# 1.1. Historical introduction

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### 1.1.1. The fundamental laws of crystallography

The documentation concerning group-theoretical aspects of group–subgroup relations and the rising importance of these relations in three-dimensional crystallography is scattered widely in the literature. This short review, therefore, cannot be exhaustive and may even be unbalanced if the authors have missed essential sources. Not included here is the progress made in the general theory of crystallographic groups, *e.g.* in higher dimensions, which is connected with the names of the mathematicians and physicists Ascher, Brown, Janner, Janssen, Neubüser, Plesken, Souvignier, Zassenhaus and others. This volume A1 of *International Tables for Crystallography*, abbreviated *IT* A1, is concerned with objects belonging to the 'classical' theory of crystallographic groups.

For a long time, the objective of crystallography, as implied by the word itself, was the description of crystals which were found in nature or which grew from solutions of salts or from melts. Crystals often display more-or-less planar faces which are symmetrically equivalent or can be made so by parallel shifting of the faces along their normals such that they form a regular body. The existence of characteristic angles between crystal faces was observed by Niels Stensen in 1669. The importance of the shape of crystals and their regularity was supported by observations on the cleavage of crystals. It was in particular this regularity which attracted mineralogists, chemists, physicists and eventually mathematicians, and led to the establishment of the laws by which this regularity was governed. The *law of symmetry* and the *law of rational indices* were formulated by René Just Haüy around 1800. These studies were restricted to the shape of macroscopic crystals and their physical properties, because only these were accessible to measurements until the beginning of the twentieth century.

Later in the nineteenth century, interest turned to 'regular systems' of points, for which the arrangement of points around every point is the same. These were studied by Wiener (1863) and Sohncke (1874). For such sets, there are isometric mappings of any point onto any other point which are such that they map the whole set onto itself. The primary aim was the classification and listing of such regular systems, while the groups of isometries behind these systems were of secondary importance. These regular systems were at first the sets of crystal faces, of face normals of crystal faces and of directions in crystals which are equivalent with respect to the physical properties or the symmetry of the external shape of the crystal. The listing and the classification of these finite sets was based on the *law of rational indices* and resulted in the derivation of the 32 crystal classes of point groups by Moritz Ludwig Frankenheim in 1826, Johann Friedrich Christian Hessel in 1830 and Axel V. Gadolin in 1867, cited by Burckhardt (1988). The list of this classification contained crystal classes that had not been observed in any crystal and included group–subgroup relations implicitly.

Crystal cleavage led Haüy in 1784 to assume small parallelepipeds as building blocks of crystals. In 1824, Ludwig August Seeber explained certain physical properties of crystals by placing molecules at the vertices of the parallelepipeds. The concepts of unit cell and of translation symmetry were thus introduced implicitly.

The classification of the 14 underlying lattices of translations was completed by Auguste Bravais (1850). In the second half of the nineteenth century, interest turned to the derivation and classification of *infinite* regular systems of points or figures, in particular by Leonhard Sohncke and Evgraf Stepanovich Fedorov. Sohncke (1879), Fedorov (1891), Arthur Schoenflies (1891) and later William Barlow (1894) turned to the investigation of the underlying groups, the *space groups* and *plane groups*. The derivation and classification of these groups were completed in the early 1890s. It was a plausible hypothesis that the structures of crystals were related to combinations of regular systems of atoms (Haag, 1887) and that the symmetry of a crystal structure should be a space group, but both conjectures were speculations at that time with no experimental proof. This also applies to the atom packings described by Sohncke and Barlow, such as a model of the NaCl structure (which they did not assign to any substance).

### 1.1.2. Symmetry and crystal-structure determination

In 1895, Wilhelm Röntgen, then at the University of Würzburg, discovered what he called X-rays. Medical applications emerged the following year, but it was 17 years later that Max von Laue suggested at a scientific discussion in Munich that a crystal should be able to act as a diffraction grating for X-rays. Two young physicists, Walther Friedrich and Paul Knipping, successfully performed the experiment in May 1912 with a crystal of copper sulfate. In von Laue's opinion, the experiment was so important that he later publicly donated one third of his 1914 Nobel prize to Friedrich and Knipping. The discovery immediately aroused the curiosity of father William Henry Bragg and son William Lawrence Bragg. The son's experiments in Cambridge, initially with NaCl and KCl, led to the development of the Bragg equation and to the first crystal-structure determinations of diamond and simple inorganic materials. Since then, the determination of crystal structures has been an ever-growing enterprise.

The diffraction of X-rays by crystals is partly determined by the space group and partly by the relative arrangement of the atoms, *i.e.* by the atomic coordinates and the lattice parameters. The presentations by Fedorov and Schoenflies of the 230 space groups were not yet appropriate for use in structure determinations with X-rays. The breakthrough came with the fundamental book of Paul Niggli (1919), who described the space groups geometrically by symmetry elements and point positions and provided the first tables of what are now called *Wyckoff positions*. Niggli emphasized the importance of the multiplicity and site symmetry of the positions and demonstrated with examples the meaning of the *reflection conditions*.

Niggli's book pointed the way. The publication of related tables by Ralph W. G. Wyckoff (1922) included diagrams of the unit cells with special positions and symmetry elements. Additional tables by Astbury & Yardley (1924) listed 'abnormal

spacings' for the space groups, *i.e.* the reflection conditions. These tables made the concepts and the data of geometric crystallography widely available and were the basis for the series *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) (abbreviated as *IT* 35), *International Tables for X-ray Crystallography*, Vol. I (1952, 1965, 1969) (abbreviated as *IT* 52) and *International Tables for Crystallography*, Vol. A (1983 and subsequent editions 1987, 1992, 1995, 2002, 2005) (abbreviated as *IT* A).

Group–subgroup relations were used in the original derivation of the space groups and plane groups. However, in the first decades of crystal-structure determinations, the derivation of geometric data (atomic coordinates) was of prime importance and the group-theoretical information in the publications was small, although implicitly present. With the growing number of crystal structures determined, however, it became essential to understand the rules and laws of crystal chemistry, to classify the incomprehensible set of structures into crystal-structure types, to develop methods for ordering the structure types in a systematic way, to show relations among them and to find common underlying principles.

To this end, different approaches were presented over time. By 1926, the number of crystal structures was already large enough for Viktor Moritz Goldschmidt to formulate basic principles of packing of atoms and ions in inorganic solids (Goldschmidt, 1926). Shortly afterwards, Linus Pauling (1928, 1929) formulated his famous rules about ionic radii, valence bonds, coordination polyhedra and the joining of these polyhedra. Later, Wilhelm Biltz (1934) focused attention on the volume requirements of atoms. Many other important factors determining crystal structures, such as chemical bonding, molecular shape, valence-electron concentration, electronic band structures, crystal-orbital overlap populations and others, have been the subject of subsequent studies. Each one of these aspects can serve as an ordering principle in crystal chemistry, giving insights from a different point of view.

For the aspects mentioned above, symmetry considerations are only secondary tools or even unimportant, and group–subgroup relations hardly play a role. Although symmetry is indispensable for the description of a specific crystal structure, for a long time crystal symmetry and the group–subgroup relations involved did not attract much attention as possible tools for working out the relations between crystal structures. This has even been the case for most textbooks on solid-state chemistry and physics. The lack of symmetry considerations is almost a characteristic feature of many of these books. There is a reason for this astonishing fact: the necessary group-theoretical material only became available in a useful form in 1965, namely as a listing of the maximal subgroups of all space groups by Neubüser & Wondratschek. However, for another 18 years this material was only distributed among interested scientists before it was finally included in the 1983 edition of *IT* A. And yet, even in the printing of 2005, the listing of the subgroups in Volume A is incomplete. It is this present Volume A1 which contains the complete listing.

### 1.1.3. Development of the theory of group–subgroup relations

The systematic survey of group–subgroup relations of space groups started with the fundamental publication by Carl Hermann (1929). This paper is the last in a series of four publications, dealing with

(I) a nomenclature of the space-group types, a predecessor of the Hermann–Mauguin nomenclature;

(II) a method for the derivation of the 230 space-group types which is related to the nomenclature in (I);

(III) the derivation of the 75 types of rod groups and the 80 types of layer groups; and

(IV) the subgroups of space groups.

In paper (IV), Hermann introduced two distinct kinds of subgroups. The *translationengleiche* subgroups of a space group $\mathcal{G}$ have retained all translations of $\mathcal{G}$ but belong to a crystal class of lower symmetry than the crystal class of $\mathcal{G}$ (Hermann used the term *zellengleiche* instead of *translationengleiche*, see footnote 10 in Section 1.2.6). The *klassengleiche* subgroups are those which belong to the same crystal class as $\mathcal{G}$, but have lost translations compared with $\mathcal{G}$. General subgroups are those which have lost translations as well as crystal-class symmetry. Hermann proved the theorem, later called *Hermann's theorem*, that any general subgroup is a *klassengleiche* subgroup of a uniquely determined *translationengleiche* subgroup $\mathcal{M}$ of $\mathcal{G}$. In particular, this implies that a *maximal* subgroup of $\mathcal{G}$ is either a *translationengleiche* subgroup or a *klassengleiche* subgroup of $\mathcal{G}$.

Because of the strong relation (*homomorphism*) between a space group $\mathcal{G}$ and its point group $\mathcal{P}_{\mathcal{G}}$, the set of *translationengleiche* subgroups of $\mathcal{G}$ is in a one-to-one correspondence with the set of subgroups of the point group $\mathcal{P}_{\mathcal{G}}$. The crystallographic point groups are groups of maximal order 48 with well known group–subgroup relations and with not more than 96 subgroups. Thus, the maximal *translationengleiche* subgroups of any space group $\mathcal{G}$ can be obtained easily by comparison with the subgroups of its point group $\mathcal{P}_{\mathcal{G}}$. The kind of derivation of the space-group types by H. Heesch (1930) also gives access to *translationengleiche* subgroups. In *IT* 35, the types of the *translationengleiche* subgroups were listed for each space group [for a list of corrections to these data, see Ascher *et al.* (1969)]. A graph of the group–subgroup relations between the crystallographic point groups can also be found in *IT* 35; the corresponding graphs for the space groups were published by Ascher (1968). In these lists and graphs the subgroups are given only by their types, not individually.

The group–subgroup relations between the space groups were first applied in Volume 1 of *Strukturbericht* (1931). In this volume, a crystal structure is described by the coordinates of the atoms, but the space-group symmetry is stated not only for spherical particles but also for molecules or ions with lower symmetry. Such particles may reduce the site symmetry and with it the space-group symmetry to that of a subgroup. In addition, the symmetry reduction that occurs if the particles are combined into larger structural units is stated. The listing of these detailed data was discontinued both in the later volumes of *Strukturbericht* and in the series *Structure Reports*. Meanwhile, experience had shown that there is no point in assuming a lower symmetry of the crystal structure if the geometrical arrangement of the centres of the particles does not indicate it.

With time, not only the classification of the crystal structures but also a growing number of investigations of (continuous) phase transitions increased the demand for data on subgroups of space groups. Therefore, when the Executive Committee of the International Union of Crystallography decided to publish a new series of *International Tables for Crystallography*, an extension of the subgroup data was planned. Stimulated and strongly supported by the mathematician J. Neubüser, the systematic derivation of the subgroups of the plane groups and the space groups

**references**