Methods in Chemistry III – Part 1
Modul M.Che.1101 WS 2010/11 – 6
Modern Methods of Inorganic Chemistry

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X-ray diffraction and the reciprocal lattice

An X-ray image corresponds to a distorted image of the reciprocal lattice. The reciprocal unit cell is 'reciprocal' to the unit-cell in real space. The diffraction experiment produces a list *h*, *k*, ℓ, intensity and σ(intensity), where the indices *h*, *k*, and ℓ define the position of a reflection in the reciprocal lattice and σ means *estimated standard deviation*.

The positions of the reflections enable the dimensions of the reciprocal cell to be calculated, from which the dimensions of the real cell can be found. The intensities of the reflections depend on the contents of the unit-cell, i.e. the nature and positions of the atoms within it.

The dimensions of the unit-cell and the intensities of the reflections are sufficient information to determine the structure. In the case of a small molecule structure there are many more reflections than atoms, so from a mathematical point of view the structure is over-determined. However the route to the structure is complicated; first we must determine the *space group*.

Determination of the space group

The space group can often, but not always, be found unambiguously by the use of the following information:

1. **The metric symmetry and lattice type (i.e. the 14 Bravais lattices).**
2. **The Laue symmetry of the diffraction pattern (taking the intensities into account). Friedel's law $F_{hk\ell}^2 = F_{-h-k-\ell}^2$ is assumed for this purpose (F^2 is proportional to the intensity).**
3. **The systematic absences.**
4. **The statistical distribution of the intensities can in principle distinguish between centrosymmetric and non-centrosymmetric structures. This assumes that the atoms are approximately equal and randomly distributed in the cell. These statistics can be misleading for heavy-atom structures, especially when the heavy atoms lie on special positions.**
5. **The frequency of the space groups in the CSD or PDB databases.**

Fortunately, several common space groups can be uniquely assigned using 1-3; 4 and 5 are less reliable. The correctness of the space group can also be checked later using the atomic coordinates!

Lattice systematic absences

reflection class	absences	lattice type	remarks
$hk\ell$	—	P	
	$h+k+\ell \neq 2n$	I	
	$k+\ell \neq 2n$	A	
	$h+\ell \neq 2n$	B	
	$h+k \neq 2n$	C	
	$k+\ell \neq 2n$, $h+\ell \neq 2n$, $h+k \neq 2n$	F	
	$-h+k+\ell \neq 3n$	R(obverse)	only trigonal
	$h-k+\ell \neq 3n$	R(reverse)	only trigonal

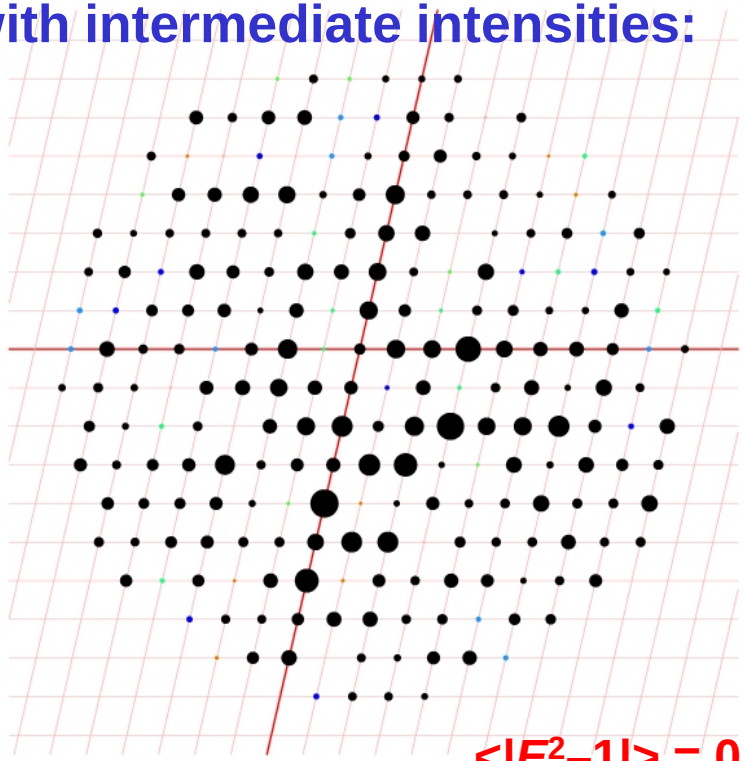
The lattice type can be determined unambiguously from the systematic absences of the general reflections h, k, ℓ.

Absences (triclinic, monoclinic and orthorhombic)

reflection class	absences	cause	remarks
*h*00	$h \neq 2n$	$2_1 \parallel$ a	
0*k*0	$k \neq 2n$	$2_1 \parallel$ b	
00ℓ	$\ell \neq 2n$	$2_1 \parallel$ c	
0*k*ℓ	$k \neq 2n$	*b* ⊥ a	
	$\ell \neq 2n$	*c* ⊥ a	
	$k+\ell \neq 2n$	*n* ⊥ a	
	$k+\ell \neq 4n$	*d* ⊥ a	only for F-lattice
*h*0ℓ	$h \neq 2n$	*a* ⊥ b	
	$\ell \neq 2n$	*c* ⊥ b	
	$h+\ell \neq 2n$	*n* ⊥ b	
	$h+\ell \neq 4n$	*d* ⊥ b	only for F-lattice
*hk*0	$h \neq 2n$	*a* ⊥ c	
	$k \neq 2n$	*b* ⊥ c	
	$h+k \neq 2n$	*n* ⊥ c	
	$h+k \neq 4n$	*d* ⊥ c	only for F-lattice

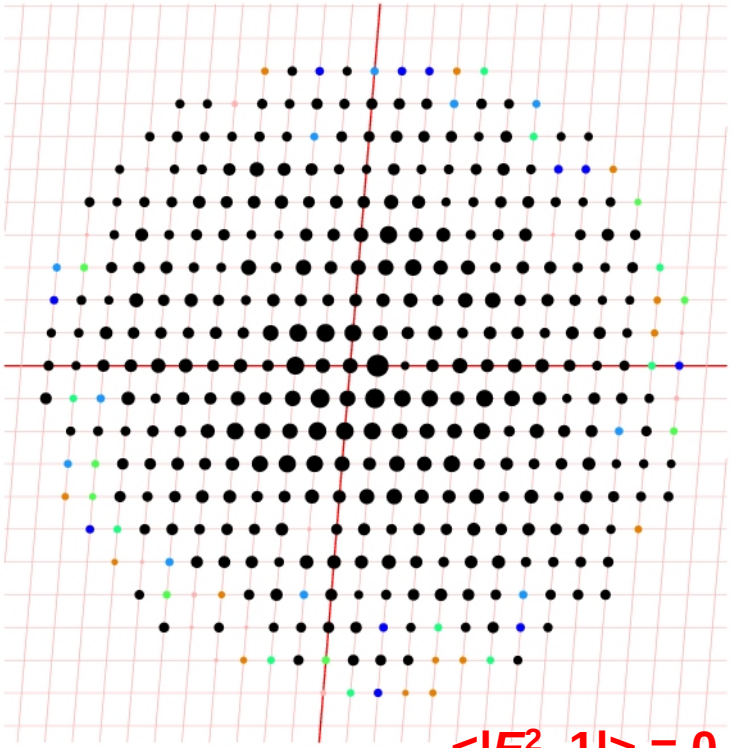
Centrosymmetric or not?

Since the Laue group always possesses a center of symmetry, indirect methods are needed to distinguish between centrosymmetric and non-centrosymmetric structures. The intensity distribution, as indicated by the $\langle|E^2-1|\rangle$ value, can help. Centrosymmetric space groups (and projections) give rise to more strong and weak reflections, but fewer with intermediate intensities:



$\langle|E^2-1|\rangle = 0.968$

The $2k\ell$ layer of reflection data for a structure in the space group $P\bar{1}$.



$\langle|E^2-1|\rangle = 0.736$

The $2k\ell$ layer of reflection data for a structure in the space group P1.

Space group frequencies

The CSD (organic structure databank), after checking suspicious cases (Wilson, 1988, 1990), contained the following distribution of space groups:

$P2_1/c$ 39%; $P\bar{1}$ 16%; $P2_12_12_1$ 12%; C2/c 7%; $P2_1$ 7%; Pbca 5%.

The **remainder (15%)** included amongst others:

P1 1.0%,; $P3_121$+$P3_221$ 0.1%; P2, Pm, P2/m < 0.1%.

In the PDB (protein databank), only the 65 (chiral) space groups that do not involve symmetry operations that would invert the configuration of a molecule need to be considered, and the distribution is somewhat different:

$P2_12_12_1$ 24%; $P3_121$+$P3_221$ 15%; $P2_1$ 14%; $P4_12_12$+$P4_32_12$ 8%; C2 6%.

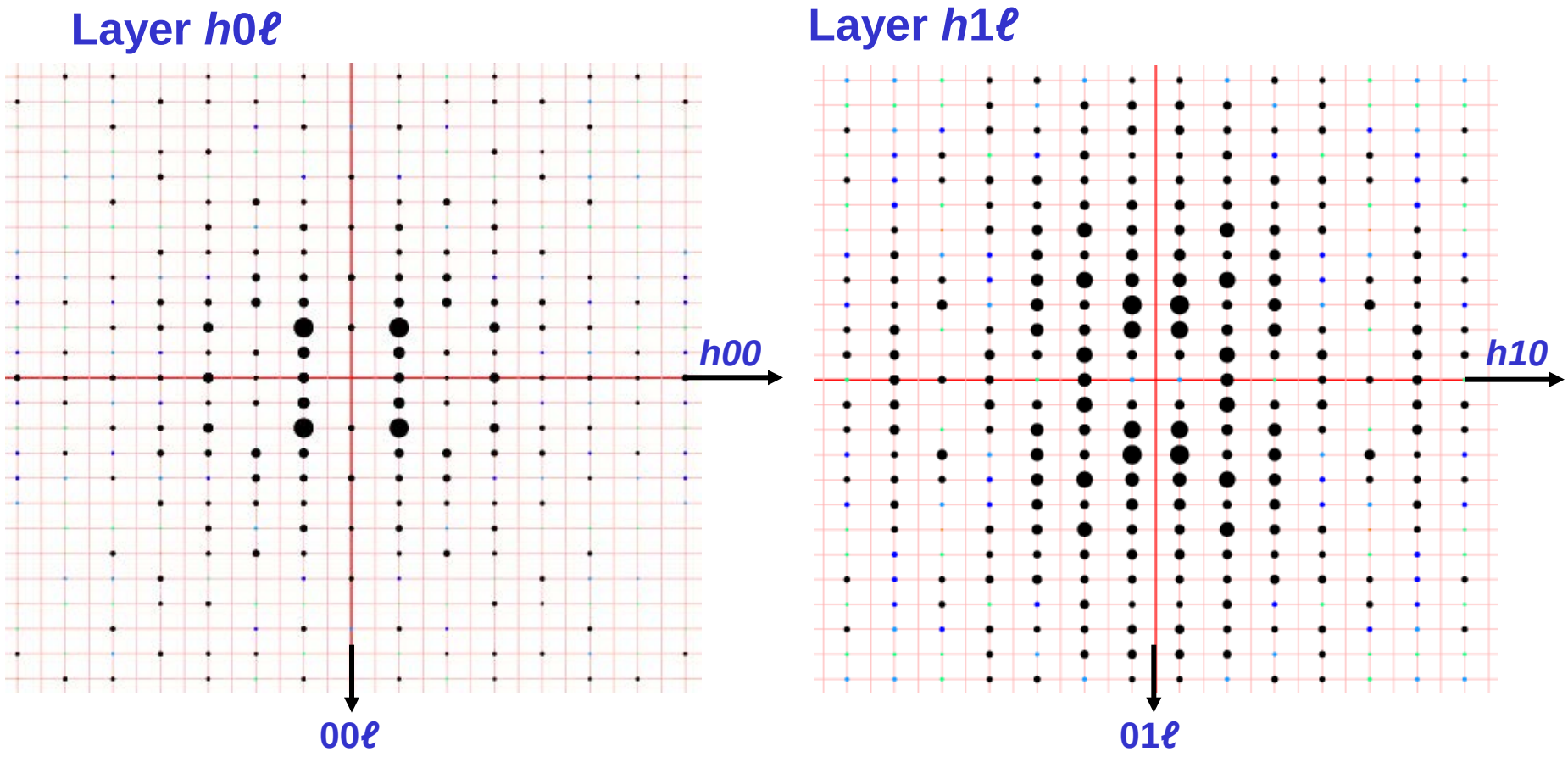
amongst the **remaining 33%** of the structures in the PDB there are significant contributions from some space groups that are very rarely observed for small molecules, e.g. **P2 1.5%.**

Triclinic, monoclinic and orthorhombic space groups

underlined = unambiguous, red = chiral, blue = non-, black = centrosymmetric

Crystal system	Laue	point group	Space groups
Triclinic	$\bar{1}$	1	P1
		$\bar{1}$	P$\bar{1}$
Monoclinic	2/*m*	2	P2, P2_1, C2
		m	P*m*, P*c*, C*m*, C*c*
		2/*m*	P2/*m*, P2_1/*m*, C2/*m*, P2/*c*, P2_1/*c*, C2/*c*
Orthorhombic	*mmm*	222	P222, P222_1, P2_12_12, P$2_12_12_1$, C222, C222_1, I222, I$2_12_12_1$, F222
		*mm*2	P*mm*2, P*mc*2_1, P*cc*2, P*ma*2, P*ca*2_1, P*nc*2, P*mn*2_1, P*ba*2, P*na*2_1, P*nn*2, C*mm*2, C*mc*2_1, C*cc*2, A*mm*2, A*bm*2, A*ma*2, A*ba*2, I*mm*2, I*ba*2, I*ma*2, F*mm*2, F*dd*2
		mmm	P*mmm*, P*nnn*, P*ccm*, P*ban*, P*mma*, P*nna*, P*mna*, P*cca*, P*bam*, P*ccn*, P*bcm*, P*nnm*, P*mmn*, P*bcn*, P*bca*, P*nma*, C*mcm*, C*mca*, C*mmm*, C*ccm*, C*mma*, C*cca*, I*mmm*, I*bam*, I*bca*, I*mma*, F*mmm*, F*ddd*

Space-group determination from absences



The Laue symmetry is mmm (orthorhombic) and the reflections $h+k\neq 2n$ are absent, so the lattice type is C. In addition, the reflections 00ℓ are absent when ℓ is odd, showing a 2_1 screw axis along c. This fits only the space group $C222_1$, one of the space groups uniquely determined by the Laue group and absences.

Space group conventions in the triclinic, monoclinic and orthorhombic systems

Triclinic: P1 possesses no symmetry, **$P\bar{1}$** only an inversion center.

Monoclinic: The principal axis is always **b**. **$P2_1/c$** implies a **2_1**-axis along **b** and a ***c*** glide plane perpendicular to **b**. The lattice type is either **P** or **C** (**I** is however sometimes used if it makes β closer to 90°; it is equivalent to **C** but with the axes chosen differently).

Orthorhombic: There is no principal axis. The full name of the space group, e.g. '**P $2_1/b$ $2/c$ $2_1/n$**', which gives the absences in full, is condensed to **P*bcn***. When this is done, priority is given to glide or mirror planes if present.

For each orthorhombic space group there is one conventional setting and up to five different non-conventional settings. For example the conventional setting of the space group **$P22_12_1$** is **$P2_12_12$**.

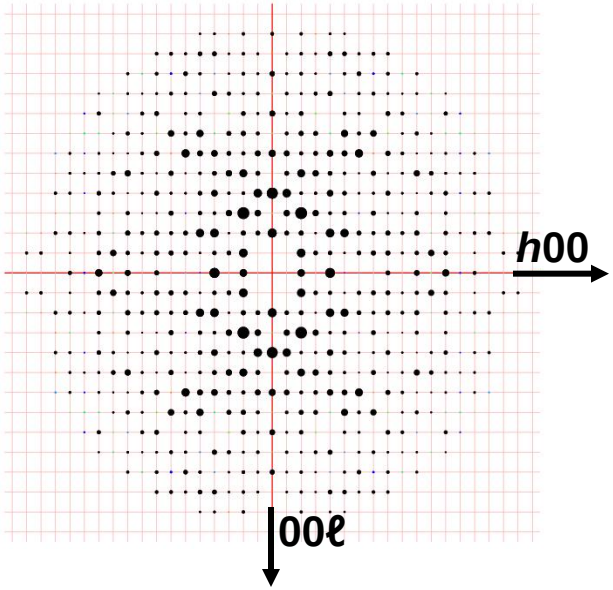
When the orientation is not (fully) determined by the symmetry, there are additional conventions: for triclinic ***c*≥*b*≥*a***, for monoclinic ***c*≥*a*** and for orthorhombic ***b*≥*a*** and/or ***c*≥*b***.

Exercises

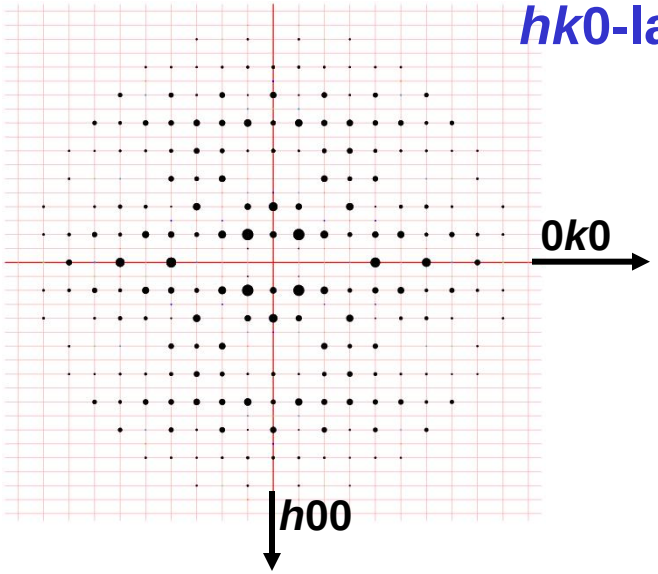
1. **Estimate the approximate percentage of small molecule structures in which the space group can be determined unambiguously from the systematic absences!**
2. **Can all triclinic, monoclinic and orthorhombic space groups be distinguished unambiguously for protein crystals?**
3. **Four layers of reciprocal space are shown on the next page. Determine the Laue group, the systematic absences and the possible space groups in the given orientation of the axes. Which space group is more likely if the reflection intensity distribution is taken into account? Luckily, in this case it should not be necessary to reorientate the axes!**

Data for exercise 3

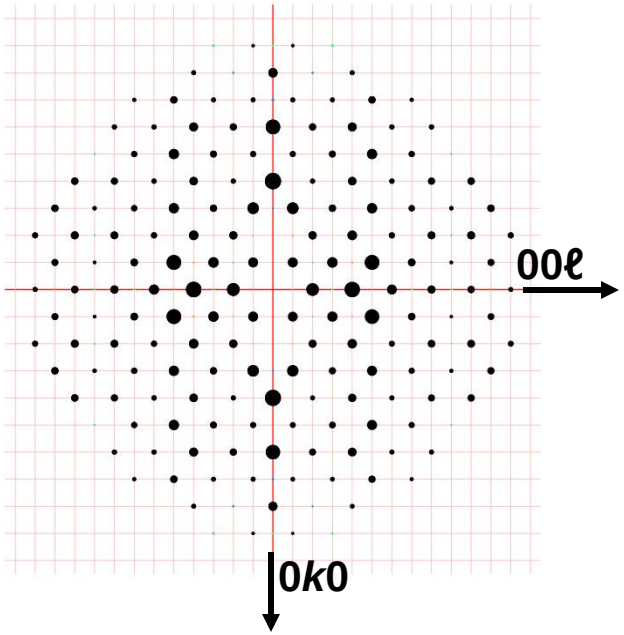
***h*0ℓ-layer**



***hk*0-layer**



0*k*ℓ-layer



***hk*1-layer**