Modular compounds

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Summary

- What is it ? What is the aim ?
- Useful properties of the superspace formalism
- The method : keys …
- Some examples, step by step …
- Conclusion

Summary

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Modular compounds consist of

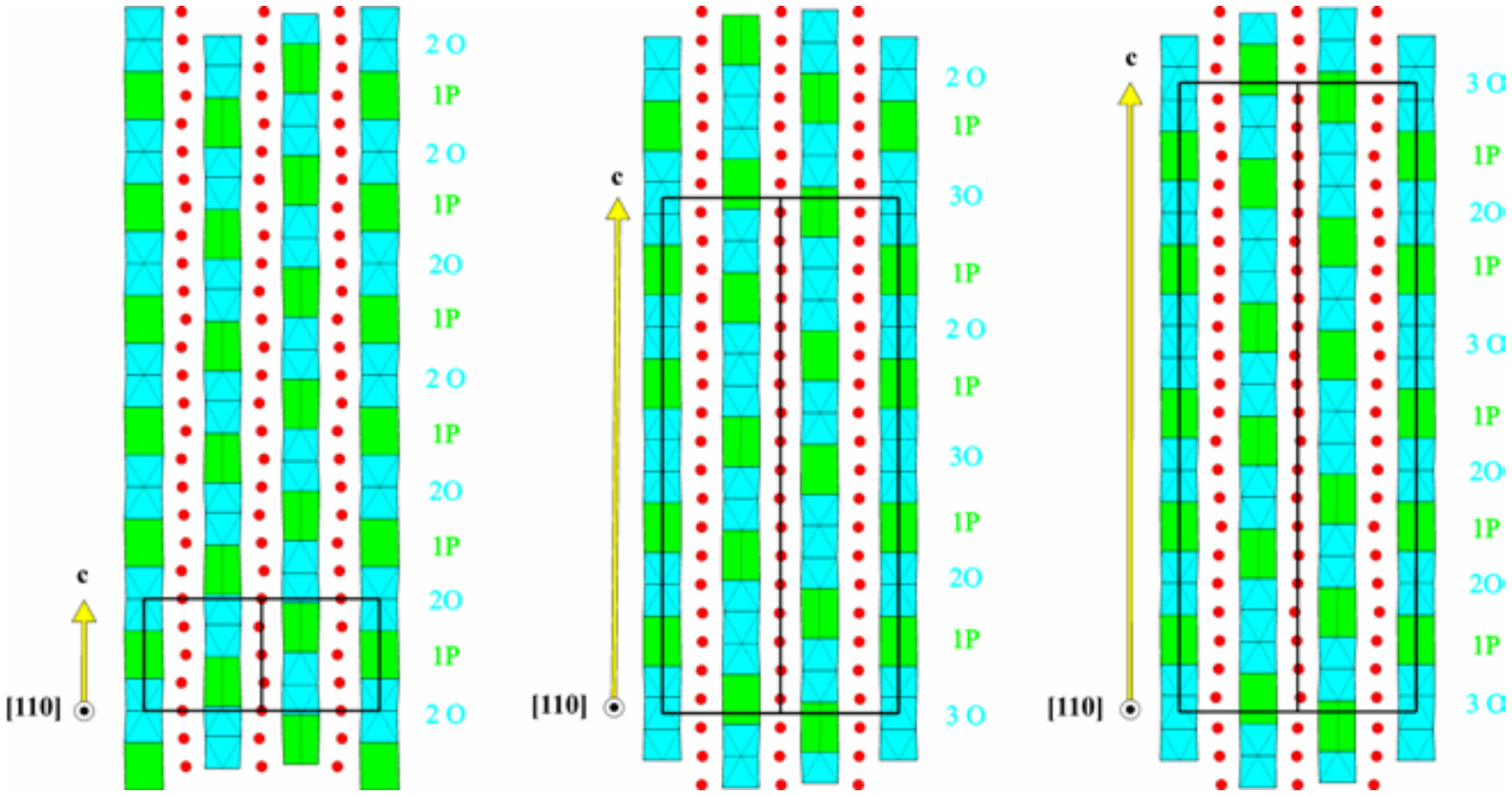
limited number of different building blocks, forming layers stacked in the third direction

Classical periodic structures …

Forms large families with :

- **structural similarities**
- **composition, cell parameters evolving for the ≠ members**
- **structural complexity increasing for the ≠ members**
- **≠ symmetries for the ≠ members**

Hexagonal phases $Ba_{1+x}[(Na_xMn_{1-x})O_3]$

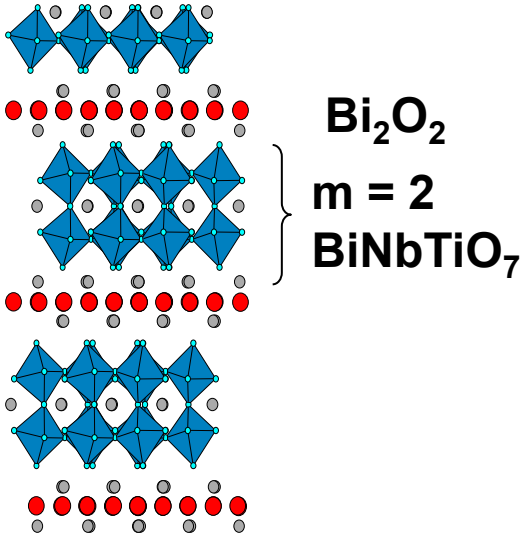


≠ sequences in the stacking direction

NaO_6 prismatic
MnO_6 octahedral

environments

Aurivillius phases



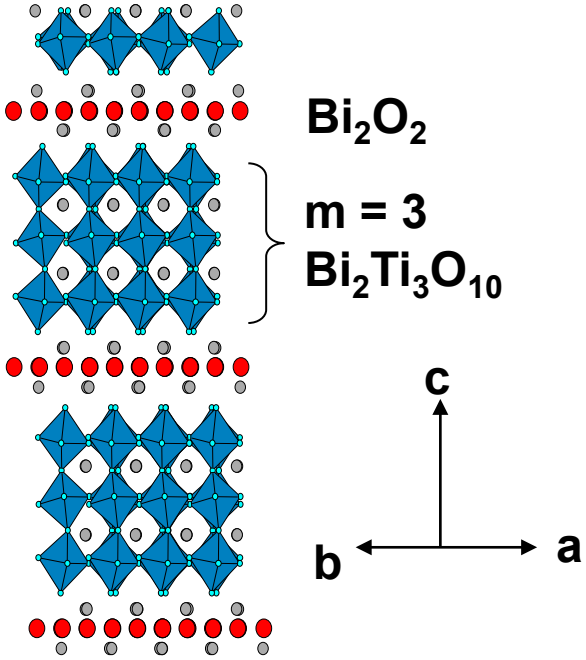
Bi_2O_2

m = 2

$BiNbTiO_7$

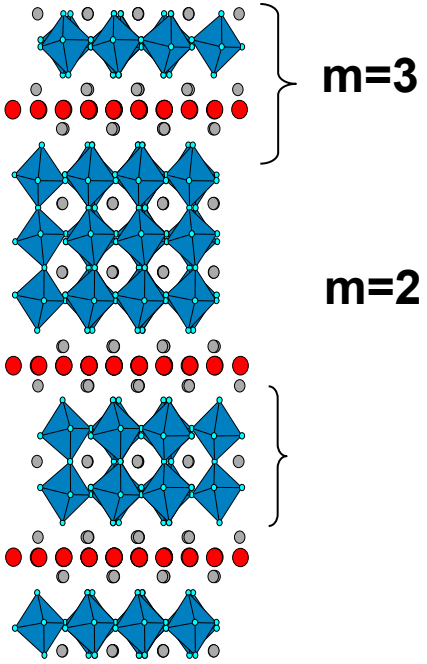
(m=2)

Bi_3NbTiO_9



(m=3)

$Bi_4Ti_3O_{12}$



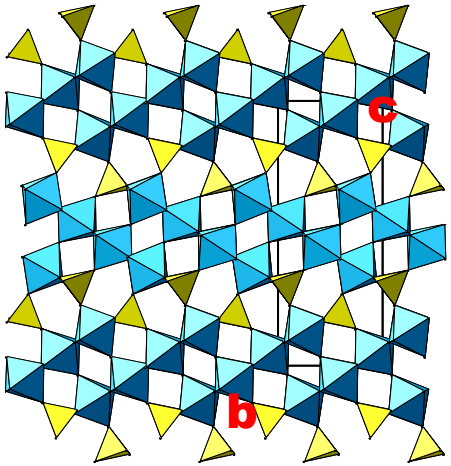
(m=2+3)

$Bi_7Ti_4NbO_{21}$

stacking of Bi_2O_2 layers and perovskite layers with variable thickness

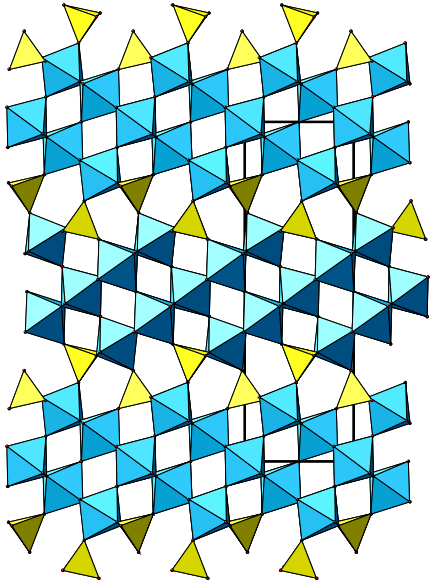
Tungsten Phosphate Bronzes $(PO_2)_4(WO_3)_{2m}$ with $4 \leq m \leq 14$

m=4, $P_4W_8O_{32}$



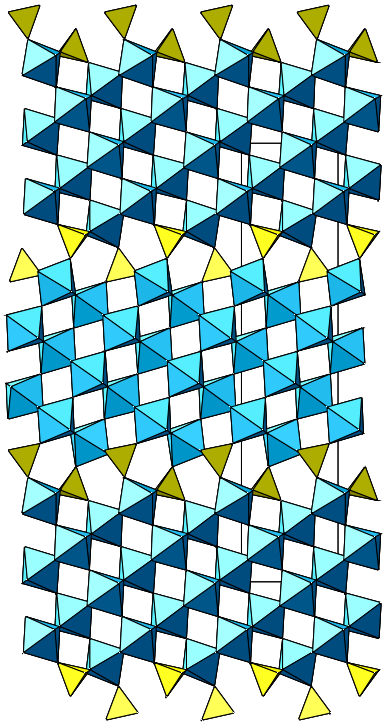
a=5.28 **b**=6.57 **c**=17.35
$P2_12_12_1$

m=5, $P_4W_{10}O_{38}$



a=5.28 **b**=6.57 **c**=20.45
β=90.40° $P2_1/n$

m=8, $P_4W_{16}O_{56}$



a=5.29 **b**=6.57 **c**=23.55
$P2_12_12_1$

Thickness of the WO_3 slabs is function of m …

Aim : to unify the description of the homologous series

using superspace formalism

to emphasize, to reveal common properties (symmetry, composition …) hidden by the overlapping of sub- and super- periodicities

to reduce the number of refinement parameters

application of superspace formalism to commensurate structures

Summary

- What is it ? What is the aim ?
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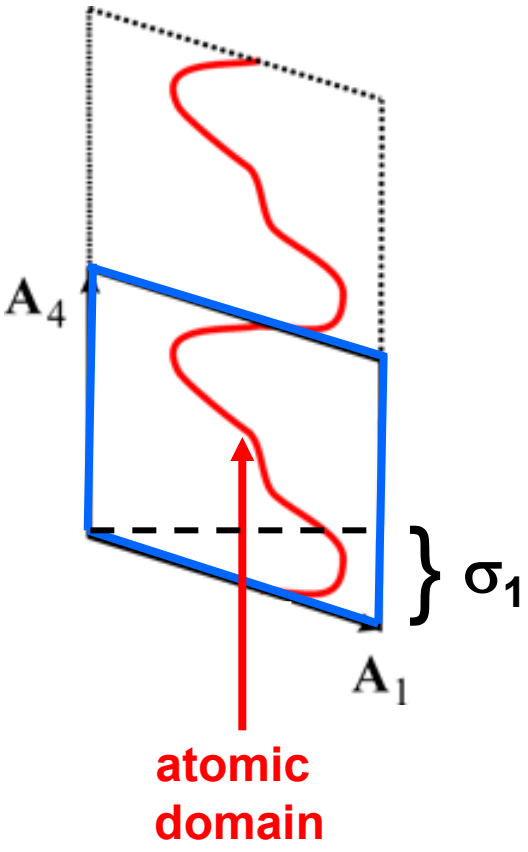
supercrystal



- **supercell :**

  $A_1 = a - \sigma_1 e_4$, $A_2 = b - \sigma_2 e_4$, $A_3 = c - \sigma_3 e_4$, $A_4 = e_4$

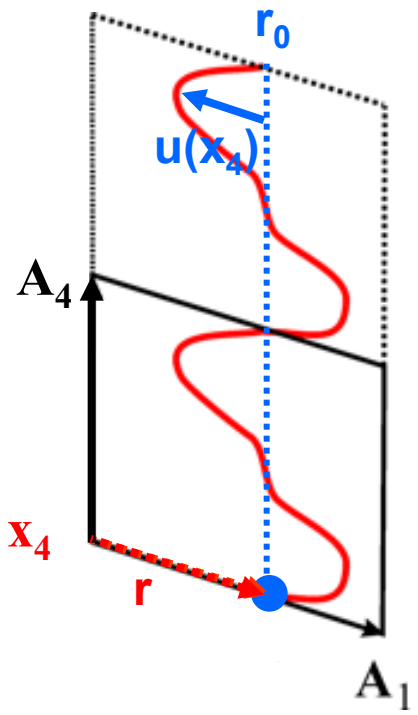
  with $q = \sigma_1 a^* + \sigma_2 b^* + \sigma_3 c^*$

- **atomic position :** $r = x_1 A_1 + x_2 A_2 + x_3 A_3$ and x_4

  $x_4 = q \,.\, (r + p)$

  $p = n_1 A_1 + n_2 A_2 + n_3 A_3$, $n_i \in \mathbb{N}$

supercrystal



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  with $q = \sigma_1 a^* + \sigma_2 b^* + \sigma_3 c^*$

- **atomic position :** $r = x_1 A_1 + x_2 A_2 + x_3 A_3 + x_4 A_4$

  $x_4 = q \,.\, (r + p)$

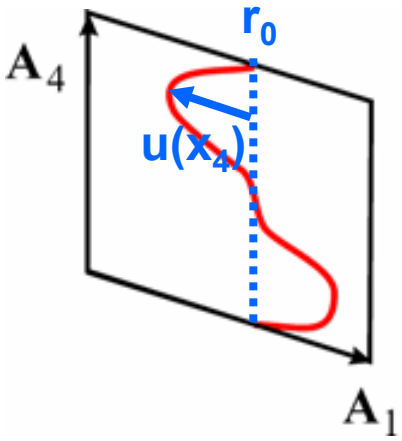
  $p = n_1 A_1 + n_2 A_2 + n_3 A_3$, $n_i \in \mathbb{N}$

- **$r(x_4)$**

  $r = r_0 + u(x_4)$ → atomic displacement

  two contributions

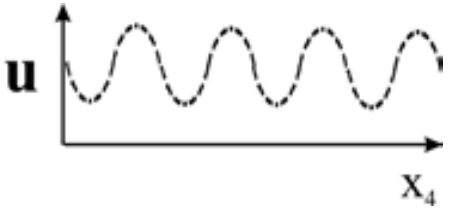
How describe u(x4) ?



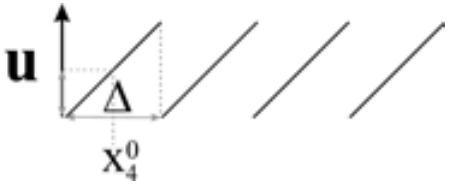
pool of periodic functions

- **Fourier series** developed up to the n order

$$u^j(x_4) = \sum_n A_n^j \sin(2n\pi i x_4) + B_n^j \cos(2n\pi i x_4)$$

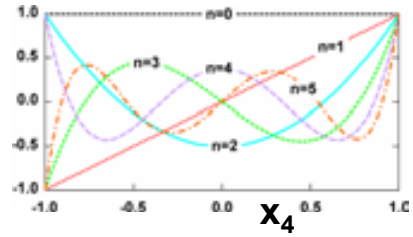


- **sawtooth functions**

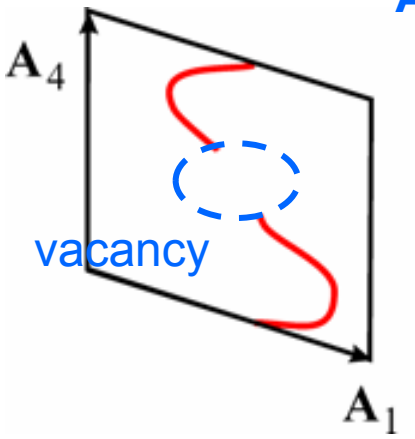


- **zigzag functions**

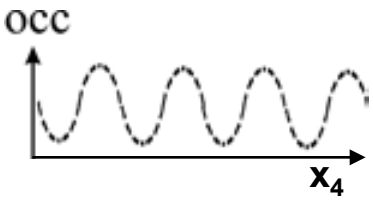
- **Legendre polynomials**



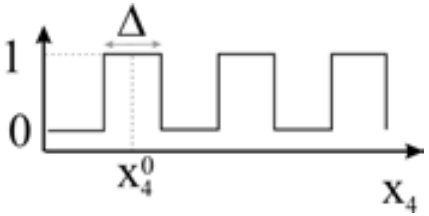
And what about the occupancy ?



- $P(x_4) = P_0 + \sum_n A_n^j \sin(2n\pi i x_4) + B_n^j \cos(2n\pi i x_4)$



- **crenel functions**

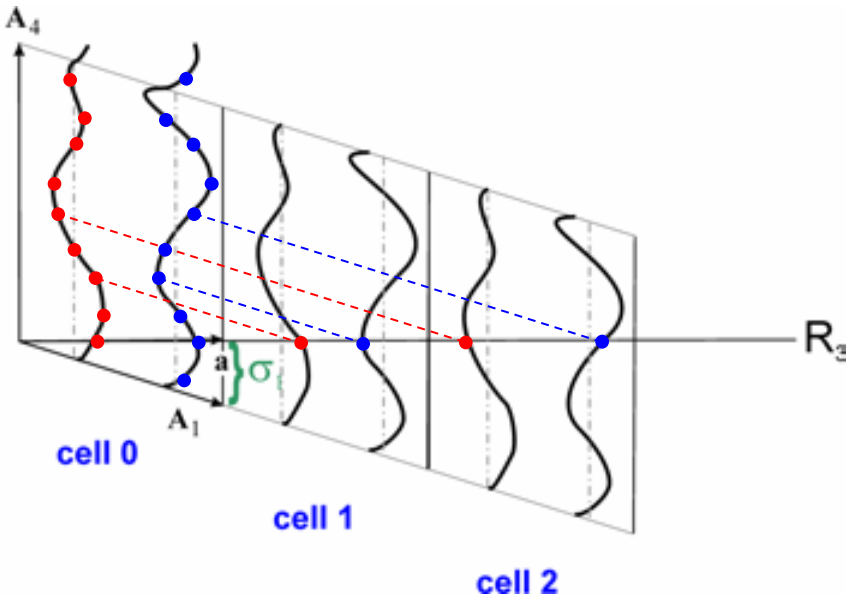


Building of the 3d structure from supercrystal ?

➡ true crystal = section of the super crystal

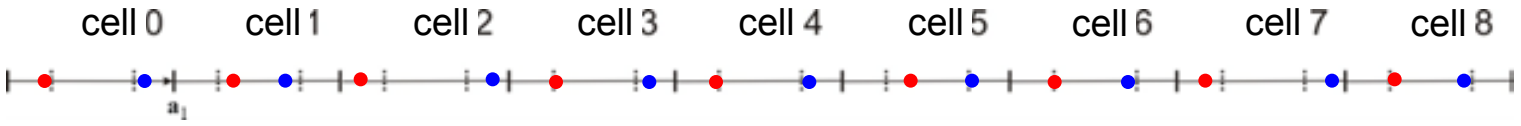
super crystal

3xq
2xq
1xq



physical space

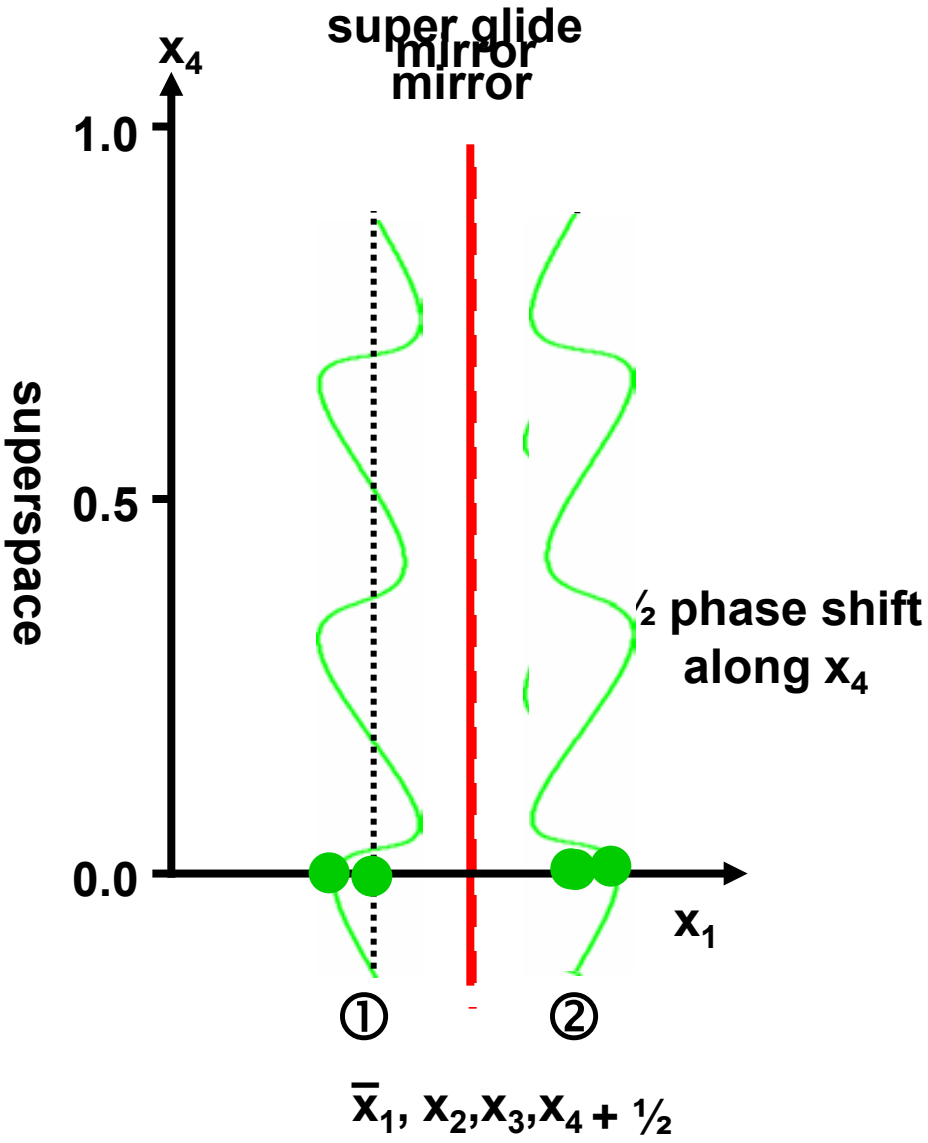
true crystal (in the physical space)

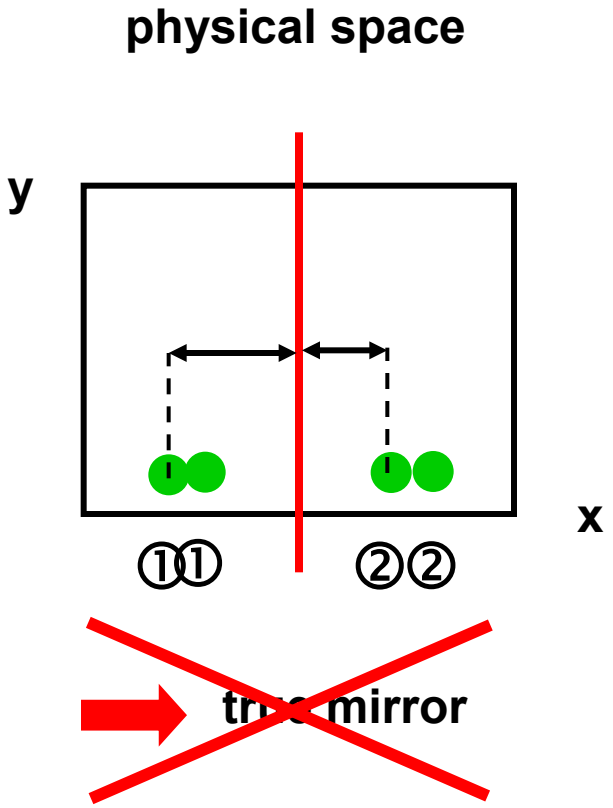


physical space

(3+1)d space

✓ multiple atoms → single atomic domain


super glide
mirror
mirror
x_4
1.0
0.5
0.0
superspace
½ phase shift
along x_4
x_1
①
②
$\bar{x}_1, x_2, x_3, x_4 + ½$

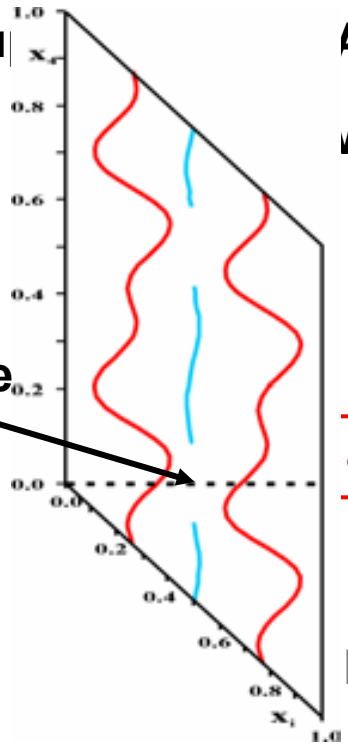

physical space
y
x
①①
②②
mirror

physical space		(3+1)d space
✓ multiple atoms	→	single atomic domain
✓ independent atoms	→	symmetry related atoms

Su

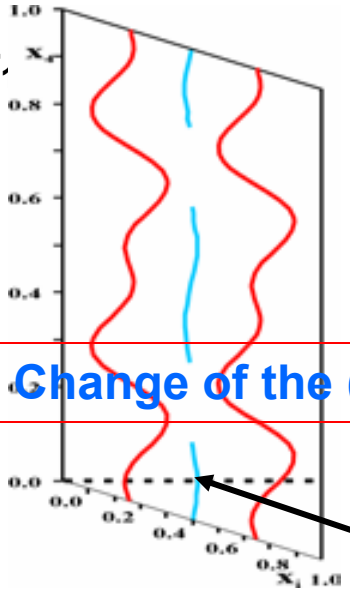
$A_1 = a - \sigma_1 e_4$, $A_2 = b - \sigma_2 e_4$, $A_3 = c - \sigma_3 e_4$, $A_4 = e_4$

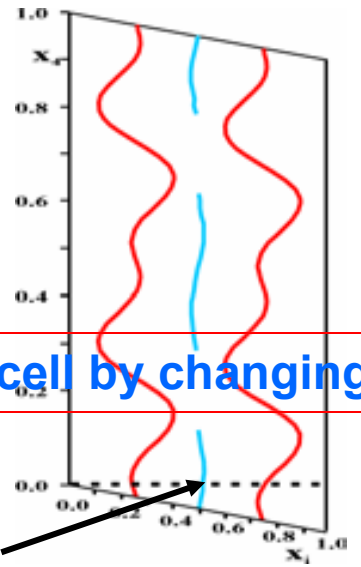
with q = σ. c*



vacancy in the 3d space

σ_i





Change of the (3+1)d cell by changing q

Physical space

no vacancy in the 3d space

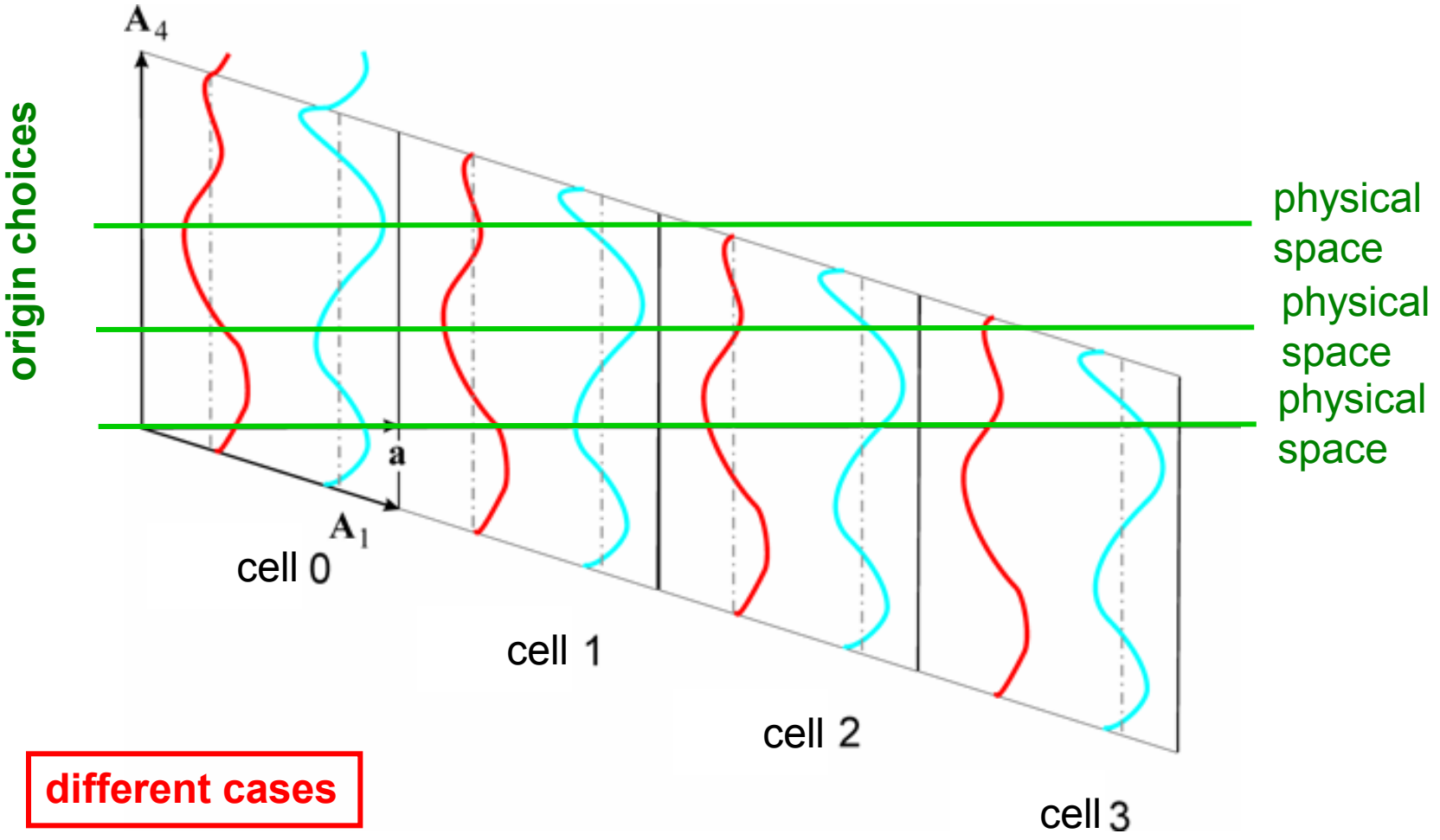
2 independant atomic domains (displacements and/or vacancies)

same modulation functions

3 choices of q vector ➡ 3 ≠ super-cells

physical space		(3+1)d space
✓ multiple atoms	→	single atomic domain
✓ independent atoms	→	symmetry related atoms
✓ different structures	→	1 model + ≠ wave vectors

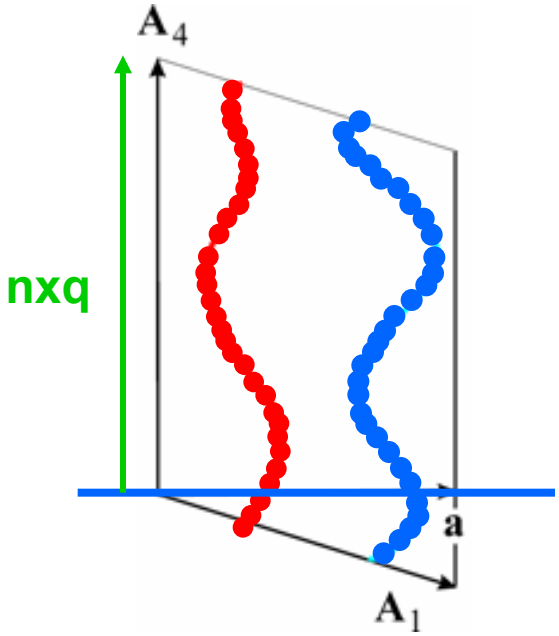
the problem of section choices



different cases

Incommensurate modulated structure

➡ **wave vector with at least one irrational component**



reading of the 3d atomic positions

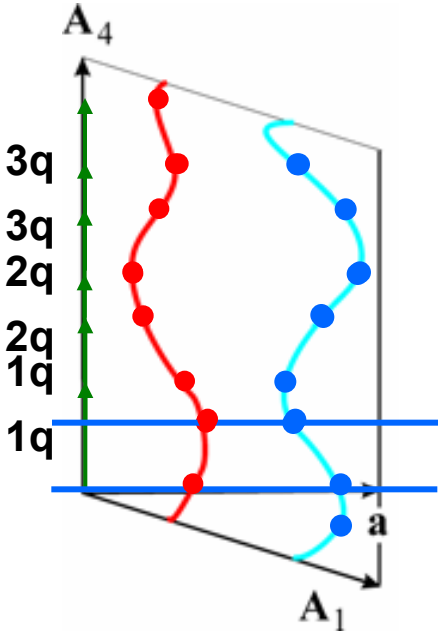
origin choice

all points of the atomic domains are physically relevant

➡ **all the 3d sections are equivalent**

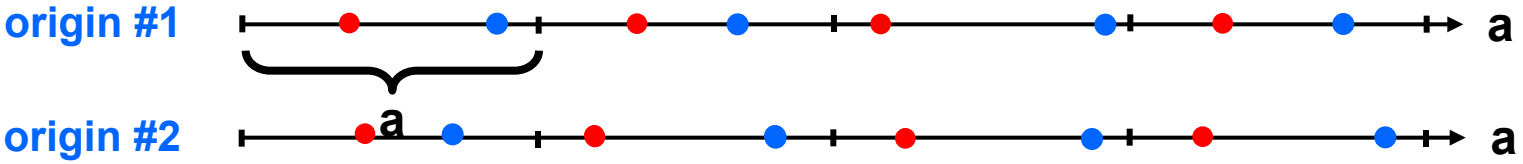
Commensurate modulated structure

➡ wave vector with rational components



only some points of the atomic domains are physically significant

2 choices of origin
=
2 different 3d structures



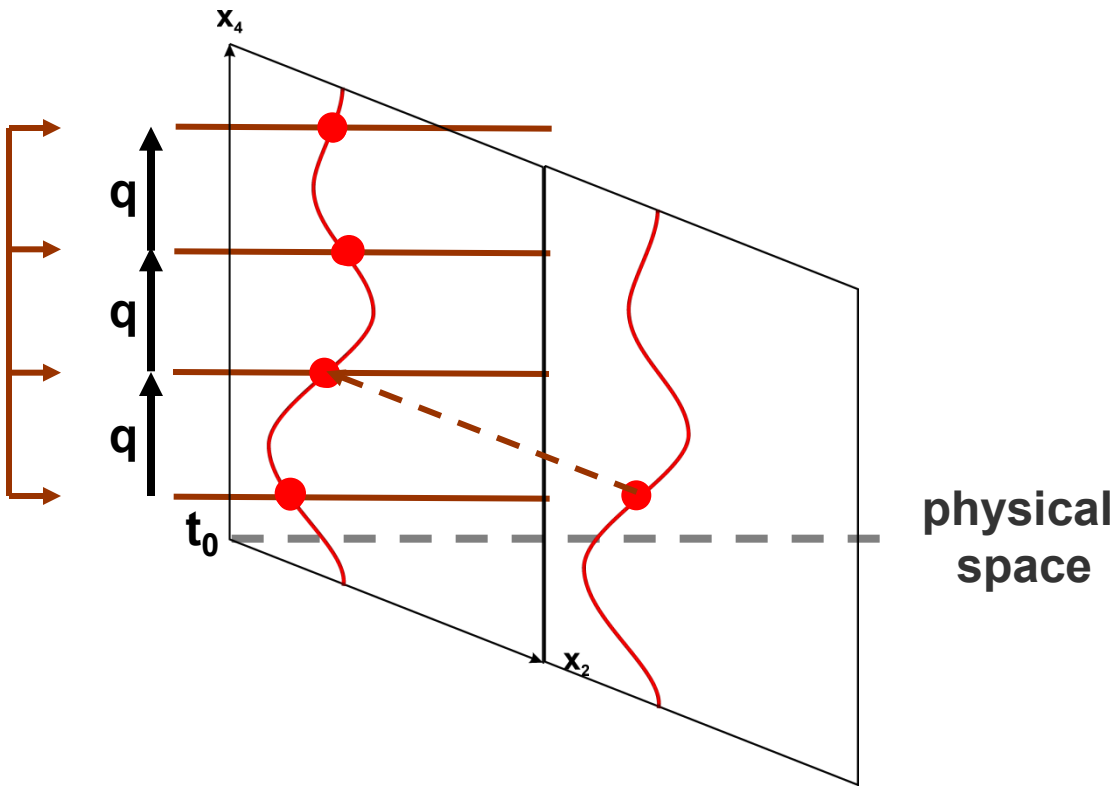
commensurate modulated structure with q= ¼ b*

atomic domain

different choices of sections

for a given t_0 relevant points on each atomic domain

grid of equivalent sections with q spacing

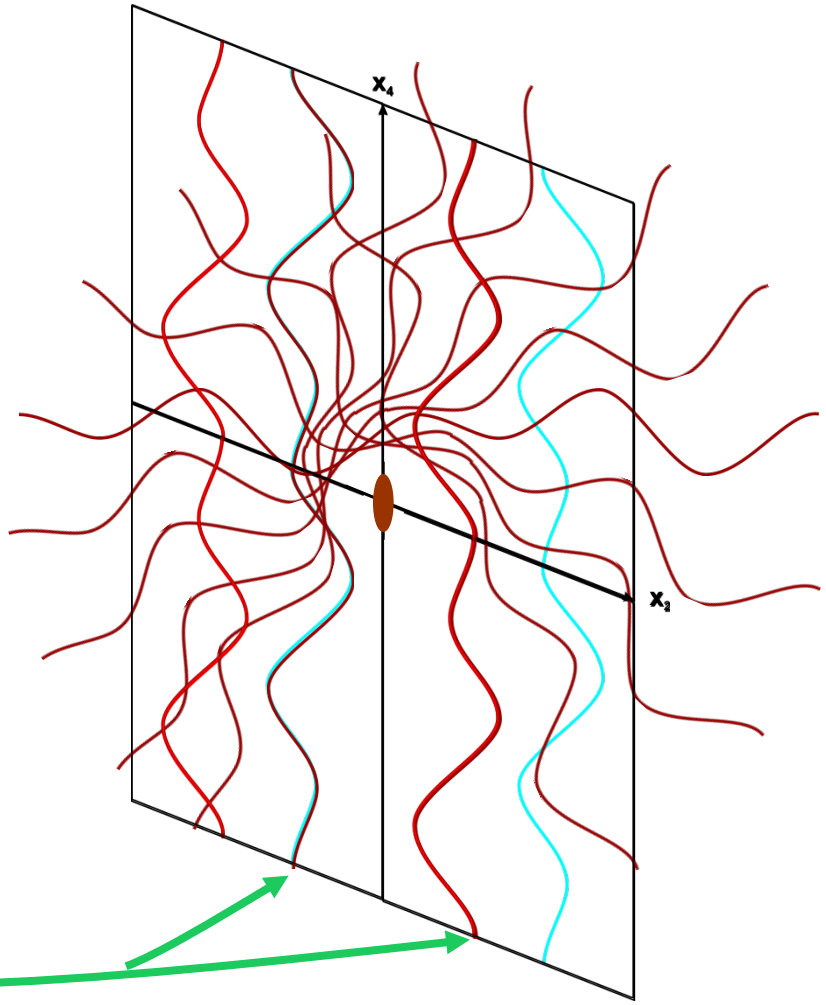


commensurate modulated structure with q= ¼ b*

m mirror $x_1,\bar{x}_2,x_3,\bar{x}_4$

≈ to 2-fold axis ⊥ (x_2,x_4)

2 equivalent atomic domains / super cell

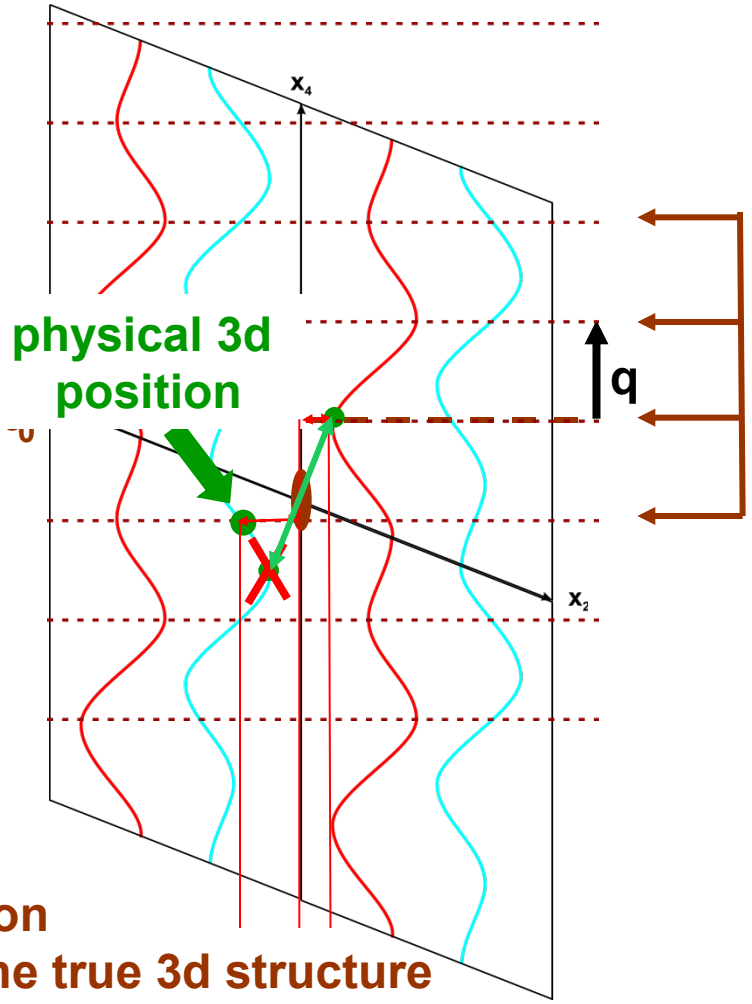


commensurate modulated structure with q= ¼ b*

m mirror $x_1,\bar{x}_2,x_3,\bar{x}_4$

general section

- ⇨ 1 physical point
- ⇨ equivalent point by m
- ⇨ grid of the equivalent sections



does not belong to an equivalent section

2 physical positions are not equivalent by m

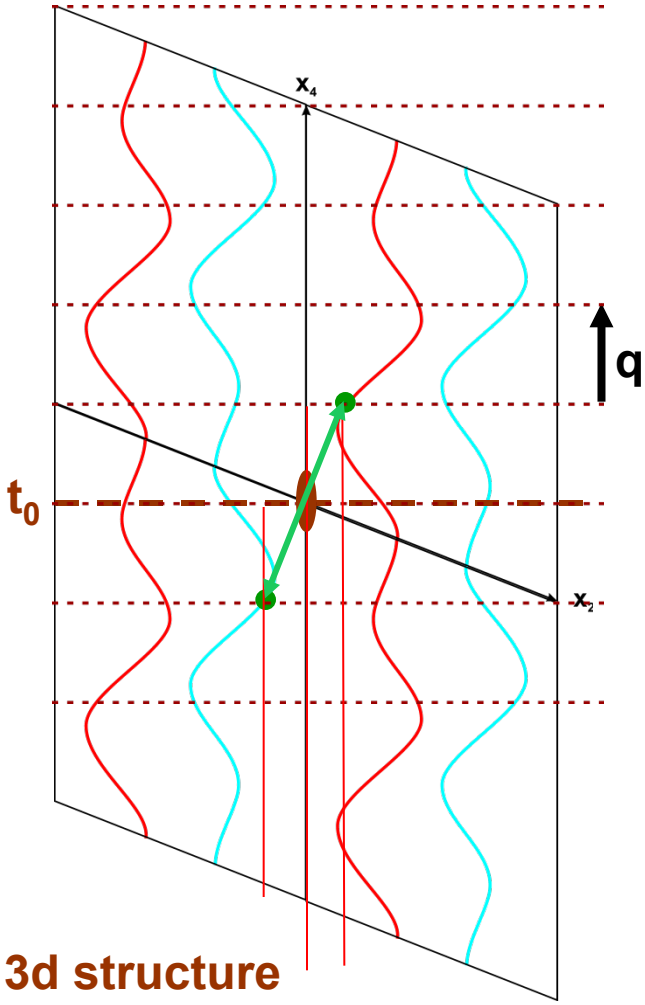
m does not belong to the t0 section
m does not belong to the SG of the true 3d structure

commensurate modulated structure with q= ¼ b*

m mirror $x_1,\bar{x}_2,x_3,\bar{x}_4$

Section t_0=0

- ⇨ 1 physical point
- ⇨ equivalent point by m
- ⇨ grid of the equivalent sections



➡ belongs to an equivalent section

➡ 2 physical positions are equivalent by m

➡ m belongs to the t_0 section
m belongs to the SG of the true 3d structure

it exists ≠ 3d sections with ≠ symmetries

make an inventory of the equivalents sections and symmetries

principle : **1 symmetry element S belongs to a section t_0 if two symmetry related atomic positions belong to t_0**

$$S = \begin{pmatrix} R_E & 0 \\ 0 & \varepsilon \end{pmatrix} \begin{pmatrix} \tau_E \\ \tau_I \end{pmatrix}$$

lattice translation $T + n_4 A_4 = n_1 A_1 + n_2 A_2 + n_3 A_3 + n_4 A_4$

$$x_4 \longrightarrow x_4' = \varepsilon x_4 + \tau_I + n_4$$

$$t = x_4 - q.r \longrightarrow t' = \varepsilon x_4 + \tau_I + n_4 - q\left[\{R_E|\tau_E\}r + T\right]$$

$$t \longrightarrow t' = \varepsilon(t + q.r) + \tau_I + n_4 - q\left[\{R_E|\tau_E\}r + T\right]$$

$$t \longrightarrow t' = \varepsilon t + \tau_I + n_4 - q\left[\tau_E + T\right]$$

principle : $t = \varepsilon t + \tau_I + n_4 - q\left[\tau_E + T\right]$

… to be applied to all the symmetry elements of the SSG **series of equations**

physical space		(3+1)d space
✓ multiple atoms	→	single atomic domain
✓ independent atoms	→	symmetry related atoms
✓ different structures	→	1 model ⊕ ≠ wave vectors
✓ different 3d symmetries	→	∃ ≠ t sections of the model

Summary

- What is it ? What is the aim ?
- Useful properties of the superspace formalism
- The method : keys …
- Some examples, step by step …
- Conclusion

Regular used of the superspace formalism …

unknown structure

diffraction pattern with different types of reflections

- **main reflections ➡ sub periodicity**
- **satellite reflections ➡ additional periodicity**

  irrationnal positions $s = ha^* + kb^* + \ell c^* + mq^*$

- **incommensurate structure**
- **superspace group**

structure solution of the average structure, of the super crystal and the of the true incommensurate structure

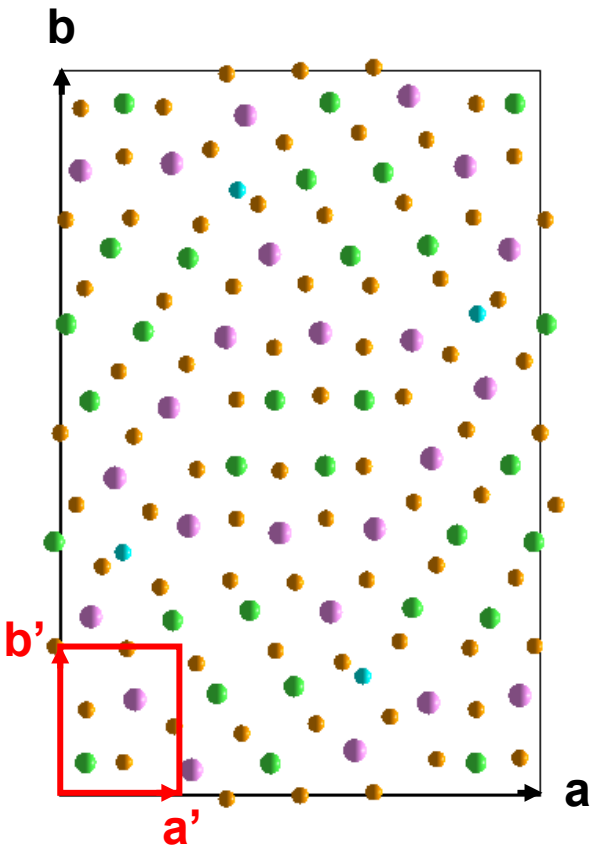
The superspace formalism for unifying a family of compounds …

family with well known structures

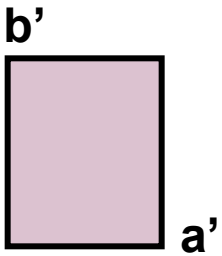
- **commensurate structures**
- **diffraction pattern with only one class of reflections**
- **sub cell common to all the members of the family ?**
  - ➡ **different types of reflections ?**
  - ➡ **sub periodicity in the 3d structure**
- **wave vector related with the composition *i.e.* with the member of the family ?**
- **superspace group compatible with 3d space groups of the family**

(3+1)d model, composition dependent, unifying the description of all the members of the family

Embedding of the 3d structure in the (3+1)d super space : principle



3d structure



geometric relationship

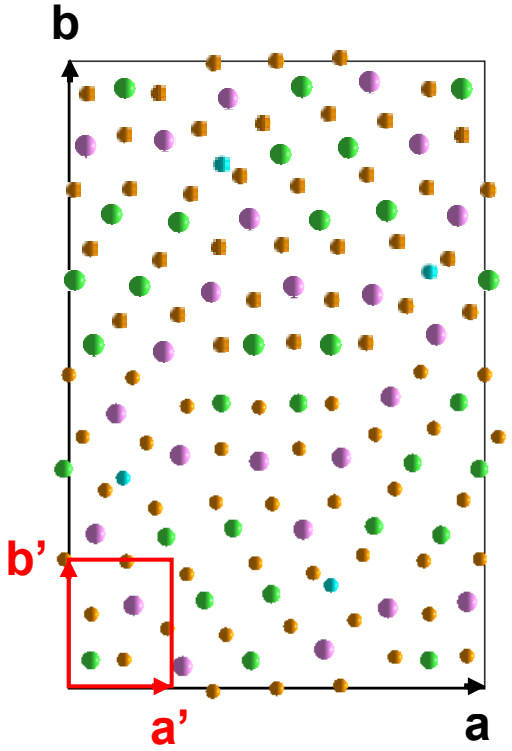
Sub-cell

$$\vec{a}' = \frac{\vec{a}}{n} \;,\; \vec{b}' = \frac{\vec{b}}{m}$$

+

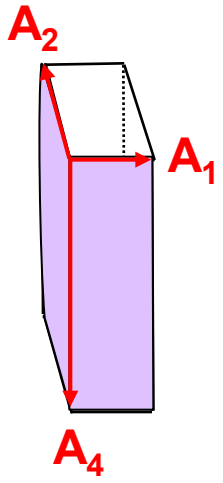
wave vector

x,y,z



3d structure

$$\vec{q} = \frac{1}{n}\vec{a}^{*\prime} + \frac{1}{m}\vec{b}^{*\prime}$$



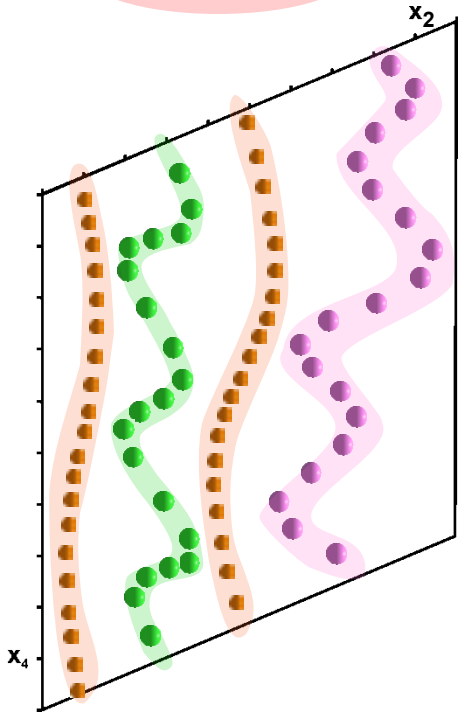
$$\vec{A}_1 = \vec{a}' - \frac{1}{n}\vec{e}_4$$

$$\vec{A}_2 = \vec{b}' - \frac{1}{m}\vec{e}_4$$

$$\vec{A}_4 = \vec{e}_4$$

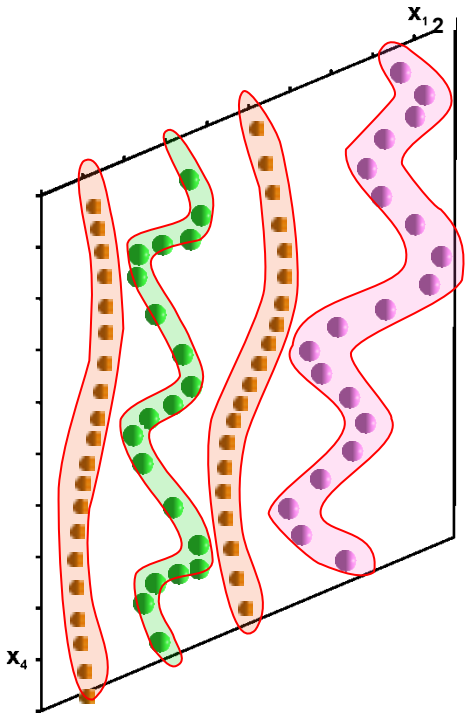
(3+1)d super cell

x_1,x_2,x_3,x_4



(3+1)d super crystal

(3+1)d super crystal



If parameters for the embedding correctly defined

→ limited number of atomic domains

- description of the atomic domains with the pool of functions
- determination of the superspace group compatible with the atomic domains
- determination of a general (3+1)d model

→ finding the rules linking the (3+1)d model, the q vector and the ≠ members of the family

- **make the inventory of the equivalents sections and symmetries *versus* the q vector and the superspace group**

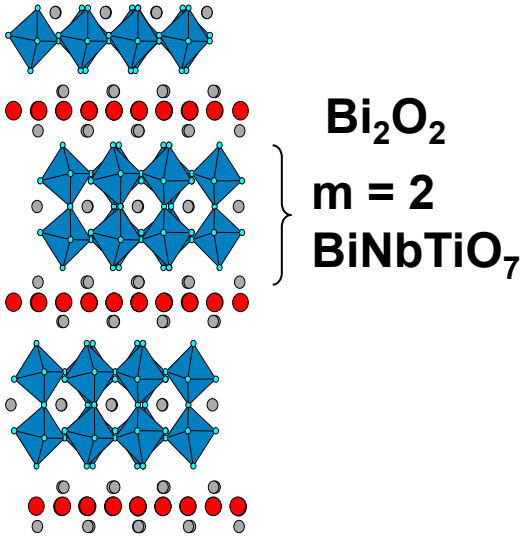
- **Verify the compatibility between**
  - **the 3d symmetries of the homologous series and the sections analysis**
  - **the structure solved using classical 3d approach and the (3+1)d model**

Summary

- What is it ? What is the aim ?
- Useful properties of the superspace formalism
- The method : keys …
- Some examples, step by step …
- Conclusion

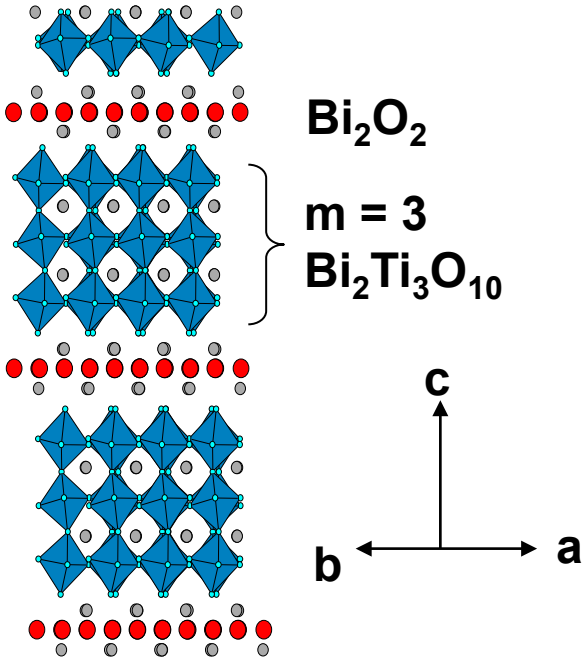
Aurivillius phases in the pseudo-binary system Bi_3TiNbO_9-$Bi_4Ti_3O_{12}$

(exemple kindly provided by Ph. Boullay)



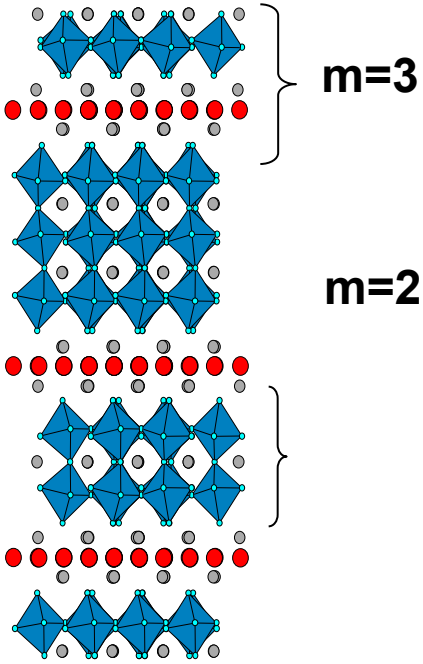
(m=2)

Bi_3NbTiO_9



(m=3)

$Bi_4Ti_3O_{12}$



(m=2+3)

$Bi_7Ti_4NbO_{21}$

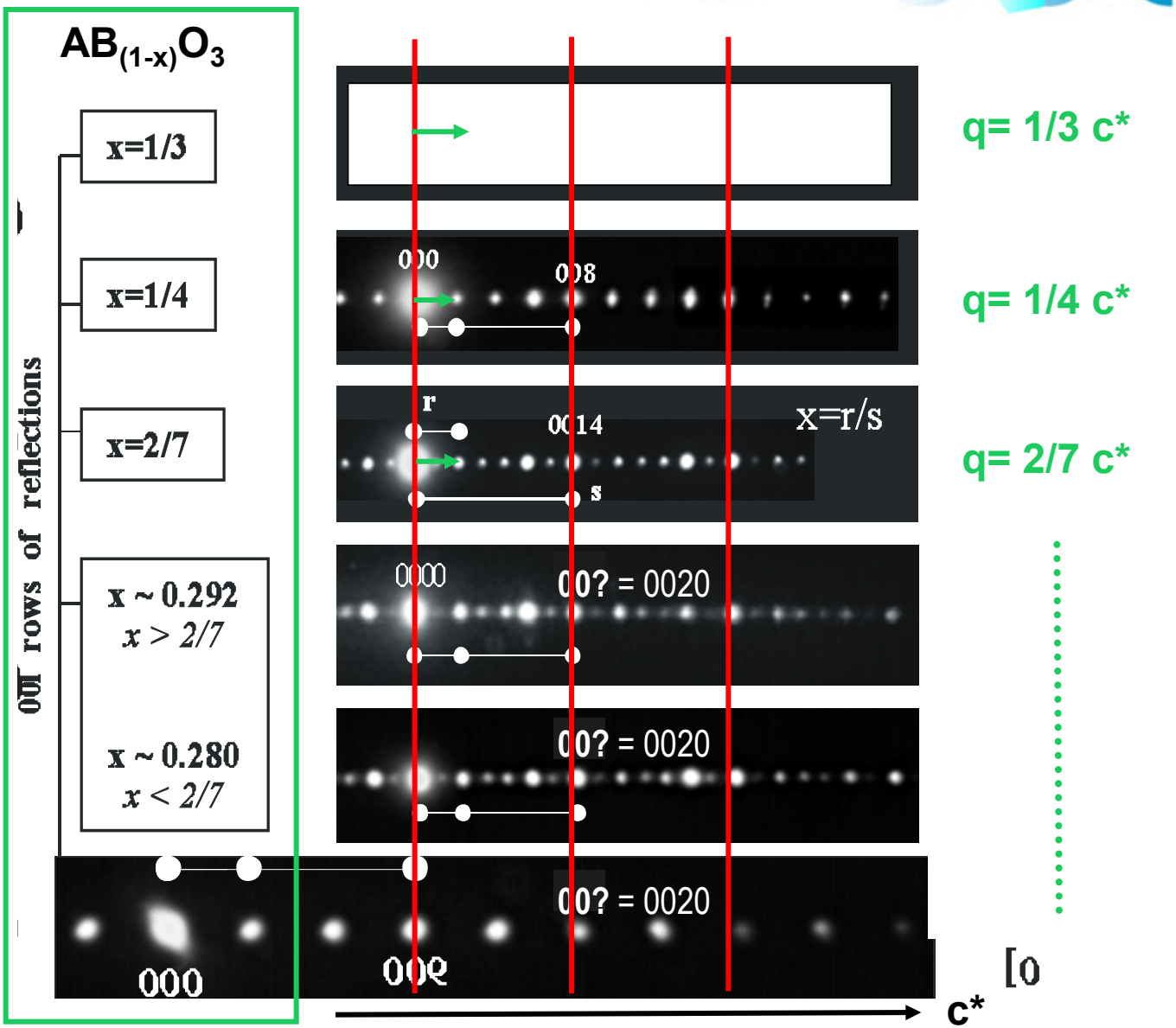
m=2 Bi_3TiNbO_9

m=3 $Bi_4Ti_3O_{12}$

2+3 $Bi_7Ti_4NbO_{21}$

$BiB_{(1-x)}O_3$

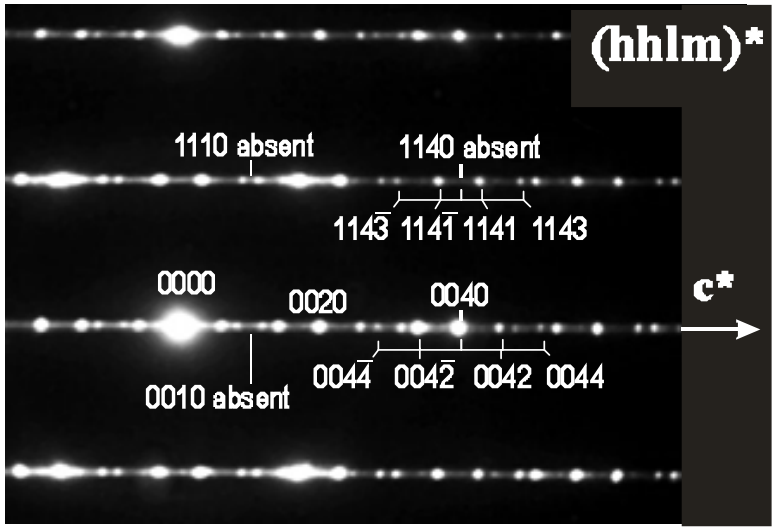
perovskite deficient

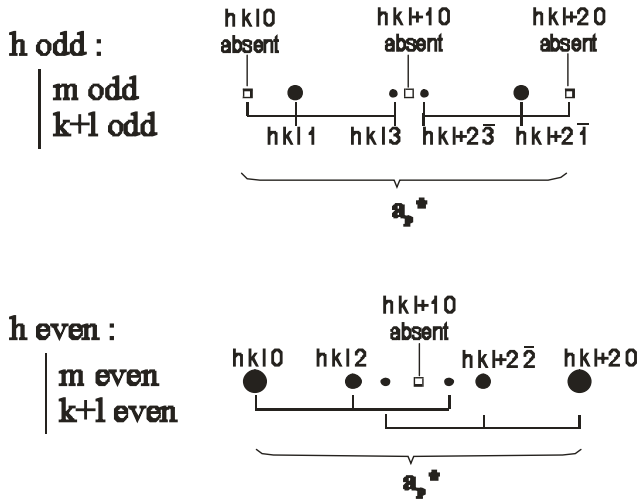


determination of the sub cell : a~ap√2, b~ap√2, c~2 ap

wave vector q = x . c* **composition dependent evolution**

systematic observation of the extinction rules

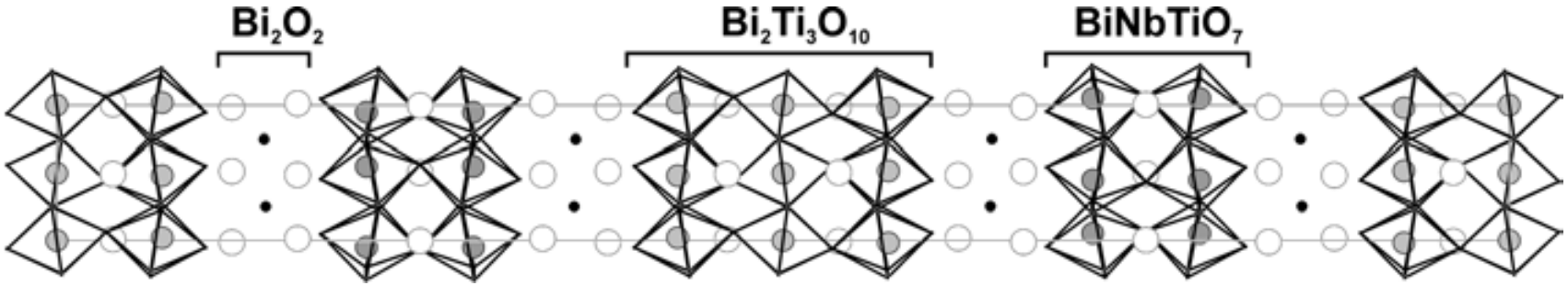




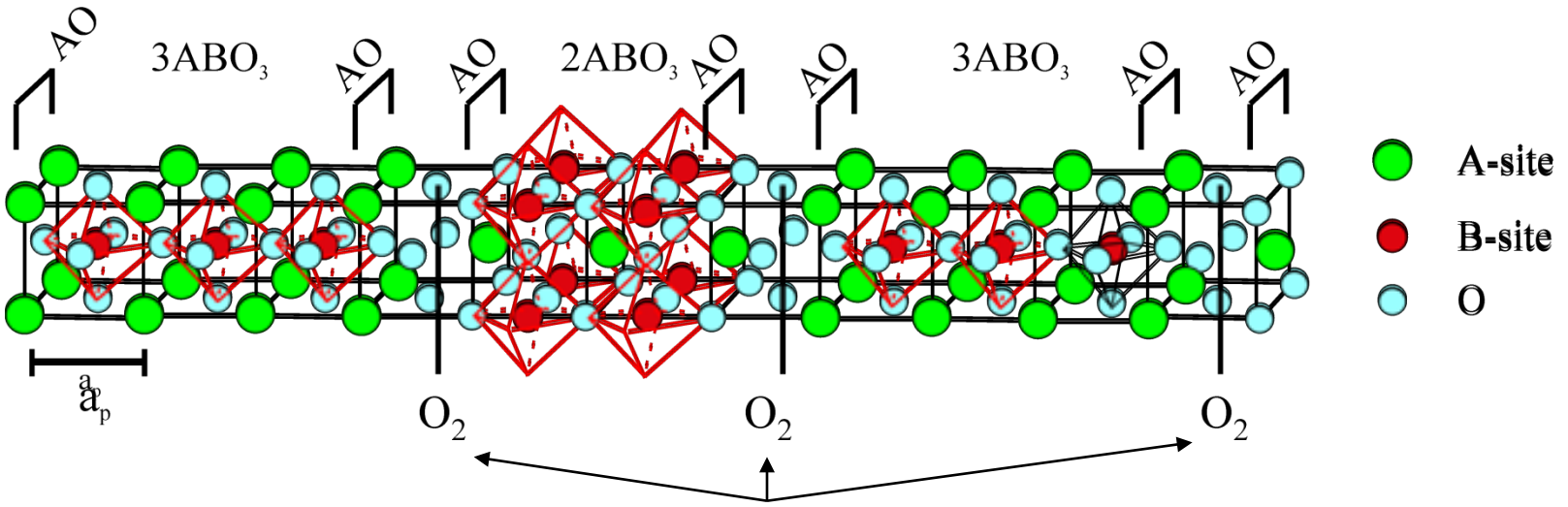
super space group X2cm(00x)000 with X {½ ½ ½ 0 / ½ 0 0 ½ / 0 ½ ½ ½ }

centring lattice vector

$Bi_7Ti_4NbO_{21}$

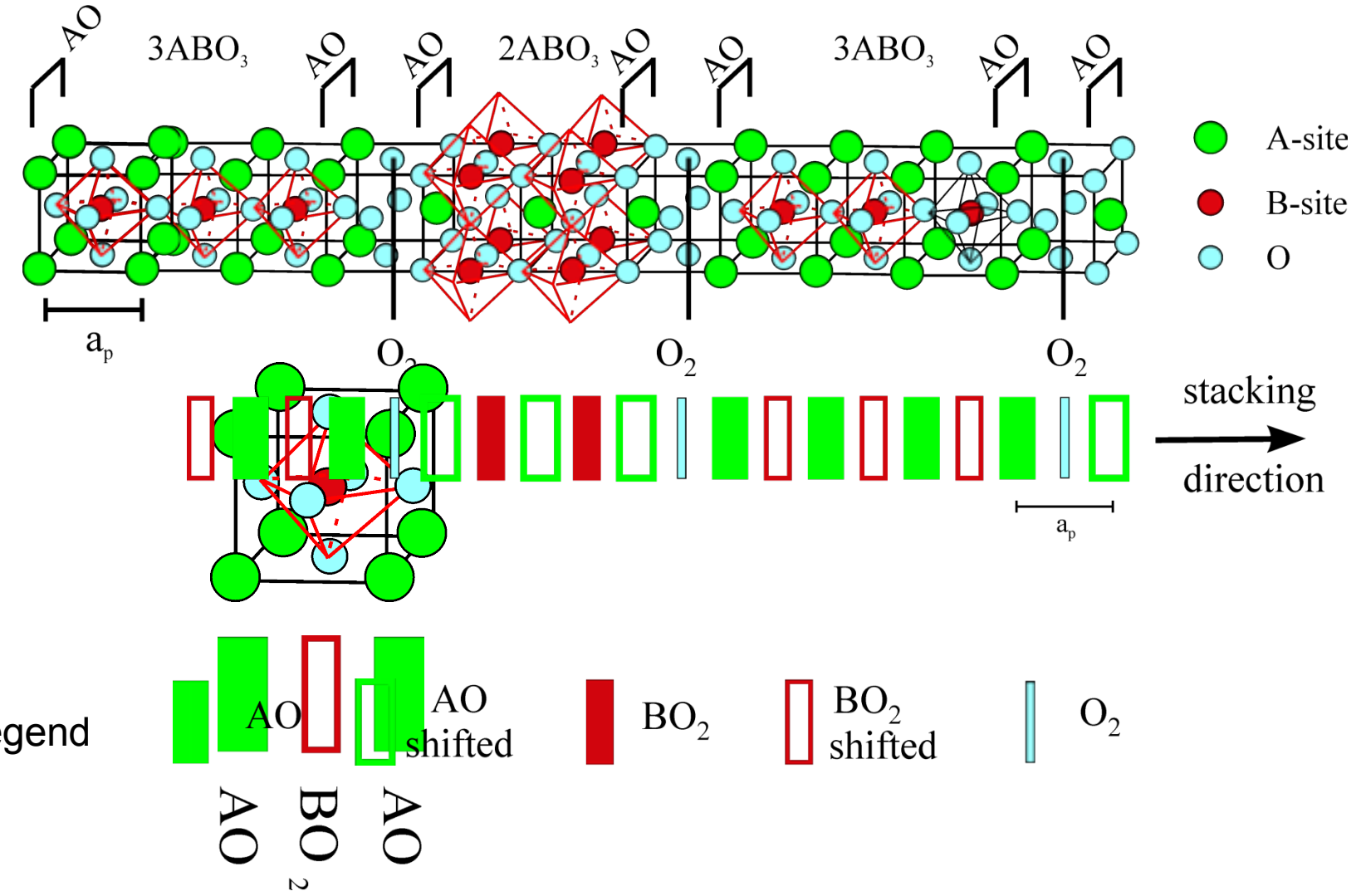


perovskite deficient material $AB_{1-x}O_3$ **structural description using layers**



B vacancies

perovskite deficient material $AB_{1-x}O_3$



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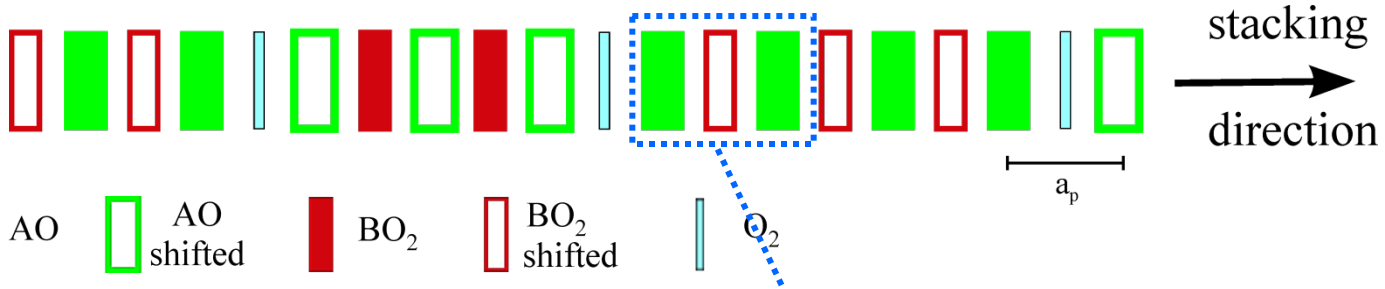
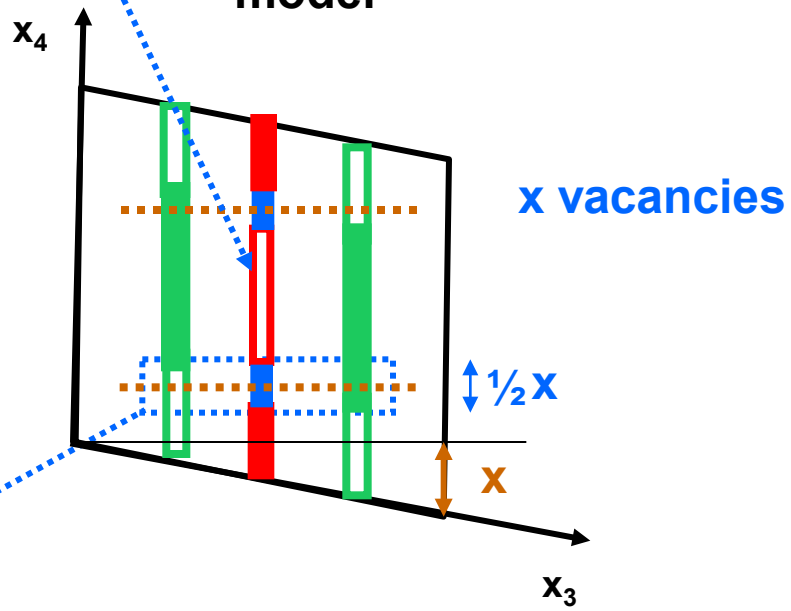
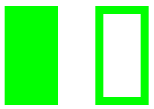


super crystal model



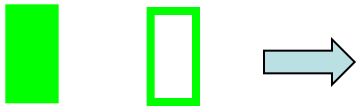
- **2 atomic domains A and B for the cations built from a sequence of :**

A

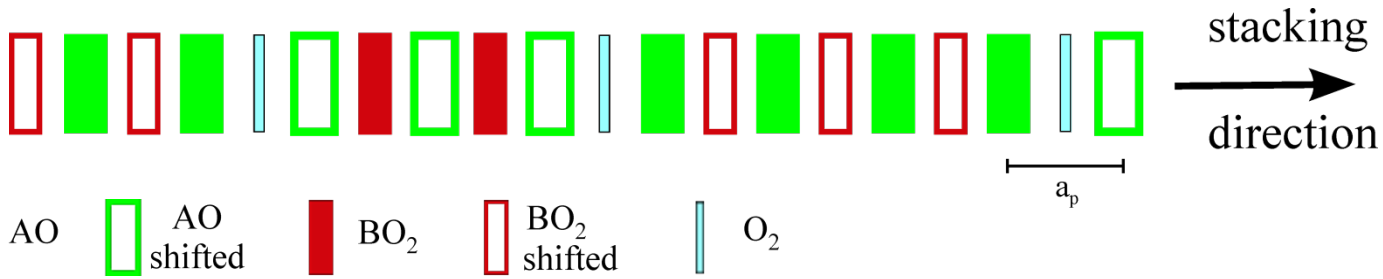


B

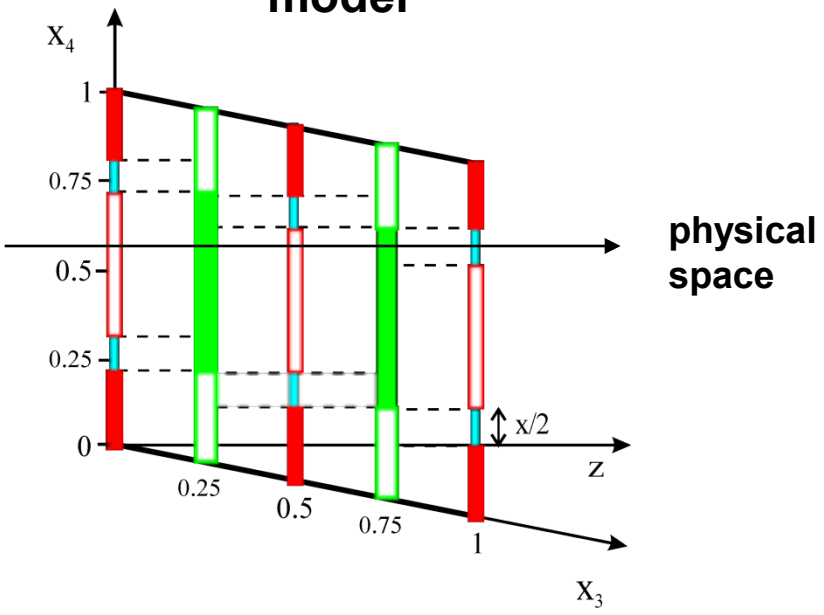
- **1 rule : between**



perovskite deficient material $AB_{1-x}O_3$



super crystal model



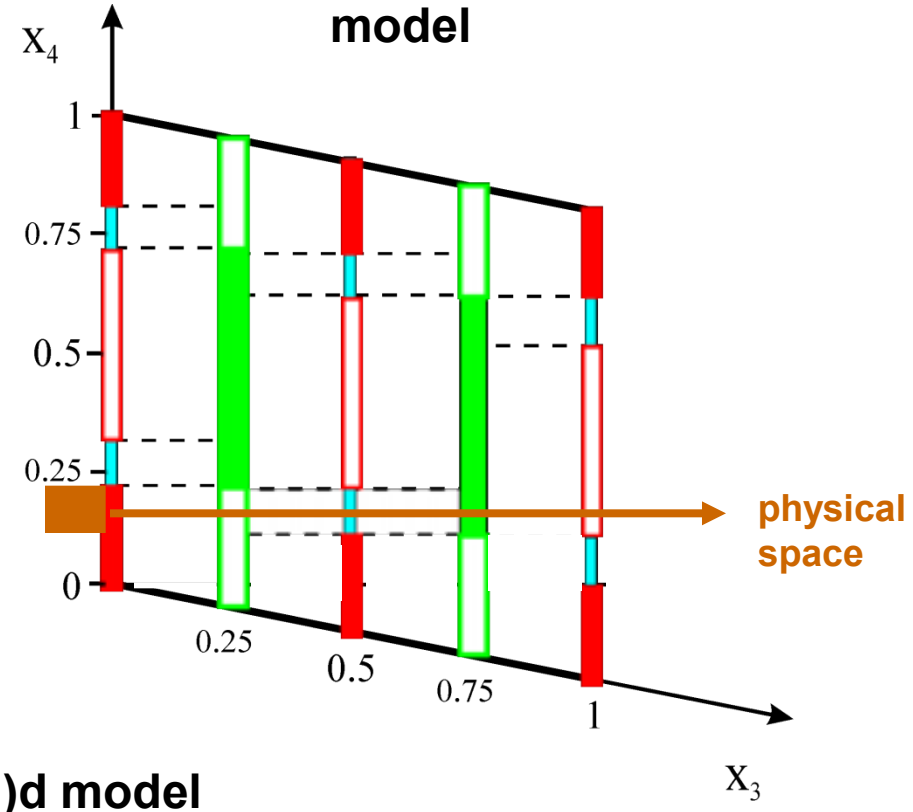
- **2 atomic domains A and B for the cations built from a sequence of :**

A

B

- **1 rule : between**

super crystal model



3d structure

stacking direction c

(3+1)d model

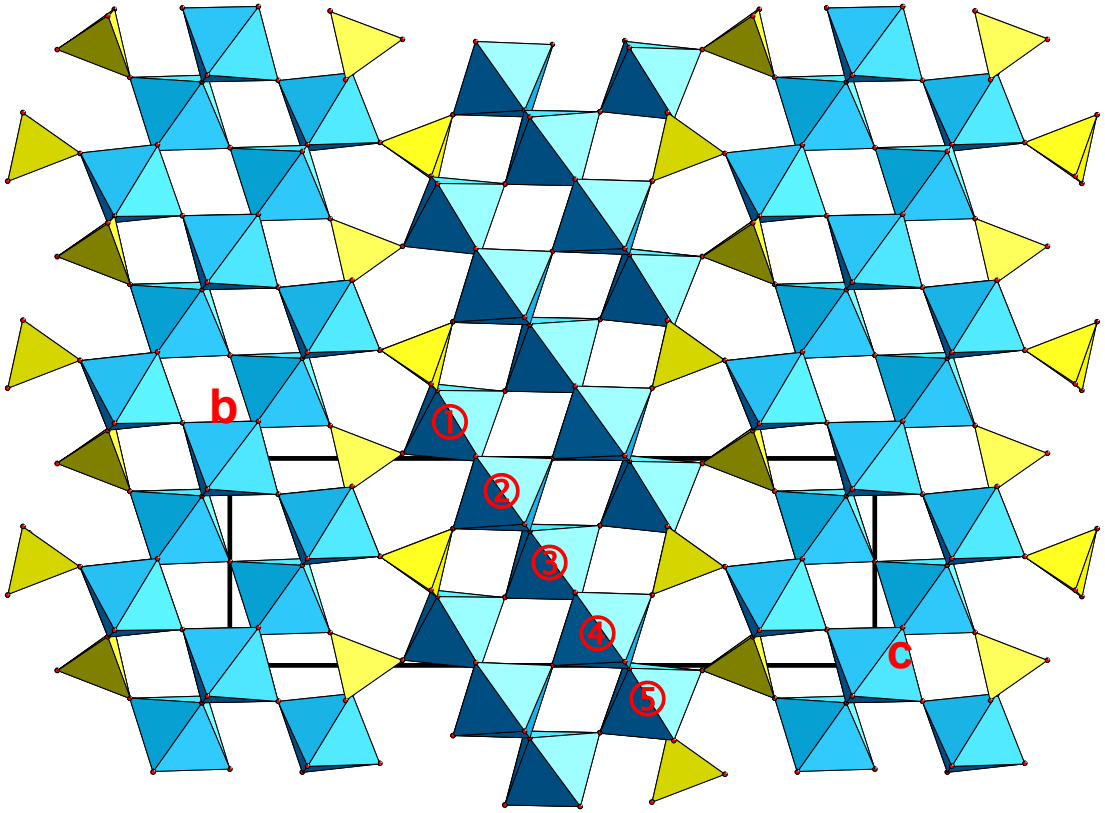
	x_1	x_2	x_3	x_4	Δ
A	0	0	¼	½	½
B	0	0	0	0	(1-x)/2

crenel functions

Mono Phosphate Tungsten Bronzes family

chemical formula $(PO_2)_4(WO_3)_{2m}$ **with 4≤m≤14**

MPTBp m=5, $P_4W_{16}O_{38}$



member (m)	chemical formula	T_{C1} (K)	cell parameters (Å) ($T \geq T_{C1}$)	Space Group ($T \geq T_{C1}$)	structural report
4	$P_4W_8O_{32}$	80	**a**=5.28 **b**=6.57 **c**=17.35	$P2_12_12_1$	Giroult *et al*, Acta Crystallogr. B37 (1981)
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12	$P_4W_{24}O_{80}$	535	**a**=5.31 **b**=6.55 **c**=42.11	$P2_12_12_1$	Roussel *et al*, Acta Crystallogr. B54 (1998)
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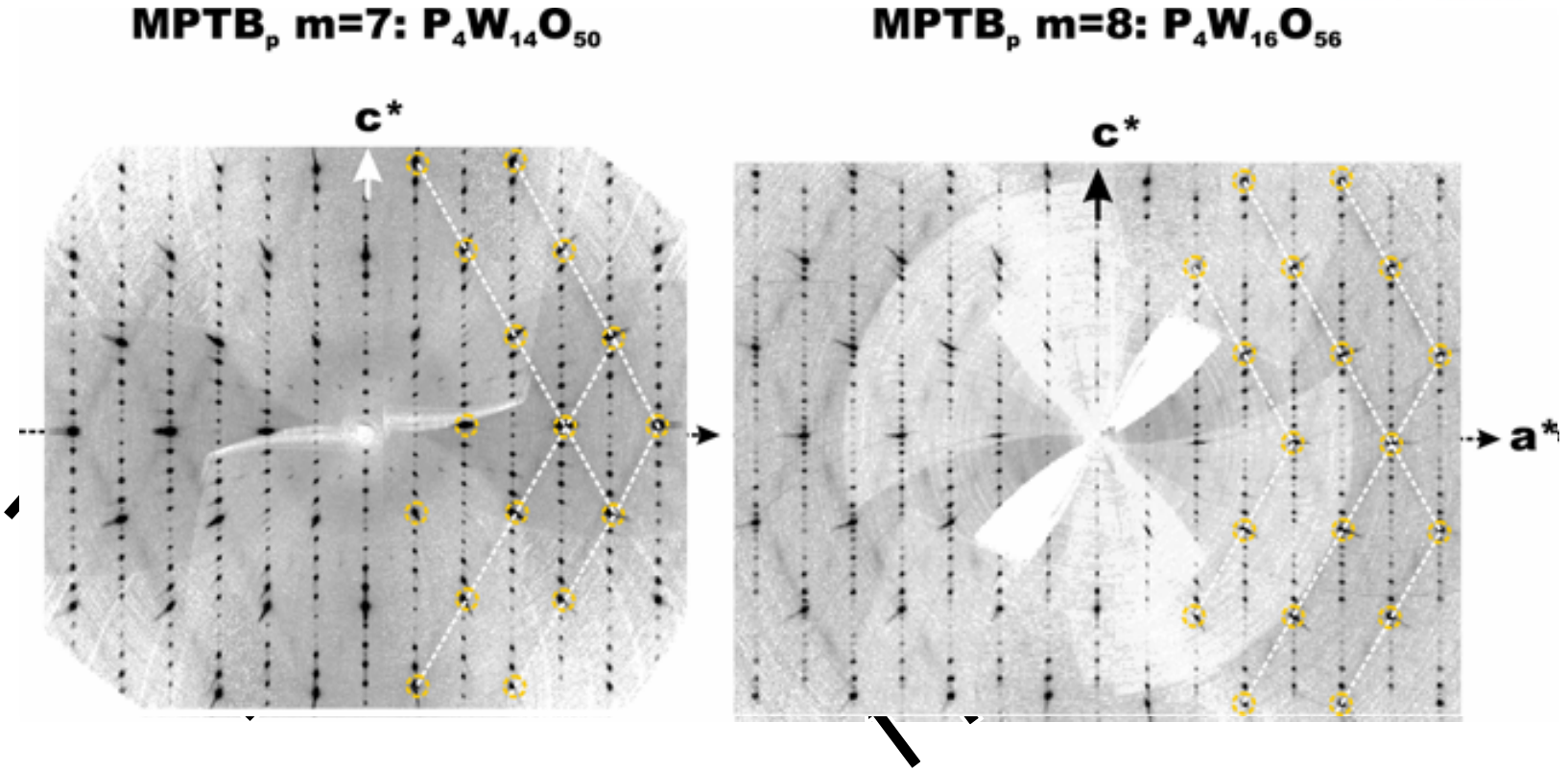
14	$P_4W_{28}O_{92}$	730	**a**=5.32 **b**=6.54 **c**=48.00	nc	Ottolenghi *et al*, J. Phys. I Fr. 6 (1996)

m even ➡ S.G. $P2_12_12_1$ **m odd ➡ S.G. $P2_1/n$**



diffuse scattering

Enlightening of intense reflections

definition of a basic subcell using the "enlightened" reflections

c=(m+2) c'

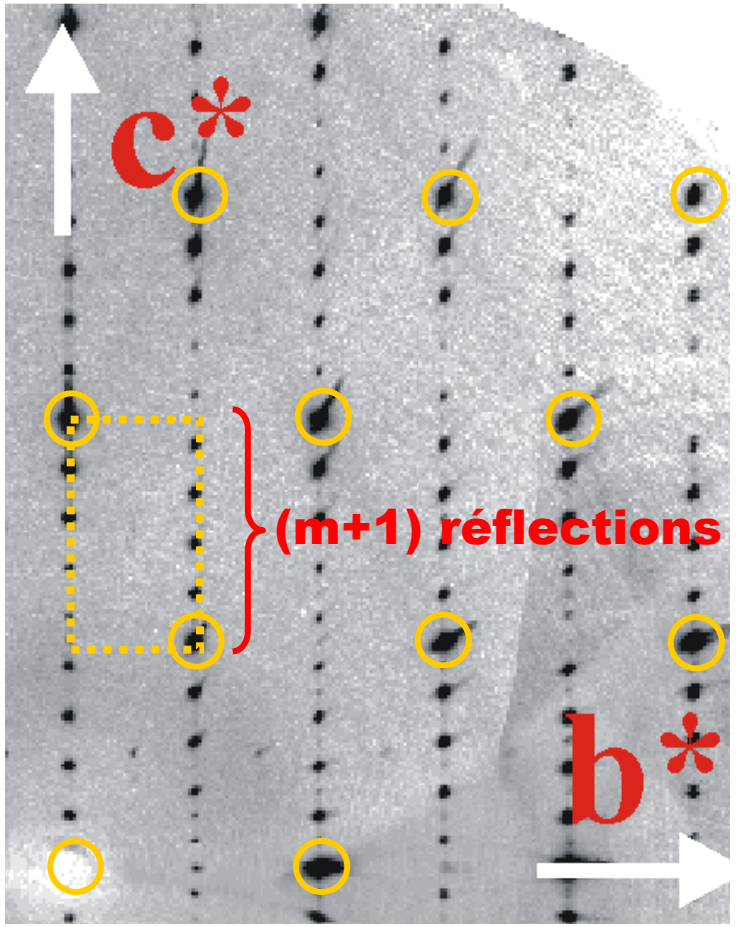
a=5.29 Å b=6.55 Å c'=2.97 Å
α=β=γ=90°

modulation vector : $q = \frac{1}{m+2} c'^{*}$

$$s = ha^{*} + kb^{*} + \ell c^{*} + mq$$

from the extinction rules :

SSG : Pnnm(00γ)0s0

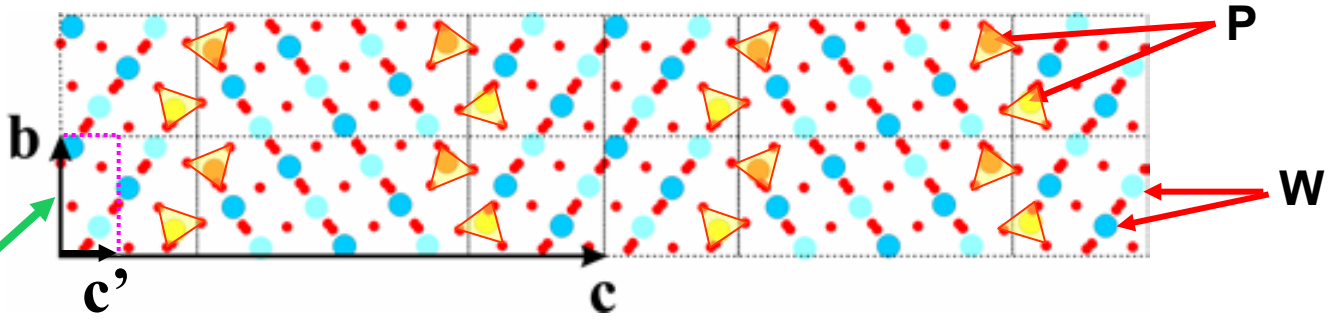


MPTBp m=8, $P_4W_8O_{56}$

cell : a=5.29 Å b=6.55 Å c'=2.97 Å β=90°, SG : $P2_12_12_1$

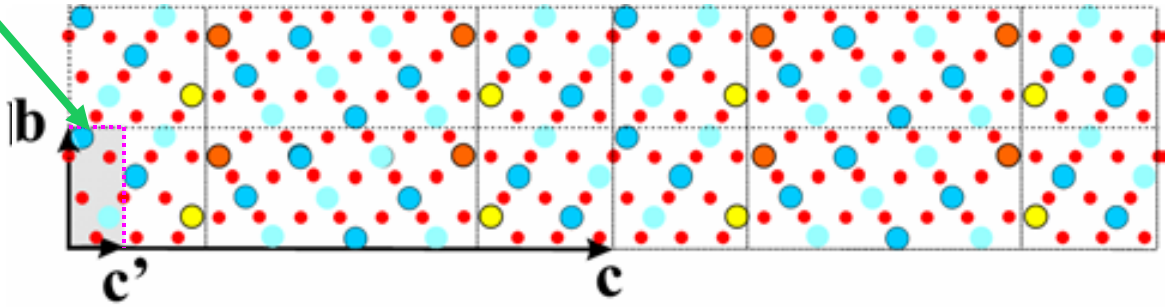
sub cell : a=5.29 Å b=6.55 Å c'=2.97 Å β=90°

real structure



subcell

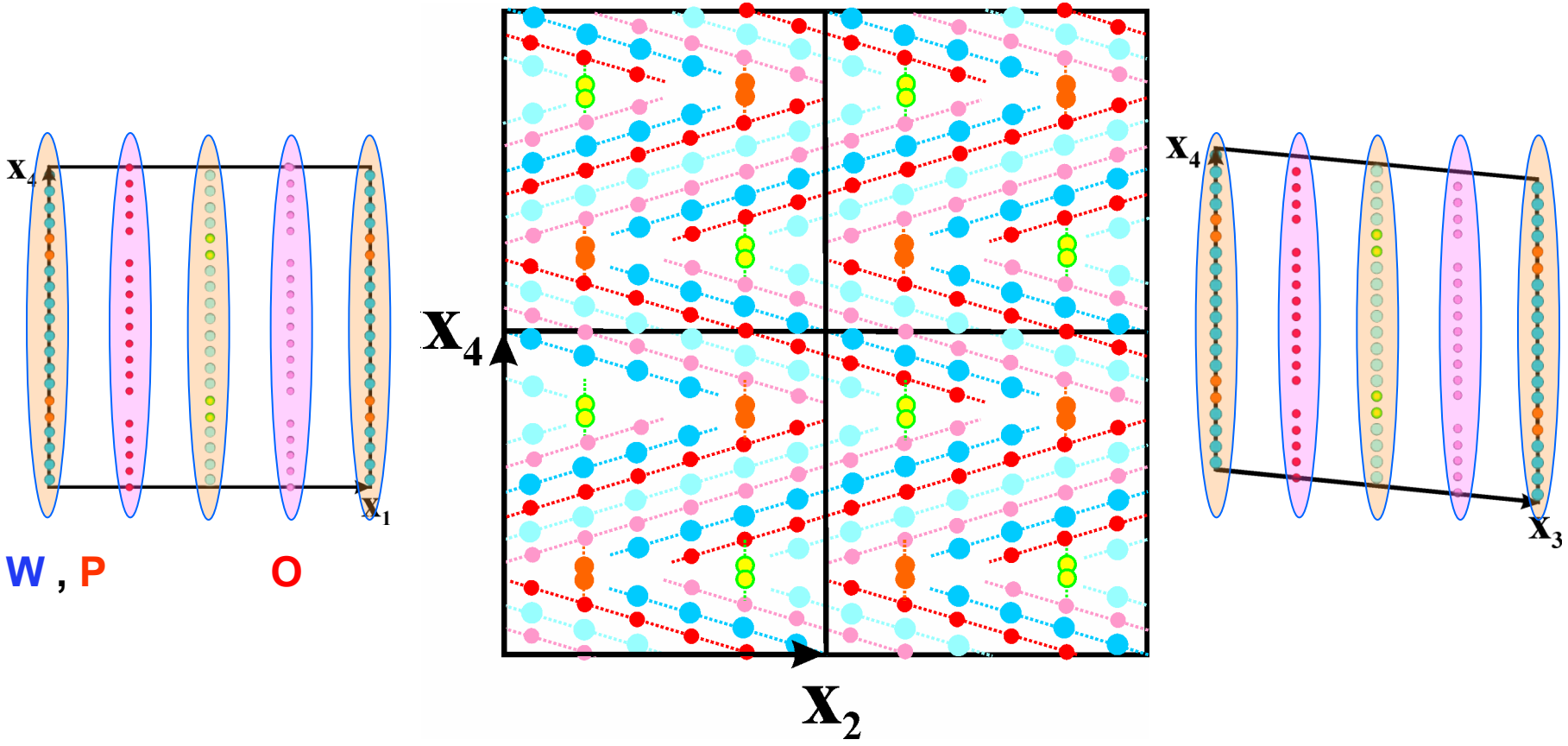
ideal structure (removing PO_4 and WO_6 tilts)



Embedding of the ideal 3d structure

sub cell : a=5.29 Å b=6.55 Å c'=2.97 Å, β=90°,

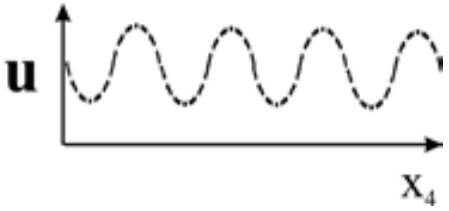
modulation vector : $q = \frac{1}{m+2} c'^{*}$ *SSG : Pnnm(00γ)0s0*



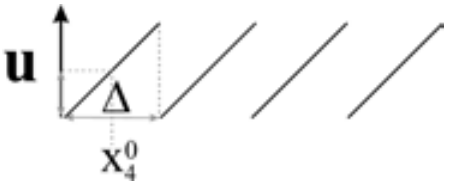
Evidence of 3 atomic domains on the (x_4x_1) and (x_4x_3) sections

Pool of periodic functions

- harmonics

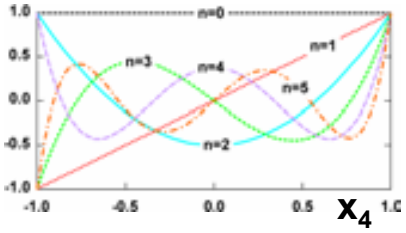


- sawtooth functions

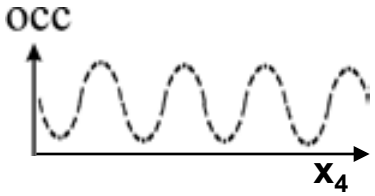


- zigzag functions

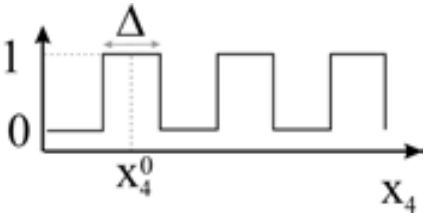
- Legendre polynomials



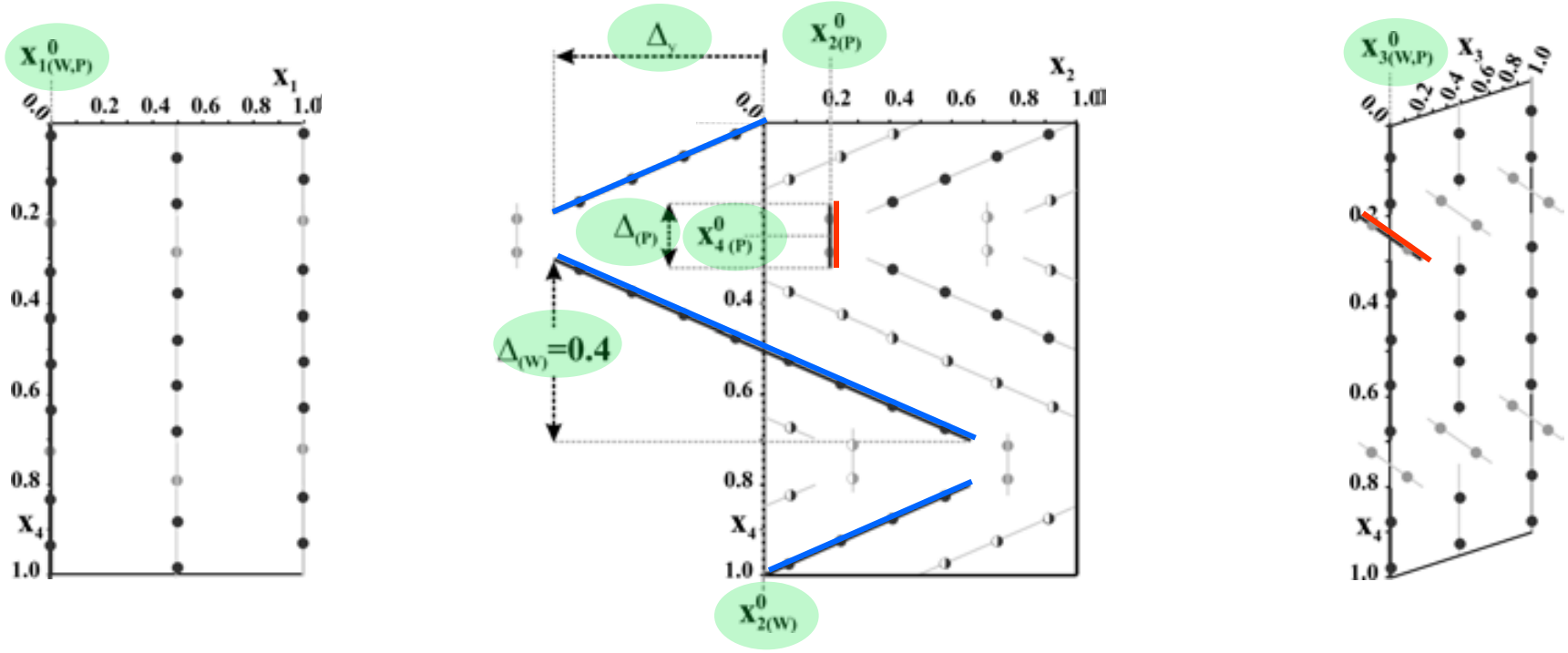
- harmonics



- crenel functions

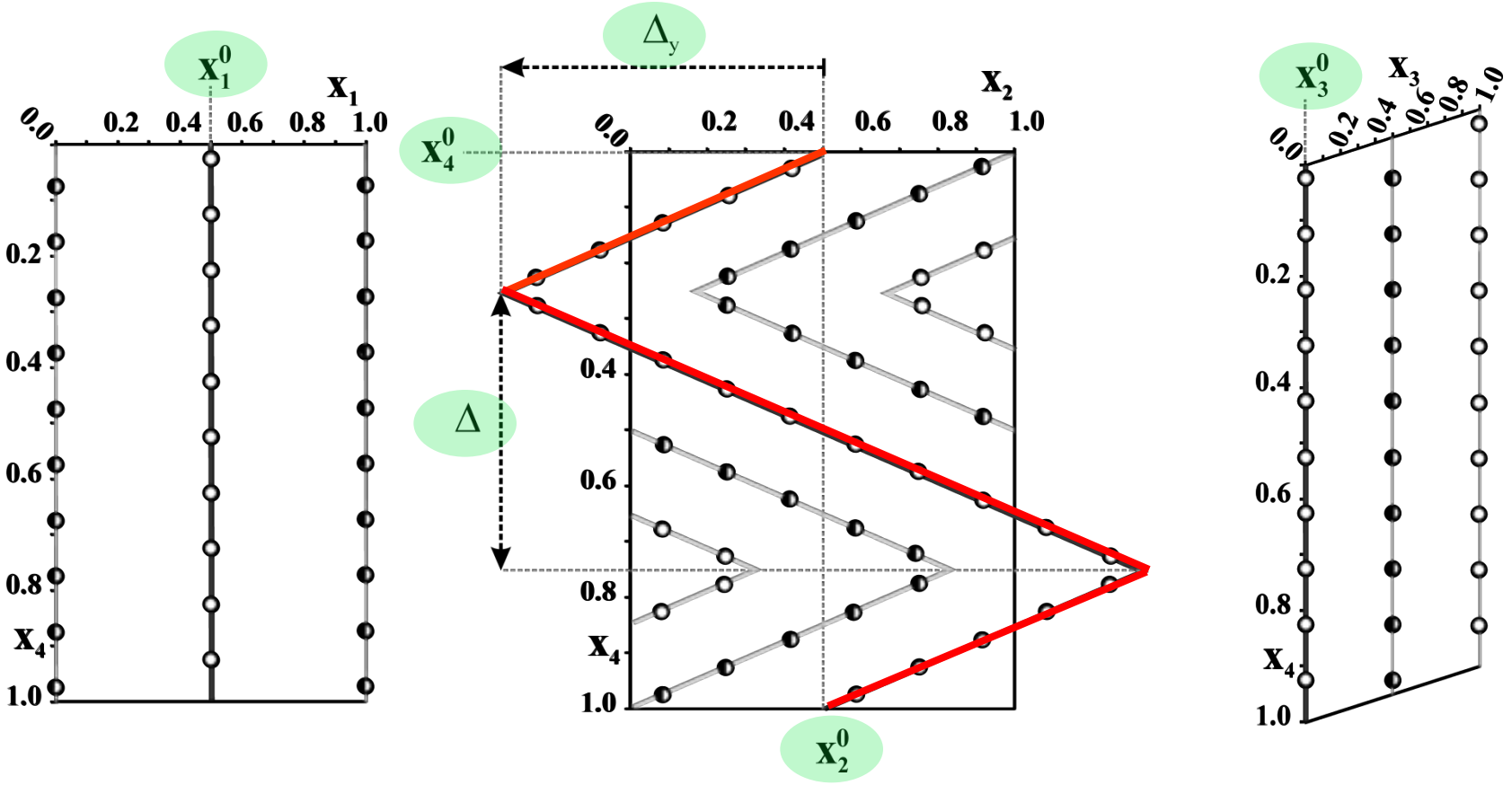


evaluation of the relevant parameters of the zig zag function for W and of the sawtooth function for P



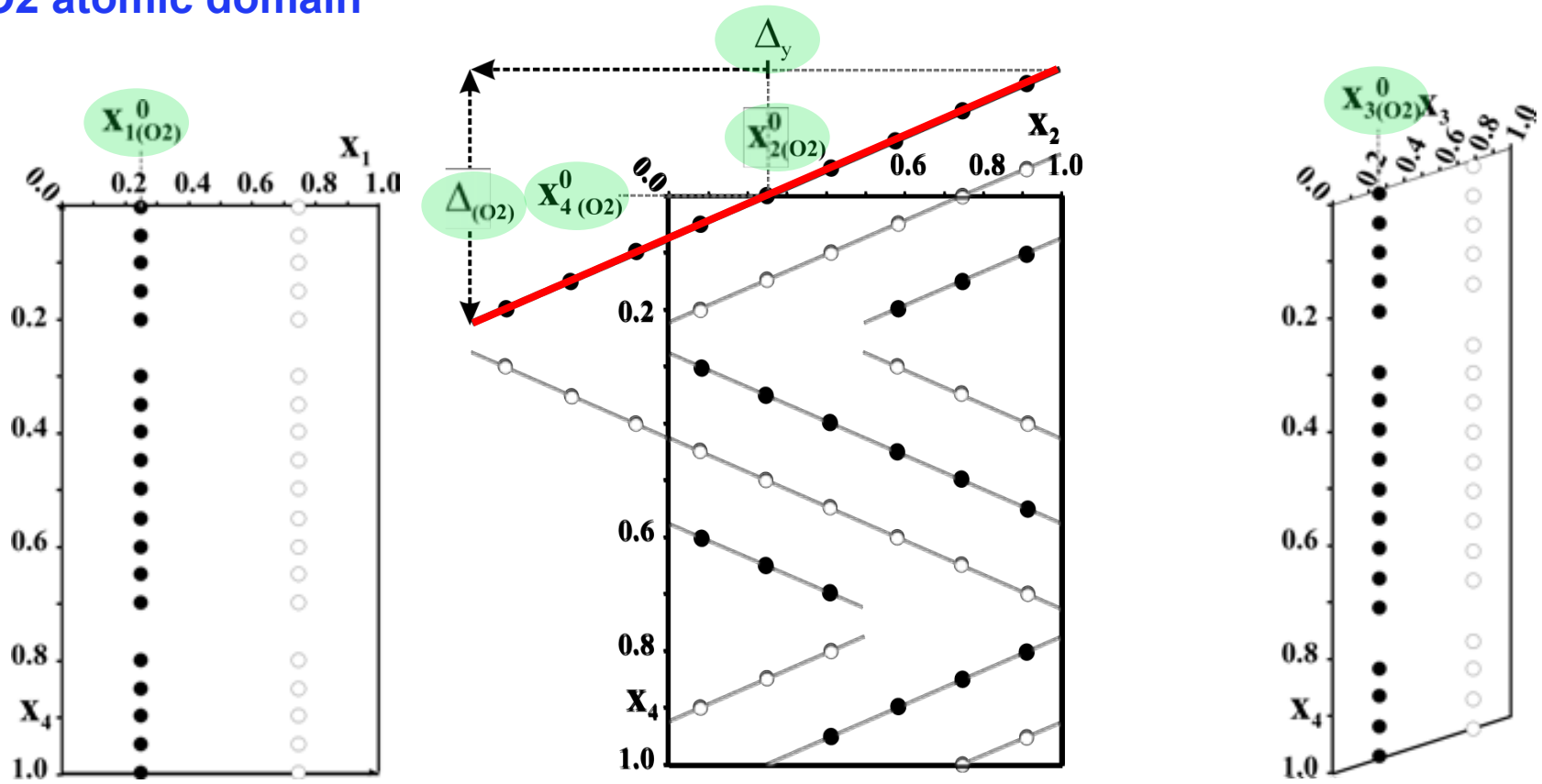
W and P atomic domains

O1 atomic domain



evaluation of the relevant parameters of the zig zag function

O2 atomic domain



evaluation of the relevant parameters of the sawtooth function

m dependent model (3+1)d model

evaluation of rules linking members and parameters

atom	x_1^0	x_2^0	x_3^0	x_4^0	Δ	Δ_x	Δ_y	Δ_z
W	0	0	0	0	$x = \frac{m}{2(m+2)}$	-	$-\frac{m}{12} = -\frac{x}{3(1-2x)}$	-
P	0	$\frac{8}{9} - \frac{m}{12}$	0	$\frac{1}{4}$	$\frac{1}{m+2} = \frac{1}{2} - x$	-	-	$\frac{1}{4}$
O1	$\frac{1}{2}$	$\frac{1}{2}$	0	0	$\frac{1}{2}$	-	$-\frac{(m+2)}{12} = \frac{1}{6(1-2x)}$	-
O2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{m+1}{2(m+2)} = \frac{1}{4} + \frac{x}{2}$	-	$-\frac{(m+1)}{12} = -\frac{(1+2x)}{12(1-2x)}$	-

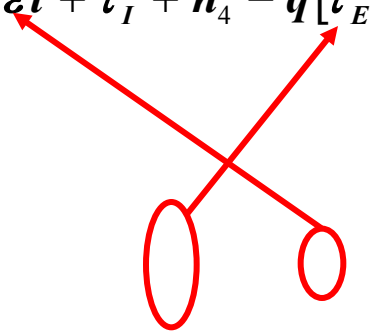
basic cell : a=5.29 Å b=6.55 Å c'=2.97 Å $\alpha=\beta=\gamma=90°$

modulation vector : $\vec{q} = \frac{1}{m+2}\vec{c} = \frac{1-2x}{2}\vec{c}$ **with** $x = \frac{m}{2(m+2)}$

$$(PO_2)_4(WO_3)_{2m} \Leftrightarrow P\frac{2}{m+2}W\frac{m}{m+2}O\frac{3m+4}{m+2} \Leftrightarrow P_{1-2x}W_{2x}O_{2x+2}$$

inventory of the equivalents sections and
versus **the q vector and the superspace g**

principle : $t = \varepsilon t + \tau_I + n_4 - q\left[\tau_E + T\right]$



$$t = -t + 0 + n_4 - \frac{1}{m+2}\left[\frac{1}{2} + n_3\right]$$

$$2t = n_4 - \frac{1}{m+2}\left[\frac{1}{2} + n_3\right]$$

$$t = \frac{1}{4(m+2)}\left[-(1+2n_3) + 2n_4(m+2)\right]$$

odd

$$t = \frac{1}{4(m+2)}\left[-1 - 2n_3 + 2n_4(m+2)\right]$$

$$t = \frac{2\nu+1}{4(m+2)}$$

S

	x_1, x_2, x	
2_1	$\frac{1}{2} + x_1,$	
	$\frac{1}{2} - x_1,$	
	$\bar{x}_1, \bar{x}_2, x_3, \frac{1}{2} + x_4$	$x_1, x_2, x_3, \frac{1}{2} - x_4$

2_1

2_1

member (m)	chemical formula	T_{C1} (K)	cell parameters (Å) ($T \geq T_{C1}$)	Space Group ($T \geq T_{C1}$)	structural report
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m even ➡ S.G. $P2_12_12_1$ **m odd ➡ S.G. $P2_1/n$**

inventory of the equivalents sections and symmetries *versus* the q vector and the superspace group

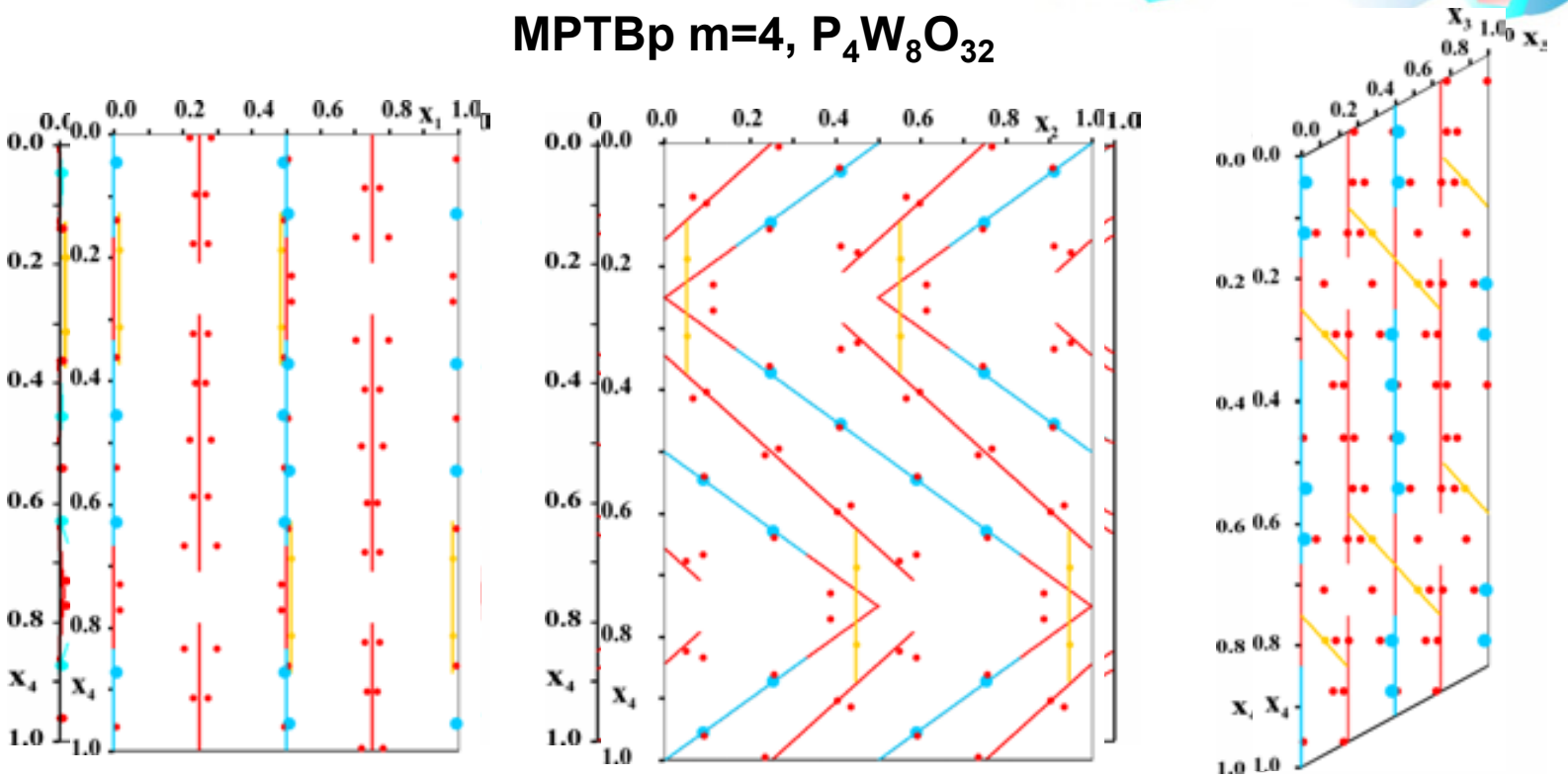
Compatibility with the observed 3d space groups

SSG Pnnm(00γ)0s0

(3+1)d Symmetry operators	
x_1, x_2, x_3, x_4	$\overline{x}_1, \overline{x}_2, \overline{x}_3, \overline{x}_4$
$\frac{1}{2}+x_1, \frac{1}{2}-x_2, \frac{1}{2}-x_3, \overline{x}_4$	$\frac{1}{2}-x_1, \frac{1}{2}+x_2, \frac{1}{2}+x_3, x_4$
$\frac{1}{2}-x_1, \frac{1}{2}+x_2, \frac{1}{2}-x_3, \frac{1}{2}-x_4$	$\frac{1}{2}+x_1, \frac{1}{2}-x_2, \frac{1}{2}+x_3, \frac{1}{2}+x_4$
$\overline{x}_1, \overline{x}_2, x_3, \frac{1}{2}+x_4$	$x_1, x_2, \overline{x}_3, \frac{1}{2}-x_4$

3d sections			
	section $t_0 = \frac{2\nu}{4m+2}$	section $t_0 = \frac{2\nu+1}{4m+2}$	section $\forall t_0$
m even	$P11\frac{2_1}{m}$	$P2_12_12_1$	$P112_1$
m odd	$P1\frac{2_1}{n}1$	$P2_1nm$	$P1n1$

MPTBp m=4, $P_4W_8O_{32}$

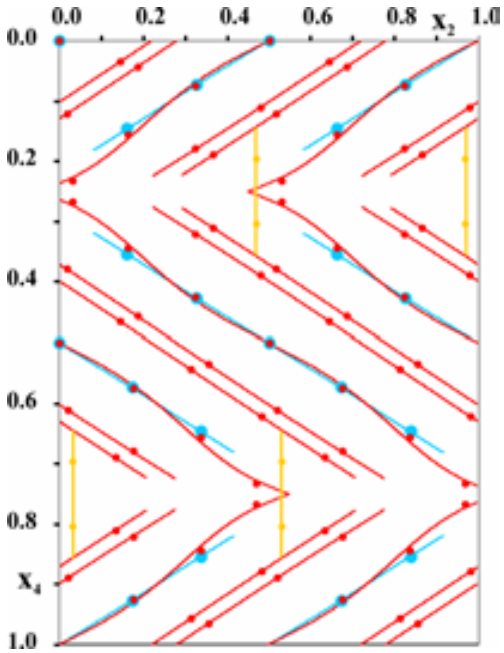


applying the (3+1)d model

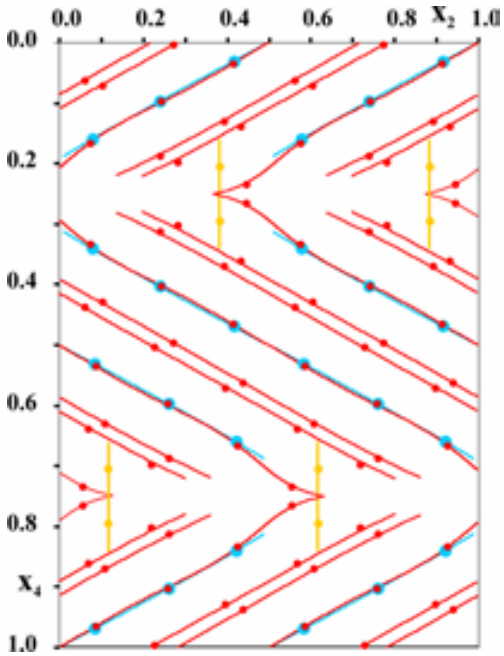
correct for P and W but too simplistic for O

using additional atomic displacements

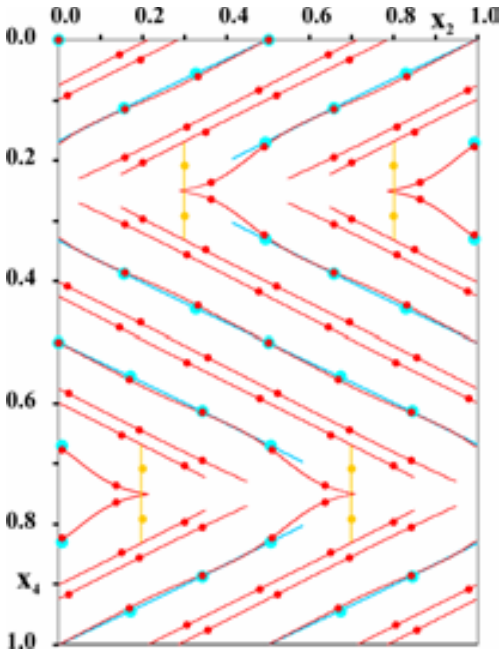
m=5, $P_4W_{10}O_{38}$



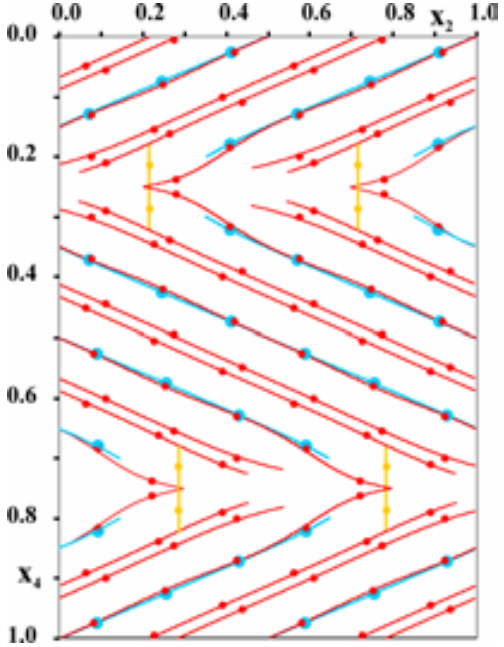
m=6, $P_4W_{12}O_{44}$



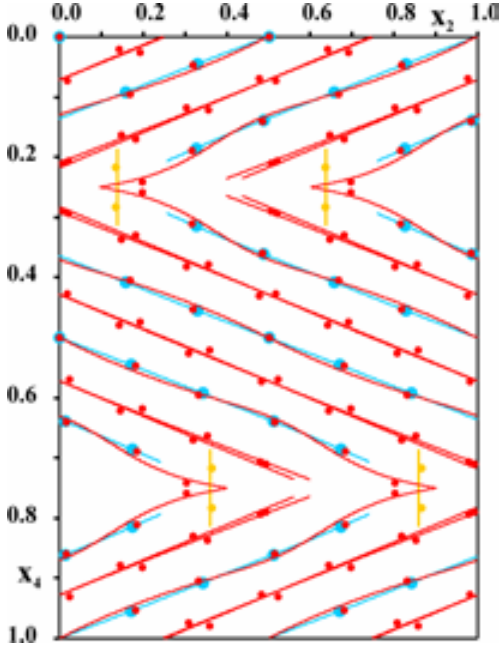
m=7, $P_4W_{14}O_{50}$



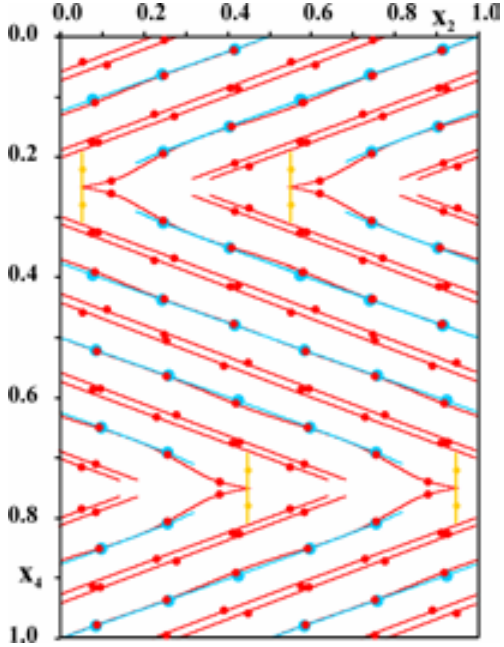
m=8, $P_4W_{16}O_{56}$



m=9, $P_4W_{18}O_{62}$



m=10, $P_4W_{20}O_{68}$



Summary

- What is it ? What is the aim ?
- Useful properties of the superspace formalism
- The method : keys …
- Some examples, step by step …
- Conclusion

- Atypical use of the superspace formalism
- Unified description of ≠ members of families of compounds
- Reveals hidden common properties (symmetry, composition …)
- Reduces the number of refinement parameters
- For more details you can also contact :

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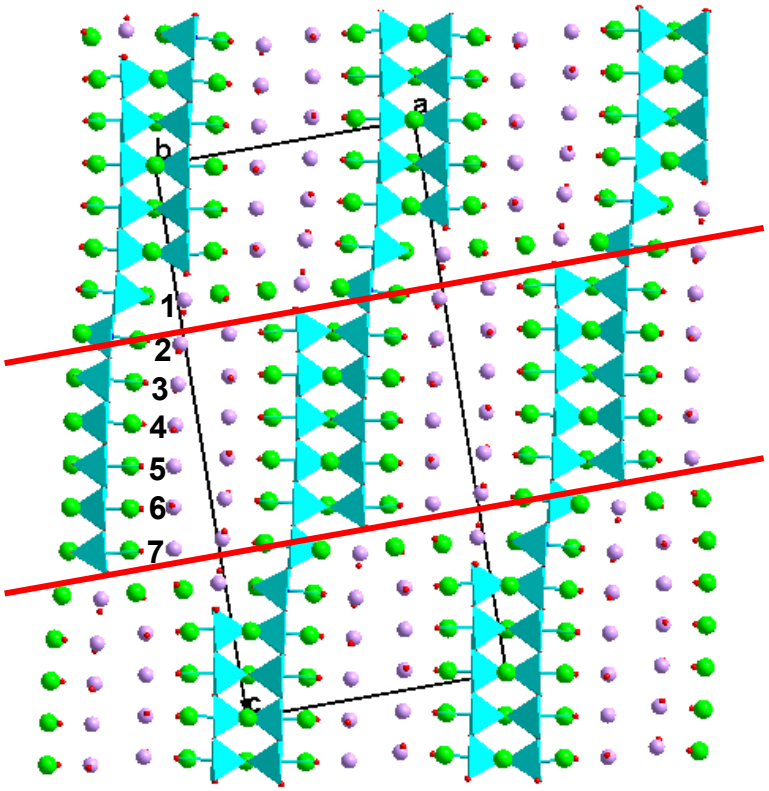
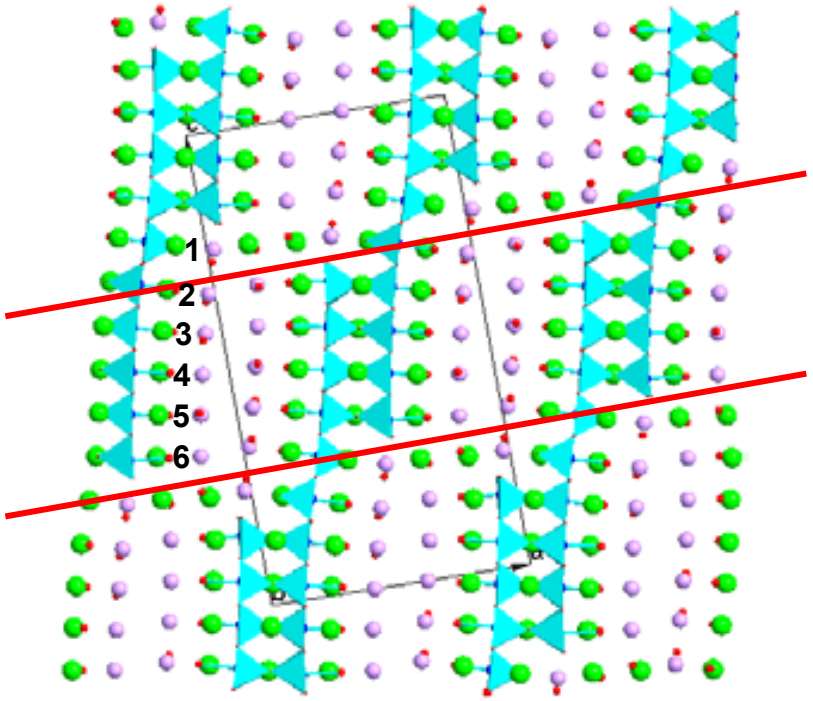
UPV 48080 BILBAO

family of terrace-like structures



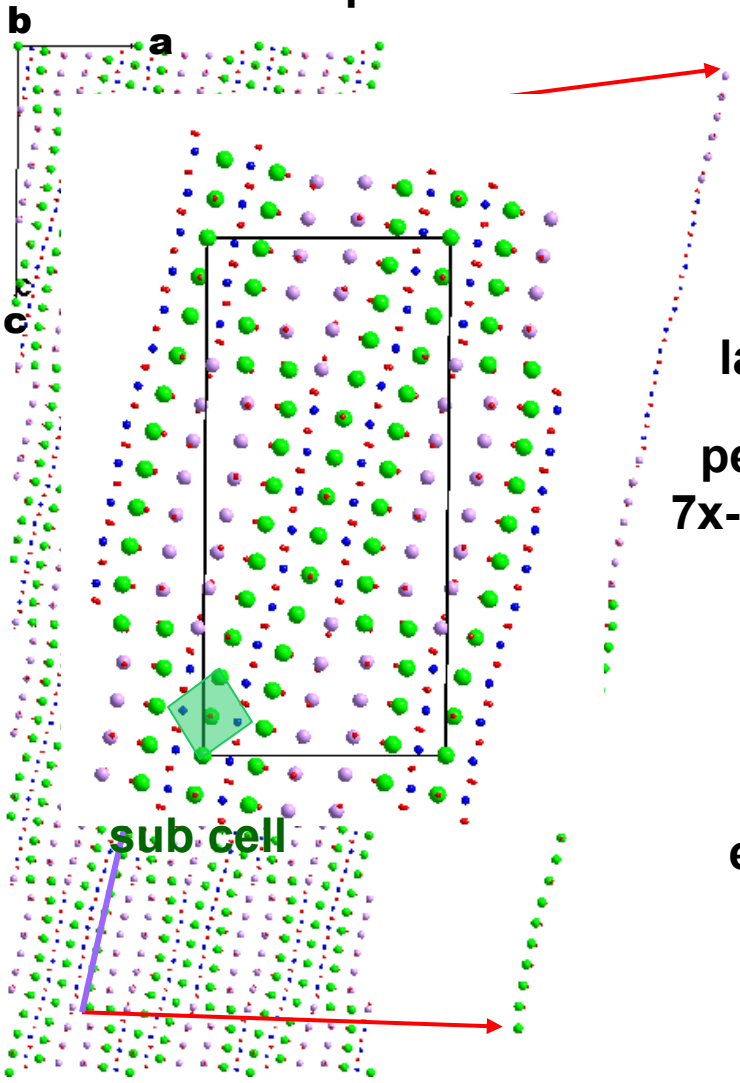
$Bi_{14}Sr_{21}Fe_{12}O_{61}$ (x=7) S.G. I2
a_1=16.55Å b_1=5.49Å c_1=35.29Å
β_1=90.52°



$Bi_{12}Sr_{18}Fe_{10}O_{52}$ (x=6) S.G. $P2_1/n$
a_1=16.48Å b_1=5.48Å c_1=30.07Å
β_1=91.40°

New definition for composition : $Bi_{2x}Sr_{3x}Fe_{2x-2}O_{9x-2}$

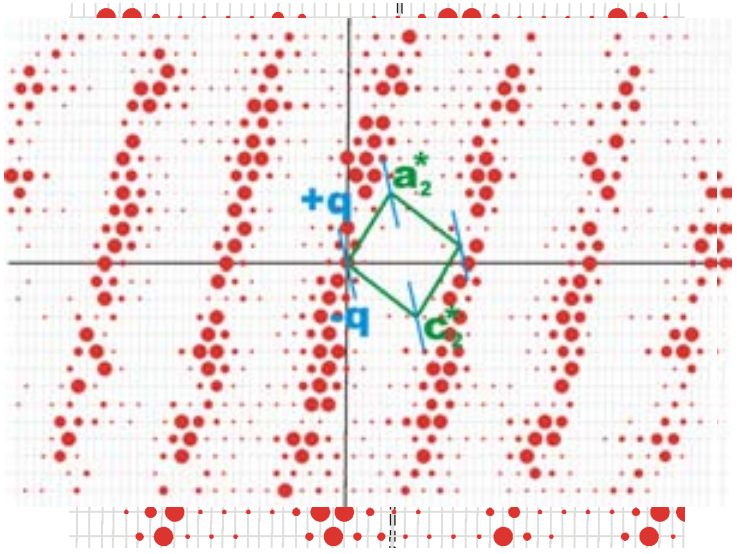
direct space



layer

period of
7x-2 cations

reciprocal space



→ different possibilities for q

embedding of the structure + symmetry

→ one choice for q

$Bi_{2x}Sr_{3x}Fe_{2x-2}O_{9x-2}$

subcell a_2=3.59Å b_2=5.49Å c_2=3.46Å β_2=81.90°

wave vector $$q = \frac{1}{7x-2}\left[(2x-1)a_2 - 2xc_2\right]$$

from the diffraction patterns : SSG X2/m(a0g)0s, with X= (½, ½, ½, ½)

relation with supercell $$a_2 = \frac{1}{7x-2}\left[(x+1)a_1 + 3c_1\right] \qquad b_2 = b_1 \qquad c_2 = \frac{1}{7x-2}\left[(2-x)a_1 + 4c_1\right]$$

	x=6	x=7
	$Bi_{12}Sr_{18}Fe_{10}O_{52}$	$Bi_{14}Sr_{21}Fe_{12}O_{61}$
q	$\frac{11}{40}a_2^* - \frac{12}{40}c_2^*$	$\frac{13}{47}a_2^* - \frac{14}{47}c_2^*$

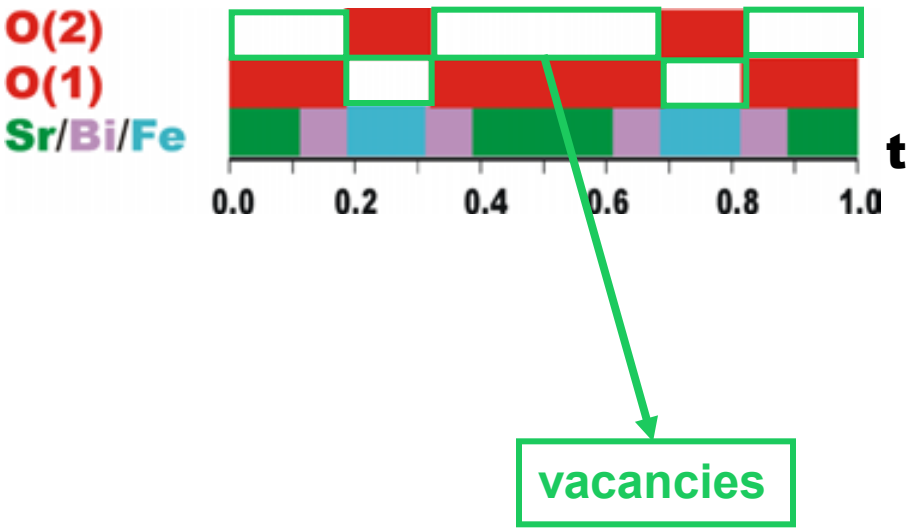
(3+1)d model with 3 independant atomic domains

atomic sites

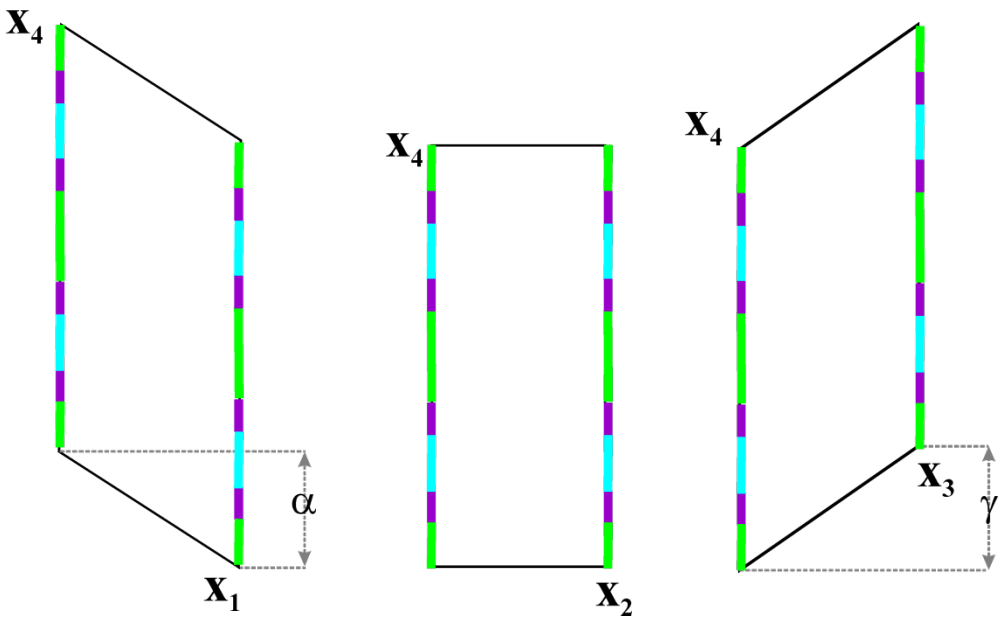
	x	y	z
Bi/Sr/Fe	0	0	0
O(1)	0	0.4477	0
O(2)	0.2611	0.2557	0.2352

average positions

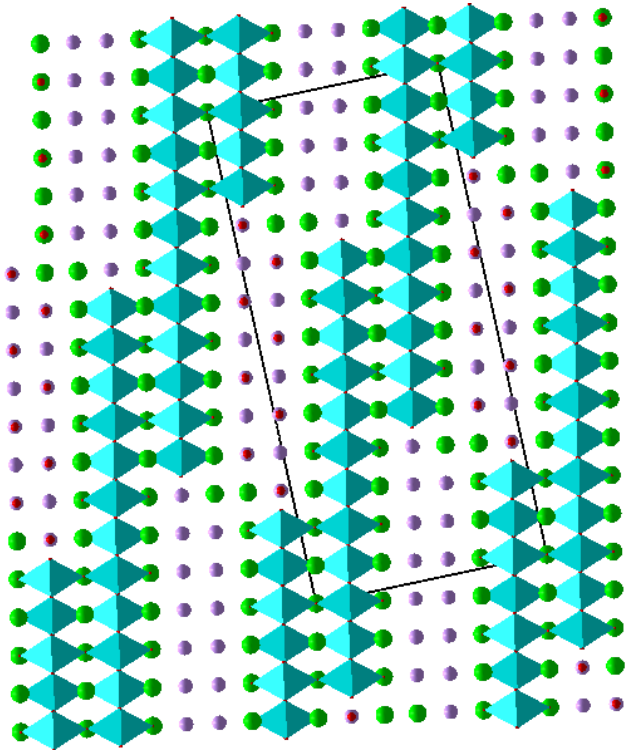
atomic occupancies using crenel functions



with crenel function

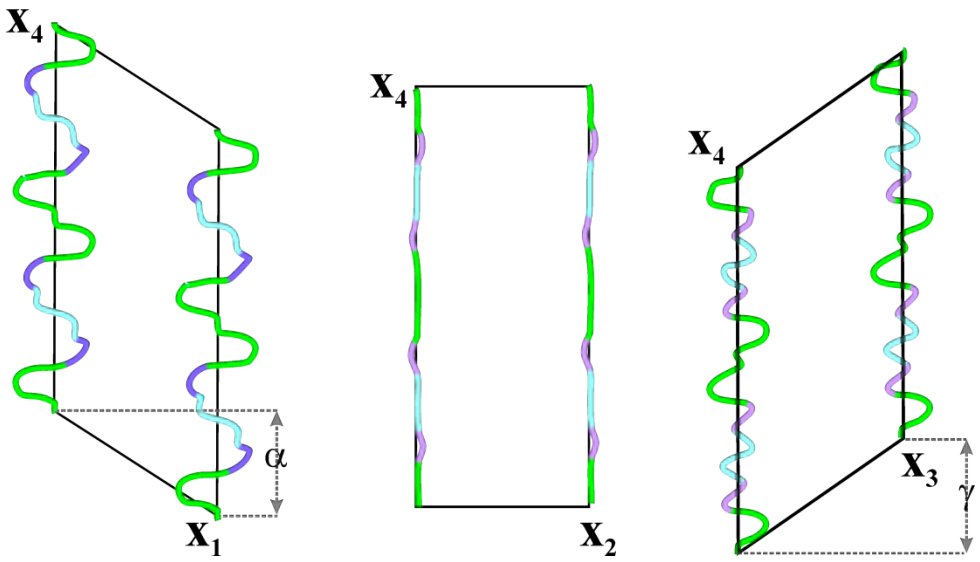


the resulting structure

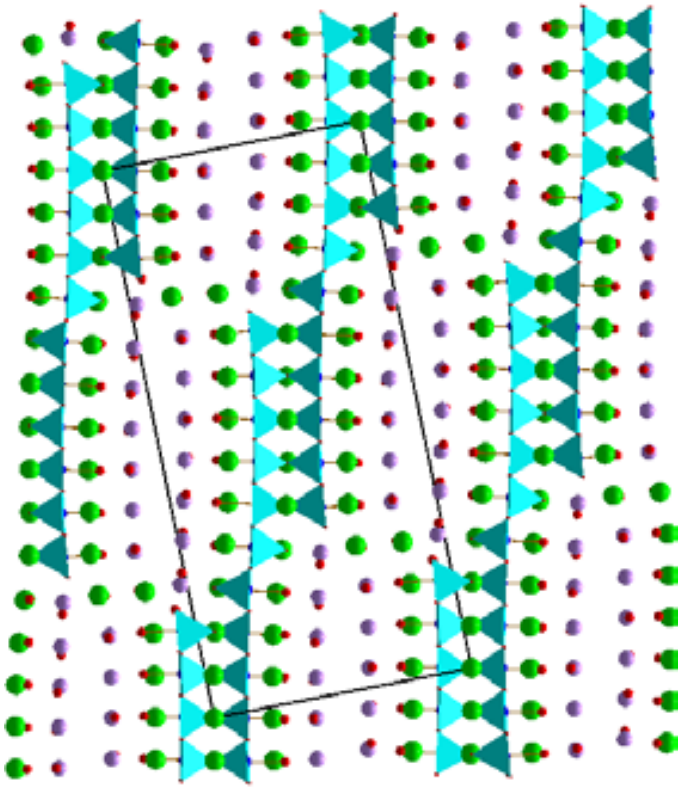


$Bi_{14}Sr_{21}Fe_{12}O_{61}$ x=7

adding atomic displacement for cations and oxygen atoms

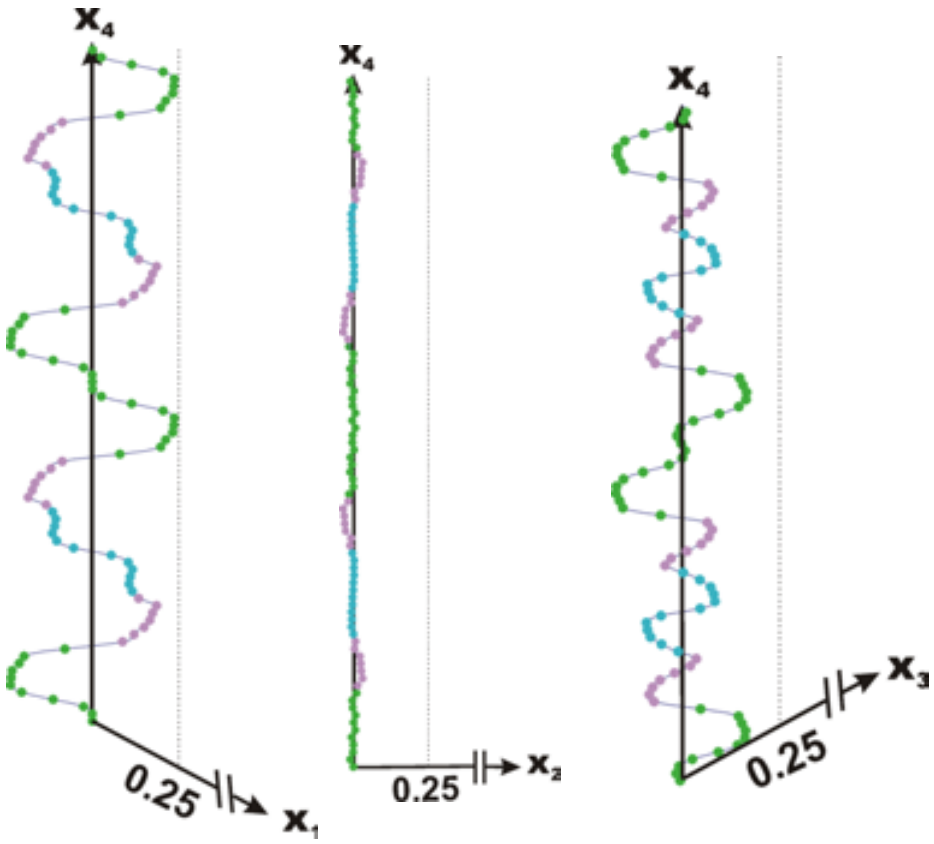


the resulting structure

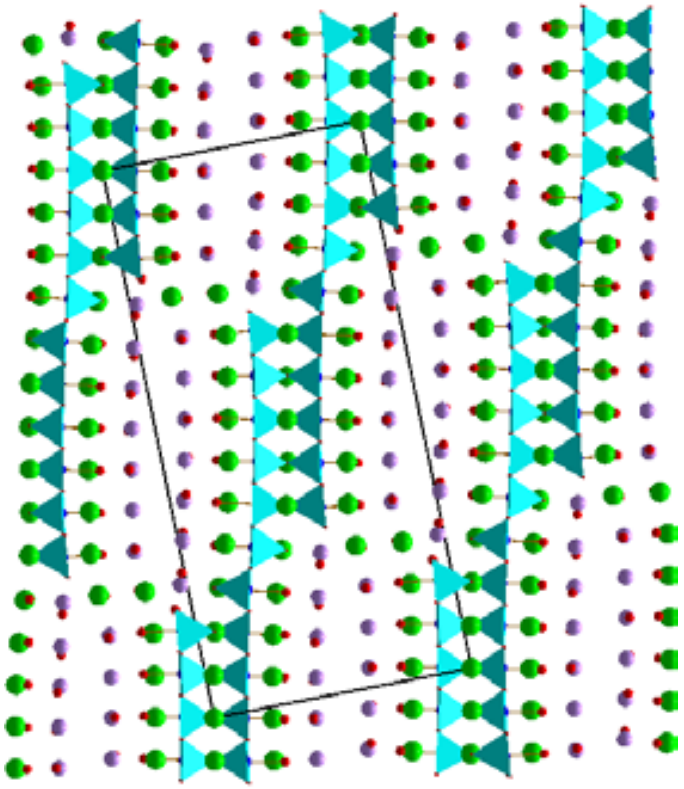


= true structure

adding atomic displacement for cations and oxygen atoms

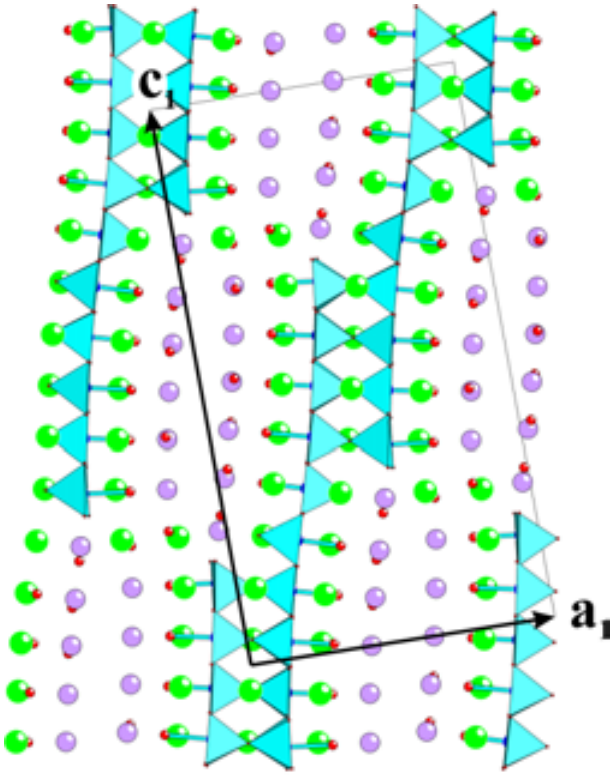


the resulting structure



= true structure

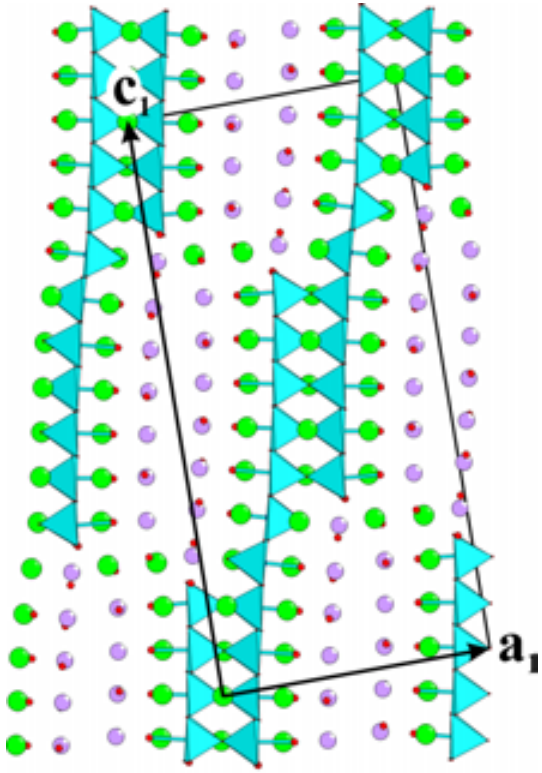
Terrace-like phases



$Bi_{12}Sr_{18}Fe_{10}O_{52}$

a=16.49Å b=5.48Å c=30.86Å

β=91.39° G.E. : $P2_1/n$



$Bi_{14}Sr_{21}Fe_{12}O_{61}$

a=16.54Å b=5.49Å c=35.29Å

β=90.52° S.G. : I2

Symmetry …

In the physical space …