Analysis of Stacking Disorder in Zeolite Beta

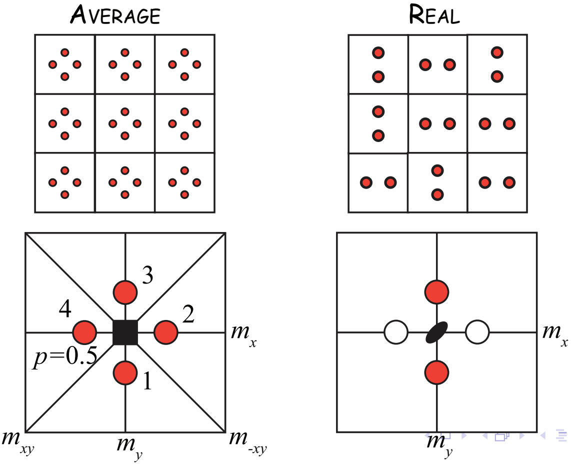
Dima Logvinovich
LfK, ETH Zurich

December 8, 2014

Thinking about substitutional disorder

Qualitatively

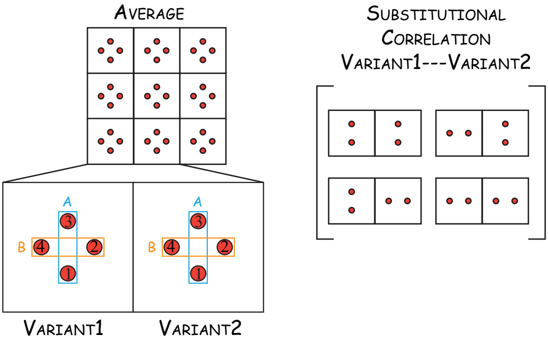
Main questions: Possible symmetry and arrangement of fragments.



Thinking about substitutional disorder

Quantitatively(in terms of variants)

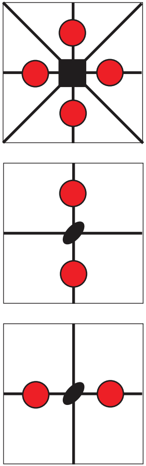
Variant can be used to describe both an average and a real crystal structures. It contains mutually exclusive fragments.

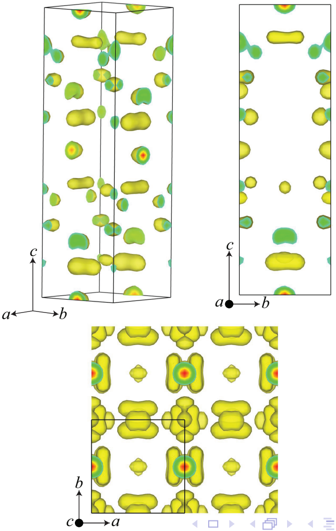


Main questions: Arrangement of fragments in a variant. Setting up joint probabilities right.

Thinking about substitutional disorder

Simple vs Complex





Meet zeolite beta(basic facts)

Synthetic zeolite beta[1]

$[x\mathrm{Na} \cdot (1-x)\mathrm{TEA}]\mathrm{AlO_2} \cdot y\mathrm{SiO_2} \cdot w\mathrm{H_2O}$

with $x \leq 1.0$, typically 0.4, $5 < y < 100$, typically 10, $w \leq 4$, and TEA–tetraethylammonium cation.

- The first of the high-silica zeolites prepared by using organic additives in synthesis
- One of the most important acidic catalysts (because of pore structure and acidity) for several organic reactions

[1] R.L. Waldinger, G.T. Kerr and E.J. Rosinski, *US Patent* 3,308,069(1967)

Early structural reports

Hybrid approach(ED study)[2]

Average structure: $a = b \approx 4.22$ Å, $c \approx 13.21$ Å, S.G. $P4_2/mmc$

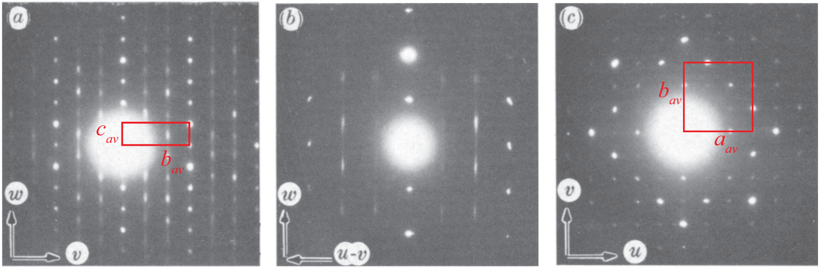
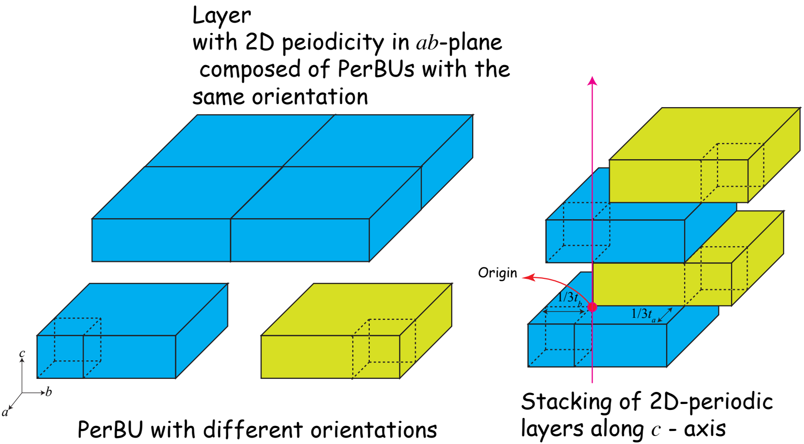


FIGURE 4. Various high symmetry diffraction patterns from isolated crystallites of zeolite beta. (a) Down the $\boldsymbol{u}$ (or $\boldsymbol{v}$) axis. (b) Down the $\boldsymbol{u}+\boldsymbol{v}$ axis, rotated *ca.* 45° from the view in (a). (c) Down an axis close to $\boldsymbol{w}$.

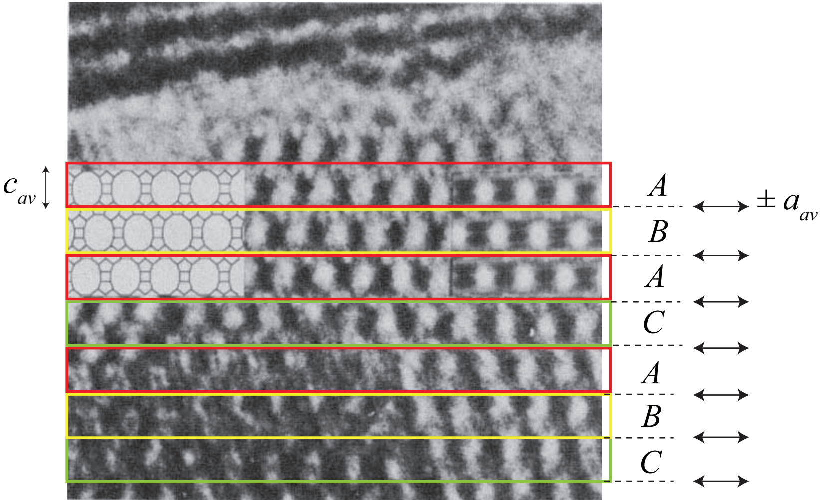
[2] J.M. Newsam, M.M.J. Treacy, W.T. Koetsier and C.B. De Gruyyter, *Proc.R. Soc.Lond.* A 420, 375-405 (1988)

Hybrid approach(basic interpretation of ED)

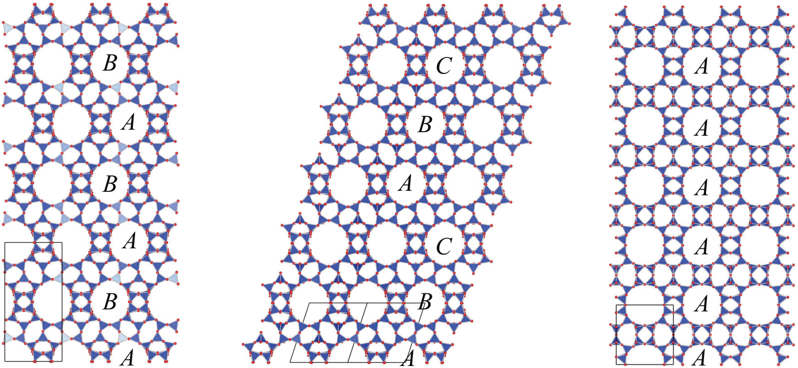


Early structural reports

Hybrid approach(HREM+sorption)

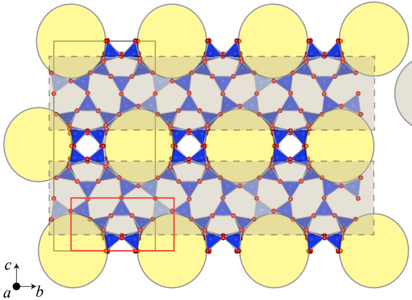


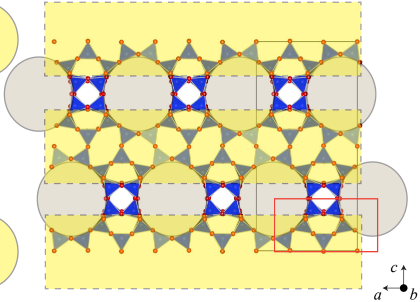
Hybrid approach(main polymorphs)



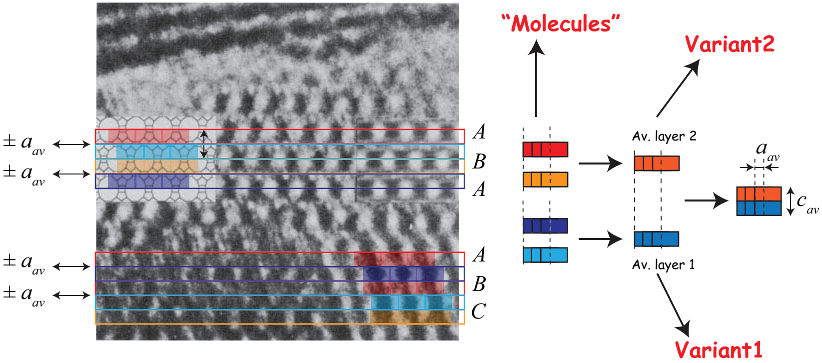
A **B** **C**

Hybrid approach(pore connectivity; PerBU)

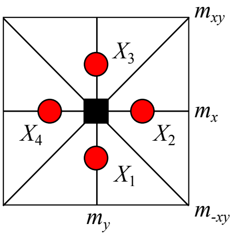




Thinking in terms of variants



Generating unique fragments (an example)



$\mathcal{G} = 4mm = \{e, 4_z^+, 4_z^-, 2_z, m_x, m_y, m_{xy}, m_{\bar{x}y}\}$

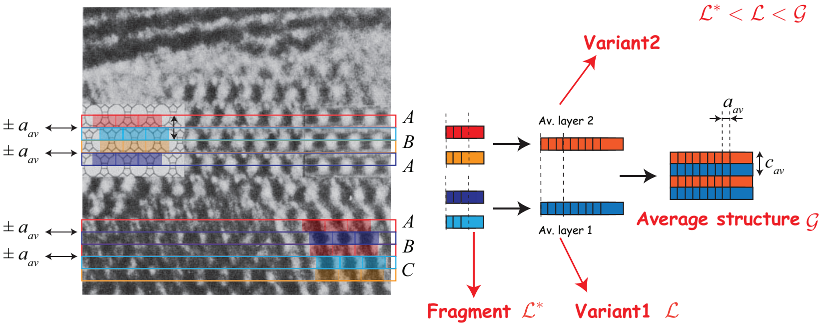
Stabilizer of X_1: $\mathcal{S}_1 < \mathcal{G}$: $\mathcal{S}_1 X_1 = X_1$
In our case $\mathcal{S}_1 = \{1, m_y\}$

Left coset decomposition $\mathcal{G} : \mathcal{S}_1$ yields unique symmetry related fragments:

$$\mathcal{G} = \bigcup_{p=1}^{i} g_p \mathcal{S}_1 = e\mathcal{S}_1 \ \cup \ 4_z^+\mathcal{S}_1 \ \cup \ 4_z^-\mathcal{S}_1 \ \cup \ 2_z\mathcal{S}_1 =$$
$$= \{1, m_y\} \ \cup \ \{4_z^+, m_{\bar{x}y}\} \ \cup \ \{4_z^-, m_{xy}\} \ \cup \ \{2_z, m_x\}$$

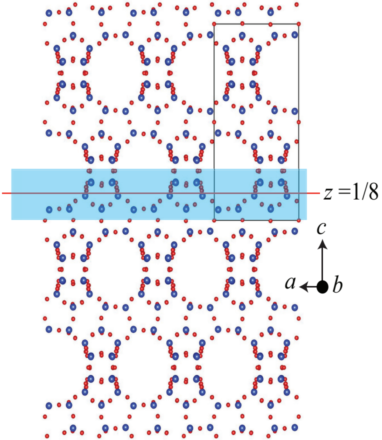
$i = |\mathcal{G}|/|\mathcal{S}_1|$-*index* of $\mathcal{S}_1$ in $\mathcal{G}$(gives the number of fragments)

Big picture



If we know the stabilizer of the layer of the real structure($\mathcal{L}^*$) and stabilizer of the layer of the average structure($\mathcal{L}$) we can learn how the latter is built from the former. If we additionally know the stabilizer of the average structure($\mathcal{G}$) we can find out how it is built from the average layer or real layers.

Definition



The subgroup of all elements of the space group $\mathcal{G}$ which leave a certain *section plane* invariant is called
a *layer group* or
a *sectional layer group*($\mathcal{L}$)
of this section plane under the action of the group $\mathcal{G}$.[3]

[3] International Tables for Crystallography Vol. E

Scanning Tables

International Tables for Crystallography (2010). Vol. E, Scanning table for space group 131, p. 493.

Laue class $D_{4h} - 4/mmm$ 6. SCANNING TABLES Tetragonal

No. 131 $P4_2/mmc$ D_{4h}^9

$$\mathcal{G} = P\frac{4_2}{m}\frac{2}{m}\frac{2}{c}$$

Orientation orbit (hkl)	Conventional basis of the scanning group $\mathbf{a}'$	$\mathbf{b}'$	$\mathbf{d}$	Scanning group $\mathcal{H}$	Linear orbit $s\mathbf{d}$	Sectional layer group $\mathcal{L}(s\mathbf{d})$	
(001)	**a**	**b**	**c**	$P4_2/mmc$	$[0\mathbf{d}, \frac{1}{2}\mathbf{d}]$	$pmmm$	L37
					$[\frac{1}{4}\mathbf{d}, \frac{3}{4}\mathbf{d}]$	$p\bar{4}m2$	L59
					$[\pm s\mathbf{d}, (\pm s + \frac{1}{2})\mathbf{d}]$	$pmm2$	L23
(100)	**b**	**c**	**a**	$Pmmm$	$0\mathbf{d}, \frac{1}{2}\mathbf{d}$	$pmmm$	L37
(010)	$-\mathbf{a}$	**c**	**b**		$[s\mathbf{d}, -s\mathbf{d}]$	$pmm2$	L23
(110)	$(-\mathbf{a}+\mathbf{b})$	**c**	$(\mathbf{a}+\mathbf{b})$	$Bbmb$	$[0\mathbf{d}, \frac{1}{2}\mathbf{d}]$	$pbmb$	L38
$(1\bar{1}0)$	$(\mathbf{a}+\mathbf{b})$	**c**	$(\mathbf{a}-\mathbf{b})$		$[\frac{1}{4}\mathbf{d}, \frac{3}{4}\mathbf{d}]$	$pbmn$ $(\mathbf{a}'/4)$	L42
					$[\pm s\mathbf{d}, (\pm s + \frac{1}{2})\mathbf{d}]$	$pbm2$ $(\mathbf{b}'/4)$	L24

No. 91 $P4_122$ D_4^3

$$\mathcal{G} = P4_122$$

Orientation orbit (hkl)	Conventional basis of the scanning group $\mathbf{a}'$	$\mathbf{b}'$	$\mathbf{d}$	Scanning group $\mathcal{H}$	Linear orbit $s\mathbf{d}$	Sectional layer group $\mathcal{L}(s\mathbf{d})$	
(001)	**a**	**b**	**c**	$P4_122$	$[0\mathbf{d}, \frac{1}{2}\mathbf{d};$	$p121$	L08
					$\frac{1}{4}\mathbf{d}, \frac{3}{4}\mathbf{d}]$	$p211$	L08
					$[\frac{1}{8}\mathbf{d}, \frac{5}{8}\mathbf{d};$	$\hat{c}211$	L10
					$\frac{3}{8}\mathbf{d}, \frac{7}{8}\mathbf{d}]$	$\hat{c}121$	L10
					$[\pm s\mathbf{d}, (\pm s + \frac{1}{4})\mathbf{d},$		
					$(\pm s + \frac{1}{2})\mathbf{d}, (\pm s + \frac{3}{4})\mathbf{d}]$	$p1$	L01

Groups modulo

Basic idea

Space groups are of an infinite order. To facilitate working with group-subgroup relations one employs *groups modulo*:

$$\mathcal{G}/\mathcal{T}_{\mathcal{G}} = \{\mathcal{T}_{\mathcal{G}}, \ldots, \mathcal{T}_{\mathcal{G}} g_i\}$$

Their distinctive property(*closure modulo*):

$$(\mathcal{T}_{\mathcal{G}} g_i)(\mathcal{T}_{\mathcal{G}} g_j) = \mathcal{T}_{\mathcal{G}}(g_i g_j) = \mathcal{T}_{\mathcal{G}}(t_l g_k) = \mathcal{T}_{\mathcal{G}}(g_k)$$

where $\{g_i,\ g_j,\ g_k\} \in \mathcal{G}$ and $t_l \in \mathcal{T}_{\mathcal{G}}$.

Relation to crystallography

$\mathcal{G}$ is a space group, $\mathcal{T}_{\mathcal{G}}$ is its translational subgroup.
Modulo group is the stabilizer for the content of the unit cell.

Where to find them

CONTINUED | No. 131 | $P4_2/mmc$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (9)

Positions

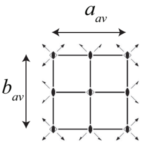
Multiplicity, Wyckoff letter, Site symmetry	Coordinates				Reflection conditions
					General:
16 r 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z+\frac{1}{2}$	(4) $y,\bar{x},z+\frac{1}{2}$	hhl : $l=2n$
	(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}+\frac{1}{2}$	(8) $\bar{y},\bar{x},\bar{z}+\frac{1}{2}$	$00l$: $l=2n$
	(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}+\frac{1}{2}$	(12) $\bar{y},x,\bar{z}+\frac{1}{2}$	
	(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z+\frac{1}{2}$	(16) $y,x,z+\frac{1}{2}$	

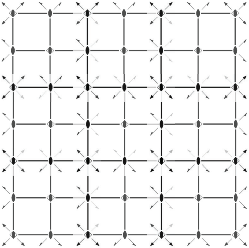
$$(3)\ \bar{y},x,z+\frac{1}{2} \ \leftrightarrow\ 4_2 \ \mapsto\ \mathcal{T}_\mathcal{G} t_{\frac{1}{2}z} 4_z$$

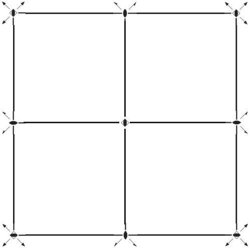
Closure: $\mathcal{T}_\mathcal{G}(t_{\frac{1}{2}z}4_z)\mathcal{T}_\mathcal{G}(t_{\frac{1}{2}z}4_z) = \mathcal{T}_\mathcal{G}(t_{1z}2_z) = \mathcal{T}_\mathcal{G}2_z \leftrightarrow (2)$

Obtaining translations

$$\mathcal{T}_{\mathcal{L}} = \bigcup_{i,j=0}^{2} \mathcal{T}_{\mathcal{L}^*}\ {t_a}^i {t_b}^j \qquad \Delta = |\mathcal{T}_{\mathcal{L}} : \mathcal{T}_{\mathcal{L}^*}| = |\mathcal{T}_{\mathcal{L}}|/|\mathcal{T}_{\mathcal{L}^*}| = 9-\text{index}$$







$$\mathcal{L}/\mathcal{T}_{\mathcal{L}} =$$

$$\{\mathcal{T}_{\mathcal{L}}, \ldots, \mathcal{T}_{\mathcal{L}} g_l\}$$

$$\bigcup_{k=1}^{l} \mathcal{T}_{\mathcal{L}}\ g_k$$

$$\mathcal{L}'/\mathcal{T}_{\mathcal{L}}* =$$

$$\{\cdots\} =$$

$$\bigcup_{i,j=0}^{2} \bigcup_{k=1}^{l} \mathcal{T}_{\mathcal{L}^*}\ {t_a}^i {t_b}^j\ g_k$$

$$\mathcal{L}/\mathcal{T}_{\mathcal{L}}* =$$

$$\{\mathcal{T}_{\mathcal{L}}*, \ldots, \mathcal{T}_{\mathcal{L}}* g_l\}$$

$$\bigcup_{k=1}^{l} \mathcal{T}_{\mathcal{L}}*\ g_k$$

Obtaining orientations

$$p\bar{4}m2 \mapsto \bar{4}m2 = \mathcal{P}_{\mathcal{L}}$$
$$c2 \mapsto 2 = \mathcal{P}_{\mathcal{L}}* = \{1, 2_{\bar{x}x}\}$$

Coordinates	$\mathcal{L}/\mathcal{T}_{\mathcal{L}^*}$	$\mathcal{P}_{\mathcal{L}^*}$
(1) x, y, z	$\mathcal{T}_{\mathcal{L}^*}1$	1
(2) $\bar{x}, \bar{y}, z$	$\mathcal{T}_{\mathcal{L}^*}2_z$	2_z
(3) $y, \bar{x}, \bar{z}$	$\mathcal{T}_{\mathcal{L}^*}\bar{4}_z^+$	$\bar{4}_z^+$
(4) $\bar{y}, x, \bar{z}$	$\mathcal{T}_{\mathcal{L}^*}\bar{4}_z^-$	$\bar{4}_z^-$
(5) $x, \bar{y}, z$	$\mathcal{T}_{\mathcal{L}^*}m_y$	m_y
(6) $\bar{x}, y, z$	$\mathcal{T}_{\mathcal{L}^*}m_x$	m_x
(7) $x, y, \bar{z}$	$\mathcal{T}_{\mathcal{L}^*}m_z$	m_z
(8) $\bar{y}, \bar{x}, \bar{z}$	$\mathcal{T}_{\mathcal{L}^*}2_{\bar{x}x}$	$2_{\bar{x}x}$

$$\mathcal{P}_{\mathcal{L}} = \mathcal{P}_{\mathcal{L}}* \cup m_x\mathcal{P}_{\mathcal{L}}* \cup m_y\mathcal{P}_{\mathcal{L}}* \cup 2_z\mathcal{P}_{\mathcal{L}}*$$

$$1 \leftrightarrow \mathcal{T}_{\mathcal{L}^*}1$$

$$m_x \leftrightarrow \mathcal{T}_{\mathcal{L}^*}m_x$$

$$m_y \leftrightarrow \mathcal{T}_{\mathcal{L}^*}m_y$$

$$2_z \leftrightarrow \mathcal{T}_{\mathcal{L}^*}2_z$$

$$\Delta = |\mathcal{P}_{\mathcal{L}} : \mathcal{P}_{\mathcal{L}^*}| = |\mathcal{P}_{\mathcal{L}}|/|\mathcal{P}_{\mathcal{L}}*| = 4 - \text{index}$$

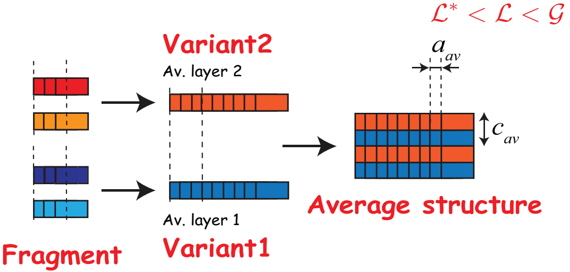
Index of a general subgroup

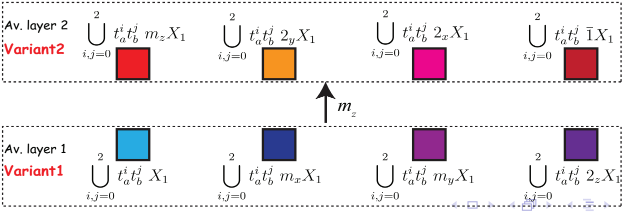
$$\Omega = \mathrm{K} \cdot \Delta = |\mathcal{P}_{\mathcal{L}} : \mathcal{P}_{\mathcal{L}^*}| \cdot |\mathcal{T}_{\mathcal{L}} : \mathcal{T}_{\mathcal{L}^*}| = 4 \cdot 9 = 36$$

- Gives the number of fragments in the variant
- Estimates and explains complexity of a problem

Groups modulo

Building beta





Groups modulo

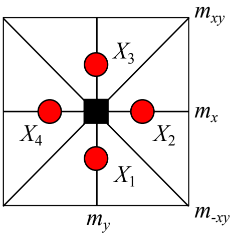
What if we don't know the symmetry of PerBU?

Every modulo-group isomorphous to the subgroups of $\bar{4}m2$ is the candidate for the modulo-group of PerBU.

Subgroup	$\lvert \mathcal{P}_{\mathcal{L}} : \mathcal{P}_{\mathcal{L}^*} \rvert$	$\lvert \mathcal{T}_{\mathcal{L}} : \mathcal{T}_{\mathcal{L}^*} \rvert$	Ω
$\bar{4}m2$	1	9	9
$\bar{4}$	2	9	18
$mm2$	2	9	18
222	2	9	18
m	4	9	36
2	4	9	36
1	8	9	72

Finding symmetry equivalent pairs

An introductory example



$$\mathcal{G} = 4mm = \{e, 4_z^+, 4_z^-, 2_z, m_x, m_y, m_{xy}, m_{\bar{x}y}\}$$

Our task: find pairs equivalent to $[X_1 - X_3]$

Find $\mathcal{S} = \mathcal{S}_{\mathcal{G}}([X_1 - X_3]) = \{e, 2_z, m_x, m_y\}$

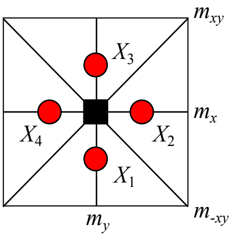
Make left coset decomposition of $\mathcal{G} : \mathcal{S}$.
The number of equivalent pairs $i = |\mathcal{G}|/|\mathcal{S}|$:

$$\mathcal{G} = \bigcup_{p=1}^{2} g_p\mathcal{S} = e\mathcal{S} \ \cup \ 4_z^+\mathcal{S}$$

Apply g_p to each of the fragments that build our pair:
$g_p\mathcal{S}[X_1 - X_3] = g_p[X_1 - X_3] = [g_pX_1 - g_pX_3] = [4_z^+X_1 - 4_z^+X_3]$

Finding symmetry equivalent pairs

Finding stabilizer of a pair



Earlier we had found the orbit of X_1:
$X = \{eX_1,\ 4_z^+X_1,\ 4_z^-X_1,\ 2_zX_1\}$

The stabilizer of X_p:

$$\mathcal{S}_p = g_p\mathcal{S}_1 g_p^{-1}$$

In our case:

$$X_3 = 2_zX_1 \Rightarrow \mathcal{S}_3 = 2_z\mathcal{S}_1 2_z^{-1} = \{e,\ m_y\}$$

The stabilizer of the pair $[X_1 - X_p]$:

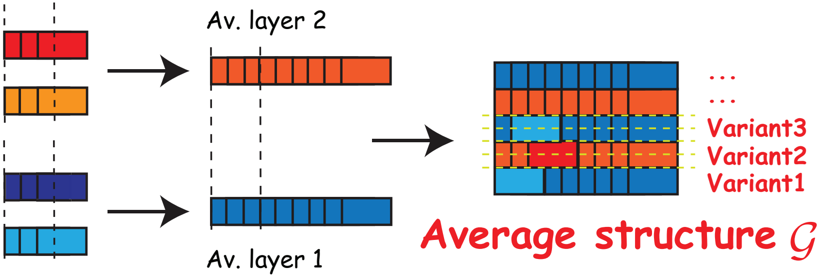
$$\mathcal{S}_{\mathcal{G}}([X_1 - X_p]) = \{s_j : s_j \in \mathcal{S}_1 \cap \mathcal{S}_p\} \cup \{g_p : g_p^2 \in \mathcal{S}_1\}$$

In our case: $2_z\mathcal{S}_1 = \{2_z,\ m_x\} \Rightarrow$

$$\mathcal{S}_{\mathcal{G}}([X_1 - X_3]) = \{e,\ m_y\} \ \cup\ \{2_z,\ m_x\} = \{e, 2_z, m_x, m_y\}$$

Finding symmetry equivalent pairs

Decompse? Ok. With respect to what?



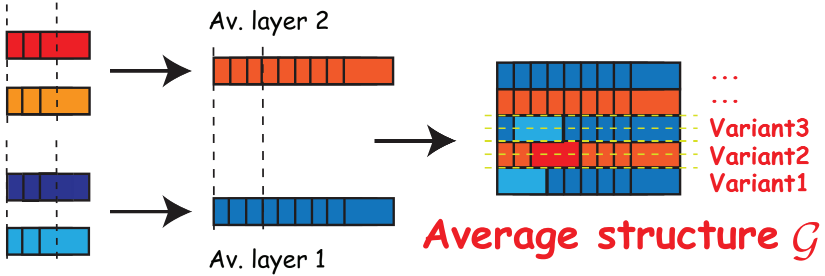
Proposition: The decomposition has to be done with respect to the stabilizer of an average bilayer.

$$\mathcal{L}_{\mathcal{G}}([L_1 - L_2]) = \cdots = pmmm$$

BUT THIS IS THE LAYER GROUP, which leaves the plane between two layers invariant !!!

Finding symmetry equivalent pairs

Decompse? Ok. With respect to what?



The planes of interest are located at $(\frac{1}{2} + \frac{1}{4}n)\mathbf{c}$, $n \in \mathbb{Z}$, which corresponds to alternating layer groups *pmmm* and $p\bar{4}m2$.

Corrolary: From here There will be *only 2 unique pair correlation matrices*. The rest will be isomorphous to these two !

Conclusions

- Applying layer groups allows greatly facilitate understanding and describing 1D-disorder in crystals.
- The used approach(because of its generality) can be applied to all cases of 1D-disorder(at least I believe so:)).
- The approach can *probably* be adopted to treat cases of 2D- and 3D-disorder.

Acknowledgement

- Prof. Dr. Walter Steurer
- Dr. Thomas Weber
- Dr! Arkadiy Simonov
- Dr. Lynne McCusker
- Dr. Christian Bärlocher
- Dr. Bernd Marler
- LfK

Diffuse scattering in zeolite beta

PILATUS experiment