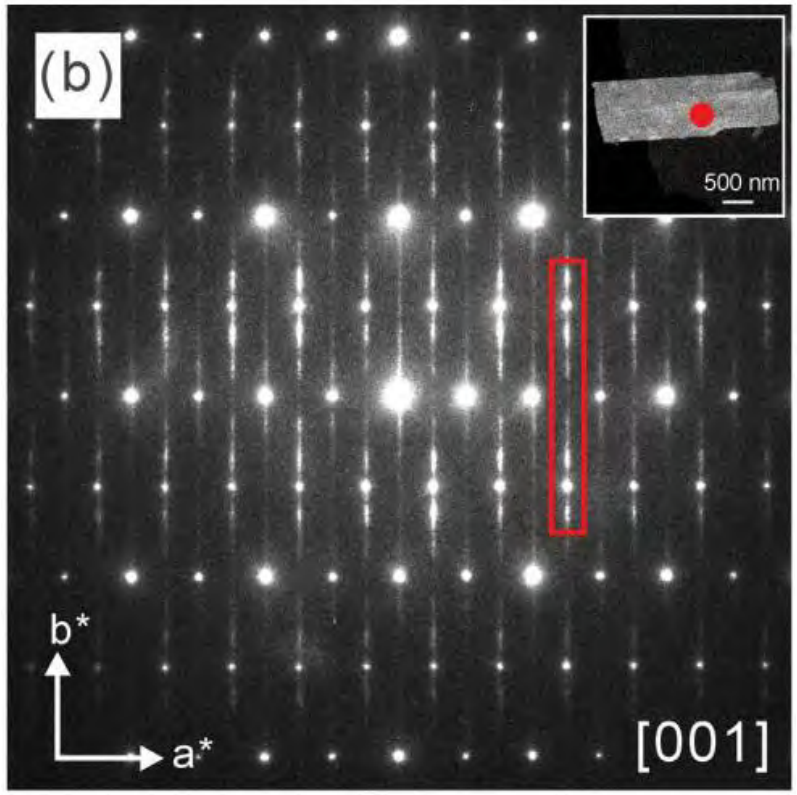


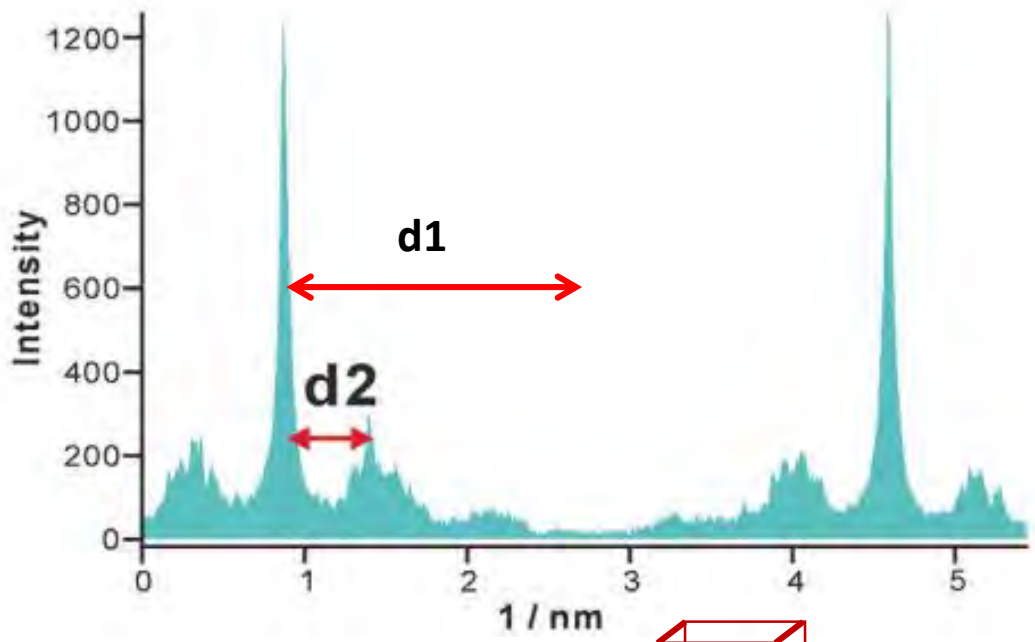


Structure solution from both data sets (ignoring diffuse scattering)

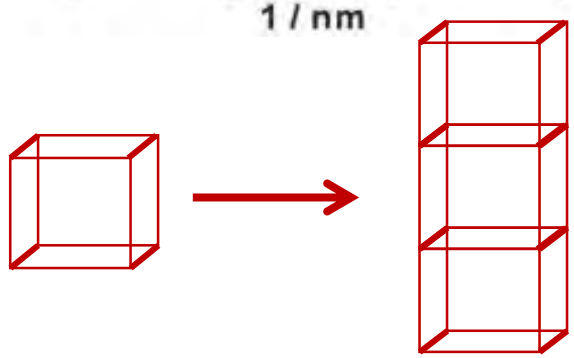
H. Zhao et al.; Journal of Solid State Chemistry 249 (2017) 114–123

Superstructure – Using additional maxima





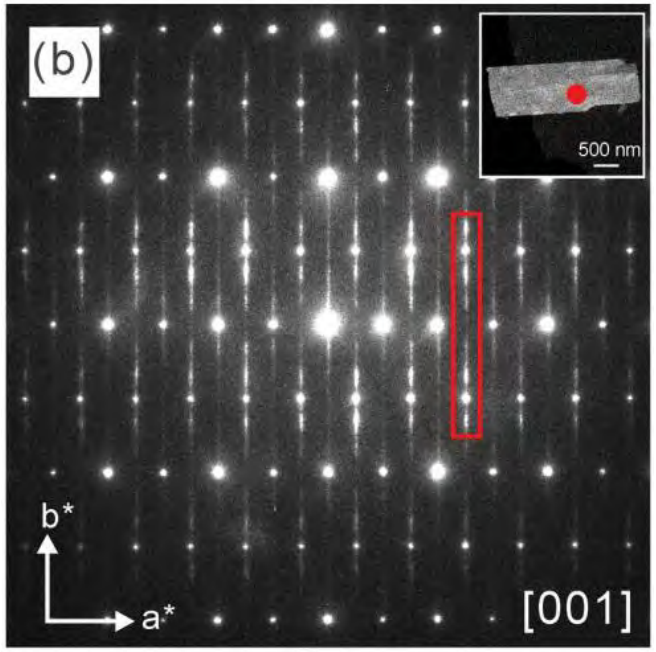
Zhao 2017



$$d_2 = \frac{1}{3} d_1 \quad \rightarrow \text{ 3-fold superstructure}$$

H. Zhao et al.; Journal of Solid State Chemistry 249 (2017) 114–123

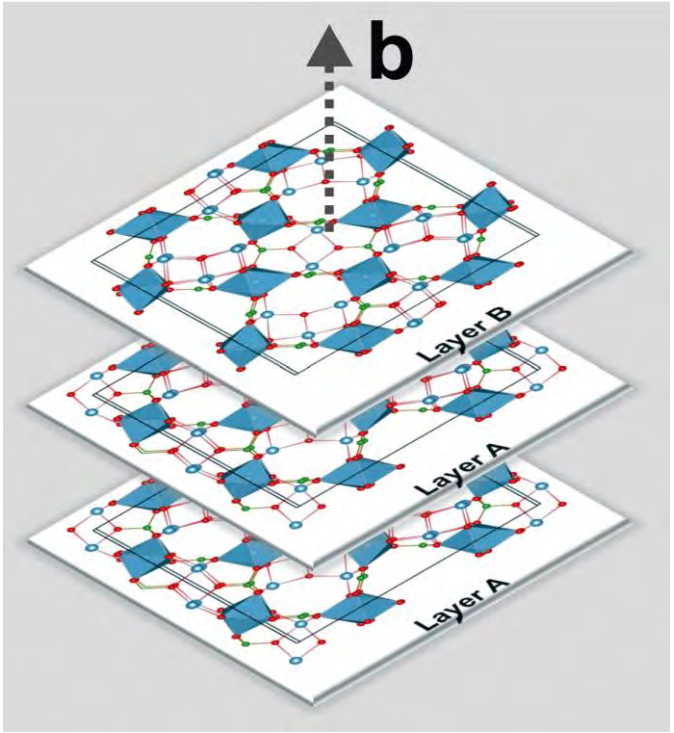
Diffuse scattering



eADT:
data reconstruction
and processing

Model set-up:
MatStudio/Vesta

DISCUS: simulation of
electron diffraction



Shift ½ a* + ½ c*

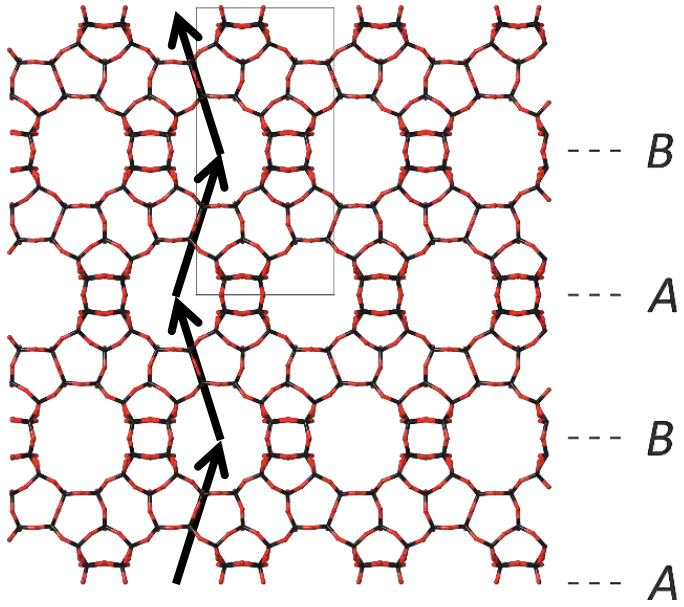
H. Zhao et al.; Journal of Solid State Chemistry 249 (2017) 114–123

For comparison: X-Ray diffuse scattering in Mullite: Shift 1/3 a* + ½ c*

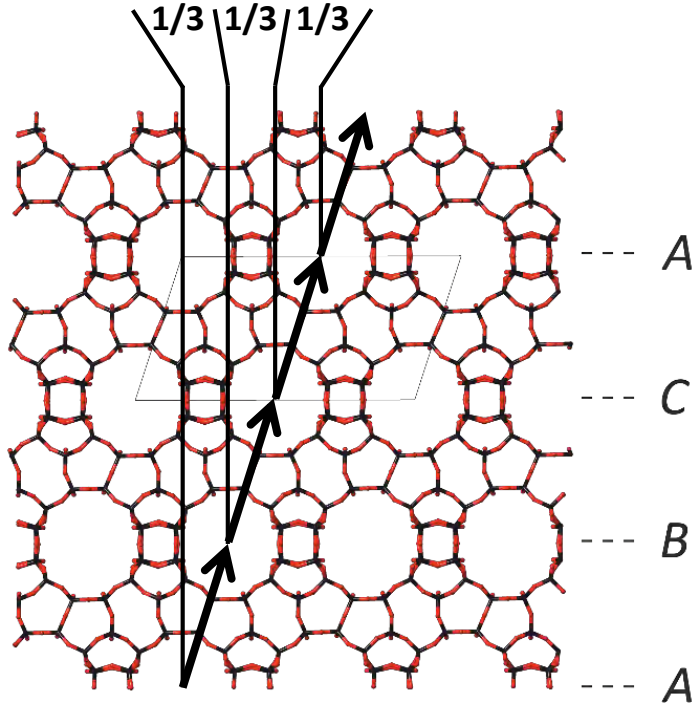
B. D. Butler, T. R. Welberry, & R. L. Withers, Phys Chem Minerals 20, 323 (1993)

Model sample – Zeolite Beta

Stacking faults in Zeolite Beta due to intergrowth of A and B polymorph



Polymorph A (BEA):
$P4_122$ or $P4_322$
a = 12.66 Å
c = 26.41 Å

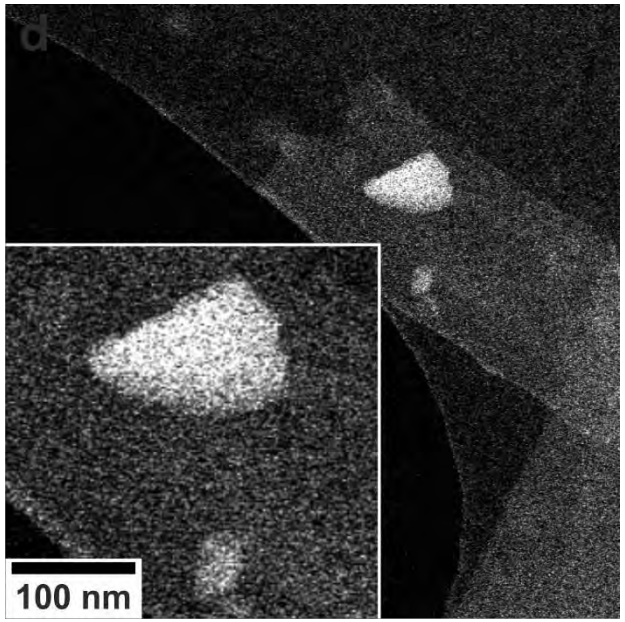


Polymorph B (BEB):
$C2/c$
a = 17.90 Å, b = 17.92 Å
c = 26.41 Å, β = 114.8°

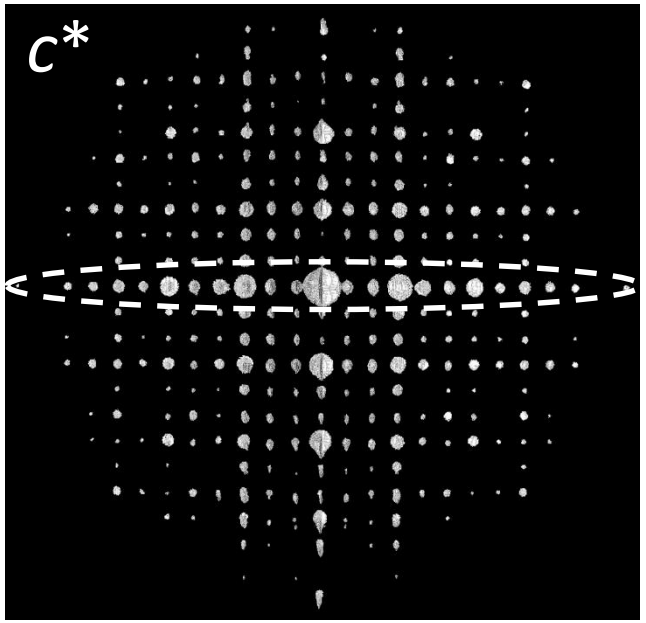
Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

Structures: J. M. Newsam et al. **1988** and Higgins et al. **1988**.

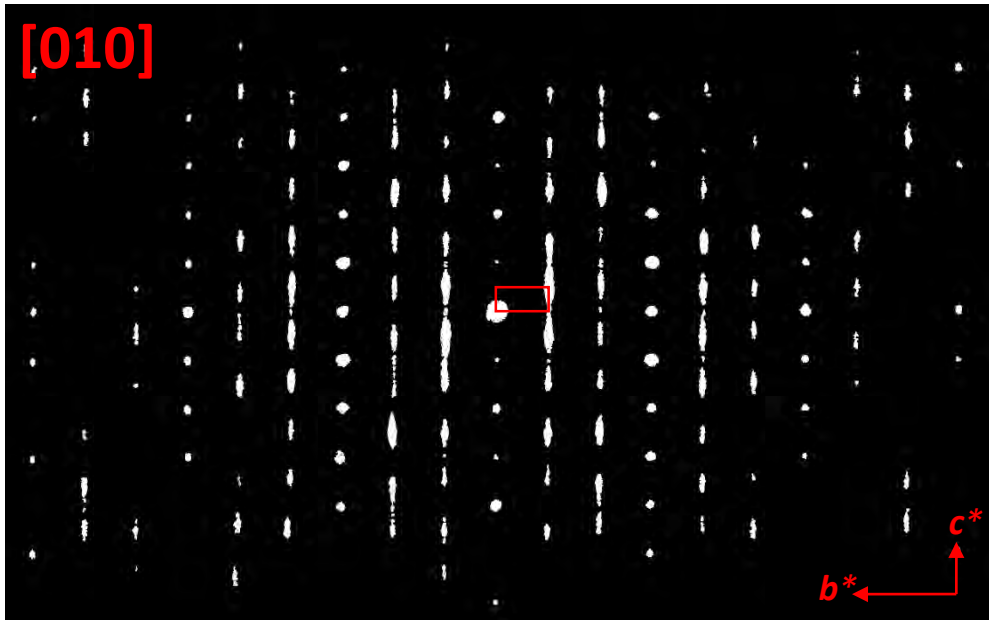
Quantitative approach – model system Zeolite Beta



µm-STEM Image



3D volume ADT-Data

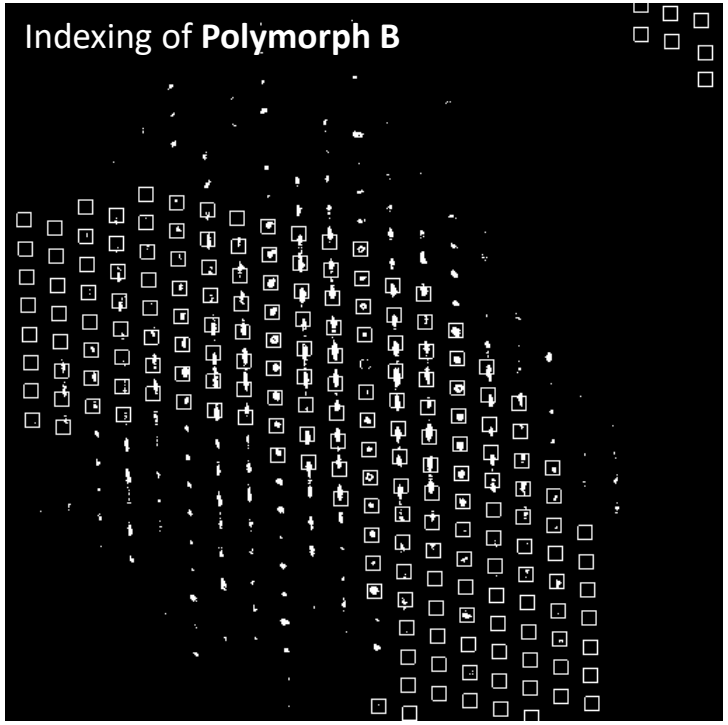


Cut of crystallographic zone

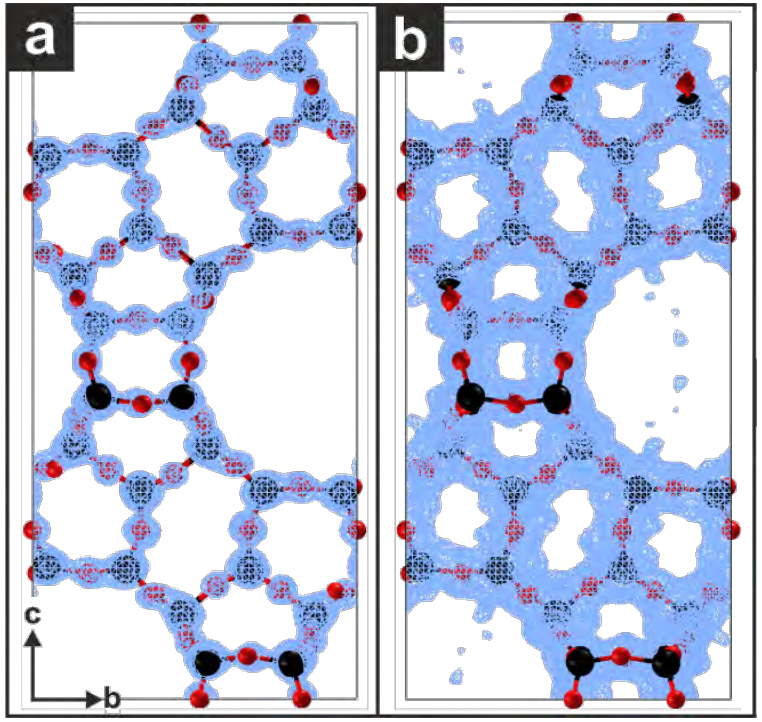
- *h*0*l* Reflections, *h* = 3n sorted along ***c****
- *h* ≠ 3n diffuse streaks parallel ***c****
- 0*kl*-Zone: Only *k* = 3n refelctions ordered

Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

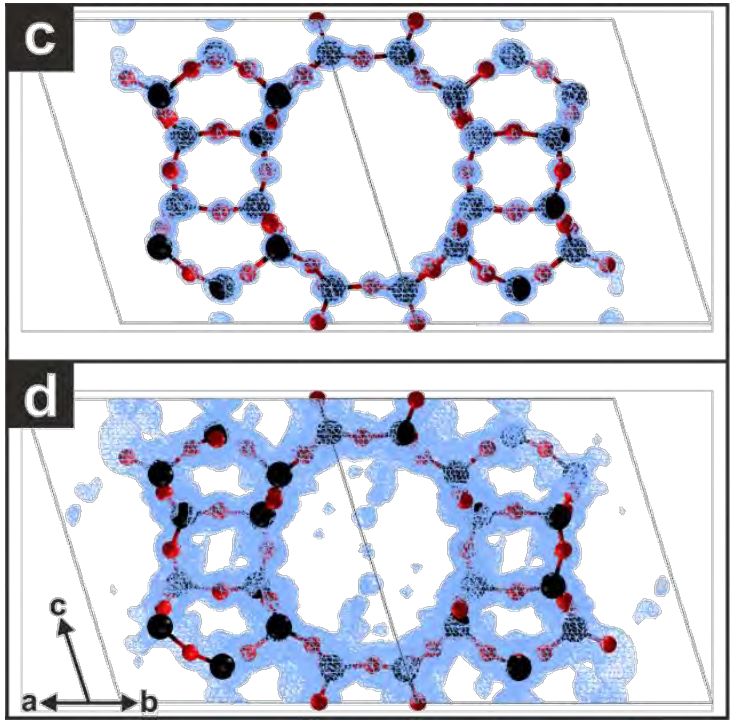
Average crystal structure solution of Zeolite Beta



$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 2/3 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$



Zeolite Beta A: potential map along [100]
Tetragonal



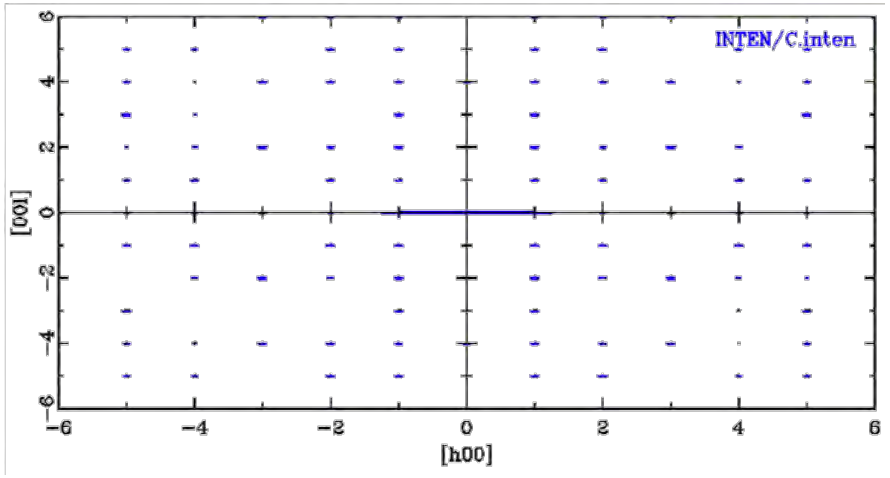
Zeolite Beta B: potential map along [110]
orthorhombisch

Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

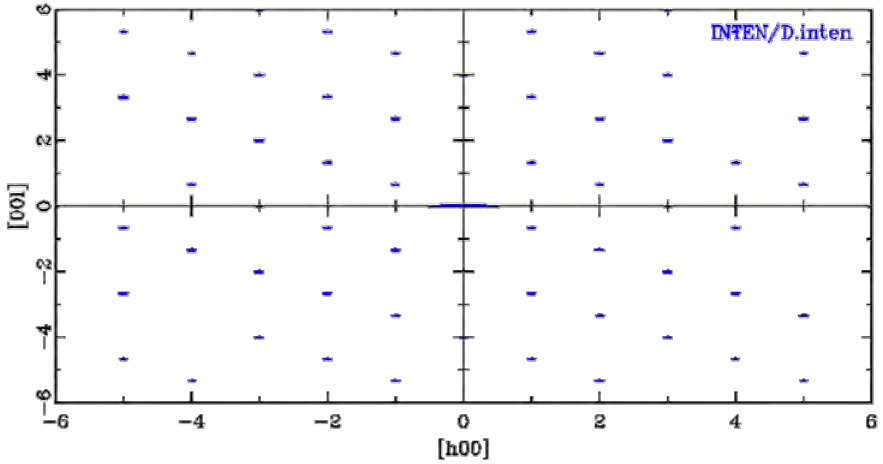
SIR2014, Burla et al., *J. Appl. Cryst.* **2015**, 48, 306-309.

Model sample – DISCUS simulation

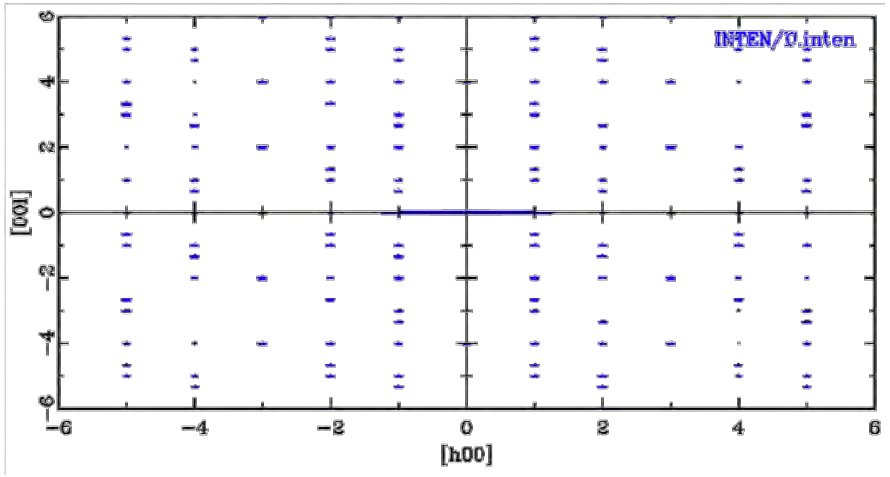
Polymorph A - tetragonal



Polymorph B - monoklin



Twinning – **ordered** → **discrete** reflections

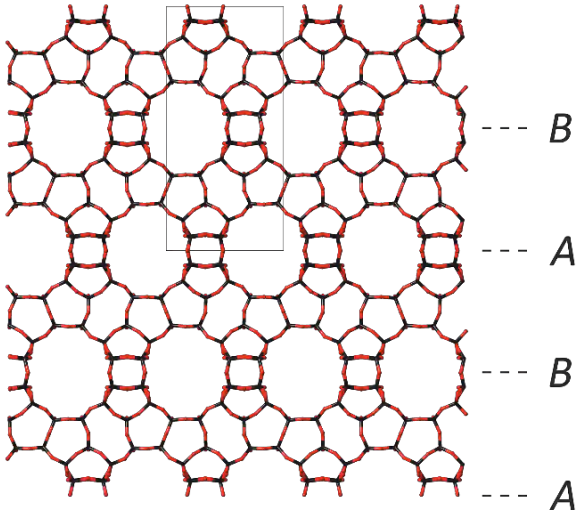


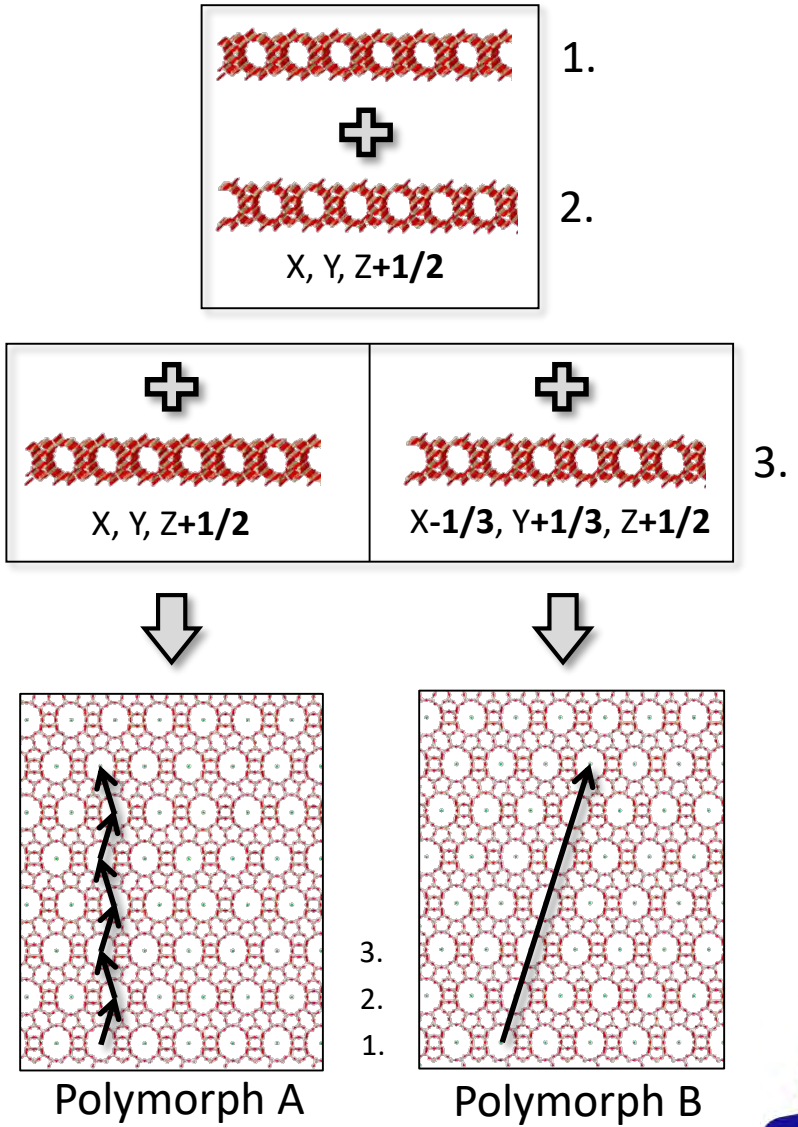
Disorder

Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

DISCUS: Th. Proffen, R. B. Neder, *J. Appl. Cryst.* **1997**, 30, 171-175.

Building up a model – Zeolite Beta



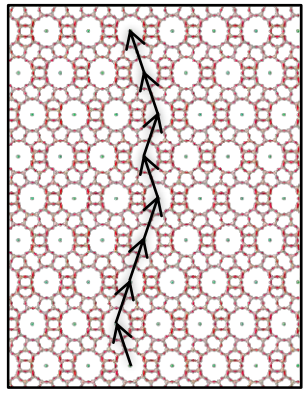


- Take two layers (*A*, *B*) aus BEA-Structure
- Inhomogenous layers separated by vector [0, 0, 1/2]
- Homogenous layers separated by vector [-1/3, 1/3, 1/2]
- Vary layer size and stacking lengths
- Probability for stacking event (1-*p* homogen, *p* inhomogen)

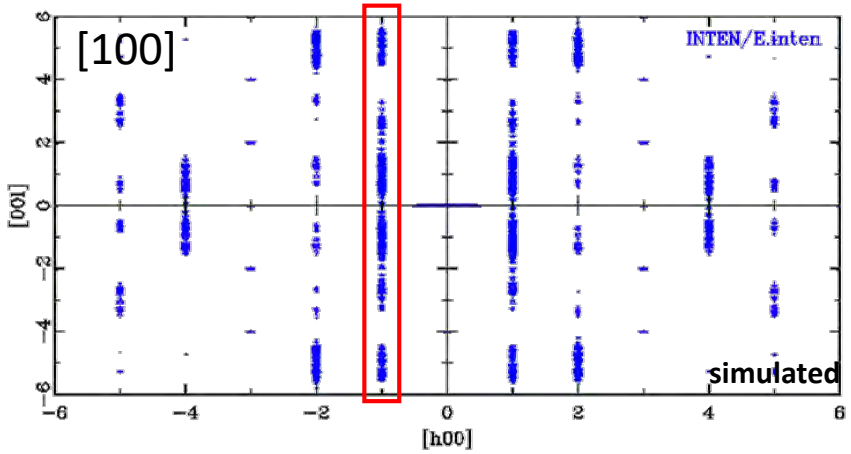
Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

Simulation and Experiment – Zeolite Beta

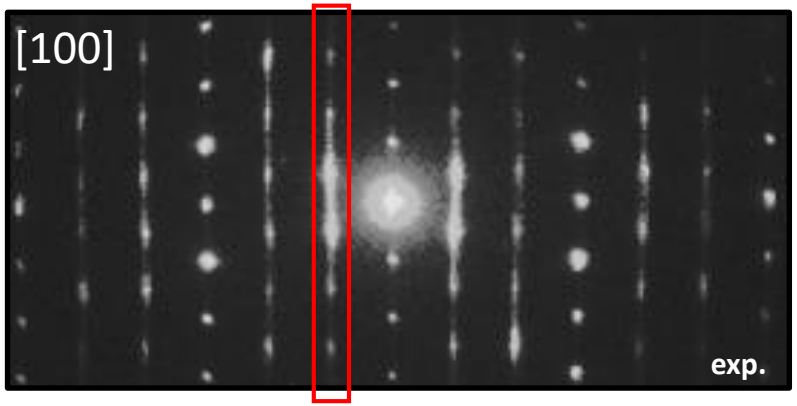
- Simulation of electron diffraction with DISCUS based on random stacks → **Comparison** with exp. Data (eADT)

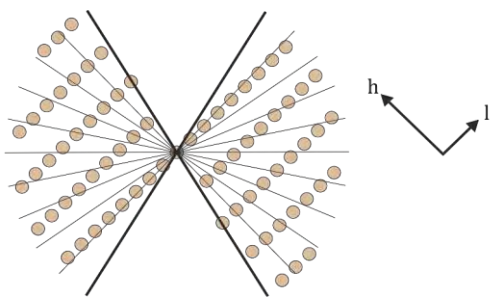


Beugung

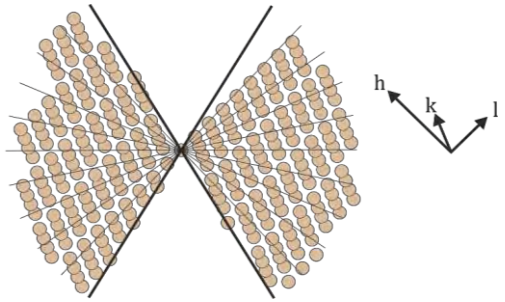


Comparison



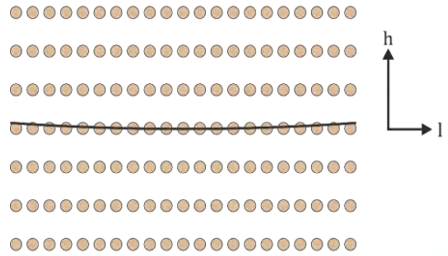


Zone recorded inside the tilt series



Zone randomly oriented

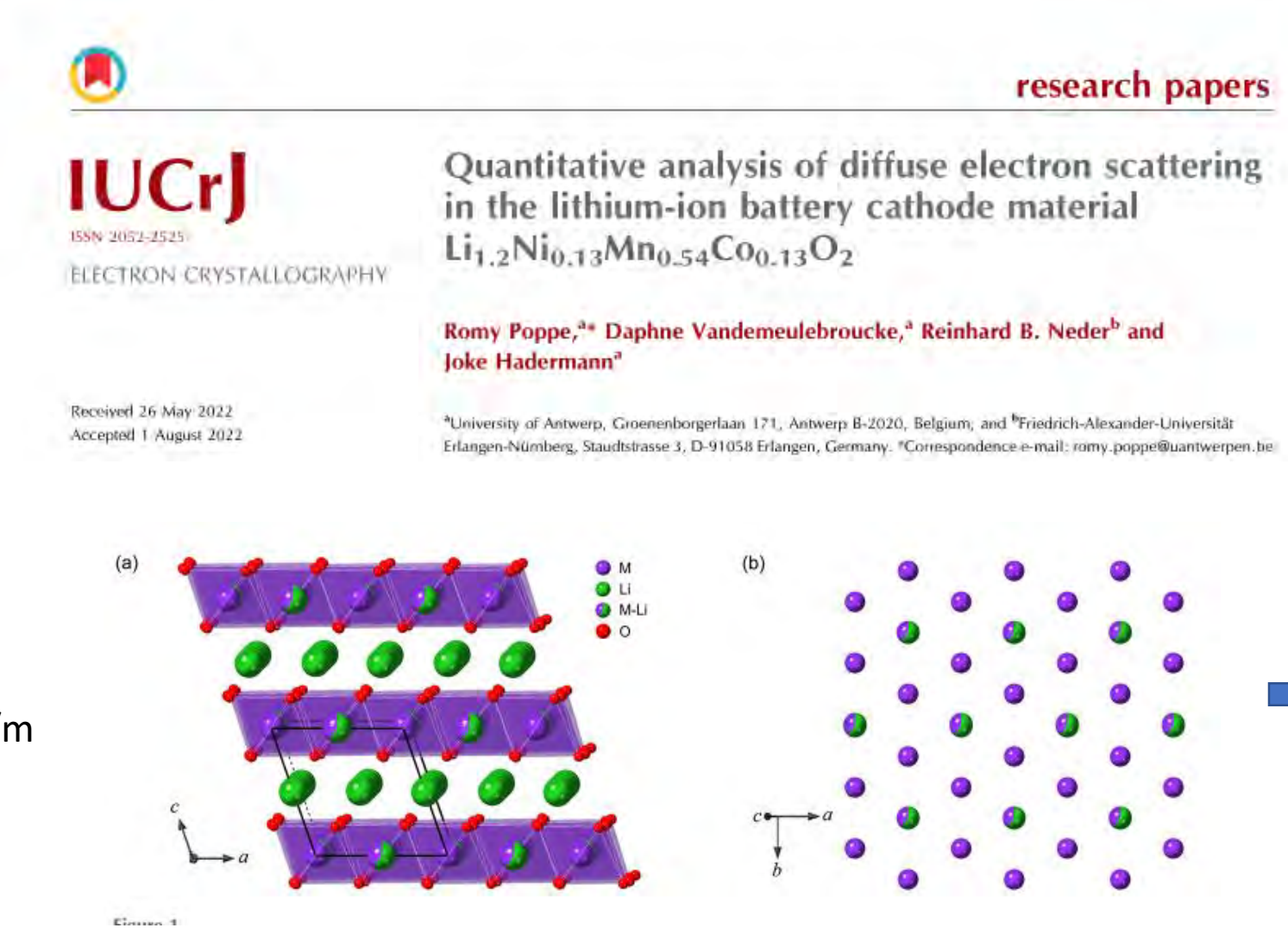
diffuse scattering



Oriented zone

Yasar Krysiak, Acta Cryst. (2018). A**74**, 93–101

Li-Ion battery cathode material



research papers

IUCrJ

ISSN 2052-2525

ELECTRON CRYSTALLOGRAPHY

Quantitative analysis of diffuse electron scattering in the lithium-ion battery cathode material $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$

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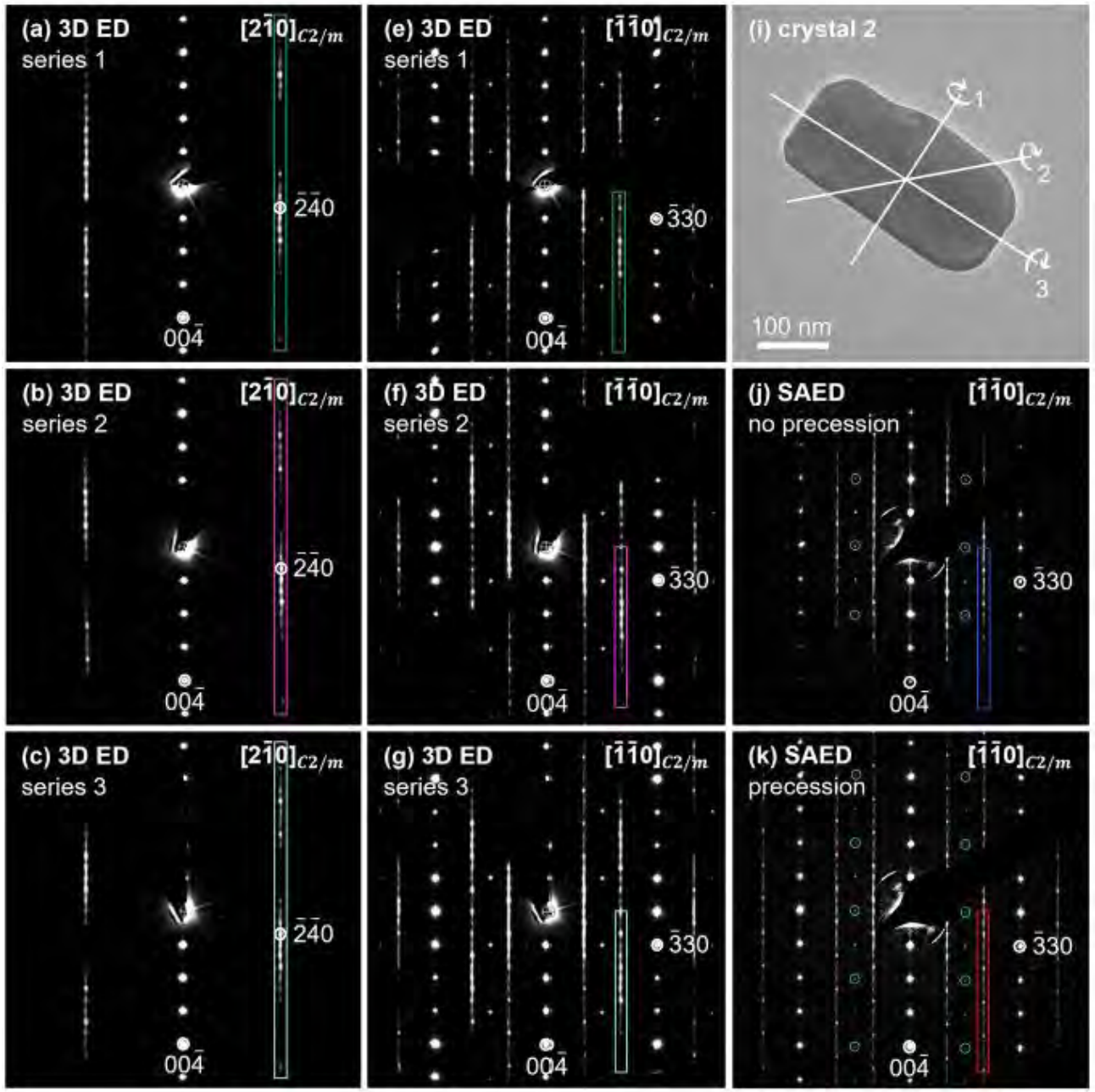
Figure 1

Sapce group: C2/m

→ Threefold twinning

A question for you:



Thermoelectrics $Cu_{2+x}Mn_{1-x}GeS_4$ (x=0-0.5)

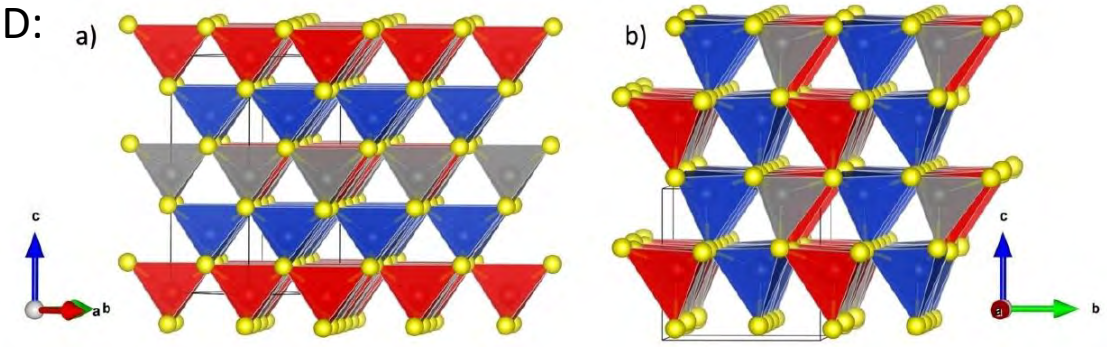
VIP Thermoelectrics Very Important Paper

How to cite: *Angew. Chem. Int. Ed.* **2022,** *61,* e202210600
International Edition: doi.org/10.1002/anie.202210600
German Edition: doi.org/10.1002/ange.202210600

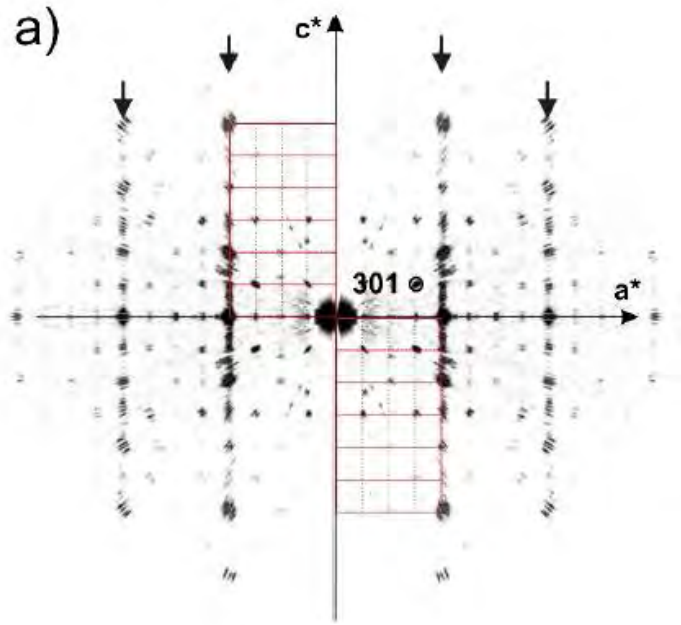
Engineering Transport Properties in Interconnected Enargite-Stannite Type $Cu_{2+x}Mn_{1-x}GeS_4$ Nanocomposites

*V. Pavan Kumar, S. Passuti, B. Zhang, S. Fujii, K. Yoshizawa, P. Boullay, S. Le Tonquesse, C. Prestipino, B. Raveau, P. Lemoine, A. Paecklar, N. Barrier, X. Zhou, M. Yoshiya, K. Suekuni, and E. Guilmeau**

PXRD:



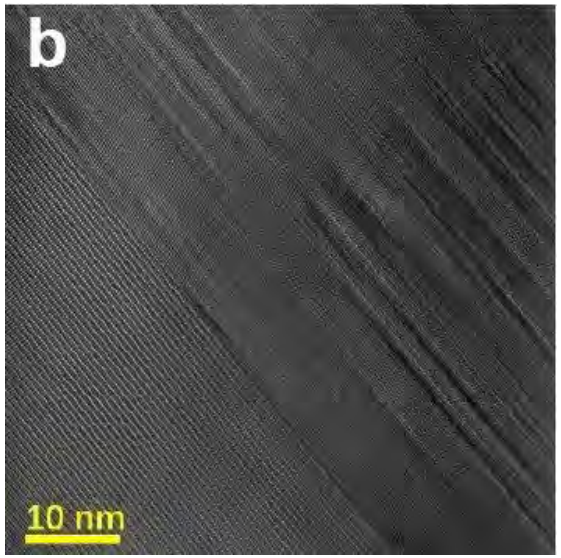
Enargite $Pmn2_1$ Stannite I-42m

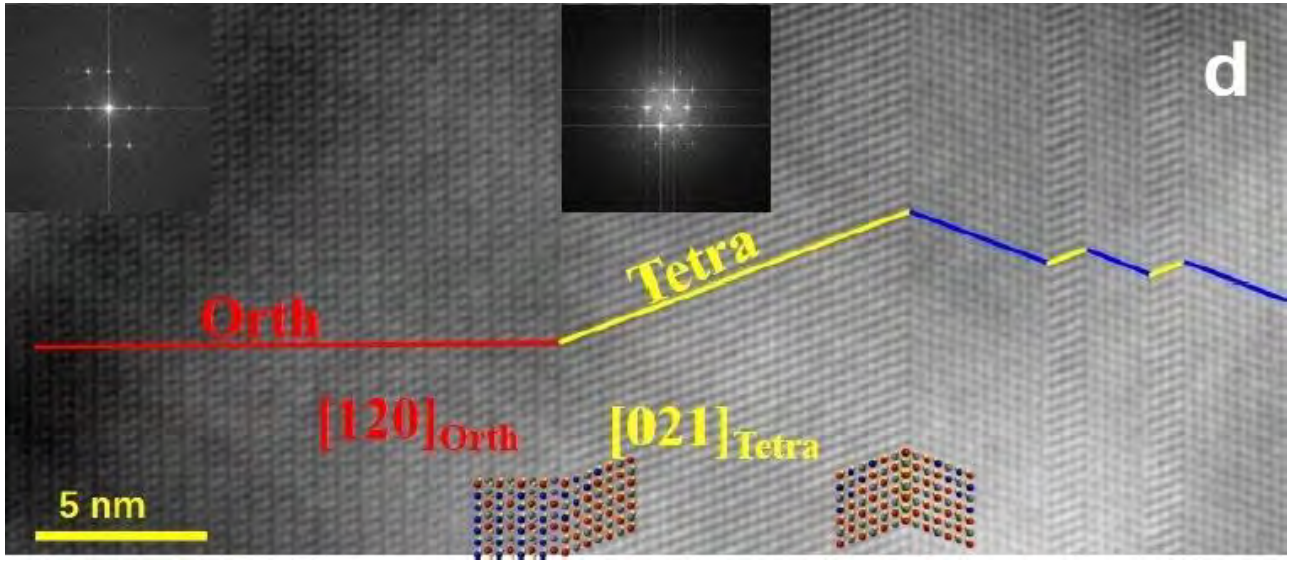


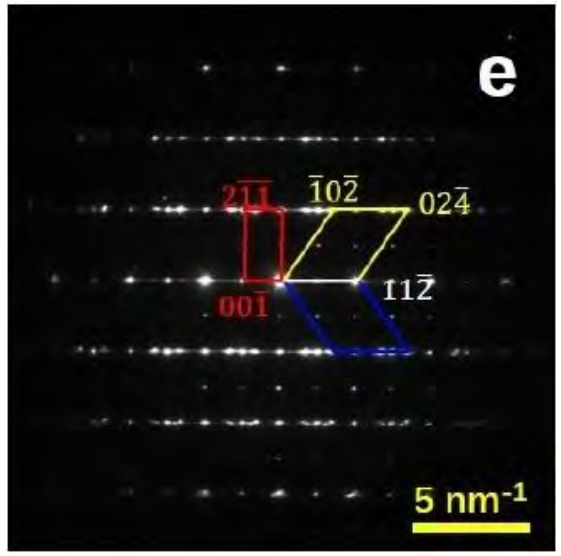
Structure solution 3DED
Diffuse lines h-2k=4n

HRTEM reveals → Nanotwins, planar defects, Dislocations, Lattice distortions

Thermoelectrics $Cu_{2+x}Mn_{1-x}GeS_4$ (x=0.3)







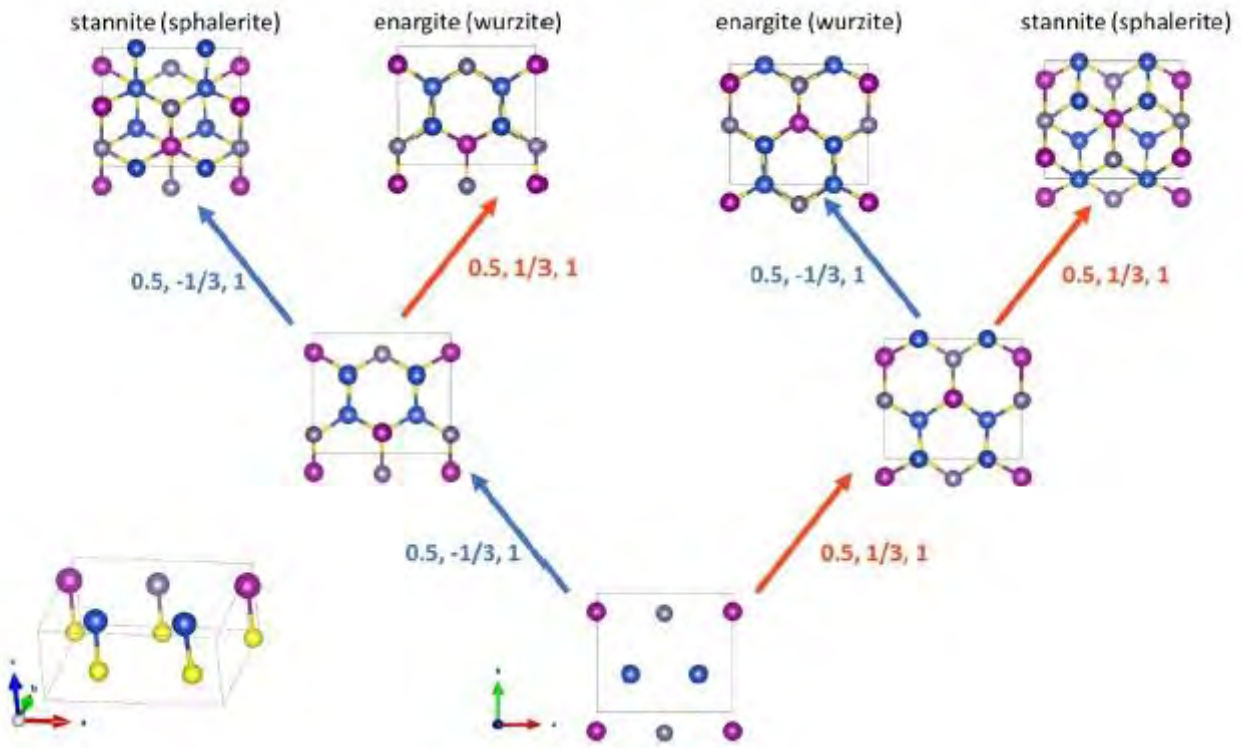
ordered or densely stacked regions

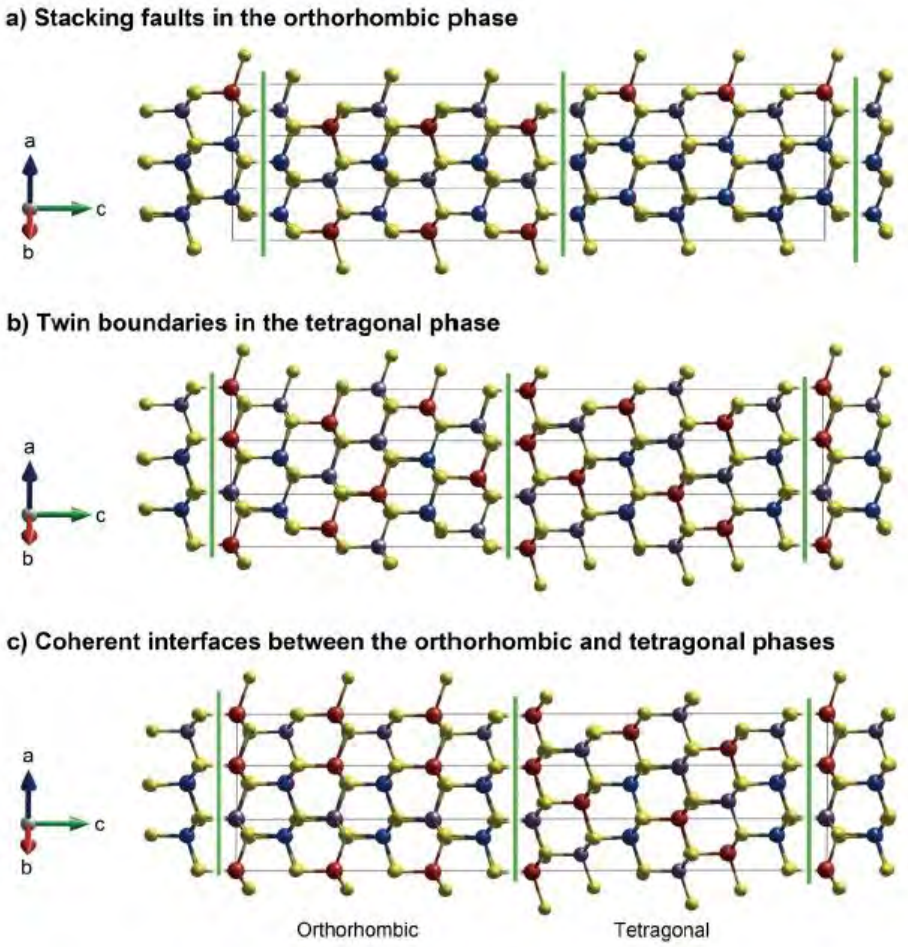
Tetragonal twins and coherent interface T-O

Diffraction pattern

Kumar et al. Angew. Chem. Int. Ed. **2022**, *61*, e202210600

Thermoelectrics $Cu_{2+x}Mn_{1-x}GeS_4$ (x=0.3)



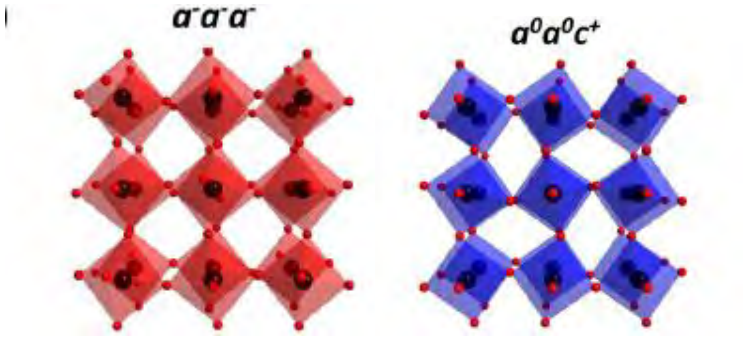


Rietveld refinement of PXRD

Piezoelectrics

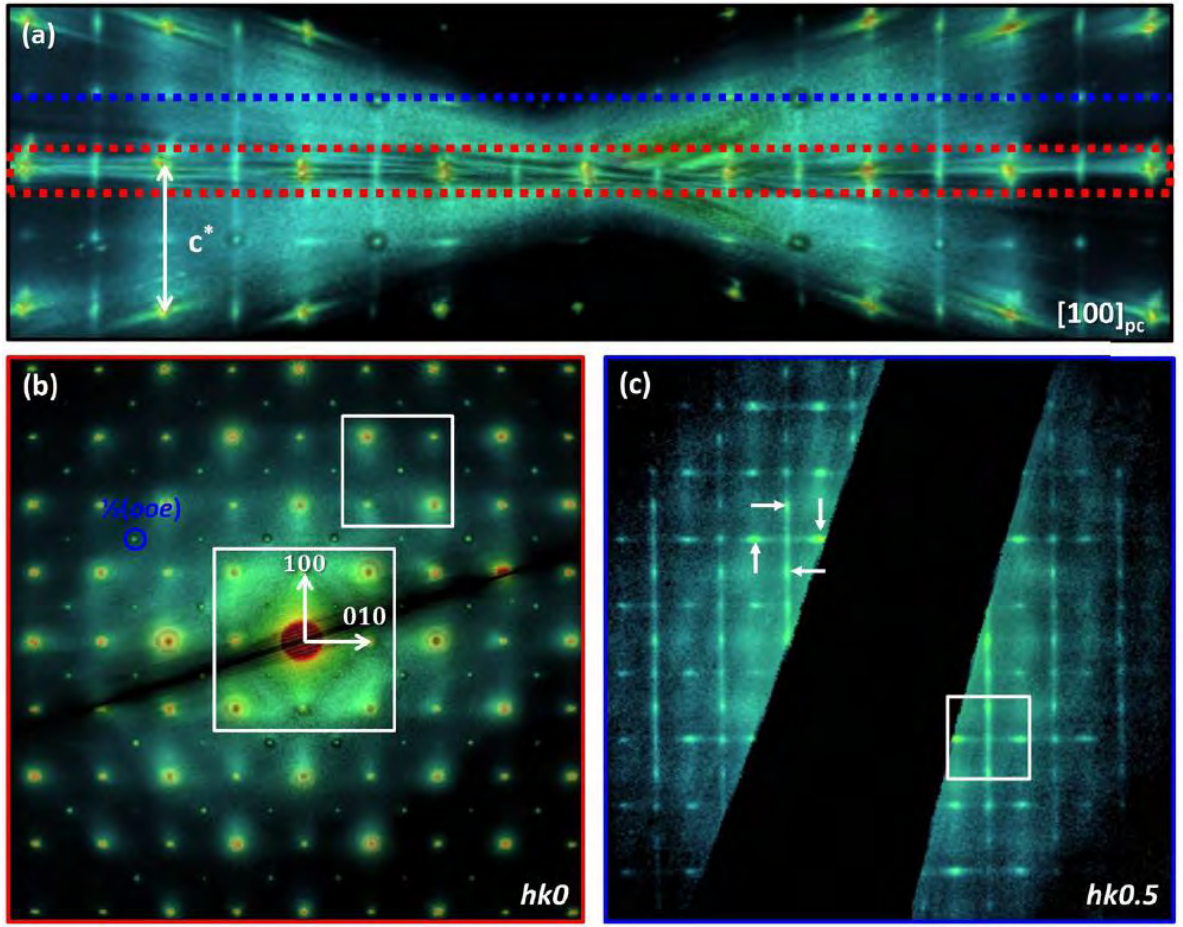
$85\%Na_{0.5}Bi_{0.5}TiO_3\text{-}10\%Bi_{0.5}K_{0.5}TiO_3\text{-}5\%BaTiO_3$

Space group: R3c or Cc or both
R3c @296°C → P4bm @ 566°C→ Pm-3m



½ ooo ½ ooe

Dark field imaging

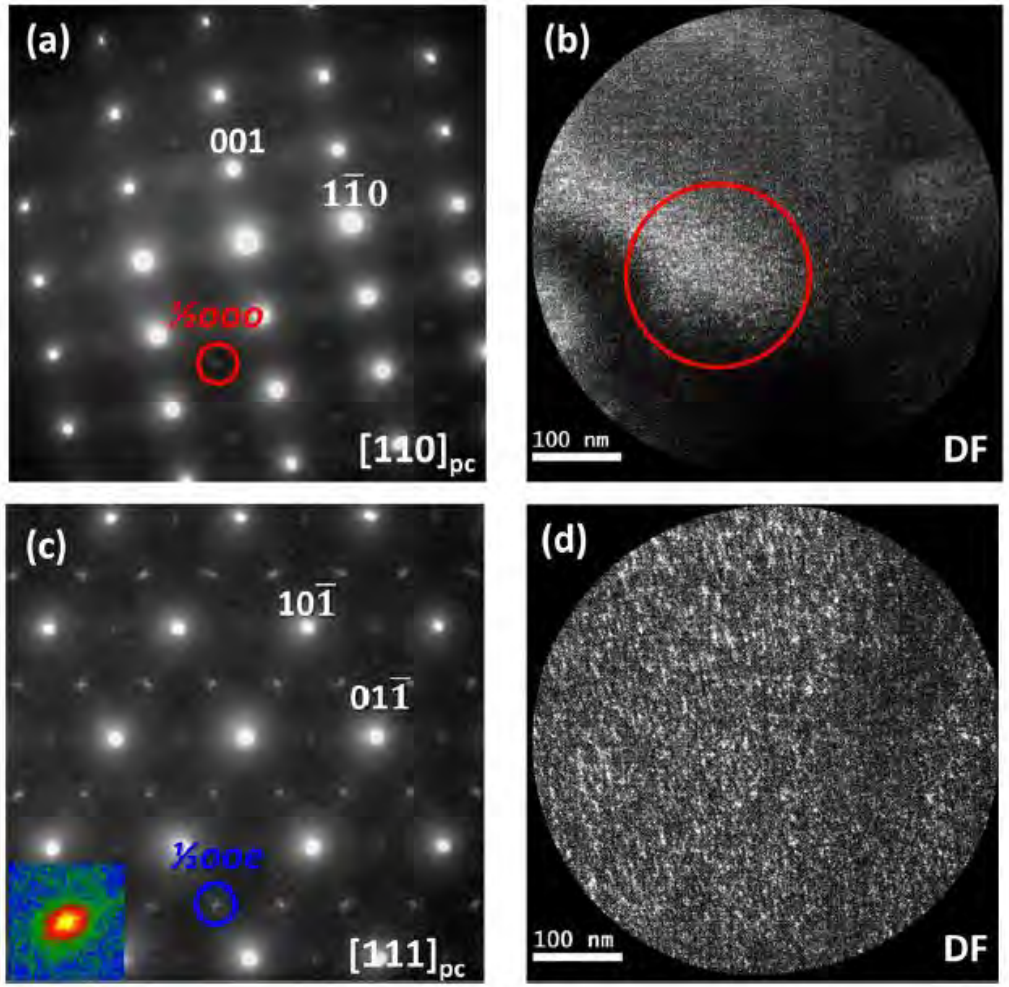


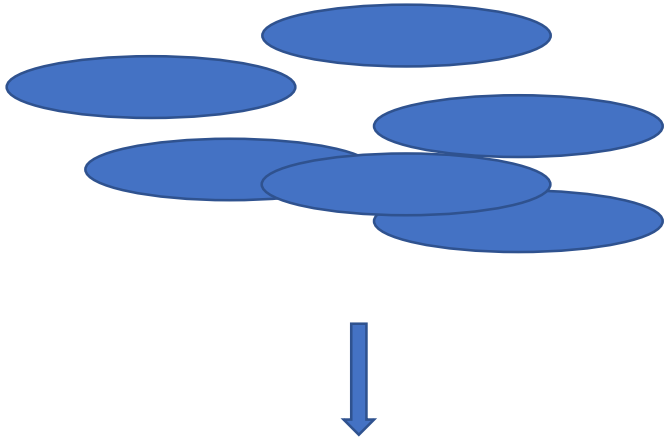
½(*ooe*) superstructure reflections and broad diffuse scattering intensity

Continuous diffuse scattering rods

A. Neagu et al. Scientific Reports| 7: 12519 | DOI:10.1038/s41598-017-12801-w 1

85%NBT-10%BKT-5%BT solid solution



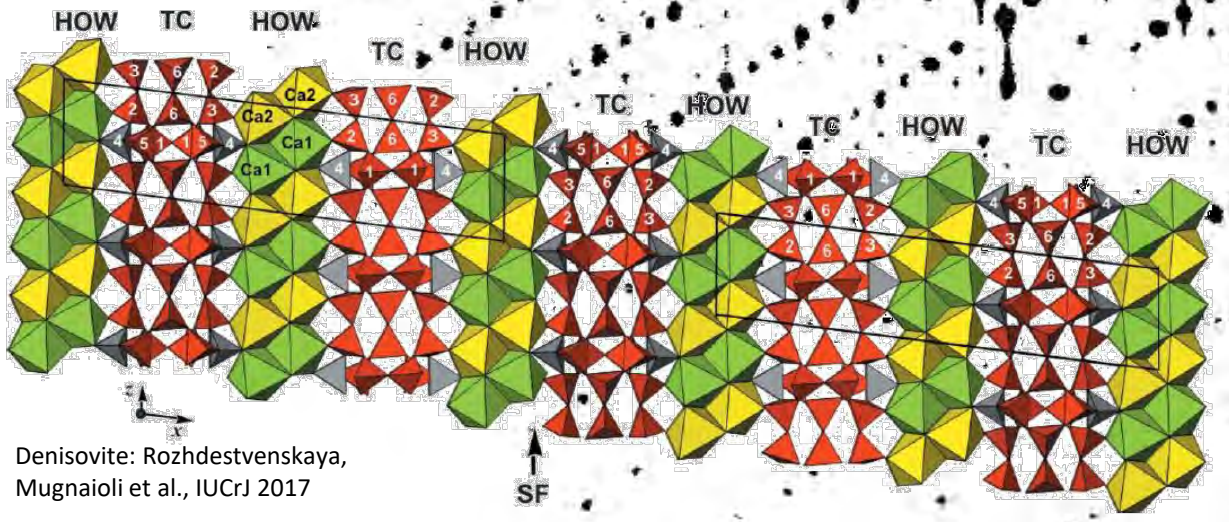


Stacking of platelets like stacking faults explains diffuse rods with increased intensity at ½ ooe

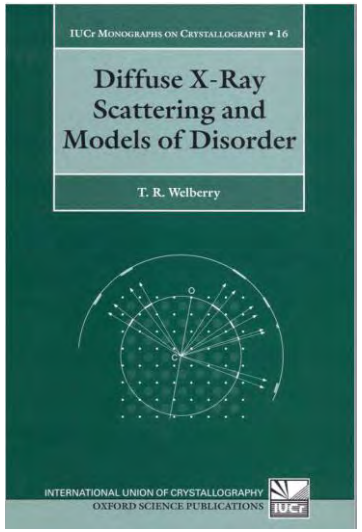
A. Neagu et al. Scientific Reports| 7: 12519 | DOI:10.1038/s41598-017-12801-w 1

Diffuse scattering further reading

Disorder electron diffraction:
Mugnaioli, Gorelik, Acta Cryst B 2019



Denisovite: Rozhdestvenskaya, Mugnaioli et al., IUCrJ 2017



Conclusion

3DED is suitable for quantification of diffuse scattering

Use preferably fine slicing

Try to get more data sets to be sure the trend stays the same

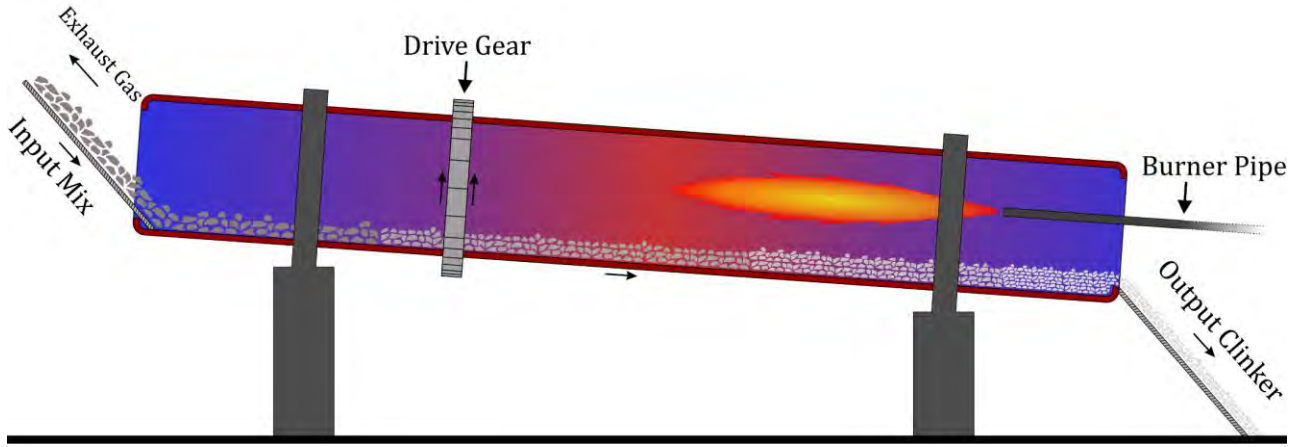
Analysis needs careful investigation

...try to break the problem down ☺

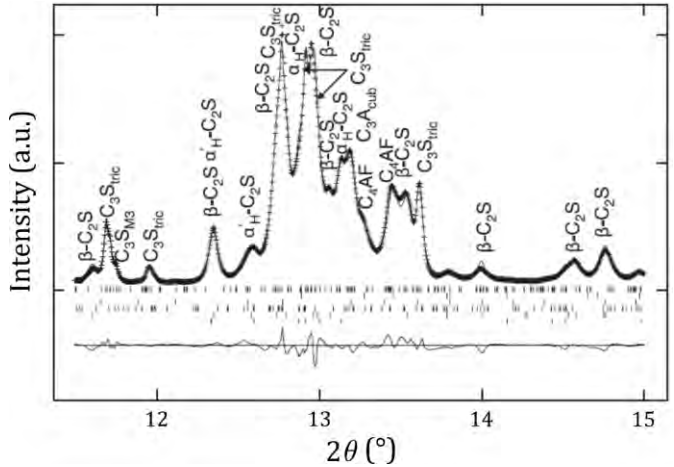
Example: Cement production process

- ✓ **Cement** → Largest Manufactured Product
- ✓ **Concrete** → Second Most Used Substance in the World
- × **~ 5%** of Global Anthropogenic **CO_2 Emissions***

- Cement = Calcium Sulfates + **Clinker**
- Clinker: *Alite* (Ca_3SiO_5; 50-70%), *Belite* (Ca_2SiO_4; 15-30%), *Aluminate* ($Ca_3Al_2O_5$; 5-10%) & *Ferrite* (Ca_2AlFeO_5; 5-15%)



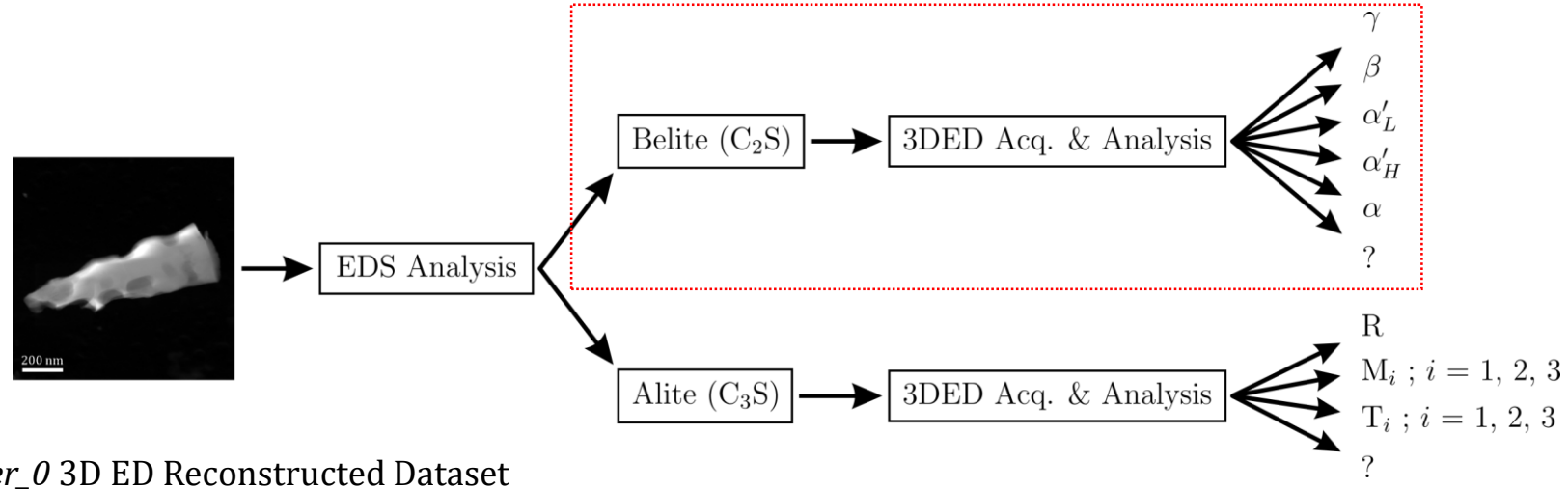
*Mahasenan et al., *Greenhouse Gas Control Technologies*, vol. II, pp. 995-1000, 2003.



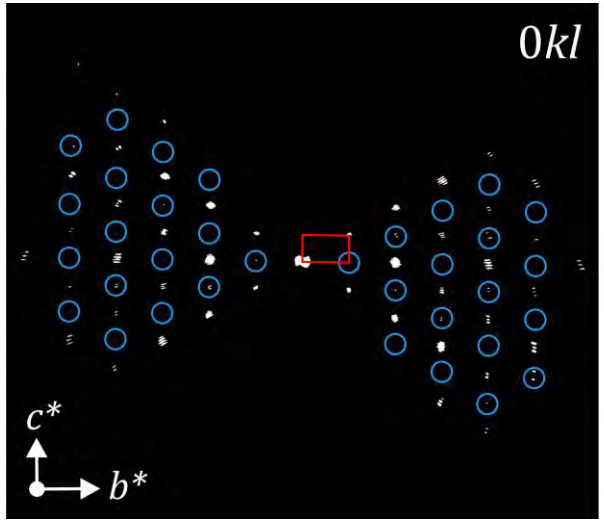
*Morsli et al., *Journal of the American Ceramic Society*, vol. 90, n. 10, pp. 3205-3212, Oct. 2007.

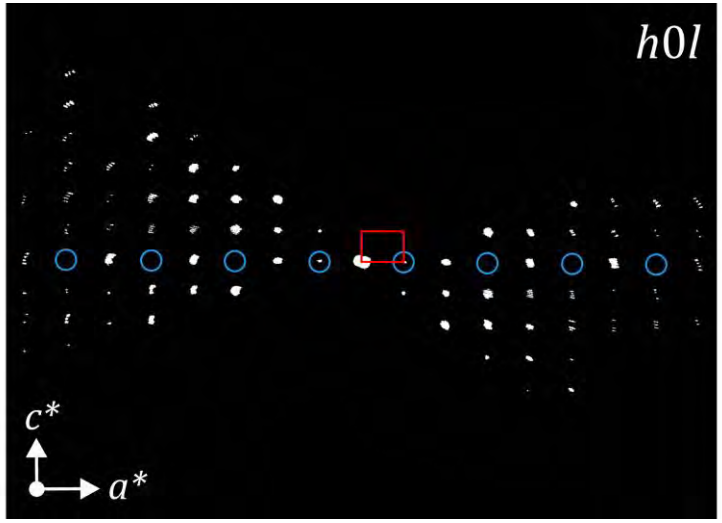
The Belite phase – FAST-ADT structure solution

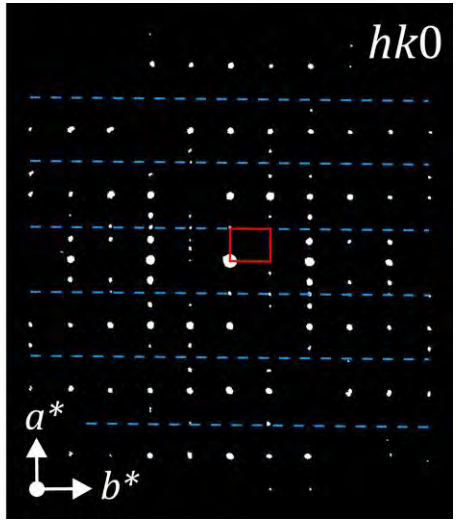
F30, µSTEM mode,
NED, PED-ADT



ODS Sections from the *clinker_0* 3D ED Reconstructed Dataset







Satellite reflections

- Systematic Extinctions according to the Extinction Symbol *Pn-a* : ⇨ Possible Space Groups: ***Pn2$_1$a*** or ***Pnma***

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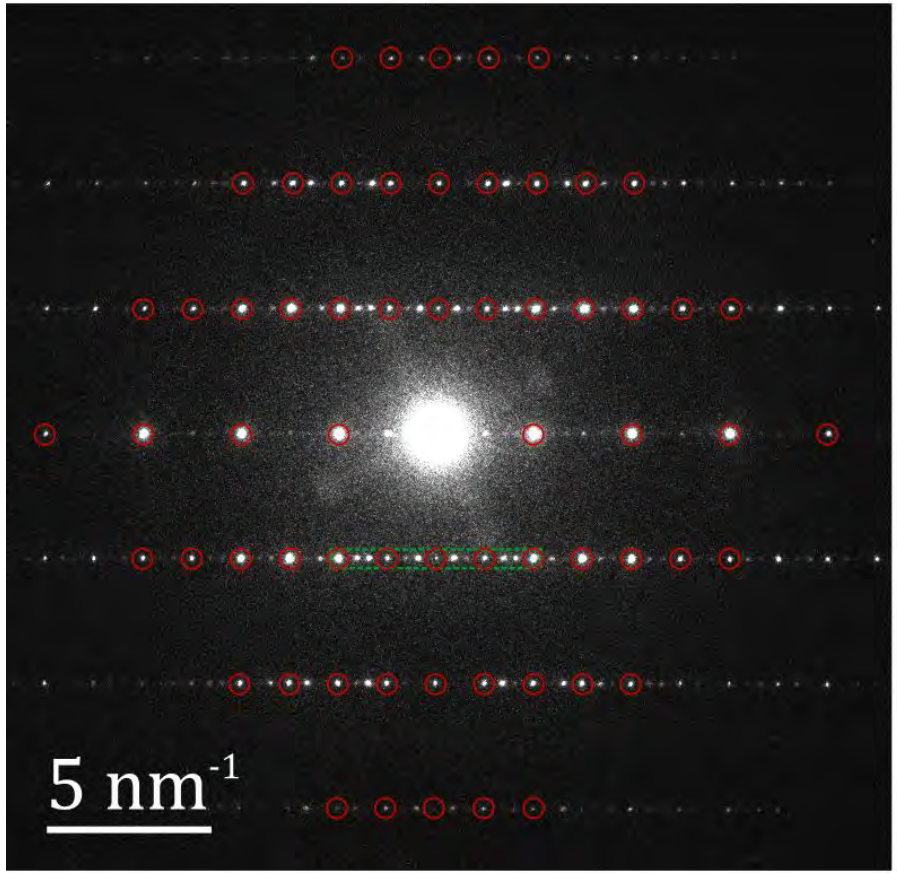
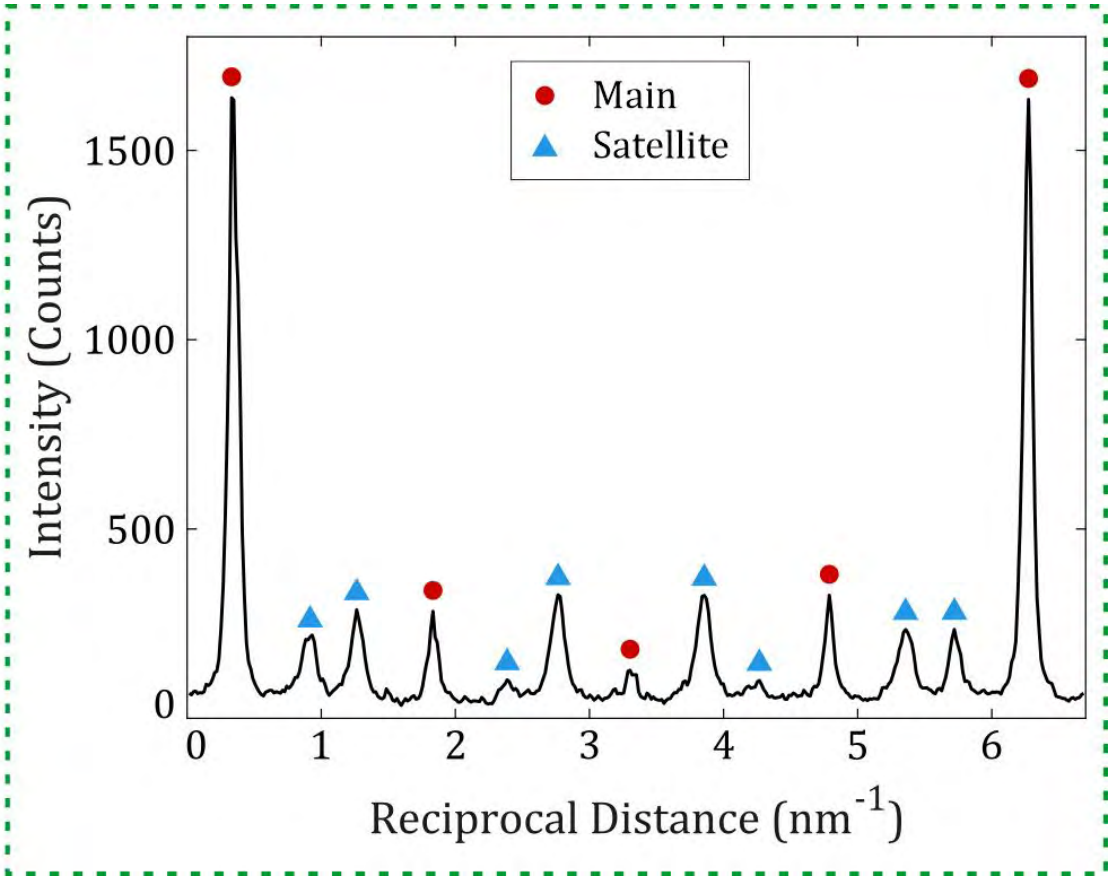
Taking satellites into account



Diffraction Pattern along [01$\bar{2}$]

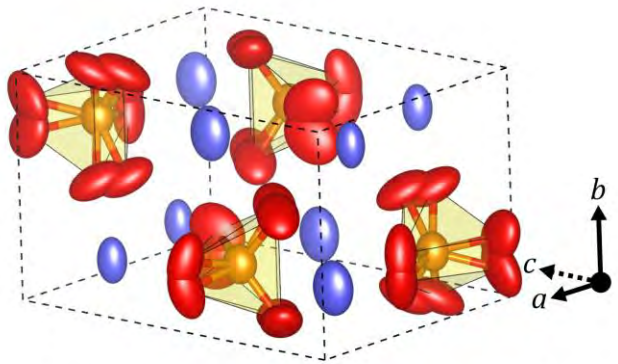


C_2S-α'$_H$: Average Structure

- ***Pn2$_1$a*** → Kinematical Refined Structures: **Unreasonable** Si-O distances & **Poor** Tetrahedra Geometry
- ***Pnma*** → Kinematical Refined Structures: **Reasonable** Si-O Distances & **Good** Tetrahedra Geometry

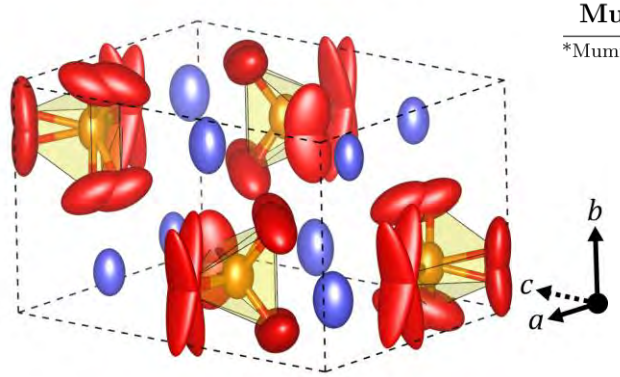
Dynamical Refinements on the *Pnma* Structure Models:

"clinker_0"



R (obs) = 5.57 % R_w (obs) = 5.62 %

"clinker_2.5"



R (obs) = 5.50 % R_w (obs) = 6.07 %

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Found Unit Cell	6.776	5.496	9.252	89.9	89.9	89.5
Mumme et al. Cell*	6.767	5.519	9.303	90.0	90.0	90.0

*Mumme et al., *Neues Jahrbuch für Mineralogie - Abhandlungen*, vol. 169, n. 1, pp 35-68, 1995.

- Retrieved Structures comparable to the XRPD-reported Model (Mumme et al.*)
- **High Anisotropy** of **DP** along the *b*-axis

⇨ **Need to take into account the Satellites**

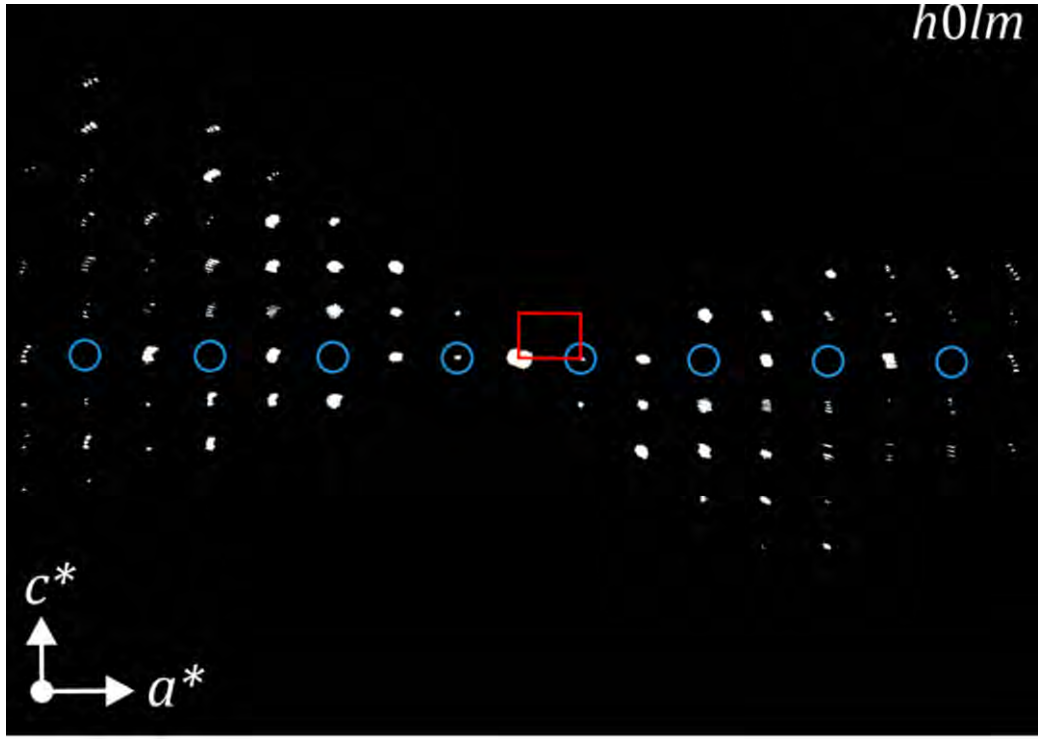
PETS. L. Palatinus, *Acta Cryst B*, vol. 75, pp. 512–522, 2019.

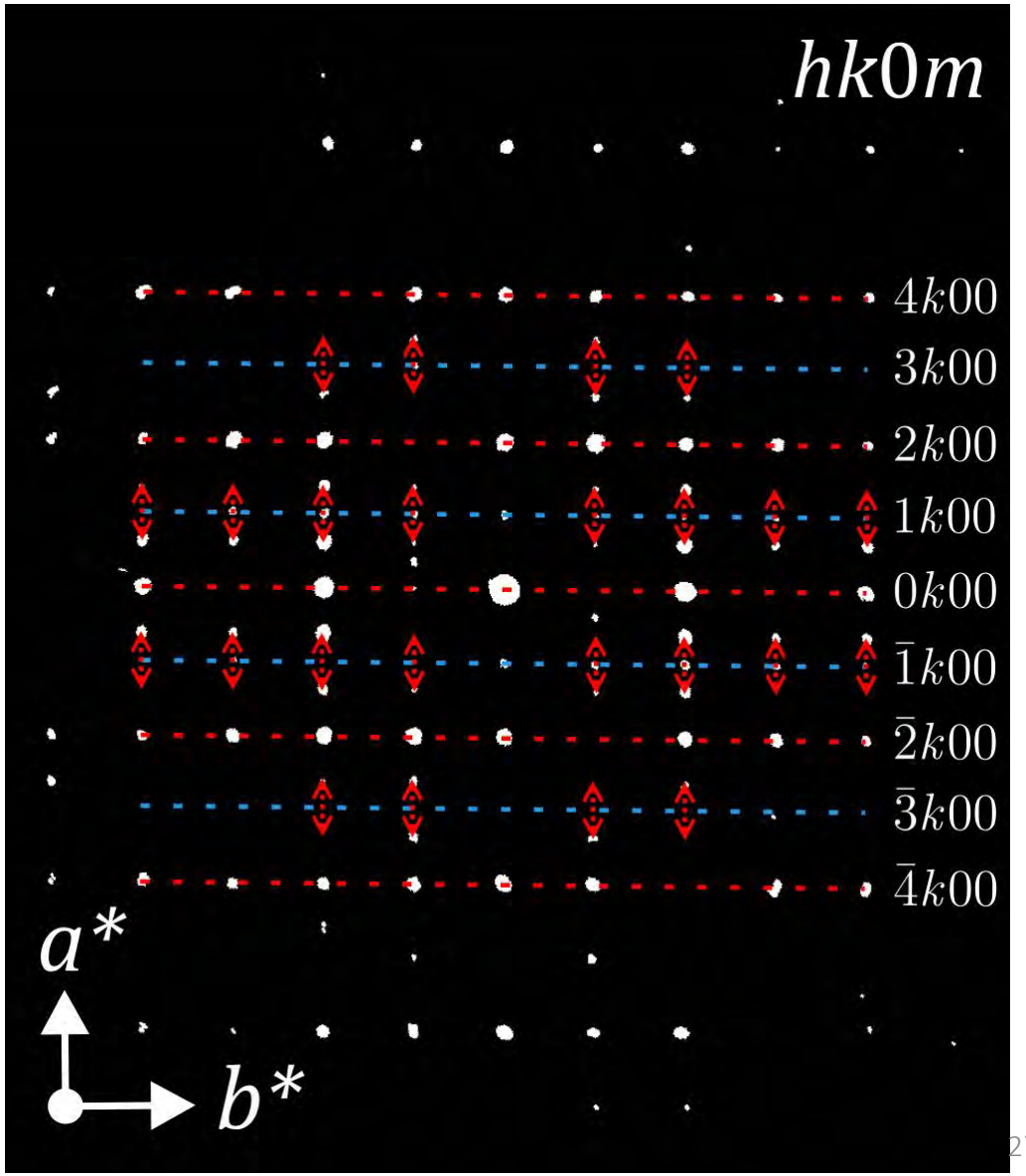
JANA, V. Petrícek,*Zeitschrift für Kristallographie - Crystalline Materials*, vol. 229, no. 5, pp. 345–352, 2014.

Taking staellites into account

Additional index: m

hklm: m=2n
hk0m: h+m=2n





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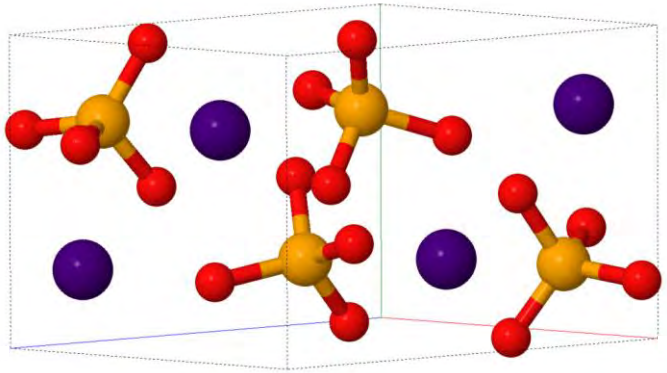
C_2S-α'$_H$: Modulated Structure

- Solution & Refinement in ***Pnma*(*α*00)0*ss***
  - All Displacement Parameters (B) around **1-2 Å^2**

clinker_0

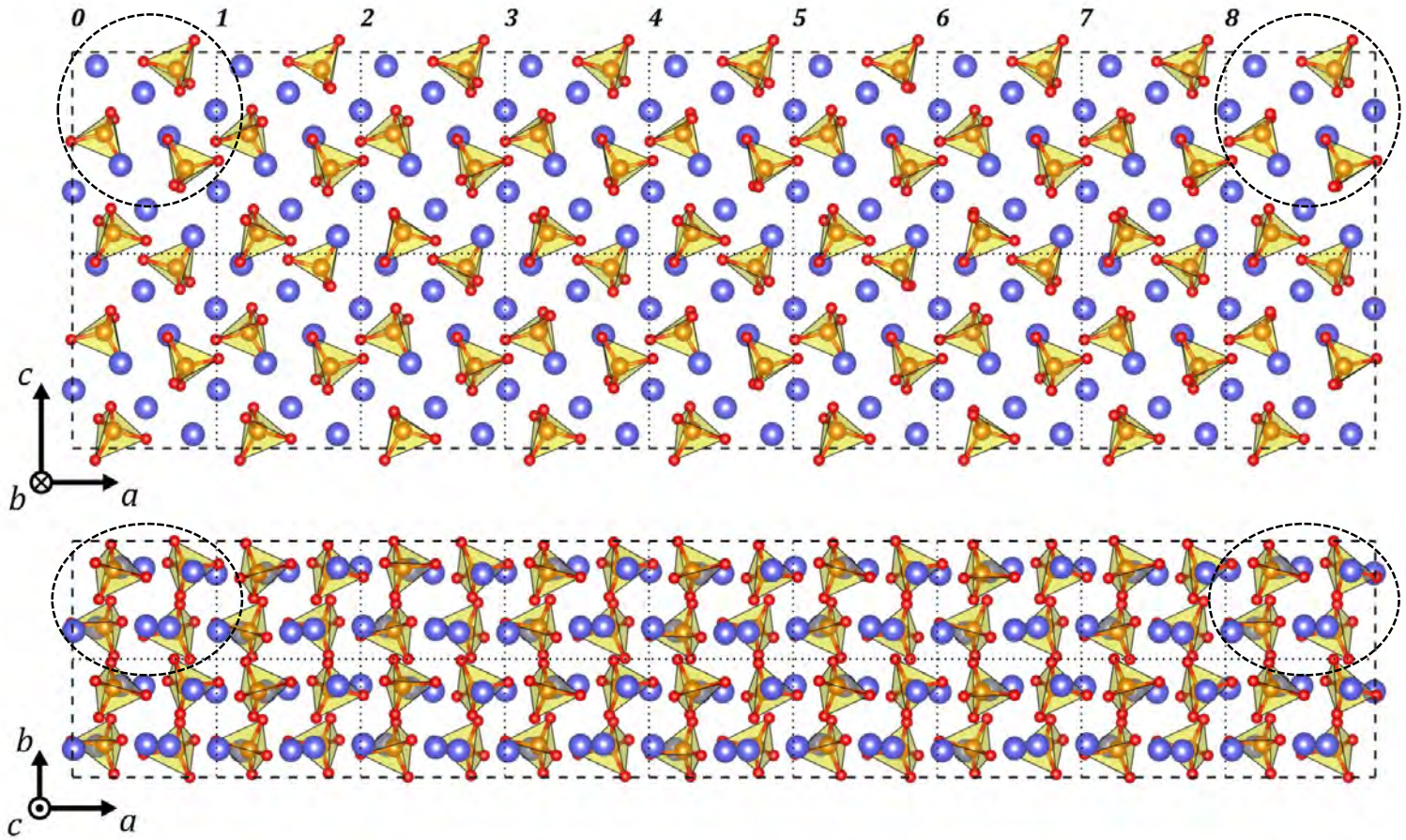


R^{main} (obs) = 7.1 % | $R^{satel.}$ (obs) = 19.9 % | R^{all} (obs) = 12.3 %
R_w^{main} (obs) = 7.3 % | $R_w^{satel.}$ (obs) = 19.5 % | R_w^{all} (obs) = 11.2 %

clinker_2.5

R^{main} (obs) = 7.6 % | $R^{satel.}$ (obs) = 15.9 % | R^{all} (obs) = 9.6 %
R_w^{main} (obs) = 8.3 % | $R_w^{satel.}$ (obs) = 17.8 % | R_w^{all} (obs) = 9.9 %

- Approximated Superstructure from the **Modulated Structure Model** (*clinker_2.5*)



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