3.1. Space-group determination and diffraction symbols

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3.1.1. Introduction

In this chapter, the determination of space groups from the Laue symmetry and the reflection conditions, as obtained from diffraction patterns, is discussed. Apart from Section 3.1.6.5, where differences between reflections hkl and $\bar{h}\bar{k}\bar{l}$ due to anomalous dispersion are discussed, it is assumed that Friedel's rule holds, *i.e.* that $|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2$. This implies that the reciprocal lattice weighted by $|F(hkl)|^2$ has an inversion centre, even if this is not the case for the crystal under consideration. Accordingly, the symmetry of the weighted reciprocal lattice belongs, as was discovered by Friedel (1913), to one of the eleven Laue classes of Table 3.1.2.1. As described in Section 3.1.5, Laue class plus reflection conditions in most cases do not uniquely specify the space group. Methods that help to overcome these ambiguities, especially with respect to the presence or absence of an inversion centre in the crystal, are summarized in Section 3.1.6.

3.1.2. Laue class and cell

Space-group determination starts with the assignment of the *Laue class* to the weighted reciprocal lattice and the determination of the *cell geometry*. The conventional cell (except for the case of a primitive rhombohedral cell) is chosen such that the basis vectors coincide as much as possible with directions of highest symmetry (*cf.* Chapters 2.1 and 9.1).

The axial system should be taken right-handed. For the different crystal systems, the symmetry directions (*blickrichtungen*) are listed in Table 2.2.4.1. The symmetry directions and the convention that, within the above restrictions, the cell should be taken as small as possible determine the axes and their labels uniquely for crystal systems with symmetry higher than orthorhombic. For orthorhombic crystals, three directions are fixed by symmetry, but any of the three may be called a, b or c. For monoclinic crystals, there is one unique direction. It has to be decided whether this direction is called b, c or a. If there are no special reasons (physical properties, relations with other structures) to decide otherwise, the standard choice b is preferred. For triclinic crystals, usually the reduced cell is taken (*cf.* Chapter 9.2), but the labelling of the axes remains a matter of choice, as in the orthorhombic system.

If the lattice type turns out to be centred, which reveals itself by systematic absences in the general reflections hkl (Section 2.2.13), examination should be made to see whether the smallest cell has been selected, within the conventions appropriate to the crystal system. This is necessary since Table 3.1.4.1 for space-group determination is based on such a selection of the cell. Note, however, that for rhombohedral space groups two cells are considered, the triple hexagonal cell and the primitive rhombohedral cell.

The Laue class determines the crystal system. This is listed in Table 3.1.2.1. Note the conditions imposed on the lengths and the directions of the cell axes as well as the fact that there are crystal systems to which two Laue classes belong.

Table 3.1.2.1. *Laue classes and crystal systems*

Laue class	Crystal system	Conditions imposed on cell geometry
$\bar{1}$	Triclinic	None
$2/m$	Monoclinic	$\alpha = \gamma = 90°$ (b unique) $\alpha = \beta = 90°$ (c unique)
mmm	Orthorhombic	$\alpha = \beta = \gamma = 90°$
$4/m$ $4/mmm$	Tetragonal	$a = b; \alpha = \beta = \gamma = 90°$
$\bar{3}$ $\bar{3}m$	Trigonal	$a = b; \alpha = \beta = 90°; \gamma = 120°$ (hexagonal axes) $a = b = c; \alpha = \beta = \gamma$ (rhombohedral axes)
$6/m$ $6/mmm$	Hexagonal	$a = b; \alpha = \beta = 90°; \gamma = 120°$
$m\bar{3}$ $m\bar{3}m$	Cubic	$a = b = c; \alpha = \beta = \gamma = 90°$

3.1.3. Reflection conditions and diffraction symbol

In Section 2.2.13, it has been shown that 'extinctions' (sets of reflections that are systematically absent) point to the presence of a centred cell or the presence of symmetry elements with glide or screw components. Reflection conditions and Laue class together are expressed by the *Diffraction symbol*, introduced by Buerger (1935, 1942, 1969); it consists of the Laue-class symbol, followed by the extinction symbol representing the observed reflection conditions. Donnay & Harker (1940) have used the concept of extinctions under the name of 'morphological aspect' (or aspect for short) in their studies of crystal habit (*cf. Crystal Data*, 1972). Although the concept of aspect applies to diffraction as well as to morphology (Donnay & Kennard, 1964), for the present tables the expression 'extinction symbol' has been chosen because of the morphological connotation of the word aspect.

The *Extinction symbols* are arranged as follows. First, a capital letter is given representing the centring type of the cell (Section 1.2.1). Thereafter, the reflection conditions for the successive symmetry directions are symbolized. Symmetry directions not having reflection conditions are represented by a dash. A symmetry direction with reflection conditions is represented by the symbol for the corresponding glide plane and/or screw axis. The symbols applied are the same as those used in the Hermann–Mauguin space-group symbols (Section 1.3.1). If a symmetry direction has more than one kind of glide plane, for the diffraction symbol the same letter is used as in the corresponding space-group symbol. An exception is made for some centred orthorhombic space groups where *two* glide-plane symbols are given (between parentheses) for one of the symmetry directions, in order to stress the relation between the diffraction symbol and the symbols of the 'possible space groups'. For the various orthorhombic settings, treated in Table 3.1.4.1, the top lines of the two-line space-group symbols in Table 4.3.2.1 are used. In the monoclinic system, dummy numbers '1' are inserted for two directions even though they are not symmetry directions, to bring out the differences between the diffraction symbols for the b, c and a settings.

references