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

- What is it? What is the aim?
- Useful properties of the superspace formalism
- The method: keys ...
- Some examples, step by step ...
- Conclusion
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 $Ba_{1+\varepsilon}[(Na_xMn_{1-x})O_3]$

≠ sequences in the stacking direction
NaO$_6$ prismatic MnO$_6$ octahedral environments
Aurivillius phases

Stacking of Bi$_2$O$_2$ layers and perovskite layers with variable thickness
Tungsten Phosphate Bronzes \( (PO_2)_4(WO_3)_{2m} \) with \( 4 \leq m \leq 14 \)

- \( m=4, \ P_4W_8O_{32} \)
- \( m=5, \ P_4W_{10}O_{38} \)
- \( m=8, \ P_4W_{16}O_{56} \)

**Parameters:**
- \( a=5.28 \ b=6.57 \ c=17.35 \ P2_12_12_1 \)
- \( a=5.28 \ b=6.57 \ c=20.45 \ \beta=90.40^\circ \ P2_1/n \)
- \( a=5.29 \ b=6.57 \ c=23.55 \ P2_12_12_1 \)

*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

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

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

\[ r = x_1 A_1 + x_2 A_2 + x_3 A_3 \]

and \( x_4 \)

\[ x_4 = q \cdot (r + p) \]

\[ p = n_1 A_1 + n_2 A_2 + n_3 A_3, \ n_i \in \mathbb{N} \]
supercell:

\[ A_1 = a - \sigma_1 e_4, \quad A_2 = b - \sigma_2 e_4, \quad A_3 = c - \sigma_3 e_4, \quad A_4 = e_4 \]

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

atomic position:

\[ r = x_1 A_1 + x_2 A_2 + x_3 A_3 + x_4 A_4 \]

\[ x_4 = q \cdot (r + p) \]

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

\( r(x_4) \)

\[ r = r_0 + u(x_4) \] atomic displacement

two contributions
How describe $u(x_4)$?

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

$$u^j(x_4) = \sum_n A^n_j \sin(2n\pi x_4) + B^n_j \cos(2n\pi x_4)$$

- sawtooth functions
- zigzag functions
- Legendre polynomials

And what about the occupancy?

$$P(x_4) = P_0 + \sum_n A^n_j \sin(2n\pi x_4) + B^n_j \cos(2n\pi x_4)$$

- crenel functions
Building of the 3d structure from supercrystal?

true crystal = section of the super crystal

super crystal

3xq
2xq
1xq

true crystal (in the physical space)
physical space  \[\rightarrow\]  \((3+1)\)d space

- multiple atoms  \[\rightarrow\]  single atomic domain
super glide mirror

\( x_1, x_2, x_3, x_4 + \frac{1}{2} \)

physical space

\( \frac{1}{2} \) phase shift along \( x_4 \)
physical space $\rightarrow$ \((3+1)d\) space

- multiple atoms $\rightarrow$ single atomic domain
- independent atoms $\rightarrow$ symmetry related atoms
Physical space

\[ A_1 = a - \sigma_1 e_4, \; A_2 = b - \sigma_2 e_4, \; A_3 = c - \sigma_3 e_4, \; A_4 = e_4 \]

with \( q = \sigma \cdot c^* \)

\( \sigma_i \rightarrow \) vacancy in the 3d space

Su

2 independent atomic domains (displacements and/or vacancies)

same modulation functions

3 choices of \( q \) vector \( \rightarrow \) 3 \( \neq \) super-cells

no vacancy in the 3d space

Change of the (3+1)d cell by changing \( q \)
physical space       \( (3+1)\text{d} \) space

- multiple atoms \( \rightarrow \) single atomic domain
- independent atoms \( \rightarrow \) symmetry related atoms
- different structures \( \rightarrow \) 1 model + \( \neq \) 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

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 \( q = \frac{1}{4} b^* \)

atomic domain

different choices of sections

for \( t_0 \) given relevant points on each atomic domain

grid of equivalent sections with \( q \) spacing
commensurate modulated structure with $q = \frac{1}{4} b^*$

$m$ mirror $x_1, x_2, x_3, x_4$

$\approx$ to 2-fold axis $\perp (x_2, x_4)$

2 equivalent atomic domains / super cell
commensurate modulated structure with \( q = \frac{1}{4} \mathbf{b}^* \)

m mirror \( x_1, \overline{x}_2, x_3, \overline{x}_4 \)

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 \( t_0 \) section
m does not belong to the SG of the true 3d structure
commensurate modulated structure with $q = \frac{1}{4} b^*$

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

**Section $t_0 = 0$**

- $\Rightarrow$ 1 physical point
- $\Rightarrow$ equivalent point by $m$
- $\Rightarrow$ 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 \( t_0 \)

\[
S = \begin{pmatrix} R_E & 0 \\ 0 & \varepsilon \end{pmatrix} \begin{pmatrix} \tau_E \\ \tau_I \end{pmatrix} \quad \text{lattice translation}
\]

\[
T + n_4 A_4 = n_1 A_1 + n_2 A_2 + n_3 A_3 + n_4 A_4
\]

\[
x_4 \rightarrow x_4' = \varepsilon x_4 + \tau_I + n_4
\]

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

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

\[
t \rightarrow t' = \varepsilon t + \tau_I + n_4 - q [\tau_E + T]
\]

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

… to be applied to all the symmetry elements of the SSG series of equations
physical space  $\rightarrow$  (3+1)d space

- multiple atoms $\rightarrow$ single atomic domain
- independent atoms $\rightarrow$ symmetry related atoms
- different structures $\rightarrow$ 1 model $\oplus \neq$ wave vectors
- different 3d symmetries $\rightarrow$ $\exists \neq t$ sections of the model
Summary

- What is it? What is the aim?
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Regular used of the superspace formalism …

unknown structure

diffraction pattern with different types of reflections

- main reflections \( \rightarrow \) sub periodicity
- satellite reflections \( \rightarrow \) additional periodicity

irrational positions \[ s = ha^* + kb^* + lc^* + mq^* \]

- 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

Sub-cell:
\[ \vec{a}' = \frac{\vec{a}}{n}, \quad \vec{b}' = \frac{\vec{b}}{m} \]

wave vector

3d structure

generic relationship
\begin{align*}
\mathbf{q} &= \frac{1}{n} \mathbf{a}^* + \frac{1}{m} \mathbf{b}^* \\
\mathbf{A}_1 &= \mathbf{a}' - \frac{1}{n} \mathbf{e}_4 \\
\mathbf{A}_2 &= \mathbf{b}' - \frac{1}{m} \mathbf{e}_4 \\
\mathbf{A}_4 &= \mathbf{e}_4
\end{align*}

3d structure

(3+1)d super crystal

(3+1)d super cell
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
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Aurivillius phases in the pseudo-binary system $\text{Bi}_3\text{TiNbO}_9$-$\text{Bi}_4\text{Ti}_3\text{O}_{12}$

(exemple kindly provided by Ph. Boullay)
$m = 2 \quad \text{Bi}_3\text{TiNbO}_9$

$m = 3 \quad \text{Bi}_4\text{Ti}_3\text{O}_{12}$

$2+3 \quad \text{Bi}_7\text{Ti}_4\text{NbO}_{21}$

$\text{BiB}_{(1-x)}\text{O}_3$

perovskite deficient

$q = 1/3 \ c^*$

$q = 1/4 \ c^*$

$q = 2/7 \ c^*$
determination of the sub cell: \( a \sim a \sqrt{2}, b \sim a \sqrt{2}, c \sim 2a \) 

wave vector \( q = x \cdot c^* \) 

composition dependent evolution 

systematic observation of the extinction rules 

super space group \( X2cm(00x)000 \) with \( X \left\{ \frac{1}{2} \frac{1}{2} \frac{1}{2} 0 \mid \frac{1}{2} 0 0 \frac{1}{2} \mid 0 \frac{1}{2} \frac{1}{2} \frac{1}{2} \right\} \) 

centring lattice vector
Bi$_7$Ti$_4$NbO$_{21}$

perovskite deficient material $\text{AB}_{1-x}\text{O}_3$ structural description using layers
perovskite deficient material \( \text{AB}_{1-x}\text{O}_3 \)
perovskite deficient material $\text{AB}_{1-x}\text{O}_3$

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

A

B

1 rule: between

super crystal model

stacking direction

x vacancies

$x$ vacancies

$\frac{1}{2}x$
perovskite deficient material $\text{AB}_{1-x}\text{O}_3$

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

- Domain A
  - Green
  - Shifted

- Domain B
  - Red
  - Shifted

1 rule: between

Physical space:

$X_3$

$X_4$

$Z$

$0.25$  $0.5$  $0.75$  $1$

$0$  $0.25$  $0.5$  $0.75$  $1$

$0$  $0.25$  $0.5$  $0.75$  $1$

Legend:
- $\text{AO}$
- $\text{AO}$ shifted
- $\text{BO}_2$
- $\text{BO}_2$ shifted
- $\text{O}_2$
super crystal model

3d structure

physical space

stacking direction c

(3+1)d model

<table>
<thead>
<tr>
<th></th>
<th>x_1</th>
<th>x_2</th>
<th>x_3</th>
<th>x_4</th>
<th>Δ</th>
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<td>A</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(1-x)/2</td>
</tr>
</tbody>
</table>
Mono Phosphate Tungsten Bronzes family

chemical formula \((PO_2)_4(WO_3)_{2m}\) with \(4 \leq m \leq 14\)

MPTBp \(m=5, P_4W_{16}O_{38}\)
<table>
<thead>
<tr>
<th>member (m)</th>
<th>chemical formula</th>
<th>T_{C1} (K)</th>
<th>cell parameters (Å)</th>
<th>Space Group</th>
<th>structural report</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>P_{4} W_{8} O_{32}</td>
<td>80</td>
<td>a=5.28 b=6.57 c=17.35</td>
<td>P_{212121}</td>
<td>Giroult et al, Acta Crystallogr. B37 (1981)</td>
</tr>
<tr>
<td>5</td>
<td>P_{4} W_{10} O_{38}</td>
<td>80</td>
<td>a=5.28 b=6.57 c=20.45 \beta=90.40</td>
<td>P_{121/n1}</td>
<td>Roussel et al, Eur. Phys. J. B 12 (1999)</td>
</tr>
<tr>
<td>4/6</td>
<td>P_{4} W_{10} O_{38}</td>
<td>158</td>
<td>a=5.28 b=6.57 c=20.57 \alpha=96.18</td>
<td>P_{21}11</td>
<td>Benmoussa et al, J. Solid State Chem. 4 (1982)</td>
</tr>
<tr>
<td>6</td>
<td>P_{4} W_{12} O_{44}</td>
<td>120</td>
<td>a=5.29 b=6.57 c=23.55</td>
<td>P_{212121}</td>
<td>Labbé et al, J. Solid State Chem. 61 (1986)</td>
</tr>
<tr>
<td>7</td>
<td>P_{4} W_{14} O_{50}</td>
<td>188</td>
<td>a=5.29 b=6.56 c=26.65 \beta=90.19</td>
<td>P_{121/n1}</td>
<td>Roussel et al, J. Solid State Chem. 122 (1996)</td>
</tr>
<tr>
<td>8</td>
<td>P_{4} W_{16} O_{56}</td>
<td>220</td>
<td>a=5.29 b=6.55 c=29.7</td>
<td>P_{212121}</td>
<td>Labbé et al, J. Solid State Chem. 61 (1986)</td>
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<tr>
<td>9</td>
<td>P_{4} W_{18} O_{62}</td>
<td>565</td>
<td>a=5.28 b=6.57 c=32.79 \beta=?</td>
<td>P_{121/n1}</td>
<td>this work</td>
</tr>
<tr>
<td>10</td>
<td>P_{4} W_{20} O_{68}</td>
<td>450</td>
<td>a=5.324 b=6.575 c=36.00</td>
<td>P_{212121}</td>
<td>this work</td>
</tr>
<tr>
<td>11</td>
<td>P_{4} W_{22} O_{74}</td>
<td>560</td>
<td>a=5.3 b=6.6 c=39 \beta=?</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
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<tr>
<td>12</td>
<td>P_{4} W_{24} O_{80}</td>
<td>535</td>
<td>a=5.31 b=6.55 c=42.11</td>
<td>P_{212121}</td>
<td>Roussel et al, Acta Crystallogr. B54 (1998)</td>
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<tr>
<td>13</td>
<td>P_{4} W_{26} O_{86}</td>
<td>550</td>
<td>a=5.28 b=6.57 c=45.04 \beta=?</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
</tr>
<tr>
<td>14</td>
<td>P_{4} W_{28} O_{92}</td>
<td>730</td>
<td>a=5.32 b=6.54 c=48.00</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
</tr>
</tbody>
</table>

\[ m \text{ even} \quad \Rightarrow \quad \text{S.G. P}_{212121} \quad \text{m odd} \quad \Rightarrow \quad \text{S.G. P}_{21/n} \]
diffuse scattering

Enlightening of intense reflections
definition of a basic subcell using the “enlightened” reflections

c=(m+2) c’

\[ a=5.29 \, \text{Å} \quad b=6.55 \, \text{Å} \quad c’=2.97 \, \text{Å} \]
\[ \alpha=\beta=\gamma=90^\circ \]

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

\[ s = ha'^* + kb'^* + \ell c'^* + mq \]

from the extinction rules :

SSG : Pnnm(00\gamma)0s0

\( (m+1) \) réflections
MPTBp m=8, $P_4W_8O_{56}$

**cell**: $a=5.29 \, \text{Å} \quad b=6.55 \, \text{Å} \quad c'=2.97 \, \text{Å} \quad \beta=90^\circ, \text{SG} : P2_12_12_1$

**sub cell**: $a=5.29 \, \text{Å} \quad b=6.55 \, \text{Å} \quad c'=2.97 \, \text{Å} \quad \beta=90^\circ$

**real structure**

**ideal structure** (removing $PO_4$ and $WO_6$ tilts)
Embedding of the ideal 3d structure

sub cell: \( a = 5.29 \, \text{Å} \), \( b = 6.55 \, \text{Å} \), \( c' = 2.97 \, \text{Å} \), \( \beta = 90^\circ \),

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

SSG: \( Pnnm(00\gamma)0s0 \)

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

<table>
<thead>
<tr>
<th>atom</th>
<th>$x_1^0$</th>
<th>$x_2^0$</th>
<th>$x_3^0$</th>
<th>$x_4^0$</th>
<th>$\Delta$</th>
<th>$\Delta_x$</th>
<th>$\Delta_y$</th>
<th>$\Delta_z$</th>
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<tbody>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$x = \frac{m}{2(m+2)}$</td>
<td>$-\frac{m}{12} = -\frac{x}{3(1-2x)}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>0</td>
<td>$\frac{8}{9} - \frac{m}{12}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{m+2} = \frac{1}{2} - x$</td>
<td>-</td>
<td>-</td>
<td>$\frac{1}{4}$</td>
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<tr>
<td>O1</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>-</td>
<td>$-\frac{(m+2)}{12} = -\frac{1}{6(1-2x)}$</td>
<td>-</td>
</tr>
<tr>
<td>O2</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
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<td>$\frac{m+1}{2(m+2)} = \frac{1}{4} + \frac{x}{2}$</td>
<td>-</td>
<td>$-\frac{(m+1)}{12} = -\frac{(1+2x)}{12(1-2x)}$</td>
<td>-</td>
</tr>
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</table>

evaluation of rules linking members and parameters

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

modulation vector : $\vec{q} = \frac{1}{m+2} \hat{c} = \frac{1-2x}{2} \hat{c}$ 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 symmetries versus the q vector and the superspace group

**Diagram:**

**Equation:**

\[ t = \varepsilon t + \tau_I + n_4 - q[\tau_E + T] \]

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

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

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

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

\[ 2_1 \]

\[ 2_1 \]
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<td>( P2_11 )</td>
<td>Benmoussa et al, J. Solid State Chem. 4 (1982)</td>
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<td>120</td>
<td>( a=5.29 \ b=6.57 \ c=23.55 )</td>
<td>( P2_12_12_1 )</td>
<td>Labbé et al, J. Solid State Chem. 61 (1986)</td>
</tr>
<tr>
<td>7</td>
<td>( P_4W_{14}O_{50} )</td>
<td>188</td>
<td>( a=5.29 \ b=6.56 \ c=26.65 ) ( \beta=90.19 )</td>
<td>( P12_1/\bar{n}1 )</td>
<td>Roussel et al, J. Solid State Chem. 122 (1996)</td>
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<tr>
<td>8</td>
<td>( P_4W_{16}O_{56} )</td>
<td>220</td>
<td>( a=5.29 \ b=6.55 \ c=29.7 )</td>
<td>( P2_12_12_1 )</td>
<td>Labbé et al, J. Solid State Chem. 61 (1986)</td>
</tr>
<tr>
<td>9</td>
<td>( P_4W_{18}O_{62} )</td>
<td>565</td>
<td>( a=5.28 \ b=6.57 \ c=32.79 ) ( \beta=? )</td>
<td>( P12_1/\bar{n}1 )</td>
<td>this work</td>
</tr>
<tr>
<td>10</td>
<td>( P_4W_{20}O_{68} )</td>
<td>450</td>
<td>( a=5.324 \ b=6.575 \ c=36.00 )</td>
<td>( P2_12_12_1 )</td>
<td>this work</td>
</tr>
<tr>
<td>11</td>
<td>( P_4W_{22}O_{74} )</td>
<td>560</td>
<td>( a=5.3 \ b=6.6 \ c=39 ) ( \beta=? )</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
</tr>
<tr>
<td>12</td>
<td>( P_4W_{24}O_{80} )</td>
<td>535</td>
<td>( a=5.31 \ b=6.55 \ c=42.11 )</td>
<td>( P2_12_12_1 )</td>
<td>Roussel et al, Acta Crystallogr. B54 (1998)</td>
</tr>
<tr>
<td>13</td>
<td>( P_4W_{26}O_{86} )</td>
<td>550</td>
<td>( a=5.28 \ b=6.57 \ c=45.04 ) ( \beta=? )</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
</tr>
<tr>
<td>14</td>
<td>( P_4W_{28}O_{92} )</td>
<td>730</td>
<td>( a=5.32 \ b=6.54 \ c=48.00 )</td>
<td>nc</td>
<td>Ottolenghi et al, J. Phys. I Fr. 6 (1996)</td>
</tr>
</tbody>
</table>

\[ m \text{ even} \rightarrow \text{S.G.} \ P2_12_12_1 \quad m \text{ odd} \rightarrow \text{S.G.} \ P2_1/\bar{n} \]
Compatibility with the observed 3d space groups

<table>
<thead>
<tr>
<th>SSG</th>
<th>\textit{Pnnm}(00\gamma)0s0</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{(3+1)d Symmetry operators}</td>
<td></td>
</tr>
<tr>
<td>$x_1, x_2, x_3, x_4$</td>
<td>$\overline{x}_1, \overline{x}_2, \overline{x}_3, \overline{x}_4$</td>
</tr>
<tr>
<td>$\frac{1}{2} + x_1, \frac{1}{2} - x_2, \frac{1}{2} - x_3, \overline{x}_4$</td>
<td>$\frac{1}{2} - x_1, \frac{1}{2} + x_2, \frac{1}{2} + x_3, x_4$</td>
</tr>
<tr>
<td>$\frac{1}{2} - x_1, \frac{1}{2} + x_2, \frac{1}{2} - x_3, \frac{1}{2} - x_4$</td>
<td>$\frac{1}{2} + x_1, \frac{1}{2} - x_2, \frac{1}{2} + x_3, \frac{1}{2} + x_4$</td>
</tr>
<tr>
<td>$\overline{x}_1, \overline{x}_2, x_3, \frac{1}{2} + x_4$</td>
<td>$x_1, x_2, \overline{x}_3, \frac{1}{2} - x_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3d sections</th>
<th>section</th>
<th>section</th>
<th>section</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_0 = \frac{2 \nu}{4m+2}$</td>
<td>$t_0 = \frac{2 \nu+1}{4m+2}$</td>
<td>$\forall t_0$</td>
</tr>
<tr>
<td>m even</td>
<td>\textit{P}1\textit{12}_m</td>
<td>\textit{P}2_1\textit{2}_1\textit{2}_1</td>
<td>\textit{P}1\textit{12}_1</td>
</tr>
<tr>
<td>m odd</td>
<td>\textit{P}1\textit{2}_n\textit{1}</td>
<td>\textit{P}2_1\textit{nm}</td>
<td>\textit{P}1\textit{n}1</td>
</tr>
</tbody>
</table>
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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Fac. Ciencia y Tecnologia, Universidad del Pais Vasco, UPV 48080 BILBAO
family of terrace-like structures

Bi$_{14}$Sr$_{21}$Fe$_{12}$O$_{61}$ (x=7)  S.G. I2
$a_1=16.55\text{Å}  b_1=5.49\text{Å}  c_1=35.29\text{Å}  
\beta_1=90.52^\circ$

Bi$_{12}$Sr$_{18}$Fe$_{10}$O$_{52}$ (x=6)  S.G. P2$_1$/n
$a_1=16.48\text{Å}  b_1=5.48\text{Å}  c_1=30.07\text{Å}  
\beta_1=91.40^\circ$
New definition for composition: $\text{Bi}_{2x}\text{Sr}_{3x}\text{Fe}_{2x-2}\text{O}_{9x-2}$
\[ \text{Bi}_{2x}\text{Sr}_{3x}\text{Fe}_{2x-2}\text{O}_{9x-2} \]

subcell

\[ a_2 = 3.59\text{Å} \quad b_2 = 5.49\text{Å} \quad c_2 = 3.46\text{Å} \]
\[ \beta_2 = 81.90^\circ \]

wave vector

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

from the diffraction patterns: \text{SSG X2/m(a0g)0s, with X= (1/2, 1/2, 1/2)}

relation with supercell

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

\[ x=6 \quad \text{Bi}_{12}\text{Sr}_{18}\text{Fe}_{10}\text{O}_{52} \quad \text{q} \]
\[ \frac{11}{40}a_2^* - \frac{12}{40}c_2^* \]

\[ x=7 \quad \text{Bi}_{14}\text{Sr}_{21}\text{Fe}_{12}\text{O}_{61} \]
\[ \frac{13}{47}a_2^* - \frac{14}{47}c_2^* \]
(3+1)d model with 3 independent atomic domains

<table>
<thead>
<tr>
<th>Bi/Sr/Fe</th>
<th>O(1)</th>
<th>O(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0.4477</td>
<td>0</td>
</tr>
<tr>
<td>0.2611</td>
<td>0.2557</td>
<td>0.2352</td>
</tr>
</tbody>
</table>

average positions

atomic occupancies using crenel functions

vacancies
with crenel function

the resulting structure

\( \text{Bi}_{14}\text{Sr}_{21}\text{Fe}_{12}\text{O}_{61} \quad x=7 \)
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

\[ a = 16.49\text{Å} \quad b = 5.48\text{Å} \quad c = 30.86\text{Å} \quad \beta = 91.39^\circ \quad \text{G.E. : P2}_1/n \]

\[ a = 16.54\text{Å} \quad b = 5.49\text{Å} \quad c = 35.29\text{Å} \quad \beta = 90.52^\circ \quad \text{S.G. : I2} \]
Symmetry ...

In the physical space ...

[Diagram showing a glide mirror with points labeled 1 and 2 along the y-axis.]