Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology in Hydrogen-Based Energy Systems

13 - 18 June 2011

Introduction to crystallography

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Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology in Hydrogen-Based Energy Systems
Trieste – Italy, 13 – 18 June 2011
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2. Symmetry operations
3. Plane and space groups
4. Crystallographic planes
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Crystalllography is the experimental science of the arrangement of atoms in solids (wikipedia).

A crystal structure is a regular arrangement of atoms or molecules.

Question:
Is there an finite ways to arrange atoms in a regular way in 2, and 3 dimensions?

If yes, how many?

How could we describe it?
There are five different ways to translate a point in two-dimensions. These are the Bravais lattices.
Bravais lattices 2 dim

|a_2| ≠ |a_1|, φ = 90°  | |a_2| ≠ |a_1|, φ = 90°  | |a_2| ≠ |a_1|, φ ≠ 90°
Oblique                      Rectangular                    Centered rectangular

|a_2| = |a_1|, φ = 120°  | |a_2| = |a_1|, φ = 90°
Hexagonal                   Square

http://en.wikipedia.org/wiki/Bravais_lattice
The space that is spanned by the translation vectors is called the unit cell. The unit cell constants define the length of the translation vectors and the angles between them. In a crystal, the unit cell contains the fundamental atomic structure that is repeated.

In 3D there is seven ‘shape’ of unit cell possible. They are called crystal system.
Seven Basic Crystal Systems

Crystals are classified into seven categories based on their overall shapes.

- **Fluorite**  
  $a = b = c$  
  $\alpha = \beta = \gamma = 90^\circ$  
  Cubic

- **Rutile**  
  $a = b \neq c$  
  $\alpha = \beta = \gamma = 90^\circ$  
  Tetragonal

- **Barite**  
  $a \neq b \neq c$  
  $\alpha = \beta = \gamma = 90^\circ$  
  Orthorhombic

- **Rhodonite**  
  $a \neq b \neq c$  
  $\alpha \neq \beta \neq \gamma \neq 90^\circ$  
  Triclinic

- **Corundum**  
  $a = b \neq c$  
  $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$  
  Hexagonal

- **Cerussite**  
  $a = b = c$  
  $\alpha = \beta = \gamma \neq 90^\circ$  
  Rhombohedral

- **Boron**  
  $a \neq b \neq c$  
  $\alpha = \gamma = 90^\circ$  
  Monoclinic
14 Bravais lattices 3 dim

CUBIC
\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

TETRAGONAL
\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

ORTHORHOMBIC
\[ a \neq b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

HEXAGONAL
\[ a = b \neq c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

MONOCLINIC
\[ a \neq b \neq c \]
\[ \alpha = \gamma = 90^\circ \]
\[ \beta \neq 120^\circ \]

TRICLINIC
\[ a \neq b \neq c \]
\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred

7 Crystal Classes
→ 14 Bravais Lattices

http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/lec1.html
Lattice points

We now have our basic unit cells. To each of these cells are associated ‘lattice points’ that define the unit cell and are related to each other by translation. They are a mathematical abstraction and do not necessarily represent a single atom. The actual atoms are part of the motif.

http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/lec1.html
Basis or motif

Symmetry operations

In addition to translation, the structure may have some symmetry. There is only a limited number of symmetry possible in two and three dimensions. Some of these are point symmetries (one point do not move when the symmetry operation is performed) other are two steps operations.

http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/lec1.html
Simple symmetry operations

Rotation

Inversion

Reflection

Translation

Symbol: \( m \) or \( \sigma \)
Graphical symbol:
These are the only rotations possible in 2 and 3D in order to completely fill the space. Certain rotations are compatible with only certain lattices (i.e., in 2D, 2 with rectangular lattice but not 4).
To the simple symmetry operation we need three more symmetry operations do fully characterize the crystals. In two dimensions we need only one of them.
Glide reflection

Graphical symbol:  

Printed symbol: $a, b \text{ or } c$

http://www.themathlab.com/dictionary/wwords/wwords.htm
Complex symmetry operations

In three dimensions we need two more two-steps symmetry operations.
Screw axes

Notation \( N_j \)
\( N \) = Rotation \((360/N)\)
\( j \) = fraction of translation \((j/N)\)
Exemple: \( 3_2 \) = rotation of 120° followed by a translation of 2/3 of the unit cell
# Screw axes

<table>
<thead>
<tr>
<th>Graphical Symbol</th>
<th>Translation</th>
<th>Printed symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>⚜</td>
<td>1/2</td>
<td>2₁</td>
</tr>
<tr>
<td>📜</td>
<td>1/3</td>
<td>3₁</td>
</tr>
<tr>
<td>📜</td>
<td>2/3</td>
<td>3₂</td>
</tr>
<tr>
<td>📜</td>
<td>1/4</td>
<td>4₁</td>
</tr>
<tr>
<td>📜</td>
<td>1/2</td>
<td>4₂</td>
</tr>
<tr>
<td>📜</td>
<td>3/4</td>
<td>4₃</td>
</tr>
<tr>
<td>📜</td>
<td>1/6</td>
<td>6₁</td>
</tr>
<tr>
<td>📜</td>
<td>1/3</td>
<td>6₂</td>
</tr>
<tr>
<td>📜</td>
<td>1/2</td>
<td>6₃</td>
</tr>
<tr>
<td>📜</td>
<td>2/3</td>
<td>6₄</td>
</tr>
<tr>
<td>📜</td>
<td>5/6</td>
<td>6₅</td>
</tr>
</tbody>
</table>
Rotoinversion

- a) $\overline{1}$ = inversion centre
- b) $\overline{2}$ = m
- c) $\Delta \equiv 3 + \overline{1}$
- d) $\Delta \equiv 3 \perp m$
## Rotoinversions

<table>
<thead>
<tr>
<th>Graphical Symbol</th>
<th>Operation</th>
<th>Printed symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>⚗</td>
<td>Inversion</td>
<td>⠠</td>
</tr>
<tr>
<td>△</td>
<td>3+₁</td>
<td>3</td>
</tr>
<tr>
<td>⬠</td>
<td>90° rotation + inversion</td>
<td>4</td>
</tr>
<tr>
<td>◇</td>
<td>3/m</td>
<td>6</td>
</tr>
</tbody>
</table>
We now have all the tools to characterize regular patterns in 2 and 3 dimensions. In two dimensions, if we combine the 5 Bravais lattices with the symmetry operations we find there is only 17 different arrangements. They are the plane groups. Let’s see a few of them.

Wallpaper of each plane group could be found at:
http://www.spsu.edu/math/tile/symm/ident17.htm
\[ p_{211} \]

No. 2

\[ p_2 \]

Origin at 2

**General:**
No conditions

**Special:**
No conditions

\[
\begin{array}{ccc}
2 & e & 1 \\
1 & d & 2 \\
1 & c & 2 \\
1 & b & 2 \\
1 & a & 2 \\
\end{array}
\]

\[
\begin{array}{ccc}
x, y; & x, y. \\
\frac{1}{2}, \frac{1}{2} & \\
\frac{1}{2}, 0 & \\
0, \frac{1}{2} & \\
0, 0 & \\
\end{array}
\]
### p6m

#### No. 17

**Co-ordinates of equivalent positions**

<table>
<thead>
<tr>
<th>Number</th>
<th>Position</th>
<th>Co-ordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>f</td>
<td>$x,y; y-x,y; y-x,y; y,x; y,y-x; x-y,y; x+y,x; \bar{x},\bar{y}; y,\bar{y}; x,\bar{x}$</td>
</tr>
<tr>
<td>6</td>
<td>e</td>
<td>$x,0; x,2x; 2x,\bar{x}; \bar{x},x; \bar{x},2\bar{x}; 2x,x$</td>
</tr>
<tr>
<td>6</td>
<td>m</td>
<td>$x,0; x,\bar{x}; \bar{x},x; \bar{x},2\bar{x}; 2x,x$</td>
</tr>
<tr>
<td>3</td>
<td>c (mm)</td>
<td>$\frac{1}{2},0; 0,\frac{1}{2}; \frac{1}{2},\frac{1}{2}$</td>
</tr>
<tr>
<td>2</td>
<td>b (3m)</td>
<td>$\frac{1}{3},\frac{1}{3}; \frac{2}{3},\frac{2}{3}$</td>
</tr>
<tr>
<td>1</td>
<td>a (6mm)</td>
<td>0,0</td>
</tr>
</tbody>
</table>

**Conditions limiting possible reflections**

- **General:** No conditions
- **Special:** No conditions

**Origin at 6mm**

**Number of positions, Wyckoff notation, and point symmetry**

- 12 f
- 6 e m
- 6 d m
- 3 c (mm)
- 2 b (3m)
- 1 a (6mm)
In 3 dimensions things are more complicated. We now combine the 14 Bravais lattices with all the symmetry operations to get the 230 possible space groups.

Wallpaper of each plane group could be found at:
http://www.spsu.edu/math/tile/symm/ident17.htm
Space group

$P 2_1$

$C_2^2$

No. 4

$P 1 1 2_1$

2 Monoclinic

1st SETTING

Number of positions, Wyckoff notation and point symmetry

1

x, y, z; $\frac{1}{2}+z$.

Origin on $2_1$; unique axis $c$

Co-ordinates of equivalent positions

Conditions limiting possible reflections

hkl: No conditions
hk0: No conditions
00l: $l=2n$

Symmetry of special projections

(001) $p2$; $a'=a$, $b'=b$

(100) $pg1$; $b'=b$, $c'=c$

(010) $p1g$; $c'=c$, $d'=a$

http://serc.carleton.edu/NAGTWorkshops/mineralogy/activities/26974.html
Crystal structures

We know how to express all possible crystal structures but how could we actually ‘see’ these structures?

Before doing this we need one more tool: **Miller indices**.
Miller indices

A family of planes is identified by its Miller indices

• The position is determined in terms of unit cell axes $a$, $b$ and $c$. (fraction)
• One plane goes through the origin
• The first plane after origin determines the Miller indices
• The indices $(h, k, l)$ are the reciprocal of the plane coordinates when it crosses one axis
• A parallel plane to an axis has a Miller index of 0

http://serc.carleton.edu/NAGTWorkshops/mineralogy/activities/26974.html
Plans cristallographiques et indices de Miller

Une famille de plans est identifié par les indices de Miller

– La position est déterminé en terme des axes $a$, $b$ et $c$. (fractionnaire)
– Un plan passe par l’origine
– Le premier plan après l’origine détermine les indices de Miller
– Les indices $(h, k, l)$ sont la réciproque des coordonnés du plan lorsqu’il coupe l’axe
– Un plan parallèle à un axe a l’indice 0
Examples (2D)

Examples

Interplanar spacings

Orthorhombic:

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}. \]

(Tetragonal: \( a = b \); cubic: \( a = b = c \).)

Hexagonal:

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}. \]

Rhombohedral:

\[ \frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}. \]

Monoclinic:

\[ \frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right). \]
Crystallographic planes are fictitious planes linking lattices points. Some directions and planes have a higher density of lattices points; these dense planes have an influence on the behaviour of the crystal:

- optical properties
- adsorption and reactivity
- surface tension
- pores and crystallites tend to have straight grain boundaries following dense planes cleavage
- dislocations

http://en.wikipedia.org/wiki/Miller_index
Bragg law

First proposed by W. L. Bragg and W. H. Bragg in 1913

**Observation:** Crystalline solids, at certain specific wavelengths and incident angles, produced intense peaks of reflected radiation (known as *Bragg peaks*).

**Explanation:** W. L. Bragg explained this result by modeling the crystal as a set of discrete parallel planes separated by a constant parameter $d$.

It was proposed that the incident X-ray radiation would produce a Bragg peak if their reflections off the various planes interfered constructively.
The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes.

Both neutron and X-ray wavelengths are comparable with inter-atomic distances (~150 pm) and thus are an excellent probe for this length scale.
Bragg law

\[ \theta, 2\theta – \text{Bragg angles} \]

\[ 2\Delta = 2d_{hkl} \sin \theta – \text{path difference} \]

\[ 2\Delta = n\lambda – \text{constructive interference} \]

Braggs’ law: 
\[ n\lambda = 2d_{hkl} \sin \theta_{hkl} \]
Single crystal diffraction

Three basic steps.

1. Obtain an adequate crystal of the material under study. (usually larger than 0.1 mm in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning. (most difficult!)

2. The crystal is placed in an beam of X-rays, (usually monochromatic) producing a regular pattern of reflections. As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal.

3. The data are combined computationally with complementary chemical information to produce the crystal structure.

Wikipedia: X-ray crystallography
Single crystal diffraction

http://serc.carleton.edu/research_education/geochemsheets/techniques/SXD.html

http://www.multiwire.com/products.html
It is not always easy (or even possible!) to get a single crystal. One could then use powder diffraction. Here, we must make sure that every possible crystalline orientation is equally represented. This puts some constraint on the particle size and amount of material needed.

**Advantages:**
- simplicity of sample preparation
- rapidity of measurement
- the ability to analyze mixed phases, e.g. soil samples
- "in situ" structure determination
Powder diffraction

Pattern obtained is a collapse of the single crystal 2D pattern into a 1D pattern.

Example
Cubic: spots from (100), (010), (001), (100), (010), (001) now are all together on the (001) line of the PDP.

Also, spots that are well separated in a single crystal diffraction pattern could be very close on the PDP.
LaB$_6$ (Pm-3m)

Cu K$_\alpha$ (0.1540598 nm)

Mo K$_\alpha$ (0.070932 nm)

Cr K$_\alpha$ (0.228976 nm)
**Phase identification**
As each crystalline solids has its own a distinctive diffraction pattern they can be identified by their PDP. A multi-phase mixture, e.g. a soil sample, will show more than one pattern superposed, allowing for determination of relative concentration. Database has more than 550,000 reference materials.

**Lattice parameters**
The position of a diffraction peak is *independent* of the atomic positions within the cell and entirely determined by the size and shape of the unit cell of the crystalline phase. Each peak represents a certain lattice plane (Miller index). If structure is known then lattice parameters could be determined.

**Phase transitions**
In ‘in situ’ experiments, changes of crystal structure upon phase transition could be observed.
**Uses**

**Crystal structure refinement and determination**
Because of overlap of reflections, the determination of crystal structure from PDP is challenging. However, the crystal structures of known materials can be refined, i.e. as a function of temperature or pressure, using the Rietveld method.

**Rietveld method**
Full pattern analysis technique where a crystal structure, together with instrumental and microstructural information is used to generate a theoretical diffraction pattern that can be compared to the observed data. A least squares procedure is then used to minimize the difference between the calculated pattern and each point of the observed pattern by adjusting model parameters.

**Size and strain determination**
Peak broadness depends on the crystallite size and strain.
crystallites
Peaks intensities

Peak position gives us the lattice parameter, peak broadness the size and strain but what about intensities?

First, let’s look at the diffraction of a single atom.
The structure factor is the sum of the diffracted amplitudes of the single atoms \( f_j \), taking into account the phase

\[
F_{hkl} = \sum_{j=1}^{m} f_j \exp \left( 2\pi i (hx_j + ky_j + lz_j) \right)
\]

The intensity of a Bragg peak is proportional to \( F_{hkl}^2 \)

Depending on the structure, there may be some systematic extinctions
## Extinction conditions

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Extinction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>none</td>
</tr>
<tr>
<td>$C$</td>
<td>$hkl; \ h + k = \text{odd}$</td>
</tr>
<tr>
<td>$B$</td>
<td>$hkl; \ h + l = \text{odd}$</td>
</tr>
<tr>
<td>$A$</td>
<td>$hkl; \ k + l = \text{odd}$</td>
</tr>
<tr>
<td>$I$</td>
<td>$hkl; \ h + k + l = \text{odd}$</td>
</tr>
<tr>
<td>$F$</td>
<td>$hkl; \ h, k, l \text{ mixed even and odd}$</td>
</tr>
<tr>
<td>$2_1 \parallel b$</td>
<td>$0k0; \ k = \text{odd}$</td>
</tr>
<tr>
<td>$c \perp b$</td>
<td>$h0l; \ l = \text{odd}$</td>
</tr>
</tbody>
</table>
Hydrogen

As the intensity scale with the number of electrons hydrogen is practically impossible to directly locate with X-ray ⇒ should use neutron. Why?

Neutrons probe the nucleus while X-ray probe the electron cloud.

Hydrogen gives a very high background ⇒ should use deuterium for neutron diffraction
MgD$_2$

Neutron

X-ray
References


