International School on Aperiodic Crystals

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Superspace symmetry and superspace groups

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Symmetry of matter is required for

Determination of crystal structures (avoiding dependent parameters)

Understanding physical properties

- Thermal expansion
- Elasticity
- Non-linear crystals (inversion center)

Neumann's Principle:

- Symmetries of a physical property of a material include the crystal point group, but may include more symmetry

Symmetry of aperiodic crystals

Aperiodic crystals lack 3D translational symmetry

Therefore, they cannot have rotational symmetry

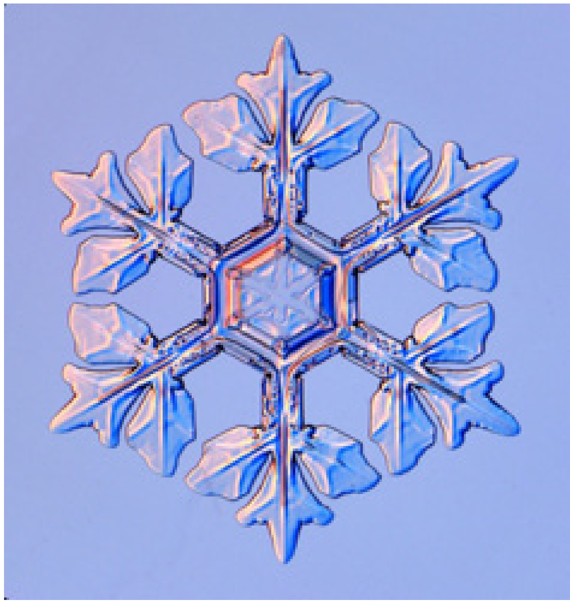
Aperiodic crystals are an ordered state of matter:

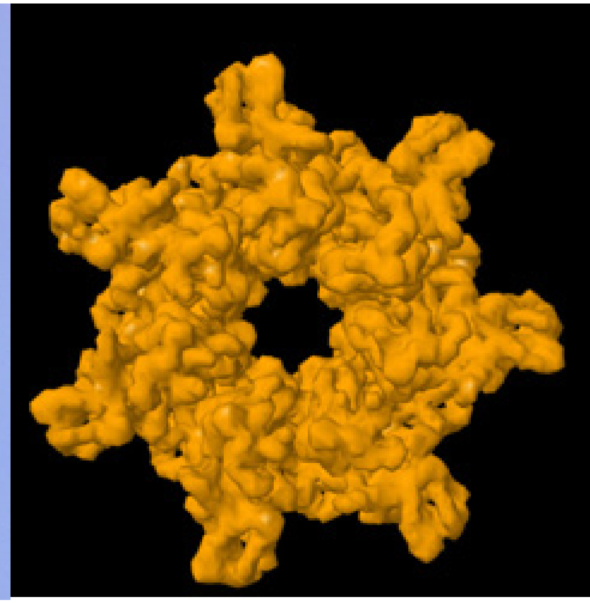
- we call them crystalline
- Diffraction gives Bragg reflections

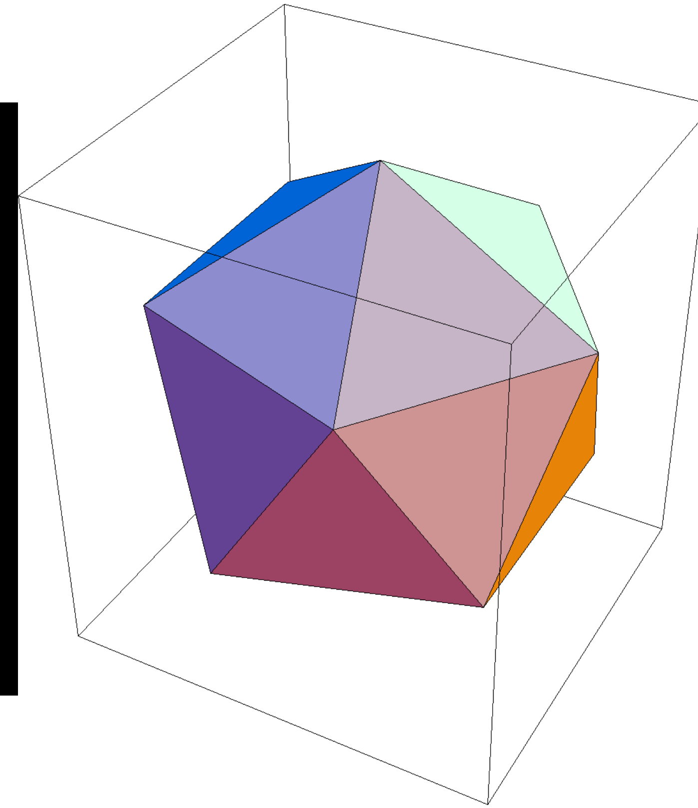
The diffraction pattern possesses 3D point symmetry

Eventually assign this symmetry to the aperiodic crystal structure (superspace groups)

Point group symmetries in 3D space







Snow crystal 6/mmm
Crystallographic point groups

Modulated and composite crystals

http://www.SnowCrystals.com

7-fold protein
n/mmm groups
for *n* = 5,7,8,...

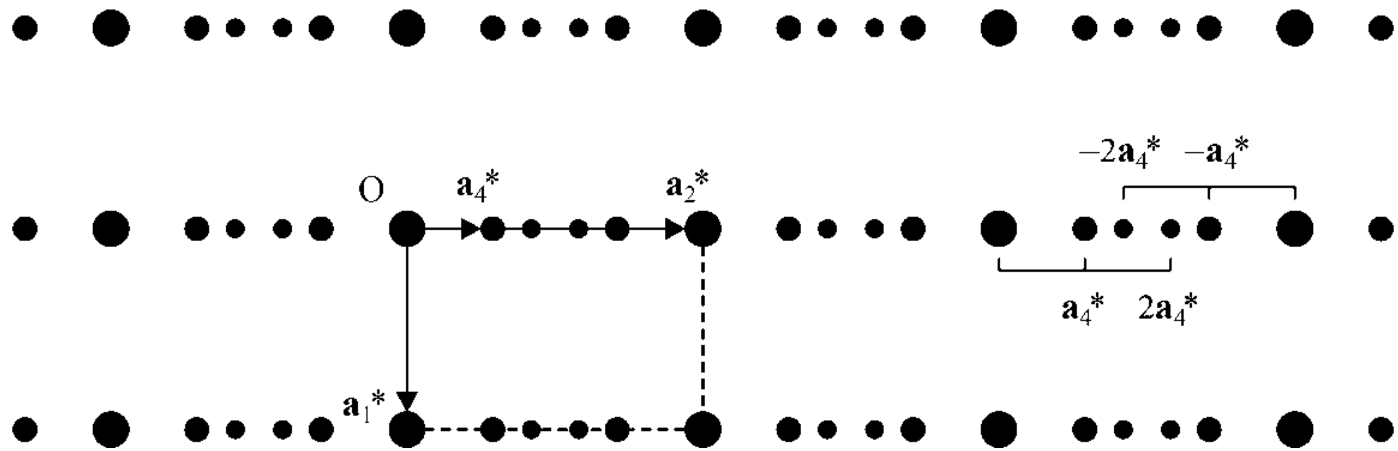
Quasicrystals

PDB: 1TZO

icosahedron 53m

Quasicrystals

Diffraction by a modulated crystal



$$\mathbf{H} = h_1\,\mathbf{a}_1^* + h_2\,\mathbf{a}_2^* + h_3\,\mathbf{a}_3^* + h_4\,\mathbf{a}_4^*$$

$$= h_1\,\mathbf{a}_1^* + h_2\,\mathbf{a}_2^* + h_3\,\mathbf{a}_3^* + m\,\mathbf{q}$$

$\mathbf{q} = \mathbf{a}_4^* = \sigma_1\,\mathbf{a}_1^* + \sigma_2\,\mathbf{a}_2^* + \sigma_3\,\mathbf{a}_3^*$ Modulation wave vector

$$\mathbf{H} = (h_1 + m\sigma_1)\,\mathbf{a}_1^* + (h_2 + m\sigma_2)\,\mathbf{a}_2^* + (h_3 + m\sigma_3)\,\mathbf{a}_3^*$$

S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

Diffraction symmetry of an incommensurately modulated crystal

Main reflections possess point symmetry according to one of the 32 crystal classes

Rotational operator *R* transforms

main reflection into main reflection

satellite reflection of order *m* into satellite of order *m*

1D modulation: $R\,\mathbf{q} \rightarrow \varepsilon\,\mathbf{q}$ with $\varepsilon = \pm 1$

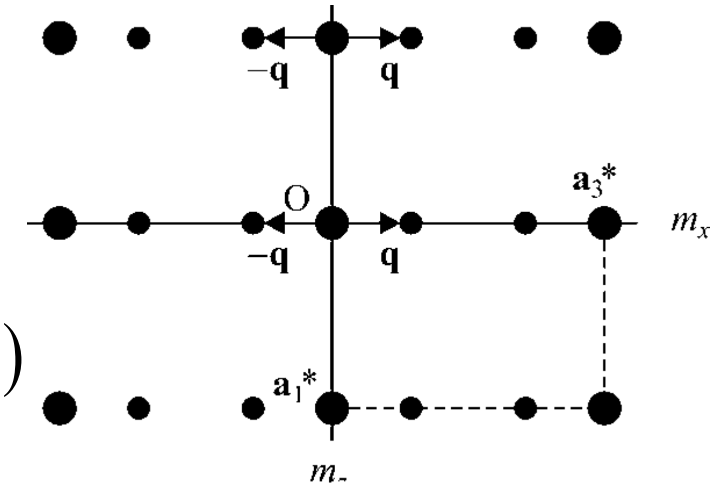
$\mathbf{q} = \sigma_1\,\mathbf{a}_1^* + \sigma_2\,\mathbf{a}_2^* + \sigma_3\,\mathbf{a}_3^* \rightarrow (\sigma_1, \sigma_2, \sigma_3)$

Condition for possible modulation wave vectors:

$(\sigma_1, \sigma_2, \sigma_3)\,R^{-1} - \varepsilon^{-1}\,(\sigma_1, \sigma_2, \sigma_3) = (0, 0, 0)$

Implications of mirror symmetry for **q**

$$R = R^{-1} = m_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$



$$(\sigma_1 \;\; \sigma_2 \;\; \sigma_3)R^{-1} - \varepsilon^{-1}(\sigma_1 \;\; \sigma_2 \;\; \sigma_3) = (0 \;\; 0 \;\; 0)$$

m_z with $\varepsilon = 1$: $(\sigma_1 \;\; \sigma_2 \;\; -\sigma_3) - (\sigma_1 \;\; \sigma_2 \;\; \sigma_3) = (0 \;\; 0 \;\; 2\sigma_3) \equiv (0 \;\; 0 \;\; 0)$

$$\mathbf{q} = (\sigma_1, \sigma_2, 0)$$

m_z with $\varepsilon = -1$: $(\sigma_1 \;\; \sigma_2 \;\; -\sigma_3) + (\sigma_1 \;\; \sigma_2 \;\; \sigma_3) = (2\sigma_1 \;\; 2\sigma_2 \;\; 0) \equiv (0 \;\; 0 \;\; 0)$

$$\mathbf{q} = (0, 0, \sigma_3)$$

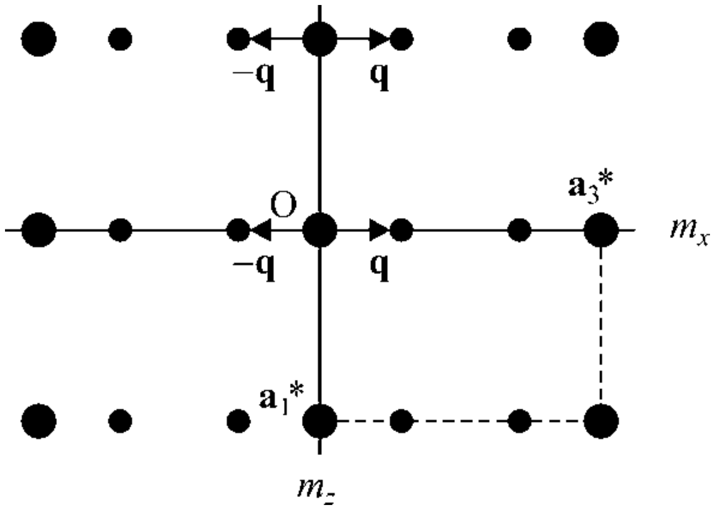
S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

Admissible incommensurate wave vectors for 1D modulations

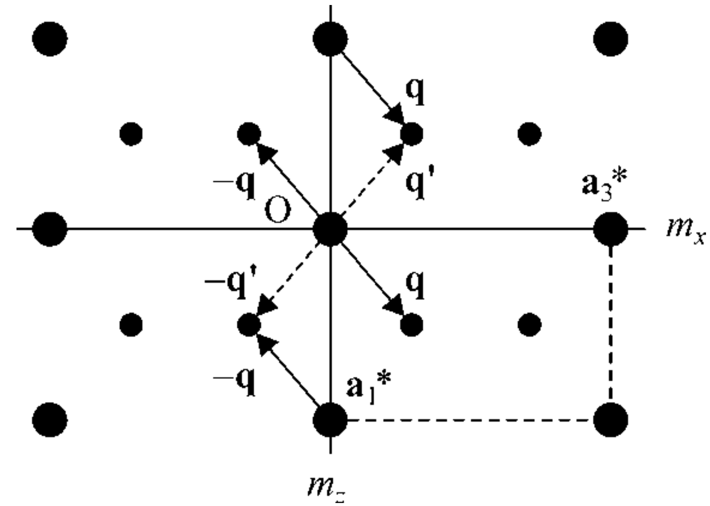
Triclinic	$(\sigma_1, \sigma_2, \sigma_3)$
Monoclinic	$(\sigma_1, \sigma_2, 0)$
	$(0, 0, \sigma_3)$
Orthorhombic	$(\sigma_1, 0, 0)$
	$(0, \sigma_2, 0)$
	$(0, 0, \sigma_3)$

Tetragonal	$(0, 0, \sigma_3)$
Trigonal	$(0, 0, \sigma_3)$
Hexagonal	$(0, 0, \sigma_3)$
Cubic	none

Umklapp terms



$$\mathbf{q} = (0, 0, \sigma_3)$$



$$\mathbf{q} = (1/2, 0, \sigma_3)$$

$$(\sigma_1, \sigma_2, \sigma_3)R^{-1} - \varepsilon^{-1}(\sigma_1, \sigma_2, \sigma_3) = (m_1^*, m_2^*, m_3^*)$$

$\mathbf{m}^* = (m_1^*, m_2^*, m_3^*)$ reciprocal lattice vector of the basic structure

$$(1/2 \;\; 0 \;\; -\sigma_3) + (1/2 \;\; 0 \;\; \sigma_3) = (1 \;\; 0 \;\; 0) \equiv (m_1^* \;\; m_2^* \;\; m_3^*)$$

S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

Admissible incommensurate wave vectors with non-zero rational components (1D)

Monoclinic—P	$(\sigma_1, \sigma_2, 1/2)$	$(1/2, 0, \sigma_3)$	$(0, 1/2, \sigma_3)$	
Monoclinic—B		$(1/2, 0, \sigma_3)$		
Monoclinic—A			$(0, 1/2, \sigma_3)$	
Orthorhombic—P	$(1/2, 0, \sigma_3)$	$(0, 1/2, \sigma_3)$	$(1/2, 1/2, \sigma_3)$	
Orthorhombic—A	$(1/2, 0, \sigma_3)$			
Orthorhombic—B		$(0, 1/2, \sigma_3)$		
Orthorhombic—C	$(1, 0, \sigma_3)$	$(0, 1, \sigma_3)$		
Orthorhombic—F	$(1, 0, \sigma_3)$	$(0, 1, \sigma_3)$		
Tetragonal—P	$(1/2, 1/2, \sigma_3)$			
Trigonal—P	$(1/3, 1/3, \sigma_3)$			

Conclusions—point symmetry

Diffraction symmetry is a 3D point group

Point symmetry restricts admissible modulation wave vectors

$\mathbf{q} = \mathbf{q}_r + \mathbf{q}_i$

Combination of 3D point group and q vectors leads to

Bravais classes of superspace groups

What about symmetry of the crystal structure?

Symmetry operators and coordinates

$\{R \,|\, \mathbf{v}\}$

$$R = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \qquad \mathbf{v} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$$ physical space coordinates

$$\mathbf{S} = \begin{pmatrix} S_1 & S_2 & S_3 \end{pmatrix}$$ reciprocal space vector

$$\{R \,|\, \mathbf{v}\} : \mathbf{x} \longrightarrow R\,\mathbf{x} + \mathbf{v} \qquad \{R \,|\, \mathbf{v}\} : \mathbf{S} \longrightarrow \mathbf{S} R^{-1}$$

$$\{R \,|\, \mathbf{v}\}^{-1} = \{R^{-1} \,|\, -R^{-1}\mathbf{v}\}$$

$\{E \,|\, \mathbf{T}\}$ lattice translation

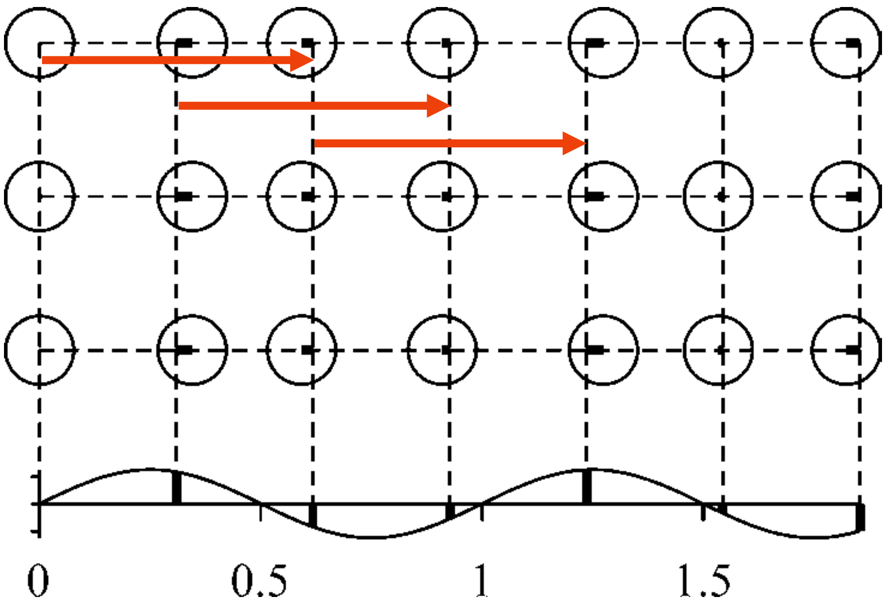
Symmetry operator $\{R\,|\,\mathbf{v}\}$ in direct and reciprocal space

$$\begin{pmatrix} x'_1 \\ x'_2 \\ x'_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

$$\begin{pmatrix} S'_1 \\ S'_2 \\ S'_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix}^{t,-1} \begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix}$$

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix}^{t,-1} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix}; \qquad \begin{pmatrix} \mathbf{a}'^*_1 \\ \mathbf{a}'^*_2 \\ \mathbf{a}'^*_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}^*_1 \\ \mathbf{a}^*_2 \\ \mathbf{a}^*_3 \end{pmatrix}$$

Lack of translational symmetry in physical space

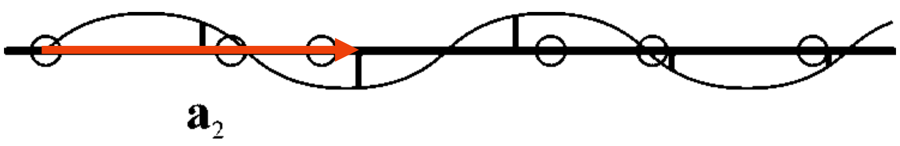


Modulation wave parallel to $\mathbf{a}_2$* : $\mathbf{q} = \sigma_2\, \mathbf{a}_2^*$

$$x_2 = l_2 + x_2^0 + u_2(\bar{x}_{s4})$$

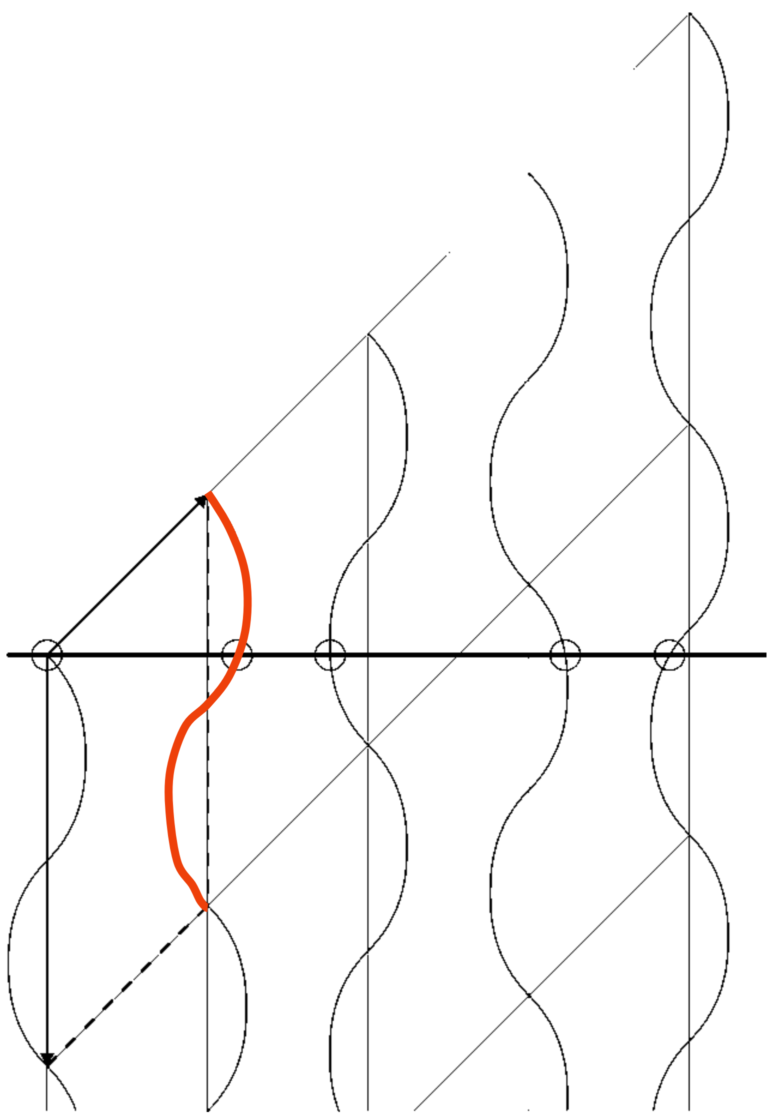
$$\bar{x}_{s4} = t + \sigma_2 (l_2 + x_2^0)$$

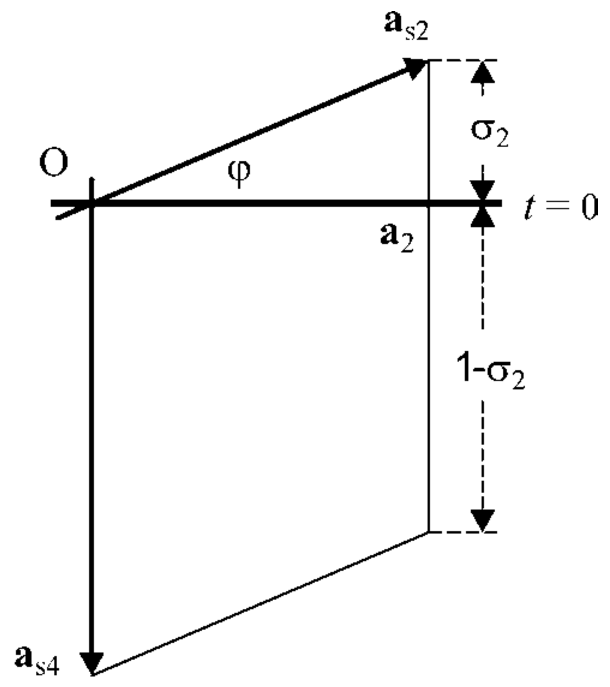
$$\{R \mid \mathbf{v}\} = \{E \mid \mathbf{T}\} = \{E \mid 2\,\mathbf{a}_2\}$$



Required phase shift $\Delta\, \bar{x}_{s4} = -\mathbf{q} \cdot \mathbf{T} = -\sigma_2\, n_2 \pmod{1}$

Translations in superspace



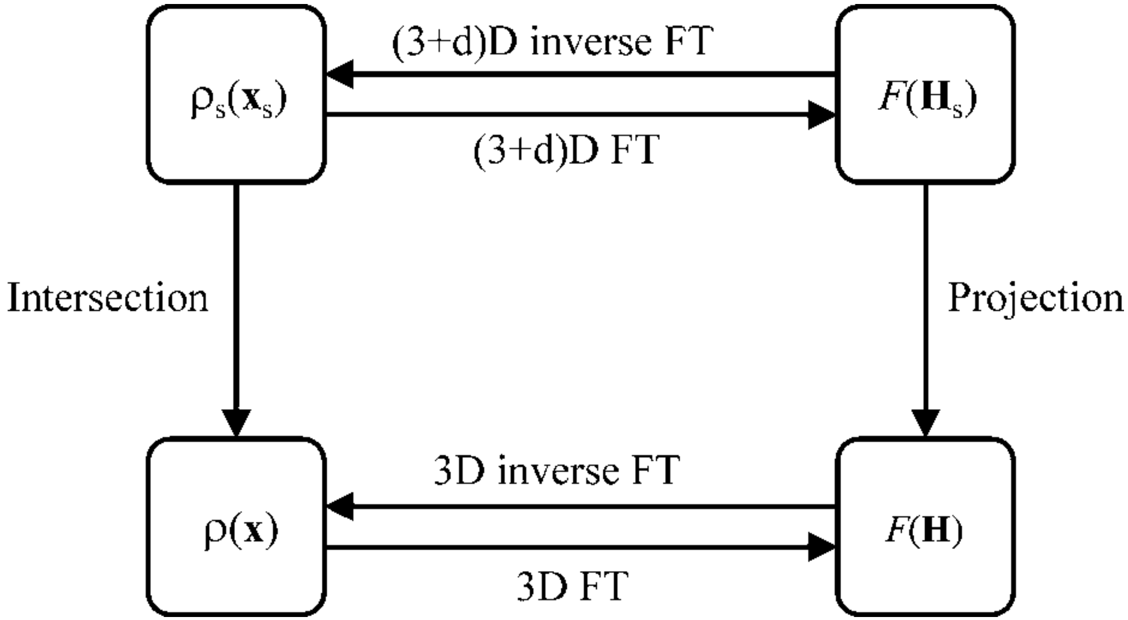


$$\{E_s \mid \mathbf{T}_s\} = \{E_s \mid \mathbf{a}_{s2}\} \quad \Rightarrow$$

$$\{E \mid \mathbf{T}\} = \{E \mid \mathbf{a}_2\}$$

plus $\quad \Delta \bar{x}_{s4} = -\mathbf{q} \cdot \mathbf{T} = -\sigma_2$

Relations between symmetry in physical space and superspace



R is point symmetry in 3D space implies symmetry operators R_s in superspace

$\mathbf{H} = h_1\, \mathbf{a}_1^* + h_2\, \mathbf{a}_2^* + h_3\, \mathbf{a}_3^* + h_4\, \mathbf{a}_4^*$

$\mathbf{a}_4^* = \mathbf{q} = \sigma_1\, \mathbf{a}_1^* + \sigma_2\, \mathbf{a}_2^* + \sigma_3\, \mathbf{a}_3^*$ Modulation wave vector

$$R_s = \begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ n_1^* & n_2^* & n_3^* & \varepsilon \end{pmatrix} = \begin{pmatrix} & 0 \\ R & 0 \\ & 0 \\ \mathbf{n}^* & \varepsilon \end{pmatrix} = (R, \varepsilon)$$

$$(\sigma_1 \;\; \sigma_2 \;\; \sigma_3) R - \varepsilon (\sigma_1 \;\; \sigma_2 \;\; \sigma_3) = (n_1^* \;\; n_2^* \;\; n_3^*) \quad \text{with} \quad \varepsilon = \pm 1$$

Transformation of reflection indices in superspace

$\mathbf{H} = h_1\, \mathbf{a}_1^* + h_2\, \mathbf{a}_2^* + h_3\, \mathbf{a}_3^* + h_4\, \mathbf{a}_4^*$

$\mathbf{H}' = h'_1\, \mathbf{a}_1^* + h'_2\, \mathbf{a}_2^* + h'_3\, \mathbf{a}_3^* + h'_4\, \mathbf{a}_4^*$

$\mathbf{H}$ and $\mathbf{H}'$ describe equivalent reflections: $F(\mathbf{H}) = F(\mathbf{H}')$

$$(R_s)^{-1} = \begin{pmatrix} & & & 0 \\ & R^{-1} & & 0 \\ & & & 0 \\ & -\varepsilon^{-1}\mathbf{n}^* R^{-1} & & \varepsilon^{-1} \end{pmatrix} = \begin{pmatrix} & & & 0 \\ & R^{-1} & & 0 \\ & & & 0 \\ & \mathbf{m}^* & & \varepsilon^{-1} \end{pmatrix}$$

$$\begin{pmatrix}\sigma_1 & \sigma_2 & \sigma_3\end{pmatrix} R^{-1} - \varepsilon^{-1}\begin{pmatrix}\sigma_1 & \sigma_2 & \sigma_3\end{pmatrix} = \begin{pmatrix}m_1^* & m_2^* & m_3^*\end{pmatrix}$$

$$\begin{pmatrix}h'_1 & h'_2 & h'_3 & h'_4\end{pmatrix} = \begin{pmatrix}h_1 & h_2 & h_3 & h_4\end{pmatrix}(R_s)^{-1}$$

Transformation of coordinates by a symmetry operator of superspace

$\mathbf{x} = x_1\, \mathbf{a}_1 + x_2\, \mathbf{a}_2 + x_3\, \mathbf{a}_3$

$\mathbf{x}_\mathrm{s} = x_{s1}\, \mathbf{a}_{\mathrm{s}1} + x_{s2}\, \mathbf{a}_{\mathrm{s}2} + x_{s3}\, \mathbf{a}_{\mathrm{s}3} + x_{s4}\, \mathbf{a}_{\mathrm{s}4}$

$x_i = x_{si}$ for $i = 1, 2, 3$

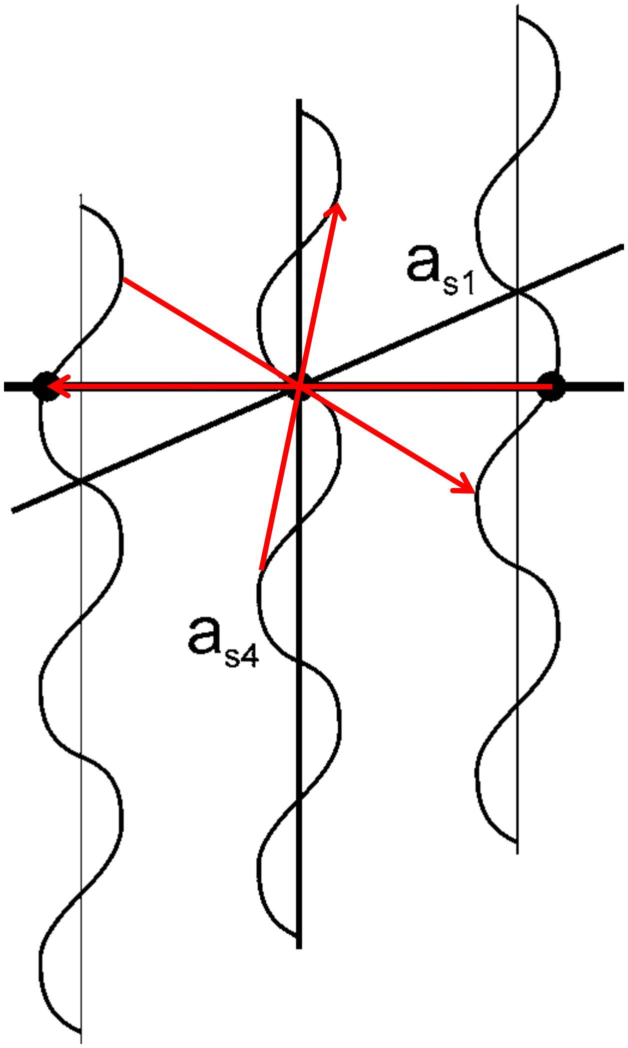
$$\{R_s \,|\, \mathbf{v}_s\} \qquad \begin{pmatrix} x'_{s1} \\ x'_{s2} \\ x'_{s3} \\ x'_{s4} \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ n_1^* & n_2^* & n_3^* & \varepsilon \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} + \begin{pmatrix} v_{s1} \\ v_{s2} \\ v_{s3} \\ v_{s4} \end{pmatrix}$$

Transformation of atoms in superspace

$$R_s = (R,\varepsilon) = (E,1): \quad (x, y, z, t) \quad \text{Identity}$$

$$(i,-1): \quad (-x,-y,-z,-t) \quad \text{inversion}$$

$$\begin{pmatrix} x'_{s1} \\ x'_{s2} \\ x'_{s3} \\ x'_{s4} \end{pmatrix} = \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix}; \quad \begin{pmatrix} v^0_{s1} \\ v^0_{s2} \\ v^0_{s3} \\ v^0_{s4} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$



inversion center at the origin

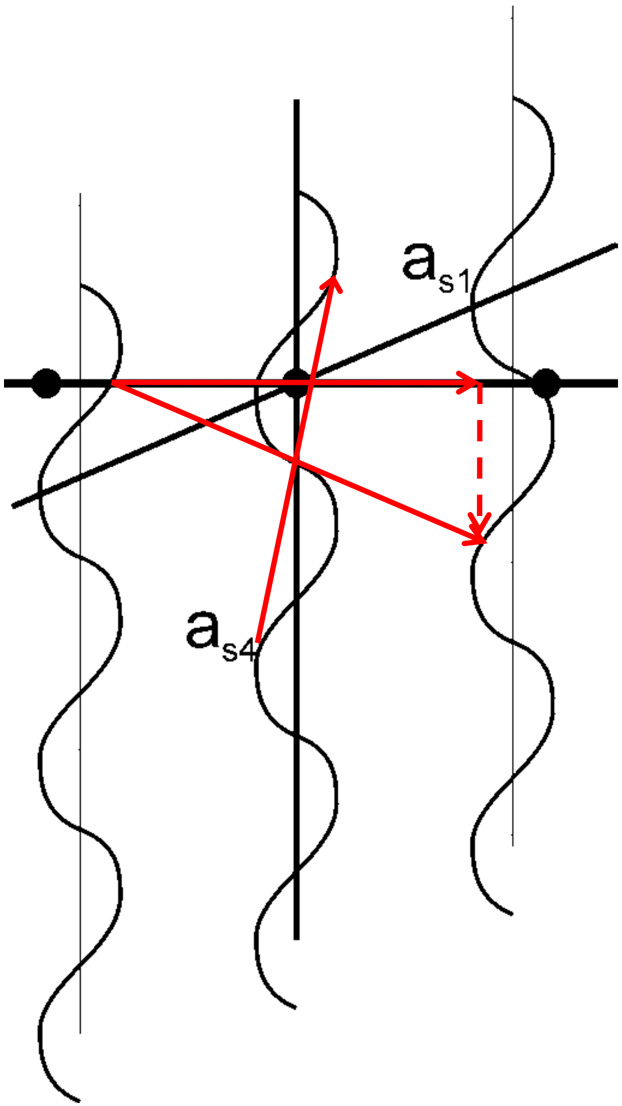
Origin-dependent translational components

$R_s = (R, \varepsilon) = (i, -1)$ inversion

$$\begin{pmatrix} x'_{s1} \\ x'_{s2} \\ x'_{s3} \\ x'_{s4} \end{pmatrix} = \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \\ v^0_{s4} \end{pmatrix}$$

$$(i, -1): \quad \left(-x, -y, -z, v^0_{s4} - t\right)$$

inversion center at $\frac{1}{2} v^0_{s4}$ along x_{s4}



Intrinsic translations

$$\{R_s\,|\,\mathbf{v}_s\}^n \;=\; \{R_s{}^n\,|\,R_s{}^{n-1}\mathbf{v}_s+\cdots+\mathbf{v}_s\} \;=\; \{E_s\,|\,\mathbf{L}_s\}$$

for $\quad R_s{}^n \;=\; E_s$

Solutions $\begin{pmatrix} v_{s1} \\ v_{s2} \\ v_{s3} \\ v_{s4} \end{pmatrix} \neq \begin{pmatrix} l_1 \\ l_2 \\ l_3 \\ l_4 \end{pmatrix}$ give intrinsic translations

Translational components of a superspace mirror plane

$$R_s = (m_z, -1): \quad (x_{s1}, x_{s2}, -x_{s4}, -x_{s4}) \quad \Rightarrow \quad \mathbf{q} = (0, 0, \sigma_3)$$

$$n = 2 \quad \Rightarrow \quad R_s\,\mathbf{v}_s + \mathbf{v}_s \;=\; \mathbf{L}_s$$

$$\{R_s \,|\, \mathbf{v}_s\} \;=\; \{m_z, -1 | v_{s1}, v_{s2}, v_{s3}, v_{s4}\} \qquad (m_z, -1) \;=\; \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

$$\begin{cases} v_{sk} = 0, 1/2 \quad (\text{mod } 1) \quad k = 1, 2 \quad \text{intrinsic translational components} \\ v_{sk} : \quad \textit{no restrictions} \quad k = 3, 4 \quad \text{origin-dependent components} \end{cases}$$

Notation of intrinsic translations

3D-part of translation by the usual symbols 2_1 screw axis, *a*-glide, *b*-glide, *c*-glide, *n*-glide and *d*-glide operators

Intrinsic translation along the additional axes by symbol:

v_{s4}	0	1/2	1/3	-1/3	1/4	-1/4	1/6	-1/6
symbol	0	s	t	$\bar{t}$	q	$\bar{q}$	h	$\bar{h}$

(*m*,-1)	(0, 0, 0, 0)	(x, y, -z, -t)	mirror
(*a*,-1)	(1/2, 0, 0, 0)	(1/2+x, y, -z, -t)	*a*-glide
(*b*,-1)	(0, 1/2, 0, 0)	(x, 1/2+y, -z, -t)	*b*-glide
(*n*,-1)	(1/2, 1/2, 0, 0)	(1/2+x, 1/2+y, -z, -t)	*n*-glide

Exercise: translational components for a twofold axis in superspace

$R_s = (2^z,\ 1):\ (-x_{s1}, -x_{s2}, x_{s4}, x_{s4})$

$\Rightarrow \quad \mathbf{q} = (0, 0, \sigma_3)$

$$(2^z, 1) = \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$\{R_s \,|\, \mathbf{v}_s\} = \{2^z, 1 | v_{s1}, v_{s2}, v_{s3}, v_{s4}\}$

$\{R_s \,|\, \mathbf{v}_s\}^n = \{R_s{}^n \,|\, R_s{}^{n-1}\mathbf{v}_s + \cdots + \mathbf{v}_s\} = \{E_s \,|\, \mathbf{L}_s\}$

Solution: translational components for a twofold axis in superspace

$\{R_s \mid \mathbf{v}_s\} = \{2^z, 1 \mid v_{s1}, v_{s2}, v_{s3}, v_{s4}\}$ $\quad (2^z,\ 1):\ (-x_{s1}, -x_{s2}, x_{s4}, x_{s4})$

$n = 2: \quad R_s\,\mathbf{v}_s + \mathbf{v}_s = \mathbf{L}_s$ $\quad (0, 0, 2v_{s3}, 2v_{s4}) = (l_1, l_2, l_3, l_4)$

$l_1 = l_2 = 0$ & v_{s1}, v_{s2}: no restrictions

origin-dependent components

$l_3, l_4 = 0,1,... \Rightarrow v_{s3}, v_{s4} = 0$, 1/2 (mod 1)

intrinsic translational components

Twofold screw axes in superspace groups

Point-symmetry operator symbol: (2,1)

Superspace group symmetry operator symbol:

(2, 0)	(0, 0, 0, 0)	(-x, -y, z, t)	twofold rotation
$(2_1, 0)$	(0, 0, 1/2, 0)	(-x, -y, 1/2+z, t)	screw
(2, *s*)	(0, 0.5, 0, 1/2)	(-x, -y, z, 1/2+t)	screw
$(2_1, s)$	(0, 0, 1/2, 1/2)	(-x, -y, 1/2+z, 1/2+t)	screw

$$\left(2^z, s\right): \quad \left(v_{s1} - x_{s1}, v_{s2} - x_{s2}, x_{s3}, 1/2 + x_{s4}\right)$$

$$\left(2_1^z, s\right): \quad \left(-x_{s1}, 0.5 - x_{s2}, 1/2 + x_{s3}, 1/2 + x_{s4}\right)$$

Equivalence of superspace groups

Coordinate transformation Q_s provides an alternative unit cell in superspace

Q_s is unimodular (3+d)x(3+d) matrix $\Rightarrow$ space groups

Q_s is (3,d)-reduced (of the same type as symmetry operators) $\Rightarrow$ superspace groups

$$\begin{pmatrix} \mathbf{a'}^*_{s1} \\ \mathbf{a'}^*_{s2} \\ \mathbf{a'}^*_{s3} \\ \mathbf{a'}^*_{s4} \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & 0 \\ Q_{21} & Q_{22} & Q_{23} & 0 \\ Q_{31} & Q_{32} & Q_{33} & 0 \\ n_1^* & n_2^* & n_3^* & Q_{44} \end{pmatrix} \begin{pmatrix} \mathbf{a}^*_{s1} \\ \mathbf{a}^*_{s2} \\ \mathbf{a}^*_{s3} \\ \mathbf{a}^*_{s4} \end{pmatrix}$$

Example of equivalence in 4D and (3+1)D spaces

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$(m_z, -1) \Leftrightarrow (2^z, 1)$ as 4D space group

$(m_z, -1) \neq (2^z, 1)$ as (3+1)D superspace group,

because Q_s is unimodular but not in (3,1)-reduced form

Sources of superspace group information

(3+1)D superspace groups

De Wolff, Janssen & Janner (1981) Acta Cryst. A **37**, 625; IT-Vol. C

Orlov & Chapuis (2005) at http://superspace.epfl.ch

(3+*d*)D Bravais classes (*d* = 1, 2, 3)

Janner, Janssen & De Wolff (1983) Acta Cryst A **39**, 658; IT-Vol. C

(3+*d*)D superspace groups (*d* = 1, 2, 3)

Yamamoto (2005) at http://quasi.nims.go.jp/yamamoto/spgr.html

NEW: Harold Stokes, Branton Campbell & S. van Smaalen (2010) submitted to Acta Crystallogr. A

Tables and WEB tool "SSG(3+d)D"

Extended information and numerous corrections for *d* = 2, 3

The number of (super-)space groups

Classification	Dimension of space or superspace						
	1	2	3	4	3+1	3+2	3+3
Bravais lattices	1	5	14	64	24	83	215
Crystal classes	2	10	32	227	31		
Space groups	2	17	219	4783	755	3338	12584

$$\begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ n_1^* & n_2^* & n_3^* & \varepsilon \end{pmatrix}$$

compare 28 927 922 space groups of dimension six

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

Numbers and symbols for superspace groups

Bravais classes as *d*.sequence number

Examples: 1.24 2.83 3.215

Superspace group 51.3.122.769

is the 769th superspace group with basic space group No. 51

it belongs to Bravais class 3.122

$$Pcmm(\alpha_1, \beta_1, 0)000(-\alpha_1, \beta_1, 0)00s(0, 0, \gamma_2)0s0$$

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

Symbol ambiguity and symbol degeneracy

Symbols for superspace groups specify generators

The symbol is not unique – already so for 3D space groups

No. 23 $I222$ and No. 24 $I2_12_12_1$ both contain 2 and 2_1 axes

Eight valid symbols for either group: $I222$ $I222_1$ $I22_12$ $I22_12_1$

$I2_122$ $I2_122_1$ $I2_12_12$ and $I2_12_12_1$

- $I222$ "Origin at intersection of 222"
- $I2_12_12_1$ "Origin at midpoint of three non-intersecting pairs of parallel 2 axes"

Choice: simplest symbol for symmorphic space group

Problem much more profound for superspace groups

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

Symbols for superspace groups

SSG(3+d)D has formulated a series of conventions and rules leading to a unique symbol for superspace groups of dimension (3+*d*), *d* = 1, 2, 3.

It is advised to always specify the symmetry operators rather than to rely on symbols. Even more so, because often a non-standard setting of the SSG is used.

Symbol of SSG depends on a mixture of the BSG setting and SCG setting of the superspace group.

54.2.29.32 $Pbcb(0, \beta_1, 0)000(0, 0, \gamma_2)s00$

Intrinsic translations from reflection conditions in SCG setting.

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

SSG(3+d)D: 11.1.6.4 $P2_1/m(1/2,0,\gamma)00$

Superspace group: 11.1.6.4 P2_1/m(1/2,0,g)00 [Y:1.37]

Bravais class: 1.6 P2/m(1/2,0,g) [JJdW:1.6]

Transformation to supercentered setting: A1=2a1+a4, A2=a2, A3=a3, A4=a4

BASIC SPACE GROUP SETTING

Modulation vectors: q1=(1/2,0,g)

Centering: (0,0,0,0)

Non-lattice generators: (-x,-y,z+1/2,-x+t); (x,y,-z+1/2,x-t)

Non-lattice operators: (x,y,z,t); (-x,-y,z+1/2,-x+t); (-x,-y,-z,-t); (x,y,-z+1/2,x-t)

SUPERCENTERED SETTING

Modulation vectors: Q1=(0,0,G), where G=g

Centering: (0,0,0,0); (1/2,0,0,1/2)

Non-lattice generators: (-X,-Y,Z+1/2,T); (X,Y,-Z+1/2,-T)

Non-lattice operators: (X,Y,Z,T); (-X,-Y,Z+1/2,T); (-X,-Y,-Z,-T); (X,Y,-Z+1/2,-T)

Reflection conditions: HKLM:H+M=2n; 00LM:L=2n

35.2.24.5 Cmm2(1,0,γ_1)000(0,0,γ_2)000

Superspace group: 35.2.24.5 Cmm2(1,0,g1)000(0,0,g2)000 [Y:2.764]

Bravais class: 2.24 Cmmm(1,0,g1)(0,0,g2) [JJdW:2.24]

Transformation to supercentered setting: A1=a1+a4, A2=a2, A3=a3, A4=a4, A5=a5

BASIC SPACE GROUP SETTING

Modulation vectors: q1=(1,0,g1), q2=(0,0,g2)

Centering: (0,0,0,0,0); (1/2,1/2,0,0,0)

Non-lattice generators: (-x,y,z,-2x+t,u); (x,-y,z,t,u); (-x,-y,z,-2x+t,u)

Non-lattice operators: (x,y,z,t,u); (-x,-y,z,-2x+t,u); (-x,y,z,-2x+t,u); (x,-y,z,t,u)

SUPERCENTERED SETTING

Modulation vectors: Q1=(0,0,G1), Q2=(0,0,G2), where G1=g1, G2=g2

Centering: (0,0,0,0,0); (1/2,1/2,0,1/2,0)

Non-lattice generators: (-X,Y,Z,T,U); (X,-Y,Z,T,U); (-X,-Y,Z,T,U)

Non-lattice operators: (X,Y,Z,T,U); (-X,-Y,Z,T,U); (-X,Y,Z,T,U); (X,-Y,Z,T,U)

Reflection conditions: HKLMN:H+K+M=2n

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

221.3.210.7 Pm-3m(0,β,β)000(β,0,β)000(β, β,0)000

Superspace group: 221.3.210.7 Pm-3m(0,b,b)000(b,0,b)000(b,b,0)000 [Y:3.11160]

Bravais class: 3.210 Pm-3m(0,b,b)(b,0,b)(b,b,0) [JJdW:3.212]

Transformation to supercentered setting: A1=a1, A2=a2, A3=a3, A4=a5+a6, A5=a4+a6, A6=a4+a5

BASIC SPACE GROUP SETTING

Modulation vectors: q1=(0,b,b), q2=(b,0,b), q3=(b,b,0)

Centering: (0,0,0,0,0,0)

Non-lattice generators: (x,y,-z,-u+v,-t+v,v); (-z,-x,-y,-v,-t,-u); (y,x,z,u,t,v)

Non-lattice operators: (x,y,z,t,u,v); (x,-y,-z,-t,-t+v,-t+u); (-x,y,-z,-u+v,-u,t-u)... (48)

SUPERCENTERED SETTING

Modulation vectors: Q1=(B,0,0), Q2=(0,B,0), Q3=(0,0,B), where B=b

Centering: (0,0,0,0,0,0); (0,0,0,1/2,1/2,1/2)

Non-lattice generators: (X,Y,-Z,T,U,-V); (-Z,-X,-Y,-V,-T,-U); (Y,X,Z,U,T,V)

Non-lattice operators: (X,Y,Z,T,U,V); (X,-Y,-Z,T,-U,-V); (-X,Y,-Z,-T,U,-V);... (48)

Reflection conditions: HKLMNP:M+N+P=2n

$P2_1(0,0,\gamma)s \Leftrightarrow P2_1(0,0,\gamma)0$

Input setting

Centering none

Operators (x,y,z,t); (-x,-y,z+1/2,t+1/2)

Standard settings

Superspace group: 4.1.5.2 P2_1(0,0,g)0 [Y:1.5]

Bravais class: 1.5 P2/m(0,0,g) [JJdW:1.5]

Transformation to supercentered setting: none

Modulation vectors: q1=(0,0,g)

Centering: (0,0,0,0)

Non-lattice generators: (-x,-y,z+1/2,t)

Non-lattice operators: (x,y,z,t); (-x,-y,z+1/2,t)

Reflection conditions: 00lm:l=2n

Transformation matrix to standard supercentered setting <deleted>

d = 1: (0, 0, γ) transformed into **c*** - (0, 0, γ) = (0, 0, 1- γ)

d = 2, 3: mixing of q vectors

Stokes, Campbell & van Smaalen, submitted to Acta Cryst. A (2010): SSG(3+d)D

Conclusions

Symmetry of aperiodic crystals is based on point symmetry in physical (3D) space

(3+*d*)D Superspace groups are a (3,*d*)-reducible subset of (3+*d*)D space groups

Equivalence of superspace groups is non-intuitive

Preferably employ the supercentered group (SCG) setting

SSG(3+*d*)D: WEB tool for *d* = 1,2,3 superspace groups.

See Harold Stokes, Branton Campbell & S. van Smaalen (2010) submitted to Acta Crystallogr. A.

International School on Aperiodic Crystals

26 September - 2 October 2010, Carqueiranne, France

Symmetry restrictions by superspace groups

Sander van Smaalen

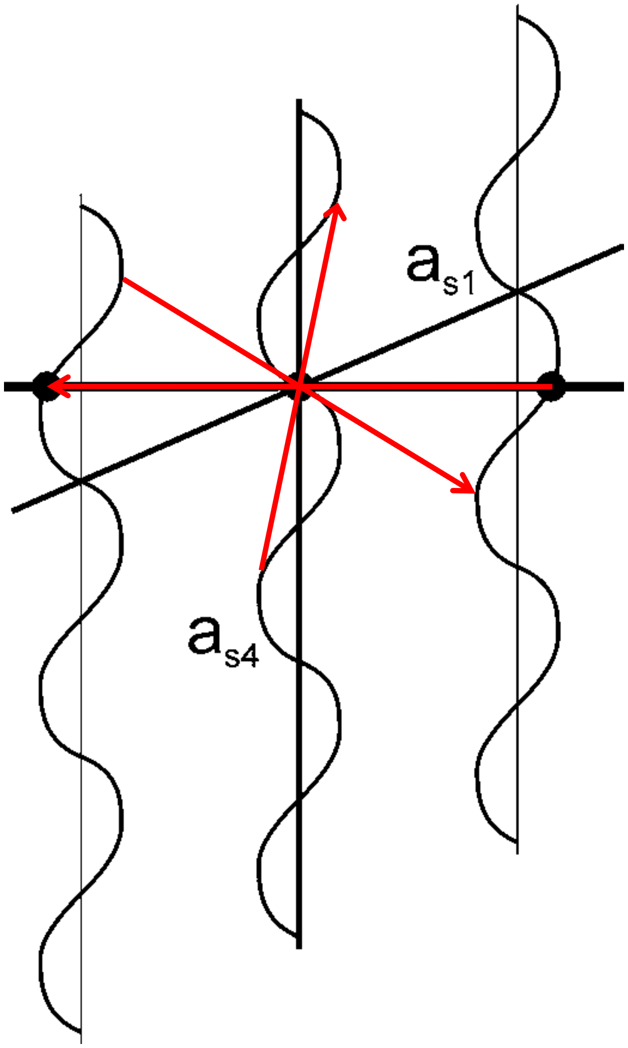
Laboratory of Crystallography

University of Bayreuth, Germany

Symmetry of the generalised electron density

$$R_s = \{R, \varepsilon \,|\, v_{s1}, v_{s2}, v_{s3}, v_{s4}\}$$

$$\begin{pmatrix} x'_{s1} \\ x'_{s2} \\ x'_{s3} \\ x'_{s4} \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ n_1^* & n_2^* & n_3^* & \varepsilon \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} + \begin{pmatrix} v_{s1} \\ v_{s2} \\ v_{s3} \\ v_{s4} \end{pmatrix}$$



x'_{s4} and x_{s4} are in different sections *t.*

One atom of the generalised electron density

$$\bar{\mathbf{x}} = \mathbf{L} + \mathbf{x}^0 \qquad \bar{x}_{s4} = t + \mathbf{q} \cdot \bar{\mathbf{x}}$$

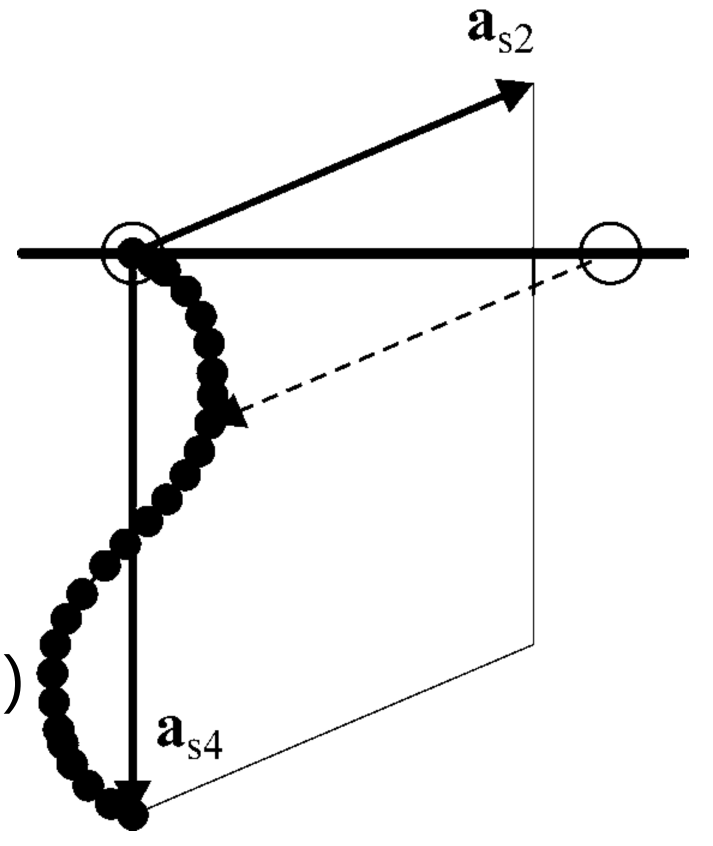
$$x_{si} = \bar{x}_{si} + u_i(t + \mathbf{q} \cdot \bar{\mathbf{x}})$$

$$x_{s4} = \bar{x}_{s4} + \mathbf{q} \cdot \mathbf{u}(t + \mathbf{q} \cdot \bar{\mathbf{x}})$$

'Line' atoms instead of point atoms:

variation of *t* from 0 to 1

$(x_{s1}, x_{s2}, x_{s3}, x_{s4})$



Atomic string: $\rho_{s\mu}(\mathbf{x}_s) = \rho_\mu(x_{s1} - x_{s1}^\mu, x_{s2} - x_{s2}^\mu, x_{s3} - x_{s3}^\mu)$

Structural parameters for a modulated structure

Each independent atom μ = 1,...,*N* of the basic structure has parameters:

$\mathbf{x}^0[\mu] = \left(x_1^0[\mu], x_2^0[\mu], x_3^0[\mu]\right)$ position in the unit cell (3)

$U_{i,j}^{\mu}$ temperature parameters (6)

$A_{n,i}^{\mu}, B_{n,i}^{\mu}$ modulation parameters ($6n_{\mathrm{max}}$)

$$u_i^{\mu}(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,i}^{\mu} \sin\left(2\pi n \bar{x}_{s4}\right) + B_{n,i}^{\mu} \cos\left(2\pi n \bar{x}_{s4}\right)$$

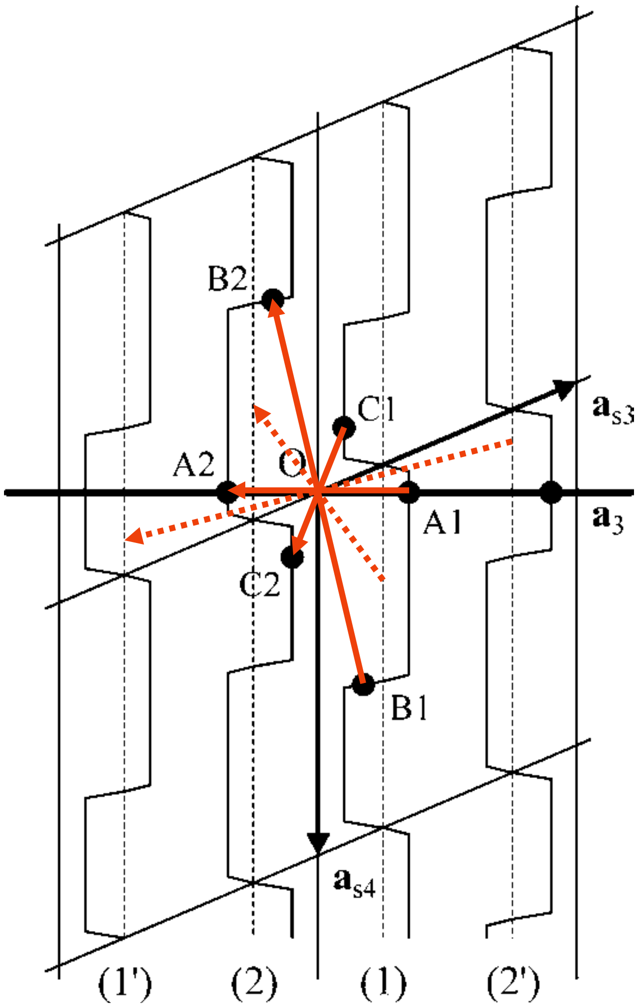
$$x_i = l_i + x_i^0(\mu) + u_i^{\mu}\left(t + \mathbf{q}\cdot(\mathbf{L} + \mathbf{x}^0)\right)$$

$\{R \mid \mathbf{v}\}$ is symmetry of the basic structure

$$R_s = \{R, \varepsilon \mid v_{s1}, v_{s2}, v_{s3}, v_{s4}\}$$

$$\begin{pmatrix} x'_{s1} \\ x'_{s2} \\ x'_{s3} \\ x'_{s4} \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ n_1^* & n_2^* & n_3^* & \varepsilon \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} + \begin{pmatrix} v_{s1} \\ v_{s2} \\ v_{s3} \\ v_{s4} \end{pmatrix}$$

$$\begin{pmatrix} \bar{x}_{s1}(2) \\ \bar{x}_{s2}(2) \\ \bar{x}_{s3}(2) \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix} + \begin{pmatrix} v_{s1} \\ v_{s2} \\ v_{s3} \end{pmatrix}$$



Transformation of modulation functions

Modulation functions are functions of the basic structure coordinates. $x_{si} = x_i = \bar{x}_i + u_i(\bar{x}_{s4})$

The transformation of a function of coordinates is

$$\mathbf{u}^2[\bar{x}_{s4}] = R\,\mathbf{u}^1[(\{R_s \mid \mathbf{v}_s\}^{-1}\bar{\mathbf{x}}_s)_{s4}] = R\,\mathbf{u}^1[\varepsilon^{-1}(\bar{\mathbf{x}}_{s4} - \mathbf{v}_{s4})]$$

in case of zero rational components (supercentered setting)

Rotation of the modulation functions (not for occupancy)

Change of their arguments

Example of mirror symmetry

$$R_s = (m_z,\ -1) \qquad \mathbf{q} = (0, 0, \gamma)$$

$$\{R_s \,|\, \mathbf{v}_s\} = \{m_z, -1 \,|\, 0,0,0,0\}$$

$$(m_z, -1) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

$$\begin{pmatrix} \bar{x}_{s1}(2) \\ \bar{x}_{s2}(2) \\ \bar{x}_{s3}(2) \end{pmatrix} = \begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ -\bar{x}_{s3}(1) \end{pmatrix}$$

$$(m, \bar{1}):\ (x, -y, z, -t)$$

$$\begin{pmatrix} u_1^2(\bar{x}_{s4}) \\ u_2^2(\bar{x}_{s4}) \\ u_3^2(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} u_1^1(-\bar{x}_{s4}) \\ u_2^1(-\bar{x}_{s4}) \\ -u_3^1(-\bar{x}_{s4}) \end{pmatrix}$$

Special positions

A special position is a position in the unit cell that is left invariant by the symmetry operator

An atom at a special position is mapped onto itself by the symmetry operator

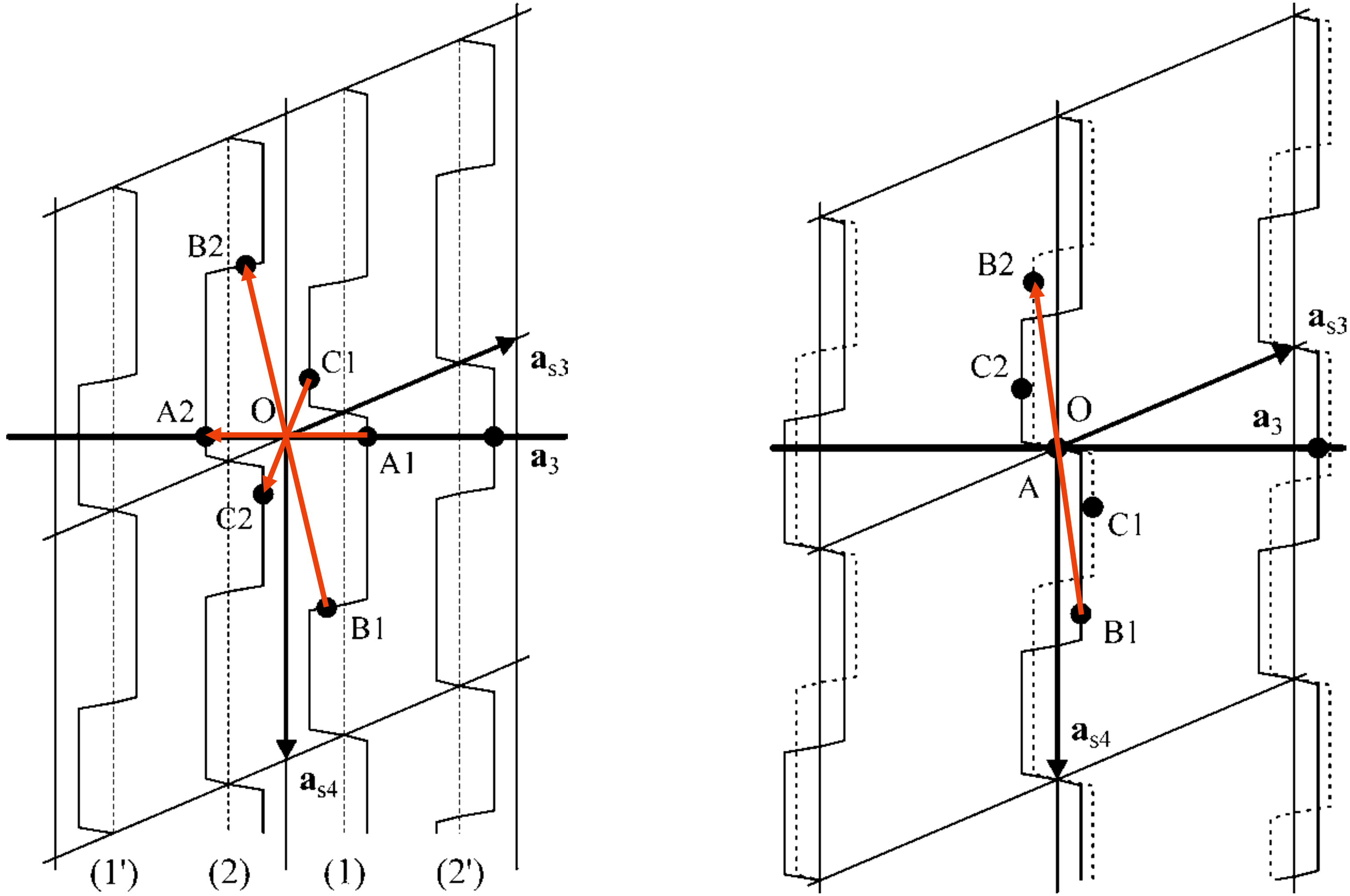
As a consequence restrictions apply to the structural parameters of this atom

But

In superspace 'atoms' are lines instead of points

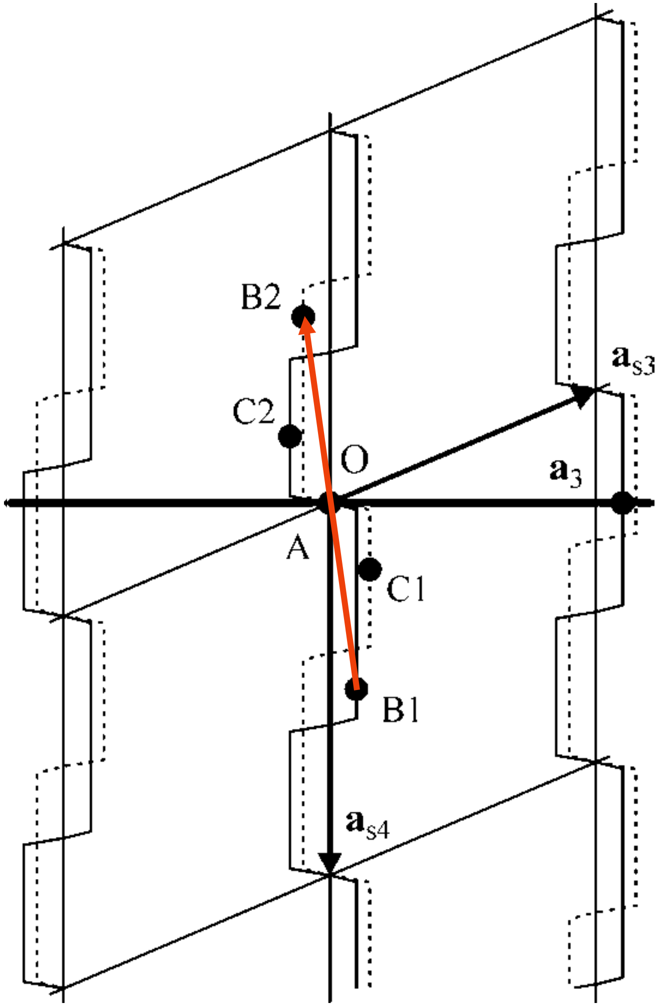
This gives additional possibilities and degrees of freedom

Symmetry of a structure in superspace



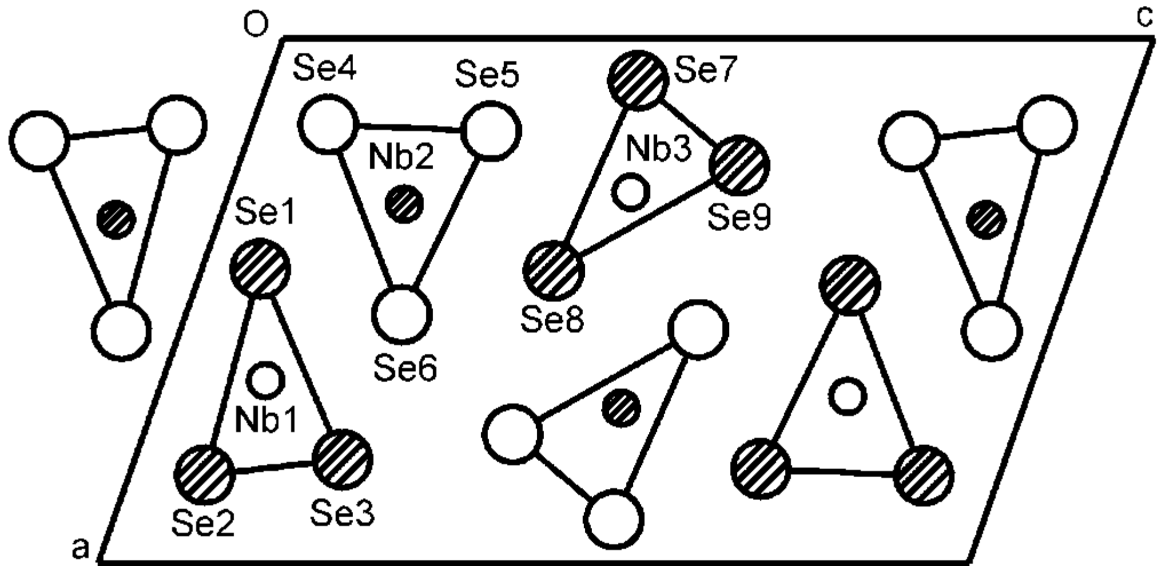
S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

Restrictions on the modulation functions



S. van Smaalen: *Incommensurate Crystallography*, Oxford University Press (2007)

$NbSe_3$ SSG 11.1.5.3 $P2_1/m(0,\beta,0)s0$



T_{c1} = 145 K **q** = (0, 0.241, 0) CDW along **b***

|**u**(Nb3)| = 0.05 Å Atomic modulation functions

Modulation of Se through elastic coupling toward Nb3

All atoms in mirror planes

S. van Smaalen *et al.*, Phys. Rev. B **45**, 3103-3106 (1992)

Mirror plane of P2$_1$/m(0,β,0)s0

$$\{R_s \mid \mathbf{v}_s\} = \{m_y, \bar{1} \mid 0, 1/2, 0, 0\}$$

$$(m_y, \bar{1}):\ (x, -y, z, -t)$$

$$\{m_y, \bar{1} \mid 0, 1/2, 0, 0\}:\ (x, 1/2 - y, z, -t)$$

$$(m_y, -1) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

$$\begin{pmatrix} \bar{x}_{s1}(2) \\ \bar{x}_{s2}(2) \\ \bar{x}_{s3}(2) \end{pmatrix} = \begin{pmatrix} \bar{x}_{s1}(1) \\ 1/2 - \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix}$$

$$\begin{pmatrix} u_1^2(\bar{x}_{s4}) \\ u_2^2(\bar{x}_{s4}) \\ u_3^2(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} u_1^1(-\bar{x}_{s4}) \\ -u_2^1(-\bar{x}_{s4}) \\ u_3^1(-\bar{x}_{s4}) \end{pmatrix}$$

Restrictions on basic-structure coordinates

$$\{R_s\,|\,v_s\} = \{m_y, \bar{1}\,|\,0, 1/2, 0, 0\}:\ (x, 1/2 - y, z, -t)$$

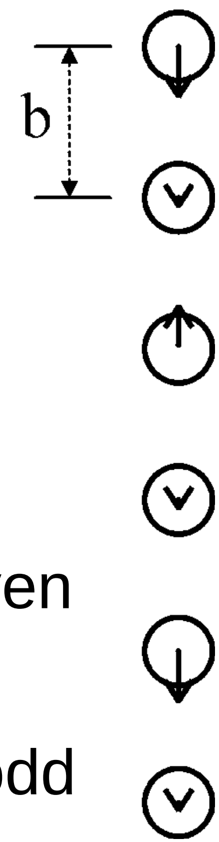
$$\begin{pmatrix} \bar{x}_1(1) \\ \bar{x}_2(1) \\ \bar{x}_3(1) \end{pmatrix} = \begin{pmatrix} \bar{x}_1(1) \\ 1/2 - \bar{x}_2(1) \\ \bar{x}_3(1) \end{pmatrix} \qquad \begin{aligned} &\Rightarrow \quad \bar{x}_2(1) = 1/2 - \bar{x}_2(1) \\ &\Leftrightarrow \quad 2\bar{x}_s(1) = 1/2 \quad (\mathrm{mod}\, 1) \\ &\Leftrightarrow \quad \bar{x}_2 = 1/4 \quad \text{or} \quad 3/4 \end{aligned}$$

$$\begin{pmatrix} \bar{x}_1(1) \\ \bar{x}_2(1) \\ \bar{x}_3(1) \end{pmatrix} = \begin{pmatrix} \bar{x}_{s1} \\ 1/4 \\ \bar{x}_{s3} \end{pmatrix}; \qquad \begin{pmatrix} \bar{x}_{s1} \\ 3/4 \\ \bar{x}_{s3} \end{pmatrix}$$

Atoms in mirror planes at x_2 = 1/4 and 3/4

Modulation functions for atom μ on (x_1,1/4,x_3)

$$\{R_s \,|\, v_s\} = \{m_y, \bar{1} \,|\, 0, 1/2, 0, 0\}:\ (x, 1/2 - y, z, -t)$$



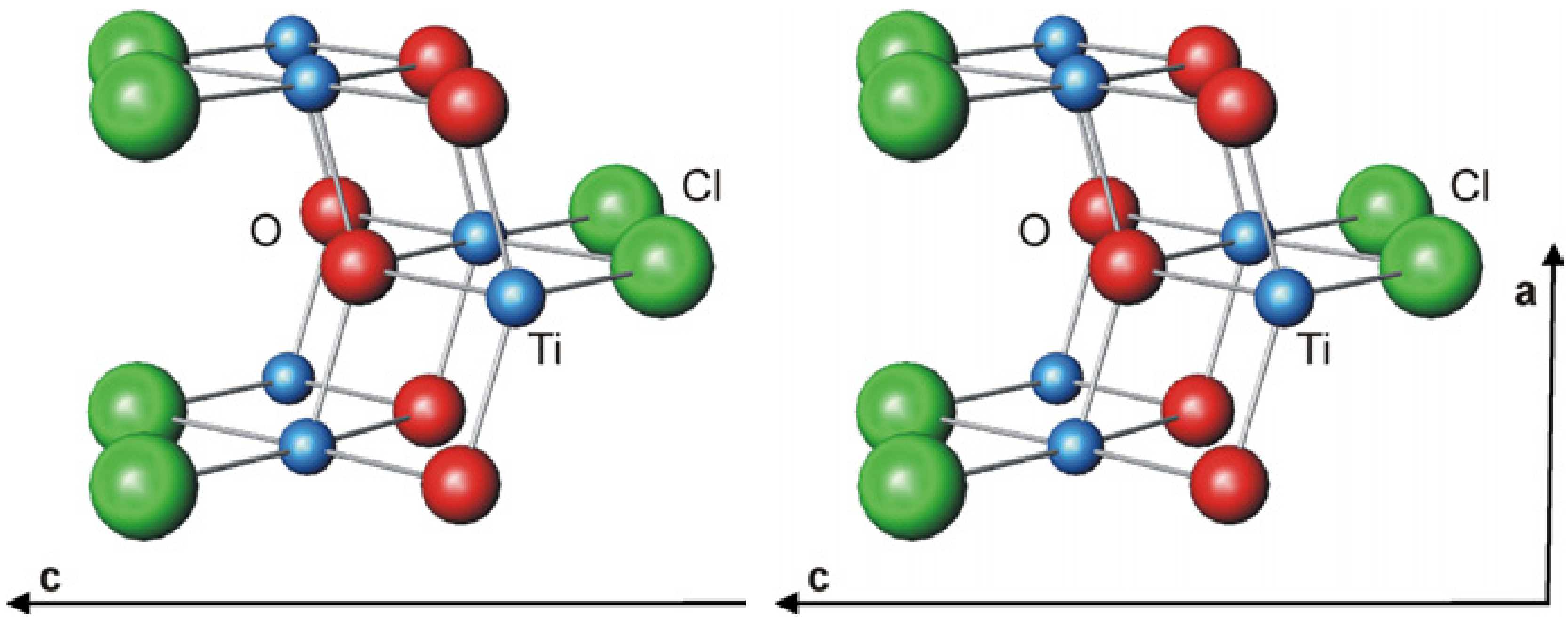
$$\begin{pmatrix} u_1^{\mu}(\bar{x}_{s4}) \\ u_2^{\mu}(\bar{x}_{s4}) \\ u_3^{\mu}(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} u_1^{\mu}(-\bar{x}_{s4}) \\ -u_2^{\mu}(-\bar{x}_{s4}) \\ u_3^{\mu}(-\bar{x}_{s4}) \end{pmatrix}$$

$$u_1(\bar{x}_{s4}) = u_1(-\bar{x}_{s4}) \quad \Rightarrow \quad u_1^{\mu}(\bar{x}_{s4}) = \sum_{n=1}^{\infty} B_{n,1}^{\mu} \cos[2\pi n \bar{x}_{s4}] \quad \text{even}$$

$$u_2(\bar{x}_{s4}) = -u_2(-\bar{x}_{s4}) \quad \Rightarrow \quad u_2^{\mu}(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,2}^{\mu} \sin[2\pi n \bar{x}_{s4}] \quad \text{odd}$$

$$u_3(\bar{x}_{s4}) = u_3(-\bar{x}_{s4}) \quad \Rightarrow \quad u_3^{\mu}(\bar{x}_{s4}) = \sum_{n=1}^{\infty} B_{n,3}^{\mu} \cos[2\pi n \bar{x}_{s4}] \quad \text{even}$$

Crystal structure of TiOCl at room temperature



- *Pmmn* a = 3.78 b = 3.34 c = 8.03 Å
- Chains of Ti along **a** and along **b**
- Isostructural compounds: TiOCl, TiOBr, VOCl, FeOCl

H. Schäfer *et al.*, Z Anorg. Allg. Chem. **295**, 268 (1958)

Monoclinic twinned incommensurate structure of TiOCl

Incommensurately modulated below T_{c2} = 90 K	
Modulation wavevector	$\mathbf{q} = (0.07, 0.511, 0)$
Superspace group	$P2/n(\alpha\ \beta\ 0)\text{-}10$ (**c** unique)
	13.1.2.1 $P2/b(\alpha,\beta,0)00$
Modulation functions (i=1,2,3)	$u_i\,[t + \mathbf{q}\cdot\mathbf{x}^0]$
Structure refinement	R(main) = 0.018
	R(sat) = 0.080

Lock-in transition toward $\mathbf{q}$ = (0 1/2 0) below T_{c1} = 67 K

Atoms on twofold axes

S. van Smaalen *et al.*, PRB **72**, 020105(R) (2005)   A. Schönleber *et al.*, Phys. Rev. B **73**, 214410 (2006)

Superspace group P2/n(α β 0)-10

Origin-dependent translational components cannot be avoided.

$$\begin{aligned}
&(E,1): && (x_{s1} \quad x_{s2} \quad x_{s3} \quad x_{s4})\\
&(2,\bar{1}): && (-x_{s1} \quad -x_{s2} \quad x_{s3} \quad -x_{s4})\\
&(i,\bar{1}): && (1/2-x_{s1} \quad 1/2-x_{s2} \quad -x_{s3} \quad -x_{s4})\\
&(m,1): && (1/2+x_{s1} \quad 1/2+x_{s2} \quad -x_{s3} \quad x_{s4})
\end{aligned}$$

SSG(3+d)D 13.1.2.1 P2/b(α,β,0)00

Exercise: twofold rotation (2, -1) at the origin

$$\{R_s \,|\, \mathbf{v}_s\} \;=\; \{2^z, -1 \,|\, 0,0,0,0\}$$

$$\mathbf{q} = (\alpha, \beta, 0)$$

$$\left(2^z, \bar{1}\right): \quad (-x, -y, z, -t)$$

$$\left(2^z, \bar{1}\right) \;=\; \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

$$\left\{2^z, \bar{1} \,|\, 0, 0, 0, 0\right\}: \; (-x, -y, z, -t)$$

$$\begin{pmatrix} \bar{x}_{s1}(2) \\ \bar{x}_{s2}(2) \\ \bar{x}_{s3}(2) \end{pmatrix} = \begin{pmatrix} -\bar{x}_{s1}(1) \\ -\bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix}$$

$$\begin{pmatrix} u_1^2(\bar{x}_{s4}) \\ u_2^2(\bar{x}_{s4}) \\ u_3^2(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} -u_1^1(-\bar{x}_{s4}) \\ -u_2^1(-\bar{x}_{s4}) \\ u_3^1(-\bar{x}_{s4}) \end{pmatrix}$$

Restrictions on basic-structure coordinates by (2, -1)

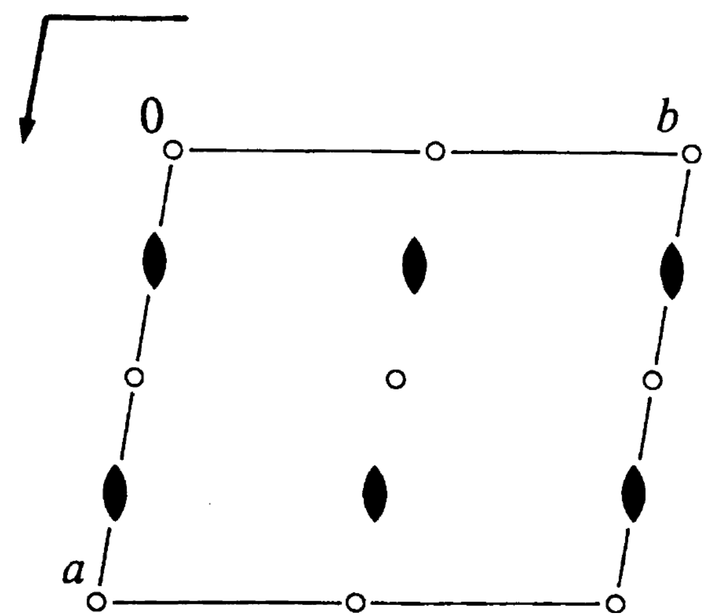
$$\begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix} = \begin{pmatrix} -\bar{x}_{s1}(1) \\ -\bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix}$$

$$\Rightarrow \quad \bar{x}_{s1}(1) = -\bar{x}_{s1}(1)$$

$$\Leftrightarrow \quad 2\bar{x}_{s1}(1) = 0 \quad (\mathrm{mod}\, 1)$$

$$\Leftrightarrow \quad \bar{x}_{s1} = 0 \quad \text{or} \quad 1/2$$

$$\begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 0 \\ 1/2 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 1/2 \\ 0 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 1/2 \\ 1/2 \\ \bar{x}_{s3} \end{pmatrix}$$



Four twofold axes in the unit cell

Modulation functions for an atom on (0, 0, x_3)

$$\begin{pmatrix} u_1^1(\bar{x}_{s4}) \\ u_2^1(\bar{x}_{s4}) \\ u_3^1(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} -u_1^1(-\bar{x}_{s4}) \\ -u_2^1(-\bar{x}_{s4}) \\ u_3^1(-\bar{x}_{s4}) \end{pmatrix}$$

$$u_1(\bar{x}_{s4}) = -u_1(-\bar{x}_{s4}) \quad \Rightarrow \quad u_1^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,1}^\mu \sin[2\pi n \bar{x}_{s4}] \quad \text{odd}$$

$$u_2(\bar{x}_{s4}) = -u_2(-\bar{x}_{s4}) \quad \Rightarrow \quad u_2^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,2}^\mu \sin[2\pi n \bar{x}_{s4}] \quad \text{odd}$$

$$u_3(\bar{x}_{s4}) = u_3(-\bar{x}_{s4}) \quad \Rightarrow \quad u_3^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} B_{n,3}^\mu \cos[2\pi n \bar{x}_{s4}] \quad \text{even}$$

Structural parameters for an atom on (0, 0, x_3)

$$\begin{pmatrix} x_1^0 \\ x_2^0 \\ x_3^0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ x_3^0 \end{pmatrix}$$

$$u_1^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,1}^\mu \sin[2\pi n \bar{x}_{s4}] \quad \text{odd}$$

$$u_2^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} A_{n,2}^\mu \sin[2\pi n \bar{x}_{s4}] \quad \text{odd}$$

$$u_3^\mu(\bar{x}_{s4}) = \sum_{n=1}^{\infty} B_{n,3}^\mu \cos[2\pi n \bar{x}_{s4}] \quad \text{even}$$

$$B_{n,1}^\mu = B_{n,2}^\mu = A_{n,3}^\mu = 0$$

$U^{11} \quad U^{22} \quad U^{33} \quad U^{12} \qquad U^{13} = U^{23} = 0$

The twofold rotation (2, -1) at (0, 0, 0, 1/4)

$$\{R_s \mid \mathbf{v}_s\} = \{2^z, -1 \mid 0,0,0,0.5\} \qquad \mathbf{q} = (\alpha, \beta, 0)$$

$$\left(2^z, \bar{1}\right): \quad (-x, -y, z, -t)$$

$$\left\{2^z, \bar{1} \mid 0, 0, 0, 0.5\right\}: \; (-x, -y, z, 0.5 - t)$$

$$\left(2^z, \bar{1}\right) = \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

$$\begin{pmatrix} \bar{x}_{s1}(2) \\ \bar{x}_{s2}(2) \\ \bar{x}_{s3}(2) \end{pmatrix} = \begin{pmatrix} -\bar{x}_{s1}(1) \\ -\bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix}$$

$$\begin{pmatrix} u_1^2(\bar{x}_{s4}) \\ u_2^2(\bar{x}_{s4}) \\ u_3^2(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} -u_1^1\left[-(\bar{x}_{s4} - 1/2)\right] \\ -u_2^1\left[-(\bar{x}_{s4} - 1/2)\right] \\ u_3^1\left[-(\bar{x}_{s4} - 1/2)\right] \end{pmatrix}$$

Restrictions on basic-structure coordinates by (2, -1) at (0, 0, 0, 1/4)

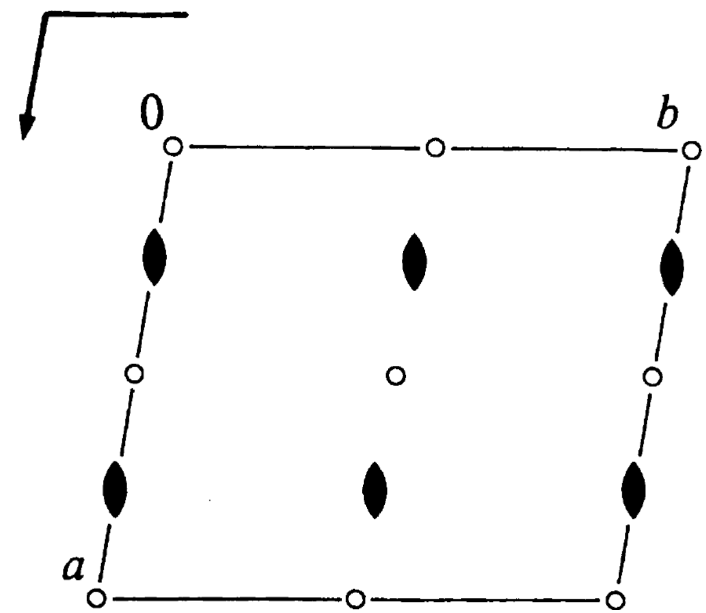
$$\begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix} = \begin{pmatrix} -\bar{x}_{s1}(1) \\ -\bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix}$$

$$\Rightarrow \quad \bar{x}_{s1}(1) = -\bar{x}_{s1}(1)$$

$$\Leftrightarrow \quad 2\bar{x}_{s1}(1) = 0 \quad (\text{mod } 1)$$

$$\Leftrightarrow \quad \bar{x}_{s1} = 0 \quad \text{or} \quad 1/2$$

$$\begin{pmatrix} \bar{x}_{s1}(1) \\ \bar{x}_{s2}(1) \\ \bar{x}_{s3}(1) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 0 \\ 1/2 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 1/2 \\ 0 \\ \bar{x}_{s3} \end{pmatrix} \quad \begin{pmatrix} 1/2 \\ 1/2 \\ \bar{x}_{s3} \end{pmatrix}$$



Restrictions on the basic-structure coordinates are the same as before

Modulation functions for an atom on (2,-1) at (0,0,0,1/4)

$$\begin{pmatrix} u_1^1(\bar{x}_{s4}) \\ u_2^1(\bar{x}_{s4}) \\ u_3^1(\bar{x}_{s4}) \end{pmatrix} = \begin{pmatrix} -u_1^1(1/2-\bar{x}_{s4}) \\ -u_2^1(1/2-\bar{x}_{s4}) \\ u_3^1(1/2-\bar{x}_{s4}) \end{pmatrix}$$

$$\Rightarrow \quad \begin{cases} u_1(\bar{x}_{s4}) = u_1(-\bar{x}_{s4}) & \text{odd harmonics} \quad \Rightarrow \quad \text{even function} \\ u_1(\bar{x}_{s4}) = -u_1(-\bar{x}_{s4}) & \text{even harmonics} \quad \Rightarrow \quad \text{odd function} \end{cases}$$

$$\Rightarrow \quad \begin{cases} u_3(\bar{x}_{s4}) = -u_3(-\bar{x}_{s4}) & \text{odd harmonics} \quad \Rightarrow \quad \text{odd function} \\ u_3(\bar{x}_{s4}) = u_3(-\bar{x}_{s4}) & \text{even harmonics} \quad \Rightarrow \quad \text{even function} \end{cases}$$

Symmetry restrictions *i* = 1 for odd harmonics

$$u_1^{\mu}(\bar{x}_{s4}) \;=\; -u_1^{\mu}(1/2 - \bar{x}_{s4}) \qquad u_1^{\mu}(\bar{x}_{s4}) \;=\; A_{1,1}^{\mu}\sin[2\pi\bar{x}_{s4}]$$

$$-A\sin[2\pi(1/2 - \bar{x}_{s4})] \;=\; A\sin[2\pi(\bar{x}_{s4} - 1/2)]$$

$$= -A\sin[2\pi\bar{x}_{s4}] \quad \equiv \quad A\sin[2\pi\bar{x}_{s4}]$$

$$\Rightarrow \quad A_{n,1}^{\mu} \;=\; 0 \quad (n = \text{odd})$$

$$-B\cos[2\pi(1/2 - \bar{x}_{s4})] \;=\; -B\cos[2\pi(\bar{x}_{s4} - 1/2)]$$

$$= B\cos[2\pi\bar{x}_{s4}] \quad \equiv \quad B\cos[2\pi\bar{x}_{s4}]$$

$$\Rightarrow \quad B_{n,1}^{\mu} \;\; \text{not restricted} \quad (n = \text{odd})$$

Symmetry restrictions i = 3 for odd harmonics

$$u_3^{\mu}(\bar{x}_{s4}) = u_3^{\mu}(1/2 - \bar{x}_{s4}) \qquad u_3^{\mu}(\bar{x}_{s4}) = A_{1,3}^{\mu} \sin[2\pi\bar{x}_{s4}]$$

$$A\sin[2\pi(1/2 - \bar{x}_{s4})] = -A\sin[2\pi(\bar{x}_{s4} - 1/2)]$$

$$= A\sin[2\pi\bar{x}_{s4}] \quad \equiv \quad A\sin[2\pi\bar{x}_{s4}]$$

$$\Rightarrow \quad A_{n,3}^{\mu} \text{ not restricted} \quad (n = \text{odd})$$

$$B\cos[2\pi(1/2 - \bar{x}_{s4})] = B\cos[2\pi(\bar{x}_{s4} - 1/2)]$$

$$= B\cos[2\pi\bar{x}_{s4}] \quad \equiv \quad B\cos[2\pi\bar{x}_{s4}]$$

$$\Rightarrow \quad B_{n,3}^{\mu} = 0 \quad (n = \text{odd})$$

Symmetry restrictions *i* = 1 for even harmonics

$$u_1^{\mu}(\bar{x}_{s4}) \;=\; -u_1^{\mu}(1/2-\bar{x}_{s4}) \qquad u_1^{\mu}(\bar{x}_{s4}) \;=\; A_{2,1}^{\mu}\sin[2\pi 2\bar{x}_{s4}]$$

$$-A\sin[2\pi 2(1/2-\bar{x}_{s4})] \;=\; A\sin[2\pi 2(\bar{x}_{s4}-1/2)]$$

$$=\; A\sin[2\pi(2\bar{x}_{s4}-1)] \;=\; A\sin[2\pi 2\bar{x}_{s4}] \quad\equiv\quad A\sin[2\pi 2\bar{x}_{s4}]$$

$$\Rightarrow \quad A_{n,1}^{\mu} \;\text{ not restricted } \quad (n=\text{even})$$

$$-B\cos[2\pi 2(1/2-\bar{x}_{s4})] \;=\; -B\cos[2\pi 2(\bar{x}_{s4}-1/2)]$$

$$=\; -B\cos[2\pi(2\bar{x}_{s4}-1)] = -B\cos[2\pi 2\bar{x}_{s4}] \quad\equiv\quad B\cos[2\pi 2\bar{x}_{s4}]$$

$$\Rightarrow \quad B_{n,1}^{\mu} = 0 \quad (n=\text{even})$$

Symmetry restrictions *i* = 3 for even harmonics

$$u_3^{\mu}(\bar{x}_{s4}) \;=\; u_3^{\mu}(1/2 - \bar{x}_{s4}) \qquad\qquad u_3^{\mu}(\bar{x}_{s4}) \;=\; A_{2,3}^{\mu}\,\sin[2\pi 2\bar{x}_{s4}]$$

$$A\sin[2\pi 2(1/2 - \bar{x}_{s4})] \;=\; -A\sin[2\pi 2(\bar{x}_{s4} - 1/2)]$$

$$=\; -A\sin[2\pi(2\bar{x}_{s4} - 1)] \;=\; -A\sin[2\pi 2\bar{x}_{s4}] \quad\equiv\quad A\sin[2\pi 2\bar{x}_{s4}]$$

$$\Rightarrow \quad A_{n,3}^{\mu} \;=\; 0 \quad (n = \text{even})$$

$$B\cos[2\pi 2(1/2 - \bar{x}_{s4})] \;=\; B\cos[2\pi 2(\bar{x}_{s4} - 1/2)]$$

$$=\; B\cos[2\pi(2\bar{x}_{s4} - 1)] \;=\; B\cos[2\pi 2\bar{x}_{s4}] \quad\equiv\quad B\cos[2\pi 2\bar{x}_{s4}]$$

$$\Rightarrow \quad B_{n,3}^{\mu} \;\; \text{not restricted} \quad (n = \text{even})$$

Special positions on (2, -1)—two origins

$$\left(-x,-y,z,-t\right)$$

$$\begin{pmatrix} x_1^0 \\ x_2^0 \\ x_3^0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ x_3^0 \end{pmatrix}$$

$$A_{n,1}^{\mu} \quad A_{n,2}^{\mu} \quad B_{n,3}^{\mu}$$

$$B_{n,1}^{\mu} = B_{n,2}^{\mu} = A_{n,3}^{\mu} = 0$$

$$U^{11} \quad U^{22} \quad U^{33} \quad U^{12}$$

$$U^{13} = U^{23} = 0$$

$$\left(-x,-y,z,0.5-t\right)$$

$$\begin{pmatrix} x_1^0 \\ x_2^0 \\ x_3^0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ x_3^0 \end{pmatrix}$$

$$n = \text{odd}: \quad B_{n,1}^{\mu} \quad B_{n,2}^{\mu} \quad A_{n,3}^{\mu}$$

$$A_{n,1}^{\mu} = A_{n,2}^{\mu} = B_{n,3}^{\mu} = 0$$

$$n = \text{even}: \quad A_{n,1}^{\mu} \quad A_{n,2}^{\mu} \quad B_{n,3}^{\mu}$$

$$B_{n,1}^{\mu} = B_{n,2}^{\mu} = A_{n,3}^{\mu} = 0$$

Conclusions

(3+*d*)D Superspace groups provide

- Restrictions on the basic-structure coordinates
- Restrictions on the shapes and phases of the modulation functions
- Mathematical form of functions depends on origin

Reduction of the independent parameters makes structure refinements possible