Symmetry of the X Ray Diffraction Pattern

• Considering a set of lattice plan (hkl), both r.l. point hkl and -h-k-l lie on the normal to the plane through the origin, but in opposite directions. The single plane through the origin of the set hkl is associated with r.l. points hkl and -h-k-l.

• Reflection hkl in position to reflect and reflection -h-k-l in a similar position correspond to reflection from opposite side of the set of planes hkl so that:

\[ I(h,k,l) = I(-h, -k, -l) \]
Symmetry of the X Ray Diffraction Pattern

- A diffraction pattern possesses at least the same or higher symmetry than the crystal.

- All diffraction patterns have a center of symmetry:
  \[ I(h,k,l) = I(-h, -k, -l) \]

These two reflections are called a Friedel pair.

- From diffraction intensity, we should be able to determine space group symmetry in most cases (symmetry of diffraction pattern, systematic absences).
Friedel’s Law

Friedel’s Law can be explained in terms of reflection from opposite sides of the same set of planes, that is:

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

Friedel’s Law can be derived as well from the expression of the Structure Factor, considering \( \hat{F}(hkl) \) as a complex number.

\[ F_{hkl} = A_{hkl} + iB_{hkl} \]
Friedel’s Law

A given complex number can equally be represented by polar coordinates, its magnitude and phase (r and α), with the following relationships between them:

\[ a + ib = f[\cos(\alpha) + i \sin(\alpha)] \]

\[ F(hkl) = A(hkl) + i B(hkl) \]

\[ |F_H| = (A^2 + B^2)^{1/2} \]

\[ r = \left( a^2 + b^2 \right)^{1/2} \]

\[ \alpha = \tan^{-1}(b/a) \]
Friedel’s Law

\[ F(\text{hkl}) = A(\text{hkl}) + i \cdot B(\text{hkl}), \quad |F_{\text{H}}| = (A^2 + B^2)^{1/2} \]

\[ A = \sum f_j \cos \phi_j = \sum f_j \cos (hx_j + ky_j + lz_j) \]

\[ B = \sum f_j \sin \phi_j = \sum f_j \sin (hx_j + ky_j + lz_j) \]

\[ \tan \phi = \frac{B}{A} \]

\( \phi_j \) phase angles from each single atom diffraction

\[ A_{\text{hkl}} = A_{\overline{\text{hkl}}} \quad B_{\text{hkl}} = -B_{\overline{\text{hkl}}} \]

\[ I = |F_{\text{H}}|^2 = (A^2 + B^2) \]

\[ I_{\text{hkl}} = I_{\overline{\text{hkl}}} \]
Friedel’s Law

For a centrosymmetric crystal, the Structure Factor is a real number

If 2N atoms are in the unit cell, they will be distributed in N couple of identical atom in the position $x_j, y_j, z_j$ and $-x_j, -y_j, -z_j$;

The contribution of each atom to the structure factor is a real number. Therefore the structure factor is a real number

$$|F_{hkl}| = |F_{hkl}|$$

$$\alpha_{hkl} = -\alpha_{hkl}$$
Friedel’s Law

Therefore $F_{hkl}$ and $F_{-h-k-l}$.

Numbers that are complex conjugate have the same module and opposite phases:

$F^*_{hkl} = F_{hkl}$

$|F_{hkl}| = |F_{\overline{hkl}}|$

“The diffraction pattern shows an inversion centre even when the crystal is not centrosymmetric”.
Friedel’s Law

When Friedel’s law holds (there are some exceptions), the intensity of half of the reciprocal lattice is provided by the other half, thus we only need to collect a hemisphere of the reciprocal lattice points within the limiting sphere.

triclinic hemisphere

\[ I(hkl) \equiv I(-h-k-l) \]

monoclinic quadrant

\[
\begin{align*}
I(hkl) &\equiv I(-h-k-l) \equiv I(-hk-l) \equiv I(h-kl) \\
I(-hkl) &\equiv I(h-k-l) \equiv I(hk-l) \equiv I(-h-kl) \\
\text{But:} & \ I(hkl) \neq I(-hkl)
\end{align*}
\]

orthorhombic octant

\[
\begin{align*}
I(hkl) &\equiv I(-hkl) \equiv I(h-kl) \equiv I(hk-l) \\
&\equiv I(-h-kl) \equiv I(-hk-l) \equiv I(h-k-l) \equiv I(-h-k-l)
\end{align*}
\]
From Diffraction to Electron Density Map

-The Structure Factor can also be seen as the addition of all waves deriving from the contribution of all the infinite small element of electron density within the unit cell.

-Considering all the electrons in an element of volume $dV$ equal to $\rho(xyz)dV$, the emitted wave from this element:

$$\rho(xyz)e^{2\pi i(hx + ky + lz)}$$

The resultant on all volume is

$$\hat{F}(hkl) = \int_v \rho(xyz)e^{2\pi i(hx + ky + lz)} \, dV$$
From Diffraction to Electron Density Map

\[ F(hkl) = \int_v \rho(xyz) e^{2\pi i(hx + ky + lz)} \, dV \]

This equation is an example of Fourier transform, that is the Structure Factor is the Fourier transform of the electron density

Therefore, to calculate the electron density:

\[ \rho(xyz) = \int_H F(hkl) e^{-2\pi i(hx + ky + lz)} \, dH \]

Since \( h, k, e, l \) are integer numbers:

\[ \rho(x, y, z) = \frac{1}{V_{\text{unit cell}}} \sum\sum\sum F(hkl) e^{-2\pi i(hx+ky+lz)} \]
From Diffraction to Electron Density Map

\[ \rho(xyz) = V^{-1} \sum \sum \sum |F_{hkl}| \exp[-2\pi i (hx + Ky + lz - \alpha_{hkl})] \]

- Square root of reflection intensity
- Phase angle of reflection
Structural Solution: the phase problem

\[ \rho(x, y, z) = \frac{1}{V_{\text{unit cell}}} \sum \sum \sum \vec{F}(hkl) e^{-2\pi i(hx+ky+lz)} \]

\[ \vec{F}(hkl) = |F_{hkl}| e^{i\Phi_{hkl}} \]

\[ \rho(x, y, z) = \frac{1}{V_{\text{unit cell}}} \sum \sum |F_{hkl}| e^{-2\pi i(hx+ky+lz - \Phi_{hkl})} \]

Wave phase: for each wave we know the magnitude but not the direction

Phases are necessary to build up the electron density map.

They are not measured.

Therefore we can calculate the magnitude of the electron density but we don’t know where it is in the unit cell.
Structural Solution: the Patterson Function

We can get the relative (not absolute) positions of atoms with respect to each other from a Patterson Map

Patterson Function: function of differences between atomic coordinates

If we consider 2 atoms in the crystal:

\[ r_1 = (x_1, y_1, z_1) \text{ and } r_2 = (x_2, y_2, z_2) \]

The coordinates of the general vector between them:

\[ \Delta r = (r_2 - r_1) = (u, v, w), u = (x_2 - x_1), v = (y_2 - y_1), w = (z_2 - z_1), \]
The Patterson function is:

\[ P(u,v,w) \sim \sum \sum \sum F^2(hkl) e^{-2\pi i(hu + kv + lw)} \]

The Patterson function does not depend on phases but only on square of the structure factors amplitude and can be calculated from the experimental data.

The Patterson function can be visualized in a tridimensional map in the interatomic vectors space of the crystal (u,v,w)
Structural Solution: the Patterson Map

A peak in the Patterson Map at \((U, V, W)\) gives two information:

- In the structure there are two atoms at a distance equal to \((U, V, W)\) from the origin \((0,0,0)\).

- The segment between two atoms is oriented in the unit cell as the segment linking the origin of the map and the point \((U, V, W)\).

Therefore the vector \((U, V, W)\) corresponds to an interatomic distance in the real space.
Using observed amplitudes, but setting all phases to 0 creates a centro-symmetric image of the molecule.
The Patterson Function of a crystal, formed by N atoms in the unit cell, will show $N^2$ maxima (all possible interatomic vectors), and even discounting the vectors of each atom with itself, this number is $N^2-N$.

Considering the $i$ atom with atomic number $Z_i$ and the $j$ atom with $Z_j$, the corresponding vector $r_{ij}$ will show a height of the peak proportional the $Z_iZ_j$ of the two atoms.
The Patterson Map shows the intermolecular vectors

In particular:

\[ H \approx m Z_i Z_j \]

The origin peak (its height is \( H_{000} = \sum Z_i^2 \)) is usually arbitrarily scaled to 999. That means the height of the other peaks is scaled to:

\[ H = 999 \frac{m Z_i Z_j}{\sum Z_i^2} \]

The sum is over all atoms in the unit cell.

The Patterson function is centro-symmetric
from Patterson Map (obtained using Patterson function) is possible to calculate the heavy atom coordinates

from heavy atom coordinates is possible to calculate:

\[ F_{hkl}^{\text{calc}} \rightarrow \phi_{hkl}(\text{approx}) \] and then \[ \rho_{\text{approx}}(xyz) \]

The position of new atoms are used to obtain new \[ F_{hkl}^{\text{calc}} \] and then new \[ \phi_{hkl}(\text{approx}) \]

continuing the process all atomic positions will be found
Structural Solution: the Patterson Function

- In P-1 the symmetry equivalent position are:

\[(u \ v \ w) = (u \ v \ w)\]

- There will always be vectors in the Patterson from an atom to its equivalent, at positions:

\[(u \ v \ w) - (u \ v \ w) = (2u \ 2v \ 2w)\]

- If we see a Patterson peak at: \((2u_1 \ 2v_1 \ 2w_1)\)

- Then there must be an atom at:

\[\left(\frac{2u_1}{2} \ \frac{2v_1}{2} \ \frac{2w_1}{2}\right) = (u_1v_1w_1)\]
The Patterson Map shows the intermolecular vectors

One Heavy Atom in P-1

For every atom at \( x, y, z \) there is a symmetry equivalent atom at \(-x, -y, -z\) and hence a Patterson peak at \( 2x, 2y, 2z \).

Example

Two gold atoms are related by the inversion center. Besides the peak on the origin (height 999) there is a peak with height 374 at
\[ u = 0.318 = 2x, \ v = 0.471 = 2y, \ w = 0.532 = 2z \]

To calculate the positions \( x, y, z \) of the gold atom in the unit cell, we can divide each of the Patterson coordinates by 2.

Thus: \( x = 0.318/2 = 0.159 \) or \( 1.318/2 = 0.659 \) \( y = 0.471/2 = 0.236 \) or \( 1.471/2 = 0.736 \) \( z = 0.532/2 = 0.266 \) or \( 1.532/2 = 0.766 \)
The Patterson Map shows the intermolecular vectors

The space group in the Patterson Map can be derived from the crystal one, adding the center of symmetry and subtracting the symmetries related to translation.

Example: \( P2_1 \)

\[
P2_1 \quad (x, y, z) \quad (-x, 1/2+y, -z)
\]

\[
Patterson(x, y, z) \quad (-x, y, -z) \quad (-x, -y, -z) \quad (x, -y, z)
\]
Solve the Patterson function means to derive the atomic positions (coordinates) in the crystal (of the heavy atom usual) from the coordinates of the maximum peaks in the Patterson Map.

Some positions (lines or planes) in the Patterson Map contain information of interatomic vectors between equivalent atoms: special positions.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Equivalent atomic positions in the crystal</th>
<th>Patterson vectors (crystal coordinate differences)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Pm )</td>
<td>((x, y, z) ) ((x, -y, -z))</td>
<td>(&lt;0, 2y, 0&gt;)</td>
</tr>
<tr>
<td></td>
<td>( P2_1 ) ((x, y, z) ) ((-x, 1/2+y, -z))</td>
<td>(&lt;2x, 1/2, 2z&gt;) Harker planes</td>
</tr>
</tbody>
</table>
**Patterson Map: Examples**

$\text{Zn(CN)}_2.\text{DMP (DMP} = \text{dimethyl-phenanthroline).}$  
Space Group $P2_1/c$, $Z = 4$

**Most relevant Patterson Map peaks:**

<table>
<thead>
<tr>
<th>#</th>
<th>$u$</th>
<th>$v$</th>
<th>$w$</th>
<th>Relative value of Patterson Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>999</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.50</td>
<td>0.45</td>
<td>342</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.05</td>
<td>0.50</td>
<td>337</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>0.45</td>
<td>0.95</td>
<td>137</td>
</tr>
<tr>
<td>5</td>
<td>0.26</td>
<td>0.92</td>
<td>0.14</td>
<td>129</td>
</tr>
</tbody>
</table>
Space Group $P2_1/c$, equivalent positions

<table>
<thead>
<tr>
<th>Symmetry operations of the space group $P2_1/c$</th>
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<tbody>
<tr>
<td>$(x, y, z)$</td>
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</table>

The Harker peaks for the Zn atom will be given by the equivalent position differences:

<table>
<thead>
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<th>Posizioni di Harker</th>
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</thead>
<tbody>
<tr>
<td>$(x, y, z)$</td>
</tr>
<tr>
<td>( -x, 1/2+y, 1/2-z )</td>
</tr>
<tr>
<td>&lt;2x, -1/2, -1/2+2z&gt;</td>
</tr>
<tr>
<td>( x, 1/2-y, 1/2+z )</td>
</tr>
<tr>
<td>&lt;0, -1/2+2y, -1/2&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Posizioni di Harker</th>
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<tbody>
<tr>
<td>2x, 1/2, 1/2+2z</td>
</tr>
<tr>
<td>2x, 2y, 2z</td>
</tr>
<tr>
<td>0, -1/2+2y, 1/2</td>
</tr>
</tbody>
</table>
Therefore we need to identify within the Patterson Map the experimental peaks corresponding the Harker sections.

The Harker peak \(<2x, 1/2, 2z-1/2>\) can be identify with the experimental peak \#2:

\[
< 2x, 1/2, 2z-1/2 > = < 0.50, 0.50, 0.45 >
\]

\[
2x = 0.50; \quad 2z-1/2 = 0.45; \quad x = 0.25 \quad z = 0.47
\]

If this is true, we can write in the first approximation the Zn: \((0.25, y, 0.47)\).
The second Harker section at $<0, -1/2+2y, 1/2>$, is needed to calculate the Zn $y$ coordinate, corresponding the experimental peak #3:

$$<0, 2y-1/2, 1/2> = <0, 0.05, 0.50>$$

$$2y-1/2 = 0.05 \; ; \; y = 0.27$$

If this is the correct solution then we need to find the third interatomic vector between Zn atoms $<2x, 2y, 2z>$ in the Patterson Map:

$$<2\times0.25, 2\times0.27, 2\times0.47> = <0.50, 0.54, 0.94>$$
Important to remember that the Patterson space has its own periodicity and symmetry, then it is necessary to find in the experimental peak the equivalent positions obtained applying the symmetry operators on \(<0.50, 0.54, 0.94>\):

| Symmetry operations of the space group \(P2_1/c\) |
|-----------------|-----------------|-----------------|-----------------|
| \((x, y, z)\)   | \((-x, 1/2+y, 1/2-z)\) | \((-x, -y, -z)\) | \((x, 1/2-y, 1/2+z)\) |

| Symmetry of the corresponding Patterson map |
|-----------------|-----------------|-----------------|-----------------|
| \((x, y, z)\)   | \((-x, y, -z)\) | \((-x, -y, -z)\) | \((x, -y, z)\) |

Applying \((x, -y, z)\) on \(<0.50, 0.54, 0.94>\) we will obtain \(<0.50, 0.46, 0.94>\),

Corresponding \#4, \(<0.51, 0.45, 0.95>\),

Then the Zn coordinates are: \(\text{Zn} (0.25, 0.27, 0.47)\)
Overall, the application of Patterson methods for structure solution can be summarized by the following steps:

1. calculate Patterson function: $P(uvw)$

2. solve for possible Heavy atom position(s)

3. use this position and the electron density to calculate an approximate phase angle ($a_{hkl}$) for each reflection

4. use these approximate $a_{hkl}$ values to calculate $r(xyz)$ and plot it

5. interpret the electron density map in a chemically sensible way
R-factor

- The R-factor is defined as:

$$R = \frac{\sum |F(\ hkl\ ) - F_{calc}|}{\sum |F(\ hkl\ )|}$$

- It’s the error between the real diffraction pattern and the calculated one.
- A R-factor of ~0.2 (20% error) is considered good enough to give a good model of the structure.
Patterson Map: Examples

Space Group $P2_1/n$, equivalent positions

<table>
<thead>
<tr>
<th>Symmetry operations of the space group $P2_1/n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x, y, z)$</td>
</tr>
</tbody>
</table>

The Harker peaks for the Ga atom will be given by the equivalent position differences:

<table>
<thead>
<tr>
<th>Posizioni di Harker</th>
<th>$( -x, 1/2+y, 1/2-z )$</th>
<th>$(-x, -y, -z)$</th>
<th>$( x, 1/2-y, 1/2+z )$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x, y, z)$</td>
<td>$&lt;1/2-2x, -1/2, -1/2+2z&gt;$</td>
<td>$&lt;2x, 2y, 2z&gt;$</td>
<td>$&lt;1/2, -1/2+2y, -1/2&gt;$</td>
</tr>
</tbody>
</table>

| Posizioni di Harker | $<1/2-2x, 1/2, 1/2+2z>$ | $<2x, 2y, 2z>$ | $<1/2, -1/2+2y, 1/2>$ |
Therefore we need to identify within the Patterson Map the experimental peaks corresponding the Harker sections.

\[ <\frac{1}{2}-2x, \frac{1}{2}, 2z-1/2> \] can be identified as peak #2:

\[ <\frac{1}{2}-2x, \frac{1}{2}, 2z-1/2> = <0.0483, 0.5000, 0.2487> \]

\[ 2x = 0.4517; \quad 2z-1/2 = 0.2487; \quad x = 0.2259 \quad z = 0.3744 \]

If this is true, we can write in the first approximation the Ga coordinates are: \( (0.2259, y, 0.3744) \).
The second Harker section \(<1/2, -1/2+2y, 1/2\>\), is needed to calculate the Zn y coordinate, corresponding the experimental peak #3:

\[
<1/2, 2y-1/2, 1/2> = <0.5000, 0.1769, 0.5000>
2y-1/2 = 0.1769 \quad y = 0.3385
\]

If this is the correct solution then we need to find the third interatomic vector between Ga atoms \(<2x, 2y, 2z>\) in the Patterson Map:

\[
<2x0.2259, 2x0.3385, 2x0.3744> = <0.4518, 0.6770, 0.7488>
\]
Important to remember that the Patterson space has its own periodicity and symmetry, then it is necessary to find in the experimental peak the equivalent positions obtained applying the symmetry operators on \(<0.4518, 0.6770, 0.7488>\):

**Symmetry operations of the space group** $P2_1/n$

\[
( x, y, z ) \quad \left( \frac{1}{2}-x, 1/2+y, 1/2-z \right) \quad (-x, -y, -z) \quad \left( \frac{1}{2}+x, 1/2-y, 1/2+z \right)
\]

**Symmetry of the corresponding Patterson map**

\[
( x, y, z ) \quad (-x, y, -z) \quad (-x, -y, -z) \quad ( x, -y, z )
\]

Applying \((x, -y, z,)\) on \(<0.4518, 0.6770, 0.7488>\) we will obtain \(<0.4518, 0.3230, 0.7488>\), corresponding the peak #4, \(<0.4527, 0.3226, 0.2517>\) reporting in the unit cell on z (1-0.7488= 0.2512)

Then the Ga coordinates are : : Ga \((0.2264, 0.1613, 0.1259)\)