2. Symmetry of Surfaces, Interfaces and Solids

2.1 Translational symmetry

So far we have considered objects of finite size. The symmetry groups for these objects leave at least one point on space unaffected (point groups). Now we consider infinite periodic arrangements of objects. For this purpose we define a new symmetry operation, the

Translation $\vec{t}$,

which moves every point of the arrangement by an vector $\vec{t}$ (lattice vector) to an equivalent position.

It follows that $\vec{t}' = N\vec{t}, N \in Z$ is also a symmetry elements (or in n dimensions $\vec{t}' = \sum_i N_i \vec{t}_i, N_i \in Z$).

(2.1: Escher, translational symmetry in 1, 2, and 3 dimensions)

2.2 Introduction: one dimensional symmetries

(2.2: left-handed dwarf and right-handed dwarf, how many periodic arrangements are there in one dimension, which are different with respect to their symmetry properties?)

For one dimensional periodic arrangements, there are 7 different symmetries, i.e. 7 different symmetry groups:

1. translational symmetry only
2. Longitudinal mirror plane
3. C_2 axis: in combination with translations, we obtain a infinite set of C_2 axes. Important: We also obtain a second set of C_2 axes, which is not equivalent to the first one (which cannot be transformed into each other by an operation of the symmetry group).
4. Perpendicular mirror plane: Again we obtain a second non-equivalent set of mirror planes.
5. Longitudinal and perpendicular mirror planes: We obtain two sets of C_2 axes.

6. Glide reflection: new symmetry element, which exists only in periodic arrangements. Translation by half of the lattice vector, followed by reflection with respect to plane parallel to the lattice vector.
7. Glide reflection and perpendicular mirror plane: a set of C_2 axes is generated.

In contrast to the point groups for finite objects, we denote these groups as the 7 space groups in one dimension.

(2.3: Determine the one dimensional space groups: polyalkene with/without alternating bond lengths)

2.3 Some important definitions

- Lattice: periodicity of the crystal, disregarding the actual structure (molecules) which fill the space.
- Lattice vector: translation by a lattice vector moves the crystal into an equivalent position.
- Primitive lattice vector: smallest lattice vectors that can be chosen.
- Primitive unit cell: parallelepiped defined by the primitive lattice vectors.
- Space group: complete set of symmetry operations of a perfect infinite crystal, i.e. an infinite periodic structure in space.
- Space group operators: elements of the space groups formed by combination of point group operator and translation.

  Seitz operator $\{R/\vec{t}\}$: Successive execution of point group operator R and a translation t. Thus $\{R/0\}$ is a space group operation and $\{E/\vec{t}\}$ is a translation.

  The set of all translations $\{E/\vec{t}\}$ forms a symmetry group contained in the space group. It is a so-called subgroup (see chapter 3), the translational subgroup.

- Crystallographic point groups are those point groups which are compatible with translational symmetry. In fact, there are only 32 crystallographic point groups in 3D space.
- Crystal class: Crystals are assigned to classes according to the crystallographic point group, which they belong to (see section 1.8).

In the following, these concepts will be discussed in detail.

2.4 Two dimensional crystals

Important cases of two dimensional crystalline structures: surfaces and interfaces

(2.4: STM images of surfaces, draw the unit cells)

In a fist step we consider the 2D lattices only. 5 types of lattices:

1. oblique
2. primitive rectangular
3. quadratic
4. hexagonal
5. centered rectangular

(2.5: Draw the different 2D lattices)

(2.6: STM images: determine the lattice type)

Remark: centering is new concept. For lattice 4, the primitive lattice constants are a=b and the angle is $\alpha <> 90°$. It is possible to define the lattice in this way. The symmetry, however, is better reflected by if a rectangular cell is chosen and we introduce the centering. Important both positions of the centered cell are equivalent by definition.

(2.7: Why is there no centered quadratic and no centered oblique lattice?)

2.5 Rotational Symmetry of Crystals

Which rotational symmetries are possible in a periodic structure?

(2.8: Geometric construction: rotational symmetry of crystals)

Only C_1, C_2, C_3 C_4 and C_6 axes are compatible with translational symmetry.

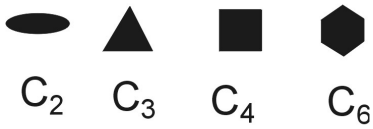
(2.9: Quasicrystals: "forbitten" symmetries in X-ray diffraction patterns)

2.6 The 2D space groups

In order to derive the 2D space groups we start from the five 2D lattices and identify all symmetry elements.

Symbols for symmetry elements:

rotation axes:



reflection plane:

glide reflection:

(2.10: All symmetry elements of the 5 2D lattices)

In a second step we consider the symmetry of the complete crystal, i.e. the lattice plus the content of the unit cell. This procedure is analogous to the 1D case. We start from a given translational lattice and add the symmetry elements, which are compatible with the lattice (see above). We obtain 17 2D space groups.

(2.11: Systematic development of the 2D space groups)

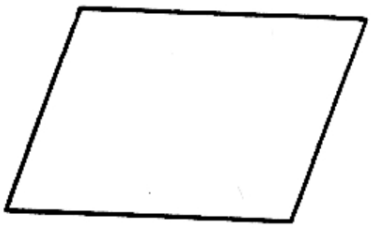
1. p1: (oblique) C_1 only
2. p2: (oblique, *) C_2
3. p3: (hexagonal) three sets of C_3
4. p4: (square) C_4 (two sets of C_2 generated)
5. p6: (hexagonal) C_6 (sets of C_2, C_3 generated)
6. pm: (rectangular) m (mirror plane, additional set of m generated)
7. pmm: (rectangular) perpendicular sets of m (sets of C_2 , n generated, *)

8. pg: (rectangular) glide reflection g (additional set of g generated)
9. pgg: (rectangular) perpendicular sets of g (C_2 generated)
10. pmg: (rectangular) perpendicular sets of m and g (sets of C_2 generated)
11. cm: (centered rectangular) m (g generated)
12. cmm: (centered rectangular) perpendicular sets of m (g, C_2 generated, *)
13. p3m1: (hexagonal) m and C_3 (C_3 generated)
14. p31m: (hexagonal) other m and C_3 (C_3 generated)
15. p4m: (square) m and C_4 (C_2, g, m generated, *)
16. p4g: (sqare) g and C_4 (C_2, g, g generated)
17. p6m: (hexagonal) m and C_6 (C_3, C_2, m generated, *)

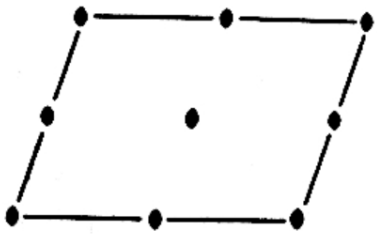
Symmetry diagrams for 2D space groups

(from F. A. Cotton)

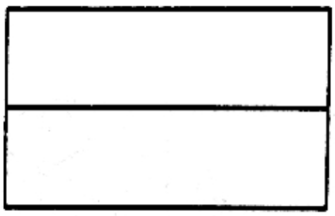
*p*1



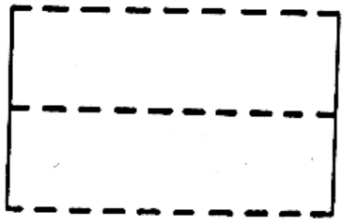
*p*2



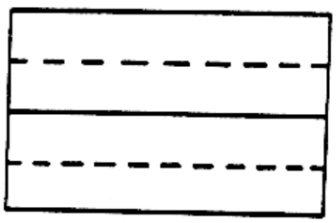
pm



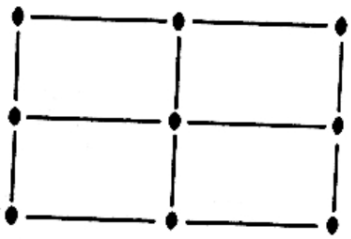
pg



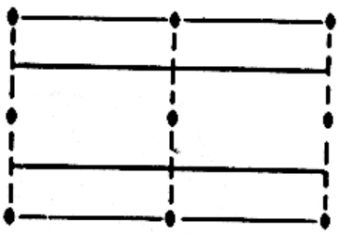
cm



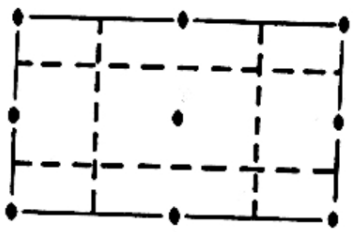
pmm



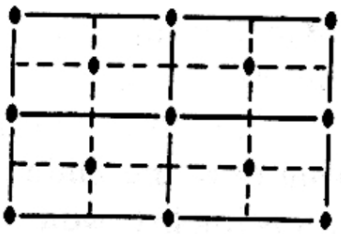
pmg



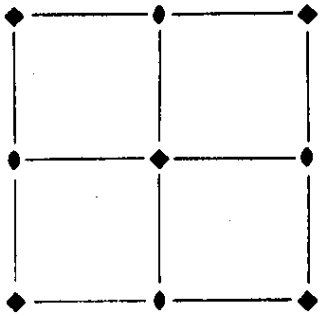
pgg



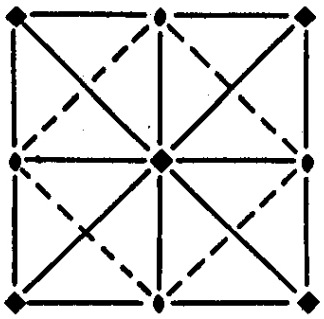
cmm



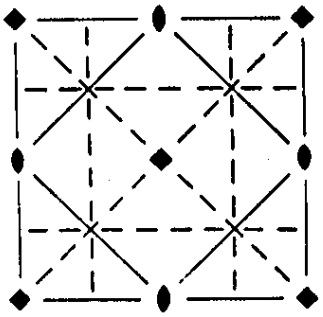
*p*4



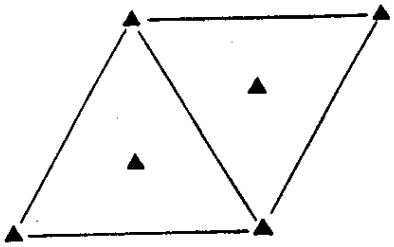
*p*4*m*



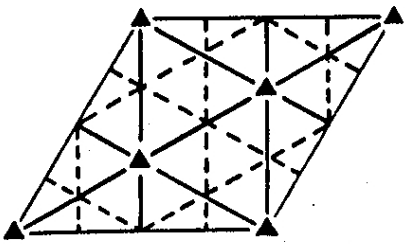
*p*4g



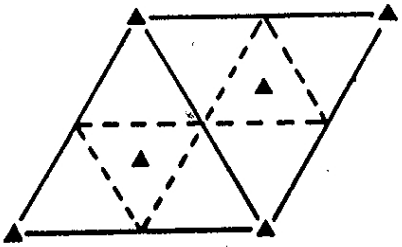
*p*3



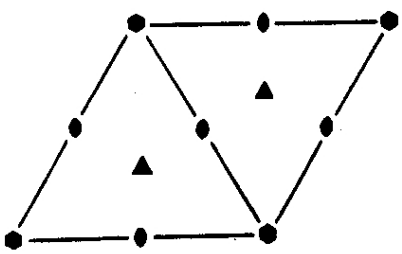
*p*3*m*1



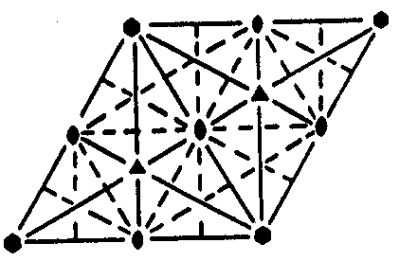
*p*31*m*



*p*6



*p*6*m*



(2.12: 2D patterns: identify symmetry elements, determine 2D space group)

(2.13: STM images: identify symmetry elements, determine 2D space group)

2.7 3D-Lattices

Similar as for the 2D case, we consider the possible lattices in three dimensions, which differ with respect to their symmetry.

In contrast to the 2D case there are three possible types of centering:

- basal plane centering (A, B, C)
- body centering (I)
- face centering (F)

(2.14: 14 Bravais lattices)

1. Triclinic lattice: $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$: only symmetry element: i; centering would not help, as the symmetry of the unit cell would remain the same, therefore only P (primitive).
2. Monoclinic lattice: $a \neq b \neq c$, $\alpha = \beta = 90° \neq \gamma$: C_2 and m are generated. Possible centering: P and I (latter is equivalent to a A or B centering)

(2.15: monoclinic lattice with I or A centering)

3. Orthorhombic lattice: $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$: more C_2 and m are generated. Possible centering: P, I, C, F
4. Tetragonal lattice: $a = b \neq c$, $\alpha = \beta = \gamma = 90°$: C_4 axis, etc.; possible centering: P, I
5. Cubic lattice: $a = b = c$, $\alpha = \beta = \gamma = 90°$: several C_4 axis, etc.; possible centering: P, I, F
6. Hexagonal / trigonal (rhombohedral) lattice: $a = b \neq c$, $\alpha = \beta = 90°$; $\gamma = 120°$: several C_3 and / or C_3 axes, etc.; possible lattices: P and rhombohedral lattice

(2.16: relation between the hexagonal and the rhombohedral lattice)

These 7 types of lattices (differentiating between trigonal and hexagonal) are denoted as the crystal systems and the 14 types of lattices the Bravais lattices.

2.8 Crystal classes

We consider the set of all space group operations $\{R|\vec{t}\}$ and set $\vec{t} = 0$. The remaining set of operations $\{R|0\}$ form the (entire) point group of the space group. Crystals are often classified via their point group, the corresponding group is denoted as the crystal class. Note: One has to be careful: not all operations of the space group are also operations of the point group, because translations belonging to glide reflections are simply disregarded. The reason to define something like a crystal class is that the macroscopic properties of a crystal are related to the point group. The reason is simply that translations of a crystals by fractions of a lattice constant do not play a role for its macroscopic properties.

There are 32 point groups which are compatible with translational sysmmetry, which we denote as the crystallographic point groups. In contrast to the symmetry of molecules the so-called crystallographic nomenclatures is used here:

- A rotoinversion $\bar{n}$ is defined instead of a rotoreflection S_m: rotation by $2\pi/n$ followed bei inversion at a center on the axis.

  relation between rotoreflection S_m and rotoinversion $\bar{n}$:

  $\bar{1} \triangleq S_2 \triangleq i$

  $\bar{2} \triangleq S_1 \triangleq \sigma$, usually written as m (mirror plane)

  $\bar{3} \triangleq S_6$

  $\bar{4} \triangleq S_4$

  $\bar{6} \triangleq S_3$

- Rotation axes C_n are simply indicated by n.

- / means "perpendicular". Example: 2/m: 2-fold axis perpendicular to mirror plane (read "two upon m").
- Only those elements are indicated, which generate the point groups symmetry.

(Actually there are some more details connected with this nomenclature, which can be found the literature).

Crystallographic point groups with Schönfliess and international symbols:

Number	Schönflies Symbol	Crystallographic Symbol	Crystal System
1	C_1	$\bar{1}$	Triclinic
2	C_i	1	
3	C_s	m	Monoclinic
4	C_2	2	
5	C_{2h}	$2/m$	
6	C_{2v}	mm	Orthorhombic
7	D_2	222	
8	D_{2h}	mmm	
9	C_4	4	Tetragonal
10	S_4	$\bar{4}$	
11	C_{4h}	$4/m$	
12	C_{4v}	$4mm$	
13	D_{2d}	$\bar{4}2m$	
14	D_4	422	
15	D_{4h}	$4/mmm$	
16	C_3	3	Trigonal—Hexagonal
17	S_6	$\bar{3}$	
18	C_{3v}	$3m$	
19	D_3	32	
20	D_{3d}	$\bar{3}m$	
21	C_{3h}	$\bar{6}$	
22	C_6	6	
23	C_{6h}	$6/m$	
24	D_{3h}	$\bar{6}m2$	
25	C_{6v}	$6mm$	
26	D_6	622	
27	D_{6h}	$6/mmm$	
28	T	23	Cubic
29	T_h	$m3$	
30	T_d	$\bar{4}3m$	
31	O	432	
32	O_h	$m3m$	

The 32 crystallographic point groups can be assigned to the crystal systems. Here, the purel lattices themselves always have the highest point group symmetry. By filling the lattice with molecules, some of he symmetry elements might be destroyed and the symmetry is reduced.

2.9 Additional symmetry elements in crystals: glide planes and screw axes

- glide planes: Translation by fraction of a lattice vector, followed by reflection with respect to a plane.
    - axial glide plane (a,b,c): translation by $\vec{t} = \vec{a}/2$ (primitive lattice vector $\vec{a}$), followed by m parallel to $\vec{t}$
    - axial glide plane (n): translation by $\vec{t} = (\vec{a} + \vec{b})/2$ or $(\vec{t} = (\vec{a} + \vec{b} + \vec{c})/2$ (primitive lattice vectors $\vec{a}, \vec{b}, \vec{c}$), followed by m parallel to $\vec{t}$
    - diamond glide plane (d): translation by $\vec{t} = (\vec{a} + \vec{b})/4$ or $(\vec{t} = (\vec{a} + \vec{b} + \vec{c})/4$ (primitive lattice vectors $\vec{a}, \vec{b}, \vec{c}$), followed by m parallel to $\vec{t}$

(2.17: d glide planes in diament)

- screw axes: rotation with respect to n-fold axis followed by translation along the axis by a fraction of the lattice vector.

  Symbol n_m: After n operations full rotation and translation by m lattice vectors

  The following scew axes are possible in a 3D crystal:

  2_1,

  3_1, 3_2,

  4_1, 4_2, 4_3,

  6_1, 6_2, 6_3, 6_4, 6_5

(2.18: representation of screw axes)

2.10 Standard symbols for space group elements

(from F. A. Cotton)

Element	Symbol	⊥ to Projection Plane	In or ∥ to Projection Plane
Simple mirror	m	———	or
Axial glide	$a,b,c,$	(glide in projection plane) / (glide ⊥ to projection plane)	or / or
Diagonal glide	n	-·-·-·-	
Diamond glide	d		
Center of inversion	$\bar{1}$	○	
Rotation axis	2, 3, 4, 6		
Rotation–inversion axis	$\bar{3}$, $\bar{4}$, $\bar{6}$		
Screw axis	2_1		
	3_1, 3_2		
	4_1, 4_2, 4_3		
	6_1, 6_2, 6_3, 6_4, 6_5		

2.11 The 3D space groups

By from the 14 Bravais lattices and successively adding symmetry elements compatible with the lattice, it is possible to derive the 230 3D space groups in an analogous fashion as for the 2D case (by combination with the pure point group operation one obtains the 73 so-called symmorphic space groups, by considering glide planes and screw axes as well, one finds 157 more space groups, the so-called non-symmorphic groups). Not surprisingly the procedure is lengthy.

Nomenclature in international notation:

- Centering: (P, C, I, F).

- 3 Symbols representing symmetry along up to three direction (nomenclature according to section 2.8).
- Symbols are often abbreviated, if possible without ambiguity (e.g. pm instead of p1m1).

Determination of the space group plays a big role e.g. for X-ray crystallography: The presence or absence of certain diffraction spots provides information on the presence or absence of symmetry elements.

(2.19: systematic absence of diffraction spots)

2.12 International tables for X-ray crystallography

All details on all space groups are summarized in a book named

"International Tables for X-Ray Crystallography",

International Union of Crystallography, Riedel, Dortrecht/Boston

Some of the information given is:

1. International symbol for space group
2. Schönfliess symbol
3. crystal system
4. crystal class
5. general point diagram: projection of unit cell, with all equivalent point positions indicated. "+" means z>0, "-" means z<0; "," means point is "inverted" (mirror operation or inversion).
6. symmetry diagram: symmetry elements of the unit cell using the symbols given in section 1.10.

7. List of point position (general points first, then special points):
    a. Multiplicity (number of equivalent points)
    b. “Wyckoff symbol“
    c. Point symmetry at the given site
    d. Coordinates of the points
8. Special conditions for the appearance for diffraction reflexes

(2.20: example from “International Tables for X-Ray Crystallography”)