International Tables for Crystallography (2006). Vol. A1, Section 1.1.3, pp. 3–4.

1965, 1969) (abbreviated as *IT* 52) and *International Tables for Crystallography*, Vol. A (1983 and subsequent editions 1987, 1992, 1995, 2002) (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 2002 edition, the listing of the subgroups in Volume A is incomplete. It is this present Volume A1 which now 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 the footnote on page 17). 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 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 Vol. 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 began. The listing was restricted to the maximal subgroups of each space group, because any subgroup of a space group can be obtained by a chain of maximal subgroups.

The derivation by Neubüser & Wondratschek started in 1965 with the *translationengleiche* subgroups of the space groups, because the complete set of these (maximally 96) subgroups could be calculated by computer. All *klassengleiche* subgroups of indices 2, 3, 4, 6, 8 and 9 were also obtained by computer. As the index of a maximal non-isomorphic subgroup of a space group is restricted to 2, 3 or 4, *all* maximal non-isomorphic subgroups of all space groups were contained in the computer outputs. First results and their application to relations between crystal structures are found in Neubüser & Wondratschek (1966). In the early tables, the subgroups were only listed by their types. For *International Tables*, an extended list of maximal non-isomorphic subgroups was prepared. For each space group the maximal *translationengleiche* subgroups and those maximal *klassengleiche* subgroups for which the reduction of the translations could be described as 'loss of centring translations' of a centred lattice are listed individually. For the other maximal *klassengleiche* subgroups, *i.e.* those for which the conventional unit cell of the subgroup is larger than that of the original space group, the description by type was retained, because the individual subgroups of this kind were not completely known in 1983. The deficiency of such a description becomes clear if one realizes that a listed subgroup type may represent 1, 2, 3, 4 or even 8 individual subgroups.

In the present Volume A1, *all* maximal non-isomorphic subgroups are listed individually, in Chapter 2.2 for the plane groups and in Chapters 2.3 and 3.2 for the space groups. In addition, graphs for the *translationengleiche* subgroups (Chapter 2.4) and for the *klassengleiche* subgroups (Chapter 2.5) supplement the tables. After several rounds of checking by hand and after comparison with other listings, *e.g.* those by H. Zimmermann (unpublished) or by Neubüser and Eick (unpublished), intensive computer checking of the hand-typed data was carried out by F. Gähler as described in Chapter 1.4.

The mathematician G. Nebe describes general viewpoints and new results in the theory of subgroups of space groups in Chapter 1.5.

The maximal *isomorphic* subgroups are a special subset of the maximal *klassengleiche* subgroups. Maximal isomorphic subgroups are treated separately because each space group $\mathcal{G}$ has an infinite number of maximal isomorphic subgroups and, in contrast to non-isomorphic subgroups, there is no limit for the index of a maximal isomorphic subgroup of $\mathcal{G}$.

An *isomorphic subgroup* of a space group seems to have first been described in a crystal–chemical relation when the crystal structure of Sb_2ZnO_6 (structure type of tapiolite, Ta_2FeO_6) was determined by Byström *et al.* (1941): 'If no distinction is drawn between zinc and antimony, this structure appears as three cassiterite-like units stacked end-on-end' (Wyckoff, 1965). The space group of Sb_2ZnO_6 is a maximal isomorphic subgroup of index 3 with $\mathbf{c}' = 3\mathbf{c}$ of the space group $P4_2/mnm$ (D_{4h}^{14}, No. 136) of cassiterite SnO_2 (rutile type).

The first systematic study attempting to enumerate all isomorphic subgroups (not just maximal ones) for each space-group type was by Billiet (1973). However, the listing was incomplete and, moreover, in the case of enantiomorphic pairs of space-group types, only those with the same space-group symbol (called *isosymbolic space groups*) were taken into account.

Sayari (1976) derived the conventional bases for all maximal isomorphic subgroups of all plane groups. The general laws of number theory which underlie these results for plane-group types $p4$, $p3$ and $p6$ and space-group types derived from point groups 4, $\overline{4}$, $4/m$, 3, $\overline{3}$, 6, $\overline{6}$ and $6/m$ were published by Müller & Brelle (1995). Bertaut & Billiet (1979) suggested a new analytical approach for the derivation of all isomorphic subgroups of space and plane groups.

Because of the infinite number of maximal isomorphic subgroups, only a few representatives of lowest index are listed in *IT* A with their lattice relations but without origin specification, *cf.* *IT* A (2002), Section 2.2.15.2. Part 13 of *IT* A (Billiet & Bertaut, 2002) is fully devoted to isomorphic subgroups, *cf.* also Billiet (1980) and Billiet & Sayari (1984).

In this volume, all maximal isomorphic subgroups are listed as members of infinite series, where each individual subgroup is specified by its index, its generators and the coordinates of its conventional origin as parameters.

The relations between a space group and its subgroups become more transparent if they are considered in connection with their normalizers in the affine group $\mathcal{A}$ and the Euclidean group $\mathcal{E}$ (Koch, 1984). Even the corresponding normalizers of Hermann's group $\mathcal{M}$ play a role in these relations, *cf.* Wondratschek & Aroyo (2001).

In addition to subgroup data, supergroup data are listed in *IT* A. If $\mathcal{H}$ is a maximal subgroup of $\mathcal{G}$, then $\mathcal{G}$ is a minimal supergroup of $\mathcal{H}$. In *IT* A, the type of a space group $\mathcal{G}$ is listed as a minimal non-isomorphic supergroup of $\mathcal{H}$ if $\mathcal{H}$ is listed as a maximal non-isomorphic subgroup of $\mathcal{G}$. Thus, for each space group $\mathcal{H}$ one can find in the tables the types of those groups $\mathcal{G}$ for which $\mathcal{H}$ is listed as a maximal subgroup. The supergroup data of *IT* A1 are similarly only an inversion of the subgroup data.

1.1.4. Applications of group–subgroup relations

Phase transitions. In 1937, Landau introduced the idea of the *order parameter* for the description of *second-order phase transitions* (Landau, 1937). Landau theory has turned out to be very useful in the understanding of phase transitions and related phenomena. Such a transition can only occur if there is a group–subgroup relation between the space groups of the two crystal structures. Often only the space group of one phase is known (usually the high-temperature phase) and subgroup relations help to eliminate many groups as candidates for the unknown space group of the other phase. Landau & Lifshitz (1980) examined the importance of group–subgroup relations further and formulated two theorems regarding the index of the group–subgroup pair. The significance of the subgroup data in second-order phase transitions was also pointed out by Ascher (1966, 1967), who formulated the *maximal-subgroup rule*: 'The symmetry group of a phase that arises in a ferroelectric transition is a maximal polar subgroup of the group of the high-temperature phase.' There are analogous applications of the maximal-subgroup rule (with appropriate modifications) to other types of continuous transitions.

The group-theoretical aspects of Landau theory have been worked out in great detail with major contributions by Birman (1966*a*,*b*), Cracknell (1975), Stokes & Hatch (1988), Tolédano & Tolédano (1987) and many others. For example, Landau theory gives additional criteria based on thermodynamic arguments for second-order phase transitions. The general statements are reformulated into group-theoretical rules which permit a phase-transition analysis without the tedious algebraic treatment involving high-order polynomials. The necessity of having complete subgroup data for the space groups for the successful implementation of these rules was stated by Deonarine & Birman (1983): '... there is a need for tables yielding for each of the 230 three-dimensional space groups a complete lattice of decomposition of all its subgroups.' Domain-structure analysis (Janovec & Přívratská, 2003) and symmetry-mode analysis (Aroyo & Perez-Mato, 1998) are further aspects of phase-transition problems where group–subgroup relations between space groups play an essential role. Domain structures are also considered in Section 1.2.7.

In treating successive phase transitions within Landau theory, Levanyuk & Sannikov (1971) introduced the idea of a hypothetical parent phase whose symmetry group is a supergroup of the observed (initial) space group. Moreover, the detection

references