Applications of X-ray and Neutron Scattering in Biological Sciences:

Symmetry in direct and reciprocal space
2012

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Biostructural Research
Mirror plane symmetry

Mirrorplane
Symmetry elements: **rotation**

Figure 3.11. A two-dimensional lattice with 3-fold symmetry axes perpendicular to the plane of the figure.
Biomolecules display rotational symmetry

- Protein from virus shell display 2-fold symmetry
Symmetry Elements

Translation

moves all the points in the asymmetric unit the same distance in the same direction. This has no effect on the handedness of figures in the plane. There are no invariant points (points that map onto themselves) under a translation.
Rotational and translational symmetry
Screw axis

120° rotation
1/3 unit cell translation

Figure 3.20. Screw axis $3_1$. 
A virus has a high symmetry
Point groups

- All symmetry operations associated with a molecule forms a point group. This group completely describes the symmetry of the molecule.
- Some point groups only contain rotations: These are called $C_2$, $C_3$ etc.
- Molecules with a principal symmetry axis of order $n$ and $n$ orthogonal to-fold symmetry axis’s belong to the D point groups ($D_2$ etc.)
- Higher symmetries are octahedral and icosahedral.

Cyclobutan is $D_4$. 
Point group symmetry diagrams

Figure 3.18. (a) Crystal with symmetry $mmm$. (b) Set of points related by symmetry $mmm$. (c) Plane representation of symmetry $mmm$. 
There are a total of 32 point groups

Figure 3.19. Plane representations of the 32 point groups.
N-fold axes with $n=5$ or $n>6$ does not occur in crystals

Adjacent spaces must be completely filled (no gaps, no overlaps).
Asymmetric unit

- Any symmetric object can be reduced to an asymmetric unit
- We can use symmetry operations to build up a lattice motif: E.g. a 2-fold axis

Asymmetric unit

Symbol for 2-folds axis
Crystals

- The crystal is built by translating the lattice motif in all 3 spatial directions.
- The crystal is a lattice. The parallelopiped that defines the lattice unit is called the unit cell.

![Unit cell and Asymmetric unit illustration]
Bravais-lattices

- Lattices has to fill all space. There are 14 Bravais lattices
- Some are centered
Bravais-lattices II

- The unit cell form restricts which symmetry operations can be used in the unit cell
- Triclinic: Only inversion center (combination of 2-fold and mirror plane)
- Monoclinic: Only 2-fold axis
- Orthorhombic: 3 mutually orthogonal 2-fold axes
- Tetragonal: 4-fold axis
- Hexagonal: 3/6 fold axis’s
- Cubic: 3 and 4-folds
Crystal systems

- Bravais lattices are grouped in crystal systems
Space groups

- If you combine the 13 Bravais lattices with the possible rotations (2, 3, 4, 6-fold rotation) including screw axis’s 2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5) and mirror planes you get 230 space groups.
### 230 space groups

#### Triclinic

<table>
<thead>
<tr>
<th>P 1</th>
<th>P -1</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2</td>
<td>P 21</td>
</tr>
<tr>
<td>P 2/C</td>
<td>P 21/C</td>
</tr>
</tbody>
</table>

#### Monoclinic

<table>
<thead>
<tr>
<th>P 2</th>
<th>P 21</th>
<th>C 2</th>
<th>P M</th>
<th>C 2/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2/C</td>
<td>P 21/C</td>
<td>C 2/C</td>
<td>P M</td>
<td>P C</td>
</tr>
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#### Orthorhombic

<table>
<thead>
<tr>
<th>P 2</th>
<th>P 21</th>
<th>C 2</th>
<th>P M</th>
<th>P C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2/C</td>
<td>P 21/C</td>
<td>C 2/C</td>
<td>P M</td>
<td>P C</td>
</tr>
</tbody>
</table>

#### Tetragonal

<table>
<thead>
<tr>
<th>P 4</th>
<th>P 41</th>
<th>P 42</th>
<th>P 43</th>
<th>I 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 4/N</td>
<td>P 42/N</td>
<td>P 42/M</td>
<td>P 42/C</td>
<td>P 42/D</td>
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</tbody>
</table>

#### Trigonal

<table>
<thead>
<tr>
<th>P 3</th>
<th>P 31</th>
<th>P 32</th>
<th>B 3</th>
<th>P -3</th>
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<tr>
<td>P 3</td>
<td>P 31</td>
<td>P 32</td>
<td>P 31</td>
<td>P 31</td>
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</tbody>
</table>

#### Hexagonal

<table>
<thead>
<tr>
<th>P 6</th>
<th>P 61</th>
<th>P 65</th>
<th>P 62</th>
<th>P 64</th>
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</thead>
<tbody>
<tr>
<td>P 6</td>
<td>P 61</td>
<td>P 62</td>
<td>P 63</td>
<td>P 64</td>
</tr>
</tbody>
</table>

#### Cubic (minus sign in front of triade optional)

<table>
<thead>
<tr>
<th>P 23</th>
<th>P 3</th>
<th>P 21</th>
<th>I 23</th>
<th>P 213</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 3</td>
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<td>P 3</td>
<td>P 3</td>
<td>P 3</td>
</tr>
</tbody>
</table>

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Chiral space groups

- Mirror planes and centers of inversion change the handedness of molecules
- Chiral molecules (like proteins) cannot crystallize in space groups with such symmetry
65 chiral space groups

Triklin
P 1
Monoklin
P 2       P 21
Orthorhombisk
P 2 2 2    P 2 2 21    P 21 2 1 2    P 21 2 1 21    C 2 2 2 1
C 2 2 2    F 2 2 2    I 2 2 2    I 21 2 1 21
Tetragonal
P 4        P 41
I 41
P 4 2 2
P 4 21 2   P 41 2 2   P 41 2 1 2   P 42 2 2   P 42 21 2
P 43 2 2   I 4 2 2    I 41 2 2
Trigonal
P 3        P 31
P 3 1 2    P 3 2 1    P 31 1 2    P 31 2 1
P 32 1 2   P 32 2 1    R 3 2
Hexagonal
P 6        P 61
P 63
P 6 2 2
P 61 2 2   P 65 2 2   P 62 2 2   P 64 2 2   P 63 2 2
Kubisk
P 2 3      F 2 3
P 4 3 2    P 42 3 2    F 4 3 2
F 41 3 2   I 4 3 2    P 43 3 2    P 41 3 2    I 41 3 2
Coordinate triplets, equivalent positions

Figure 3.15. This crystal has a 2-fold axis along c. The point P with coordinate triplet \(x, y, z\), is related by the symmetry operation to point \(P'\) with coordinate triplet \(-x, -y, z\).

\[ r = ax + by + cz, \]

Therefore, each point can be described by its fractional coordinates, that is, by its coordinate triplet \((x, y, z)\).
A diagram from International Table of Crystallography

$P2_12_12_1$  $P 2_1 2_1 2_1$  222  No. 19

1. $x, y, z$
2. $\frac{1}{2} + x, \bar{y}, \frac{1}{2} - z$
3. $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$
4. $\bar{x}, \frac{1}{2} - y, \frac{1}{2} + z$
Identification of the Space Group is called indexing the crystal. The International Tables for X-ray Crystallography tell us a huge amount of information about any given space group. For instance, if we look up space group P2, we find it has a 2-fold rotation axis and the following symmetry equivalent positions:

\[
\begin{align*}
X & , \ Y & , \ Z \\
-X & , \ Y & , \ -Z 
\end{align*}
\]

and an asymmetric unit defined by:

\[
0 \leq x \leq 1 \\
0 \leq y \leq 1 \\
0 \leq z \leq 1/2
\]

An interactive tutorial on Space Groups can be found on-line in Bernhard Rupp’s Crystallography 101 Course: http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm
Rotation matrices and translation vectors

\[ \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2} \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z + \frac{1}{2} \end{pmatrix} \]

\[ \mathbf{R} \cdot \mathbf{x} + \mathbf{t} = \mathbf{x}' \]

Two equivalent positions \((x \ y \ z)\) and \((-x \ -y \ z+\frac{1}{2})\) are related by a rotation matrix \(\mathbf{R}\) and a translation matrix \(\mathbf{t}\).
Space group P1

Point group 1 + Bravais lattice P1

Figure 3.23. P1, equivalent positions x, y, z.
Space group $P\bar{1}$

Figure 3.24. $P\bar{1}$, equivalent positions 
(1) $x, y, z$; (2) $\bar{x}, \bar{y}, \bar{z}$.

Point group $1\bar{1}$ + Bravais lattice $P\bar{1}$
Space group P2

Figure 3.25. $P_2$, equivalent positions
(1) $x, y, z$; (2) $\bar{x}, y, \bar{z}$.

Point group 2 + Bravais lattice “primitive monoclinic”
Space group $P2_1$

Figure 3.26. $P2_1$, equivalent positions
(1) $x, y, z$; (2) $\bar{x}, y + \frac{1}{2}, z$.

Point group 2 + Bravais lattice “primitive monoclinic”, but consider screw axis
BPTI example from Livermore lab III
The diffraction pattern also forms a lattice

Most contemporary x-ray data collection used the rotation geometry, in which the crystal makes a simple rotation of a degree or so while the image is being collected. The geometry of the diffraction pattern is less obvious than for a precession photograph, although data collection is more efficient.

**Oscillation (rotation) photograph.**
The diffraction pattern forms a lattice that is related to the crystal lattice. The lattice of diffracted x-rays is very obvious in a precession photograph (a camera geometry that used to be popular).

Indexing is the process of assigning hkl indices to the reflections. In a precession photograph this is done by counting out from the direct beam position.

The geometry of diffraction is like reflection from the Miller planes.

This reflection has indices h=10, k=7, l=0. Its intensity is \( I_{(10,7,0)} = |F_{(10,7,0)}|^2 \).
Structure factor expression

The structure factor $F(h)$ can be written as below:

$$F(h) = \sum_{i=1}^{N} f_i(|h|) e^{2\pi i h r_i}$$

Here $h$ is the scattering vector

$$h = ha^* + kb^* + lc^*$$

where $a^*$, $b^*$ and $c^*$ are the reciprocal lattice vectors, $f_i(|h|)$ is the atomic scattering factor and $r_i$ is the coordinate vector of the $i$'th atom

$$r_i = x_i a + y_i b + z_i c$$

and $a$, $b$ and $c$ are the direct lattice vectors.
Intensity of reflections

The intensity of the scattered wave is proportional to the square of the structure factor

\[ I(h) \propto F(h)^2 = \left( \sum_{i=1}^{N} f_i(|h|)e^{2\pi i h r_i} \right) \left( \sum_{i=1}^{N} f_i(|h|)e^{-2\pi i h r_i} \right) \]
Friedels law

\[ I(h) \propto F(h)^2 = (\sum_{i=1}^{N} f_i(|h|)e^{2\pi i hr_i})(\sum_{i=1}^{N} f_i(|h|)e^{-2\pi i hr_i}) \]

From the intensity equation it can be seen

\[ I(h, k, l) = I(-h, -k, -l) \]

Thus in the absence of anomalous scatterers (heavy atoms) the intensity weighted reciprocal lattice is always centrosymmetric. This is referred to as Friedels law.
Rotational symmetry

If the space group of the crystal is P2 then the following symmetry operators are present

\[ x, y, z \text{ and } -x, y, -z \]

The structure factor for the reflection with indices \( h,k,l \) can then be written

\[
F(h, k, l) = \sum_{i=1}^{N/2} f_i(|h|) (e^{2\pi i (hx_i + ky_i + lz_i)} + e^{2\pi i (-hx_i + ky_i - lz_i)})
\]
Hypothesis

Symmetry in real space will also introduce symmetry in the intensity weighted reciprocal lattice

• True for the space group P2_1?
True

The expression for the \(-h, k, -l\) reflection

\[
F(-h, k, -l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\mathbf{h}|)(e^{2\pi i(-hx_i+ky_i-lz_i)} + e^{2\pi i(hx_i+ky_i+lz_i)})
\]

is seen to be identical to the expression for the \(h, k, l\) reflection

\[
F(h, k, l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\mathbf{h}|)(e^{2\pi i(hx_i+ky_i+lz_i)} + e^{2\pi i(-hx_i+ky_i-lz_i)})
\]

Consequently two-fold symmetry in direct space also imposes two-fold symmetry in reciprocal space. Thus in space group P2 the following relations hold

\[
I(h, k, l) = I(-h, k, -l) = I(-h, -k, -l) = I(h, -k, l)
\]

\(\text{i.e. only one fourth of the possible reflections are unique.}\)
Screw axis symmetry

Space group P2$_1$ has the following equivalent positions

\[ x, y, z \text{ and } -x, y + \frac{1}{2}, -z \]

\[
F(h, k, l) = \sum_{i=1}^{N/2} f_i(|h|) \left( e^{2\pi i(hx_i+ky_i+lz_i)} + e^{2\pi i(-hx_i+k(y_i+1/2)-lz_i)} \right)
\]

\[
= \sum_{i=1}^{N/2} f_i(|h|) \left( e^{2\pi i(hx_i+ky_i+lz_i)} + e^{\pi k} e^{2\pi i(-hx_i+ky_i-lz_i)} \right)
\]

\[
F(-h, k, -l) = \sum_{i=1}^{N/2} f_i(|h|) \left( e^{2\pi i(-hx_i+ky_i-lz_i)} + e^{2\pi i(hx_i+k(y_i+1/2)+lz_i)} \right)
\]

\[
= \sum_{i=1}^{N/2} f_i(|h|) \left( e^{2\pi i(-hx_i+ky_i-lz_i)} + e^{\pi k} e^{2\pi i(hx_i+ky_i+lz_i)} \right)
\]
Screw axis

If $k$ even then $e^{\pi k} = 1$ then

$$F(h, k, l) = F(-h, k, -l)$$

As for the P2 case

If $k$ odd then $e^{\pi k} = -1$ then

$$F(h, k, l) = \sum_{i=1}^{\frac{N}{2}} f_i(|h|) (e^{2\pi i (hx_i + ky_i + lz_i)} - e^{2\pi i (-hx_i + ky_i - lz_i)})$$

$$F(-h, k, -l) = \sum_{i=1}^{\frac{N}{2}} f_i(|h|) (e^{2\pi i (-hx_i + ky_i - lz_i)} - e^{2\pi i (hx_i + ky_i + lz_i)})$$

$$= -F(h, k, l)$$

And in general for all $k$ and for P2$_1$

$$I(h, k, l) = I(-h, k, -l)$$
Rotational/screw axis in reciprocal space

So generalizing:
- All rotational symmetry is conserved in reciprocal space
- Centrosymmetry is induced
- Screw axis induce the same symmetry as the corresponding rotational axis.
The combination of rotational symmetry and a center of inversion can give rise to mirror plane symmetry in the diffraction pattern.

hk0 layer of the reciprocal lattice

Identify symmetry elements!
Systematic extinctions

Look again at the structure factor expression in $P2_1$

$$F(h, k, l) = \sum_{i=1}^{N/2} f_i(|h|)(e^{2\pi i(hx_i+ky_i+lz_i)} + e^{2\pi i(-hx_i+k(y_i+1/2)-lz_i)})$$

When looking at reflections of type $0k0$

$$F(0, k, 0) = \sum_{i=1}^{N/2} f_i(|h|)(e^{2\pi iky_i} + e^{\pi ik}e^{2\pi iky_i})$$

If $k$ even

$$F(0, k, 0) = \sum_{i=1}^{N/2} f_i(|h|)(e^{2\pi iky_i} + e^{2\pi iky_i})$$

$$= 2\sum_{i=1}^{N/2} f_i(|h|)e^{2\pi iky_i}$$
Systematic extinctions

If \( k \) odd

\[
F(0, k, 0) = \sum_{i=1}^{N/2} f_i(|h|)(e^{2\pi i k y_i} - e^{2\pi i k y_i}) = 0
\]

So the presence of a 2-fold screw axis along the b axis will implicate that the reflections of class 0,k,0 will have those with odd \( k \) systematically extinct.
Systematic absences

This SAED pattern of Ta$_2$P shows mm-, but not 4-fold symmetry as seen from the intensities of diffraction spots. Notice that all odd reflections along both the h and k axes are absent. This shows there must be 2$_1$ screw axes along and/or glide planes perpendicular to both axes.
The symmetry of the lattice belongs to a laue class

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Point Group</th>
<th>Laue Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2</td>
<td>2/m</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>222</td>
<td>mmm</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4</td>
<td>4/m</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>4/mmm</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3</td>
<td>-3</td>
</tr>
<tr>
<td></td>
<td>32 (312 and 321)</td>
<td>-3m</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6</td>
<td>6/m</td>
</tr>
<tr>
<td></td>
<td>622</td>
<td>6/mmm</td>
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<td>Cubic</td>
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<td></td>
<td>432</td>
<td>m-3m</td>
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</table>
Systematic extinctions give information on centerings, glide plans and screw axis

<table>
<thead>
<tr>
<th>Symmetry Element</th>
<th>Types</th>
<th>Reflection Condition</th>
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<tbody>
<tr>
<td>A centered</td>
<td>hkl</td>
<td>k + l = 2n</td>
</tr>
<tr>
<td>B centered</td>
<td>h + l = 2n</td>
<td></td>
</tr>
<tr>
<td>C centered</td>
<td>h + k = 2n</td>
<td></td>
</tr>
<tr>
<td>F centered</td>
<td>k + l = 2n, h + l = 2n, h + k = 2n</td>
<td></td>
</tr>
<tr>
<td>I centered</td>
<td>h + k + l = 2n</td>
<td></td>
</tr>
<tr>
<td>R (obverse)</td>
<td>-h + k + l = 3n</td>
<td></td>
</tr>
<tr>
<td>R (reverse)</td>
<td>h - k + l = 3n</td>
<td></td>
</tr>
<tr>
<td>Glide reflecting in a</td>
<td>hkl</td>
<td>k = 2n</td>
</tr>
<tr>
<td>b glide</td>
<td>i = 2n</td>
<td></td>
</tr>
<tr>
<td>c glide</td>
<td>k + l = 2n</td>
<td></td>
</tr>
<tr>
<td>n glide</td>
<td>k + i = 2n</td>
<td></td>
</tr>
<tr>
<td>d glide</td>
<td>k + l = 4n</td>
<td></td>
</tr>
<tr>
<td>Glide reflecting in b</td>
<td>h0l</td>
<td>h = 2n</td>
</tr>
<tr>
<td>a glide</td>
<td>i = 2n</td>
<td></td>
</tr>
<tr>
<td>c glide</td>
<td>k = 2n</td>
<td></td>
</tr>
<tr>
<td>n glide</td>
<td>k + i = 2n</td>
<td></td>
</tr>
<tr>
<td>d glide</td>
<td>h + l = 2n</td>
<td></td>
</tr>
<tr>
<td>Glide reflecting in c</td>
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<td>k = 2n</td>
</tr>
<tr>
<td>b glide</td>
<td>h = 2n</td>
<td></td>
</tr>
<tr>
<td>a glide</td>
<td>k = 2n</td>
<td></td>
</tr>
<tr>
<td>n glide</td>
<td>k + h = 2n</td>
<td></td>
</tr>
<tr>
<td>d glide</td>
<td>k + h = 4n</td>
<td></td>
</tr>
<tr>
<td>Glide reflecting in (110)</td>
<td>hhl</td>
<td>h = 2n</td>
</tr>
<tr>
<td>b glide</td>
<td>h + l = 2n</td>
<td></td>
</tr>
<tr>
<td>n glide</td>
<td>h + k + l = 4n</td>
<td></td>
</tr>
<tr>
<td>Screw</td>
<td></td>
<td>[100]</td>
</tr>
<tr>
<td>2i, 4i</td>
<td>h = 4n</td>
<td></td>
</tr>
<tr>
<td>4i, 6i</td>
<td></td>
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</tr>
<tr>
<td>Screw</td>
<td></td>
<td>[010]</td>
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<tr>
<td>2i, 4i</td>
<td>k = 4n</td>
<td></td>
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<tr>
<td>4i, 6i</td>
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<tr>
<td>Screw</td>
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<td>[001]</td>
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<td>2i, 4i, 6i</td>
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<td></td>
</tr>
<tr>
<td>4i, 4i, 4i</td>
<td>l = 4n</td>
<td></td>
</tr>
<tr>
<td>6i, 6i</td>
<td>l = 6n</td>
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</tr>
<tr>
<td>Screw</td>
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<td>[110]</td>
</tr>
<tr>
<td>2i</td>
<td></td>
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</table>

Copenhagen February 8
Dias 48