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Introduction to crystallography

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Introduction to crystallography

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Crystallography

Crystallography 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?





Unit cell (2D)



There are five different ways to translate a point in two-dimensions. These are the Bravais lattices





Bravais lattices 2 dim







http://en.wikipedia.org/wiki/Bravais_lattice

Unit cell

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



cmbe.engr.uga.edu

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14 Bravais lattices 3 dim





http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lect ure1/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/lect ure1/lec1.html



Basis or motif





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P. Hofmann, Solid State Physics. An Introduction, 1st edition, 2008, Wiley-VCH.

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 symetry operation is performed) other are two steps operations.



http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lect ure1/lec1.html



Simple symmetry operations









Reflection



Symbol: m or σ Graphical symbol:







V.K. Pecharsky and P.Z. Zavalij, *Fundamentals of Powder diffraction and Structural Characterization of Materials*, Springer, 2nd edition (2008)



Rotations

Graphical Symbol	Operation	Printed symbol
•	180° rotation	2
	120° rotation	3
•	90° rotation	4
۲	60° rotation	6

These are the only rotations possible in 2 and 3 D 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)





Complex symmetry operations

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* 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

capsicum.me.utexas.edu/ChE386K/docs/14_**Screw_Axes**.ppt

Screw axes

Graphical Symbol	Translation	Printed symbol
ý	1/2	21
À	1/3	31
	2/3	32
*	1/4	41
*	1/2	42
*	3/4	43
1	1/6	61
	1/3	6 ₂
•	1/2	6 ₃
•	2/3	64
٠	5/6	6 ₅

Rotoinversion

Rotoinversions

Graphical Symbol	Operation	Printed symbol
0	Inversion	1
۵	3 +Ī	3
\diamond	90° rotation + inversion	4
	3/m	6

Plane groups

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

Space groups

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

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 trhough the origin
- •The first plane after origin determine the Miller indices
- •The indices (*h, k, l*) are the reciproqual of the plane coordinates when it cross one axe
- •A parallel plane to an axe has a Miller index of 0

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

a

P. Hofmann, Solid State Physics. An Introduction, 1st edition, 2008, Wiley-VCH.

(11)

21

(41)

Examples

P. Hofmann, Solid State Physics. An Introduction, 1st edition, 2008, Wiley-VCH.

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

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.

Bragg law

The concept of *Bragg diffraction* applies equally to neutron diffraction and electron diffraction processes.

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

V.K. Pecharsky and P.Z. Zavalij, *Fundamentals of Powder diffraction and* Structural Characterization of Materials, Springer, 2nd edition (2008)

Single crystal diffraction

Three basic steps.

- 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.

Single crystal diffraction

http://www.multiwire.com/products.html

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

Powder diffraction

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 put 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

<u>Cubic:</u> spots from (100), (010), (001), ($\overline{1}00$), ($0\overline{1}0$), ($00\overline{1}$) 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.

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

P. Hofmann, Solid State Physics. An Introduction, 1st edition, 2008, Wiley-VCH.

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.

Power scale as the number of electrons

Fig. 3-15. Diffracting power of a few common atoms and ions (after C. W. Bunn, *Chemical Crystallography*, Oxford University Press, 1945).

Structure factor

The structure factor is the sum of the diffracted amplitudes of the single atoms (f_j) , taking into account the phase

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

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

Depending on the structure, there may be some systematic extinctions

Extinction conditions

Symmetry	Extinction Conditions
Р	none
С	hkl; h + k = odd
В	hkl; h + l = odd
A	hkl; k + l = odd
Ι	hkl; h + k + l = odd
F	hkl; h, k, l mixed even and odd
$2_1 \parallel b$	0k0: k = odd
$c \perp b$	h0l: l = odd

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.

http://www.ne.ncsu.edu/nrp/npdf.html

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

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