Space Group Determination

Determining the Space Group

1. $I_{\text{rel}}$ is the same as $I_{\text{int}}$

   Friedel's Law

   Georges Friedel
   French
   (1865-1933)

   unique reflections reduced by symmetry
   identical reflections can be averaged for better statistics

2. space groups with screw axes, glide planes and/or centering give diffraction patterns with certain reflections "missing"

   systematic absences (or extinctions)

visualize diffraction pattern (reciprocal lattice) and relate symmetry of reciprocal lattice to direct lattice
find systematic absences that reveal some of the symmetry

three instruments have been used to do this:
1. Weissenberg camera
2. precession camera
3. diffractometer

Weissenberg Method

Karl Weissenberg
Austrian
(1893-1976)

Martin J. Buerger
American
(1903-1986)
The Weissenberg Method and the Precession Method are two techniques used in X-ray crystallography for structure determination. The Weissenberg Method involves a distorted view of the reciprocal lattice, while the Precession Method involves a crystal axis precessing about the x-ray beam and the film following the precession motion, ensuring the film is always perpendicular to the crystal axis. The Precession Technique is easier to describe but more challenging to execute, requiring a complex apparatus.

M. F. C. Ladd and R. A. Palmer, *Structure Determination by X-ray Crystallography*

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**Weissenberg Method**

Distorted view of reciprocal lattice.

**Precession Method**

“Crystal axis precesses about the x-ray beam and the film follows the precession motion in such a way that the film is always perpendicular to the crystal axis.” This is much easier to say than carry out, and an apparatus of appreciable mechanical complexity is required.”

M. F. C. Ladd and R. A. Palmer

*Structure Determination by X-ray Crystallography*

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**Precession Method**

Undistorted view of reciprocal lattice.

**Precession Photograph**

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**Model Precession Photograph of Two Layers**

$h = 0$

$h = 1$

**Four-circle Diffractometer**
Four-circle Diffractometer

Kappa Geometry Diffractometer

Kappa Geometry Diffractometer

Kappa Geometry Diffractometer

Desktop Diffractometer

Rotation Photograph
15-25 measurements (2x, 2y) allow computer to calculate \( \theta, \phi, \psi, \) and \( \chi \) angles to bring each reflection onto sphere of reflection; reflections then carefully centered

Computer generates sets of vectors and angles to index \((h k l)\) the 15-25 reflections; possible direct lattice axes and angles determined; choose a high symmetry unit cell and input in computer; computer calculates an orientation matrix that relates unit cell to diffractometer geometry; can locate Bragg reflections.

Advantages:
1. quick
2. crystal orientation does not matter
3. can try several crystals to find the best
4. computer does most of the work

Disadvantages:
1. can miss symmetry – especially if it is high

Richard E. Marsh
American
(1922– )

Some 60 new space-group corrections.
More space-group corrections:
The centrosymmetric-noncentrosymmetric ambiguity: some more examples.
More space-group changes.
More space-group corrections: from triclinic to centered monoclinic and to rhombohedral: also from P1 to P \( \bar{1} \) and from Cc to C2/c.
Changes in space and Laue groups of some published crystal structures.
Some incorrect space groups: an update.
Some incorrect space groups in *Inorganic Chemistry*, Vol 16.

Systematic Absences

\[
\begin{align*}
\text{h = 0} & & \text{h = 1} \\
\begin{array}{cccc}
\text{a} & \text{b} & \text{c} & \text{d} \\
1 & 2 & 3 & 4 \\
5 & 6 & 7 & 8 \\
9 & 10 & 11 & 12 \\
13 & 14 & 15 & 16 \\
\end{array}
\end{align*}
\]
## Systematic Absences

### Affected Reflections and Absent Conditions

<table>
<thead>
<tr>
<th>Element</th>
<th>Affected Reflection</th>
<th>Reflection Absent when</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2_1$ along $a$</td>
<td>$h \ 0 \ 0$</td>
<td>$h = 2n + 1 \quad \text{odd}$</td>
</tr>
<tr>
<td>$2_1$ along $b$</td>
<td>$0 \ k \ 0$</td>
<td>$k = 2n + 1$</td>
</tr>
<tr>
<td>$2_1$ along $c$</td>
<td>$0 \ 0 \ t$</td>
<td>$t = 2n + 1$</td>
</tr>
<tr>
<td>Glide plane $\perp a$</td>
<td>$0 \ k \ t$</td>
<td>$k = 2n + 1$</td>
</tr>
<tr>
<td>$b$</td>
<td></td>
<td>$t = 2n + 1$</td>
</tr>
<tr>
<td>$c$</td>
<td></td>
<td>$k = 2n + 1$</td>
</tr>
<tr>
<td>$n$</td>
<td></td>
<td>$k + t = 2n + 1$</td>
</tr>
<tr>
<td>$d$</td>
<td></td>
<td>$k + t = 4n + 1, 2, \text{or } 3$</td>
</tr>
</tbody>
</table>

## Space Groups and Systematic Absences

Some space groups are completely determined by absences:

- **Monoclinic:** $P2_1/c$  
  -  
  $0 \ k \ 0, \quad k = 2n + 1$  
  $h \ 0 \ t, \quad t = 2n + 1$  
  $0 \ 0 \ t, \quad t = 2n + 1$  

- **Orthorhombic:** $P2_12_12_1$  
  - $Pmm$  
  - $Pnma$  
  - $Pcma$  
  - $Pbcn$  
  - $Abma$  
  - $Cmca$  
  - $Fd3d$  
  - $Ibca$
Space Groups and Systematic Absences

often two space groups have identical systematic absences, but one is centric and the other not; half general positions identical

\[
P_{na2_1} \quad \begin{cases} 0 \ k \ l, & k + l = 2n + 1 \quad x, y, z \\ h \ 0 \ l, & h = 2n + 1 \quad \bar{x}, \bar{y}, \bar{z} + \frac{1}{2} \end{cases}
\]

\[
(h \ 0 \ 0, & h = 2n + 1) \quad x + \frac{1}{2}, y + \frac{1}{2}, z \\
(0 \ k \ 0, & k = 2n + 1) \quad x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2} \\
(0 \ 0 \ l, & l = 2n + 1)
\]

\[
P_{nam} \quad \text{(non-standard setting of } P_{nma} \text{ – switch } y \text{ and } z)
\]

\[
\begin{align*}
x, y, z & \quad \bar{x}, \bar{y}, \bar{z} \\
\bar{x}, \bar{y}, \bar{z} + \frac{1}{2} & \quad x, y, z + \frac{1}{2} \\
x + \frac{1}{2}, y + \frac{1}{2}, z & \quad \bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} \\
\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2} & \quad x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}
\end{align*}
\]

Data

now have a space group (or choice of usually no more than two)
to solve the structure, need to measure the intensity of as many indexed reflections as we can get