Methods in Chemistry III – Part 1
Modul M.Che.1101 WS 2010/11 – 7
Modern Methods of Inorganic Chemistry

Mi 10:15-12:00, Hörsaal II

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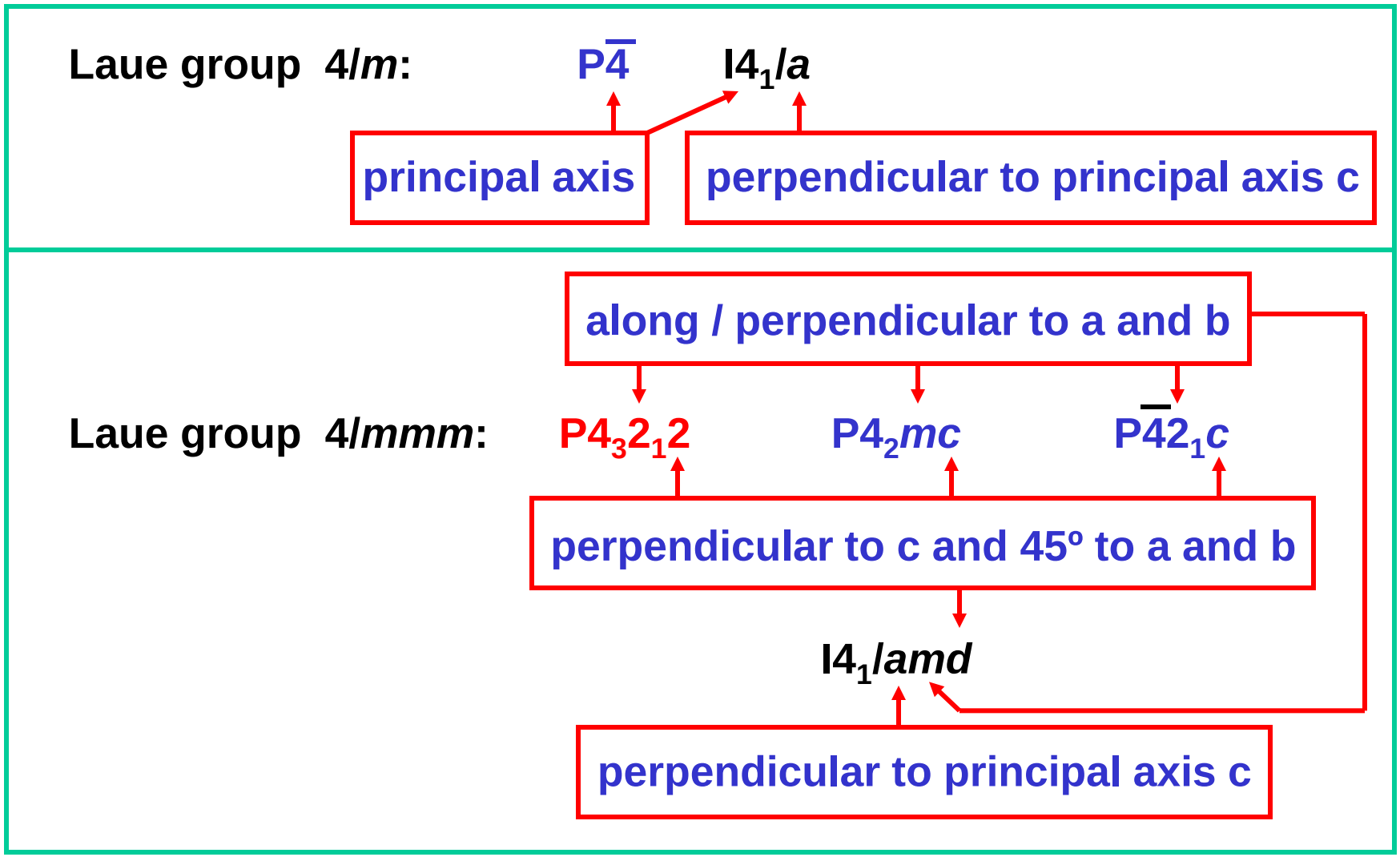
Further systematic absences (tetragonal, trigonal, hexagonal and cubic)

reflection class	absences	cause	remarks
$h00$	$h \neq 2n$	$2_1,4_2 \parallel a$	tetragonal, cubic
	$h \neq 4n$	$4_1,4_3 \parallel a$	cubic
$0k0$	$k \neq 2n$	$2_1,4_2 \parallel b$	tetragonal, cubic
	$k \neq 4n$	$4_1,4_3 \parallel b$	cubic
00ℓ	$\ell \neq 2n$	$2_1 \parallel c$	cubic
	$\ell \neq 2n$	$4_2 \parallel c$	tetragonal, cubic
	$\ell \neq 2n$	$6_3 \parallel c$	hexagonal
	$\ell \neq 3n$	$3_1,3_2 \parallel c$	trigonal
	$\ell \neq 3n$	$6_2,6_4 \parallel c$	hexagonal
	$\ell \neq 4n$	$4_1,4_3 \parallel c$	tetragonal, cubic
	$\ell \neq 6n$	$6_1,6_5 \parallel c$	hexagonal
$hh\ell$	$\ell \neq 2n$	$c \perp [110]$	tetragonal, cubic
		$c \perp [120]$	trigonal
	$2h+ \ell \neq 4n$	$d \perp [110]$	tetragonal, cubic (only for I-lattice)
$h\bar{h}\ell$	$\ell \neq 2n$	$c \perp a$	trigonal, hexagonal

Tetragonal space group symbols

There are two Laue groups, 4/*m* and 4/*mmm*. The principal axis is always c. Typical space group symbols are:



Tetragonal space groups

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

Crystal system	Laue	Point group	Space groups
Tetragonal	4/*m*	4	P4, $P4_1$, $P4_2$, $P4_3$, I4, $I4_1$
		$\bar{4}$	$P\bar{4}$, $I\bar{4}$
		4/*m*	P4/*m*, $P4_2/m$, P4/*n*, $P4_2/n$, I4/*m*, $I4_1/a$
Tetragonal	4/*mmm*	422	P422, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, I422, $I4_122$
		4*mm*	P4*mm*, P4*bm*, $P4_2cm$, $P4_2nm$, P4*cc*, P4*nc*, $P4_2mc$, $P4_2bc$, I4*mm*, I4*cm*, $I4_1md$, $I4_1cd$
		$\bar{4}m$	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}2_1c$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
		4/*mmm*	P4/*mmm*, P4/*mcc*, P4/*nbm*, P4/*nnc*, P4/*mbm*, P4/*mnc*, P4/*nmm*, P4/*ncc*, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$, $P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$, I4/*mmm*, I4/*mcm*, $I4_1/amd$, $I4_1/acd$

Trigonal and hexagonal space groups

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

Crystal system	Laue	Point group	Space groups
Trigonal	$\bar{3}$	3	P3, $P3_1$, $P3_2$, R3
		$\bar{3}$	$P\bar{3}$, $R\bar{3}$
Trigonal	$\bar{3}m$	32	P312, P321, $P3_112$, $P3_121$, $P3_212$, $P3_221$, R32
		3*m*	P3*m*1, P31*m*, P3*c*1, P31*c*, R3*m*, R3*c*
		$\bar{3}m$	$P\bar{3}m1$, $P\bar{3}1m$, $P\bar{3}c1$, $P\bar{3}1c$, $R\bar{3}m$, $R\bar{3}c$
Hexagonal	6/*m*	6	P6, $P6_1$, $P6_2$, $P6_3$, $P6_4$, $P6_5$
		$\bar{6}$	$P\bar{6}$
		6/*m*	P6/*m*, $P6_3/m$
Hexagonal	6/*mmm*	622	P622, $P6_122$, $P6_222$, $\underline{P6_322}$, $P6_422$, $P6_522$
		6*mm*	P6*mm*, P6*cc*, $P6_3cm$, $P6_3mc$
		$\bar{6}m2$ oder $\bar{6}2m$	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
		6/*mmm*	P6/*mmm*, P6/*mcc*, $P6_3/mcm$, $P6_3/mmc$

Hexagonal and rhombohedral axes

Crystals with primitive rhombohedral lattices (a=b=c, $\alpha=\beta=\gamma$) are often described by a centered hexagonal cell (a=b≠c, $\alpha=\beta=90^o$, $\gamma=120^o$). This hexagonal cell is three times as large as the primitive rhombohedral cell and shows lattice absences $-h+k+\ell \neq 3n$. Although it is difficult to draw a projection of the rhombohedral cell, the symmetry operations appear simpler:

R3, primitive rhombohedral axes: *x*, *y*, *z*; *y*, *z*, *x*; *z*, *x*, *y*

R3, hexagonal axes: *x*, *y*, *z*; –*y*, *x*–*y*, *z*; *y*–*x*, –*x*, *z*;

2/3+*x*, 1/3+*y*, 1/3+*z*; 2/3–*y*, 1/3+*x*–*y*, 1/3+*z*; 2/3+*y*–*x*, 1/3–*x*, 1/3+*z*;

1/3+*x*, 2/3+*y*, 2/3+*z*; 1/3–*y*, 2/3+*x*–*y*, 2/3+*z*; 1/3+*y*–*x*, 2/3–*x*, 2/3+*z*.

Cubic space groups

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

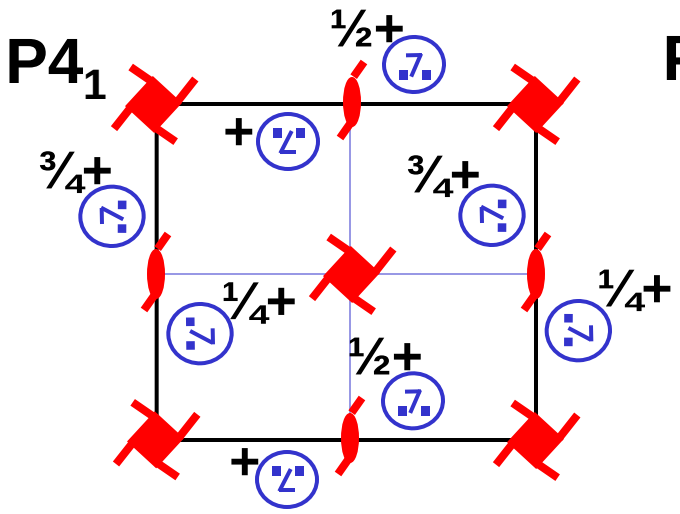
Crystal system	Laue/Point group		Space groups
Cubic	$m\bar{3}$	23	P23, P2$_1$3, I23, I2$_1$3, F23
		$m\bar{3}$	P$m\bar{3}$, P$n\bar{3}$, P$a\bar{3}$, I$m\bar{3}$, I$a\bar{3}$, F$m\bar{3}$, F$d\bar{3}$
Cubic	$m\bar{3}m$	432	P432, P4$_1$32, P4$_2$32, P4$_3$32, I432, I4$_1$32, F432, F4$_1$32
		$\bar{4}3m$	P$\bar{4}3m$, P$\bar{4}3n$, I$\bar{4}3m$, I$\bar{4}3d$, F$\bar{4}3m$, F$\bar{4}3c$
		$m\bar{3}m$	P$m\bar{3}m$, P$n\bar{3}n$, P$m\bar{3}n$, P$n\bar{3}m$, I$m\bar{3}m$, I$a\bar{3}d$, F$m\bar{3}m$, F$m\bar{3}c$, F$d\bar{3}m$, F$d\bar{3}c$

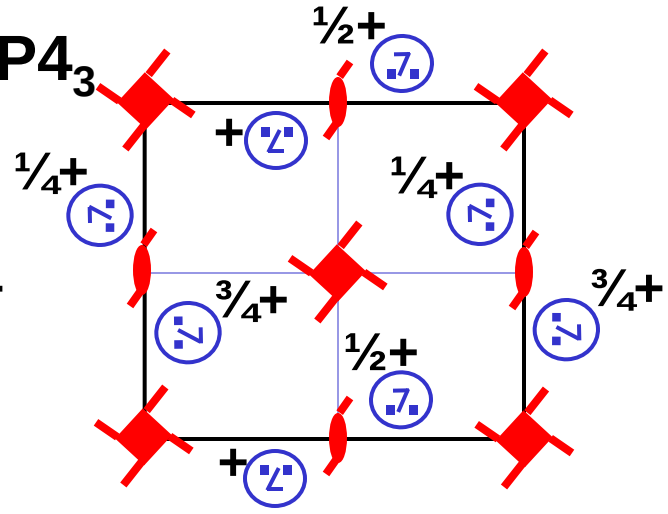
Trigonal and hexagonal space group symbols are similar to tetragonal (the third direction is at 30º to a). The second direction in cubic space group symbols is always a threefold axis, the third is (as in tetragonal) at 45º to two of the axes and at right angles to the other.

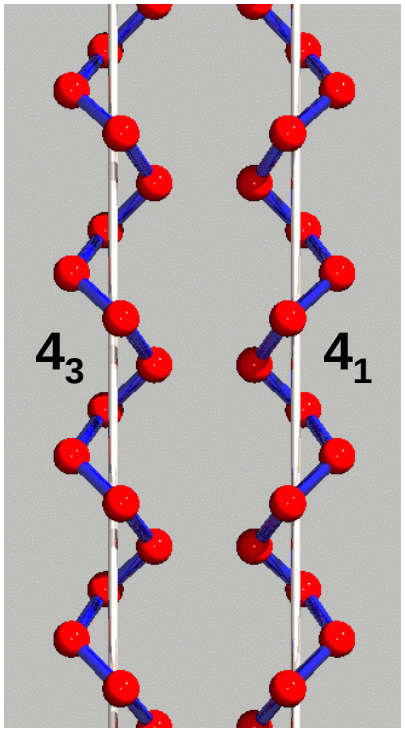
A *d glide plane* at the first position in a cubic symbol reflects and shifts x, y, z to x+¼, y+¼, –z; in the third position it transforms x, y, z to y+¼, x+¼, z+¼.

Enantiomeric pairs of space groups

There are 11 pairs of space groups that are enantiomers of each other, e.g. $P4_1$ und $P4_3$:







A further example is $P4_12_12$ and $P4_32_12$. Since the diffraction pattern possesses an inversion center, the structure can be solved (using the usual small molecule methods) in either space group, but one is the correct enantiomer and the other is its mirror image.

Note that non-chiral molecules may also crystallize in such space groups; although the molecule is non-chiral the way they pack together is chiral. For example α-Se crystallizes in $P3_121/P3_221$, α-Quarz (SiO_2) in $P3_121/P3_221$ and β-Quarz (>573°C) in $P6_222/P6_422$.

The structure factor F and the electron density ρ

$$I_{hk\ell} \text{ is proportional to } |F_{hk\ell}|^2$$

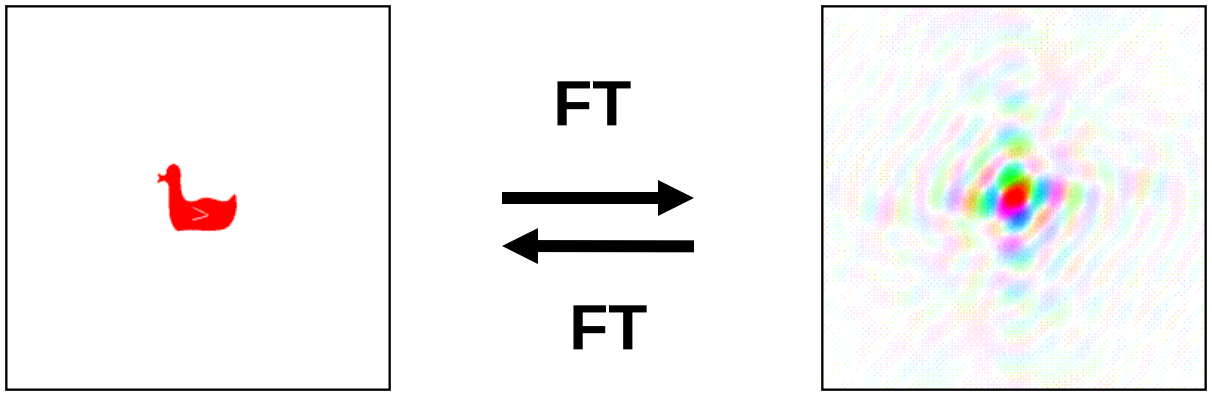
$$F_{hk\ell} = \int_V \rho_{xyz} \exp[+2\pi i(hx+ky+\ell z)]\, dV$$

$$\rho_{xyz} = (1/V) \sum_{hk\ell} F_{hk\ell} \exp[-2\pi i(hx+ky+\ell z)]$$

$F_{hk\ell}$ and ρ_{xyz} are related to each other by means of these *Fourier transformations*. The electron density ρ is real and positive, but the struktur factor F is a complex number: to calculate the electron density from the structure factors, we also need the *phase* (ϕ) of *F*.

Under normal conditions we can only measure the diffracted intensities *I* and not the phase ϕ of a reflection *h*,*k*,ℓ, so it appears that we are faced with an insoluble problem, the *crystallographic phase problem!*

A duck in reciprocal space

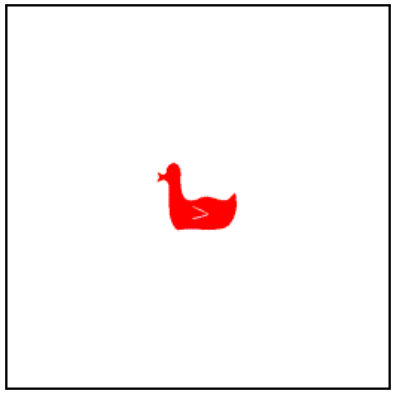


duck

Fourier transform of a duck

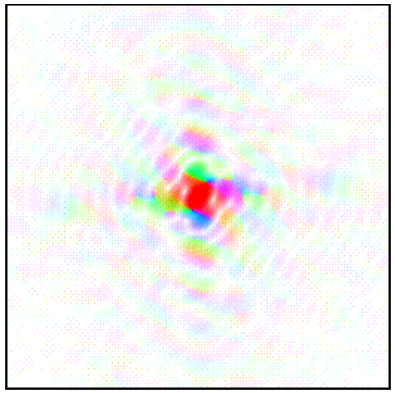
Kevin Cowtan www.ysbl.ac.uk/~cowtan/fourier/fourier.html

Amplitude (F) and phase (ϕ)



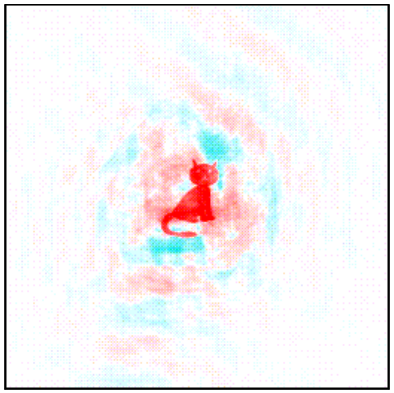
FT

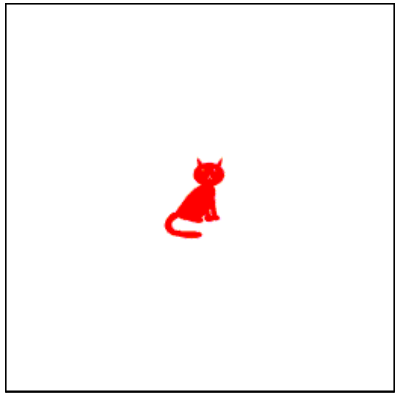
the amplitudes of the duck



FT

?





FT

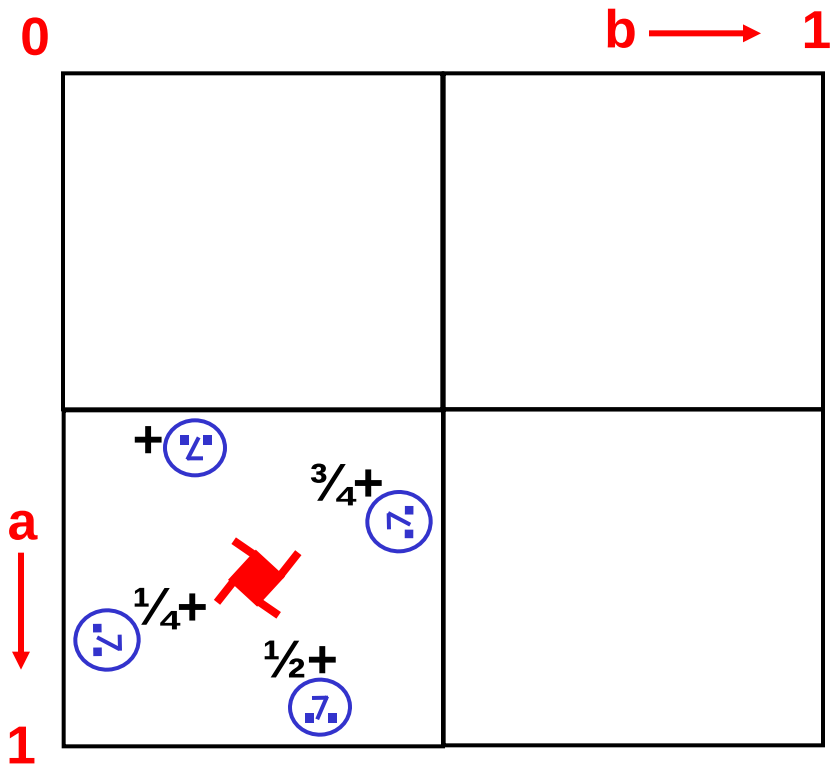
are combined with the phases of the cat

Kevin Cowtan www.ysbl.ac.uk/~cowtan/fourier/fourier.html

Exercises

1. **Find the 11 enantiomorphic pairs of space groups (hint: all are of course chiral and possess 3_N, 4_N or 6_N axes).**

2. **The incomplete picture should show the space group $I4_1$. Add the effect of the I-lattice by marking the additional symmetry elements and molecules that it generates. Why is there no space group $I4_3$?**



3. **Assign the space group of a tetragonal crystal with the systematic absences: *hkℓ*, *h*+*k*+ℓ ≠ 2*n*; *hk*0, h ≠ 2*n* or *k* ≠ 2*n*; *hh*ℓ, 2*h*+ℓ ≠ 4*n*.**