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SPACE-GROUP SYMMETRY

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MOIS I. AROYO

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Contributing authors

- H. ARNOLD: Institut für Kristallographie, Rheinisch-Westfälische Technische Hochschule, Aachen, Germany. [1.2, 1.5]
- M. I. AROYO: Departamento de Física de la Materia Condensada, Universidad del País Vasco (UPV/EHU), Bilbao, Spain. [1.2, 1.4, 1.5, 2.1, 3.2]
- E. F. BERTAUT†: Laboratoire de Cristallographie, CNRS, Grenoble, France. [1.5]
- H. BURZLAFF: Universität Erlangen–Nürnberg, Robert-Koch-Strasse 4a, D-91080 Uttenreuth, Germany. [3.1, 3.3]
- G. CHAPUIS: École Polytechnique Fédérale de Lausanne, BSP/Cubotron, CH-1015 Lausanne, Switzerland. [1.4, 1.5]
- W. FISCHER: Institut für Mineralogie, Petrologie und Kristallographie, Philipps-Universität, D-35032 Marburg, Germany. [3.4, 3.5]
- H. D. FLACK: Chimie minérale, analytique et appliquée, University of Geneva, Geneva, Switzerland. [1.6, 2.1]
- A. M. GLAZER: Department of Physics, University of Oxford, Parks Road, Oxford, United Kingdom. [1.4]
- H. GRIMMER: Research with Neutrons and Muons, Paul Scherrer Institut, WHGA/342, Villigen PSI, CH-5232, Switzerland. [3.1]
- B. GRUBER†: Department of Applied Mathematics, Faculty of Mathematics and Physics, Charles University, Malostranské nám. 25, CZ-11800 Prague 1, Czech Republic. [3.1]
- TH. HAHN†: Institut für Kristallographie, RWTH Aachen University, 52062 Aachen, Germany. [2.1, 3.2]
- H. KLAPPER: Institut für Kristallographie, RWTH Aachen University, 52062 Aachen, Germany. [3.2]
- E. KOCH: Institut für Mineralogie, Petrologie und Kristallographie, Philipps-Universität, D-35032 Marburg, Germany. [3.4, 3.5]
- P. KONSTANTINOV: Institute for Nuclear Research and Nuclear Energy, 72 Tzarigradsko Chaussee, BG-1784 Sofia, Bulgaria. [2.1]
- V. KOPSKÝ†: Bajkalska 1170/28, 100 00 Prague 10, Czech Republic. [1.7]
- D. B. LITVIN: Department of Physics, The Eberly College of Science, Penn State – Berks Campus, The Pennsylvania State University, PO Box 7009, Reading, PA 19610-6009, USA. [1.7, 3.6]
- A. LOOIJENGA-VOS: Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, The Netherlands. [2.1]
- ULRICH MÜLLER: Fachbereich Chemie, Philipps-Universität, D-35032 Marburg, Germany. [1.7, 3.2, 3.5]
- K. MOMMA: National Museum of Nature and Science, 4-1-1 Amakubo, Tsukuba, Ibaraki 305-0005, Japan. [2.1]
- U. SHMUELI: School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel. [1.6]
- B. SOUVIGNIER: Radboud University Nijmegen, Faculty of Science, Mathematics and Computing Science, Institute for Mathematics, Astrophysics and Particle Physics, Postbus 9010, 6500 GL Nijmegen, The Netherlands. [1.1, 1.3, 1.4, 1.5]
- J. C. H. SPENCE: Department of Physics, Arizona State University, Rural Rd, Tempe, AZ 85287, USA. [1.6]
- P. M. DE WOLFF†: Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands. [3.1]
- H. WONDRAUSCHEK†: Laboratorium für Applikationen der Synchrotronstrahlung (LAS), Universität Karlsruhe, Germany. [1.2, 1.4, 1.5, 1.7]
- H. ZIMMERMANN: Institut für Angewandte Physik, Lehrstuhl für Kristallographie und Strukturphysik, Universität Erlangen–Nürnberg, Bismarckstrasse 10, D-91054 Erlangen, Germany. [3.1, 3.3]

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Foreword to the Sixth Edition

Standardizing the space-group tables has been a priority for crystallographers since at least 1929. The 1935 publication of the first set of such tables predated the founding of the International Union of Crystallography (IUCr) by 12 years. That book was one of the two volumes of *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (or *International Tables for the Determination of Crystal Structures*). It established conventions so fundamental to the field that it is hard to imagine the confusion they prevented.

Major revisions of the space-group tables were published by the IUCr in 1952 (*International Tables for X-ray Crystallography* Volume I: *Symmetry Groups*) and 1983 (*International Tables for Crystallography* Volume A: *Space-Group Symmetry*). The considerably revised fifth edition of Volume A was made available online in 2006 at <http://it.iucr.org/> along with the other seven volumes of the series as *International Tables Online*, which features many links within and between the electronic versions of the volumes. In 2011 the online series was complemented by the addition of the *Symmetry Database*, which provides more extensive symmetry information than do the volumes themselves.

Over the decades the information about space-group symmetry has been expanded so greatly that no single volume can contain it all. Some information about group–subgroup relationships was present in the 1935 volume but was left out of the 1952 edition. That information, augmented by some group–supergroup relationships, reappeared in the 1983 book. A full treatment of the subject was published in 2004 as the new Volume A1: *Symmetry Relations Between Space Groups*. The ability to follow electronic links back and forth between the online versions of Volumes A and A1 makes their combination very powerful.

In 2002 the new Volume E, *Subperiodic Groups*, was published. It contains the tables for the space groups of two-dimensional patterns that are periodic in only one dimension (the frieze groups) and three-dimensional patterns that are periodic in only one dimension (the rod groups) or two dimensions (the layer groups). The distinction between the 80 layer groups and the 17 plane groups is important. The latter had been included since 1952 along with the 230 space groups because the plane groups are so useful for teaching; they do not, however, allow for layer thickness. Layer groups may have more symmetry elements than are allowed for a plane group, *i.e.* inversion centers, a mirror plane within the layer, and 2 and 2_1 axes within the layer.

The new Volume C: *Mathematical, Physical and Chemical Tables* appeared in 1992 as a successor to Volume II of *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, which had grown to Volumes II–IV of the series *International Tables for X-ray Crystallography*; Volume C includes a section on the

symmetry descriptions of commensurately and incommensurately modulated structures. Since then, that field has grown so much that the material is currently being expanded and relocated to the next edition of Volume B, *Reciprocal Space*.

Symmetry descriptions of magnetic structures are still under development. The number of magnetic groups is so large that any volume of *International Tables* listing them will have to be electronic only. In 2014, as an interim step, the IUCr published an e-book by D. B. Litvin (*Magnetic Group Tables*) that is available for downloading from the IUCr website at <http://www.iucr.org/publ/978-0-9553602-2-0>.

Because Volume A is usually the first volume of *International Tables* encountered by non-experts, an important aim of this edition has been to make its contents more accessible. The text sections have been completely reorganized and new introductory chapters have been written by authors experienced in teaching crystallography at all levels. Many explanatory examples have been added, and the terms and symbols used have been made consistent throughout. Diagrams for the cubic space groups have been redrawn so that they are easier to comprehend and axis labels have been added for the orthorhombic groups. Introductions to the topics covered in Volumes A1 and E, as well as to magnetic symmetry, have been added.

Volume A continues to evolve; this new edition, the sixth, is a major revision intended to meet the needs of scientists in the Electronic Age: users of the online version will also have access to the *Symmetry Database*, which is under continuous development and contains far more data than can be presented in print. The database can be used to calculate, among other things, the symmetry operations and Wyckoff positions for nonstandard settings in order to facilitate the tracking of symmetry relationships through a series of phase transitions or chemical substitutions.

We are all greatly indebted to Mois Aroyo, the Editor of this edition, for having had the vision for this revision of Volume A and for then having seen the project through. Getting experts to write for a wide group of readers and to agree on consistent terminology required erudition, tact and patience, all of which Mois has displayed in abundance.

Those who have been involved with this sixth edition are also indebted to all the crystallographers who contributed to previous editions. Two of the longtime architects of Volumes A and A1, Theo Hahn and Hans Wondratschek, recently passed on, but not before making very significant contributions towards the preparation of this new edition. It is an honor to acknowledge their many contributions.

CAROLYN PRATT BROCK

Editor-in-Chief, *International Tables for Crystallography*

Preface

Like its predecessors, this new sixth edition of *International Tables for Crystallography*, Volume A (referred to as *ITA 6*) treats the symmetries of two- and three-dimensional space groups and point groups in direct space. It is the reference work for crystal symmetry and provides standard symmetry data which are indispensable for any crystallographic or structural study. The text and data in *ITA 6* fall into three main parts: Part 1 serves as a didactic introduction to space-group symmetry; Part 2 contains the authoritative tabulations of plane and space groups, and a guide to the tabulated data; and Part 3 features articles on more specialized, advanced topics.

Apart from new topics and developments, this sixth edition includes important modifications of the contents and of the arrangement of the text and the tabulated material of the previous (fifth) edition (*ITA 5*). The most salient feature of this edition is the introductory material in Part 1, which offers a homogeneous text of educational and teaching nature explaining the different kinds of symmetry information found in the tables. Although the first part is designed to provide a didactic introduction to symmetry in crystallography, suitable for advanced undergraduate and postgraduate students and for researchers from other fields, it is not meant to serve as an elementary textbook: readers are expected to have a basic understanding of the subject. The following aspects of symmetry theory are dealt with in Part 1:

Chapter 1.1 (Souvignier) offers a general introduction to group theory, which provides the mathematical background for considering symmetry properties. Starting from basic principles, those properties of groups are discussed that are of particular interest in crystallography. Essential topics like group–subgroup relationships, homomorphism and isomorphism, group actions and Wyckoff positions, conjugacy and equivalence relations or group normalizers are treated in detail and illustrated by crystallographic examples.

Chapter 1.2 (Wondratschek and Aroyo) deals with the types of crystallographic symmetry operations and the application of the matrix formalism in their description. The procedure for the geometric interpretation of a matrix–column pair of a symmetry operation is thoroughly explained and demonstrated by several instructive examples. The last section of the chapter provides a detailed discussion of the key concepts of a symmetry element and its constituents, a geometric element and an element set.

Chapter 1.3 (Souvignier) presents an introduction to the structure and classification of crystallographic space groups. Fundamental concepts related to translation lattices, such as the metric tensor, the unit cell and the distinction into primitive and centred lattices are rigorously defined. The action of point groups on translation lattices and the interplay between point groups and lattices is discussed in detail and, in particular, the distinction between symmorphic and non-symmorphic groups is explained. The final part of this chapter deals with various classification schemes of crystallographic space groups, including the classification into space-group types, geometric crystal classes and Bravais types of lattices.

Chapter 1.4 (Souvignier, Wondratschek, Aroyo, Chapuis and Glazer) handles various crystallographic terms used for the presentation of the symmetry data in the space-group tables. It starts with a detailed introduction to Hermann–Mauguin symbols for space, plane and crystallographic point groups, and to their Schoenflies symbols. A description is given of the symbols used for symmetry operations, and of their listings in the general-position and in the symmetry-operations blocks of the space-group tables. The Seitz notation for symmetry operations adopted by the Commission on Crystallographic Nomenclature as the standard convention for Seitz symbolism of the International Union of Crystallography [Glazer *et al.* (2014). *Acta Cryst. A* **70**, 300–302] is described and the Seitz symbols for the plane- and space-group symmetry operations are tabulated. The so-called additional symmetry operations of space groups resulting from the combination of the generating symmetry operations with lattice translations are introduced and illustrated. The classification of points in direct space into general and special Wyckoff positions, and the study of their site-symmetry groups and Wyckoff multiplicities are presented in detail. The final sections of the chapter offer a helpful introduction to two-dimensional sections and projections of space groups and their symmetry properties.

Chapter 1.5 (Wondratschek, Aroyo, Souvignier and Chapuis) introduces the mathematical tools necessary for performing coordinate transformations. The transformations of crystallographic data (point coordinates, space-group symmetry operations, metric tensors of direct and reciprocal space, indices of reflection conditions *etc.*) under a change of origin or a change of the basis are discussed and demonstrated by examples. More than 40 different types of coordinate-system transformations representing the most frequently encountered cases are listed and illustrated. Finally, synoptic tables of the space and plane groups show a large selection of alternative settings and their Hermann–Mauguin symbols covering most practical cases. It is worth pointing out that, in contrast to *ITA 5*, the extended Hermann–Mauguin symbols shown in the synoptic tables follow their original definition according to which the characters of the symbols indicate symmetry operations, and not symmetry elements.

Chapter 1.6 (Shmueli, Flack and Spence) offers a detailed presentation of methods of determining the symmetry of single-domain crystals from diffraction data, followed by a brief discussion of intensity statistics and their application to real intensity data from a $P\bar{1}$ crystal structure. The theoretical background for the derivation of the possible general reflections is introduced along with a brief discussion of special reflection conditions. An extensive tabulation of general reflection conditions and possible space groups is presented. The chapter concludes with a description and illustration of symmetry determination based on electron-diffraction methods, principally using convergent-beam electron diffraction.

Chapter 1.7 (Wondratschek, Müller, Litvin and Kopský) gives a short outline of the content of *International Tables for Crystallography* Volume A1, which is devoted to symmetry relations

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between space groups, and also of the content of *International Tables for Crystallography* Volume E, in which two- and three-dimensional subperiodic groups are treated. The chapter starts with a brief introduction to the different kinds of maximal subgroups and minimal supergroups of space groups. The relations between the Wyckoff positions for group-subgroup-related space groups and their crystallographic applications are discussed. Illustrative examples of the application of the relationship between a crystal space group and the subperiodic-group symmetry of planes that transect the crystal in the determination of the layer-group symmetry of such planes and of domain walls are also given.

The essential data in Volume A are the diagrams and tables of the 17 types of plane groups and of the 230 types of space groups shown in Chapters 2.2 and 2.3 of Part 2. For each group type the following symmetry data are presented: a headline block with the relevant group symbols; diagrams of the symmetry elements and of the general positions; specifications of the origin and of the asymmetric unit; symmetry operations; generators; general and special Wyckoff positions with multiplicities, site symmetries, coordinate triplets and reflection conditions; and symmetries of special projections (for the space-group types). Compared to the tabulated symmetry data in *ITA* 5, two important differences are to be noted:

- (i) The subgroups and supergroups of the space groups were listed as part of the space-group tables in the first to fifth editions of Volume A (from 1983 to 2005), but the listing was incomplete and lacked additional information on any basis transformations and origin shifts that may be involved. A complete listing of all maximal subgroups and minimal supergroups of all plane and space groups is now given in Volume A1 of *International Tables for Crystallography*, and to avoid repetition of the data tabulated there, the maximal-subgroup and minimal-supergroup data are omitted from the plane-group and space-group tables of *ITA* 6.
- (ii) To improve the visualization and to aid interpretation of the complicated general-position diagrams of the cubic space groups, the stereodiagrams that were used for them in the previous editions of Volume A have been replaced by orthogonal-projection diagrams of the type given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). In the new diagrams the points of the general position are shown as vertices of transparent polyhedra whose origins are chosen at special points of highest site symmetry. To provide a clearer three-dimensional style overview of the arrangements of the polyhedra, additional general-position diagrams in perspective projection are shown for each of the ten space groups of the $m\bar{3}m$ crystal class, and are included in a new four-page arrangement of the data for each of these space groups. The general-position diagrams of the cubic groups in both orthogonal and perspective projections were generated using the program *VESTA* [Momma & Izumi (2011). *J. Appl. Cryst.* **44**, 1272–1276].

There are further modifications of the symmetry data in the space-group tables, some of which deserve special mention:

- (iii) To simplify the use of the symmetry-element diagrams for the three different projections of the orthorhombic space groups, the corresponding origins and basis vectors are explicitly labelled, as in the tables of the monoclinic space groups.

- (iv) Modifications to the tabulated data and diagrams of the seven trigonal space groups of the rhombohedral lattice system (the so-called *rhombohedral* space groups) include: (a) changes in the sequence of coordinate triplets of some special Wyckoff positions of five rhombohedral groups [namely $R\bar{3}$ (148): Wyckoff positions $3d$ and $3e$; $R32$ (155): $3d$ and $3e$; $R3m$ (160): $3b$; $R\bar{3}m$ (166): $3d$, $3e$ and $6h$; $R\bar{3}c$ (167): $6d$] in the rhombohedral-axes settings in order to achieve correspondence between the sequences of coordinate triplets of the rhombohedral and hexagonal descriptions; (b) labelling of the basis vectors (cell edges) of the primitive rhombohedral cell in the general-position diagrams of the rhombohedral-axes setting descriptions of all rhombohedral space groups.

The diagrams and tables of the plane and space groups in Part 2 are preceded by a guide to their use, which includes lists of the symbols and terms used in them. In general, this guide (Chapter 2.1) follows the presentation of the material in *ITA* 5 but with several important exceptions related to the modifications of the content and the rearrangement of the material as discussed above. The improvements include new sections on: (i) symmetry elements (Hahn and Aroyo), explaining the important modifications of the tables of symbols of symmetry elements; (ii) Patterson symmetry (Flack), with tables of Patterson symmetries and symmetries of Patterson functions for all space and plane groups; and (iii) the general-position diagrams of the cubic groups (Momma and Aroyo). An extended section on the computer preparation of *ITA* 6 (Konstantinov and Momma) discusses the specific features of the computer programs and layout macros applied in the preparation of the set of diagrams and tables for this new edition.

Advanced and more specialized topics on space-group symmetry are treated in Part 3 of the volume. Most of the articles are substantially revised, upgraded and extended with respect to the versions in *ITA* 5. The major changes can be briefly described as follows:

In Chapter 3.1 on crystal lattices and their properties, the discussion of the Delaunay reduction procedure and the resulting classification of lattices into 24 Delaunay sorts (*'Symmetrische Sorten'*) by Burzlaff and Zimmermann is supplemented by illustrative examples and a new table of data. Gruber and Grimmer broaden the description of conventional cells, showing that the conditions characterizing the conventional cells of the 14 Bravais types of lattices are only necessary and to make them sufficient they have to be extended to a more comprehensive system.

Chapter 3.2 on point groups and crystal classes (Hahn, Klapper, Müller and Aroyo) is substantially revised and new material has been added. The new developments include: (i) graphical presentations of the 47 face and point forms; (ii) enhancement of the tabulated Wyckoff-position data of the 10 two-dimensional and the 32 three-dimensional crystallographic point groups by the inclusion of explicit listings of the coordinate triplets of symmetry-equivalent points, and (iii) a new section on molecular symmetry (Müller), which treats noncrystallographic symmetries, the symmetry of polymeric molecules, and symmetry aspects of chiral molecules and crystal structures.

The revised text of Chapter 3.4 (Fischer and Koch) on lattice complexes is complemented by a thorough discussion of the concepts of orbit types, characteristic and non-characteristic orbits, and their comparison with the concepts of lattice complexes and limiting complexes.

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Chapter 3.5 (Koch, Fischer and Müller) introduces and fully tabulates for the first time the chirality-preserving Euclidean normalizers of plane and space groups. Illustrative examples demonstrate the importance of the chirality-preserving Euclidean normalizers in the treatment of chiral crystal structures.

The new Chapter 3.6 (Litvin) on magnetic groups addresses the revival of interest in magnetic symmetry. The magnetic groups considered are the magnetic point groups, the two- and three-dimensional magnetic subperiodic groups, *i.e.* the magnetic frieze, rod and layer groups, and the one-, two- and three-dimensional magnetic space groups. After an introduction to magnetic symmetry groups, the existing nomenclatures for magnetic space groups are discussed and compared. The structure, symbols and properties of the magnetic groups and their maximal subgroups as listed in the electronic book by Litvin [*Magnetic Group Tables* (2014). IUCr: Chester. <http://www.iucr.org/publ/978-0-9553602-2-0>] are presented and illustrated.

Work on this sixth edition extended over the last eight years and many people have contributed to the successful completion of this complicated project. My acknowledgements should start with H. Wondratschek (Universität, Karlsruhe) and Th. Hahn (RWTH, Aachen), to whose memory this volume is dedicated. Their constant interest, support and sometimes hard but always constructive criticism were decisive during the preparation of this volume.

It is my great pleasure to thank all the authors of *ITA 6* who have contributed new material or have updated and substantially revised articles from the previous edition. Also, I should like to express my gratitude to B. Gruber and V. Kopský for their important contributions to *ITA 6*; unfortunately, and to my deep regret, they both passed away in 2016. My sincere thanks go to P. Konstantinov (INRNE, Sofia) and K. Momma (National Museum of Nature and Science, Tsukuba) for their hard work and the effort they invested in the computer production of the plane- and space-group tables of the volume. This sixth edition is a result of numerous discussions (some of them difficult and controversial, but always stimulating and fruitful) with different people: H. Wondratschek, B. Souvignier (Radboud University,

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I am particularly grateful to my colleagues and friends J. M. Perez-Mato, G. Madariaga and F. J. Zuñiga (Universidad del País Vasco, Bilbao) for their constant support and understanding during the work on *ITA 6*, and for motivating discussions on the content and presentation of the crystallographic data. It is also my great pleasure to thank the useful comments and assistance provided by our PhD students and post-doctoral researchers, especially E. Kroumova, C. Capillas, D. Orobengoa, G. de la Flor and E. S. Tasci.

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MOIS I. AROYO

Editor, *International Tables for Crystallography Volume A*

SAMPLE PAGES

1.1. A general introduction to groups

B. SOUVIGNIER

In this chapter we give a general introduction to group theory, which provides the mathematical background for considering symmetry properties. Starting from basic principles, we discuss those properties of groups that are of particular interest in crystallography. To readers interested in a more elaborate treatment of the theoretical background, the standard textbooks by Armstrong (2010), Hill (1999) or Sternberg (2008) are recommended; an account from the perspective of crystallography can also be found in Müller (2013).

1.1.1. Introduction

Crystal structures may be investigated and classified according to their symmetry properties. But in a strict sense, crystal structures in nature are never perfectly symmetric, due to impurities, structural imperfections and especially their finite extent. Therefore, symmetry considerations deal with *idealized* crystal structures that are free from impurities and structural imperfections and that extend infinitely in all directions. In the mathematical model of such an idealized crystal structure, the atoms are replaced by points in a three-dimensional point space and this model will be called a *crystal pattern*.

A symmetry operation of a crystal pattern is a transformation of three-dimensional space that preserves distances and angles and that leaves the crystal pattern as a whole unchanged. The symmetry of a crystal pattern is then understood as the collection of all symmetry operations of the pattern.

The following simple statements about the symmetry operations of a crystal pattern are almost self-evident:

- (a) If two symmetry operations are applied successively, the crystal pattern is still invariant, thus the combination of the two operations (called their *composition*) is again a symmetry operation.
- (b) Every symmetry operation can be reversed by simply moving every point back to its original position.

These observations (together with the fact that leaving all points in their position is also a symmetry operation) show that the symmetry operations of a crystal pattern form an algebraic structure called a *group*.

1.1.2. Basic properties of groups

Although groups occur in innumerable contexts, their basic properties are very simple and are captured by the following definition.

Definition. Let \mathcal{G} be a set of elements on which a binary operation is defined which assigns to each pair (g, h) of elements the composition $g \circ h \in \mathcal{G}$. Then \mathcal{G} , together with the binary operation \circ , is called a *group* if the following hold:

- (i) the binary operation is associative, *i.e.* $(g \circ h) \circ k = g \circ (h \circ k)$;
- (ii) there exists a *unit element* or *identity element* $e \in \mathcal{G}$ such that $g \circ e = g$ and $e \circ g = g$ for all $g \in \mathcal{G}$;
- (iii) every $g \in \mathcal{G}$ has an inverse element, denoted by g^{-1} , for which $g \circ g^{-1} = g^{-1} \circ g = e$.

In most cases, the composition of group elements is regarded as a *product* and is written as $g \cdot h$ or even gh instead of $g \circ h$. An exception is groups where the composition is addition, *e.g.* a group of translations. In such a case, the composition $\mathbf{a} \circ \mathbf{b}$ is more conveniently written as $\mathbf{a} + \mathbf{b}$.

Examples

- (i) The group consisting only of the identity element e (with $e \circ e = e$) is called the *trivial group*.
- (ii) The group $3m$ of all symmetries of an equilateral triangle is a group with the composition of symmetry operations as binary operation. The group contains six elements, namely three reflections, two rotations and the identity element. It is schematically displayed in Fig. 1.1.2.2.
- (iii) The set \mathbb{Z} of all integers forms a group with addition as operation. The identity element is 0, the inverse element for $a \in \mathbb{Z}$ is $-a$.
- (iv) The set of complex numbers with absolute value 1 forms a circle in the complex plane, the *unit circle* S^1 . The unit circle can be described by $S^1 = \{\exp(2\pi i t) \mid 0 \leq t < 1\}$ and forms a group with (complex) multiplication as operation.
- (v) The set of all real $n \times n$ matrices with determinant $\neq 0$ is a group with matrix multiplication as operation. This group is called the *general linear group* and denoted by $GL_n(\mathbb{R})$.

If a group \mathcal{G} contains finitely many elements, it is called a *finite group* and the number of its elements is called the *order* of the group, denoted by $|\mathcal{G}|$. A group with infinitely many elements is called an *infinite group*.

For a group element g , its *order* is the smallest integer $n > 0$ such that $g^n = e$ is the identity element. If there is no such integer, then g is said to be of *infinite order*.

The group operation is not required to be *commutative*, *i.e.* in general one will have $gh \neq hg$. However, a group \mathcal{G} in which $gh = hg$ for all g, h is said to be a *commutative* or *abelian group*.

The inverse of the product gh of two group elements is the product of the inverses of the two elements in reversed order, *i.e.* $(gh)^{-1} = h^{-1}g^{-1}$.

A particularly simple type of groups is *cyclic groups* in which all elements are powers of a single element g . A finite cyclic group C_n of order n can be written as $C_n = \{g, g^2, \dots, g^{n-1}, g^n = e\}$. For example, the rotations that are symmetry operations of an equilateral triangle constitute a cyclic group of order 3.

The group \mathbb{Z} of integers (with addition as operation) is an example of an infinite cyclic group in which negative powers also have to be considered, *i.e.* where $\mathcal{G} = \{\dots, g^{-2}, g^{-1}, e = g^0, g^1, g^2, \dots\}$.

Groups of small order may be displayed by their *multiplication table*, which is a square table with rows and columns indexed by the group elements and where the intersection of the row labelled by g and of the column labelled by h is the product gh . It follows immediately from the invertibility of the group elements that each row and column of the multiplication table contains every group element precisely once.

1. INTRODUCTION TO SPACE-GROUP SYMMETRY

Table 1.2.3.1

Symmetry elements in point and space groups

Name of symmetry element	Geometric element	Defining operation (d.o.)	Operations in element set
Mirror plane	Plane p	Reflection through p	D.o. and its coplanar equivalents [†]
Glide plane	Plane p	Glide reflection through p ; $2\mathbf{v}$ (not \mathbf{v}) a lattice-translation vector	D.o. and its coplanar equivalents [†]
Rotation axis	Line l	Rotation around l , angle $2\pi/N$, $N = 2, 3, 4$ or 6	1st ... $(N - 1)$ th powers of d.o. and their coaxial equivalents [‡]
Screw axis	Line l	Screw rotation around l , angle $2\pi/N$, $u = j/N$ times shortest lattice translation along l , right-hand screw, $N = 2, 3, 4$ or 6 , $j = 1, \dots, (N - 1)$	1st ... $(N - 1)$ th powers of d.o. and their coaxial equivalents [‡]
Rotoinversion axis	Line l and point P on l	Rotoinversion: rotation around l , angle $2\pi/N$, followed by inversion through P , $N = 3, 4$ or 6	D.o. and its inverse
Centre	Point P	Inversion through P	D.o. only

[†] That is, all glide reflections through the same reflection plane, with glide vectors \mathbf{v} differing from that of the d.o. (taken to be zero for reflections) by a lattice-translation vector. The glide planes a, b, c, n, d and e are distinguished (cf. Table 2.1.2.1). [‡] That is, all rotations and screw rotations around the same axis l , with the same angle and sense of rotation and the same screw vector \mathbf{u} (zero for rotation) up to a lattice-translation vector.

In crystallography these group elements, however, were the symmetry operations of the symmetry groups, not the crystallographic symmetry elements. Therefore, the IUCr Commission on Crystallographic Nomenclature appointed an *Ad-hoc* Committee on the Nomenclature of Symmetry with P. M. de Wolff as Chairman to propose definitions for terms of crystallographic symmetry and for several classifications of crystallographic space groups and point groups.

In the reports of the *Ad-hoc* Committee, de Wolff *et al.* (1989) and (1992) with *Addenda*, Flack *et al.* (2000), the results were published. To define the term *symmetry element* for any symmetry operation was more complicated than had been envisaged previously, in particular for unusual screw and glide components.

According to the proposals of the Committee the following procedure has been adopted (cf. also Table 1.2.3.1):

- (1) No symmetry element is defined for the identity and the (lattice) translations.
- (2) For any symmetry operation of point groups and space groups with the exception of the rotoinversions $\bar{3}$, $\bar{4}$ and $\bar{6}$, the *geometric element* is defined as the *set of fixed points* (the second column of Table 1.2.3.1) of the *reduced operation*, cf. equation (1.2.2.17). For reflections and glide reflections this is a plane; for rotations and screw rotations it is a line, for the inversion it is a point. For the rotoinversions $\bar{3}$, $\bar{4}$ and $\bar{6}$ the geometric element is a line with a point (the inversion centre) on this line.
- (3) The *element set* (cf. the last column of Table 1.2.3.1) is defined as a set of operations that share the same geometric element. The element set can consist of symmetry operations of the same type (such as the powers of a rotation) or of different types, e.g. by a reflection and a glide reflection through the same plane. The *defining operation* (d.o.) may be any symmetry operation from the element set that suffices to identify the symmetry element. In most cases, the 'simplest' symmetry operation from the element set is chosen as the d.o. (cf. the third column of Table 1.2.3.1). For reflections and glide reflections the element set includes the defining operation and all glide reflections through the same reflection plane but with glide vectors differing by a lattice-translation vector, i.e. the so-called *coplanar equivalents*. For rotations and screw rotations of angle $2\pi/k$ the element set is the defining operation, its 1st ... $(k - 1)$ th powers and all rotations and screw rotations with screw vectors differing from that of the defining operation by a lattice-translation vector, known as *coaxial equivalents*. For a rotoinversion the element set includes the defining operation and its inverse.

- (4) The combination of the geometric element and its element set is indicated by the name *symmetry element*. The names of the symmetry elements (first column of Table 1.2.3.1) are combinations of the name of the defining operation attached to the name of the corresponding geometric element. Names of symmetry elements are *mirror plane*, *glide plane*, *rotation axis*, *screw axis*, *rotoinversion axis* and *centre*.² This allows such statements as *this point lies on a rotation axis* or *these operations belong to a glide plane*.

Examples

- (1) *Glide and mirror planes*. The element set of a glide plane with a glide vector \mathbf{v} consists of infinitely many different glide reflections with glide vectors that are obtained from \mathbf{v} by adding any lattice-translation vector parallel to the glide plane, including centring translations of centred cells.
 - (a) It is important to note that if among the infinitely many glide reflections of the element set of the same plane there exists one operation with zero glide vector, then this operation is taken as the *defining operation* (d.o.). Consider, for example, the symmetry operation $x + 1/2, y + 1/2, -z + 1/2$ of *Cmcm* (63) [*General position* (1/2, 1/2, 0) block]. This is an n -glide reflection through the plane $x, y, 1/4$. However, the corresponding symmetry element is a mirror plane, as among the glide reflections of the element set of the plane $x, y, 1/4$ one finds the reflection $x, y, -z + 1/2$ [symmetry operation (6) of the *General position* (0, 0, 0) block].
 - (b) The symmetry operation $x + 5/2, y - 7/2, -z + 3$ is a glide reflection. Its geometric element is the plane $x, y, 3/2$. Its symmetry element is a glide plane in space group *Pmmm* (59) because there is no lattice translation by which the glide vector can be changed to $\mathbf{0}$. If, however, the same mapping is a symmetry operation of space group *Cmmm* (65), then its symmetry element is a reflection plane because the glide vector with components $5/2, -7/2, 0$ can be cancelled through a translation $(2 + \frac{1}{2})\mathbf{a} + (-4 + \frac{1}{2})\mathbf{b}$, which is a lattice translation in a *C* lattice. Evidently, the correct specification of the symmetry element is possible only with respect to a specific translation lattice.

² The proposal to introduce the symbols for the symmetry elements $Em, Eg, En, En_j, E\bar{n}$ and $E\bar{1}$ was not taken up in practice. The printed and graphical symbols of symmetry elements used throughout the space-group tables of Part 2 are introduced in Section 2.1.2 and listed in Tables 2.1.2.1 to 2.1.2.7.

1.3. GENERAL INTRODUCTION TO SPACE GROUPS

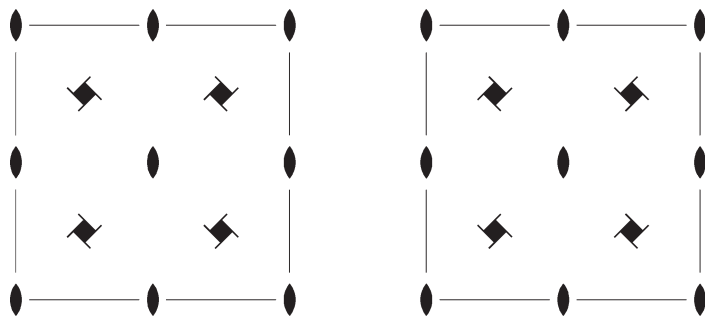


Figure 1.3.4.2
Space-group diagram of $I4_1$ (left) and its reflection in the plane $z = 0$ (right).

rotation g' : $-y, x + 1/2, z - 1/4$, and one might suspect that \mathcal{G}' is a space group of the same affine type but of a different crystallographic space-group type as \mathcal{G} . However, this is not the case because conjugating \mathcal{G} by the translation $n = t(0, 1/2, 0)$ conjugates g to $g' = ngn^{-1}$: $-y + 1/2, x + 1, z + 1/4$. One sees that g'' is the composition of g' with the centring translation t and hence g'' belongs to \mathcal{G}' . This shows that conjugating \mathcal{G} by either the reflection m or the translation n both result in the same group \mathcal{G}' . This can also be concluded directly from the space-group diagrams in Fig. 1.3.4.2. Reflecting in the plane $z = 0$ turns the diagram on the left into the diagram on the right, but the same effect is obtained when the left diagram is shifted by $\frac{1}{2}\mathbf{a}$ or \mathbf{b} .

The groups \mathcal{G} and \mathcal{G}' thus belong to the same crystallographic space-group type because \mathcal{G} is transformed to \mathcal{G}' by a shift of the origin by $\frac{1}{2}\mathbf{b}$, which is clearly an orientation-preserving coordinate transformation.

Enantiomorphism

The 219 affine space-group types in dimension 3 result in 230 crystallographic space-group types. Since an affine type either forms a single space-group type (in the case where the group obtained by an orientation-reversing coordinate transformation can also be obtained by an orientation-preserving transformation) or splits into two space-group types, this means that there are 11 affine space-group types such that an orientation-reversing coordinate transformation cannot be compensated by an orientation-preserving transformation.

Groups that differ only by their handedness are closely related to each other and share many properties. One addresses this phenomenon by the concept of *enantiomorphism*.

Example

Let \mathcal{G} be a space group of type $P4_1$ (76) generated by a fourfold right-handed screw rotation $(4_{001}^+, (0, 0, 1/4))$ and the translations of a primitive tetragonal lattice. Then transforming the coordinate system by a reflection in the plane $z = 0$ results in a space group \mathcal{G}' with fourfold left-handed screw rotation $(4_{001}^-, (0, 0, 1/4)) = (4_{001}^+, (0, 0, -1/4))^{-1}$. The groups \mathcal{G} and \mathcal{G}' are isomorphic because they are conjugate by an affine mapping, but \mathcal{G}' belongs to a different space-group type, namely $P4_3$ (78), because \mathcal{G} does not contain a fourfold left-handed screw rotation with translation part $\frac{1}{4}\mathbf{c}$.

Definition

Two space groups \mathcal{G} and \mathcal{G}' are said to form an *enantiomorphic pair* if they are conjugate under an affine mapping, but not under an orientation-preserving affine mapping.

If \mathcal{G} is the group of isometries of some crystal pattern, then its enantiomorphic counterpart \mathcal{G}' is the group of isometries of the mirror image of this crystal pattern.

The splitting of affine space-group types of three-dimensional space groups into pairs of crystallographic space-group types gives rise to the following 11 enantiomorphic pairs of space-group types: $P4_1/P4_3$ (76/78), $P4_122/P4_322$ (91/95), $P4_12_12/P4_32_12$ (92/96), $P3_1/P3_2$ (144/145), $P3_112/P3_212$ (151/153), $P3_121/P3_221$ (152/154), $P6_1/P6_5$ (169/173), $P6_2/P6_4$ (170/172), $P6_122/P6_522$ (178/179), $P6_222/P6_422$ (180/181), $P4_332/P4_132$ (212/213). These groups are easily recognized by their Hermann–Mauguin symbols, because they are the primitive groups for which the Hermann–Mauguin symbol contains one of the screw rotations $3_1, 3_2, 4_1, 4_3, 6_1, 6_2, 6_4$ or 6_5 . The groups with fourfold screw rotations and body-centred lattices do not give rise to enantiomorphic pairs, because in these groups the orientation reversal can be compensated by an origin shift, as illustrated in the example above for the group of type $I4_1$.

Example

A well known example of a crystal that occurs in forms whose symmetry is described by enantiomorphic pairs of space groups is quartz. For low-temperature α -quartz there exists a left-handed and a right-handed form with space groups $P3_121$ (152) and $P3_221$ (154), respectively. The two individuals of opposite chirality occur together in the so-called Brazil twin of quartz. At higher temperatures, a phase transition leads to the higher-symmetry β -quartz forms, with space groups $P6_422$ (181) and $P6_222$ (180), which still form an enantiomorphic pair.

1.3.4.2. Geometric crystal classes

We recall that the point group of a space group is the group of linear parts occurring in the space group. Once a basis for the underlying vector space is chosen, such a point group is a group of 3×3 matrices. A point group is characterized by the relative positions between the rotation and rotoinversion axes and the reflection planes of the operations it contains, and in this sense a point group is independent of the chosen basis. However, a suitable choice of basis is useful to highlight the geometric properties of a point group.

Example

A point group of type $3m$ is generated by a threefold rotation and a reflection in a plane with normal vector perpendicular to the rotation axis. Choosing a basis $\mathbf{a}, \mathbf{b}, \mathbf{c}$ such that \mathbf{c} is along the rotation axis, \mathbf{a} is perpendicular to the reflection plane and \mathbf{b} is the image of \mathbf{a} under the threefold rotation (*i.e.* \mathbf{b} lies in the plane perpendicular to the rotation axis and makes an angle of 120° with \mathbf{a}), the matrices of the threefold rotation and the reflection with respect to this basis are

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and } \begin{pmatrix} -1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

A different useful basis is obtained by choosing a vector \mathbf{a}' in the reflection plane but neither along the rotation axis nor perpendicular to it and taking \mathbf{b}' and \mathbf{c}' to be the images of \mathbf{a}' under the threefold rotation and its square. Then the matrices of the threefold rotation and the reflection with respect to the basis $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ are

1.4. Space groups and their descriptions

B. SOUVIGNIER, H. WONDRATSCHEK, M. I. AROYO, G. CHAPUIS AND A. M. GLAZER

1.4.1. Symbols of space groups

BY H. WONDRATSCHEK

1.4.1.1. Introduction

Space groups describe the symmetries of crystal patterns; the point group of the space group is the symmetry of the macroscopic crystal. Both kinds of symmetry are characterized by symbols of which there are different kinds. In this section the space-group numbers as well as the Schoenflies symbols and the Hermann–Mauguin symbols of the space groups and point groups will be dealt with and compared, because these are used throughout this volume. They are rather different in their aims. For the Fedorov symbols, mainly used in Russian crystallographic literature, *cf.* Chapter 3.3. In that chapter the Hermann–Mauguin symbols and their use are also discussed in detail. For computer-adapted symbols of space groups implemented in crystallographic software, such as *Hall symbols* (Hall, 1981*a,b*) or *explicit symbols* (Shmueli, 1984), the reader is referred to Chapter 1.4 of *International Tables for Crystallography*, Volume B (2008).

For the definition of space groups and plane groups, *cf.* Chapter 1.3. The plane groups characterize the symmetries of two-dimensional periodic arrangements, realized in sections and projections of crystal structures or by periodic wallpapers or tilings of planes. They are described individually and in detail in Chapter 2.2. Groups of one- and two-dimensional periodic arrangements embedded in two-dimensional and three-dimensional space are called *subperiodic groups*. They are listed in Vol. E of *International Tables for Crystallography* (2010) (referred to as *IT E*) with symbols similar to the Hermann–Mauguin symbols of plane groups and space groups, and are related to these groups as their subgroups. The space groups *sensu stricto* are the symmetries of periodic arrangements in three-dimensional space, *e.g.* of normal crystals, see also Chapter 1.3. They are described individually and in detail in the space-group tables of Chapter 2.3. In the following, if not specified separately, both space groups and plane groups are covered by the term *space group*.

The description of each space group in the tables of Chapter 2.3 starts with two headlines in which the different symbols of the space group are listed. All these names are explained in this section with the exception of the data for *Patterson symmetry* (*cf.* Chapter 1.6 and Section 2.1.3.5 for explanations of Patterson symmetry).

1.4.1.2. Space-group numbers

The space-group numbers were introduced in *International Tables for X-ray Crystallography* (1952) [referred to as *IT* (1952)] for plane groups (Nos. 1–17) and space groups (Nos. 1–230). They provide a short way of specifying the type of a space group uniquely, albeit without reference to its symmetries. They are particularly convenient for use with computers and have been in use since their introduction.

There are no numbers for the point groups.

1.4.1.3. Schoenflies symbols

The Schoenflies symbols were introduced by Schoenflies (1891, 1923). They describe the point-group type, also known as the geometric crystal class or (for short) crystal class (*cf.* Section 1.3.4.2), of the space group geometrically. The different space-group types within the same crystal class are denoted by a superscript index appended to the point-group symbol.

1.4.1.3.1. Schoenflies symbols of the crystal classes

Schoenflies derived the point groups as groups of crystallographic symmetry operations, but described these crystallographic point groups geometrically by their representation through axes of rotation or roto-reflection and reflection planes (also called mirror planes), *i.e.* by *geometric elements*; for geometric elements of symmetry elements, *cf.* Section 1.2.3, de Wolff *et al.* (1989, 1992) and Flack *et al.* (2000). Rotation axes dominate the description and planes of reflection are added when necessary. Rotore-reflection axes are also indicated when necessary. The orientation of a reflection plane, whether *horizontal*, *vertical* or *diagonal*, refers to the plane itself, not to its normal.

A coordinate basis may be chosen by the user: the basis vectors start at the origin which is placed in front of the user. The basis vector **c** points vertically upwards, the basis vectors **a** and **b** lie

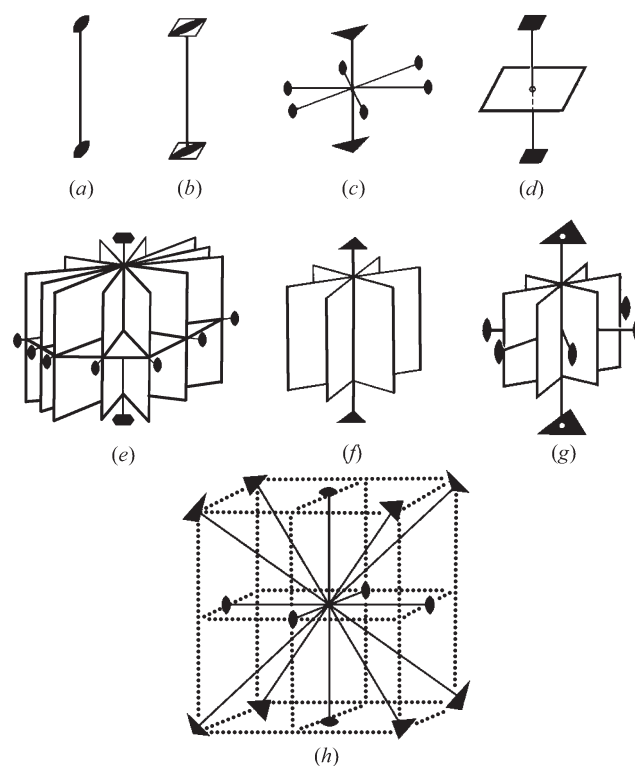
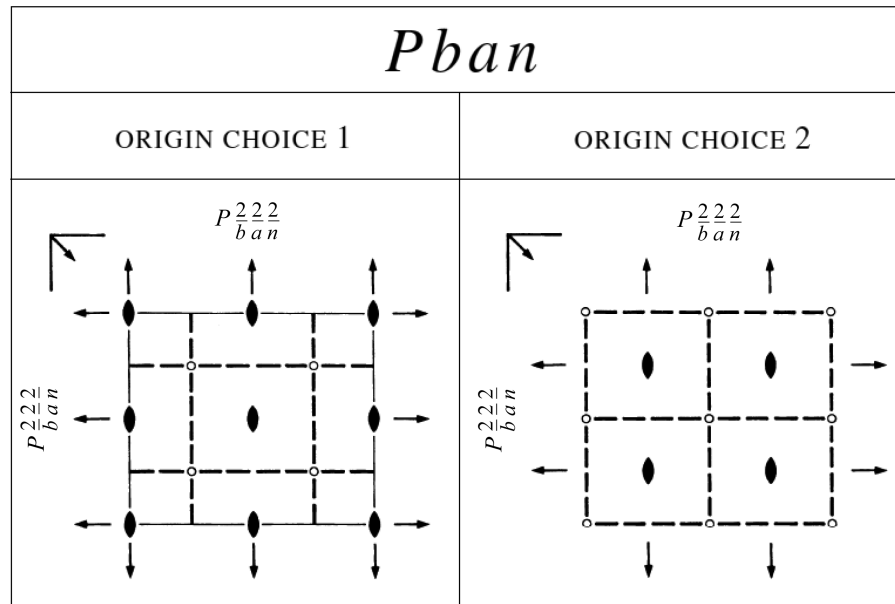


Figure 1.4.1.1

Symmetry-element diagrams of some point groups [adapted from Vainshtein (1994)]. The point groups are specified by their Schoenflies and Hermann–Mauguin symbols. (a) $C_2 = 2$, (b) $S_4 = 4$, (c) $D_3 = 32$, (d) $C_{4h} = 4/m$, (e) $D_{6h} = 6/m\ 2/m\ 2/m$, (f) $C_{3v} = 3m$, (g) $D_{3d} = \bar{3}2/m$, (h) $T = 23$. [The cubic frame in part (h) has no crystallographic meaning: it has been included to aid visualization of the orientation of the symmetry elements.]


Figure 1.5.3.2

Two possible origin choices for the orthorhombic space group $Pban$ (50). Origin choice 1 is on 222 , whereas origin choice 2 is on $\bar{1}$.

hexagonal cell ($|\mathbf{a}_{\text{hex}}| = |\mathbf{b}_{\text{hex}}|$; $\mathbf{c}_{\text{hex}} \perp \mathbf{a}_{\text{hex}}, \mathbf{b}_{\text{hex}}$; $\gamma = 120^\circ$) with a volume three times larger than that of the primitive rhombohedral cell. The second presentation is given with a primitive rhombohedral cell with $a_{\text{rh}} = b_{\text{rh}} = c_{\text{rh}}$ and $\alpha_{\text{rh}} = \beta_{\text{rh}} = \gamma_{\text{rh}}$. The relation between the two types of cell is illustrated in Fig. 1.5.3.3 for the space group $R3m$ (160). In the hexagonal cell, the coordinates of the special position with site symmetry $3m$ are $0, 0, z$, whereas in the rhombohedral cell the same special position has coordinates x, x, x . If we refer to the transformations of the primitive rhombohedral cell cited in Table 1.5.1.1, we observe two different centring with three possible orientations R_1, R_2 and R_3 which are related by $\pm 120^\circ$ to each other. The two kinds of centring, called *obverse* and *reverse*, are illustrated in Fig. 1.5.1.6. A rotation of 180° around the rhombohedral axis relates the obverse and reverse descriptions of the rhombohedral lattice. The obverse triple R cells have lattice points at $0, 0, 0$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$, whereas the reverse R cells have lattice points at $0, 0, 0$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$; $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$. The triple hexagonal cell R_1 of the obverse setting (*i.e.* $\mathbf{a}_{\text{hex}} = \mathbf{a}_{\text{rh}} - \mathbf{b}_{\text{rh}}$, $\mathbf{b}_{\text{hex}} = \mathbf{b}_{\text{rh}} - \mathbf{c}_{\text{rh}}$, $\mathbf{c}_{\text{hex}} = \mathbf{a}_{\text{rh}} + \mathbf{b}_{\text{rh}} + \mathbf{b}_{\text{rh}}$) has been used in the description of the rhombohedral space groups in this volume (*cf.* Table 1.5.1.1 and Fig. 1.5.3.3).

The hexagonal lattice can be referred to a centred rhombohedral cell, called the D cell (*cf.* Table 1.5.1.1). The centring points of this cell are $0, 0, 0$, $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$. However, the D cell is rarely used in crystallography.

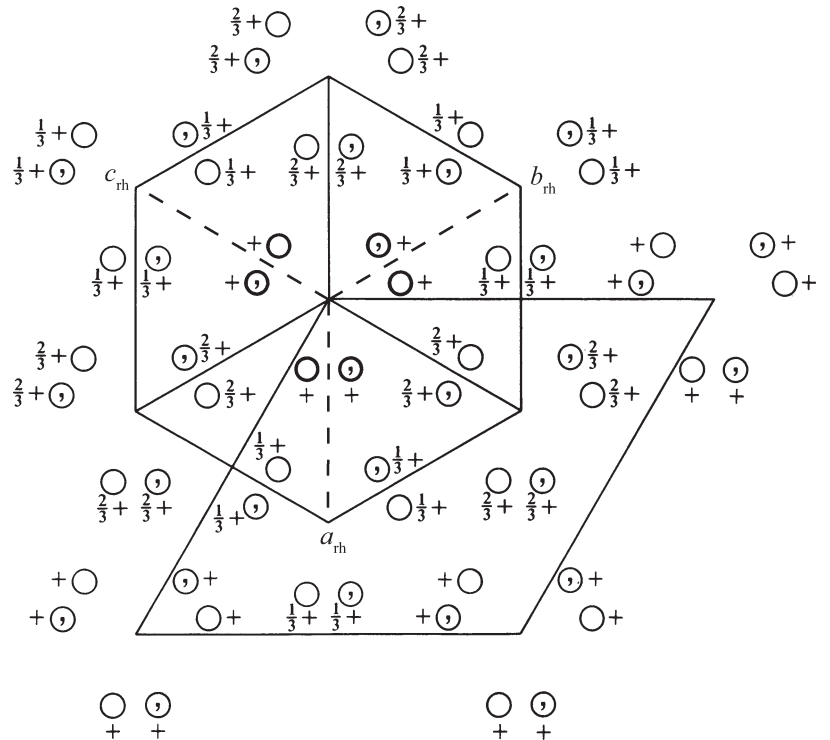
1.5.3.2. Examples

1.5.3.2.1. Transformations between different settings of $P2_1/c$

In the space-group tables of this volume, the monoclinic space group $P2_1/c$ (14) is described in six different settings: for each of the ‘unique axis b ’ and ‘unique axis c ’ settings there are three descriptions specified by different cell choices (*cf.* Section 2.1.3.15). The different settings are identified by the appropriate full Hermann–Mauguin symbols. The basis transfor-

mations (\mathbf{P}, \mathbf{p}) between the different settings are completely specified by the linear part of the transformation, the 3×3 matrix \mathbf{P} [*cf.* equation (1.5.1.4)], as all settings of $P2_1/c$ refer to the same origin, *i.e.* $\mathbf{p} = \mathbf{o}$. The transformation matrices \mathbf{P} necessary for switching between the different descriptions of $P2_1/c$ can either be read off directly or constructed from the transformation-matrix data listed in Table 1.5.1.1.

(A) Transformation from $P12_1/c1$ (unique axis b , cell choice 1) to $P112_1/a$ (unique axis c , cell choice 1). The change of the direction of the screw axis 2_1 indicates that the unique direction \mathbf{b}


Figure 1.5.3.3

General-position diagram of the space group $R3m$ (160) showing the relation between the hexagonal and rhombohedral axes in the obverse setting: $\mathbf{a}_{\text{rh}} = \frac{1}{3}(2\mathbf{a}_{\text{hex}} + \mathbf{b}_{\text{hex}} + \mathbf{c}_{\text{hex}})$, $\mathbf{b}_{\text{rh}} = \frac{1}{3}(-\mathbf{a}_{\text{hex}} + \mathbf{b}_{\text{hex}} + \mathbf{c}_{\text{hex}})$, $\mathbf{c}_{\text{rh}} = \frac{1}{3}(-\mathbf{a}_{\text{hex}} - 2\mathbf{b}_{\text{hex}} + \mathbf{c}_{\text{hex}})$.

1.6. Methods of space-group determination

U. SHMUELI, H. D. FLACK AND J. C. H. SPENCE

1.6.1. Overview

This chapter describes and discusses several methods of symmetry determination of single-domain crystals. A detailed presentation of symmetry determination from diffraction data is given in Section 1.6.2.1, followed by a brief discussion of intensity statistics, ideal as well as non-ideal, with an application of the latter to real intensity data from a $P\bar{1}$ crystal structure in Section 1.6.2.2. Several methods of retrieving symmetry information from a solved crystal structure are then discussed (Section 1.6.2.3). This is followed by a discussion of chemical and physical restrictions on space-group symmetry (Section 1.6.2.4), including some aids in symmetry determination, and by a brief section on pitfalls in space-group determination (Section 1.6.2.5).

The following two sections deal with reflection conditions. Section 1.6.3 presents the theoretical background of conditions for possible general reflections and their corresponding derivation. A brief discussion of special reflection conditions is included. Section 1.6.4 presents an extensive tabulation of general reflection conditions and possible space groups.

Other methods of space-group determination are presented in Section 1.6.5. Section 1.6.5.1 deals with an account of methods of space-group determination based on resonant (also termed ‘anomalous’) scattering. Section 1.6.5.2 is a brief description of approaches to space-group determination in macromolecular crystallography. Section 1.6.5.3 deals with corresponding approaches in powder-diffraction methods.

The chapter concludes with a description and illustration of symmetry determination based on electron-diffraction methods (Section 1.6.6), and principally focuses on convergent-beam electron diffraction.

This chapter deals only with single crystals. A supplement (Flack, 2015) deals with twinned crystals and those displaying a specialized metric.

1.6.2. Symmetry determination from single-crystal studies

BY U. SHMUELI AND H. D. FLACK

1.6.2.1. Symmetry information from the diffraction pattern

The extraction of symmetry information from the diffraction pattern takes place in three stages.

In the first stage, the unit-cell dimensions are determined and analyzed in order to establish to which Bravais lattice the crystal belongs. A conventional choice of lattice basis (coordinate system) may then be chosen. The determination of the Bravais lattice¹ of the crystal is achieved by the process of cell reduction, in which the lattice is first described by a basis leading to a primitive unit cell, and then linear combinations of the unit-cell vectors are taken to reduce the metric tensor (and the cell dimensions) to a standard form. From the relationships amongst

the elements of the metric tensor, one obtains the Bravais lattice, together with a conventional choice of the unit cell, with the aid of standard tables. A detailed description of cell reduction is given in Chapter 3.1 of this volume and in Part 9 of earlier editions (*e.g.* Burzlaff *et al.*, 2002). An alternative approach (Le Page, 1982) seeks the Bravais lattice directly from the cell dimensions by searching for all the twofold axes present. All these operations are automated in software. Regardless of the technique employed, at the end of the process one obtains an indication of the Bravais lattice and a unit cell in a conventional setting for the crystal system, primitive or centred as appropriate. These are usually good indications which, however, must be confirmed by an examination of the distribution of diffracted intensities as outlined below.

In the second stage, it is the point-group symmetry of the intensities of the Bragg reflections which is determined. We recall that the average reduced intensity of a pair of Friedel opposites (hkl and $\bar{h}\bar{k}\bar{l}$) is given by

$$\begin{aligned} |F_{\text{av}}(\mathbf{h})|^2 &= \frac{1}{2}[|F(\mathbf{h})|^2 + |F(\bar{\mathbf{h}})|^2] \\ &= \sum_{i,j} [(f_i + f'_i)(f_j + f'_j) + f''_i f''_j] \cos[2\pi\mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)] \equiv A(\mathbf{h}), \end{aligned} \quad (1.6.2.1)$$

where the atomic scattering factor of atom j , taking into account resonant scattering, is given by

$$\mathbf{f}_j = f_j + f'_j + if''_j,$$

the wavelength-dependent components f'_j and f''_j being the real and imaginary parts, respectively, of the contribution of atom j to the resonant scattering, \mathbf{h} contains in the (row) matrix (1×3) the diffraction orders (hkl) and \mathbf{r}_j contains in the (column) matrix (3×1) the coordinates (x_j, y_j, z_j) of atom j . The components of the \mathbf{f}_j are assumed to contain implicitly the displacement parameters. Equation (1.6.2.1) can be found *e.g.* in Okaya & Pepinsky (1955), Rossmann & Arnold (2001) and Flack & Shmueli (2007). It follows from (1.6.2.1) that

$$|F_{\text{av}}(\mathbf{h})|^2 = |F_{\text{av}}(\bar{\mathbf{h}})|^2 \text{ or } A(\mathbf{h}) = A(\bar{\mathbf{h}}),$$

regardless of the contribution of resonant scattering. Hence the averaging introduces a centre of symmetry in the (averaged) diffraction pattern.² In fact, working with the average of Friedel opposites, one may determine the Laue group of the diffraction pattern by comparing the intensities of reflections which should be symmetry equivalent under each of the Laue groups. These are the 11 centrosymmetric point groups: $\bar{1}$, $2/m$, mmm , $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $6/m$, $6/mmm$, $m\bar{3}$ and $m\bar{3}m$. For example, the reflections of which the intensities are to be compared for the Laue group $\bar{3}$ are: hkl , kil , ihl , $\bar{h}\bar{k}\bar{l}$, $\bar{k}\bar{i}\bar{l}$ and $\bar{i}\bar{h}\bar{l}$, where $i = -h - k$. An extensive listing of the indices of symmetry-related reflections in all the point groups, including of course the Laue groups, is

¹ The Bravais lattice symbol consists of two characters. The first is the first letter of the name of a crystal family and the second is the centring mode of a conventional unit cell. For details see Tables 3.1.2.1 and 3.1.2.2.

² We must mention the well known Friedel's law, which states that $|F(\mathbf{h})|^2 = |F(\bar{\mathbf{h}})|^2$ and which is only a reasonable approximation for noncentrosymmetric crystals if resonant scattering is negligibly small. This law holds well for centrosymmetric crystals, independently of the resonant-scattering contribution.

completely. Correspondingly, the seven subgroups of index 4 with the same translations as the original space group $P6_3/mcm$ are obtained *via* the 21 different chains of Fig. 1.7.1.1.

While all group–subgroup relations considered here are relations between individual space groups, they are valid for all space groups of a space-group type, as the following example shows.

Example

A particular space group $P121$ has a subgroup $P1$ which is obtained from $P121$ by retaining all translations but eliminating all rotations and combinations of rotations with translations. For every space group of space-group type $P121$ such a subgroup $P1$ exists.

From this example it follows that the relationship exists, in an extended sense, for the two space-group types involved. One can, therefore, list these relationships by means of the symbols of the space-group types.

A three-dimensional space group may have subgroups with no translations (*i.e.* site-symmetry groups; *cf.* Section 1.4.5), or with one- or two-dimensional lattices of translations (*i.e.* line groups, frieze groups, rod groups, plane groups and layer groups), *cf.* Volume E of *International Tables for Crystallography*, or with a three-dimensional lattice of translations (space groups).

The number of subgroups of a space group is always infinite. Not only the number of all subgroups but even the number of all maximal subgroups of a given space group is infinite.

In this section, only those subgroups of a space group that are also space groups will be considered. All *maximal* subgroups of space groups are themselves space groups. To simplify the discussion, let us suppose that we know all maximal subgroups of a space group \mathcal{G} . In this case, *any* subgroup \mathcal{H} of \mathcal{G} may be obtained *via* a chain of maximal subgroups $\mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_{r-1}, \mathcal{H}_r$ such that $\mathcal{G} (= \mathcal{H}_0) > \mathcal{H}_1 > \mathcal{H}_2 > \dots > \mathcal{H}_{r-1} > \mathcal{H}_r (= \mathcal{H})$, where \mathcal{H}_j is a maximal subgroup of \mathcal{H}_{j-1} of index $[i_j]$, with $j = 1, \dots, r$. There may be many such chains between \mathcal{G} and \mathcal{H} . On the other hand, all subgroups of \mathcal{G} of a given index $[i]$ are obtained if all chains are constructed for which $[i_1] \times [i_2] \times \dots \times [i_r] = [i]$ holds.

The index $[i]$ of a subgroup has a geometric significance. It determines the ‘dilution’ of symmetry operations of \mathcal{H} compared with those of \mathcal{G} . The number of symmetry operations of \mathcal{H} is $1/i$ times the number of symmetry operations of \mathcal{G} ; since space groups are infinite groups, this is to be understood in the same

way as ‘the number of even numbers is one half of the number of all integer numbers’.

The infinite number of subgroups only occurs for a certain kind of subgroup and can be reduced as described below. It is thus useful to consider the different kinds of subgroups of a space group in the way introduced by Hermann (1929):

- (1) By reducing the order of the point group, *i.e.* by eliminating all symmetry operations of some kind. The example $P12_11 \rightarrow P1$ mentioned above is of this type;
- (2) By loss of translations, *i.e.* by ‘thinning out’ the lattice of translations. For the space group $P121$ mentioned above this may happen in different ways:
 - (a) by suppressing all translations of the kind $(2u + 1)\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u, v and w are integers. The new basis is normally written $\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$ and, hence, half of the twofold axes have been eliminated; or
 - (b) by $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = 2\mathbf{b}$, $\mathbf{c}' = \mathbf{c}$, *i.e.* by thinning out the translations parallel to the twofold axes; or
 - (c) again by $\mathbf{b}' = 2\mathbf{b}$ but replacing the twofold rotation axes by twofold screw axes.
- (3) By combination of (1) and (2), *e.g.* by reducing the order of the point group and by thinning out the lattice of translations.

Subgroups of the first kind, (1), are called *translationengleiche* (or *t*-) subgroups because the set \mathcal{T} of all (pure) translations is retained. In case (2), the point group \mathcal{P} and thus the crystal class of the space group is unchanged. These subgroups are called *klassengleiche* or *k*-subgroups. In the general case (3), both the translation subgroup \mathcal{T} of \mathcal{G} and the point group \mathcal{P} are reduced; the subgroup has lost translations *and* belongs to a crystal class of lower order: these are *general* subgroups.

Obviously, the general subgroups are more difficult to survey than kinds (1) and (2). Fortunately, a theorem of Hermann (1929) states that if \mathcal{H} is a proper subgroup of \mathcal{G} , then there always exists an intermediate group \mathcal{M} such that $\mathcal{G} > \mathcal{M} > \mathcal{H}$, where \mathcal{M} is a *t*-subgroup of \mathcal{G} and \mathcal{H} is a *k*-subgroup of \mathcal{M} . If $\mathcal{H} < \mathcal{G}$ is maximal, then either $\mathcal{M} = \mathcal{G}$ and \mathcal{H} is a *k*-subgroup of \mathcal{G} or $\mathcal{M} = \mathcal{H}$ and \mathcal{H} is a *t*-subgroup of \mathcal{G} . It follows that a maximal subgroup of a space group \mathcal{G} is either a *t*-subgroup or a *k*-subgroup of \mathcal{G} . According to this theorem, general subgroups can never occur among the maximal subgroups. They can, however, be derived by a stepwise process of linking maximal *t*-subgroups and maximal *k*-subgroups by the chains discussed above.

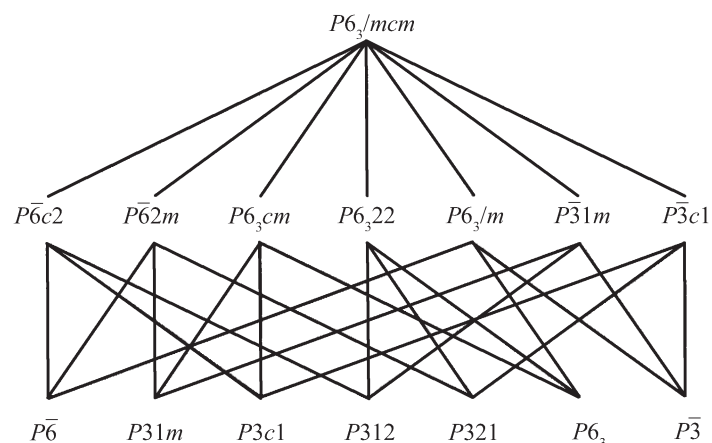


Figure 1.7.1.1

Space group $P6_3/mcm$ with *t*-subgroups of index 2 and 4. All 21 possible subgroup chains are displayed by lines.

1.7.1.1. Translationengleiche (or *t*-) subgroups of space groups

The ‘point group’ \mathcal{P} of a given space group \mathcal{G} is a finite group, *cf.* Chapter 1.3. Hence, the number of subgroups and consequently the number of maximal subgroups of \mathcal{P} is finite. There exist, therefore, only a finite number of maximal *t*-subgroups of \mathcal{G} . The possible *t*-subgroups were first listed in *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Band 1 (1935); corrections have been reported by Ascher *et al.* (1969). All maximal *t*-subgroups are listed individually for each space group \mathcal{G} in *IT A1* with the index, the (unconventional) Hermann–Mauguin symbol referred to the coordinate system of \mathcal{G} , the space-group number and conventional Hermann–Mauguin symbol, their general position and the transformation to the conventional coordinate system of \mathcal{H} . This may involve a change of basis and an origin shift from the coordinate system of \mathcal{G} .

1. INTRODUCTION TO SPACE-GROUP SYMMETRY

decimal value indicates that the coordinate is not fixed by symmetry). Simultaneously, the site symmetry of the metal atom is reduced from $4/m\bar{m}m$ to $4mm$ and the z coordinate becomes independent. In fact, the W atom is shifted from $z = 0$ to $z = 0.066$, *i.e.* it is not situated in the centre of the octahedron of the surrounding O atoms. This shift is the cause of the symmetry reduction. There is no splitting of the Wyckoff positions in this step of symmetry reduction, but a decrease of the site symmetries of all atoms.

When cooled, at 1170 K $HT\text{-}WO_3$ is transformed to $\alpha\text{-}WO_3$. This involves mutual rotations of the coordination octahedra along c and requires another step of symmetry reduction. Again, the Wyckoff positions do not split in this step of symmetry reduction, but the site symmetries of all atoms are further decreased.

Upon further cooling, WO_3 undergoes several other phase transitions that involve additional distortions and, in each case, an additional symmetry reduction to another subgroup (not shown in Fig. 1.7.2.2). For more details see Müller (2013), Section 11.6, and references therein.

1.7.2.4. Domain structures

In the case of phase transitions and of topotactic reactions³ that involve a symmetry reduction, the kind of group–subgroup relation determines how many kinds of domains and what domain states can be formed. If the lower-symmetry product results from a *translationengleiche* group–subgroup relation, twinned crystals are to be expected. A *klassengleiche* group–subgroup relation will cause antiphase domains. The number of different kinds of twin or antiphase domains corresponds to the index of the symmetry reduction. For example, the phase transition from $HT\text{-}WO_3$ to $\alpha\text{-}WO_3$ involves a *klassengleiche* group–subgroup relation of index 2 (k_2 in Fig. 1.7.2.2); no twins will be formed, but two kinds of antiphase domains can be expected.

1.7.2.5. Presentation of the relations between the Wyckoff positions among group–subgroup-related space groups

Group–subgroup relations as outlined in the preceding sections can only be correct if all atomic positions of the hettotypes result directly from those of the aristotype.

Every group–subgroup relation between space groups entails specific relations between their Wyckoff positions. If the index of symmetry reduction is 2, a Wyckoff position either splits into two symmetry-independent positions that keep the site symmetry, or there is no splitting and the site symmetry is reduced. If the index is 3 or higher, a Wyckoff position either splits, or its site symmetry is reduced, or both happen. Given the relative settings and origin choices of a space group and its subgroup, there exist unique relations between their Wyckoff positions. Laws governing these relations are considered in Chapter 1.5 of the second edition of *IT A1*.

Volume A1, Part 3, *Relations between the Wyckoff positions*, contains tables for all space groups. For every one of them, all maximal subgroups are listed, including the corresponding coordinate transformations. For all Wyckoff positions of a space group the relations to the Wyckoff positions of the subgroups are given. This includes the infinitely many maximal isomorphic subgroups, for which general formulae are given. Isomorphic subgroups are a special kind of *klassengleiche* subgroup that

³ A topotactic reaction is a chemical reaction in the solid state where the orientation of the product crystal is determined by the orientation of the educt crystal.

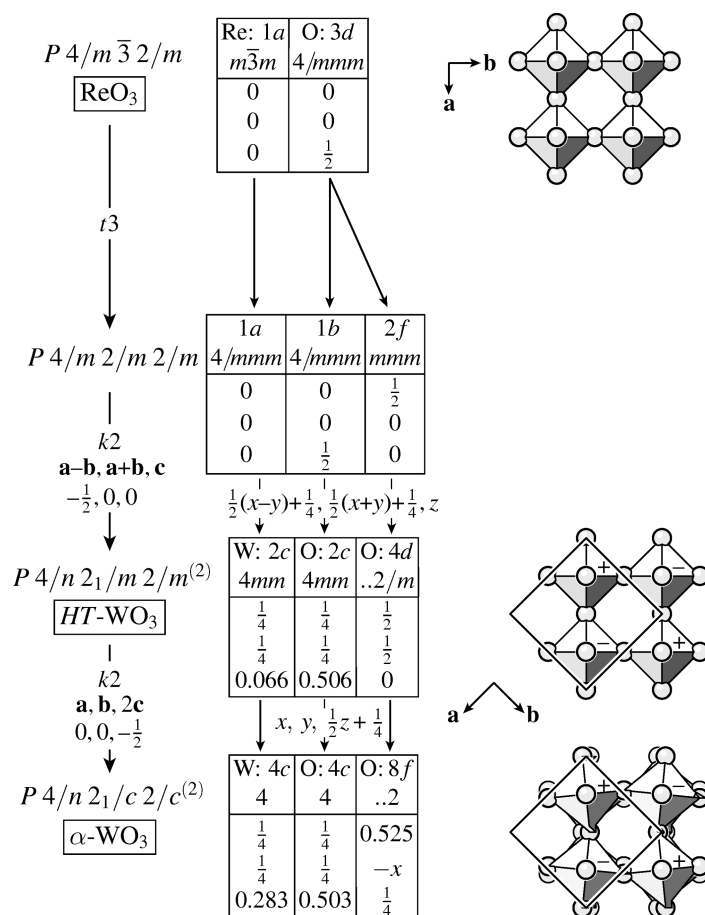


Figure 1.7.2.2 Group–subgroup relations (Bärnighausen tree) from the ReO_3 type to two polymorphic forms of WO_3 . The superscript (2) after the space-group symbols states the origin choice. + and – in the images of high-temperature WO_3 and $\alpha\text{-}WO_3$ indicate the direction of the z shifts of the W atoms from the octahedron centres. Structural data for WO_3 are taken from Locherer *et al.* (1999).

belong to the same or the enantiomorphic space-group type, *i.e.* group and subgroup have the same or the enantiomorphic space-group symbol; the unit cell of the subgroup is increased by some integral factor, which is p , p^2 or p^3 (p = prime number) in the case of maximal isomorphic subgroups.

1.7.3. Relationships between space groups and subperiodic groups

BY D. B. LITVIN AND V. KOPSKÝ

The present volume in the series *International Tables for Crystallography* (Volume A: *Space-Group Symmetry*) treats one-, two- and three-dimensional space groups. Volume E in the series, *Subperiodic Groups* (2010), treats two- and three-dimensional subperiodic groups: frieze groups (groups in two-dimensional space with translations in a one-dimensional subspace), rod groups (groups in three-dimensional space with translations in a one-dimensional subspace) and layer groups (groups in three-dimensional space with translations in a two-dimensional subspace). In the same way in which three-dimensional space groups are used to classify the atomic structure of three-dimensional crystals, the subperiodic groups are used to classify the atomic structure of other crystalline structures, such as liquid crystals, domain interfaces, twins and thin films.

Hexagonal

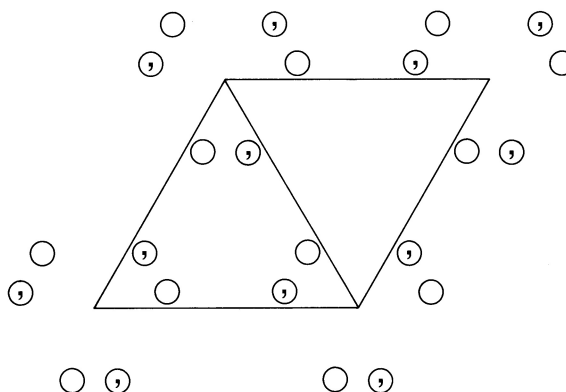
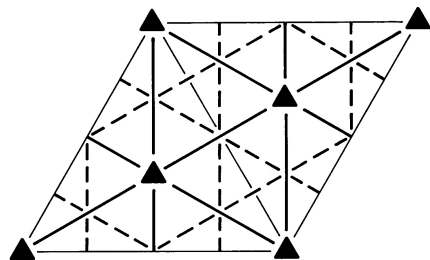
$3m$

$p3m1$

Patterson symmetry $p6mm$

$p3m1$

No. 14



Origin at $3m1$

Asymmetric unit $0 \leq x \leq \frac{2}{3}; 0 \leq y \leq \frac{2}{3}; x \leq 2y; y \leq \min(1-x, 2x)$

Vertices $0,0 \quad \frac{2}{3}, \frac{1}{3} \quad \frac{1}{3}, \frac{2}{3}$

Symmetry operations

- (1) 1 (2) $3^+ 0,0$ (3) $3^- 0,0$
 (4) $m \ x, \bar{x}$ (5) $m \ x, 2x$ (6) $m \ 2x, x$

Generators selected (1); $t(1,0)$; $t(0,1)$; (2); (4)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

6 *e* 1 (1) x, y (2) $\bar{y}, x-y$ (3) $\bar{x}+y, \bar{x}$
 (4) \bar{y}, \bar{x} (5) $\bar{x}+y, y$ (6) $x, x-y$

General:

no conditions

Special: no extra conditions

3 *d* . *m* . x, \bar{x} $x, 2x$ $2\bar{x}, \bar{x}$

1 *c* $3m$. $\frac{2}{3}, \frac{1}{3}$

1 *b* $3m$. $\frac{1}{3}, \frac{2}{3}$

1 *a* $3m$. $0,0$

Orthorhombic

$mm2$

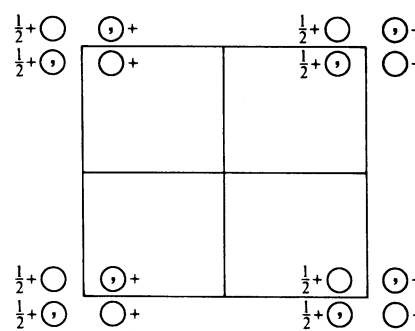
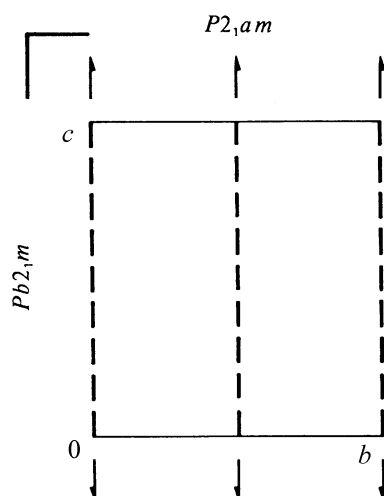
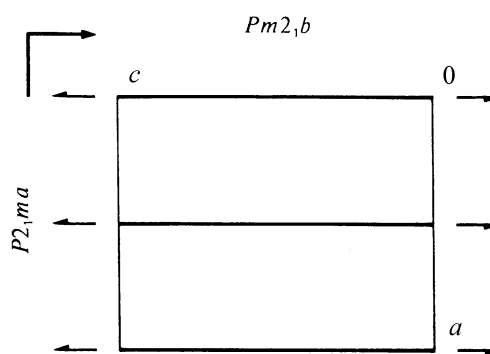
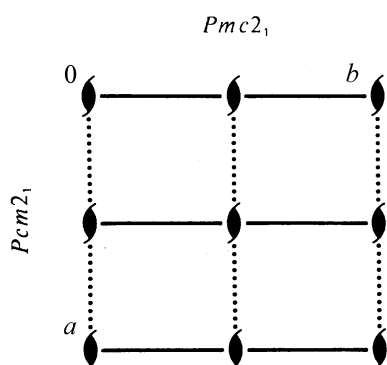
C_{2v}^2

$Pmc2_1$

Patterson symmetry $Pmmm$

$Pmc2_1$

No. 26



Origin on $mc2_1$

Asymmetric unit $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq \frac{1}{2}; 0 \leq z \leq 1$

Symmetry operations

(1) 1 (2) $2(0,0,\frac{1}{2})$ $0,0,z$ (3) c $x,0,z$ (4) m $0,y,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

4 c 1 (1) x,y,z (2) $\bar{x},\bar{y},z+\frac{1}{2}$ (3) $x,\bar{y},z+\frac{1}{2}$ (4) \bar{x},y,z

General:

$h0l: l = 2n$

$00l: l = 2n$

Special: no extra conditions

2 b $m..$ $\frac{1}{2},y,z$ $\frac{1}{2},\bar{y},z+\frac{1}{2}$

2 a $m..$ $0,y,z$ $0,\bar{y},z+\frac{1}{2}$

Symmetry of special projections

Along $[001]$ $p2mm$

$\mathbf{a}' = \mathbf{a}$ $\mathbf{b}' = \mathbf{b}$

Origin at $0,0,z$

Along $[100]$ $p1g1$

$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}$

Origin at $x,0,0$

Along $[010]$ $p11m$

$\mathbf{a}' = \frac{1}{2}\mathbf{c}$ $\mathbf{b}' = \mathbf{a}$

Origin at $0,y,0$

$Ia\bar{3}d$

O_h^{10}

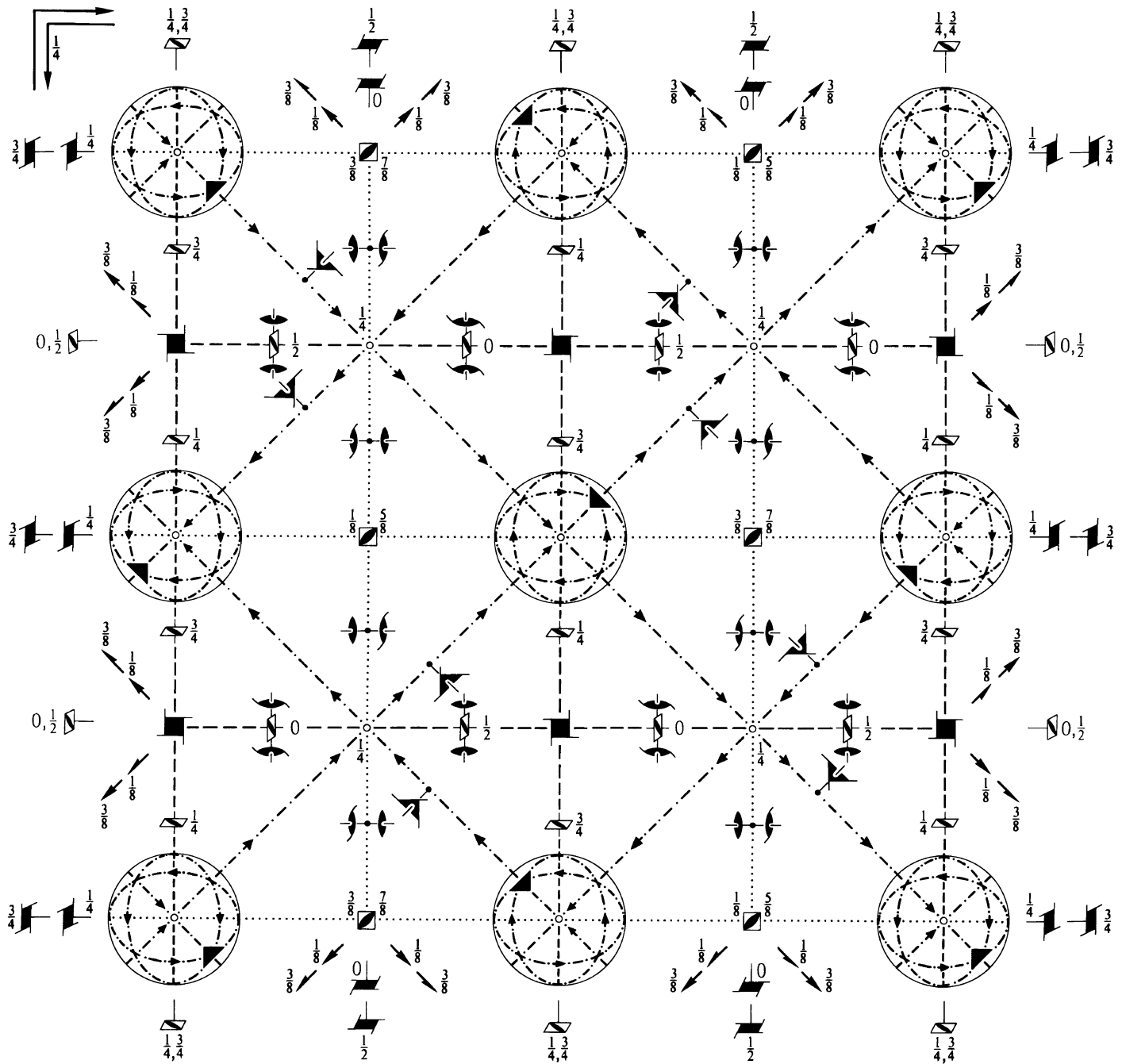
$m\bar{3}m$

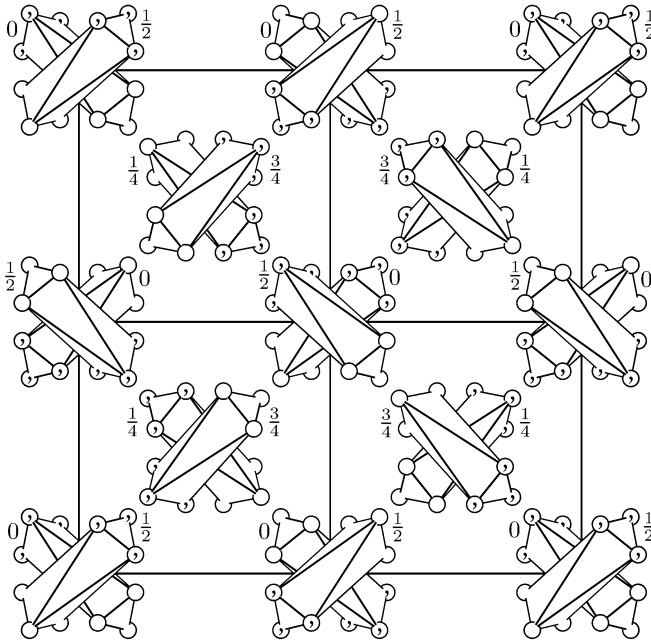
Cubic

No. 230

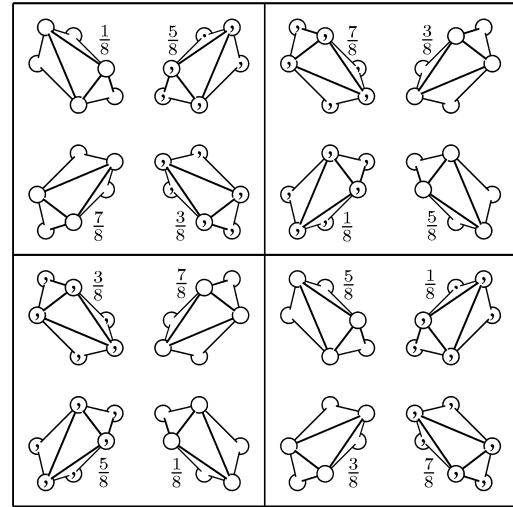
$I 4_1/a \bar{3} 2/d$

Patterson symmetry $Im\bar{3}m$





Polyhedron centre at 0, 0, 0



Polyhedron centre at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$

Origin at centre ($\bar{3}$)

Asymmetric unit $-\frac{1}{8} \leq x \leq \frac{1}{8}; -\frac{1}{8} \leq y \leq \frac{1}{8}; 0 \leq z \leq \frac{1}{4}; \max(x, -x, y, -y) \leq z$
Vertices $0, 0, 0$ $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ $-\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ $-\frac{1}{8}, -\frac{1}{8}, \frac{1}{8}$ $\frac{1}{8}, -\frac{1}{8}, \frac{1}{8}$
 $\frac{1}{8}, \frac{1}{8}, \frac{1}{4}$ $-\frac{1}{8}, \frac{1}{8}, \frac{1}{4}$ $-\frac{1}{8}, -\frac{1}{8}, \frac{1}{4}$ $\frac{1}{8}, -\frac{1}{8}, \frac{1}{4}$

Symmetry operations

For (0,0,0)+ set

- | | | | |
|---|---|---|---|
| (1) 1 | (2) $2(0, 0, \frac{1}{2})$ $\frac{1}{4}, 0, z$ | (3) $2(0, \frac{1}{2}, 0)$ $0, y, \frac{1}{4}$ | (4) $2(\frac{1}{2}, 0, 0)$ $x, \frac{1}{4}, 0$ |
| (5) 3^+ x, x, x | (6) 3^+ $\bar{x} + \frac{1}{2}, x, \bar{x}$ | (7) 3^+ $x + \frac{1}{2}, \bar{x} - \frac{1}{2}, \bar{x}$ | (8) 3^+ $\bar{x}, \bar{x} + \frac{1}{2}, x$ |
| (9) 3^- x, x, x | (10) 3^- $(-\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ $x + \frac{1}{6}, \bar{x} + \frac{1}{6}, \bar{x}$ | (11) 3^- $(\frac{1}{3}, \frac{1}{3}, -\frac{1}{3})$ $\bar{x} + \frac{1}{3}, \bar{x} + \frac{1}{6}, x$ | (12) 3^- $(\frac{1}{3}, -\frac{1}{3}, \frac{1}{3})$ $\bar{x} - \frac{1}{6}, x + \frac{1}{3}, \bar{x}$ |
| (13) $2(\frac{1}{2}, \frac{1}{2}, 0)$ $x, x - \frac{1}{4}, \frac{1}{8}$ | (14) 2 $x, \bar{x} + \frac{3}{4}, \frac{3}{8}$ | (15) $4^-(0, 0, \frac{3}{4})$ $\frac{1}{4}, 0, z$ | (16) $4^+(0, 0, \frac{3}{4})$ $-\frac{1}{4}, \frac{1}{2}, z$ |
| (17) $4^-(\frac{3}{4}, 0, 0)$ $x, \frac{1}{4}, 0$ | (18) $2(0, \frac{1}{2}, \frac{1}{2})$ $\frac{1}{8}, y + \frac{1}{4}, y$ | (19) 2 $\frac{3}{8}, y + \frac{3}{4}, \bar{y}$ | (20) $4^+(\frac{1}{4}, 0, 0)$ $x, -\frac{1}{4}, \frac{1}{2}$ |
| (21) $4^+(0, \frac{1}{4}, 0)$ $\frac{1}{2}, y, -\frac{1}{4}$ | (22) $2(\frac{1}{2}, 0, \frac{1}{2})$ $x - \frac{1}{4}, \frac{1}{8}, x$ | (23) $4^-(0, \frac{3}{4}, 0)$ $0, y, \frac{1}{4}$ | (24) 2 $\bar{x} + \frac{3}{4}, \frac{3}{8}, x$ |
| (25) $\bar{1}$ $0, 0, 0$ | (26) a $x, y, \frac{1}{4}$ | (27) c $x, \frac{1}{4}, z$ | (28) b $\frac{1}{4}, y, z$ |
| (29) $\bar{3}^+$ $x, x, x; 0, 0, 0$ | (30) $\bar{3}^+$ $\bar{x} - \frac{1}{2}, x + 1, \bar{x}; 0, \frac{1}{2}, \frac{1}{2}$ | (31) $\bar{3}^+$ $x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x}; \frac{1}{2}, \frac{1}{2}, 0$ | (32) $\bar{3}^+$ $\bar{x} + 1, \bar{x} + \frac{1}{2}, x; \frac{1}{2}, 0, \frac{1}{2}$ |
| (33) $\bar{3}^-$ $x, x, x; 0, 0, 0$ | (34) $\bar{3}^-$ $x + \frac{1}{2}, \bar{x} - \frac{1}{2}, \bar{x}; 0, 0, \frac{1}{2}$ | (35) $\bar{3}^-$ $\bar{x}, \bar{x} + \frac{1}{2}, x; 0, \frac{1}{2}, 0$ | (36) $\bar{3}^-$ $\bar{x} + \frac{1}{2}, x, \bar{x}; \frac{1}{2}, 0, 0$ |
| (37) $d(-\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ $x + \frac{1}{2}, \bar{x}, z$ | (38) $d(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ x, x, z | (39) $\bar{4}^-$ $0, \frac{3}{4}, z; 0, \frac{3}{4}, \frac{1}{8}$ | (40) $\bar{4}^+$ $\frac{1}{2}, -\frac{1}{4}, z; \frac{1}{2}, -\frac{1}{4}, \frac{3}{8}$ |
| (41) $\bar{4}^-$ $x, 0, \frac{3}{4}; \frac{1}{8}, 0, \frac{3}{4}$ | (42) $d(\frac{3}{4}, -\frac{1}{4}, \frac{1}{4})$ $x, y + \frac{1}{2}, \bar{y}$ | (43) $d(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ x, y, y | (44) $\bar{4}^+$ $x, \frac{1}{2}, -\frac{1}{4}; \frac{3}{8}, \frac{1}{2}, -\frac{1}{4}$ |
| (45) $\bar{4}^+$ $-\frac{1}{4}, y, \frac{1}{2}; -\frac{1}{4}, \frac{3}{8}, \frac{1}{2}$ | (46) $d(\frac{1}{4}, \frac{3}{4}, -\frac{1}{4})$ $\bar{x} + \frac{1}{2}, y, x$ | (47) $\bar{4}^-$ $\frac{3}{4}, y, 0; \frac{3}{4}, \frac{1}{8}, 0$ | (48) $d(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ x, y, x |

For ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)+ set

- | | | | |
|---|--|---|--|
| (1) $i(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | (2) 2 $0, \frac{1}{4}, z$ | (3) 2 $\frac{1}{4}, y, 0$ | (4) 2 $x, 0, \frac{1}{4}$ |
| (5) $3^+(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ x, x, x | (6) $3^+(\frac{1}{6}, -\frac{1}{6}, \frac{1}{6})$ $\bar{x} - \frac{1}{6}, x + \frac{1}{3}, \bar{x}$ | (7) $3^+(\frac{1}{6}, -\frac{1}{6}, \frac{1}{6})$ $x + \frac{1}{6}, \bar{x} + \frac{1}{6}, \bar{x}$ | (8) $3^+(\frac{1}{6}, \frac{1}{6}, -\frac{1}{6})$ $\bar{x} + \frac{1}{3}, \bar{x} + \frac{1}{6}, x$ |
| (9) $3^-(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ x, x, x | (10) $3^-(\frac{1}{6}, -\frac{1}{6}, -\frac{1}{6})$ $x + \frac{1}{6}, \bar{x} + \frac{1}{6}, \bar{x}$ | (11) $3^-(\frac{1}{6}, -\frac{1}{6}, \frac{1}{6})$ $\bar{x} + \frac{1}{3}, \bar{x} + \frac{1}{6}, x$ | (12) $3^-(\frac{1}{6}, \frac{1}{6}, -\frac{1}{6})$ $\bar{x} - \frac{1}{6}, x + \frac{1}{3}, \bar{x}$ |
| (13) $2(\frac{1}{2}, \frac{1}{2}, 0)$ $x, x + \frac{1}{4}, \frac{3}{8}$ | (14) 2 $x, \bar{x} + \frac{1}{4}, \frac{1}{8}$ | (15) $4^-(0, 0, \frac{3}{4})$ $\frac{3}{4}, 0, z$ | (16) $4^+(0, 0, \frac{3}{4})$ $\frac{1}{4}, \frac{1}{2}, z$ |
| (17) $4^-(\frac{1}{4}, 0, 0)$ $x, \frac{3}{4}, 0$ | (18) $2(0, \frac{1}{2}, \frac{1}{2})$ $\frac{3}{8}, y - \frac{1}{4}, y$ | (19) 2 $\frac{1}{8}, y + \frac{1}{4}, \bar{y}$ | (20) $4^+(\frac{3}{4}, 0, 0)$ $x, \frac{1}{4}, \frac{1}{2}$ |
| (21) $4^+(0, \frac{3}{4}, 0)$ $\frac{1}{2}, y, \frac{1}{4}$ | (22) $2(\frac{1}{2}, 0, \frac{1}{2})$ $x + \frac{1}{4}, \frac{3}{8}, x$ | (23) $4^-(0, \frac{1}{4}, 0)$ $0, y, \frac{3}{4}$ | (24) 2 $\bar{x} + \frac{1}{4}, \frac{1}{8}, x$ |
| (25) $\bar{1}$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ | (26) b $x, y, 0$ | (27) a $x, 0, z$ | (28) c $0, y, z$ |
| (29) $\bar{3}^+$ $x, x, x; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ | (30) $\bar{3}^+$ $\bar{x} - \frac{1}{2}, x, \bar{x}; -\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}$ | (31) $\bar{3}^+$ $x - \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x}; -\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}$ | (32) $\bar{3}^+$ $\bar{x}, \bar{x} - \frac{1}{2}, x; \frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}$ |
| (33) $\bar{3}^-$ $x, x, x; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ | (34) $\bar{3}^-$ $x + \frac{1}{2}, \bar{x} - \frac{1}{2}, \bar{x}; \frac{1}{4}, -\frac{1}{4}, \frac{1}{4}$ | (35) $\bar{3}^-$ $\bar{x}, \bar{x} + \frac{1}{2}, x; -\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ | (36) $\bar{3}^-$ $\bar{x} + \frac{1}{2}, x, \bar{x}; \frac{1}{4}, \frac{1}{4}, -\frac{1}{4}$ |
| (37) $d(\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$ $x + \frac{1}{2}, \bar{x}, z$ | (38) $d(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ x, x, z | (39) $\bar{4}^-$ $0, \frac{1}{4}, z; 0, \frac{1}{4}, \frac{3}{8}$ | (40) $\bar{4}^+$ $\frac{1}{2}, \frac{1}{4}, z; \frac{1}{2}, \frac{1}{4}, \frac{1}{8}$ |
| (41) $\bar{4}^-$ $x, 0, \frac{1}{4}; \frac{3}{8}, 0, \frac{1}{4}$ | (42) $d(\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})$ $x, y + \frac{1}{2}, \bar{y}$ | (43) $d(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ x, y, y | (44) $\bar{4}^+$ $x, \frac{1}{2}, \frac{1}{4}; \frac{1}{8}, \frac{1}{2}, \frac{1}{4}$ |
| (45) $\bar{4}^+$ $\frac{1}{4}, y, \frac{1}{2}; \frac{1}{4}, \frac{1}{8}, \frac{1}{2}$ | (46) $d(-\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ $\bar{x} + \frac{1}{2}, y, x$ | (47) $\bar{4}^-$ $\frac{1}{4}, y, 0; \frac{1}{4}, \frac{3}{8}, 0$ | (48) $d(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ x, y, x |

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

$(0,0,0)+ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$

Reflection conditions

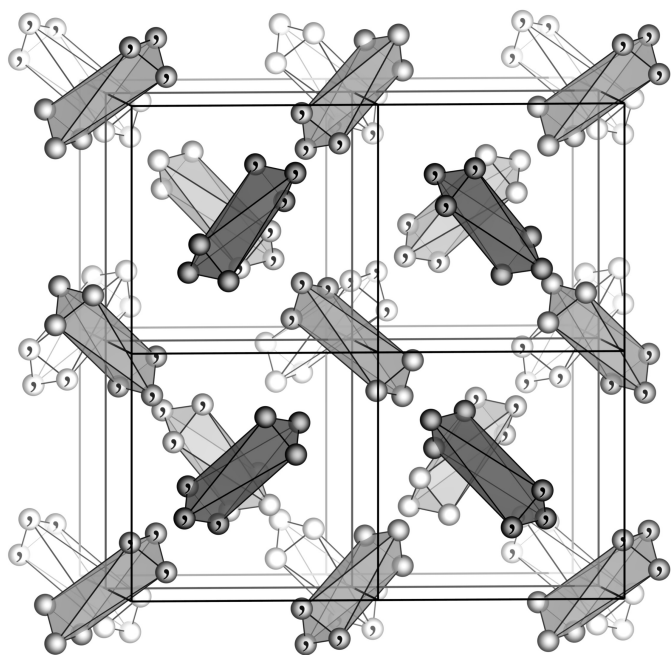
h, k, l permutable

General:

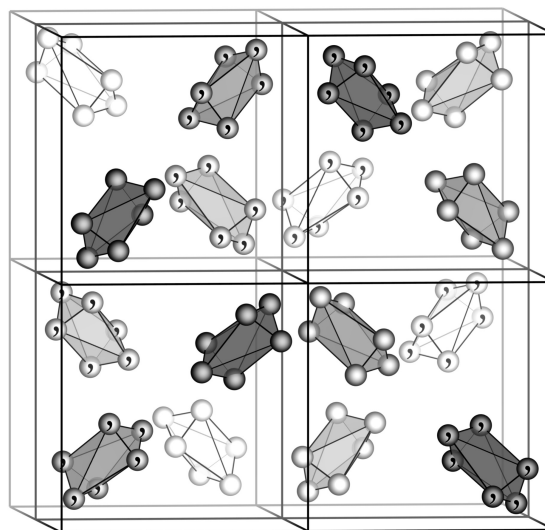
96	h	1	(1) x, y, z	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	(3) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$
			(5) z, x, y	(6) $z + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{y}$	(7) $\bar{z} + \frac{1}{2}, \bar{x}, y + \frac{1}{2}$	(8) $\bar{z}, x + \frac{1}{2}, \bar{y} + \frac{1}{2}$
			(9) y, z, x	(10) $\bar{y}, z + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(11) $y + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{x}$	(12) $\bar{y} + \frac{1}{2}, \bar{z}, x + \frac{1}{2}$
			(13) $y + \frac{3}{4}, x + \frac{1}{4}, \bar{z} + \frac{1}{4}$	(14) $\bar{y} + \frac{3}{4}, \bar{x} + \frac{3}{4}, \bar{z} + \frac{3}{4}$	(15) $y + \frac{1}{4}, \bar{x} + \frac{1}{4}, z + \frac{3}{4}$	(16) $\bar{y} + \frac{1}{4}, x + \frac{3}{4}, z + \frac{1}{4}$
			(17) $x + \frac{3}{4}, z + \frac{1}{4}, \bar{y} + \frac{1}{4}$	(18) $\bar{x} + \frac{1}{4}, z + \frac{3}{4}, y + \frac{1}{4}$	(19) $\bar{x} + \frac{3}{4}, \bar{z} + \frac{3}{4}, \bar{y} + \frac{3}{4}$	(20) $x + \frac{1}{4}, \bar{z} + \frac{1}{4}, y + \frac{3}{4}$
			(21) $z + \frac{3}{4}, y + \frac{1}{4}, \bar{x} + \frac{1}{4}$	(22) $z + \frac{1}{4}, \bar{y} + \frac{1}{4}, x + \frac{3}{4}$	(23) $\bar{z} + \frac{1}{4}, y + \frac{3}{4}, x + \frac{1}{4}$	(24) $\bar{z} + \frac{3}{4}, \bar{y} + \frac{3}{4}, \bar{x} + \frac{3}{4}$
			(25) $\bar{x}, \bar{y}, \bar{z}$	(26) $x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$	(27) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(28) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$
			(29) $\bar{x}, \bar{x}, \bar{y}$	(30) $\bar{z} + \frac{1}{2}, x + \frac{1}{2}, y$	(31) $z + \frac{1}{2}, x, \bar{y} + \frac{1}{2}$	(32) $z, \bar{x} + \frac{1}{2}, y + \frac{1}{2}$
			(33) $\bar{y}, \bar{z}, \bar{x}$	(34) $y, \bar{z} + \frac{1}{2}, x + \frac{1}{2}$	(35) $\bar{y} + \frac{1}{2}, z + \frac{1}{2}, x$	(36) $y + \frac{1}{2}, z, \bar{x} + \frac{1}{2}$
			(37) $\bar{y} + \frac{1}{4}, \bar{x} + \frac{3}{4}, z + \frac{3}{4}$	(38) $y + \frac{1}{4}, x + \frac{1}{4}, z + \frac{1}{4}$	(39) $\bar{y} + \frac{3}{4}, x + \frac{3}{4}, \bar{z} + \frac{1}{4}$	(40) $y + \frac{3}{4}, \bar{x} + \frac{1}{4}, \bar{z} + \frac{3}{4}$
			(41) $\bar{x} + \frac{1}{4}, \bar{z} + \frac{3}{4}, y + \frac{3}{4}$	(42) $x + \frac{3}{4}, \bar{z} + \frac{1}{4}, \bar{y} + \frac{3}{4}$	(43) $x + \frac{1}{4}, z + \frac{1}{4}, y + \frac{1}{4}$	(44) $\bar{x} + \frac{3}{4}, z + \frac{3}{4}, \bar{y} + \frac{1}{4}$
			(45) $\bar{z} + \frac{1}{4}, \bar{y} + \frac{3}{4}, x + \frac{3}{4}$	(46) $\bar{z} + \frac{3}{4}, y + \frac{3}{4}, \bar{x} + \frac{1}{4}$	(47) $z + \frac{3}{4}, \bar{y} + \frac{1}{4}, \bar{x} + \frac{3}{4}$	(48) $z + \frac{1}{4}, y + \frac{1}{4}, x + \frac{1}{4}$

Special: as above, plus

48	g	$\dots 2$	$\frac{1}{8}, y, \bar{y} + \frac{1}{4}$	$\frac{3}{8}, \bar{y}, \bar{y} + \frac{3}{4}$	$\frac{7}{8}, y + \frac{1}{2}, y + \frac{1}{4}$	$\frac{5}{8}, \bar{y} + \frac{1}{2}, y + \frac{3}{4}$	$hkl: h = 2n + 1$ $or h = 4n$			
			$\bar{y} + \frac{1}{4}, \frac{1}{8}, y$	$\bar{y} + \frac{3}{4}, \frac{3}{8}, \bar{y}$	$y + \frac{1}{4}, \frac{7}{8}, y + \frac{1}{2}$	$y + \frac{3}{4}, \frac{5}{8}, \bar{y} + \frac{1}{2}$				
			$y, \bar{y} + \frac{1}{4}, \frac{1}{8}$	$\bar{y}, \bar{y} + \frac{3}{4}, \frac{3}{8}$	$y + \frac{1}{2}, y + \frac{1}{4}, \frac{7}{8}$	$\bar{y} + \frac{1}{2}, y + \frac{3}{4}, \frac{5}{8}$				
			$\frac{7}{8}, \bar{y}, y + \frac{3}{4}$	$\frac{5}{8}, y, y + \frac{1}{4}$	$\frac{1}{8}, \bar{y} + \frac{1}{2}, \bar{y} + \frac{3}{4}$	$\frac{3}{8}, y + \frac{1}{2}, \bar{y} + \frac{1}{4}$				
			$y + \frac{3}{4}, \frac{7}{8}, \bar{y}$	$y + \frac{1}{4}, \frac{5}{8}, y$	$\bar{y} + \frac{3}{4}, \frac{1}{8}, \bar{y} + \frac{1}{2}$	$\bar{y} + \frac{1}{4}, \frac{3}{8}, y + \frac{1}{2}$				
			$\bar{y}, y + \frac{3}{4}, \frac{7}{8}$	$y, y + \frac{1}{4}, \frac{5}{8}$	$\bar{y} + \frac{1}{2}, \bar{y} + \frac{3}{4}, \frac{1}{8}$	$y + \frac{1}{2}, \bar{y} + \frac{1}{4}, \frac{3}{8}$				
48	f	$2 \dots$	$x, 0, \frac{1}{4}$	$\bar{x} + \frac{1}{2}, 0, \frac{3}{4}$	$\frac{1}{4}, x, 0$	$\frac{3}{4}, \bar{x} + \frac{1}{2}, 0$	$0, \frac{1}{4}, x$	$0, \frac{3}{4}, \bar{x} + \frac{1}{2}$	$hkl: 2h + l = 4n$	
			$\frac{3}{4}, x + \frac{1}{4}, 0$	$\frac{3}{4}, \bar{x} + \frac{3}{4}, \frac{1}{2}$	$x + \frac{3}{4}, \frac{1}{2}, \frac{1}{4}$	$\bar{x} + \frac{1}{4}, 0, \frac{1}{4}$	$0, \frac{1}{4}, \bar{x} + \frac{1}{4}$	$\frac{1}{2}, \frac{1}{4}, x + \frac{3}{4}$		
			$\bar{x}, 0, \frac{3}{4}$	$x + \frac{1}{2}, 0, \frac{1}{4}$	$\frac{3}{4}, \bar{x}, 0$	$\frac{1}{4}, x + \frac{1}{2}, 0$	$0, \frac{3}{4}, \bar{x}$	$0, \frac{1}{4}, x + \frac{1}{2}$		
			$\frac{1}{4}, \bar{x} + \frac{3}{4}, 0$	$\frac{1}{4}, x + \frac{1}{4}, \frac{1}{2}$	$\bar{x} + \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$	$x + \frac{3}{4}, 0, \frac{3}{4}$	$0, \frac{3}{4}, x + \frac{3}{4}$	$\frac{1}{2}, \frac{3}{4}, \bar{x} + \frac{1}{4}$		
32	e	$\dots 3$	x, x, x	$\bar{x} + \frac{1}{2}, \bar{x}, x + \frac{1}{2}$	$\bar{x}, x + \frac{1}{2}, \bar{x} + \frac{1}{2}$	$x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x}$	$hkl: h = 2n + 1$ $or h + k + l = 4n$			
			$x + \frac{3}{4}, x + \frac{1}{4}, \bar{x} + \frac{1}{4}$	$\bar{x} + \frac{3}{4}, \bar{x} + \frac{3}{4}, \bar{x} + \frac{3}{4}$	$x + \frac{1}{4}, \bar{x} + \frac{1}{4}, x + \frac{3}{4}$	$\bar{x} + \frac{1}{4}, x + \frac{3}{4}, x + \frac{1}{4}$				
			$\bar{x}, \bar{x}, \bar{x}$	$x + \frac{1}{2}, x, \bar{x} + \frac{1}{2}$	$x, \bar{x} + \frac{1}{2}, x + \frac{1}{2}$	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, x$				
			$\bar{x} + \frac{1}{4}, \bar{x} + \frac{3}{4}, x + \frac{3}{4}$	$x + \frac{1}{4}, x + \frac{1}{4}, x + \frac{1}{4}$	$\bar{x} + \frac{3}{4}, x + \frac{3}{4}, \bar{x} + \frac{1}{4}$	$x + \frac{3}{4}, \bar{x} + \frac{1}{4}, \bar{x} + \frac{3}{4}$				
24	d	$\bar{4} \dots$	$\frac{3}{8}, 0, \frac{1}{4}$	$\frac{1}{8}, 0, \frac{3}{4}$	$\frac{1}{4}, \frac{3}{8}, 0$	$\frac{3}{4}, \frac{1}{8}, 0$	$0, \frac{1}{4}, \frac{3}{8}$	$0, \frac{3}{4}, \frac{1}{8}$	$hkl: h, k = 2n, h + k + l = 4n$ $or h, k = 2n + 1, l = 4n + 2$ $or h = 8n, k = 8n + 4$ and $h + k + l = 4n + 2$	
			$\frac{3}{4}, \frac{5}{8}, 0$	$\frac{3}{4}, \frac{3}{8}, \frac{1}{2}$	$\frac{1}{8}, \frac{1}{2}, \frac{1}{4}$	$\frac{7}{8}, 0, \frac{1}{4}$	$0, \frac{1}{4}, \frac{7}{8}$	$\frac{1}{2}, \frac{1}{4}, \frac{1}{8}$		
24	c	$2 \dots 22$	$\frac{1}{8}, 0, \frac{1}{4}$	$\frac{3}{8}, 0, \frac{3}{4}$	$\frac{1}{4}, \frac{1}{8}, 0$	$\frac{3}{4}, \frac{3}{8}, 0$	$0, \frac{1}{4}, \frac{1}{8}$	$0, \frac{3}{4}, \frac{3}{8}$		
			$\frac{7}{8}, 0, \frac{3}{4}$	$\frac{5}{8}, 0, \frac{1}{4}$	$\frac{3}{4}, \frac{7}{8}, 0$	$\frac{1}{4}, \frac{5}{8}, 0$	$0, \frac{3}{4}, \frac{7}{8}$	$0, \frac{1}{4}, \frac{5}{8}$		
16	b	$\dots 32$	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	$\frac{3}{8}, \frac{7}{8}, \frac{5}{8}$	$\frac{7}{8}, \frac{5}{8}, \frac{3}{8}$	$\frac{5}{8}, \frac{3}{8}, \frac{7}{8}$	$\frac{7}{8}, \frac{7}{8}, \frac{7}{8}$	$\frac{5}{8}, \frac{1}{8}, \frac{3}{8}$	$\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$	$hkl: h, k = 2n + 1, l = 4n + 2$ $or h, k, l = 4n$
								$\frac{3}{8}, \frac{5}{8}, \frac{1}{8}$		
16	a	$\dots \bar{3}$	$0, 0, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$	$\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	$\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$	$hkl: h, k = 2n, h + k + l = 4n$
								$\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$		



Polyhedron centre at 0, 0, 0

Polyhedron centre at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ **Symmetry of special projections**Along $[001]$ $p4mm$ $\mathbf{a}' = \frac{1}{2}\mathbf{a}$ $\mathbf{b}' = \frac{1}{2}\mathbf{b}$ Origin at $\frac{1}{4}, 0, z$ Along $[111]$ $p6mm$ $\mathbf{a}' = \frac{1}{3}(2\mathbf{a} - \mathbf{b} - \mathbf{c})$ $\mathbf{b}' = \frac{1}{3}(-\mathbf{a} + 2\mathbf{b} - \mathbf{c})$ Origin at x, x, x Along $[110]$ $c2mm$ $\mathbf{a}' = \frac{1}{2}(-\mathbf{a} + \mathbf{b})$ $\mathbf{b}' = \frac{1}{2}\mathbf{c}$ Origin at $x, x + \frac{1}{4}, \frac{1}{8}$

3.1. CRYSTAL LATTICES

Table 3.1.2.3 (continued)

Delaunay–Voronoi type	Metric conditions	Selling tetrahedron	Projections along symmetry directions	Dirichlet domain in the unit cell			Transformation to the conventional cell
M5 V3 $m(AC)I$ $\frac{2}{m}$ v	$b^2 = r^2 - q^2$						$\begin{pmatrix} -1 & 0 & 1 \\ -1 & 1 & 0 \\ -2 & 0 & 0 \end{pmatrix}$ $\begin{pmatrix} 1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & -1 & -1 \end{pmatrix}$
				A: $b^2 = f^2 - a^2$ C: $b^2 = f^2 - c^2$ I: $b^2 = c^2 - a^2$			
M6 V4 mP $\frac{2}{m}$ s	—						$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
T1 V1 aP 1	—						$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
T2 V2 aP 1	$\mathbf{a} \cdot \mathbf{b} = 0$						$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
T3 V3 aP 1	$\mathbf{a} \cdot \mathbf{b} = 0$ $(\mathbf{a} + \mathbf{b} + \mathbf{c}) \cdot \mathbf{c} = 0$						$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

In some cases, different Selling patterns are given for one ‘Symmetrische Sorte’. This procedure avoids a final reduction step (cf. Patterson & Love, 1957) and simplifies the computational treatment significantly. The number of ‘Symmetrische Sorten’, and thus the number of transformations which have to be applied, is smaller than the number of lattice characters according to Niggli. Note that the introduction of reduced bases using shortest lattice vectors causes complications in more than three dimensions (cf. Schwarzenberger, 1980).

3.1.2.4. Example of Delaunay reduction and standardization of the basis

Let the basis $\mathbf{B} = (\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ given by the scalar products

$$\begin{pmatrix} g_{11} & g_{22} & g_{33} \\ g_{23} & g_{31} & g_{12} \end{pmatrix} = \begin{pmatrix} 6 & 8 & 8 \\ 4 & 2 & 3 \end{pmatrix}$$

or by $b_1 = 2.449 (\sqrt{6})$, $b_2 = b_3 = 2.828 (\sqrt{8})$ (in arbitrary units), β_{23}

$= 60^\circ$ ($\cos \beta_{23} = \frac{1}{2}$), $\beta_{13} = 73.22^\circ$ ($\cos \beta_{13} = \sqrt{3}/6$), $\beta_{12} = 64.34^\circ$ ($\cos \beta_{12} = \sqrt{3}/4$).

The aim is to find a standardized basis of shortest lattice vectors using Delaunay reduction. This example, given by B. Gruber (cf. Burzlaff & Zimmermann, 1985), shows the standardization problems remaining after the reduction.

The general reduction step can be described using Selling four flats. The corners are designated by the vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d} = -\mathbf{a} - \mathbf{b} - \mathbf{c}$. The edges are marked by the scalar products among these vectors. If positive scalar products can be found, choose the largest: $\mathbf{a} \cdot \mathbf{b}$ (indicated as \mathbf{ab} in Fig. 3.1.2.2a). The reduction transformation is: $\mathbf{a}_D = \mathbf{a}$, $\mathbf{b}_D = -\mathbf{b}$, $\mathbf{c}_D = \mathbf{c} + \mathbf{b}$, $\mathbf{d}_D = \mathbf{d} + \mathbf{b}$ (see Fig. 3.1.2.2a). In this example, this results in the Selling four flat shown in Fig. 3.1.2.2(b). The next step, shown in Fig. 3.1.2.2(c), uses the (maximal) positive scalar product for further reduction. Finally, using $\mathbf{b}_2 + \mathbf{b}_3 + \mathbf{b}_4 = -\mathbf{b}_1$ we get the result shown in Fig. 3.1.2.2(d).

The complete procedure can be expressed in a table, as shown in Table 3.1.2.4. Each pair of lines contains the starting basis and

3.2. POINT GROUPS AND CRYSTAL CLASSES

Table 3.2.3.2

The 32 three-dimensional crystallographic point groups

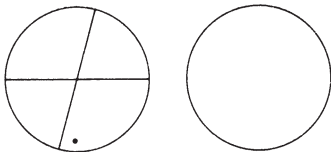
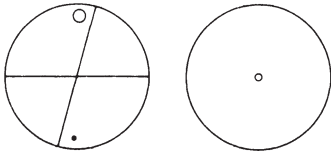
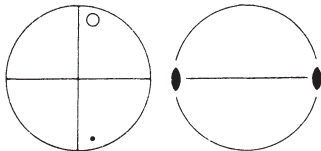
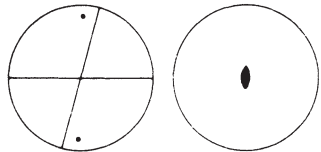
The point groups are listed in blocks according to crystal system and are specified by their short and (if different) full Hermann–Mauguin symbols and their Schoenflies symbols. For each point group, the stereographic projections show (on the left) the general position and (on the right) the symmetry elements.

The list of Wyckoff positions includes:

Columns 1 to 4: multiplicity, Wyckoff letter, oriented site-symmetry symbol, coordinate triplets;

Under the stereographic projections: face forms (in roman type) and point forms (in italics); if there is more than one entry, subsequent entries refer to limiting (noncharacteristic) forms;

Last column: Miller indices of equivalent faces [for trigonal and hexagonal groups, Bravais–Miller indices (*hkl*) are used if referred to hexagonal axes].

TRICLINIC SYSTEM					
1	C_1		Pedion or monohedron <i>Single point</i>	(hkl)	
1	<i>a</i>	1	x, y, z	Symmetry of special projections Along any direction 1	
$\bar{1}$	C_i		Pinacoid or parallelohedron <i>Line segment through origin</i> Point in origin	(hkl) $(\bar{h}\bar{k}\bar{l})$	
2	<i>a</i>	1	x, y, z $\bar{x}, \bar{y}, \bar{z}$	Symmetry of special projections Along any direction 2	
1	<i>o</i>	$\bar{1}$	$0, 0, 0$		
MONOCLINIC SYSTEM					
2	C_2		Sphenoid or dihedron <i>Line segment</i> Pinacoid or parallelohedron <i>Line segment through origin</i>	(hkl) $(\bar{h}\bar{k}l)$	
2	<i>b</i>	1	x, y, z \bar{x}, y, \bar{z}	Symmetry of special projections Along [100] Along [010] Along [001] <i>m</i> 2 <i>m</i>	$(h0l)$ $(\bar{h}0l)$
1	<i>a</i>	2	$0, y, 0$		(010) or $(0\bar{1}0)$
2	C_2		Sphenoid or dihedron <i>Line segment</i> Pinacoid or parallelohedron <i>Line segment through origin</i>	(hkl) $(\bar{h}\bar{k}l)$	
2	<i>b</i>	1	x, y, z \bar{x}, \bar{y}, z	Symmetry of special projections Along [100] Along [010] Along [001] <i>m</i> <i>m</i> 2	$(hk0)$ $(\bar{h}\bar{k}0)$
1	<i>a</i>	2	$0, 0, z$		(001) or $(00\bar{1})$

3.2.4. Molecular symmetry

BY U. MÜLLER

3.2.4.1. Introduction

In this section, by ‘molecule’ we mean a separate set of closely bonded atoms; this definition includes molecular ions. The term ‘molecule’ as used here also includes molecular aggregates held together by hydrogen bonds or other important molecular interactions. We consider only the symmetry of isolated molecules, *i.e.* we act as if the molecule had no surroundings or a completely isotropic surrounding (even if it is a molecular ion that in reality has nearby counter ions), and we do not consider any vibrational distortions. Of course, in crystals the surroundings are not isotropic; their anisotropy is reflected in the site symmetry of the molecule. The site symmetry of the molecule in the crystal may not be higher than the molecular symmetry, and, in most cases, it is lower, *i.e.* it is a subgroup of the point group of the isolated molecule. From experience we know that the actual deviation of the molecular symmetry in crystals as compared to the symmetry in an isotropic surrounding is usually unimportant; generally, only conformation angles are affected significantly.

According to the statistical data for organic molecules (molecules having C–C or C–H bonds), the point group 1 is the most frequent (70.9%), followed by $\bar{1}$ (8.1%), 2 (7.5%), m (6.5%), $2/m$ (2.1%) and $mm2$ (1.7%); all others are <1% (Pidcock *et al.*, 2003). In crystals, the site symmetry of organic molecules is 1 with a frequency of 80.7%, followed by $\bar{1}$ (~11%). Centrosymmetric molecules ($\bar{1}$ and higher centrosymmetric point groups) almost always crystallize in centrosymmetric space groups (99%) and lie on centrosymmetric sites ($\bar{1}$ and higher) with a frequency of 97% (Pidcock *et al.*, 2003; Müller, 1978).

Since all real molecules are objects of three-dimensional space, we consider only three-dimensional symmetry groups. This choice also applies to so-called ‘zero-’, ‘one-’ and ‘two-dimensional’ molecules; these misleading terms are sometimes used for, respectively, finite molecules, polymeric chain molecules and polymeric layer molecules. For chemists who use these terms, the ‘dimensionality’ mostly refers to the linkage by covalent bonds; for physicists, ‘dimensionality’ may refer to some other anisotropic property, *e.g.* conductivity.

3.2.4.2. Definitions

The set of all isometries that map a molecule onto itself is its *molecular symmetry*. Its symmetry operations form a group which is the *point group* \mathcal{P}_M of the molecule.

The group \mathcal{P}_M is finite if the molecule consists of a finite number of atoms and is mapped onto itself by a finite number of isometries. However, the group is infinite for linear molecules like HCl and CO₂, because of the infinite order of the molecular axis. For the symmetry of polymeric molecules see below (Section 3.2.4.4).

All symmetry operations of a finite molecule leave its centre of mass unchanged. If this point is chosen as the origin, all symmetry operations can be represented by 3×3 matrices \mathbf{W}_i , referred to some predefined coordinate system.

According to their equivalence, point groups are classified into *point-group types*. Two point groups \mathcal{P}_{M1} and \mathcal{P}_{M2} belong to the same *point-group type* if, after selection of appropriate coordinate systems, the matrix groups of \mathcal{P}_{M1} and \mathcal{P}_{M2} coincide. Why point groups and point-group types have to be distinguished is shown in the following example of metaldehyde; however, for

most molecules the distinction is usually of only minor importance.

In Section 1.1.7 a general definition is given for an *orbit* under the action of a group. Applied to molecules, we formulate this definition in the following way:

The set of points symmetry-equivalent to a point X of a molecule is the *orbit of X under \mathcal{P}_M* .

A point X in a molecule has a definite *site symmetry* \mathcal{S}_X (site-symmetry group). It consists of all those symmetry operations of the point group \mathcal{P}_M which leave the point fixed. The site-symmetry group \mathcal{S}_X is always a subgroup of the point group of the molecule: $\mathcal{S}_X \leq \mathcal{P}_M$.

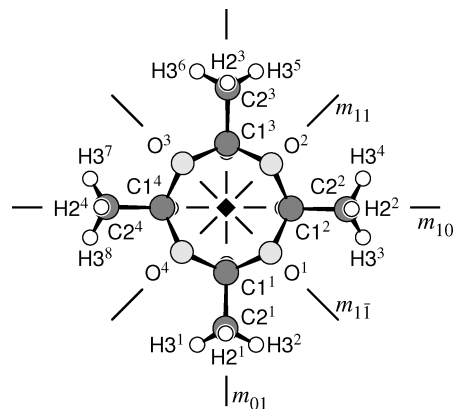
A point X is on a *general position* if its site symmetry \mathcal{S}_X consists of nothing more than the identity, $\mathcal{S}_X = \mathcal{I}$. Otherwise, if $\mathcal{S}_X > \mathcal{I}$, the point is on a *special position*.

The *multiplicity* of a point X in a molecule is equal to the number of points which are symmetry-equivalent to this point, *i.e.* the number of points in its orbit. If the point is on a general position, its multiplicity is equal to the group order $|\mathcal{P}_M|$. If $|\mathcal{S}_X|$ is the order of the site symmetry of a point on a special position, the multiplicity of X is $|\mathcal{P}_M|/|\mathcal{S}_X|$.

Two points X and Y of a molecule belong to the same *Wyckoff position* if the site-symmetry groups \mathcal{S}_X and \mathcal{S}_Y are conjugate subgroups of \mathcal{P}_M , *i.e.* if \mathcal{S}_X and \mathcal{S}_Y are symmetry-equivalent under a symmetry operation of \mathcal{P}_M ; expressed mathematically, this is $\mathcal{S}_Y = g\mathcal{S}_Xg^{-1}$ with $g \in \mathcal{P}_M$. The special case $\mathcal{S}_X = \mathcal{S}_Y$ is included.

Example

A molecule of metaldehyde [tetrameric acetaldehyde, 2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclooctane, (H₃CCHO)₄] has the point group $\mathcal{P}_M = 4mm$ (C_{4v}) of order $|\mathcal{P}_M| = 8$, consisting of the symmetry operations 1, 4^+ , 2 , 4^- , m_{10} , m_{01} , m_{11} and $m_{\bar{1}\bar{1}}$.



The atoms C1¹...C1⁴, the four H atoms bonded to them (not labelled in the figure and largely hidden), C2¹...C2⁴ and H2¹...H2⁴ make up four sets of symmetry-equivalent atoms and thus form four orbits. All these atoms are placed on the mirror planes m_{10} and m_{01} ; their site-symmetry groups are $\{1, m_{10}\}$ or $\{1, m_{01}\}$. $\{1, m_{10}\}$ and $\{1, m_{01}\}$ are conjugate subgroups of $4mm$ because they are equivalent by a fourfold rotation, *i.e.* $\{1, m_{01}\} = 4^+\{1, m_{10}\}4^-$. All of these atoms belong to *one* Wyckoff position, labelled $4c$ in Table 3.2.3.2. The symmetry-equivalent atoms O¹...O⁴ make up another orbit which belongs to a different Wyckoff position, labelled $4b$, with the conjugate site symmetries $\{1, m_{11}\}$ and $\{1, m_{\bar{1}\bar{1}}\}$. Although the site symmetries of both $4b$ and $4c$ consist of the identity and one reflection, they are not conjugate because there is no symmetry operation of $4mm$ that relates them. The subgroups $\{1, m_{10}\}$ and $\{1, m_{11}\}$ are different point groups of the same point-group type.

Table 3.4.1.1

Reference symbols of the 31 Weissenberg complexes with $f \geq 1$ degrees of freedom in \mathbb{E}^3

Weissenberg complex	f	Weissenberg complex	f
$P2_1/m e$	2	$I\bar{4}2d d$	1
$P2/c e$	1	$P4/nmm c$	1
$C2/c e$	1	$I4_1/acd e$	1
$P2_12_12_1 a$	3	$P3_2 a$	2
$Pmma e$	1	$P3_212 a$	1
$Pbcm d$	2	$P3_221 a$	1
$Pmnm a$	1	$P\bar{3}m1 d$	1
$Pnma c$	2	$P6_1 a$	2
$Cmcm c$	1	$P6_122 a$	1
$Cmme g$	1	$P6_122 b$	1
$Imma e$	1	$P2_13 a$	1
$P4_3 a$	2	$I2_13 a$	1
$P4_322 a$	1	$I2_13 b$	1
$P4_322 c$	1	$Ia\bar{3} d$	1
$P4_32_12 a$	1	$I\bar{4}3d c$	1
$I4_122 f$	1		

distance between any two symmetry-equivalent points belonging to $Pmma e$ cannot become shorter than the minimum of $\frac{1}{2}a$, b and c .

A lattice complex refers either to Wyckoff positions exclusively of the first or exclusively of the second kind. Most lattice complexes are related to Wyckoff positions of the first kind.

There exist, however, 67 lattice complexes without point configurations with infinitesimally short distances between symmetry-related points [cf. *Hauptgitter* (Weissenberg, 1925)]. These lattice complexes were called *Weissenberg complexes* by Fischer *et al.* (1973). The 36 invariant lattice complexes are trivial examples of Weissenberg complexes. The other 31 Weissenberg complexes with degrees of freedom (24 univariant, 6 bivariant, 1 trivariant) are compiled in Table 3.4.1.1. They have the following common property: each Weissenberg complex contains at least two invariant limiting complexes belonging to the same crystal family (see also Section 3.4.3.1.3).

Example

The Weissenberg complex $Pmma 2e \frac{1}{4}, 0, z$ is a comprehensive complex of $Pmmm a$ and of $Cmmm a$. Within the characteristic Wyckoff position, $\frac{1}{4}, 0, 0$ refers to $Pmmm a$ and $\frac{1}{4}, 0, \frac{1}{4}$ to $Cmmm a$.

Apart from the seven invariant plane lattice complexes, there exists only one further Weissenberg complex within the plane groups, namely the univariant rectangular complex $p2mg c$.

3.4.2. The concept of characteristic and non-characteristic orbits, comparison with the lattice-complex concept

3.4.2.1. Definitions

The generating space group of any crystallographic orbit may be compared with the eigensymmetry of its point configuration. If both groups coincide, the orbit is called a *characteristic crystallographic orbit*, otherwise it is named a *non-characteristic crystallographic orbit* (Wondratschek, 1976; Engel *et al.*, 1984; see also Section 1.1.7). If the eigensymmetry group contains additional translations in comparison with those of the generating space

group, the term *extraordinary orbit* is used (cf. also Matsumoto & Wondratschek, 1979). Each class of configuration-equivalent orbits contains exactly one characteristic crystallographic orbit.

The set of all point configurations in \mathbb{E}^3 can be divided into 402 equivalence classes by means of their eigensymmetry: two point configurations belong to the same *symmetry type of point configuration* if and only if their characteristic crystallographic orbits belong to the same type of Wyckoff set.

As each crystallographic orbit is uniquely related to a certain point configuration, each equivalence relationship on the set of all point configurations also implies an equivalence relationship on the set of all crystallographic orbits: two crystallographic orbits are assigned to the same *orbit type* (cf. also Engel *et al.*, 1984) if and only if the corresponding point configurations belong to the same symmetry type.

In contrast to lattice complexes, neither symmetry types of point configuration nor orbit types can be used to define equivalence relations on Wyckoff positions, Wyckoff sets or types of Wyckoff set. Two crystallographic orbits coming from the same Wyckoff position belong to different orbit types, if – owing to special coordinate values – they differ in the eigensymmetry of their point configurations. Furthermore, two crystallographic orbits with the same coordinate description, but stemming from different space groups of the same type, may belong to different orbit types because of a specialization of the metrical parameters.

Example

The eigensymmetry of orbits from Wyckoff position $P\bar{4}3m 4e x, x, x$ with $x = \frac{1}{4}$ or $x = \frac{3}{4}$ is enhanced to $Fm\bar{3}m 4a, b$ and hence they belong to a different orbit type to those with $x \neq \frac{1}{4}, \frac{3}{4}$.

Example

In general, an orbit belonging to the type of Wyckoff set $I4/m 2a, b$ corresponds to a point configuration with eigensymmetry $I4/mmm 2a, b$. If, however, the space group $I4/m$ has specialized metrical parameters, e.g. $c/a = 1$ or $c/a = 2^{1/2}$, then the eigensymmetry of the point configuration is enhanced to $Im\bar{3}m 2a$ or $Fm\bar{3}m 4a, b$, respectively.

3.4.2.2. Comparison of the concepts of lattice complexes and orbit types

It is the common intention of the lattice-complex and the orbit-type concepts to subdivide the point configurations and crystallographic orbits in \mathbb{E}^3 into subsets with certain common properties. With only a few exceptions, the two concepts result in different subsets. As similar but not identical symmetry considerations are used, each lattice complex is uniquely related to a certain symmetry type of point configuration and to a certain orbit type, and *vice versa*. Therefore, the two concepts result in the same number of subsets: there exist 402 lattice complexes and 402 symmetry types of point configuration and orbit types. The differences between the subsets are caused by the different properties of the point configurations and crystallographic orbits used for the classifications (cf. also Koch & Fischer, 1985).

The concept of orbit types is entirely based on the eigensymmetry of the particular point configurations: a crystallographic orbit is regarded as an isolated entity, *i.e.* detached from its Wyckoff position and its type of Wyckoff set. On the contrary, lattice complexes result from a hierarchy of classifications of crystallographic orbits into Wyckoff positions, Wyckoff sets, types of Wyckoff set and classes of configuration-equivalent types of

3.6. Magnetic subperiodic groups and magnetic space groups

D. B. LITVIN

3.6.1. Introduction

The *magnetic subperiodic groups* in the title refer to generalizations of the crystallographic subperiodic groups, *i.e.* frieze groups (two-dimensional groups with one-dimensional translations), crystallographic rod groups (three-dimensional groups with one-dimensional translations) and layer groups (three-dimensional groups with two-dimensional translations). There are seven frieze-group types, 75 rod-group types and 80 layer-group types, see *International Tables for Crystallography*, Volume E, *Subperiodic Groups* (2010; abbreviated as *IT E*). The magnetic *space groups* refer to generalizations of the one-, two- and three-dimensional crystallographic space groups, n -dimensional groups with n -dimensional translations. There are two one-dimensional space-group types, 17 two-dimensional space-group types and 230 three-dimensional space-group types, see Part 2 of the present volume (*IT A*).

Generalizations of the crystallographic groups began with the introduction of an operation of ‘change in colour’ and the ‘two-colour’ (black and white, antisymmetry) crystallographic point groups (Heesch, 1930; Shubnikov, 1945; Shubnikov *et al.*, 1964). Subperiodic groups and space groups were also extended into two-colour groups. Two-colour subperiodic groups consist of 31 two-colour frieze-group types (Belov, 1956*a,b*), 394 two-colour rod-group types (Shubnikov, 1959*a,b*; Neronova & Belov, 1961*a,b*; Galyarski & Zamorzaev, 1965*a,b*) and 528 two-colour layer-group types (Neronova & Belov, 1961*a,b*; Palistrant & Zamorzaev, 1964*a,b*). Of the two-colour space groups, there are seven two-colour one-dimensional space-group types (Neronova & Belov, 1961*a,b*), 80 two-colour two-dimensional space-group types (Heesch, 1929; Cochran, 1952) and 1651 two-colour three-dimensional space-group types (Zamorzaev, 1953, 1957*a,b*; Belov *et al.*, 1957). See also Zamorzaev (1976), Shubnikov & Koptsik (1974), Koptsik (1966, 1967), and Zamorzaev & Palistrant (1980). [Extensive listings of references on colour symmetry, magnetic symmetry and related topics can be found in the books by Shubnikov *et al.* (1964), Shubnikov & Koptsik (1974), and Opechowski (1986).]

The so-called *magnetic groups*, groups to describe the symmetry of spin arrangements, were introduced by Landau & Lifschitz (1951, 1957) by re-interpreting the operation of ‘change in colour’ in two-colour crystallographic groups as ‘time inversion’. This chapter introduces the structure, properties and symbols of *magnetic subperiodic groups* and *magnetic space groups* as given in the extensive tables by Litvin (2013), which are an extension of the classic tables of properties of the two- and three-dimensional subperiodic groups found in *IT E* and the one-, two- and three-dimensional space groups found in the present volume. A survey of magnetic group types is also presented in Litvin (2013), listing the elements of one representative group in each *reduced superfamily* of the two- and three-dimensional magnetic subperiodic groups and one-, two- and three-dimensional magnetic space groups. Two notations for magnetic groups, the Opechowski–Guccione notation (OG notation) (Guccione, 1963*a,b*; Opechowski & Guccione, 1965; Opechowski, 1986) and the Belov–Neronova–Smirnova notation

(BNS notation) (Belov *et al.*, 1957) are compared. The maximal subgroups of index ≤ 4 of the magnetic subperiodic groups and magnetic space groups are also given.

3.6.2. Survey of magnetic subperiodic groups and magnetic space groups

We review the concept of a reduced magnetic superfamily (Opechowski, 1986) to provide a classification scheme for magnetic groups. This is used to obtain the survey of the two- and three-dimensional magnetic subperiodic group types and the one-, two- and three-dimensional magnetic space groups given in Litvin (2013). In that survey a specification of a single representative group from each group type is provided.

3.6.2.1. Reduced magnetic superfamilies of magnetic groups

Let \mathcal{F} denote a crystallographic group. The magnetic superfamily of \mathcal{F} consists of the following set of groups:

- (1) The group \mathcal{F} .
- (2) The group $\mathcal{F}1' \equiv \mathcal{F} \times 1'$, the direct product of the group \mathcal{F} and the time-inversion group $1'$, the latter consisting of the identity 1 and time inversion $1'$.
- (3) All groups $\mathcal{F}(\mathcal{D}) \equiv \mathcal{D} \cup (\mathcal{F} - \mathcal{D})1' \equiv \mathcal{F} \times 1'$, subdirect products of the groups \mathcal{F} and $1'$. \mathcal{D} is a subgroup of index 2 of \mathcal{F} . Groups of this kind will also be denoted by \mathcal{M} .

The third subset is divided into two subdivisions:

- (3a) Groups \mathcal{M}_T , where \mathcal{D} is an equi-translational (*translationalengleiche*) subgroup of \mathcal{F} .
- (3b) Groups \mathcal{M}_R , where \mathcal{D} is an equi-class (*klassengleiche*) subgroup of \mathcal{F} .¹

Two magnetic groups $\mathcal{F}_1(\mathcal{D}_1)$ and $\mathcal{F}_2(\mathcal{D}_2)$ are called *equivalent* if there exists an affine transformation that maps \mathcal{F}_1 onto \mathcal{F}_2 and \mathcal{D}_1 onto \mathcal{D}_2 (Opechowski, 1986). If only non-equivalent groups $\mathcal{F}(\mathcal{D})$ are included, then the above set of groups is referred to as the reduced magnetic superfamily of \mathcal{F} .

Example

We consider the crystallographic point group $\mathcal{F} = 2_x 2_y 2_z$. The magnetic superfamily of the group $2_x 2_y 2_z$ consists of five groups: $\mathcal{F} = 2_x 2_y 2_z$, the group $\mathcal{F}1' = 2_x 2_y 2_z 1'$, and the three groups $\mathcal{F}(\mathcal{D}) = 2_x 2_y 2_z(2_x)$, $2_x 2_y 2_z(2_y)$ and $2_x 2_y 2_z(2_z)$. Since the latter three groups are all equivalent, the reduced magnetic superfamily of the group $\mathcal{F} = 2_x 2_y 2_z$ consists of only three groups: $2_x 2_y 2_z$, $2_x 2_y 2_z 1'$, and one of the three groups $2_x 2_y 2_z(2_x)$, $2_x 2_y 2_z(2_y)$ and $2_x 2_y 2_z(2_z)$.

Example

In the reduced magnetic space group superfamily of $\mathcal{F} = Pnn2$ there are five groups: $\mathcal{F} = Pnn2$, $\mathcal{F}1' = Pnn21'$, and three groups $\mathcal{F}(\mathcal{D}) = Pnn2(Pc)$, $Pnn2(P2)$ and $Pnn2(Fdd2)$. The

¹ Replacing time inversion $1'$ by an operation of ‘changing two colours’, the two-colour groups corresponding to the types 1, 2, 3a and 3b magnetic groups are known as type I, II, III and IV Shubnikov groups, respectively (Bradley & Cracknell, 1972).