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## 15.3. EXAMPLES OF THE USE OF NORMALIZERS

characteristic type of Wyckoff sets (*cf.* Part 14) and the inherent symmetry of all corresponding point configurations is enhanced.

#### Example

The Euclidean and affine normalizer of P6 is  $P^{1}6/mmm$  (**a**, **b**,  $\varepsilon$ **c**). As a consequence of the continuous translations, the site symmetry of any point is at least m. in  $P^{1}6/mmm$ . With the aid of the 'additional generators', one calculates four subsets of point configurations that are equivalent to a given general point configuration 6d xyz with  $x = x_0$ ,  $y = y_0$ ,  $z = z_0$ :  $x_0, y_0, z_0 + t$ ;  $-x_0, -y_0, -z_0 + t$ ;  $y_0, x_0, z_0 + t$ ;  $-y_0, -x_0, -z_0 + t$ . The first two and the second two subsets coincide, however.

According to the above examples, Euclidean- (affine-) equivalent point configurations may or may not belong to the same Wyckoff position. Consequently, normalizers also define equivalence relations on Wyckoff positions:

Two Wyckoff positions of a space group  $\mathcal{G}$  are called *Euclidean*or  $\mathcal{N}_{\mathcal{E}}$ -equivalent (affine- or  $\mathcal{N}_{\mathcal{A}}$ -equivalent) if their point configurations are mapped onto each other by the Euclidean (affine) normalizer of  $\mathcal{G}$ .

Euclidean-equivalent Wyckoff positions are important for the description or comparison of crystal structures in terms of atomic coordinates. Affine-equivalent Wyckoff positions result in *Wyckoff sets (cf.* Section 8.3.2 and Chapter 14.1) and form the necessary basis for the *definition of lattice complexes*. All site-symmetry groups corresponding to equivalent Wyckoff positions are conjugate in the respective normalizer.

## Examples

The Euclidean and affine normalizer of  $I\overline{4}m2$  is I4/mmm  $(\frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{c})$ . It maps the point configurations  $2a \ 000, 2b \ 00\frac{1}{2}, 2c \ 0\frac{1}{2}\frac{1}{4}$  and  $2d \ 0\frac{1}{2}\frac{3}{4}$  (body-centred tetragonal lattices) onto each other. Accordingly, Wyckoff positions a to d are affine-equivalent and together form a Wyckoff set. Analogous point configurations exist in subgroup  $P\overline{4}n2$  of  $I\overline{4}m2$  (again Wyckoff positions a to d). The Euclidean and affine normalizer of  $P\overline{4}n2$ , however, is P4/mmm  $(\frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{c})$ , not containing  $t(\frac{1}{2}0\frac{1}{4})$ . Therefore, Wyckoff positions a and b form one Wyckoff set, c and d a different one. This is also reflected in the site-symmetry groups  $\overline{4}$ .. and 2.22.

The existence of Euclidean-equivalent point configurations results in different but *equivalent descriptions of crystal structures* (exception: crystal structures with symmetry  $Im\overline{3}m$  or  $Ia\overline{3}d$ ). All such equivalent descriptions are derived by applying the additional generators of the Euclidean normalizer of the space group  $\mathcal{G}$  to all point configurations of the original description. Since an adequate description of a crystal structure always displays the full symmetry group of that structure, the number of equivalent descriptions must equal the index of  $\mathcal{G}$  in  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ .

### Example

Ag<sub>3</sub>PO<sub>4</sub> crystallizes with symmetry  $P\overline{4}3n$  (cf. Masse et al., 1976): P at 2a 000, Ag at  $6d \frac{1}{4}0\frac{1}{2}$  and O at 8e xxx with x = 0.1486.  $\mathcal{N}_{\mathcal{E}}(P\overline{4}3n) = Im\overline{3}m$  with index 4 gives rise to three additional equivalent descriptions:  $t(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  yields P at 2a 000, Ag at  $6c \frac{1}{4}\frac{1}{2}0$  and O at 8e xxx with x = 0.1486; inversion through the origin results in P at 2a 000, Ag at  $6d \frac{1}{4}0\frac{1}{2}$ , O at 8e xxx with x = -0.1486 and in P at 2a 000, Ag at  $6c \frac{1}{4}\frac{1}{2}0$  and O at 8e xxx with x = -0.1486. Although the phosphorus configuration is the same for all descriptions and the silver and oxygen atoms refer to only two configurations each, their combinations result in a total of four different equivalent descriptions of the structure. If the Euclidean normalizer of a space group contains continuous translations, each crystal structure with that symmetry refers to an infinite set of equivalent descriptions. This set may be subdivided into a finite number of subsets in such a way that the descriptions of each subset vary according to the continuous translations. The number of these subsets is given by the product of the finite factors listed in the last column of Tables 15.2.1.3 and 15.2.1.4.

#### Example

The tetragonal form of BaTiO<sub>3</sub> has been described in space group P4mm (cf. e.g. Buttner & Maslen, 1992): Ba at  $1a \ 00z$  with z = 0, Ti at  $1b \ \frac{1}{21}z$  with z = 0.482, O1 at  $1b \ \frac{1}{21}z$  with z = 0.016, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.515.  $\mathcal{N}_{\mathcal{E}}(P4mm) = P^{1}4/mmm$   $(\frac{1}{2}(\mathbf{a} - \mathbf{b}), \frac{1}{2}(\mathbf{a} + \mathbf{b}), \varepsilon \mathbf{c})$  gives rise to  $(2 \cdot \infty) \cdot 2 \cdot 1$  equivalent descriptions of this structure. The continuous translation with vector (00t) yields a first infinite subset of equivalent descriptions: Ba at  $1a \ 00z$  with z = t, Ti at  $1b \ \frac{1}{21}z$  with z = 0.482 + t, O1 at  $1b \ \frac{1}{21}z$  with z = 0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.515 + t. The translation with vector  $(\frac{1}{21}2)$  generates a second infinite subset: Ba at  $1b \ \frac{1}{21}z$  with z = t, Ti at  $1a \ 00z$  with z = 0.482 + t, O1 at  $1a \ 00z$  with z = 0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.515 + t. Inversion through the origin causes two further infinite subsets of equivalent coordinate descriptions of BaTiO<sub>3</sub>: first, Ba at  $1a \ 00z$  with z = -0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.485 + t; second, Ba at  $1b \ \frac{1}{21}z$  with z = t, Ti at  $1b \ \frac{1}{21}z$  with z = -0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.485 + t; second, Ba at  $1b \ \frac{1}{21}z$  with z = -0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.485 + t; Second, Ba at  $1b \ \frac{1}{2}z$  with z = -0.016 + t, and O2 at  $2c \ \frac{1}{2}0z$  with z = 0.518 + t, O1 at  $1a \ 00z$  with z = -0.016 + t.

More details on Euclidean-equivalent point configurations and descriptions of crystal structures have been given by Fischer & Koch (1983).

#### 15.3.3. Equivalent lists of structure factors

All the different but equivalent descriptions of a crystal structure refer to different but equivalent lists of structure factors. These lists contain the same moduli of the structure factors  $|F(\mathbf{h})|$ , but they differ in their indices  $\mathbf{h} = (h, k, l)$  and phases  $\varphi(\mathbf{h})$ .

In the previous section, the unit cell (basis and origin) of a space group  $\mathcal{G}$  has been considered fixed, whereas the crystal structure or its enantiomorph was embedded into the pattern of symmetry elements at different but equivalent locations. In the present context, however, it is advantageous to regard the crystal structure as being fixed and to let  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  transform the basis and the origin with respect to which the crystal structure is described. This matches the usual approach to resolve the ambiguities in direct methods by fixing the origin and the absolute structure.

Each matrix–vector pair (P, p) representing an element of  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  describes a unit-cell transformation of  $\mathcal{G}$ . According to Section 5.1.3 the following equations hold:

$$(\mathbf{a}',\mathbf{b}',\mathbf{c}'), = (\mathbf{a},\mathbf{b},\mathbf{c})P, \qquad \begin{pmatrix} \mathbf{a}^{*'}\\ \mathbf{b}^{*'}\\ \mathbf{c}^{*'} \end{pmatrix} = P^{-1} \begin{pmatrix} \mathbf{a}^{*}\\ \mathbf{b}^{*}\\ \mathbf{c}^{*} \end{pmatrix}, \qquad h' = h P.$$

As a consequence, the phase  $\varphi(\mathbf{h})$  of a certain structure factor also changes into  $\varphi'(\mathbf{h}') = \varphi(\mathbf{h}) - 2\pi\mathbf{h}\mathbf{p}$ .

Similar to equivalent descriptions of a crystal structure, it is possible to derive all equivalent lists of structure factors: The additional generators of  $\mathcal{K}(\mathcal{G})$  are pure translations that leave the indices **h** of all structure factors unchanged but transform their phases according to  $\varphi'(\mathbf{h}) = \varphi(\mathbf{h}) - 2\pi \mathbf{h} \mathbf{p}$ . Therefore, the origin for the description of the crystal structure may be fixed by appropriate restrictions of some phases. The number of these phases equals the

	h + k + l =			
F222	4 <i>n</i>	4n + 2	4n + 1	4n + 3
$t(000) \\ t(\frac{1}{4}\frac{1}{4}\frac{1}{4}) \\ t(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \\ t(\frac{3}{4}\frac{3}{4}\frac{3}{4})$	$egin{aligned} arphi(m{h}) \ arphi(m{h}) \ arphi(m{h}) \ arphi(m{h}) \ arphi(m{h}) \ arphi(m{h}) \ arphi(m{h}) \end{aligned}$	$ \begin{aligned} \varphi(\boldsymbol{h}) \\ \pi + \varphi(\boldsymbol{h}) \\ \varphi(\boldsymbol{h}) \\ \pi + \varphi(\boldsymbol{h}) \end{aligned} $	$\varphi(\boldsymbol{h})$ $\frac{3}{2}\pi + \varphi(\boldsymbol{h})$ $\pi + \varphi(\boldsymbol{h})$ $\frac{1}{2}\pi + \varphi(\boldsymbol{h})$	$\varphi(\boldsymbol{h})$ $\frac{1}{2}\pi + \varphi(\boldsymbol{h})$ $\pi + \varphi(\boldsymbol{h})$ $\frac{3}{2}\pi + \varphi(\boldsymbol{h})$
$  \frac{\bar{1}(000)}{\bar{1}(\frac{1}{8}\frac{1}{8}\frac{1}{8})} \\ \bar{1}(\frac{1}{4}\frac{1}{4}\frac{1}{4}) \\ \bar{1}(\frac{3}{8}\frac{3}{8}\frac{3}{8}) $	$egin{aligned} & -arphi(m{h}) \ & -arphi(m{h}) \end{aligned}$	$egin{aligned} & -arphi(m{h}) \ & \pi - arphi(m{h}) \ & -arphi(m{h}) \ & \pi - arphi(m{h}) \ & \pi - arphi(m{h}) \end{aligned}$	$-\varphi(\boldsymbol{h})$ $\frac{1}{2}\pi - \varphi(\boldsymbol{h})$ $\pi - \varphi(\boldsymbol{h})$ $\frac{3}{2}\pi - \varphi(\boldsymbol{h})$	$-\varphi(\boldsymbol{h})$ $\frac{3}{2}\pi - \varphi(\boldsymbol{h})$ $\pi - \varphi(\boldsymbol{h})$ $\frac{1}{2}\pi - \varphi(\boldsymbol{h})$

Table 15.3.3.1. Changes of structure-factor phases for the equivalent descriptions of a crystal structure in F222

number of additional generators of  $\mathcal{K}(\mathcal{G})$ , given in Table 15.2.1.3 or 15.2.1.4. These generators [together with the inversion that generates  $\mathcal{L}(\mathcal{G})$ , if present] also determine the parity classes of the structure factors and the ranges for the phase restrictions.

The inversion that generates  $\mathcal{L}(\mathcal{G})$  changes the handedness of the coordinate system in direct space and in reciprocal space and, therefore, gives rise to different absolute crystal structures. The indices of a given structure factor change from h to h' = -h, whereas the phase is influenced only if the symmetry centre is not located at 000.

If no anomalous scattering is observed, Friedel's rule holds and the moduli of any two structure factors with indices h and -h are equal. As a consequence, different absolute crystal structures result in lists of structure factors and indices that differ only in their phases. Therefore, one phase may be restricted to an appropriate range of length  $\pi$  to fix the absolute structure. This is not possible if anomalous scattering has been observed.

If  $\mathcal{L}(\mathcal{G})$  differs from  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ , *i.e.* if  $\mathcal{G}$  and  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  belong to different Laue classes, the further generators of  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  always change the orientation of the basis in direct and in reciprocal space. Therefore, the indices of the structure factors are permuted, but their phases are transformed only if  $p \neq 0$ . The choice between these equivalent descriptions of the crystal structure is made when indexing the reflection pattern. In the case of anomalous scattering, the similar choice between the absolute structures is also combined with the indexing procedure.

#### Example

According to Table 15.2.1.3, eight equivalent descriptions exist for each crystal structure with symmetry F222. Four of them differ only by an origin shift and the other four are enantiomorphic to the first four.  $t(\frac{11}{444})$  transforms all phases according to  $\varphi'(\mathbf{h}) = \varphi(\mathbf{h}) - (\pi/2)(\mathbf{h} + \mathbf{k} + \mathbf{l})$ , which gives rise to four parity classes of structure factors: h + k + l = 4n, 4n + 1, 4n + 2 and 4n + 3 (*n* integer). As  $t(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  generates all additional translations of  $\mathcal{K}(F222)$ , restriction of one phase  $\varphi(\mathbf{h}_1)$  to a range of length  $\pi/2$  fixes the origin. Restriction of a second phase  $\varphi(\mathbf{h}_2)$  to an appropriately chosen range of length  $\pi$  discriminates between pairs of enantiomorphic descriptions in the absence of anomalous scattering. For  $\overline{1}(000)$ , the corresponding change of phases is  $\varphi'(\mathbf{h}) = -\varphi(\mathbf{h})$ . Table 15.3.3.1 shows, for structure factors from all parity classes, how their phases depend on the chosen description of the crystal structure. Only phases from parity classes h + k + l = 4n + 1 or 4n + 3 determine the origin in a unique way. The phase  $\varphi(h_2)$  that fixes the absolute structure

may be chosen from any parity class but the appropriate range for its restriction depends on the parity classes of  $\varphi(\mathbf{h}_1)$  and  $\varphi(\mathbf{h}_2)$  and, moreover, on the range chosen for  $\varphi(\mathbf{h}_1)$ . If, for instance,  $\varphi(\mathbf{h}_1)$  with h+k+l=4n+1 is restricted to  $\pi/2 \leq \varphi(\mathbf{h}_1) < \pi$ , one of the following restrictions may be chosen for  $\varphi(\mathbf{h}_2): 0 < \varphi(\mathbf{h}_2) < \pi$  for  $h+k+l=4n; -\pi/2 < \varphi(\mathbf{h}_2) < \pi/2$  for  $h+k+l=4n+2; -\pi/4 < \varphi(\mathbf{h}_2) < 3\pi/4$  for  $h+k+l=4n+1; -3\pi/4 < \varphi(\mathbf{h}_2) < \pi/4$  for h+k+l=4n+4 and h+k+l=4n+4. If, however, the phase  $\varphi(\mathbf{h}_1)$  of the same first reflection was restricted to  $-\pi/4 \leq \varphi(\mathbf{h}_1) < 3\pi/4$ , the possible restrictions for the second phase change to:  $0 < \varphi(\mathbf{h}_2) < \pi$  for h+k+l=4n+4 or 4n+3 (for further details, *cf.* Koch, 1986).

# 15.3.4. Euclidean- and affine-equivalent sub- and supergroups

The Euclidean or affine normalizer of a space group  $\mathcal{G}$  maps any subgroup or supergroup of  $\mathcal{G}$  either onto itself or onto another subgroup or supergroup of  $\mathcal{G}$ . Accordingly, these normalizers define equivalence relationships on the sets of subgroups and supergroups of  $\mathcal{G}$  (Koch, 1984*b*):

Two subgroups or supergroups of a space group  $\mathcal{G}$  are called *Euclidean-* or  $\mathcal{N}_{\mathcal{E}}$ - equivalent (affine- or  $\mathcal{N}_{\mathcal{A}}$ - equivalent) if they are mapped onto each other by an element of the Euclidean (affine) normalizer of  $\mathcal{G}$ , *i.e.* if they are conjugate subgroups of the Euclidean (affine) normalizer.

In the following, the term 'equivalent subgroups (supergroups)' is used if a statement is true for Euclidean-equivalent *and* affine-equivalent subgroups (supergroups), and  $\mathcal{N}(\mathcal{G})$  is used to designate the Euclidean as well as the affine normalizer.

The knowledge of Euclidean-equivalent subgroups is necessary in connection with the possible deformations of a crystal structure due to subgroup degradation. Affine-equivalent subgroups play an important role for the derivation and classification of black-andwhite groups (magnetic groups) and of colour groups (cf. for example Schwarzenberger, 1984). Information on equivalent supergroups is useful for the determination of the idealized type of a crystal structure.

For any pair of space groups  $\mathcal{G}$  and  $\mathcal{H}$  with  $\mathcal{H} < \mathcal{G}$ , the relation between the two normalizers  $\mathcal{N}(\mathcal{G})$  and  $\mathcal{N}(\mathcal{H})$  controls the subgroups of  $\mathcal{G}$  that are equivalent to  $\mathcal{H}$  and the supergroups of  $\mathcal{H}$ equivalent to  $\mathcal{G}$ . The intersection group of both normalizers,  $\mathcal{M}(\mathcal{G}, \mathcal{H}) = \mathcal{N}(\mathcal{G}) \cap \mathcal{N}(\mathcal{H}) \geq \mathcal{H}$  may or may not coincide with  $\mathcal{N}(\mathcal{G})$  and/or with  $\mathcal{N}(\mathcal{H})$ . The following two statements hold generally:

(i) The index  $i_g$  of  $\mathcal{M}(\mathcal{G}, \mathcal{H})$  in  $\mathcal{N}(\mathcal{G})$  equals the number of subgroups of  $\mathcal{G}$  which are equivalent to  $\mathcal{H}$ . Each coset of  $\mathcal{M}(\mathcal{G}, \mathcal{H})$  in  $\mathcal{N}(\mathcal{G})$  maps  $\mathcal{H}$  onto another equivalent subgroup of  $\mathcal{G}$ .

(ii) The index  $i_h$  of  $\mathcal{M}(\mathcal{G}, \mathcal{H})$  in  $\mathcal{N}(\mathcal{H})$  equals the number of supergroups of  $\mathcal{H}$  equivalent to  $\mathcal{G}$ . Each coset of  $\mathcal{M}(\mathcal{G}, \mathcal{H})$  in  $\mathcal{N}(\mathcal{H})$  maps  $\mathcal{G}$  onto another equivalent supergroup of  $\mathcal{H}$ .

Equivalent subgroups are *conjugate* in  $\mathcal{G}$  if and only if  $\mathcal{G} \cap \mathcal{N}(\mathcal{H}) \neq \mathcal{G}$ . In this case,  $\mathcal{G}$  contains elements not belonging to  $\mathcal{N}(\mathcal{H})$  and the cosets of  $\mathcal{G} \cap \mathcal{N}(\mathcal{H})$  in  $\mathcal{G}$  refer to the different conjugate subgroups.

Examples

(1)  $\mathcal{G} = Cmmm$  has four monoclinic subgroups of type P2/m with the same orthorhombic metric and the same basis as Cmmm:  $\mathcal{H}_1 = P2/m11$ ,  $\mathcal{H}_2 = P12/m1$ ,  $\mathcal{H}_3 = P112/m$  ( $\overline{1}$  at 000),  $\mathcal{H}_4 = P112/m$  ( $\overline{1}$  at  $\frac{11}{44}$ 0). According to Table 15.2.1.3, the