

## 3.4. LATTICE COMPLEXES

crystal structures (Smirnova, 1962), of Patterson diagrams (Koch & Hellner, 1971), of Dirichlet domains (Koch, 1973, 1984) and of sphere packings for subperiodic groups (Koch & Fischer, 1978b).

The 30 lattice complexes in two-dimensional space correspond uniquely to the 'henomeric types of dot pattern' introduced by Grünbaum and Shephard (*cf. e.g.* Grünbaum & Shephard, 1981; Grünbaum, 1983).

## 3.4.4.2. Relations between crystal structures

Different crystal structures frequently show the same geometrical arrangement for some of their atoms, even though their space groups do not belong to the same type. In such cases, the corresponding Wyckoff positions either belong to the same lattice complex or there exists a close relationship between them, *e.g.* a limiting-complex relation.

## Examples

- (1) The Fe atoms in pyrite  $\text{FeS}_2$  occupy Wyckoff position  $4a \bar{3}. 0, 0, 0$  of  $Pa\bar{3}$  (descriptive symbol  $F$ ) that belongs to the invariant lattice complex  $Fm\bar{3}m a$ . Accordingly, the Fe atoms in pyrite form a face-centred cubic lattice, as do the Cu atoms in the element structure of copper.
- (2) Cuprite  $\text{Cu}_2\text{O}$  crystallizes with symmetry  $Pn\bar{3}m$ . The oxygen atoms occupy Wyckoff position  $2a \bar{4}3m 0, 0, 0$  (descriptive symbol  $I$ ) and the copper atoms position  $4b \bar{3}m \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$  (descriptive symbol  $\frac{1}{4}\frac{1}{4}\frac{1}{4} F$ ). Position  $2a$  belongs to lattice complex  $Im\bar{3}m a$  and position  $4b$  to  $Fm\bar{3}m a$ . Therefore, the O atoms form a body-centred cubic lattice like the W atoms in the structure of tungsten, and the copper atoms form a face-centred cubic lattice. The tungsten configuration is shifted by  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$  with respect to the copper configuration.
- (3)  $\text{K}_2\text{NaAlF}_6$  (elpasolite, *cf.* Morss, 1974) and  $\text{K}_2\text{PbNi}(\text{NO}_2)_6$  (*cf.* Takagi *et al.*, 1975) crystallize with symmetry  $Fm\bar{3}m$  and  $Fm\bar{3}$ , respectively.



Al	4a	$m\bar{3}m$	0, 0, 0	$F$
Na	4b	$m\bar{3}m$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2} F$
K	8c	$\bar{4}3m$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$\frac{1}{4}\frac{1}{4}\frac{1}{4} P_2$
F	24e	$4m.m$	$x, 0, 0$	$F6z$
			$x = 0.219$	



Ni	4a	$m\bar{3}$ .	0, 0, 0	$F$
Pb	4b	$m\bar{3}$ .	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2} F$
K	8c	23.	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$\frac{1}{4}\frac{1}{4}\frac{1}{4} P_2$
N	24e	$mm2..$	$x, 0, 0$	$F6z$
			$x = 0.1966$	
O	48h	$m..$	0, $y, z$	$F6z2x$

As the descriptive lattice-complex symbols for the various atomic positions show immediately, the two crystal structures are very similar. The only difference originates from the replacement of the fluorine atoms in elpasolite by  $\text{NO}_2$  groups in  $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ , which causes the symmetry reduction from  $Fm\bar{3}m$  to  $Fm\bar{3}$ .

- (4) The crystal structure of CoU (Baenziger *et al.*, 1950) may be interpreted as a slightly distorted CsCl (or  $\beta$ -brass, CuZn)-type structure. CsCl corresponds to Wyckoff posi-

tions  $1a$  and  $1b$  of  $Pm\bar{3}m$  with descriptive symbols  $P$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2} P$ , respectively; Co and U both occupy Wyckoff position  $8a .3. x, x, x$  of  $I2_13$  with  $x = 0.0347$  for U and  $x = 0.294$  for Co. As the descriptive symbol  $2_12_1.. P_2 Y^* 1xxx$  shows, this Wyckoff position belongs to a Weissenberg complex with two invariant limiting complexes, namely  $P (Pm\bar{3}m a)$  and  $Y^* (I4_132 a)$ .  $x = 0$  corresponds to  $P_2$ ,  $x = \frac{1}{4}$  to  $\frac{1}{4}\frac{1}{4}\frac{1}{4} P_2$ ,  $x = \frac{1}{8}$  to  $^+ Y^*$  and  $x = \frac{7}{8}$  to  $^- Y^*$ . Consequently, the uranium and cobalt atoms form approximately a  $P_2$  and a  $\frac{1}{4}\frac{1}{4}\frac{1}{4} P_2$  configuration, respectively.

Publications by Hellner (1965, 1976a,b,c, 1977, 1979), Loeb (1970), Smirnova & Vasserman (1971), Sakamoto & Takahashi (1971), Niggli (1971), Fischer & Koch (1974b), Hellner *et al.* (1981) and Hellner & Sowa (1985) refer to this aspect.

## 3.4.4.3. Reflection conditions

Wyckoff positions belonging to the same lattice complex show analogous reflection conditions. Therefore, lattice complexes have also been used to check the reflection conditions for all Wyckoff positions in the space-group tables of this volume.

## Example

The lattice complex  $oF$  consists of all face-centred point lattices with orthorhombic symmetry. For its characteristic Wyckoff position  $Fmmm 4a$ , only the general conditions for reflections  $hkl$  in space group  $Fmmm$  are valid, namely  $h + k, h + l, k + l = 2n$  (*cf.* Chapter 2.3). The non-characteristic Wyckoff position  $Ccce 4a$  also belongs to this lattice complex. The general reflection condition for  $Ccce$  is  $hkl: h + k = 2n$ . This has to be combined with  $k + l = 2n$ , the special condition for Wyckoff position  $a$ . Together the two conditions produce  $h + l = 2n$ , the third condition for a face-centred point lattice.

The descriptive symbols may supply information on the reflection conditions. If the symbol does not contain any distribution-symmetry part, the reflection conditions of the Wyckoff position are indicated by the symbol of the invariant lattice complex in the central part (*e.g.*  $P4/nmm g: C4xx$  shows that the reflection condition is that of a  $C$  lattice,  $hkl: h + k = 2n$ ). In cases where the site set consists of only one point, *i.e.* the Wyckoff position belongs to a Weissenberg complex, all conditions for general reflections  $hkl$  that may arise from special choices of the coordinates can be read from the central part of the symbol (*e.g.*  $P4/nmm c: 0\frac{1}{2}0 .2 CI1z$  indicates that, by special choice of  $z$ , either  $hkl: h + k = 2n$  or  $hkl: h + k + l = 2n$  may be produced).

## 3.4.4.4. Phase transitions

If a crystal undergoes a phase transition from a high- to a low-symmetry modification, the transition may be connected with a group-subgroup transition. In such cases, the comparison of the lattice complexes corresponding to the Wyckoff positions of the original space group on the one hand and of its various subgroups on the other hand very often shows which of these subgroups are suitable for the low-symmetry modification.

This kind of procedure will be demonstrated with the aid of the space group  $R\bar{3}m$  and its three *translationengleiche* subgroups with index 2, namely  $R32$ ,  $R\bar{3}$  and  $R3m$ . In the course of the restriction to a subgroup, the Wyckoff positions of  $R\bar{3}m$  behave differently:

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The descriptive symbols  $R$  and  $00\frac{1}{2}R$  refer to Wyckoff positions  $R\bar{3}m$   $3a$  and  $3b$  as well as to Wyckoff positions  $R32$   $3a$  and  $3b$  and  $R\bar{3}$   $3a$  and  $3b$ . Therefore, all corresponding point configurations and atomic arrangements remain unchanged in these subgroups. In subgroup  $R3m$ , however, the respective Wyckoff position is  $3a$  with descriptive symbol  $R[z]$ , i.e. a shift parallel to  $[001]$  of the entire point configuration is allowed.

The descriptive symbol  $R2z$  for  $R\bar{3}m$   $6c$  also occurs for  $R32$   $6c$  and  $R\bar{3}$   $6c$ . Again, neither subgroup allows any deformations of the corresponding point configurations or atomic arrangements. Symmetry reduction to  $R3m$ , however, yields a splitting of each  $R2z$  configuration into two  $R[z]$  configurations. The two  $z$  parameters may be chosen independently.

As  $M$  and  $00\frac{1}{2}M$  are the descriptive symbols not only of  $R\bar{3}m$   $9e$  and  $9d$  but also of  $R\bar{3}$   $9e$  and  $9d$ ,  $R\bar{3}$  does not enable any deformation of the corresponding atomic arrangements. In  $R32$  and in  $R3m$ , however, the respective point configurations may be differently deformed, as the descriptive symbols show:  $R3x$  and  $00\frac{1}{2}R3x$  ( $R32$   $9d$  and  $9e$ ),  $R3x\bar{x}[z]$  ( $R3m$   $9b$ ).

Wyckoff positions  $R\bar{3}m$   $18f$  and  $18g$  ( $R6x$  and  $00\frac{1}{2}R6x$ ) correspond to  $R32$   $9d$  and  $9e$  ( $R3x$  and  $00\frac{1}{2}R3x$ ), to  $R\bar{3}$   $18f$  ( $R6xyz$ ), and to  $R3m$   $18c$  ( $R3x\bar{x}2y[z]$ ). In  $R32$ , the hexagons  $6x$  around the points of the  $R$  lattice are split into two oppositely oriented triangles  $3x$ , which may have different size. In  $R\bar{3}$  and in  $R3m$ , the hexagons may be differently deformed.

Wyckoff position  $R\bar{3}m$   $18h$  ( $R6x\bar{x}z$ ) corresponds to sets of trigonal antiprisms around the points of an  $R$  lattice. These antiprisms may be distorted in  $R32$   $18f$  ( $R3x2yz$ ) or rotated in  $R\bar{3}$   $18f$  ( $R6xyz$ ). In  $R3m$   $9b$  ( $R3x\bar{x}[z]$ ), each antiprism is split into two parallel triangles that may differ in size.

In each of the three subgroups, any point configuration belonging to the general position  $R\bar{3}m$   $36i$  splits into two parts. Each of these parts may be differently deformed.

#### 3.4.4.5. Incorrect space-group assignment

In the literature, some crystal structures are still described within space groups that are only subgroups of the correct symmetry groups. Many such mistakes (but not all of them) could be avoided by simply looking at the lattice complexes (and their descriptive symbols) that correspond to the Wyckoff positions of the different kinds of atoms. Whenever the same (or an analogous) lattice-complex description of a crystal structure is also possible within a supergroup, then the crystal structure has at least that symmetry.

#### Examples

- (1) The crystal structure of  $\beta$ -LiRhO<sub>2</sub> has been refined in space group  $F4_132$  (cf. Hobbie & Hoppe, 1986).

Rh	16c	.32	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	$T$
Li	16d	.32	$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2} T$
O	32e	.3.	$x, x, x$	..2 $D4xxx$

The same atomic arrangement is possible in the supergroup  $Fd\bar{3}m$  of  $F4_132$ , as can easily be read from Table 3.4.3.3:

Rh	16c	$\bar{3}m$	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	$T$
Li	16d	$\bar{3}m$	$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2} T$
O	32e	$.3m$	$x, x, x$	..2 $D4xxx$

Therefore,  $\beta$ -LiRhO<sub>2</sub> should be described in  $Fd\bar{3}m$ .

- (2) KIA<sub>4</sub>S<sub>4</sub>O<sub>6</sub> (Pertlik, 1988) has been described with symmetry  $P622$ .

I	1a	622	0, 0, 0	$P$
K	1b	622	0, 0, $\frac{1}{2}$	$00\frac{1}{2}P$
As	4h	3..	$\frac{1}{3}, \frac{2}{3}, z$	$G2z$
O	6i	2..	$\frac{1}{2}, 0, z$	$N2z$

Space group  $P6/mmm$  allows the same atomic arrangement:

I	1a	6/mmm	0, 0, 0	$P$
K	1b	6/mmm	0, 0, $\frac{1}{2}$	$00\frac{1}{2}P$
As	4h	3m.	$\frac{1}{3}, \frac{2}{3}, z$	$G2z$
O	6i	2mm	$\frac{1}{2}, 0, z$	$N2z$

Therefore, KIA<sub>4</sub>S<sub>4</sub>O<sub>6</sub> should be described in  $P6/mmm$ .

#### 3.4.4.6. Application of descriptive lattice-complex symbols

Descriptive symbols of lattice complexes – at least those of the invariant lattice complexes – have been used for the description of crystal structures (cf. Section 3.4.4.2 and the literature cited there), for the nomenclature of three-periodic surfaces (von Schnering & Nesper, 1987) and in connection with orbifolds of space groups (Johnson *et al.*, 2001).

#### 3.4.4.7. Weissenberg complexes

In general, each lattice complex involves point configurations that cannot be related to any crystal structure because the shortest distances between the atoms in a corresponding arrangement would become too small. Only the 67 Weissenberg complexes (cf. Section 3.4.1.5.2) form an exception from this rule. Assuming that the metrical parameters are chosen adequately, each point configuration stemming from a Weissenberg complex may, in principle, refer to the arrangement of some atoms in a crystal structure. In case of the 36 invariant lattice complexes this property is immediately evident. The further 31 Weissenberg complexes have one or more degrees of freedom (cf. Section 3.4.1.5.2 and Table 3.4.1.1). Nevertheless, varying the corresponding free coordinate parameters never results in point configurations with infinitesimally small distances.

#### References

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