DICP Course 2 - Dalian, 2012
POWDER X-RAY DIFFRACTION
Part I – CRYSTALLOGRAPHY

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Charles Kappenstein, Professor Emeritus, University of Poitiers, France

DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES

1431 Université de Poitiers

中国科学院 CHINESE ACADEMY OF SCIENCES

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Faculté des Sciences Fondamentales et Appliquées
UFR SFA
Université de Poitiers

Institut de Chimie des Milieux et Matériaux de Poitiers
IC2MP

Outline of the course

I – CRISTALLOGRAPHY

II – X-RAY DIFFRACTION

III – POWDER DIFFRACTOMETRY

Outline of the course

1. – POINT LATTICES

1.1. - Crystal space lattice

1.1.1. - Definitions

1.1.2. - Lines and planes

1.1.3. - Set of planes - Miller indices (h k l)

1.2. - Reciprocal lattice

1.2.1. - Diffraction condition

1.2.2. - Properties of the reciprocal lattice

1.3. - Applications of reciprocal lattice

1.3.1. - Miller indices of a set of planes defined by two lines

1.3.2. - Indices [u v w] of a line defined by two planes

1.3.3. - Angle between two planes (or faces of a crystal)

1.3.4. - Building the reciprocal lattice

1.3.5. - d-spacing determination

1.4. - Axis changes

Outline of the course

2. – CRYSTALLOGRAPHIC GROUPS

- ***2.1. - Crystal lattices***
- ***2.2. - 14 Bravais lattices***
- ***2.3. - Space groups***
  - 2.3.1. - 7 one-dimensional space groups
  - 2.3.2. - 17 two-dimensional space groups
  - 2.3.3. - 230 three-dimensional space groups

INTRODUCTION

Cristalline state: defined by a 3-D periodic ordering of atoms

- perfect (no defect)
- infinite

Crystal: limited part of crystalline state

- smooth faces
- regular geometric shapes: set of equal faces (cube, octahedron, prismatic…)
- possibility of cleavage (not possible for amorphous solids)

Geometric model of crystalline state

- infinite point lattices
- 3 non-coplanar vectors: **a**, **b, c** (in bold) or $\vec{a}, \vec{b}, \vec{c}$ (with arrows)

1. – POINT LATTICES

1-D ➔ line lattice: **a**

2-D ➔ plane lattice: **a , b**

3-D ➔ space lattice: **a, b, c**

1. – POINT LATTICES

1.1. - Crystal space lattice (or direct space)

1.1.1. - Definitions

- three vectors + origin point
- lattice translations from origin to any point P_i

$$\mathbf{OP}_i = u_i\,\mathbf{a} + v_i\,\mathbf{b} + w_i\,\mathbf{c} \quad \text{or} \quad \overrightarrow{\mathbf{OP}} = \mathbf{u_i}\vec{\mathbf{a}} + \mathbf{v_i}\vec{\mathbf{b}} + \mathbf{w_i}\vec{\mathbf{c}}$$

- u_i, v_i and w_i are relative integers

Translation vector between two lattice points: $\mathbf{P_1P_2}$ (see figure)

- $\mathbf{OP}_1 = u_1\,\mathbf{a} + v_1\,\mathbf{b} + w_1\,\mathbf{c}$
- $\mathbf{OP}_2 = u_2\,\mathbf{a} + v_2\,\mathbf{b} + w_2\,\mathbf{c}$
- $\mathbf{P_1P_2} = \mathbf{OP_2} - \mathbf{OP_1} = (u_2 - u_1)\,\mathbf{a} + (v_2 - v_1)\,\mathbf{b} + (w_2 - w_1)\,\mathbf{c}$

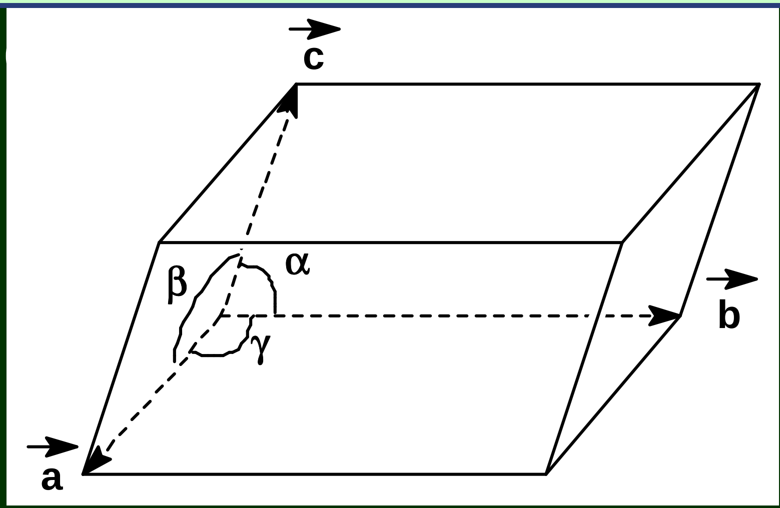
1. – POINT LATTICES

The vectors **a**, **b** and **c** define the **unit cell**

6 cell or lattice parameters:

a b c α β γ

a = |**a**| = modulus of **a**



The unit cell must be **right-handed** (like cork-screw)

This corresponds to a **direct rotation**

Different vector products

- Scalar product: **a . b**

  Do you remember the analytical relation?

  a . b = |**a**| . |**b**| cos (angle between **a** and **b**)

- Cross product: **a** x **b**

  The cross product defines a new vector perpendicular to **a** and **b** and right-handed

  Do you remember the analytical relation for the modulus of this new vector?

  |**a** x **b**| = |**a**| . |**b**| sin (angle between **a** and **b**)

1. – POINT LATTICES

Volume of unit cell: V = (**a** x **b**) . **c** = (**a**, **b**, **c**)

triple or mixed product

$$V = (\vec{a} \times \vec{b}) \cdot \vec{c} = (\vec{a}, \vec{b}, \vec{c})$$

With any 3 non-coplanar vectors we can build a cell:

$\mathbf{OP_1}$, $\mathbf{OP_2}$, $\mathbf{OP_3}$ with $\mathbf{OP_i} = u_i\mathbf{a} + v_i\mathbf{b} + w_i\mathbf{c}$

Or $\overrightarrow{OP}_1, \overrightarrow{OP}_2, \overrightarrow{OP}_3$

$$\overrightarrow{OP}_i = u_i\vec{a} + v_i\vec{b} + w_i\vec{c}$$

Volume of this cell?

$$(\overrightarrow{OP}_1, \overrightarrow{OP}_2, \overrightarrow{OP}_3) = \begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{vmatrix} (\vec{a}, \vec{b}, \vec{c})$$

Value m of this determinant? m is an integer (number of lattice points in the cell)

- $m > 0$ ➔ right-handed cell
- $m < 0$ ➔ left-handed-cell
- $|m| = 1$ ➔ primitive cell $|m| > 1$ ➔ multiple cell

1. – POINT LATTICES

The unit cell displays the symmetry of the crystal
It can be simple or multiple
Ex.: cubic system

simple cell	m = 1	lattice mode P	
multiple cell	m = 2	lattice mode I	(body centered cell)
multiple cell	m = 4	lattice mode F	(face centered cell)

the simple cell is rhombohedral

Position of any point inside the cell:

$$\overrightarrow{OX} = x\,\vec{a} + y\,\vec{b} + z\,\vec{c}$$

x, y and z: fractional coordinates, dimensionless numbers in the range 0 to 1

1.1. - Crystal space lattice (or direct space)

1.1.2. – Lines and planes

Any line is defined by one translation **OP** which is repeated

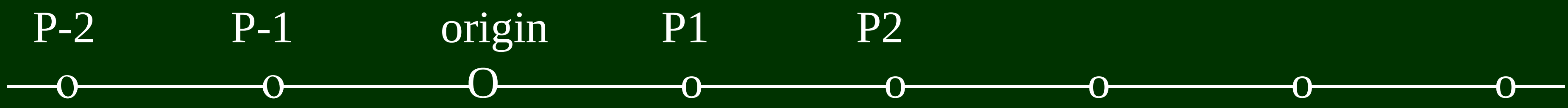
$$\vec{OP} = u\,\vec{a} + v\,\vec{b} + w\,\vec{c}$$

Notation: [u v w]

Distance between two successive points on the line:

line parameter N_{uvw} = **| OP |**

The origin of the line can be choosen at any point



Therefore [u v w] represents a set of parallel lines displaying the same line parameter

1. – POINT LATTICES

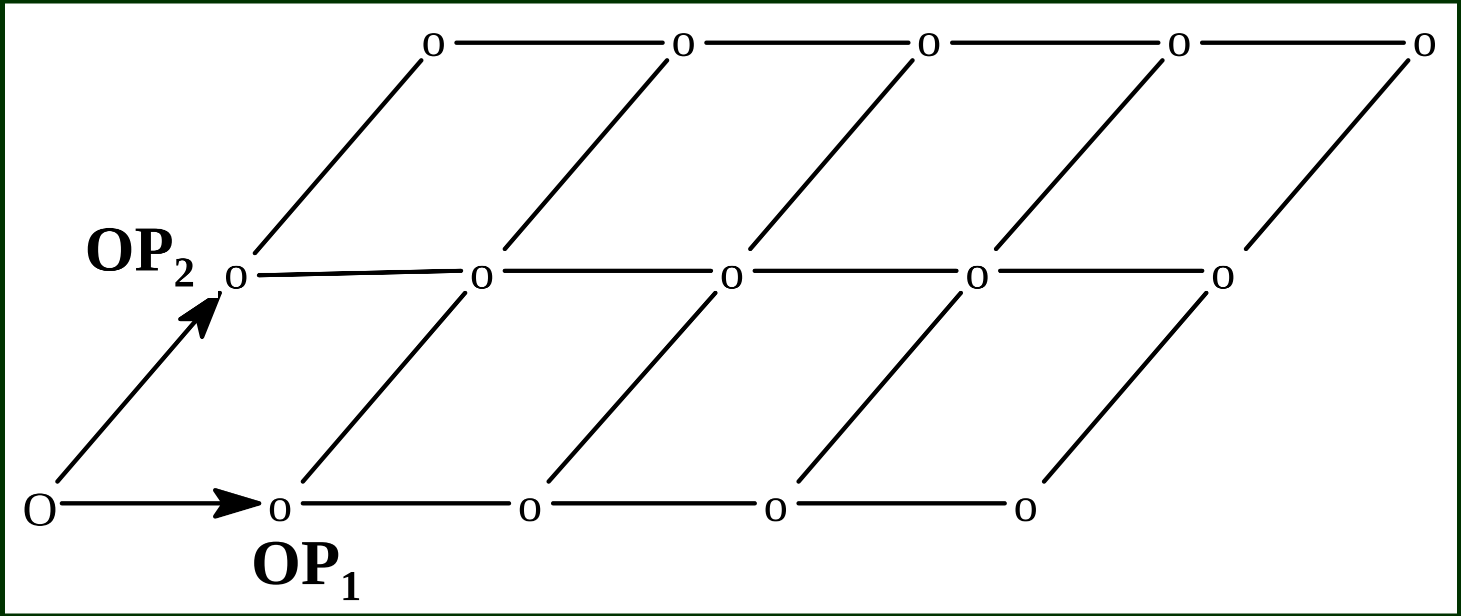
1.1. - Crystal space lattice (or direct space)

1.1.2. – Lines and planes

A plane is defined by two translations $\mathbf{OP_1}$ and $\mathbf{OP_2}$

Any translation in the plane is represented by

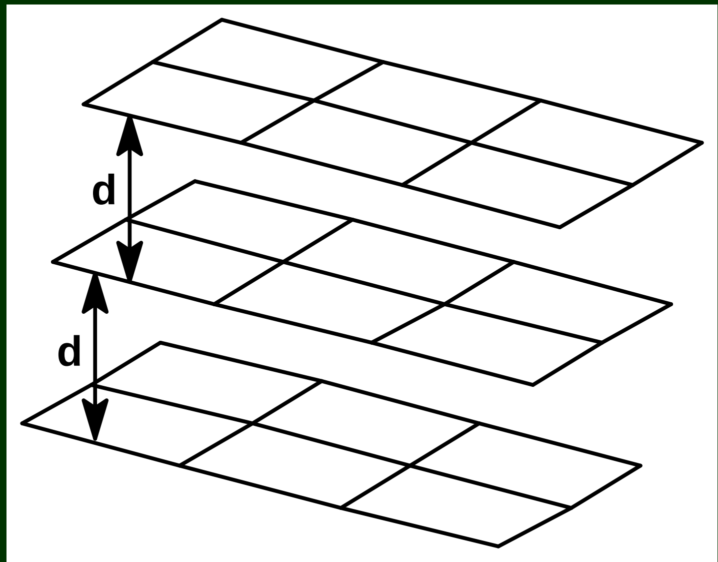
$\mathbf{T} = u\,\mathbf{OP_1} + v\,\mathbf{OP_2}$ u and v are integers



1.1. - Crystal space lattice (or direct space)

1.1.3. – Set of planes – Miller indices

The distance between two successive planes is a constant: d-spacing



If the planes are based on the vectors **a** and **b,** how to determine d?

V = (**a** x **b**) . **c** = |**a** x **b**| . d or

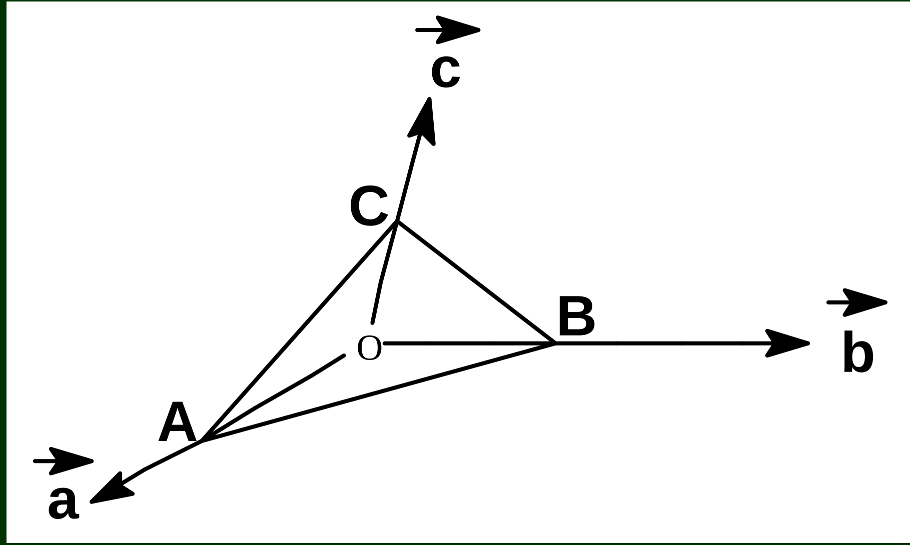
$$V = (\vec{a}_{\wedge}\vec{b}) \cdot \vec{c} = \left|\vec{a}_{\wedge}\vec{b}\right| \cdot d$$

1. – POINT LATTICES

1.1.3. – Set of planes – Miller indices

Orientation of a set of planes?

We consider the first plane from origin



$$\vec{a} = h\overrightarrow{OA}\ ; \qquad \vec{b} = k\overrightarrow{OB}\ ; \qquad \vec{c} = l\overrightarrow{OC}$$

The three indices h, k and l define the orientation of the plane family: (h k l)

Ex: Fractional coordinates:

A 1 0 0, B 0 1 0, C 0 0 1/2 :

➔ (1 1 2)

A 1 0 0, B 0 -1 0, C 0 0 ∞ (plane parallel to **c**) :

➔ (1 -1 0) equivalent to (-1 1 0)

$(h\ k\ l) \equiv (-h\ –k\ –l)$ same plane family

d-spacing of the family (h k l)

$$d_{hkl} = f\,(h, k, l, a, b, c, \alpha, \beta, \gamma)$$

Exercices

Ex. 1. Determine the multiplicity of the cell based on the following vectors:

$$a)\ \vec{a}-\vec{b},\ \vec{a},\ -\vec{a}+\vec{c} \qquad b)\ \vec{a},\ 4\vec{a}+\vec{b},\ 3\vec{a}-\vec{c}$$

Ex. 2. The angle between the perpendicular lines to the two faces (h k 0) and (h –k 0) has been determined for a tetragonal (quadratic) crystal. The experimental value is 53°10'. What are the values of the indices h and k?

Ex. 3. Determine the indices of the line going through the points 3 2 1 et 2 -4 0.

Ex. 4. Is the line [-2 1 0] contained in the plane (1 2 3)?

Ex. 5. What are the indices of the plane which contains the lines [1 1 1] and [3 2 1]?

Ex. 6. Determine the indices of the line common to the planes (3 2 1) and (1 2 3).

Exercices

Ex. 7. What is the value of the angle between the lines [1 1 1] and [1 1 0] for a tetragonal lattice with cell parameters a = 5.00 Å and c = 3.00 Å?

Ex. 8. Determine the value of the angle between the planes (1 1 1) and (1 1 0) for a cubic lattice with cell parameter a. Same question for the planes (1 0 0) et (1 1 0).

Ex. 9. Can you show that the lines [-1 0 1], [-1 1 0] and [-2 1 1] are lying in the same plane, whatever the lattice? Determine the indices of this plane.

Ex. 10. Determine the indices of the line defines by two planes, the first going through the lattice points 3 2 1; 2 -4 0 and 3 3 -1, and the second one through the lattice points -1 2 1; 1 1 1 and -2 1 2.

Ex. 11. Draw the seven 1-D space groups, using a rectangular triangle as asymmetrical unit.