Determining symmetry from phases

ECM29 Computing School, Rovinj,
21st August 2015

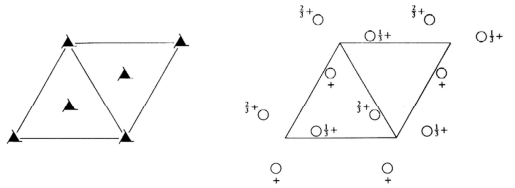
George M. Sheldrick

http://shelx.uni-ac.gwdg.de/SHELX/

International Tables vol A: space group $P3_1$

$P3_1$ C_3^2 3 Trigonal

No. 144 $P3_1$ Patterson symmetry $P\bar{3}$



Coordinates of the general position:

m*=1: *x*, *y*, *z

***m*=2: –*y*, *x*–*y*, *z*+⅓**

***m*=3: –*x*+*y*, –*x*, *z*+⅔**

Origin on 3_1

Asymmetric unit $0 \le x \le 1;\ 0 \le y \le 1;\ 0 \le z \le \frac{1}{3}$

Vertices 0,0,0 1,0,0 1,1,0 0,1,0 0,0,⅓ 1,0,⅓ 1,1,⅓ 0,1,⅓

Symmetry operations

(1) 1 (2) 3^+ (0,0,⅓) 0,0,*z* (3) 3 (0,0,⅔) 0,0,*z*

Generators selected (1); *t*(1,0,0); *t*(0,1,0); *t*(0,0,1); (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates
3 *a* 1	(1) *x*,*y*,*z*	(2) $\bar{y}$,*x*−*y*,*z*+⅓ (3) $\bar{x}+y$,$\bar{x}$,*z*+⅔

Symmetry of special projections

Along [001] *p*3 **a**′ = **a** **b**′ = **b** Origin at 0,0,*z*

Along [100] *p*1 **a**′ = ½(**a**+2**b**) **b**′ = **c** Origin at *x*,0,0

Along [210] *p*1 **a**′ = ½**b** **b**′ = **c** Origin at *x*,½*x*,0

Symmetry generators

Systematic absences:

Reflection conditions

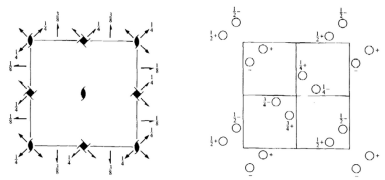
General:

000*l* : *l* = 3*n*

Space group $P4_12_12$

$P4_12_12$ D_4^4 422 Tetragonal

No. 92 $P4_12_12$ Patterson symmetry $P4/mmm$



Coordinates of the general position:

Origin on 2[110] at 2, 1 (1,2)

Asymmetric unit $0 \le x \le 1;\ 0 \le y \le 1;\ 0 \le z \le \frac{1}{8}$

Symmetry operations

(1) 1 (2) 2(0,0,½) 0,0,*z* (3) 4^-(0,0,½) 0,½,*z* (4) 4^+(0,0,½) ½,0,*z*

(5) 2(0,½,0) ½,*y*,¼ (6) 2(½,0,0) *x*,½,¼ (7) 2 *x*,*x*,0 (8) 2 *x*,$\bar{x}$,¼

Generators selected (1); *t*(1,0,0); *t*(0,1,0); *t*(0,0,1); (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates	Reflection conditions
8 *b* 1	(1) *x*,*y*,*z*	(2) $\bar{x}$,$\bar{y}$,*z*+½ (3) $\bar{y}$+½,*x*+½,*z*+¼ (4) *y*+½,$\bar{x}$+½,*z*+¾	General:
	(5) $\bar{x}$+½,*y*+½,$\bar{z}$+¼	(6) *x*+½,$\bar{y}$+½,$\bar{z}$+½ (7) *y*,*x*,$\bar{z}$ (8) $\bar{y}$,$\bar{x}$,$\bar{z}$+½	00*l* : *l* = 4*n*
			*h*00 : *h* = 2*n*
			Special: as above, plus
4 *a* ..2	*x*,*x*,0	$\bar{x}$,$\bar{x}$,½ $\bar{x}$+½,*x*+½,¼ *x*+½,$\bar{x}$+½,¾	0*kl* : *l* = 2*n*+1 or 2*k*+*l* = 4*n*

Symmetry of special projections

Along [001] *p*4*gm* **a**′ = **a** **b**′ = **b** Origin at 0,½,*z*

Along [100] *p*2*gg* **a**′ = **b** **b**′ = **c** Origin at *x*,¼,¼

Along [110] *p*2*gm* **a**′ = ½(−**a**+**b**) **b**′ = **c** Origin at *x*,*x*,0

Systematic absences:

Special position:

The symmetry operators

All symmetry-dependent information in real or reciprocal space can be derived from the symmetry operators! E.g. Space group $P3_1$:

m = 1: *x*, *y*, *z*; *m*=2: –*y*, *x*–*y*, *z*+⅓; *m*=3: –*x*+*y*, –*x*, *z*+⅔

These operators may also be expressed as 3x3 matrices **R** plus vectors **t**:

$$\begin{pmatrix} x_m \\ y_m \\ z_m \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

Or: $\mathbf{x_m = R_m x + t_m}$, which in the case of operator *m*=3 is:

$$\begin{pmatrix} x_m \\ y_m \\ z_m \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ ⅔ \end{pmatrix}$$

Symmetry operators for $P4_12_12$

For the examples in this talk we will use the space groups $P3_1$ and $P4_12_12$; for the latter the general positions are:

m=1: x, y, z	m=2: $-x, -y, z+½$
m=3: $½-y, ½+x, z+¼$	m=4: $-y, -x, ½-z$
m=5: $½+y, ½-x, z+¾$	m=6: $½-x, ½+y, ¼-z$
m=7: $½+x, ½-y, ¾-z$	m=8: $y, x, -z$

i.e. for m=5:

$$\mathbf{R} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{t} = \begin{pmatrix} ½ \\ ½ \\ ¾ \end{pmatrix}$$

To obtain the general positions of the enantiomorphous space group $P4_32_12$, just exchange ¼ and ¾ !

Properties of R and t

The *determinant* of the matrix **R** must be +1 or –1. If it is –1 it produces an inverted image, so the space group in *not chiral* (but may still be non-centrosymmetric).

When one row of **R** is never negative for any operator [e.g. the third row (R_{31} R_{32} R_{33}) in $P3_1$] the space group is *polar*.

If all elements of **t** are zero for all operators (not including lattice centering) the space group is *symmorphic* (and has no systematic absences apart from lattice absences).

If t includes elements that are not multiples of ½ and the lattice is primitive the space group is *one member of an enantiomorphic pair*; if either all elements of **t** are multiples of ½ or the lattice is centered the space group does not belong to an enantiomorphic pair (!)

Symmetry in reciprocal space

For the symmetry operator m: $\mathbf{x_m = R_m x + t_m}$

The calculated structure factor $\mathbf{F_c}$ is given by the complex number

$\mathbf{F_c} = (A + iB)$ where:

$$A_{hkl} = \sum_{atoms} \sum_{symm} f_j \cos[2\pi(hx_m+ky_m+\ell z_m)]$$
$$B_{hkl} = \sum_{atoms} \sum_{symm} f_j \sin[2\pi(hx_m+ky_m+\ell z_m)]$$

(the exponential term for atomic displacements has been included in the scattering factor f_j here for simplicity). But

$hx_m+ky_m+\ell z_m = \mathbf{h}\,(\mathbf{R_m x+t_m}) = h_m x + k_m y + \ell_m z + ht_1 + kt_2 + \ell t_3$

where: $h_m = R_{11}h + R_{21}k + R_{31}\ell$
$k_m = R_{12}h + R_{22}k + R_{32}\ell$
$\ell_m = R_{13}h + R_{23}k + R_{33}\ell$

So to find the *equivalent indices* (h_m,k_m,ℓ_m) we multiply (h,k,ℓ) by the *transpose* of the matrix **R**.

The phases of equivalent reflections

The phase ϕ_m of the equivalent reflection $\mathbf{h_m}$ is derived from the phase ϕ of the (prime) reflection **h** by:

$\phi_m = \phi - 2\pi\mathbf{ht_m} = \phi - 2\pi\,(ht_1 + kt_2 + \ell t_3)$

For example in $P3_1$: $h_2 = 0h + 1k + 0\ell = k$
$k_2 = -1h - 1k + 0\ell = -h-k$
$\ell_2 = 0h + 0k + 1\ell = \ell$

So $\mathbf{h_2}$ is k, $-h-k$, ℓ with phase:

$\phi_2 = \phi - 2\pi\mathbf{ht_2} = \phi - 2\pi\,(0h + 0k + ⅓\ell) = \phi - (⅔)\pi\ell$

These are the true equivalent reflections; they have the same intensities and exactly the above phase shifts whether anomalous scatterers (that would cause Friedel's law to break down) are present or not.

Friedel's law

Friedels law states that $|F_{-m}| = |F_m|$ and $\phi_{-m} = -\phi_m$ where ϕ_{-m} is the phase of $(-h_m,-k_m,-\ell_m)$. Friedel's law is strictly valid only when f" is equal (or zero) for all atoms in the structure, but it is almost always a good approximation. In space group $P3_1$:

$$|F_{h,k,\ell}| = |F_{k,-h-k,\ell}| = |F_{-h-k,h,\ell}| \quad \text{(exact equivalents) and}$$

$$|F_{-h,-k,-\ell}| = |F_{-k,h+k,-\ell}| = |F_{h+k,-h,-\ell}| \quad \text{(exact equivalents)}$$

but these two groups are only approximately equal because they are related by Friedel's law. For non-centrosymmetric space groups (chiral or not) there are always two groups of exact equivalents; if Friedel's law holds, the |F| values of the two groups are also the same.

Equivalents in $P4_12_12$

For $P4_12_12$ the two groups of equivalents are:

$$h,k,\ell = -h,-k,\ell = k,-h,\ell = -k,-h,-\ell = -k,h,\ell = -h,k,-\ell = h,-k,-\ell = k,h,-\ell$$

$$-h,-k,-\ell = h,k,-\ell = -k,h,-\ell = k,h,\ell = k,-h,-\ell = h,-k,\ell = -h,k,\ell = -k,-h,\ell$$

The space group P4*mm* has the same Laue group as $P4_12_12$ but different Friedel-related groups:

$$h,k,\ell = -h,-k,\ell = k,-h,\ell = -k,-h,\ell = -k,h,\ell = -h,k,\ell = h,-k,\ell = k,h,\ell$$

$$-h,-k,-\ell = h,k,-\ell = -k,h,-\ell = k,h,-\ell = k,-h,-\ell = h,-k,-\ell = -h,k,-\ell = -k,-h,-\ell$$

To derive these groups of equivalents correctly, it is necessary to know the point group (or space group). The Laue group contains an inversion center and so is not sufficient. It should be noted that for chiral compounds (i.e. for macromolecules) there is only one possible point group for each Laue group (the one that has rotation axes but no planes, inversion centers or inverse tetrads).

Systematic absences

A reflection is *systematically absent* when $h_m = h$ but ϕ_m is not equal to ϕ $(+2n\pi$ where n is an integer). In $P3_1$:

$$\phi_{k,-h-k,\ell} = \phi_{h,k,\ell} - 2\pi\ell/3 \ (+2n\pi)$$

so when $h = k = 0$:

$$\phi_{0,0,\ell} = \phi_{0,0,\ell} - 2\pi\ell/3 \ (+2n\pi)$$

which can only be true when $\ell = 3n$, i.e. reflections 0,0,ℓ with ℓ not equal to $3n$ are *systematically absent*. Note that the reflection is absent if this applies for *any* operator m. E.g. in $P4_12_12$:

$$m{=}2: \quad \phi_{-h,-k,\ell} = \phi_{h,k,l} - \pi\ell \ (+2n\pi)$$

which implies 0,0,ℓ absent for ℓ not equal to $2n$, but:

$$m{=}3: \quad \phi_{k,-h,\ell} = \phi_{h,k,\ell} - \pi h - \pi k - \tfrac{1}{2}\pi\ell \ (+2n\pi)$$

which requires 0,0,ℓ absent for ℓ not $4n$, so 0,0,2 is also absent.

Symmetry-restricted phases

If $\mathbf{h}_{-\mathbf{m}} = \mathbf{h}$ then:

$$\phi_{-m} = -(\phi - 2\pi\mathbf{h}\mathbf{t}_\mathbf{m}) = \phi \ (+2n\pi)$$

which gives the equation:

$$2\phi = 2\pi\mathbf{h}\mathbf{t}_\mathbf{m} + 2n\pi \quad (n \text{ integer})$$

$$\text{or} \quad \phi = \pi\,(ht_1 + kt_2 + \ell t_3 + n)$$

So there can only be two possible values for ϕ (corresponding to odd and even n) and they must differ by π. Such reflections belong to a *centrosymmetric projection*. In $P3_1$, for no values of m and h,k,ℓ (except 0,0,0) is $\mathbf{h}_{-\mathbf{m}} = \mathbf{h}$, so there are no centrosymmetric projections. This is clearly also true in real space from inspection of the IT diagram.

Centric reflections in $P4_12_12$

$P4_12_12$ has several classes of reflections with restricted phases, e.g.:

$$m=2: \quad \mathbf{h}_{-\mathbf{m}} = -(-h,-k,\ell)$$

which is equal to h,k,ℓ when $\ell=0$, which gives:

$$\phi_{h,k,0} = \pi\,(\,0h + 0k + (\tfrac{1}{2})0\,) + n\pi = n\pi$$

so the $h,k,0$ reflections have phases restricted to 0 or π. Similarly, $m=6$ gives $\mathbf{h}_{-\mathbf{m}} = -(-h, k, -\ell)$ which is equal to h,k,ℓ if $k = 0$. Then:

$$\phi_{h,0,\ell} = \pi\,(\,\tfrac{1}{2}h + \tfrac{1}{2}(0) + \tfrac{1}{4}\ell\,) + n\pi = \pi\,(\,\tfrac{1}{2}h + \tfrac{1}{4}\ell\,) + n\pi$$

So for example the reflection 1,0,1 has two possible phases of $3\pi/4$ or $7\pi/4$.

In the case $m=4$, $\mathbf{h}_{-\mathbf{m}} = -(-k,-h,-\ell)$ which is equal to h,k,ℓ when $h = k$. Thus it can be shown that reflections h,h,ℓ are restricted to $\pi/2$ or $3\pi/2$.

Phases and translation

If the whole structure is shifted by Δx we can write: $x_j' = x_j + \Delta x$

Thus $\mathbf{F_h'} = \sum_j f_j \exp(2\pi i\, hx'_j) = \sum_j f_j \exp(2\pi i\,(h(x_j+\Delta x))$

$= [\,\sum_j f_j \exp(2\pi i\, hx_j)]\exp(2\pi i\, h\Delta x)$

$= F_h \exp(2\pi i\, h\Delta x)$

i.e. $\phi' = \phi + 2\pi h\Delta x$

Only those origin shifts are allowed that do not alter the symmetry of the space group. Phases that do not change on any allowed origin shift are called *seminvariant phases*.

If there are two phase sets (e.g. from direct methods) with phase differences $\Delta\phi_h$, a Fourier synthesis:

$$Q_{\Delta x} = \sum_h |F|^2 \exp(i\Delta\phi_h) \exp(-2\pi i\, \mathbf{h\Delta x})$$

Should give a maximum at $\mathbf{\Delta x}$ equal to the translation between the two structures.

Using phases to find the correct origin and space group

PLATON can find the space group and place its origin correctly starting from atom positions in P1. The disadvantage of this approach is that tolerances are required to decide whether atom positions are the same within experimental error in the higher space group.

Giacovazzo [*J. Appl. Cryst* 33 (2000) 307] and Palatinus [*J. Appl. Cryst.* 41 (2008) 975] suggested ways of finding the space group and the required origin shift using only the phases. The two approaches are similar but Giacovazzo finds the full space group directly (but at his own admission, slowly) whereas Palatinus searches for individual symmetry elements and then uses them to construct the space group.

An advantage of this approach is that it is possible to define a single figure of merit to decide which possible space group is more likely.

The phases of equivalent reflections

The phase ϕ_m of the equivalent reflection $\mathbf{h}_\mathbf{m}$ is derived from the phase ϕ of the (prime) reflection $\mathbf{h}$ by:

$$\phi_m = \phi - 2\pi\mathbf{h}\mathbf{t}_\mathbf{m} = \phi - 2\pi\,(\,ht_1 + kt_2 + \ell t_3)$$

For example in $P3_1$: (for symmetry operator #2)

$h_2 = 0h + 1k + 0\ell = k$

$k_2 = -1h - 1k + 0\ell = -h-k$

$\ell_2 = 0h + 0k + 1\ell = \ell$

So $\mathbf{h_2}$ is $k, -h-k, \ell$ with phase:

$$\phi_2 = \phi - 2\pi\mathbf{h}\mathbf{t_2} = \phi - 2\pi\,(\,0h + 0k + \tfrac{1}{3}\ell\,) = \phi - (\tfrac{2}{3})\pi\ell$$

This relation is only valid if the space group is correct and the structure has been shifted so that the origin is correctly placed.

Phases and translation

If the whole structure is shifted by **Δx** we can write: $\mathbf{x_j'} = \mathbf{x_j} + \mathbf{\Delta x}$

Thus $\mathbf{F_h'} = \sum_j f_j \exp(2\pi i\, \mathbf{h x_j'}) = \sum_j f_j \exp(2\pi i\, (\mathbf{h(x_j+\Delta x)})$

$= [\sum_j f_j \exp(2\pi i\, \mathbf{h x_j})] \exp(2\pi i\, \mathbf{h\Delta x})$

$= \mathbf{F_h} \exp(2\pi i\, \mathbf{h\Delta x})$

i.e. $\phi' = \phi + 2\pi\mathbf{h\Delta x}$

This provides us with a way to find the origin shift **Δx** using the phases, by fitting the phase differences between equivalent reflections **h'** and **h** to **2πhΔx.** This calculation has to be performed modulo 2π!

The α figure of merit

In my hands both the Giacovazzo and Palatinus figures of merit performed well. The related α value used in SHELXT has a direct physical meaning (the normalized mean square phase error). For a prime reflection **h** and a symmetry equivalent $\mathbf{h_m}$ we define:

$$q = \{ \phi_m - \phi + 2\pi[\mathbf{ht_m} + \mathbf{\Delta x(h_m - h)}] \} \text{ modulo } 2\pi$$

For the correct origin shift **Δx** and the correct space group q should be close to zero if the phases of the symmetry equivalents are consistent. An F^2-weighted sum of q^2 over all pairs of equivalents for all reflections, normalized so that it would have a value of 1.0 for random phases, is then the figure of merit α.

Finding the origin in a centrosymmetric space group

Only when the inversion center of a centrosymmetric structure is at the origin will the phases be 0 or π, otherwise they have general values. To find the origin shift needed to bring an inversion center to the origin, we can double the phases (so that they should all be zero if the origin is correct) and then perform a Fourier transformation:

$$\mathbf{P_X} = \sum_h |\mathbf{F_h}|^2 \exp(-2\pi i \bullet 2\phi_h) \exp(-2\pi i\, \mathbf{hX})$$

The electron density should then be shifted by **X/2** to bring it to the true origin, where **X** is the position of the maximum of this *origin shifted Patterson function*. In SHELXT the α figure of merit for this P1 to $P\bar{1}$ conversion is referred to as α_0. It should be less than about 0.25 for a centrosymmetric space group.

It is still necessary to take into account that not all inversion centers are equivalent in all space groups. However it is still much faster to test all possible non-equivalent inversion centers than to do a full 3D grid search to find the best value of α.

Calculating α in non-centrosymmetric space groups

A 3D grid search for α would be slow because it is not suitable for a FFT, so it is divided into 2D and 1D searches. All non-centrosymmetric space groups in the given Laue group are tested as follows, taking axis transformations to obtain conventional settings into account where necessary.

1. For P1 no search is required, α is undefined (set to zero).
2. For the space groups Pm, Pc, Pn, Cm and Cc a 1D line search is performed.
3. For all other polar space groups, a 2D grid search is performed.
4. For all other space groups, a 2D grid search is followed by a 1D line search.

In all cases (including centrosymmetric) the **Δx** value obtained by interpolation is then refined further to minimize α.