*International Tables for Crystallography* (2006). Vol. A, Section 3.1.6, pp. 51–53.



Table 3.1.4.1. *Reflection conditions, diffraction symbols and possible space groups* (*cont.*)

TETRAGONAL, Laue classes $4/m$ and $4/mmm$ (*cont.*)

| Reflection conditions | | | | | | | Extinction symbol | Laue class: $4/m$ — Point group | | | Laue class: $4/mmm$ ($4/m\ 2/m\ 2/m$) — Point group | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *hkl* | *hk*0 | 0*kl* | *hhl* | 00*l* | 0*k*0 | *hh*0 | | 4 | $\bar{4}$ | $4/m$ | 422 | 4*mm* | $\bar{4}2m$ $\bar{4}m2$ | $4/mmm$ |
| | $h+k$ | $k$ | | | $k$ | | $Pnb-$ | | | | | | | $P4/nbm$ (125) |
| | $h+k$ | $k$ | $l$ | $l$ | $k$ | | $Pnbc$ | | | | | | | $P4_2/nbc$ (133) |
| | $h+k$ | $l$ | | $l$ | $k$ | | $Pnc-$ | | | | | | | $P4_2/ncm$ (138) |
| | $h+k$ | $l$ | $l$ | $l$ | $k$ | | $Pncc$ | | | | | | | $P4/ncc$ (130) |
| | $h+k$ | $k+l$ | | $l$ | $k$ | | $Pnn-$ | | | | | | | $P4_2/nnm$ (134) |
| | $h+k$ | $k+l$ | $l$ | $l$ | $k$ | | $Pnnc$ | | | | | | | $P4/nnc$ (126) |
| $h+k+l$ | $h+k$ | $k+l$ | $l$ | $l$ | $k$ | | $I---$ | $I4$ (79) | $I\bar{4}$ (82) | $I4/m$ (87) | $I422$ (97) | $I4mm$ (107) | $I\bar{4}2m$ (121) $I\bar{4}m2$ (119) | $I4/mmm$ (139) |
| $h+k+l$ | $h+k$ | $k+l$ | $l$ | $l=4n$ | $k$ | | $I4_1--$ | $I4_1$ (80) | | | $I4_122$ (98) | | | |
| $h+k+l$ | $h+k$ | $k+l$ | ‡ | $l=4n$ | $k$ | $h$ | $I--d$ | | | | | $I4_1md$ (109) | $I\bar{4}2d$ (122) | |
| $h+k+l$ | $h+k$ | $k, l$ | $l$ | $l$ | $k$ | | $I-c-$ | | | | | $I4cm$ (108) | $I\bar{4}c2$ (120) | $I4/mcm$ (140) |
| $h+k+l$ | $h+k$ | $k, l$ | ‡ | $l=4n$ | $k$ | $h$ | $I-cd$ | | | | | $I4_1cd$ (110) | | |
| $h+k+l$ | $h, k$ | $k+l$ | $l$ | $l=4n$ | $k$ | | $I4_1/a--$ | | | $I4_1/a$ (88) | | | | |
| $h+k+l$ | $h, k$ | $k+l$ | ‡ | $l=4n$ | $k$ | $h$ | $Ia-d$ | | | | | | | $I4_1/amd$ (141) |
| $h+k+l$ | $h, k$ | $k, l$ | ‡ | $l=4n$ | $k$ | $h$ | $Iacd$ | | | | | | | $I4_1/acd$ (142) |

† Pair of enantiomorphic space groups, *cf.* Section 3.1.5.
‡ Condition: $2h+l=4n$; $l$.

(as well as for the $R$ space groups of the trigonal system), the different cell choices and settings of one space group are disregarded, 101 extinction symbols* and 122 diffraction symbols for the 230 space-group types result.

Only in 50 cases does a diffraction symbol uniquely identify just one space group, thus leaving 72 diffraction symbols that correspond to more than one space group. The 50 unique cases can be easily recognized in Table 3.1.4.1 because the line for the possible space groups in the particular Laue class contains just one entry.

The non-uniqueness of the space-group determination has two reasons:

(i) Friedel's rule, *i.e.* the effect that, with neglect of anomalous dispersion, the diffraction pattern contains an inversion centre, even if such a centre is not present in the crystal.

*Example*

A monoclinic crystal (with unique axis $b$) has the diffraction symbol $1\,2/m\,1P1c1$. Possible space groups are $P1c1$ (7) without an inversion centre, and $P12/c1$ (13) with an inversion centre. In both cases, the diffraction pattern has the Laue symmetry $1\,2/m\,1$.

One aspect of Friedel's rule is that the diffraction patterns are the same for two enantiomorphic space groups. Eleven diffraction symbols each correspond to a pair of enantiomorphic space groups. In Table 3.1.4.1, such pairs are grouped between braces. Either of the two space groups may be chosen for structure solution. If due to anomalous scattering Friedel's rule does not hold, at the refinement stage of structure determination it may be possible to determine the absolute structure and consequently the correct space group from the enantiomorphic pair.

(ii) The occurrence of four space groups in two 'special' pairs, each pair belonging to the same point group: $I222$ (23) & $I2_12_12_1$ (24) and $I23$ (197) & $I2_13$ (199). The two space groups of each pair differ in the location of the symmetry elements with respect to each other. In Table 3.1.4.1, these two special pairs are given in square brackets.

### 3.1.6. Space-group determination by additional methods

#### 3.1.6.1. *Chemical information*

In some cases, chemical information determines whether or not the space group is centrosymmetric. For instance, all proteins crystallize in noncentrosymmetric space groups as they are constituted of L-amino acids only. Less certain indications may be obtained by considering the number of molecules per cell and the possible space-group symmetry. For instance, if experiment shows that there are two molecules of formula $A_\alpha B_\beta$ per cell in either space group $P2_1$ or $P2_1/m$ and if the molecule $A_\alpha B_\beta$ cannot possibly have either a mirror plane or an inversion centre, then there is a strong indication that the correct space group is $P2_1$. Crystallization of $A_\alpha B_\beta$ in $P2_1/m$ with random disorder of the molecules cannot be excluded, however. In a similar way, multiplicities of Wyckoff positions and the number of formula units per cell may be used to distinguish between space groups.

* The increase from 97 (*IT*, 1952) to 101 extinction symbols is due to the separate treatment of the trigonal and hexagonal crystal systems in Table 3.1.4.1, in contradistinction to *IT* (1952), Table 4.4.3, where they were treated together. In *IT* (1969), diffraction symbols were listed by Laue classes and thus the number of extinction symbols is the same as that of diffraction symbols, namely 122.

Table 3.1.4.1. *Reflection conditions, diffraction symbols and possible space groups* (*cont.*)

TRIGONAL, Laue classes $\bar{3}$ and $\bar{3}m$

| Reflection conditions | | | | Extinction symbol | Laue class | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\bar{3}$ | | $\bar{3}m1$ ($\bar{3}\ 2/m\ 1$) $\bar{3}m$ | | | $\bar{3}1m$ ($\bar{3}\ 1\ 2/m$) | | |
| Hexagonal axes | | | | | Point group | | | | | | | |
| $hkil$ | $h\bar{h}0l$ | $hh\overline{2h}l$ | $000l$ | | 3 | $\bar{3}$ | 321 32 | $3m1$ $3m$ | $\bar{3}m1$ $\bar{3}m$ | 312 | $31m$ | $\bar{3}1m$ |
| | | | | $P - - -$ | $P3$ (143) | $P\bar{3}$ (147) | $P321$ (150) | $P3m1$ (156) | $P\bar{3}m1$ (164) | $P312$ (149) | $P31m$ (157) | $P\bar{3}1m$ (162) |
| | | | $l = 3n$ | $P3_1 - -$ | $\{P3_1(144), P3_2(145)\}$ § | | $\{P3_121$ (152), $P3_221$ (154)$\}$ § | | | $\{P3_112$ (151), $P3_212$ (153)$\}$ § | | |
| | | $l$ | $l$ | $P - - c$ | | | | | | | $P31c$ (159) | $P\bar{3}1c$ (163) |
| | $l$ | | $l$ | $P - c -$ | | | | $P3cl$ (158) | $P\bar{3}c1$ (165) | | | |
| $-h+k+l=3n$ | $h+l=3n$ | $l=3n$ | $l=3n$ | $R$(obv)$- -$ ¶ | $R3$ (146) | $R\bar{3}$ (148) | $R32$ (155) | $R3m$ (160) | $R\bar{3}m$ (166) | | | |
| $-h+k+l=3n$ | $h+l=3n$; $l$ | $l=3n$ | $l=6n$ | $R$(obv)$- c$ | | | | $R3c$ (161) | $R\bar{3}c$ (167) | | | |
| $h-k+l=3n$ | $-h+l=3n$ | $l=3n$ | $l=3n$ | $R$(rev)$- -$ | $R3$ (146) | $R\bar{3}$ (148) | $R32$ (155) | $R3m$ (160) | $R\bar{3}m$ (166) | | | |
| $h-k+l=3n$ | $-h+l=3n$; $l$ | $l=3n$ | $l=6n$ | $R$(rev)$- c$ | | | | $R3c$ (161) | $R\bar{3}c$ (167) | | | |
| Rhombohedral axes | | | | Extinction symbol | Point group | | | | | | | |
| $hkl$ | | $hhl$ | $hhh$ | | 3 | $\bar{3}$ | 32 | $3m$ | $\bar{3}m$ | | | |
| | | | | $R - -$ | $R3$(146) | $R\bar{3}$ (148) | $R32$ (155) | $R3m$ (160) | $R\bar{3}m$ (166) | | | |
| | | $l$ | $h$ | $R - c$ | | | | $R3c$ (161) | $R\bar{3}c$ (167) | | | |

§ Pair of enantiomorphic space groups; *cf.* Section 3.1.5.
¶ For obverse and reverse settings *cf.* Section 1.2.1. The obverse setting is standard in these tables.
The transformation reverse → obverse is given by **a**(obv.) = −**a**(rev.), **b**(obv.) = −**b**(rev.), **c**(obv.) = **c**(rev.).

HEXAGONAL, Laue classes $6/m$ and $6/mmm$

| Reflection conditions | | | Extinction symbol | Laue class | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $6/m$ | | | $6/mmm$ ($6/m\ 2/m\ 2/m$) | | | |
| | | | | Point group | | | | | | |
| $h\bar{h}0l$ | $hh\overline{2h}l$ | $000l$ | | 6 | $\bar{6}$ | $6/m$ | 622 | $6mm$ | $\bar{6}2m$ $\bar{6}m2$ | $6/mmm$ |
| | | | $P - - -$ | $P6$ (168) | $P\bar{6}$ (174) | $P6/m$ (175) | $P622$ (177) | $P6mm$ (183) | $P\bar{6}2m$ (189) $P\bar{6}m2$ (187) | $P6/mmm$ (191) |
| | | $l$ | $P6_3 - -$ | $P6_3$ (173) | | $P6_3/m$ (176) | $P6_322$ (182) | | | |
| | | $l=3n$ | $P6_2 - -$ | $\{P6_2$ (171), $P6_4$ (172)$\}$ ** | | | $\{P6_222$ (180), $P6_422$ (181)$\}$ ** | | | |
| | | $l=6n$ | $P6_1 - -$ | $\{P6_1$ (169), $P6_5$ (170)$\}$ ** | | | $\{P6_122$ (178), $P6_522$ (179)$\}$ ** | | | |
| | $l$ | $l$ | $P - - c$ | | | | | $P6_3mc$ (186) | $P\bar{6}2c$ (190) | $P6_3/mmc$ (194) |
| $l$ | | $l$ | $P - c -$ | | | | | $P6_3cm$ (185) | $P\bar{6}c2$ (188) | $P6_3/mcm$ (193) |
| $l$ | $l$ | $l$ | $P - cc$ | | | | | $P6cc$ (184) | | $P6/mcc$ (192) |

** Pair of enantiomorphic space groups, *cf.* Section 3.1.5.

Table 3.1.4.1. *Reflection conditions, diffraction symbols and possible space groups* (*cont.*)

CUBIC, Laue classes $m\bar{3}$ and $m\bar{3}m$

| Reflection conditions (Indices are permutable, apart from space group No. 205) †† | | | | Extinction symbol | Laue class: $m\bar{3}$ ($2/m\ \bar{3}$) | | Laue class: $m\bar{3}m$ ($4/m\ \bar{3}\ 2/m$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Point group | | | | |
| $hkl$ | $0kl$ | $hhl$ | $00l$ | | 23 | $m\bar{3}$ | 432 | $\bar{4}3m$ | $m\bar{3}m$ |
| | | | | $P---$ | $P23$ (195) | $Pm\bar{3}$ (200) | $P432$ (207) | $P\bar{4}3m$ (215) | $Pm\bar{3}m$ (221) |
| | | | $l$ | $\{P2_1--$, $P4_2--\}$ | $P2_13$ (198) | | $P4_232$ (208) | | |
| | | | $l=4n$ | $P4_1--$ | | | $\{P4_132$ (213), $P4_332$ (212)$\}$ ‡‡ | | |
| | | $l$ | $l$ | $P--n$ | | | | $P\bar{4}3n$ (218) | $Pm\bar{3}n$ (223) |
| | $k$†† | | $l$ | $Pa--$ | | $Pa\bar{3}$ (205) | | | |
| | $k+l$ | | $l$ | $Pn--$ | | $Pn\bar{3}$ (201) | | | $Pn\bar{3}m$ (224) |
| | $k+l$ | $l$ | $l$ | $Pn-n$ | | | | | $Pn\bar{3}n$ (222) |
| $h+k+l$ | $k+l$ | $l$ | $l$ | $I---$ | $[I23$ (197), $I2_13$ (199)$]$ §§ | $Im\bar{3}$ (204) | $I432$ (211) | $I\bar{4}3m$ (217) | $Im\bar{3}m$ (229) |
| $h+k+l$ | $k+l$ | $l$ | $l=4n$ | $I4_1--$ | | | $I4_132$ (214) | | |
| $h+k+l$ | $k+l$ | $2h+l=4n, l$ | $l=4n$ | $I--d$ | | | | $I\bar{4}3d$ (220) | |
| $h+k+l$ | $k, l$ | $l$ | $l$ | $Ia--$ | | $Ia\bar{3}$ (206) | | | |
| $h+k+l$ | $k, l$ | $2h+l=4n, l$ | $l=4n$ | $Ia-d$ | | | | | $Ia\bar{3}d$ (230) |
| $h+k, h+l, k+l$ | $k, l$ | $h+l$ | $l$ | $F---$ | $F23$ (196) | $Fm\bar{3}$ (202) | $F432$ (209) | $F\bar{4}3m$ (216) | $Fm\bar{3}m$ (225) |
| $h+k, h+l, k+l$ | $k, l$ | $h+l$ | $l=4n$ | $F4_1--$ | | | $F4_132$ (210) | | |
| $h+k, h+l, k+l$ | $k, l$ | $h, l$ | $l$ | $F--c$ | | | | $F\bar{4}3c$ (219) | $Fm\bar{3}c$ (226) |
| $h+k, h+l, k+l$ | $k+l=4n, k, l$ | $h+l$ | $l=4n$ | $Fd--$ | | $Fd\bar{3}$ (203) | | | $Fd\bar{3}m$ (227) |
| $h+k, h+l, k+l$ | $k+l=4n, k, l$ | $h, l$ | $l=4n$ | $Fd-c$ | | | | | $Fd\bar{3}c$ (228) |

†† For No. 205, only cyclic permutations are permitted. Conditions are $0kl$: $k=2n$; $h0l$: $l=2n$; $hk0$: $h=2n$.
‡‡ Pair of enantiomorphic space groups, *cf.* Section 3.1.5.
§§ Pair of space groups with common point group and symmetry elements but differing in the relative location of these elements.

### 3.1.6.2. *Point-group determination by methods other than the use of X-ray diffraction*

This is discussed in Chapter 10.2. In favourable cases, suitably chosen methods can prove the absence of an inversion centre or a mirror plane.

### 3.1.6.3. *Study of X-ray intensity distributions*

X-ray data can give a strong clue to the presence or absence of an inversion centre if not only the symmetry of the diffraction pattern but also the distribution of the intensities of the reflection spots is taken into account. Methods have been developed by Wilson and others that involve a statistical examination of certain groups of reflections. For a textbook description, see Lipson & Cochran (1966) and Wilson (1970). In this way, the presence of an inversion centre in a three-dimensional structure or in certain projections can be tested. Usually it is difficult, however, to obtain reliable conclusions from projection data. The same applies to crystals possessing pseudo-symmetry, such as a centrosymmetric arrangement of heavy atoms in a noncentrosymmetric structure. Several computer programs performing the statistical analysis of the diffraction intensities are available.

### 3.1.6.4. *Consideration of maxima in Patterson syntheses*

The application of Patterson syntheses for space-group determination is described by Buerger (1950, 1959).

### 3.1.6.5. *Anomalous dispersion*

Friedel's rule, $|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2$, does not hold for noncentrosymmetric crystals containing atoms showing anomalous dispersion. The difference between these intensities becomes particularly strong when use is made of a wavelength near the resonance level (absorption edge) of a particular atom in the crystal. Synchrotron radiation, from which a wide variety of wavelengths can be chosen, may be used for this purpose. In such cases, the diffraction pattern reveals the symmetry of the actual point group of the crystal (including the orientation of the point group with respect to the lattice).

### 3.1.6.6. *Summary*

One or more of the methods discussed above may reveal whether or not the point group of the crystal has an inversion centre. With this information, in addition to the diffraction symbol, 192 space groups can be uniquely identified. The rest consist of the eleven pairs of enantiomorphic space groups, the two 'special pairs' and six further ambiguities: 3 in the orthorhombic system (Nos. 26 & 28, 35 & 38, 36 & 40), 2 in the tetragonal system (Nos. 111 & 115, 119 & 121), and 1 in the hexagonal system (Nos. 187 & 189). If not only the point group but also its orientation with respect to the lattice can be determined, the six ambiguities can be resolved. This implies that 204 space groups can be uniquely identified, the only exceptions being the eleven pairs of enantiomorphic space groups and the two 'special pairs'.



references