Applications of X-ray and Neutron Scattering in Biological Sciences:

Symmetry in direct and reciprocal space
2012

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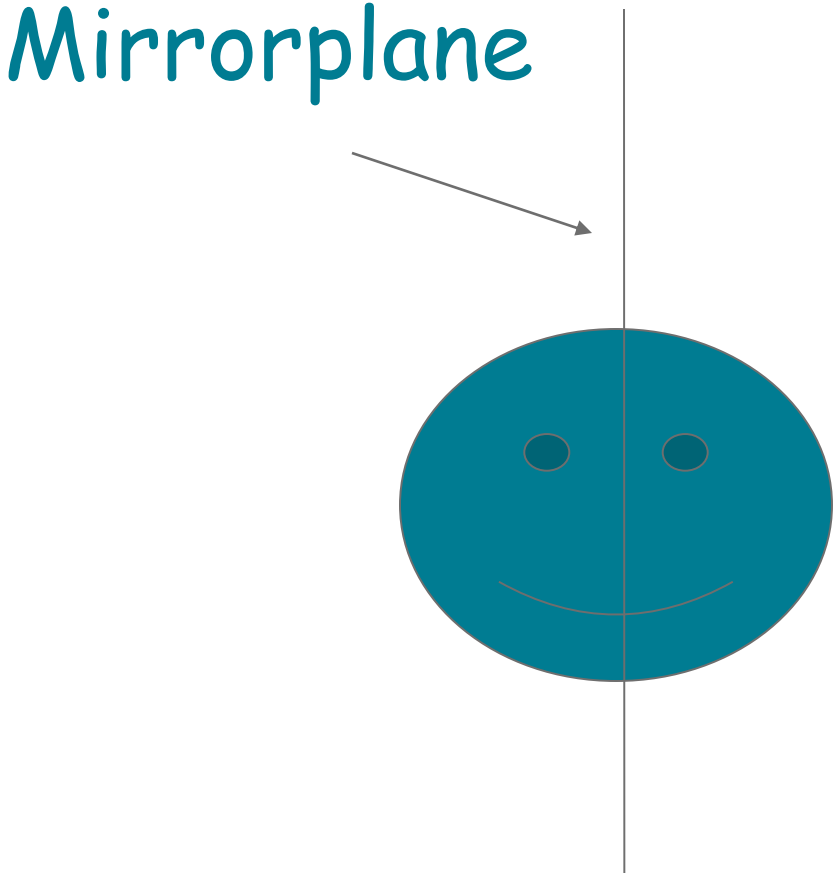
Biostructural Research

Mirror plane symmetry



Symmetry elements: rotation

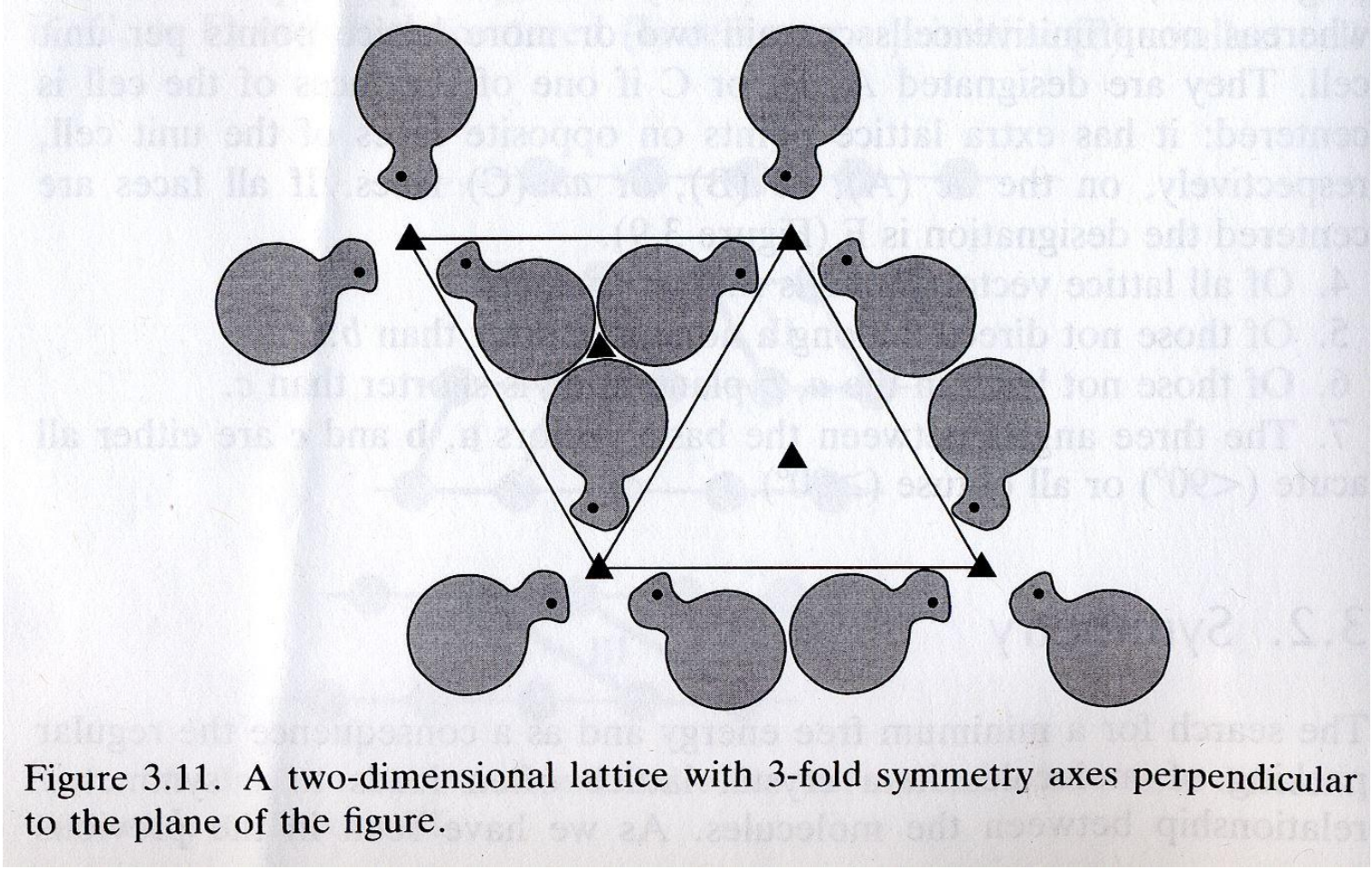
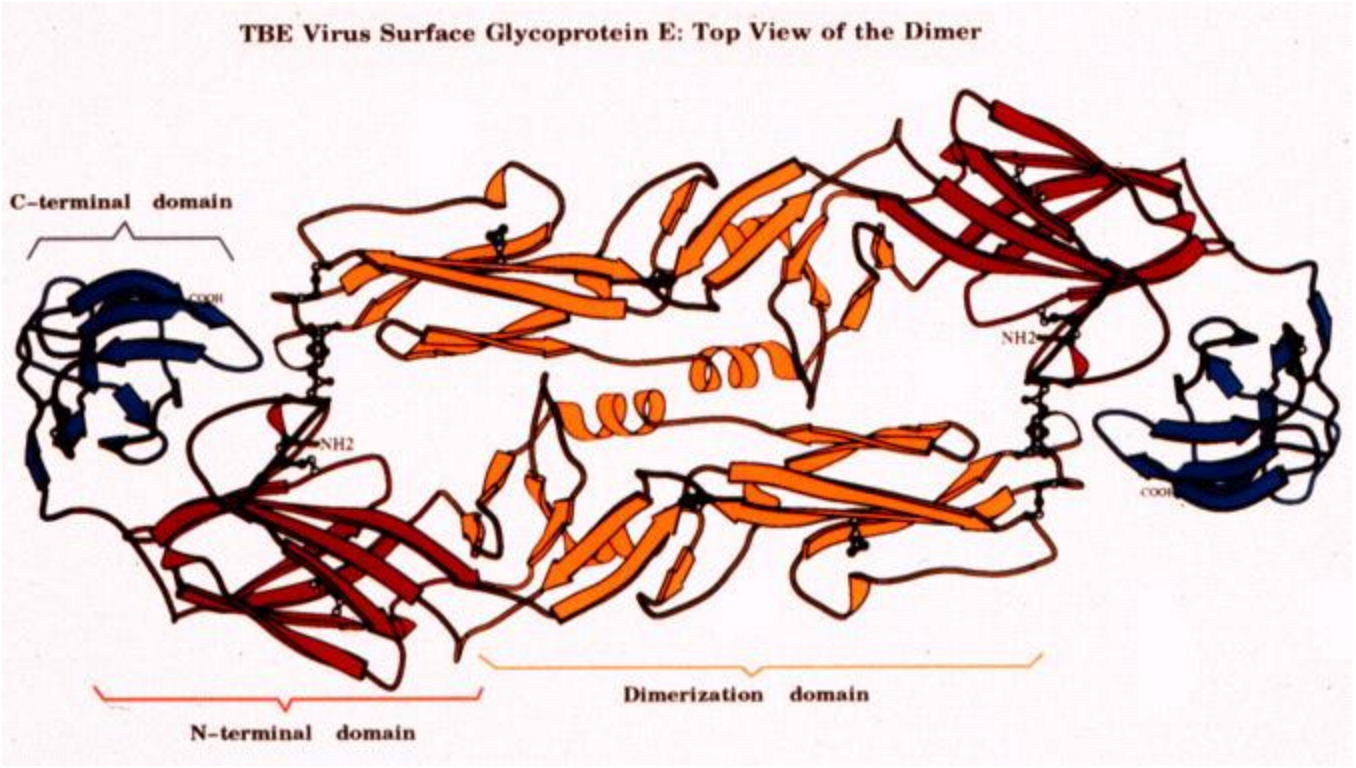


Figure 3.11. A two-dimensional lattice with 3-fold symmetry axes perpendicular to the plane of the figure.

Biomolecules display rotational symmetry

- Protein from virus shell display 2-fold symmetry

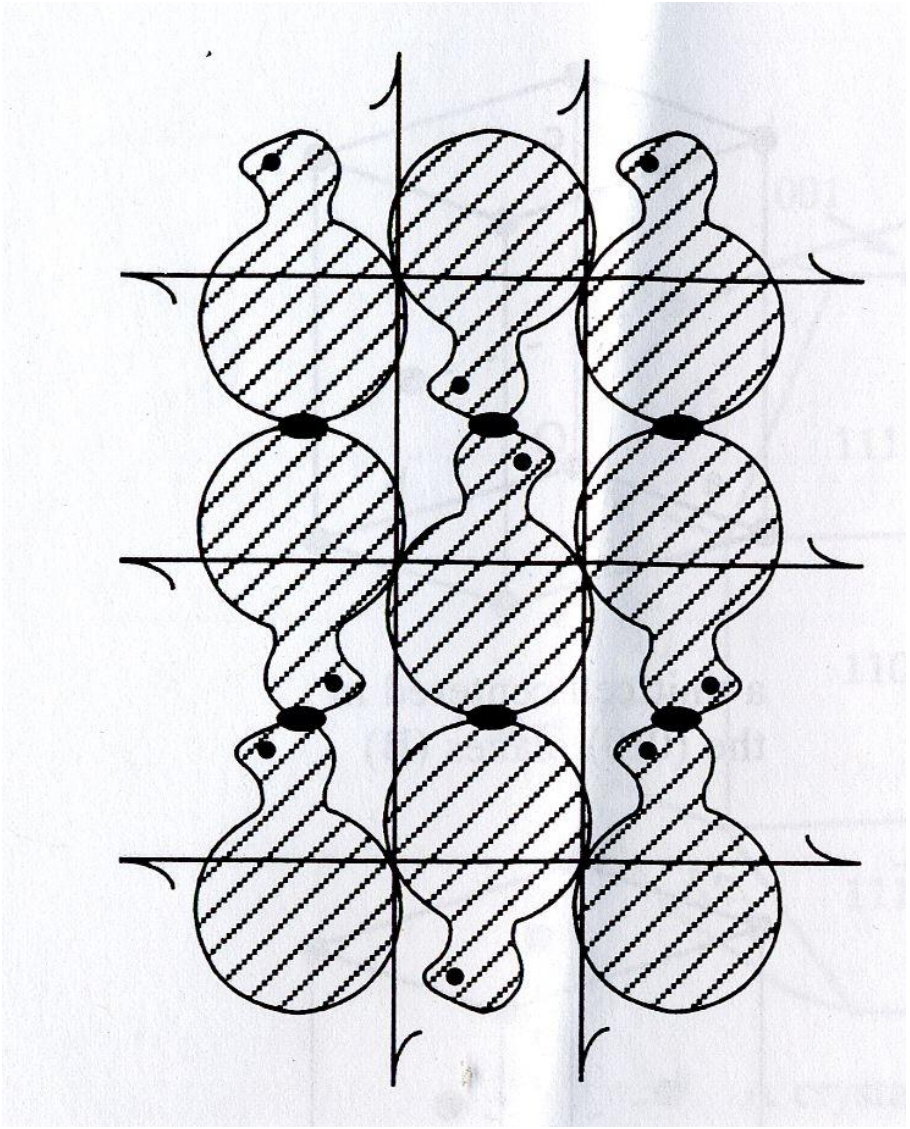


Symmetry Elements

Translation

moves all the points in the asymmetric unit the same distance in the same direction. This has no effect on the handedness of figures in the plane. There are no invariant points (points that map onto themselves) under a translation.

Rotational and translational symmetry



Screw axis

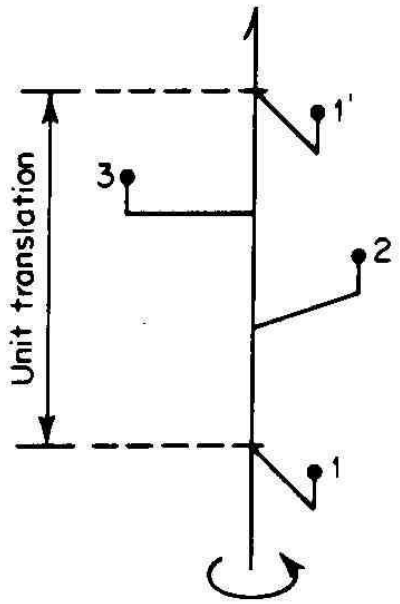
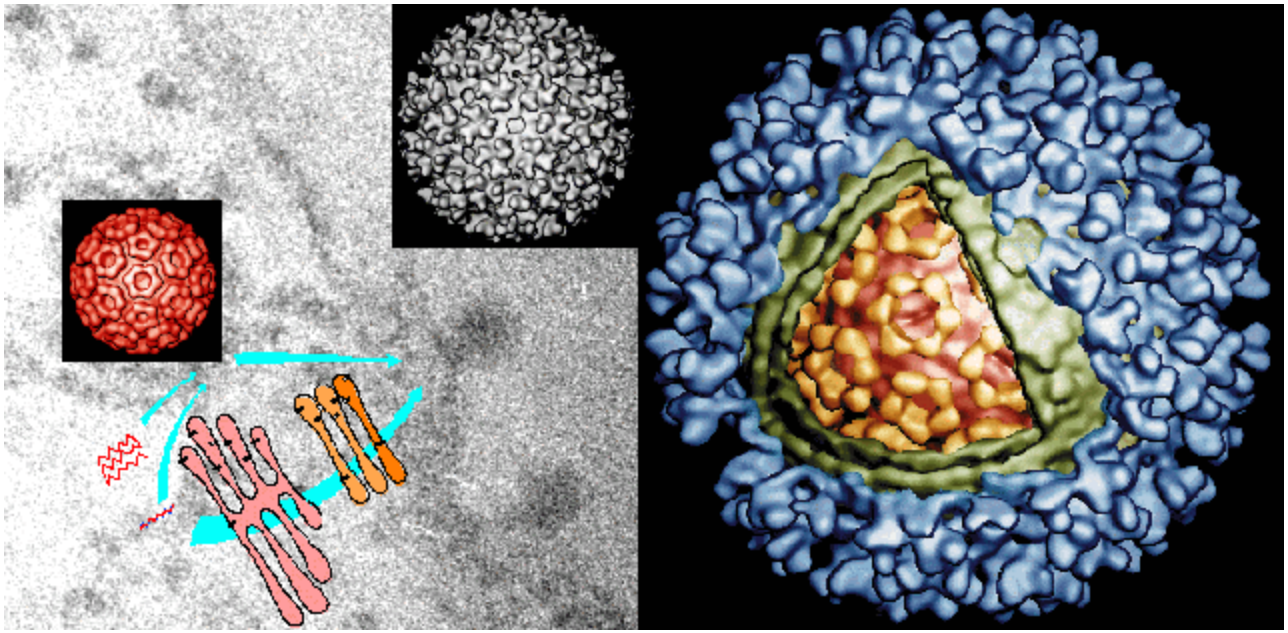


Figure 3.20. Screw axis 3_1.

120° rotation
1/3 unit cell translation

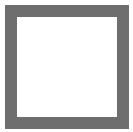
A virus has a high symmetry



Point groups

- All symmetry operations associated with a molecules forms a point group. This groups completely describes the symmetry of the molecule
- Some point groups only contain rotations: These are called C_2, C_3 etc.
- Molecules with a principal symmetry axis of order n and n orthogonal to-fold symmetry axis's belong to the D point groups (D_2 etc.)
- Higher symmetries are octahedral and icosahedral

Cyclobutan is D_4



Point group symmetry diagrams

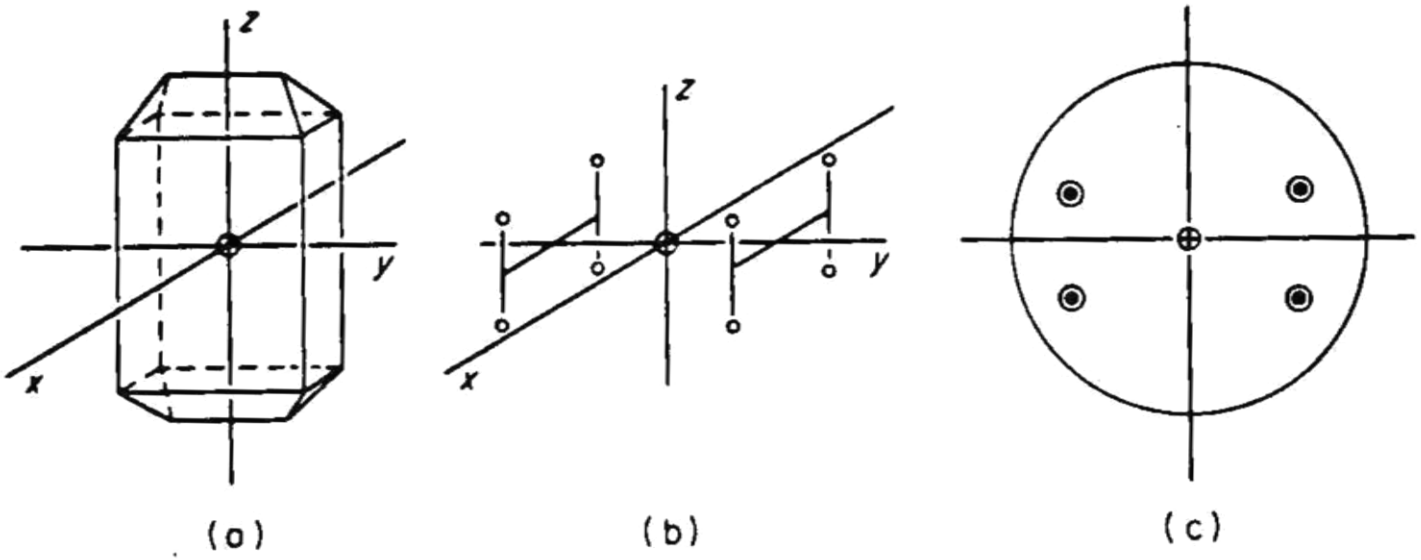


Figure 3.18. (*a*) Crystal with symmetry *mmm*. (*b*) Set of points related by symmetry *mmm*. (*c*) Plane representation of symmetry *mmm*.

There are a total of 32 point groups

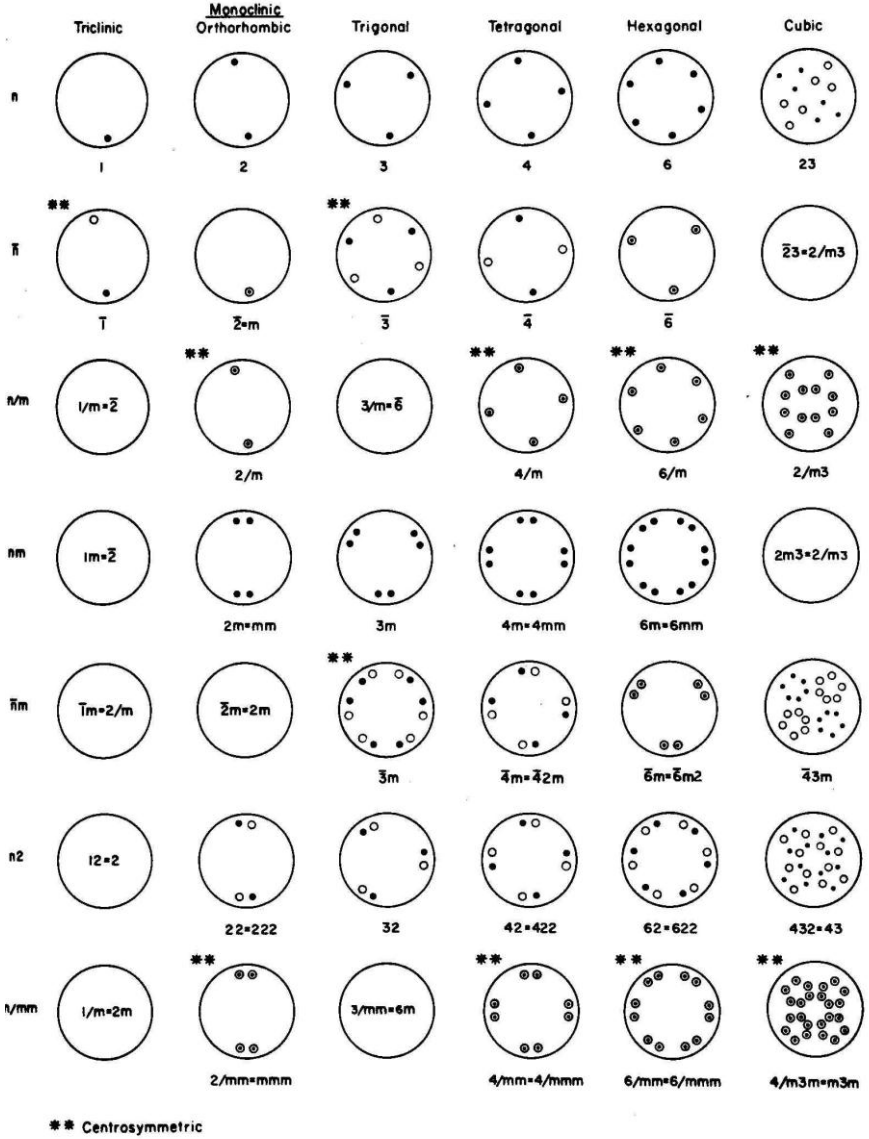
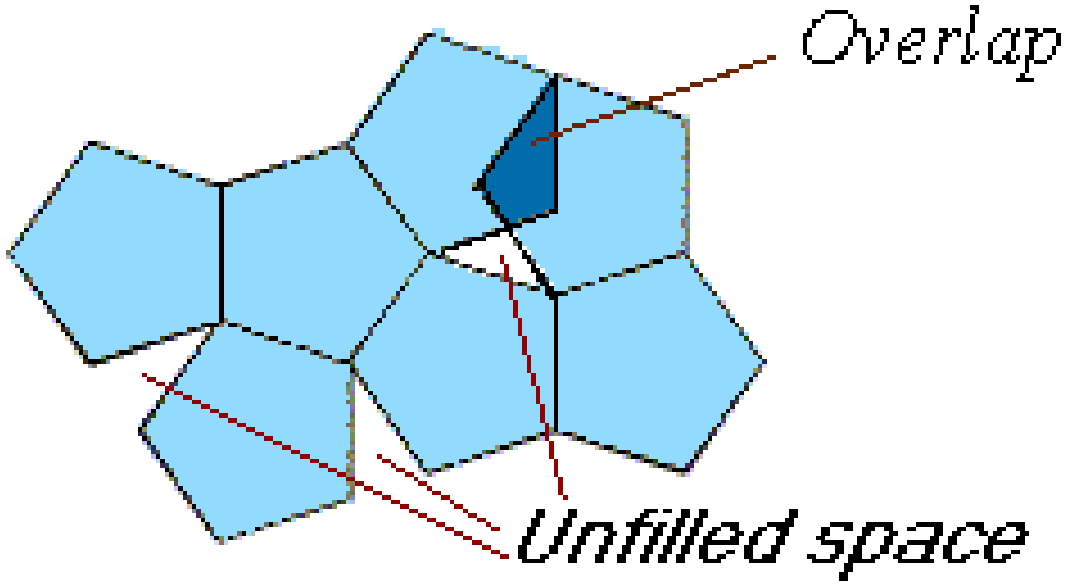


Figure 3.19. Plane representations of the 32 point groups.

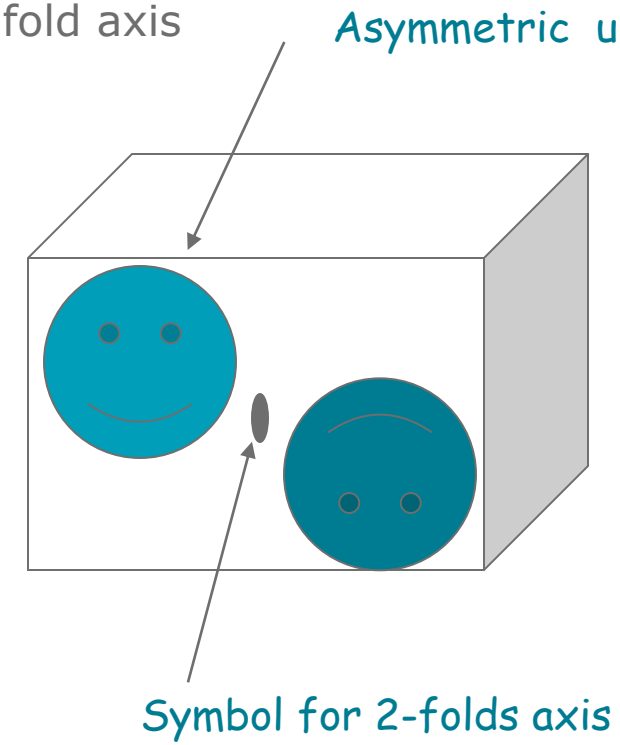
N-fold axes with n=5 or n>6 does not occur in crystals



Adjacent spaces must be completely filled (no gaps, no overlaps).

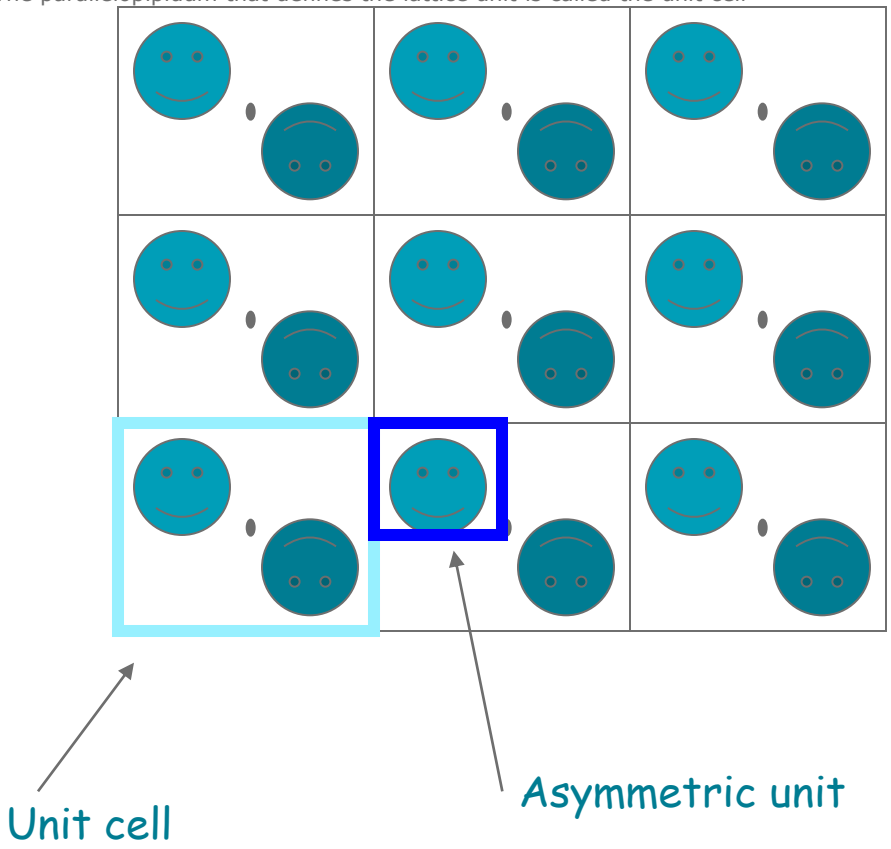
Asymmetric unit

- Any symmetric object can bed reduced to an asymmetric unit
- We can use symmetri operations to build up a lattice motif: E.g a 2-fold axis



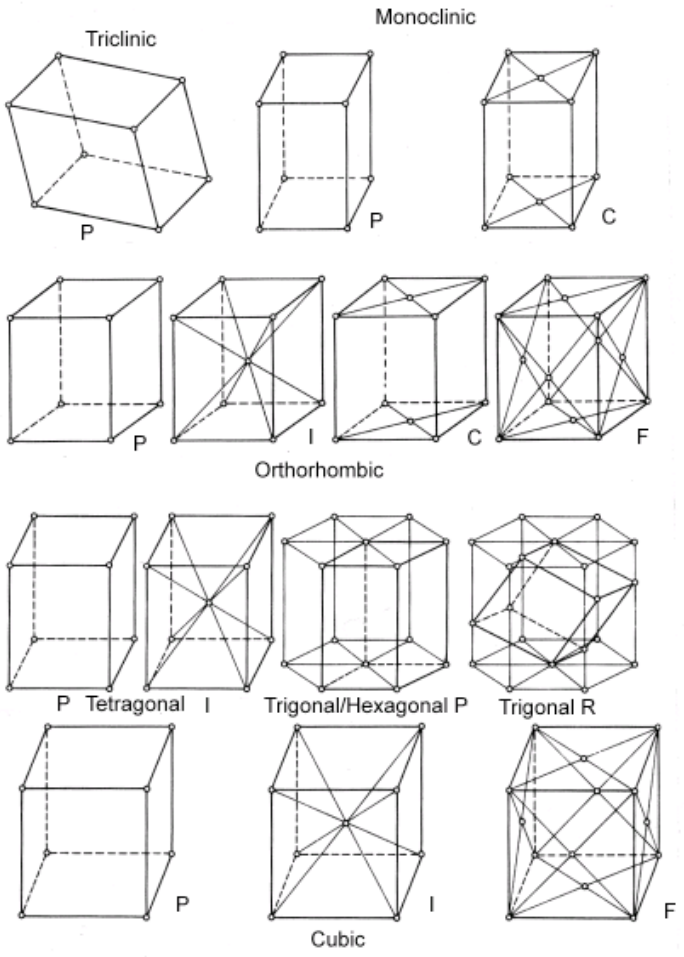
Crystals

- The crystal is build by translating the lattice motif in all 3 spatial directions
- The crystal is a lattice. The parallelopipidum that defines the lattice unit is called the unit cell



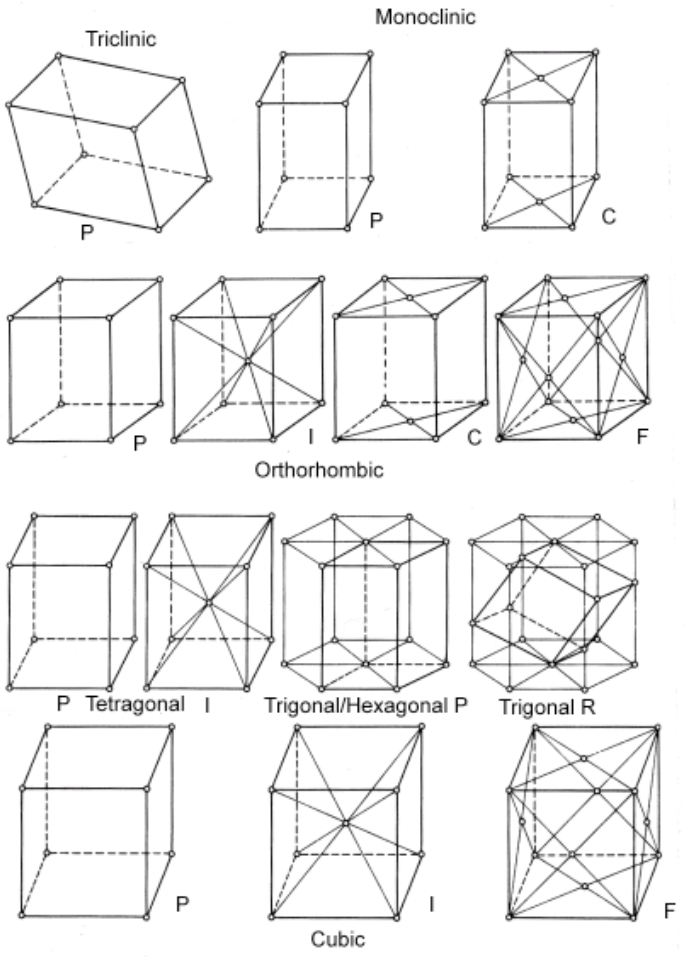
Bravais-lattices

- Lattices has to fill all space. Th
  Bravais lattices
- Some are centered



Bravais-lattices II

- The unit cell form restricts which symmetry oper
  unit cell
- Triclinic: Only inversion center (combination of
- Monoclinic: Only 2-fold axis
- Orthorhombic: 3 mutually orthogonal 2-fold axis
- Tetragonal: 4-fold axis
- Hexagonal: 3/6 fold axis's
- Cubic: 3 and 4-folds

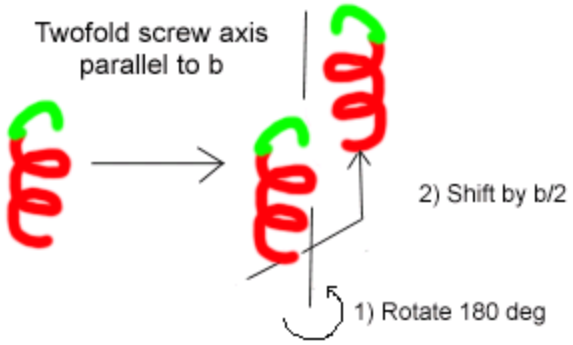


Crystal systems

- Bravais lattices are grouped in crystal systems

Space groups

- If you combine the 13 Bravais lattices with the possible rotations (2,3,4,6-fold rotation) including screw axis's 2_1, 3_1,3_2, 4_1, 4_2,4_3, 6_1, 6_2, 6_3, 6_4, 6_5) and mirror planes you get 230 space groups



230 space groups

TRICLINIC

P 1	P -1

MONOCLINIC

P 2	P 21	C 2	P M	P C
C M	C C	P 2/M	P 21/M	C 2/M
P 2/C	P 21/C	C 2/C		

ORTHORHOMBIC

P 2 2 2	P 2 2 21	P 21 21 2	P 21 21 21	C 2 2 21
C 2 2 2	F 2 2 2	I 2 2 2	I 21 21 21	P M M 2
P M C 21	P C C 2	P M A 2	P C A 21	P N C 2
P M N 21	P B A 2	P N A 21	P N N 2	C M M 2
C M C 21	C C C 2	A M M 2	A B M 2	A M A 2
A B A 2	F M M 2	F D D 2	I M M 2	I B A 2
I M A 2	P M M M	P N N N	P C C M	P B A N
P M M A	P N N A	P M N A	P C C A	P B A M
P C C N	P B C M	P N N M	P M M N	P B C N
P B C A	P N M A	C M C M	C M C A	C M M M
C C C M	C M M A	C C C A	F M M M	F D D D
I M M M	I B A M	I B C A	I M M A	

TETRAGONAL

P 4	P 41	P 42	P 43	I 4
I 41	P -4	I -4	P 4/M	P 42/M
P 4/N	P 42/N	I 4/M	I 41/A	P 4 2 2
P 4 21 2	P 41 2 2	P 41 21 2	P 42 2 2	P 42 21 2
P 43 2 2	P 43 21 2	I 4 2 2	I 41 2 2	P 4 M M
P 4 B M	P 42 C M	P 42 N M	P 4 C C	P 4 N C
P 42 M C	P 42 B C	I 4 M M	I 4 C M	I 41 M D
I 41 C D	P -4 2 M	P -4 2 C	P -4 21 M	P -4 21 C
I -4 M 2	P -4 C 2	P -4 B 2	P -4 N 2	P -4 M 2
I -4 C 2	P -4 2 M	I -4 2 D	P 4/M M M	P 4/M C C
P 4/N B M	P 4/N N C	P 4/M B M	P 4/M N C	P 4/N M M
P 4/N C C	P 42/M M C	P 42/M C M	P 42/N B C	P 42/N N M
P 42/M B C	P 42/M N M	P 42/N M C	P 42/N C M	I 4/M M M
I 4/M C M	I 41/A M D	I 41/A C D		

TRIGONAL

P 3	P 31	P 32	R 3	P -3
R -3	P 3 1 2	P 3 2 1	P 31 1 2	P 31 2 1
P 32 1 2	P 32 2 1	R 3 2	P 3 M 1	P 3 1 M
P 3 C 1	P 3 1 C	R 3 M	R 3 C	P -3 1 M
P -3 1 C	P -3 M 1	P -3 C 1	R -3 M	R -3 C

HEXAGONAL

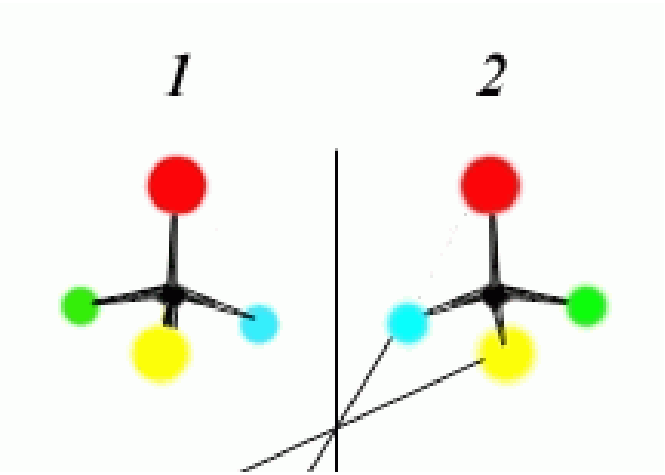
P 6	P 61	P 65	P 62	P 64
P 63	P -6	P 6/M	P 63/M	P 6 2 2
P 61 2 2	P 65 2 2	P 62 2 2	P 64 2 2	P 63 2 2
P 6 M M	P 6 C C	P 63 C M	P 63 M C	P -6 M 2
P -6 C 2	P -6 2 M	P -6 2 C	P 6/M M M	P 6/M C C
P 63/M C M	P 63/M M C			

CUBIC (minus sign in front of triade optional)

P 2 3	F 2 3	I 2 3	P 21 3	I 21 3
P M 3	P N 3	F M 3	F D 3	I M 3
P A 3	I A 3	P 4 3 2	P 42 3 2	F 4 3 2
F 41 3 2	I 4 3 2	P 43 3 2	P 41 3 2	I 41 3 2
P -4 3 M	F -4 3 M	I -4 3 M	P -4 3 N	F -4 3 C
I -4 3 D	P M 3 M	P N 3 N	P M 3 N	P N 3 M
F M 3 M	F M 3 C	F D 3 M	F D 3 C	I M 3 M
I A 3 D				

Chiral space groups

- Mirror planes and centers of inversion change the handedness of molecules
- Chiral molecules (like protei groups with such symmetry



65 chiral space groups

Triklin				
P 1				
Monoklin				
P 2	P 21	C 2		
Orthorhombisk				
P 2 2 2	P 2 2 21	P 21 21 2	P 21 21 21	C 2 2 21
C 2 2 2	F 2 2 2	I 2 2 2	I 21 21 21	
Tetragonal				
P 4	P 41	P 42	P 43	I 4
I 41	P 4 2 2			
P 4 21 2	P 41 2 2	P 41 21 2	P 42 2 2	P 42 21 2
P 43 2 2	P 43 21 2	I 4 2 2	I 41 2 2	
Trigonal				
P 3	P 31	P 32	R 3	
P 3 1 2	P 3 2 1	P 31 1 2	P 31 2 1	
P 32 1 2	P 32 2 1	R 3 2		
Hexagonal				
P 6	P 61	P 65	P 62	P 64
P 63	P 6 2 2			
P 61 2 2	P 65 2 2	P 62 2 2	P 64 2 2	P 63 2 2
Kubisk				
P 2 3	F 2 3	I 2 3	P 21 3	I 21 3
P 4 3 2	P 42 3 2	F 4 3 2		
F 41 3 2	I 4 3 2	P 43 3 2	P 41 3 2	I 41 3 2

Coordinate triplets, equivalent positions

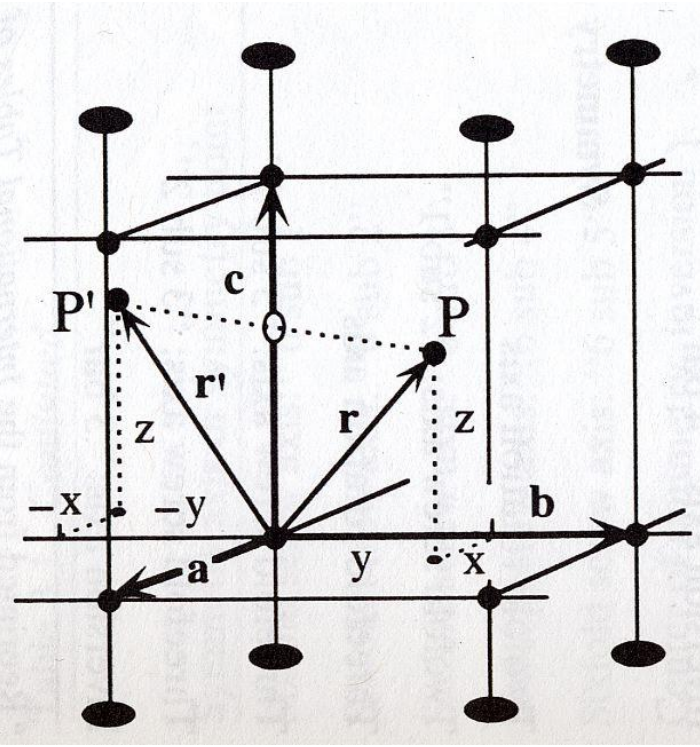


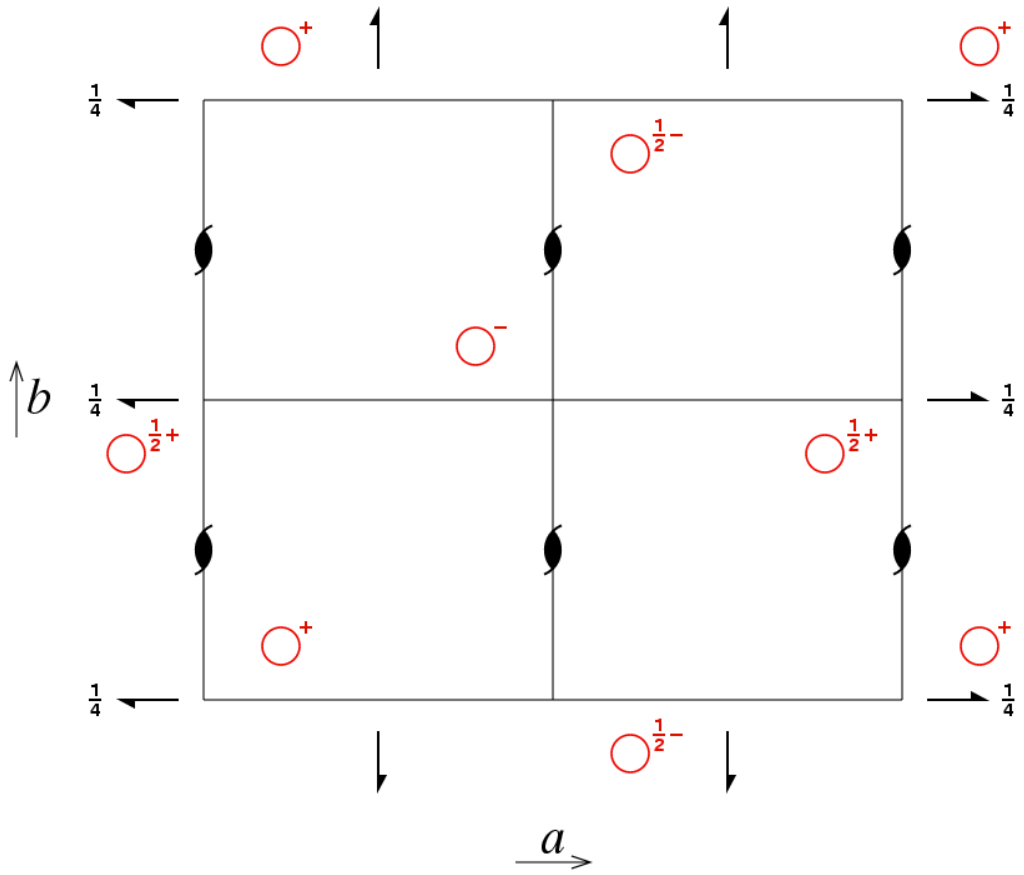
Figure 3.15. This crystal has a 2-fold axis along c. The point P with coordinate triplet x, y, z, is related by the symmetry operation to point P' with coordinate triplet $-x, -y, z$.

$\mathbf{r} = \mathbf{a}x + \mathbf{b}y + \mathbf{c}z,$

Therefore, each point can be described by its fractional coordinates, that is, by its coordinate triplet (x, y, z)

A diagram from International Table of Crystallography

$P2_12_12_1$ $P\,2_1\,2_1\,2_1$ 222 No. 19



1 x, y, z

2 $\frac{1}{2}+x, \bar{y}, \frac{1}{2}-z$

3 $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$

4 $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$

Identification of the Space Group is called indexing the crystal. The International Tables for X-ray Crystallography tell us a huge amount of information about any given space group. For instance, If we look up space group P2, we find it has a 2-fold rotation axis and the following symmetry equivalent positions:

```
 X   ,  Y   ,  Z
-X   ,  Y   , -Z
```

and an asymmetric unit defined by:

$$0 \leq x \leq 1$$
$$0 \leq y \leq 1$$
$$0 \leq z \leq 1/2$$

An interactive tutorial on Space Groups can be found on-line in Bernhard Rupp's Crystallography 101 Course: http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm

Rotation matrices and translation vectors

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ ½ \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z + ½ \end{pmatrix}$$

$$\mathbf{R \cdot x + t = x'}$$

Two equivalent positions ($x\ y\ z$) and ($-x\ -y\ z+½$) are related by a rotation matrix **R** and a translation matrix **t**.

Space group P1

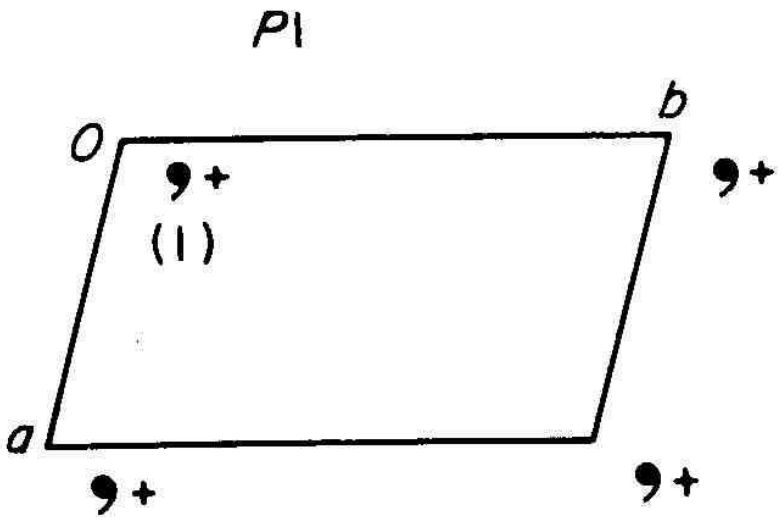


Figure 3.23. *P*1, equivalent positions *x*, *y*, *z*.

Point group 1 + Bravais lattice P1

Space group P1bar

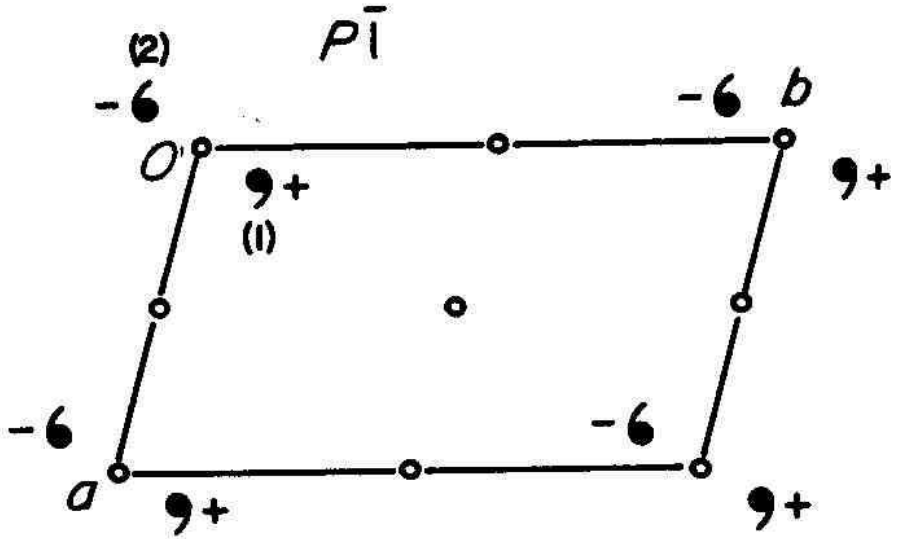


Figure 3.24. $P\bar{1}$, equivalent positions (1) x, y, z; (2) $\bar{x}, \bar{y}, \bar{z}$.

Point group 1bar + Bravais lattice P1

Space group P2

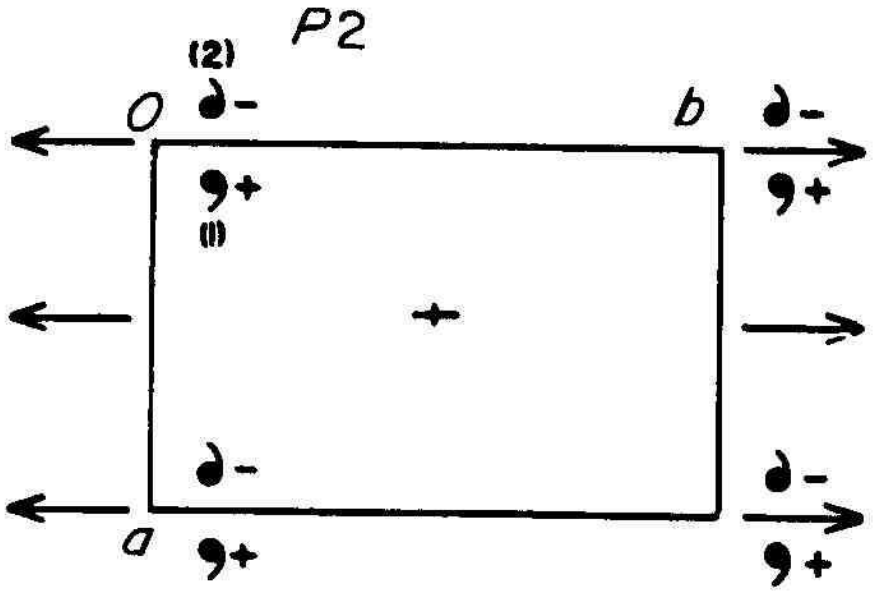


Figure 3.25. $P2$, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}$.

Point group 2 + Bravais lattice “primitive monoclinic”

Space group $P2_1$

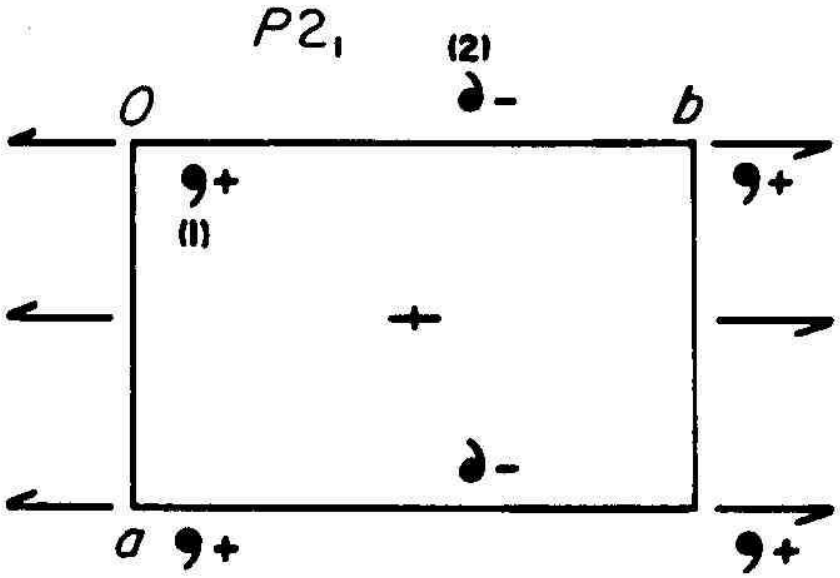
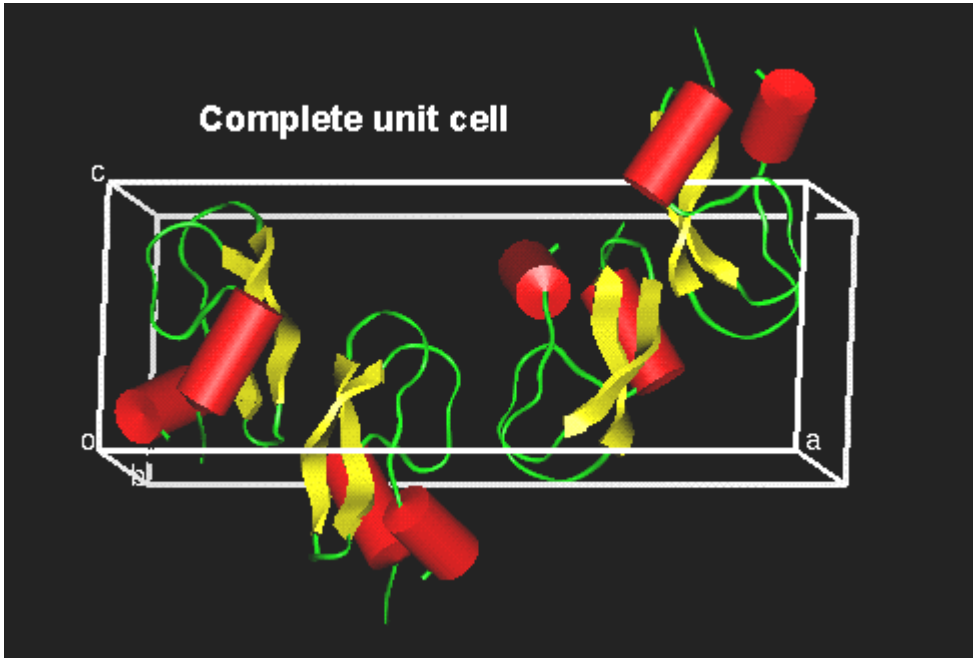


Figure 3.26. $P2_1$, equivalent positions (1) x, y, z; (2) $\bar{x}, y+\frac{1}{2}, \bar{z}$.

Point group 2 + Bravais lattice "primitive monoclinic", but consider screw axis

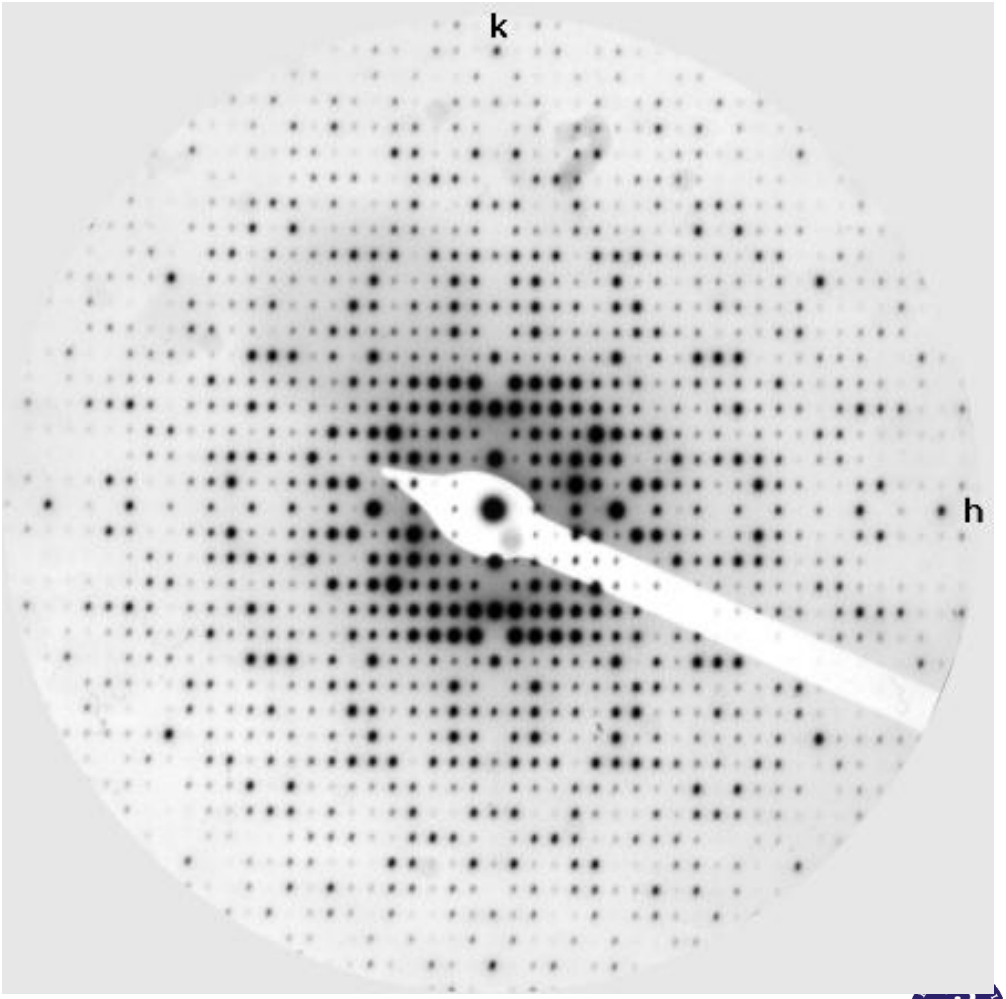
BPTI example from Livermore lab III



Systematic absences

This SAED pattern of Ta_2P shows mm-, but not 4-fold symmetry as seen from the intensities of diffraction spots.

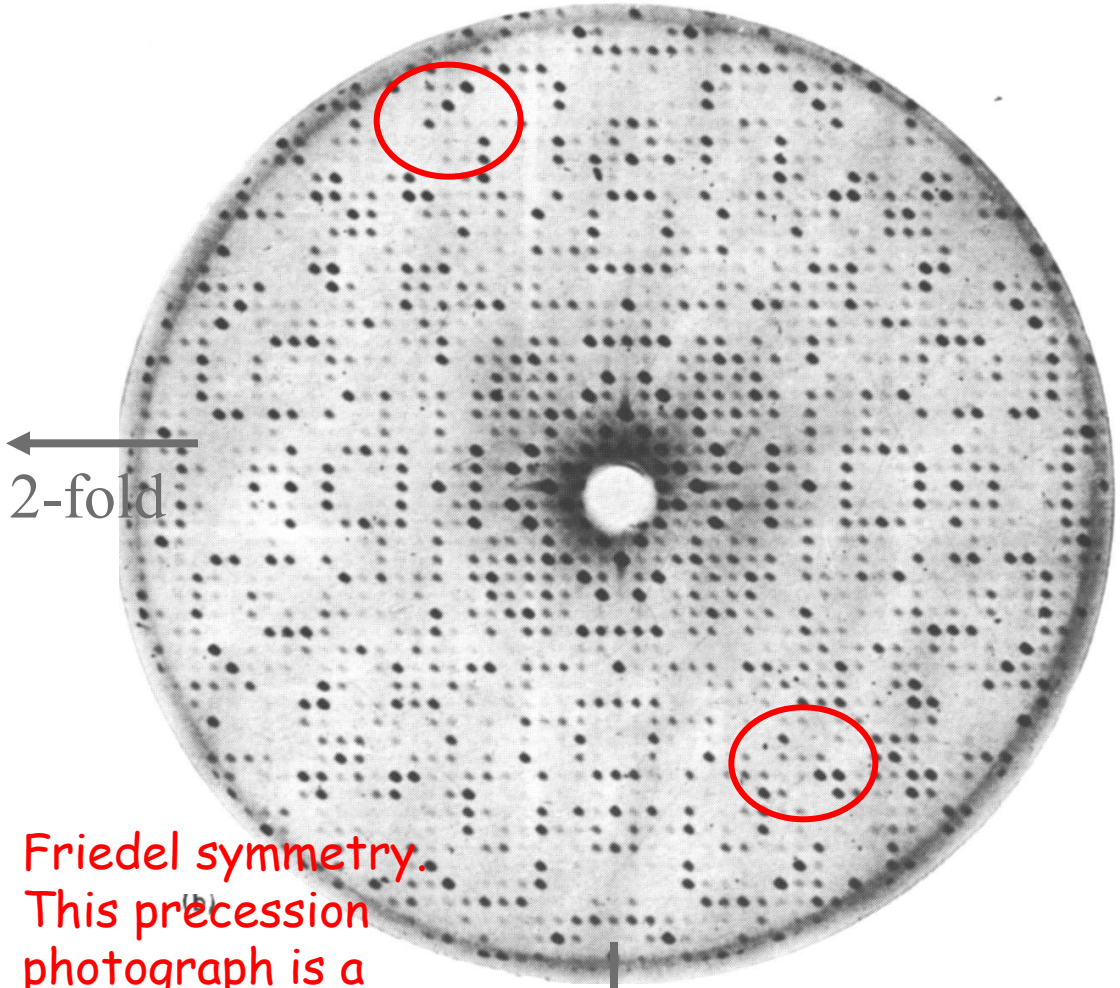
Notice that all odd reflections along both the h and k axes are absent. This shows there must be 2_1 screw axes along and/or glide planes perpendicular to both axes. The very faint forbidden reflections (9 0) and (-9 0) are caused by multiple diffraction.



Symmetry of the Diffraction Pattern

The diffraction pattern has almost the same symmetry as the crystal. One important difference is that the diffraction pattern also contains a center of inversion (Friedel symmetry). The combination of rotational symmetry and a center of inversion can give rise to mirror plane symmetry in the diffraction pattern – which of course is not possible in the crystal.

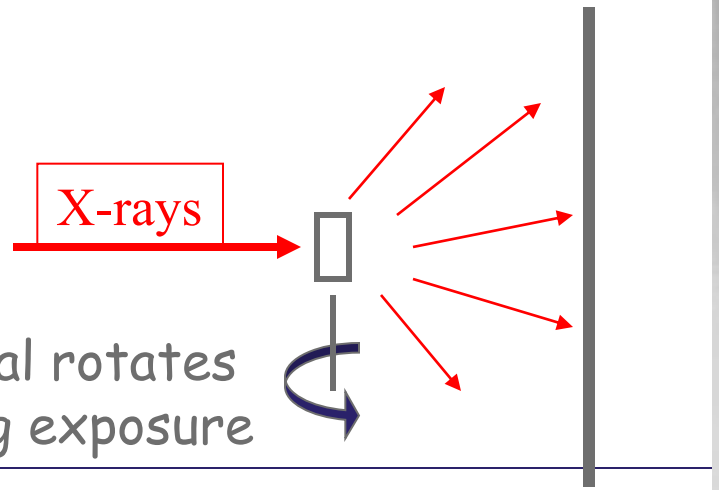
The diffraction pattern looses information about translational symmetry.



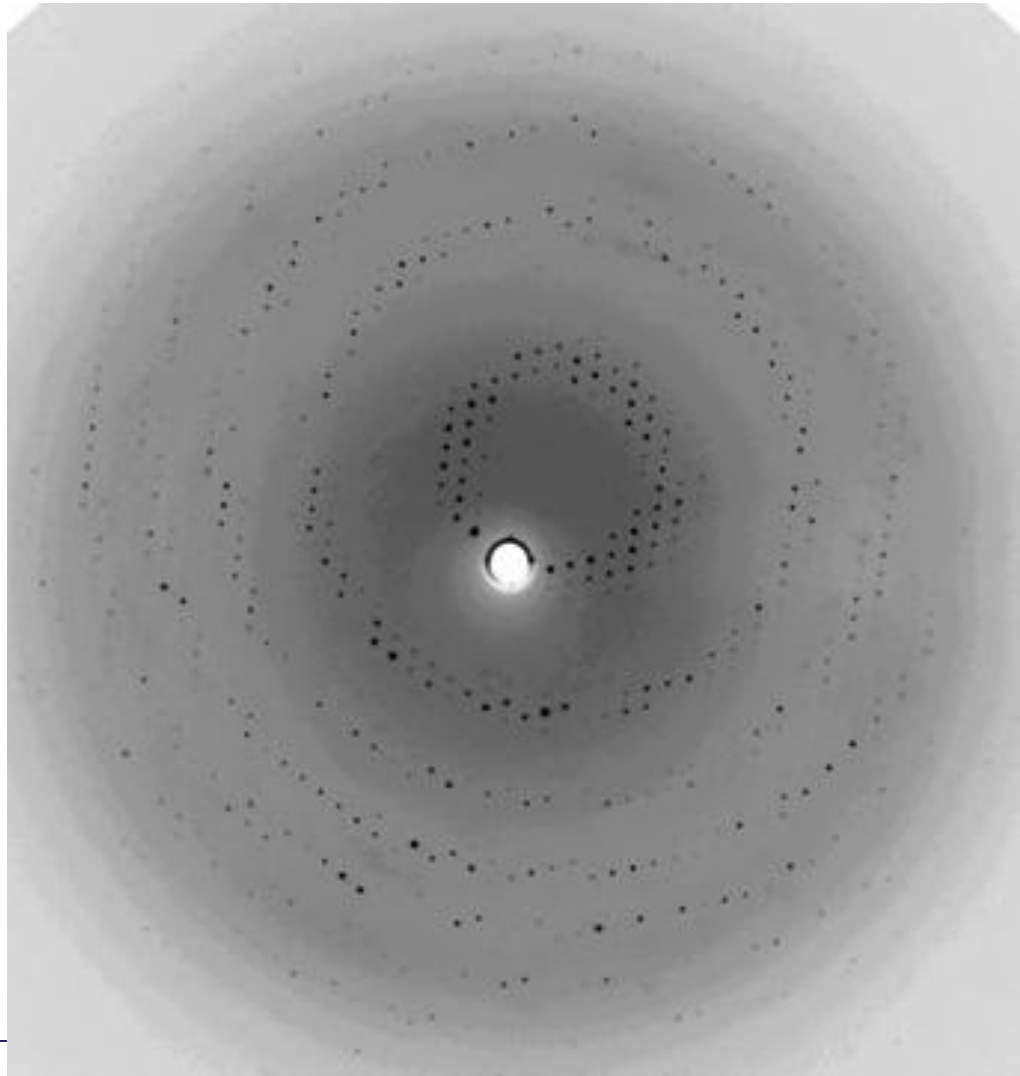
Friedel symmetry. This precession photograph is a slice through the center of the reciprocal lattice

The diffraction pattern also forms a lattice

Most contemporary x-ray data collection used the rotation geometry, in which the crystal makes a simple rotation of a degree or so while the image is being collected. The geometry of the diffraction pattern is less obvious than for a precession photograph, although data collection is more efficient.

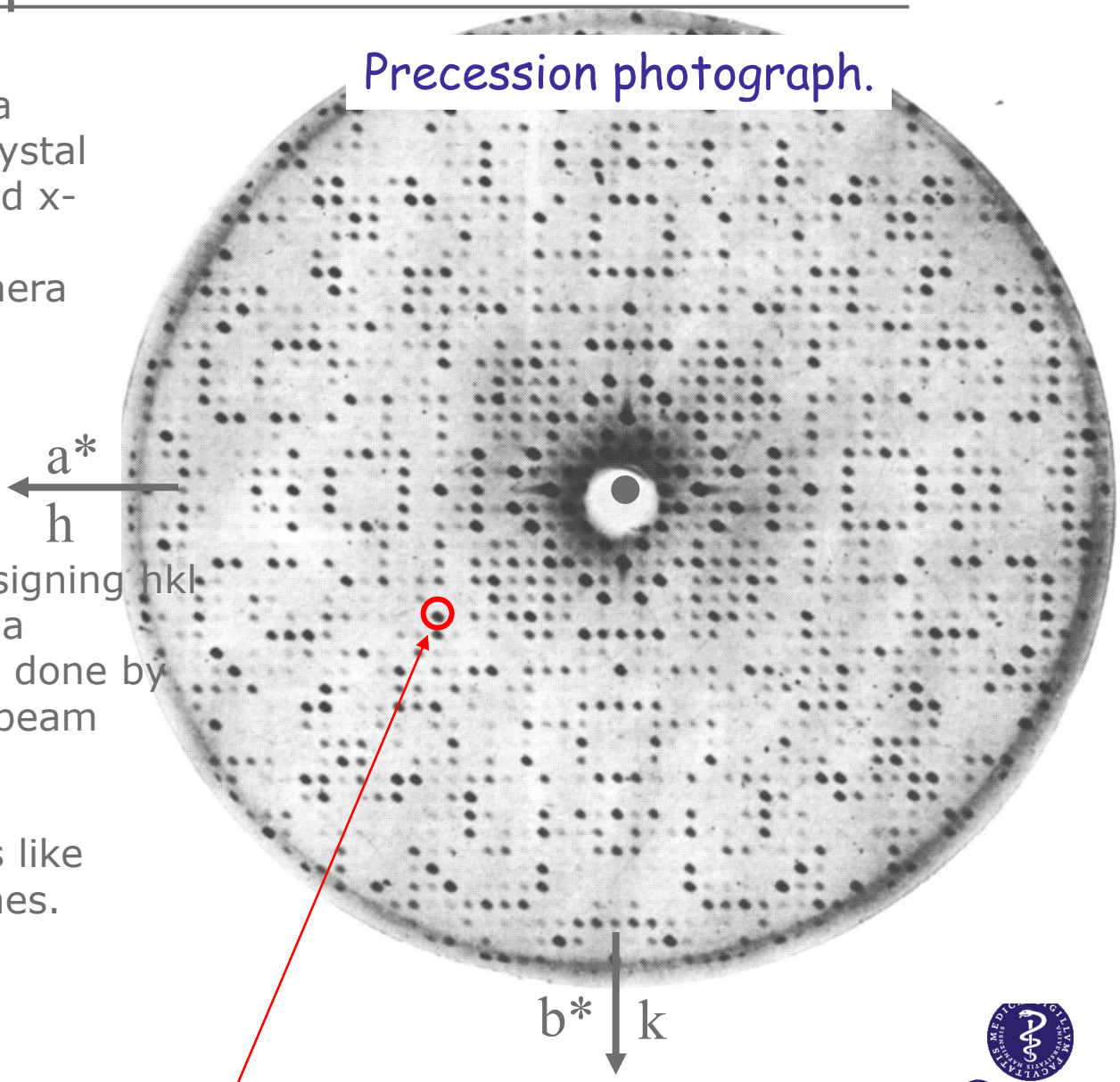


Oscillation (rotation) photograph.



The diffraction pattern also forms a lattice

The diffraction pattern forms a lattice that is related to the crystal lattice. The lattice of diffracted x-rays is very obvious in a precession photograph (a camera geometry that used to be popular).



Indexing is the process of assigning hkl indices to the reflections. In a precession photograph this is done by counting out from the direct beam position.

The geometry of diffraction is like reflection from the Miller planes.

This reflection has indices h=10 , k=7, l=0. Its intensity is $I_{(10,7,0)} = |F_{(10,7,0)}|^2$

Structure factor expression

The structure factor $F(\mathbf{h})$ can be written as below:

$$F(\boldsymbol{h}) = \sum_{i=1}^{N} f_i(|\boldsymbol{h}|) e^{2\pi i \boldsymbol{h} \boldsymbol{r}_i}$$

Here $\boldsymbol{h}$ is the scattering vector

$$\boldsymbol{h} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$$

where **a***, **b*** and **c*** are the reciprocal lattice vectors, $f_i(|\mathbf{h}|)$ is the atomic scattering factor and $\mathbf{r}_i$ is the coordinate vector of the *i*'th atom

$$\boldsymbol{r}_i = x_i\boldsymbol{a} + y_i\boldsymbol{b} + z_i\boldsymbol{c}$$

and **a**, **b** and **c** are the direct lattice vectors.

Intensity of reflections

The intensity of the scattered wave is proportional to the square of the structure factor

$$I(\boldsymbol{h}) \propto F(\boldsymbol{h})^2$$

$$= \left(\sum_{i=1}^{N} f_i(|\boldsymbol{h}|) e^{2\pi i \boldsymbol{h}\boldsymbol{r}_i}\right)\left(\sum_{i=1}^{N} f_i(|\boldsymbol{h}|) e^{-2\pi i \boldsymbol{h}\boldsymbol{r}_i}\right)$$

Friedels law

$$I(\boldsymbol{h}) \propto F(\boldsymbol{h})^2 = (\sum_{i=1}^{N} f_i(|\boldsymbol{h}|)e^{2\pi i \boldsymbol{h}\boldsymbol{r}_i})(\sum_{i=1}^{N} f_i(|\boldsymbol{h}|)e^{-2\pi i \boldsymbol{h}\boldsymbol{r}_i})$$

From the intensity equation it can be seen

$$I(h,k,l) = I(-h,-k,-l)$$

Thus in the absence of anomalous scatterers (heavy atoms) the intensity weighted reciprocal lattice is always centrosymmetric. This is referred to as Friedels law.

Rotational symmetry

If the space group of the crystal is P2 then the following symmetry operators are present

$$x, y, z \; and - x, y, -z$$

The structure factor for the reflection with indices *h,k,l* can then be written

$$F(h,k,l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(hx_i+ky_i+lz_i\right)} + e^{2\pi i\left(-hx_i+ky_i-lz_i\right)})$$

Hypothesis

Symmetry in real space will also introduce symmetry in the intensity weighted reciprocal lattice

- True for the space group P2 ?

True

The expression for the *–h,k,-l* reflection

$$F(-h,k,-l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i(-hx_i+ky_i-lz_i)} + e^{2\pi i(hx_i+ky_i+lz_i)})$$

is seen to be identical to the expression for the *h,k,l* reflection

$$F(h,k,l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i(hx_i+ky_i+lz_i)} + e^{2\pi i(-hx_i+ky_i-lz_i)})$$

Consequently two-fold symmetry in direct space also imposes two-fold symmetry in reciprocal space. Thus in space group P2 the following relations hold

$$I(h,k,l) = I(-h,k,-l) = I(-h,-k,-l) = I(h,-k,l)$$

i.e. only one fourth of the possible reflections are unique.

Screw axis symmetry

Space group $P2_1$ has the following equivalent positions

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

$$F(h,k,l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(hx_i+ky_i+lz_i\right)} + e^{2\pi i\left(-hx_i+k(y_i+1/2)-lz_i\right)})$$

$$= \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(hx_i+ky_i+lz_i\right)} + e^{\pi k}e^{2\pi i\left(-hx_i+ky_i-lz_i\right)})$$

$$F(-h,k,-l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(-hx_i+ky_i-lz_i\right)} + e^{2\pi i\left(hx_i+k(y_i+\frac{1}{2})+lz_i\right)})$$

$$= \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(-hx_i+ky_i-lz_i\right)} + e^{\pi k}e^{2\pi i\left(hx_i+ky_i+lz_i\right)})$$

Screw axis

If k even then $e^{\pi k} = 1$ then

$$F(h,k,l) = F(-h,k,-l)$$

As for the P2 case

If *k* odd then $e^{\pi k} = -1$ then

$$F(h,k,l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(hx_i+ky_i+lz_i\right)} - e^{2\pi i\left(-hx_i+ky_i-lz_i\right)})$$

$$F(-h,k,-l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i\left(-hx_i+ky_i-lz_i\right)} - e^{2\pi i\left(hx_i+k(y_i+lz_i\right)})$$

$$= -F(h,k,l)$$

And in general for all *k* and for $P2_1$

$$I(h,k,l) = I(-h,k,-l)$$

Rotational/screw axis in reciprocal space

So generalizing:

- All rotational symmetry is conserved in reciprocal space
- Centrosymmetry is induced
- Screw axis induce the same symmetry as the corresponding rotational axis.

Systematic extinctions

Look again at the structure factor expression in $P2_1$

$$F(h,k,l) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i(hx_i+ky_i+lz_i)} + e^{2\pi i(-hx_i+k(y_i+1/2)-lz_i)})$$

When looking at reflections of type 0k0

$$F(0,k,0) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi iky_i} + e^{\pi ik}e^{2\pi iky_i})$$

If *k* even

$$F(0,k,0) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi iky_i} + e^{2\pi iky_i})$$

$$= 2\sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)e^{2\pi iky_i}$$

Systematic extinctions

If *k* odd

$$F(0,k,0) = \sum_{i=1}^{\frac{N}{2}} f_i(|\boldsymbol{h}|)(e^{2\pi i k y_i} - e^{2\pi i k y_i}) = 0$$

So the presence of a 2-fold screw axis along the b axis will implicate that the reflections of class *0,k,0* will have those with odd *k* systematically extinct.

The symmetry of the lattice belongs to a laue class

Crystal System	Point Group	Laue Class
Triclinic	1	-1
Monoclinic	2	2/m
Orthorhombic	222	mmm
Tetragonal	4	4/m
	422	4/mmm
Trigonal	3	-3
	32 (312 and 321)	-3m
Hexagonal	6	6/m
	622	6/mmm
Cubic	23	m-3
	432	m-3m

Systematic extinctions give information on centerings, glide plans and screw axis

Table 4. Systematically Absent Reflection Conditions.

Symmetry Element	Types	Reflection Condition
A centered	*hkl*	$k + l = 2n$
B centered		$h + l = 2n$
C centered		$h + k = 2n$
F centered		$k + l = 2n$, $h + l = 2n$, $h + k = 2n$
I centered		$h + k + l = 2n$
R (obverse)		$-h + k + l = 3n$
R (reverse)		$h - k + l = 3n$
Glide reflecting in **a**	0*kl*	
b glide		$k = 2n$
c glide		$l = 2n$
n glide		$k + l = 2n$
d glide		$k + l = 4n$
Glide reflecting in **b**	*h*0*l*	
a glide		$h = 2n$
c glide		$l = 2n$
n glide		$h + l = 2n$
d glide		$h + l = 4n$
Glide reflecting in **c**	*hk*0	
b glide		$k = 2n$
a glide		$h = 2n$
n glide		$k + h = 2n$
d glide		$k + h = 4n$
Glide reflecting in (110)	*hhl*	
b glide		$h = 2n$
n glide		$h + l = 2n$
d glide		$h + k + l = 4n$
Screw || [100]	*h*00	
2_1, 4_2		$h = 2n$
4_1, 4_3		$h = 4n$
Screw || [010]	0*k*0	
2_1, 4_2		$k = 2n$
4_1, 4_3		$k = 4n$
Screw || [001]	00*l*	
2_1, 4_2, 6_3		$l = 2n$
3_1, 3_2, 6_2, 6_4		$l = 3n$
4_1, 4_3		$l = 4n$
6_1, 6_5		$l = 6n$
Screw || [110]	*hh*0	
2_1		$h = 2n$