1. INTRODUCTION TO SPACE-GROUP SYMMETRY

These reflection conditions that are not related to space-group operations are given in Chapter 2.3 only for special positions. They may arise, however, also for different reasons. For example, a heavy atom at the origin of the space group $P2_12_12_1$ would generate F-centring with corresponding apparent absences (*cf.* the special position 4*a* of the space group *Pbca* and the absences it generates).

We wish to point out that the most common 'special-position absence' in molecular structures is due to a heavy atom at the origin of the space group $P2_1/c$.

1.6.4. Tables of reflection conditions and possible space groups

By H. D. Flack and U. Shmueli

1.6.4.1. Introduction

The primary order of presentation of these tables of reflection conditions of space groups is the Bravais lattice. This order has been chosen because cell reduction on unit-cell dimensions leads to the Bravais lattice as described as stage 1 in Section 1.6.2.1. Within the space groups of a given Bravais lattice, the entries are arranged by Laue class, which may be obtained as described as stage 2 in Section 1.6.2.1. As a consequence of these decisions about the way the tables are structured, in the hexagonal family one finds for the Bravais lattice *hP* that the Laue classes $\bar{3}$, $\bar{3}m1$, $\bar{3}1m$, $6/m$ and $6/mmm$ are grouped together.

As an aid in the study of naturally occurring macromolecules and compounds made by enantioselective synthesis, the space groups of enantiomerically pure compounds (Sohncke space groups) are typeset in bold.

The tables show, on the left, sets of reflection conditions and, on the right, those space groups that are compatible with the given set of reflection conditions. The reflection conditions, *e.g.* h or $k + l$, are to be understood as $h = 2n$ or $k + l = 2n$, respectively. All of the space groups in each table correspond to the same Patterson symmetry, which is indicated in the table header. This makes for easy comparison with the entries for the individual space groups in Chapter 2.3 of this volume, in which the Patterson symmetry is also very clearly shown. All space groups with a conventional choice of unit cell are included in Tables 1.6.4.2–1.6.4.30. All alternative settings displayed in Chapter 2.3 are thus included. The following further alternative settings, not displayed in Chapter 2.3, are also included: space group $Pb\bar{3}$ (205) and all the space groups with an *hR* Bravais lattice in the reverse setting with hexagonal axes.

Table 1.6.2.1 gives some relevant statistics drawn from Tables 1.6.4.2–1.6.4.30. The total number of space-group settings mentioned in these tables is 416. This number is considerably larger than the 230 space-group types described in Part 2 of this volume. The following example shows why the tables include data for several descriptions of the space-group types. At the stage of space-group determination for a crystal in the crystal class *mm*2, it is not yet known whether the twofold rotation axis lies along **a**, **b** or **c**. Consequently, space groups based on the three point groups $2mm$, $m2m$ and $mm2$ need to be considered.

In some texts dealing with space-group determination, a 'diffraction symbol' (sometimes also called an 'extinction symbol') in the form of a Hermann–Mauguin space-group symbol is used as a shorthand code for the reflection conditions and Laue class. These symbols were introduced by Buerger (1935, 1942,

1969) and a concise description is to be found in Looijenga-Vos & Buerger (2002). Nespolo *et al.* (2014) use them.

1.6.4.2. Examples of the use of the tables

(1) If the Bravais lattice is *oI* and the Laue class is *mmm*, Table 1.6.4.1 directs us to Table 1.6.4.11. Given the observed reflection conditions

hkl: $h + k + l = 2n$, $0kl$: $k = 2n, l = 2n$, $h0l$: $h + l = 2n$,
$hk0$: $h + k = 2n$, $h00$: $h = 2n$, $0k0$: $k = 2n$, $00l$: $l = 2n$,

it is seen from Table 1.6.4.11 that the possible settings of the space groups are: *Ibm*2 (46), *Ic*2*m* (46), *Ibmm* (74) and *Icmm* (74).

(2) If the Bravais lattice is *oP* and the Laue class is *mmm*, Table 1.6.4.1 directs us to Table 1.6.4.7. If there are no conditions on $0kl$, the space groups $P222$ to $Pmnn$ should be searched. If the condition is $0kl$: $k = 2n$ or $l = 2n$, the space groups $Pbm2$ to $Pcnn$ should be searched. If the condition is $0kl$: $k + l = 2n$, the space groups $Pnm2_1$ to $Pnnn$ should be searched.

(3) If the Bravais lattice is *cP* and the Laue class is $m\bar{3}$, Table 1.6.4.1 directs us to Table 1.6.4.25. If the conditions are $0kl$: $k = 2n$ and $h00$: $h = 2n$, it is readily seen that the space group is $Pa\bar{3}$.

(4) If only the Bravais lattice is known or assumed, which is the case in powder-diffraction work (see Section 1.6.5.3), all tables of this section corresponding to this Bravais lattice need to be consulted. For example, if it is known that the Bravais lattice is of type *cP*, Table 1.6.4.1 tells us that the possible Laue classes are $m\bar{3}$ and $m\bar{3}m$, and the possible space groups can be found in Tables 1.6.4.25 and 1.6.4.26, respectively. The appropriate reflection conditions are of course given in these tables. All relevant tables can thus be located with the aid of Table 1.6.4.1 if the Bravais lattice is known.

1.6.5. Specialized methods of space-group determination

By H. D. Flack

1.6.5.1. Applications of resonant scattering to symmetry determination

1.6.5.1.1. Introduction

In small-molecule crystallography, it has been customary in crystal-structure analysis to make no use of the contribution of resonant scattering (otherwise called anomalous scattering and in older literature anomalous dispersion) other than in the specific area of absolute-structure and absolute-configuration determination. One may trace the causes of this situation to the weakness of the resonant-scattering contribution, to the high cost in time and labour of collecting intensity data sets containing measurements of all Friedel opposites and for a lack of any perceived or real need for the additional information that might be obtained from the effects of resonant scattering.

On the experimental side, the turning point came with the widespread distribution of area detectors for small-molecule crystallography, giving the potential to measure, at no extra cost, full-sphere data sets leading to the intensity differences between Friedel opposites hkl and $\overline{hkl}$. In 2015, the new methods of data analysis briefly presented here are in the stage of development

references