

## 14.3. Applications of the lattice-complex concept

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## 14.3.1. Geometrical properties of point configurations

To study the geometrical properties of all point configurations in three-dimensional space, it is not necessary to consider all Wyckoff positions of the space groups or all 1128 types of Wyckoff set. Instead, one may restrict the investigations to the characteristic Wyckoff positions of the 402 lattice complexes. The results can then be transferred to all noncharacteristic Wyckoff positions of the lattice complexes, as listed in Tables 14.2.3.1 and 14.2.3.2.

The determination of all types of sphere packings with cubic or tetragonal symmetry forms an example for this kind of procedure (Fischer, 1973, 1974, 1991*a,b*, 1993). The cubic lattice complex  $I4xxx$ , for example, allows two types of sphere packings within its characteristic Wyckoff position  $I43m\ 8c\ xxx\ .3m$ , namely  $9/3/c2$  for  $x = 3/16$  and  $6/4/c1$  for  $3/16 \leq x < 1/4$  (cf. Fischer, 1973).  $Ag_3PO_4$  crystallizes with symmetry  $P43n$  (Deschizeaux-Cheruy *et al.*, 1982) and the oxygen atoms occupy Wyckoff position  $8e\ xxx\ .3$ , which also belongs to  $I4xxx$ . Comparison of the coordinate parameter  $x = 0.1491$  for the oxygen atoms with the sphere-packing parameters listed for  $I43m\ c$  shows directly that the oxygen arrangement in this crystal structure does not form a sphere packing.

Other examples for this approach are the derivation of crystal potentials (Naor, 1958), of coordinate restrictions in 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, 1978).

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).

## 14.3.2. Relations between crystal structures

Frequently, different crystal structures show the same geometrical arrangement for some of their atoms, even though their space groups do not belong to the same type. In these cases, the corresponding Wyckoff positions either belong to the same lattice complex or there exist close relationships between them, e.g. limiting-complex relations.

## Examples

- (1) The Fe atoms in pyrite  $FeS_2$  occupy Wyckoff position  $4a\ 000\ .3$  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  $Cu_2O$  crystallizes with symmetry  $Pn\bar{3}m$ . The oxygen atoms occupy Wyckoff position  $2a\ 000\ 43m$  (descriptive symbol  $I$ ) and the copper atoms position  $4b\ \frac{1}{4}\frac{1}{4}\frac{1}{4}\ .3m$  (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)  $K_2NaAlF_6$  (elpasolite, cf. Morss, 1974) and  $K_2PbNi(NO_2)_6$  (cf. Takagi *et al.*, 1975) crystallize with symmetry  $Fm\bar{3}m$  and  $Fm\bar{3}$ , respectively.

 $K_2NaAlF_6$ 

Al	4a	$m\bar{3}m$	000	$F$
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	x00	$F6z$

$$x = 0.219$$

 $K_2PbNi(NO_2)_6$ 

Ni	4a	$m\bar{3}$	000	$F$
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	$mm2..$	x00	$F6z$

$$x = 0.1966$$

O	48h	$m..$	0yz	$F6z2x$
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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  $NO_2$  groups in  $K_2PbNi(NO_2)_6$ , 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 positions  $1a$  and  $1b$  of  $Pm\bar{3}m$  with descriptive symbol  $P$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}\ P$ , respectively; Co and U both occupy Wyckoff position  $8a\ .3\ .xxx$  of  $I2_13$  with  $x = 0.0347$  for U and  $x = 0.294$  for Co. As the descriptive symbol  $2_12_1.. P_2Y^*1xxx$  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, 1976*a,b,c*, 1977, 1979), Loeb (1970), Smirnova & Vasserman (1971), Sakamoto & Takahasi (1971), Niggli (1971), Fischer & Koch (1974), Hellner *et al.* (1981) and Hellner & Sowa (1985) refer to this aspect.

## 14.3.3. 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.

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 the case that 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.  $P4/nmm$   $c: 0\frac{1}{2}0 ..2 C1z$  indicates that, by special choice of  $z$ , either  $hkl: h+k=2n$  or  $hkl: h+k+l=2n$  may be produced).

#### 14.3.4. 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 degradation. In such a case, 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 a space group  $R\bar{3}m$  and its three translation-equivalent subgroups with index 2, namely  $R32$ ,  $R\bar{3}$  and  $R3m$ . In the course of the subgroup degradation, the Wyckoff positions of  $R\bar{3}m$  behave differently:

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  $R\bar{3}m$   $6c$  occurs also for  $R32$   $6c$  and  $R\bar{3}$   $6c$ . Again both subgroups do not allow 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 deformed differently, 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 deformed differently.

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 deformed differently.

#### 14.3.5. 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	$\frac{111}{888}$	$T$
Li	16d	.32	$\frac{555}{888}$	$\frac{111}{222} T$
O	32e	.3.	xxx	..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 14.2.3.2:

Rh	16c	$\bar{3}m$	$\frac{111}{888}$	$T$
Li	16d	$\bar{3}m$	$\frac{555}{888}$	$\frac{111}{222} T$
O	32e	$\bar{3}m$	xxx	..2 $D4xxx$

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

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

I	1a	622	000	$P$
K	1b	622	$00\frac{1}{2}$	$00\frac{1}{2} P$
As	4h	3..	$\frac{1}{3}z$	$G2z$
O	6i	2..	$\frac{1}{2}0z$	$N2z$

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

I	1a	$6/mmm$	000	$P$
K	1b	$6/mmm$	$00\frac{1}{2}$	$00\frac{1}{2} P$
As	4h	$3m.$	$\frac{1}{3}z$	$G2z$
O	6i	$2mm$	$\frac{1}{2}0z$	$N2z$

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

#### 14.3.6. 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 14.3.2 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).

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## 14.1

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