International Tables for Crystallography (2011). Vol. A1, Chapter 1.7, pp. 57–69.

1.7. The Bilbao Crystallographic Server

By Mois I. Aroyo, J. Manuel Perez-Mato, Cesar Capillas and Hans Wondratschek

1.7.1. Introduction

The Bilbao Crystallographic Server, http://www.cryst.ehu.es, is a web site of crystallographic databases and programs. It can be used free of charge from any computer with a web browser *via* the Internet.

The server is built on a core of databases and contains different shells. The set of databases includes data from the 5th edition of *International Tables for Crystallography* Volume A, *Space-Group Symmetry* (2005) (hereafter referred to as *IT* A) and the data for maximal subgroups of space groups as listed in Part 2 of this volume (hereafter referred to as *IT* A1). Access is also provided to the crystallographic data for the subperiodic layer and rod groups [*International Tables for Crystallography*, Volume E, *Subperiodic Groups* (2002)] and their maximal subgroups. A database on incommensurate structures incorporating modulated structures and composites, and a **k**-vector database with Brillouin-zone figures and classification tables of the wavevectors for space groups are also available.

Communication with the databases is achieved by simple retrieval tools. They allow access to the information on space groups or subperiodic groups in different types of formats: HTML, text ASCII or XML. The next shell includes programs related to group–subgroup relations of space groups. These programs use the retrieval tools for accessing the necessary space-group information and apply group-theoretical algorithms in order to obtain specific results which are not available in the databases. There follows a shell with programs on representation theory of space groups and point groups and further useful symmetry information. Parallel to the crystallographic software, a shell with programs facilitating the study of specific problems related to solid-state physics, structural chemistry and crystallography has also been developed.

The server has been operating since 1998, and new programs and applications are being added (Kroumova, Perez-Mato, Aroyo *et al.*, 1998; Aroyo, Perez-Mato *et al.*, 2006; Aroyo, Kirov *et al.*, 2006). The aim of the present chapter is to report on the different databases and programs of the server related to the subject of this volume. Parts of these databases and programs have already been described in Aroyo, Perez-Mato *et al.* (2006), and here we follow closely that presentation. The chapter is completed by the description of the new developments up to 2007.

The relevant databases and retrieval tools that access the stored symmetry information are presented in Section 1.7.2. The discussion of the accompanying applications is focused on the crystallographic computing programs related to group–subgroup and group–supergroup relations between space groups (Section 1.7.3). The program for the analysis of the relations of the Wyckoff positions for a group–subgroup pair of space groups is presented in Section 1.7.4. The underlying group-theoretical background of the programs is briefly explained and details of the necessary input data and the output are given. The use of the programs is demonstrated by illustrative examples.

1.7.2. Databases and retrieval tools

The databases form the core of the Bilbao Crystallographic Server and the information stored in them is used by all computer programs available on the server. The following description is restricted to the databases related to the symmetry relations between space groups; these are the databases that include space-group data from *IT* A and subgroup data from *IT* A1.

1.7.2.1. Space-group data

The programs and databases of the Bilbao Crystallographic Server use specific settings of space groups (hereafter referred to as *standard* or *default* settings) that coincide with the conventional space-group descriptions found in *IT* A. For space groups with more than one description in *IT* A, the following settings are chosen as standard: unique axis *b* setting, cell choice 1 for monoclinic groups; hexagonal axes setting for rhombohedral groups; and origin choice 2 (origin at $\overline{1}$) for the centrosymmetric groups listed with respect to two origins in *IT* A.

The space-group database includes the following symmetry information:

(i) The generators and the representatives of the general position of each space group specified by its *IT* A number and Hermann–Mauguin symbol;
(ii) The special Wyckoff positions including the Wyckoff letter, Wyckoff multiplicity, the site-symmetry group and the set of coset representatives, as given in *IT* A;
(iii) The reflection conditions including the general and special conditions;
(iv) The affine and Euclidean normalizers of the space groups (*cf. IT* A, Part 15). They are described by sets of additional symmetry operations that generate the normalizers successively from the space groups. The database includes the additional generators of the Euclidean normalizers for the general-cell metrics as listed in Tables 15.2.1.3 and 15.2.1.4 of *IT* A. These Euclidean normalizers are also affine normalizers for all cubic, hexagonal, trigonal, tetragonal and part of the orthorhombic space-group types. For the rest of the orthorhombic space groups, the type of the affine normalizer coincides with the highest-symmetry Euclidean normalizer of that space group and the corresponding additional generators form part of the database (*cf.* Table 15.2.1.3 of *IT* A). The affine normalizers of triclinic and monoclinic groups are not isomorphic to groups of motions and they are not included in the normalizer database of the Bilbao Crystallographic Server.
(v) The assignment of Wyckoff positions to Wyckoff sets as found in Table 14.2.3.2 of *IT* A.

The data from the databases can be accessed using the simple retrieval tools, which use as input the number of the space group (*IT* A numbers). It is also possible to select the group from a table of *IT* A numbers and Hermann–Mauguin symbols. The output of the program *GENPOS* contains a list of the generators or the general positions and provides the possibility to obtain the same data in different settings either by specifying the transformation

matrix to the new basis or selecting one of the 530 settings listed in Table 4.3.2.1 of *IT* A. A list of the Wyckoff positions for a given space group in different settings can be obtained using the program *WYCKPOS*. The Wyckoff-position representatives for the nonstandard settings of the space groups are specified by the transformed coordinates of the representatives of the corresponding default settings. The assignments of the Wyckoff positions to Wyckoff sets are retrieved by the program *WYCKSETS*. This program also lists a set of coset representatives of the decompositions of the normalizers with respect to the space groups and the transformation of the Wyckoff positions under the action of these coset representatives. The programs *NORMALIZER* and *HKLCOND* give access to the data for normalizers and reflection conditions.

1.7.2.2. Database on maximal subgroups

1.7.2.2.1. Maximal subgroups of indices 2, 3 and 4 of the space groups

All maximal non-isomorphic subgroups and maximal isomorphic subgroups of indices 2, 3 and 4 of each space group can be retrieved from the database using the program *MAXSUB*. Each subgroup $\mathcal{H}$ is specified by its *IT* A number, the index in the group $\mathcal{G}$ and the transformation matrix–column pair $(\boldsymbol{P}, \boldsymbol{p})$ that relates the bases of $\mathcal{H}$ and $\mathcal{G}$:

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}')_{\mathcal{H}} = (\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{G}}\boldsymbol{P}. \qquad (1.7.2.1)$$

The column $\boldsymbol{p} = (p_1, p_2, p_3)$ of coordinates of the origin $O_{\mathcal{H}}$ of $\mathcal{H}$ is referred to the coordinate system of $\mathcal{G}$.

It is important to note that, in contrast to the data listed in *IT* A1, the matrix–column pairs $(\boldsymbol{P}, \boldsymbol{p})$ used by the programs of the server transform the *standard* basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{G}}$ of $\mathcal{G}$ to the *standard* basis of $\mathcal{H}$ (see Section 2.1.2.5 for the special rules for the settings of the subgroups used in *IT* A1). The different maximal subgroups are distributed in classes of conjugate subgroups. For certain applications it is necessary to represent the subgroups $\mathcal{H}$ as subsets of the elements of $\mathcal{G}$. This is achieved by an option in *MAXSUB* which transforms the general-position representatives of $\mathcal{H}$ by the corresponding matrix–column pair $(\boldsymbol{P}, \boldsymbol{p})^{-1}$ to the coordinate system of $\mathcal{G}$. In addition, one can obtain the splittings of all Wyckoff positions of $\mathcal{G}$ to those of $\mathcal{H}$.

1.7.2.2.2. Maximal isomorphic subgroups

Maximal subgroups of index higher than 4 have indices p, p^2 or p^3, where p is a prime. They are isomorphic subgroups and are infinite in number. In *IT* A1, the isomorphic subgroups are listed as members of series under the heading 'Series of maximal isomorphic subgroups'. In addition, the isomorphic subgroups of indices 2, 3 and 4 are listed individually. The program *SERIES* provides access to the database of maximal isomorphic subgroups on the Bilbao Crystallographic Server. Apart from the parametric *IT* A1 descriptions of the series, its output provides the individual listings of all maximal isomorphic subgroups of indices as high as 27 for all space groups, except for the cubic ones where the maximum index is 125. The format and content of the subgroup data are similar to those of the *MAXSUB* access tool. In addition, there is a special tool (under 'define a maximal index' on the *SERIES* web form) that permits the online generation of maximal isomorphic subgroups of any index up to 131 for all space groups. [Note that these data are only generated online and do not form part of the (static) database of isomorphic subgroups.]

1.7.3. Group–subgroup and group–supergroup relations between space groups

1.7.3.1. Subgroups of space groups

If two space groups $\mathcal{G}$ and $\mathcal{H}$ form a group–subgroup pair $\mathcal{G} > \mathcal{H}$, it is always possible to represent their relation by a chain of intermediate maximal subgroups $\mathcal{Z}_k$: $\mathcal{G} > \mathcal{Z}_1 > \ldots > \mathcal{Z}_n = \mathcal{H}$. For a specified index of $\mathcal{H}$ in $\mathcal{G}$ there are, in general, a number of possible chains relating both groups, and a number of different subgroups $\mathcal{H}_j < \mathcal{G}$ isomorphic to $\mathcal{H}$. We have developed two basic tools for the analysis of the group–subgroup relations between space groups: *SUBGROUPGRAPH* (Ivantchev *et al.*, 2000) and *HERMANN* (Capillas, 2006). Given the space-group types $\mathcal{G}$ and $\mathcal{H}$ and an index $[i]$, both programs determine all different subgroups $\mathcal{H}_j$ of $\mathcal{G}$ with the given index and their distribution into classes of conjugate subgroups with respect to $\mathcal{G}$. Owing to its importance in a number of group–subgroup problems, the program *COSETS* is included as an independent application. It performs the decomposition of a space group in cosets with respect to one of its subgroups. Apart from these basic tools, there are two complementary programs which are useful in specific crystallographic problems that involve group–subgroup relations between space groups. The program *CELLSUB* calculates the subgroups of a space group for a given multiple of the unit cell. The common subgroups of two or three space groups are calculated by the program *COMMONSUBS*.

1.7.3.1.1. The program SUBGROUPGRAPH

This program is based on the data for the maximal subgroups of index 2, 3 and 4 of the space groups of *IT* A1. These data are transformed into a graph with 230 nodes corresponding to the 230 space-group types. If two nodes in the graph are connected by an edge, the corresponding space groups form a group–maximal subgroup pair. Each one of these pairs is characterized by a group–subgroup index. The different maximal subgroups of the same space-group type are distinguished by corresponding matrix–column pairs $(\boldsymbol{P}, \boldsymbol{p})$ which give the relations between the standard coordinate systems of the group and the subgroup. The index and the set of transformation matrices are considered as attributes of the edge connecting the group with the subgroup.

The specification of the group–subgroup pair $\mathcal{G} > \mathcal{H}$ leads to a reduction of the total graph to a subgraph with $\mathcal{G}$ as the top node and $\mathcal{H}$ as the bottom node, see Example 1.7.3.1.1 at the end of this section. In addition, the $\mathcal{G} > \mathcal{H}$ subgraph, referred to as the *general* $\mathcal{G} > \mathcal{H}$ graph, contains all possible groups $\mathcal{Z}_k$ which appear as intermediate maximal subgroups between $\mathcal{G}$ and $\mathcal{H}$. It is important to note that in the general $\mathcal{G} > \mathcal{H}$ graphs the space-group symbols indicate space-group types, *i.e.* all space groups belonging to the same space-group type are represented by one node on the graph. Such graphs are called *contracted*. The contracted graphs have to be distinguished from the *complete* graphs where all space groups occurring in a group–subgroup graph are indicated by different space-group nodes.

The number of the nodes in the general $\mathcal{G} > \mathcal{H}$ graph may be further reduced if the index of $\mathcal{H}$ in $\mathcal{G}$ is specified. The subgraph obtained is again of the contracted type.

The comparison of complete graphs and contracted graphs shows that the use of contracted graphs for the analysis of specific group–subgroup relations $\mathcal{G} > \mathcal{H}_j$ can be very misleading (see Example 1.7.3.1.1, Fig. 1.7.3.2 and Fig. 1.7.3.3). The complete graphs produced by *SUBGROUPGRAPH* are equal for subgroups of a conjugacy class; the different orientations and/

or origin shifts of the conjugate subgroups $\mathcal{H}_s$ are manifested by the different transformation matrices $(\boldsymbol{P}, \boldsymbol{p})_s$ listed by the program.

Different chains of maximal subgroups for the group–subgroup pair $\mathcal{G} > \mathcal{H}$ are obtained following the possible paths connecting the top of the graph (the group $\mathcal{G}$) with the bottom (the group $\mathcal{H}$). Each group–maximal subgroup pair determines one step of this chain. The index of $\mathcal{H}$ in $\mathcal{G}$ equals the product of the indices for each one of the intermediate edges. The transformation matrices relating the standard bases of $\mathcal{G}$ and $\mathcal{H}$ are obtained by multiplying the matrices of each step of the chain. Thus, for each pair of group–subgroup types with a given index there is a set of transformation matrices $(\boldsymbol{P}, \boldsymbol{p})_j$, where each matrix corresponds to a subgroup $\mathcal{H}_j$ isomorphic to $\mathcal{H}$. Some of these subgroups could coincide. To find the different $\mathcal{H}_j$ of $\mathcal{G}$, the program transforms the elements of the subgroup $\mathcal{H}$ to the basis of the group $\mathcal{G}$ using the different matrices $(\boldsymbol{P}, \boldsymbol{p})_j$ and compares the elements of the subgroups $\mathcal{H}_j$ in the basis of $\mathcal{G}$. Two subgroups that are characterized by different transformation matrices are considered identical if their elements, transformed to the basis of the group $\mathcal{G}$, coincide.

The different subgroups $\mathcal{H}_j$ are distributed into classes of conjugate subgroups with respect to $\mathcal{G}$ by checking directly their conjugation relations with elements of $\mathcal{G}$.

Input to *SUBGROUPGRAPH*:

(i) As input, the program needs the specification of the space groups $\mathcal{G}$ and $\mathcal{H}$. The groups $\mathcal{G}$ and $\mathcal{H}$ can be defined either by their sequential *IT* A numbers or by their Hermann–Mauguin symbols. The default settings of all space groups are used.

(ii) If the index of $\mathcal{H}$ in $\mathcal{G}$ is specified, then the program determines the chains of maximal subgroups relating these groups and classifies the isomorphic subgroups $\mathcal{H}_j$ into classes of conjugate subgroups.

Output of *SUBGROUPGRAPH*:

The output is illustrated by Example 1.7.3.1.1.

(i) Group–subgroup pairs with non-specified indices.

When the index of the subgroup $\mathcal{H}$ in $\mathcal{G}$ is not specified, the program returns a list of the possible intermediate space groups $\mathcal{Z}_k$ relating $\mathcal{G}$ and $\mathcal{H}$. The list is given as a table whose rows correspond to the intermediate space groups $\mathcal{Z}_k$, specified by their Hermann–Mauguin symbols. In addition, the table contains the maximal subgroups of $\mathcal{Z}_k$, specified by their *IT* A numbers and the corresponding indices given in brackets.

This list is also represented as a contracted graph. Each space-group type in the list corresponds to one node in the graph, and the maximal subgroups are the neighbours (successors) of this node. Group–subgroup relations occurring in both directions are represented by nodes connected by two edges with opposite arrows. Maximal isomorphic subgroups are shown by loop edges (nodes connected to themselves), see Fig. 1.7.3.1.

(ii) Group–subgroup pairs with specified indices. As an example, see Table 1.7.3.1 and Figs. 1.7.3.2 and 1.7.3.3.

(*a*) Chains of maximal subgroups.

If the index of the subgroup $\mathcal{H}$ in the group $\mathcal{G}$ is specified, the program returns a list of all possible chains of maximal subgroups relating $\mathcal{G}$ and $\mathcal{H}$ with this index. (The program has no access to data for maximal isomorphic subgroups with indices higher than four.) The different transformation matrices and a link to a list of these matrices are given for each of the possible chains.

The graphical representation contains the intermediate groups that connect $\mathcal{G}$ and $\mathcal{H}$ with the specified index. This graph is a subgraph of the general graph of maximal subgroups with unspecified index and is also of the contracted type.

(*b*) Classification of the different subgroups $\mathcal{H}_j$ of $\mathcal{G}$.

Once the index of $\mathcal{H}$ in $\mathcal{G}$ is given, the different subgroups $\mathcal{H}_j$ of that index are calculated and distributed into classes of conjugate subgroups of $\mathcal{G}$. The subgroups of a conjugacy class form a block where each subgroup is specified by the corresponding transformation matrix–column pair $(\boldsymbol{P}, \boldsymbol{p})_j$ that relates the standard bases of $\mathcal{G}$ and $\mathcal{H}_j$. There is also a link to a list of the elements of the subgroups transformed to the basis of the group $\mathcal{G}$, which allows the identification of those elements of $\mathcal{G}$ that are retained in the subgroup. The list of transformation matrices that give the same (identical) subgroup is accessible under a separate link (see Table 1.7.3.1).

The graph contains the intermediate space groups $\mathcal{Z}_k$ for the pair $\mathcal{G} \overset{i}{>} \mathcal{H}$ but contrary to the graph of the previous step, the different isomorphic subgroups are represented by different nodes, *i.e.* the graph is a complete one. All isomorphic subgroups $\mathcal{H}_j$ are given at the bottom of the graph. Their labels are formed by the short Hermann–Mauguin symbol of the subgroup followed by a number given in parentheses which specifies the class of conjugate subgroups to which the subgroup $\mathcal{H}_j$ belongs.

Note that for group–subgroup pairs with high indices, where a lot of intermediate maximal subgroups occur, the resulting complete graph with all subgroups $\mathcal{H}_j$ can be very complicated and difficult to overview. Alternatively, a simpler graph associated with a single specific subgroup $\mathcal{H}_j$ can also be obtained (the graphs are the same for all subgroups within a conjugacy class).

Example 1.7.3.1.1

Consider the group–subgroup relations between the groups $\mathcal{G} = P4_12_12$, No. 92, and $\mathcal{H} = P2_1$, No. 4. If no index is specified then the graph of maximal subgroups that relates $P4_12_12$ and $P2_1$ is represented as a table indicating the space-group types of the possible intermediate space groups $\mathcal{Z}_k$ and the corresponding indices. The contracted general $P4_12_12 > P2_1$ graph is shown in Fig. 1.7.3.1. Two edges with opposite arrows between a group–subgroup pair correspond to group–subgroup relations in both directions, *e.g.* the pair $P4_1$ and $P4_3$.

Table 1.7.3.1. *Group–subgroup relations for $P4_12_12$ (No. 92) > $P2_1$ (No. 4), index 4*

There are three different subgroups $\mathcal{H}_j = (P2_1)_j$ of $P4_12_12$ distributed into two classes of conjugate subgroups. The possible chains of maximal subgroups and the corresponding matrices $(\boldsymbol{P}, \boldsymbol{p})_j$ (written in concise form) are also shown. (Note that the standard setting for $P2_1$ is the unique axis b setting.) The different transformation matrices for the subgroup $(P2_1)_3$ correspond to the different group–subgroup chains that relate the same subgroup to $P4_12_12$, *cf.* Fig. 1.7.3.3.

Class	$\mathcal{H}_j$	Chains	$(\boldsymbol{P}, \boldsymbol{p})_j$
Class 1	$(P2_1)_1 = P2_{1\,[010]}$	$P4_12_12 > P2_12_12_1 > P2_1$	$\mathbf{a}, \mathbf{b}, \mathbf{c}; \frac{1}{4}\ 0\ \frac{5}{8}$
	$(P2_1)_2 = P2_{1\,[100]}$	$P4_12_12 > P2_12_12_1 > P2_1$	$\mathbf{c}, \mathbf{a}, \mathbf{b}; \frac{1}{4}\ \frac{1}{4}\ \frac{3}{8}$
Class 2	$(P2_1)_3 = P2_{1\,[001]}$	$P4_12_12 > P2_12_12_1 > P2_1$	$\mathbf{b}, \mathbf{c}, \mathbf{a}; \frac{1}{2}\ 0\ \frac{3}{8}$
		$P4_12_12 > P4_1 > P2_1$	$\mathbf{b}, \mathbf{c}, \mathbf{a}; 0\ \frac{1}{2}\ 0$
		$P4_12_12 > C222_1 > P2_1$	$\mathbf{a}, \mathbf{c}, -\mathbf{b}; 0\ 0\ \frac{1}{4}$

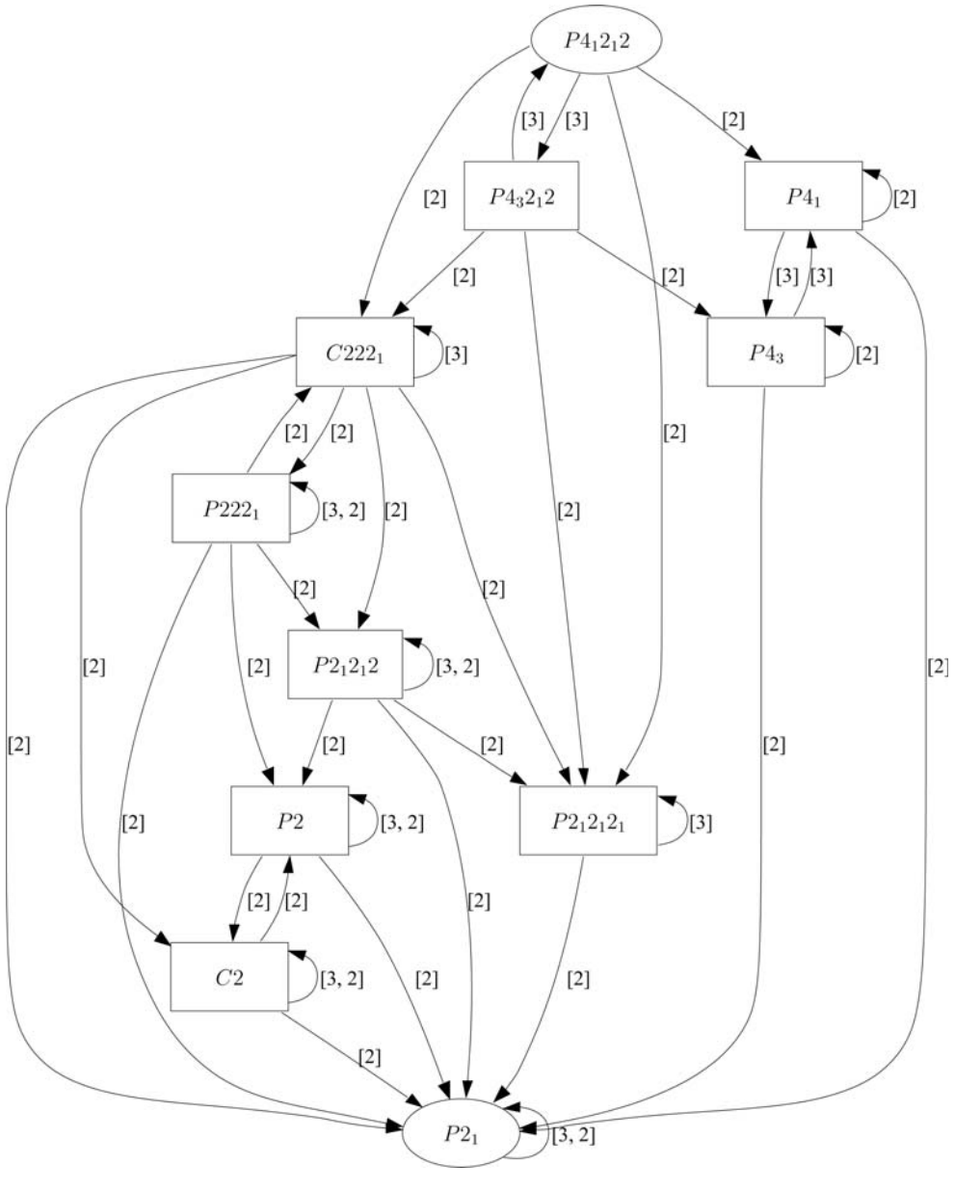

Fig. 1.7.3.1. General contracted graph for $P4_12_12$ (No. 92) > $P2_1$ (No. 4) as given by the program *SUBGROUPGRAPH*. The nodes of the graph correspond to the space-group types that can appear as intermediate groups in the chain of the group–subgroup pair $P4_12_12 > P2_1$. Each edge of the graph corresponds to a maximal subgroup pair of the indicated index [*i*]. Isomorphic subgroups (of indices 2 and 3) are shown as loops.

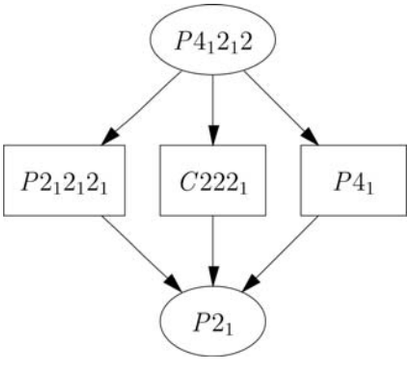

Fig. 1.7.3.2. Contracted graph for the pair of space groups $P4_12_12$ (No. 92) > $P2_1$ (No. 4), index 4, as given by the program *SUBGROUPGRAPH*. The nodes of the graph correspond to space-group types. The directed edges represent the possible group–maximal subgroup pairs.

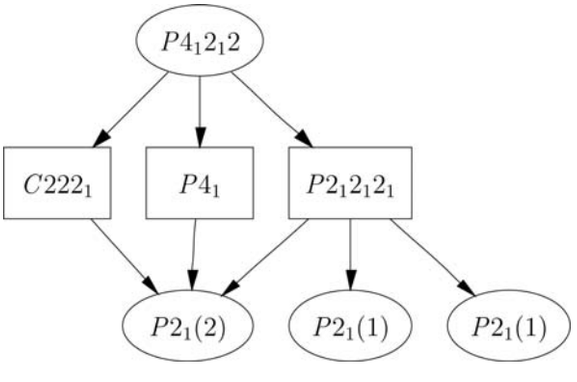

Fig. 1.7.3.3. Complete graph for $P4_12_12$ (No. 92) > $P2_1$ (No. 4), index 4, as given by the program *SUBGROUPGRAPH*. The nodes represent space groups and not space-group types. The three subgroups of the type $P2_1$ are distributed into two classes of conjugate subgroups, which are indicated in parentheses after the space-group symbol. The two subgroups $P2_1(1)$ with twofold screw axes along [100] and [010] of $P4_12_12$ belong to the same conjugacy class. Their complete single graphs look alike and differ considerably from the graph of $P2_1(2)$. The latter corresponds to the subgroup whose twofold screw axes point along the tetragonal axes.

When the index [i] of the subgroup in the group is specified, the resultant graph is reduced to the chains of maximal subgroups that correspond to the value of [i]. For example, in Fig. 1.7.3.2 the contracted graph $P4_12_12 > P2_1$ of index 4 is shown. The data in Table 1.7.3.1 and the complete graph shown in Fig. 1.7.3.3 indicate that there are three different $P2_1$ subgroups of $P4_12_12 > P2_1$ of index 4, distributed over two classes of conjugate subgroups. The three different subgroups of space-group type $P2_1$ of index 4 correspond to three sets of twofold screw axes in $P4_12_12$: those pointing along [100] and [010] of the tetragonal cell give rise to the two conjugate subgroups, and the third one (forming a class of conjugate subgroups by itself) is along the tetragonal axis. Their full Hermann–Mauguin symbols are $P2_111$, $P12_11$ and $P112_1$. The corresponding transformations are listed in Table 1.7.3.1. The complete graph $P4_12_12 > P2_1$, index 4 (Fig. 1.7.3.3) also shows that three different maximal subgroup chains end at the same $P2_1(P112_1)$ subgroup, each of them specified by a different transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$ (Table 1.7.3.1). The three different transformation matrices are related by elements of the normalizer of the subgroup.

1.7.3.1.2. The program HERMANN

The method of calculation of the subgroups and their distribution into classes of conjugate subgroups used in *SUBGROUPGRAPH* is not adequate for group–subgroup pairs of indices greater than 50. The program *HERMANN* has been developed to treat the cases of such considerable reduction of symmetry. It is a modification of *SUBGROUPGRAPH* and is based on Hermann's theorem (*cf.* Lemma 1.2.8.1.1). Consider a group–subgroup pair $\mathcal{G} > \mathcal{H}$, with $\mathcal{H}$ a general subgroup of index [i]. The existence and the uniqueness of Hermann's group $\mathcal{M}$, $\mathcal{G} > \mathcal{M} > \mathcal{H}$, implies the possibility of factorizing the group–subgroup chain $\mathcal{G} > \mathcal{H}$ and its index [i] into two subchains of smaller indices with $[i] = [i_P] \cdot [i_L]$. The first one, the so-called *translationengleiche* or *t*-chain $\mathcal{G} \overset{i_P}{>} \mathcal{M}$, is related to the reduction of the point-group symmetry in the subgroup. The second one is known as the *klassengleiche* or *k*-chain $\mathcal{M} \overset{i_L}{>} \mathcal{H}$, and it takes account of the loss of translations. (The [i_L] index is equal to the cell-multiplication factor of the volumes of the primitive cells of the lattices.)

The program *HERMANN* calculates all subgroups $\mathcal{H}_j$ of $\mathcal{G}$ of index [i] and distributes them into conjugacy classes with respect to $\mathcal{G}$. In addition, the program indicates the corresponding Hermann groups. It is important to note that for a given pair of space-group types $\mathcal{G} \overset{i}{>} \mathcal{H}$ and index [i], Hermann groups $\mathcal{M}$ of different space-group types can exist that belong to the same crystal class, *cf.* Example 1.7.3.1.2. However, there is a unique Hermann group for any group–subgroup pair of specific space groups.

The space-group types of the possible Hermann groups $\mathcal{M}$ for the pair $\mathcal{G} \overset{i}{>} \mathcal{H}$ are determined by the following conditions: (i) the groups $\mathcal{M}$ are subgroups of $\mathcal{G}$ of index [i_P] where i_P is equal to the ratio of the point-group orders of $\mathcal{G}$ and $\mathcal{H}$; (ii) the point groups of $\mathcal{M}$ coincide with the point group of $\mathcal{H}$, $\mathcal{P}_\mathcal{H}$; (iii) the groups $\mathcal{M}$ have subgroups $\mathcal{H}$ of index $[i_L] = [i]/[i_P]$. The complete set of the subgroups $\mathcal{H}_j$ of $\mathcal{G}$ is calculated by the consecutive application of *SUBGROUPGRAPH* to the two subchains $\mathcal{G} \overset{i_P}{>} \mathcal{M}$ and $\mathcal{M} \overset{i_L}{>} \mathcal{H}$. At this stage, the subgroups $\mathcal{H}_j$ are distributed into conjugacy classes with respect to the corresponding Hermann groups only. Finally, the program determines the conjugacy classes of $\mathcal{H}_j$ with respect to $\mathcal{G}$: these either coincide with conjugacy classes relative to $\mathcal{M}$, or some of the classes relative to $\mathcal{M}$ merge together to form conjugacy classes with respect to $\mathcal{G}$.

Input to *HERMANN*:

The data needed are the space-group types of $\mathcal{G}$ and $\mathcal{H}$ and their index.

Output of *HERMANN*:

Essentially, the output of the program is a list of all subgroups $\mathcal{H}_j$ of $\mathcal{G}$ of index $[i] = [i_P] \cdot [i_L]$, distributed into conjugacy classes with respect to $\mathcal{G}$. The classes of conjugate subgroups are listed in different blocks depending on the space-group type of the Hermann groups $\mathcal{M} \overset{i_P}{<} \mathcal{G}$. The subgroups $\mathcal{H}_j$ in each class are listed explicitly and are distinguished by the transformation matrices $(\boldsymbol{P}, \boldsymbol{p})_j$. Options for transforming the elements of $\mathcal{H}_j$ to the basis of $\mathcal{G}$ and for decomposing $\mathcal{G}$ in right cosets with respect to $\mathcal{H}_j$ are available. In addition, it is possible to calculate the splittings of the Wyckoff positions of $\mathcal{G}$ relative to $\mathcal{H}_j$ (*cf.* Section 1.7.4, program *WYCKSPLIT*). There is an optional link to the program *SYMMODES*, which carries out a symmetry analysis of the possible distortions compatible with $\mathcal{H}_j$ for the symmetry break $\mathcal{G} \longrightarrow \mathcal{H}_j$.

Example 1.7.3.1.2

Consider the pair of group–subgroup types $P422$ (No. 89) > $P2_1$ (No. 4), index [i] = 8 (Fig. 1.7.3.4). The factorization of the index into $[i_P] = 4$ and $[i_L] = 2$ follows from the ratio of the orders of the point groups of $\mathcal{G}$ and $\mathcal{H}$. The two space-group types $P2$, No. 3, and $C2$, No. 5, satisfy the conditions for Hermann subgroups for the pair $P422 \overset{i=8}{>} P2_1$. There are three $P2$ Hermann subgroups of $\mathcal{G}$ distributed in two conjugacy classes: the subgroups with twofold axes along [100] and [010] form a conjugacy class, and $P2_{[001]}(P2)$ is a normal subgroup in $P422$. The two $C2$ Hermann subgroups with twofold axes along [110] and $[1\bar{1}0]$ form a single conjugacy class. Each Hermann subgroup has just one normal subgroup of $P2_1$ type of index $[i_L] = 2$. Altogether there are five different $P2_1$ subgroups of $P422$ of index [i] = 8, distributed in three conjugacy classes, following the conjugacy relationships of the corresponding Hermann groups.

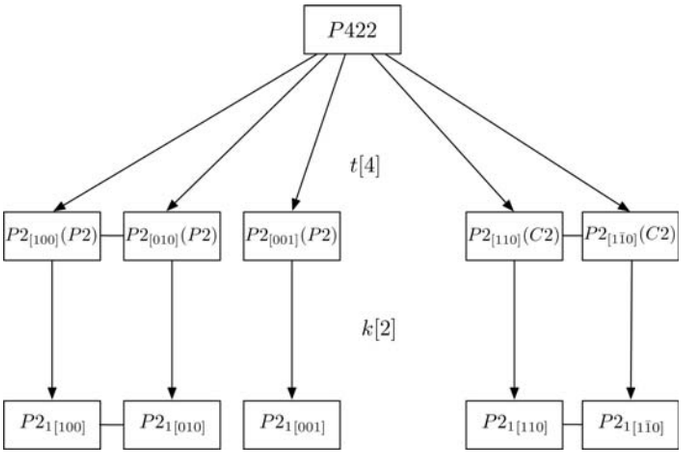

Fig. 1.7.3.4. Group–subgroup graph for $P422$ (No. 89) > $P2_1$ (No. 4), index 8. The nodes represent space groups and not space-group types. The directional symbols [100] *etc.* state the orientations of the monoclinic axes referred to the basis of $P422$. Horizontal lines connect subgroups conjugate in $P422$. There are two space-group types of Hermann subgroups in the intermediate level of the figure: $P2$ and $C2$. The distribution of the five $P2_1$ subgroups into conjugacy classes with respect to $P422$ follows the conjugacy-class distribution of the corresponding Hermann subgroups.

1.7.3.1.3. The program COSETS

The coset decomposition of a group $\mathcal{G}$ with respect to a subgroup $\mathcal{H} < \mathcal{G}$ is a basic step in many problems that involve group–subgroup relations between space groups, *e.g.* the distribution of subgroups into conjugacy classes (*cf.* Section 1.2.6.3) or the determination of supergroups of space groups (*cf.* Section 2.1.7.4). The procedure for the coset decomposition $\mathcal{G} : \mathcal{H}$ is well defined: one transforms $\mathcal{G}$ to the basis of $\mathcal{H}$ by the transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$ that relates the two bases, and then one distributes the transformed elements of $\mathcal{G}$ into left $g_r\mathcal{H}$ or right $\mathcal{H}g_s$ cosets with respect to $\mathcal{H}$ (*cf.* Section 1.2.4.2). The elements g_r and g_s are called the *coset representatives*. Consider the space-group pair $\mathcal{G} > \mathcal{H}$ with the corresponding transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$. The coset decomposition $\mathcal{G} : \mathcal{H}$ can be easily achieved if both $\mathcal{G}$ and $\mathcal{H}$ are decomposed into cosets with respect to the translation subgroup $\mathcal{T}'_{\mathcal{H}}$ of $\mathcal{H}$, consisting of integer translations only (*i.e.* the coset decomposition is performed with respect to a primitive lattice of $\mathcal{H}$). The determination of the coset representatives of $\mathcal{G} : \mathcal{T}'_{\mathcal{H}}$ for the right-coset decomposition is simplified by the fact that two elements of $\mathcal{G}$ that differ by an integer translation $t_{\mathcal{H}}$ of $\mathcal{H}$ belong to the same coset $\mathcal{T}'_{\mathcal{H}}g_q$. This is, however, not in general true for the left-coset decomposition: in that case, two elements of $\mathcal{G}$ belong to the same coset $g_q\mathcal{T}'_{\mathcal{H}}$ if they differ by the translation $\boldsymbol{W}_q t_{\mathcal{H}}$ where $g_q = (\boldsymbol{W}_q, \boldsymbol{w}_q)$. In other words, two elements of $\mathcal{G}$ (with the same rotational part) belong to the same coset $g_q\mathcal{T}'_{\mathcal{H}}$ if the difference Δ_q between their translational parts satisfies $(\boldsymbol{W}_q)^{-1}\Delta_q \in \mathcal{T}'_{\mathcal{H}}$.

Given the space-group pair $\mathcal{G} > \mathcal{H}$ with the corresponding transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$, the program *COSETS* decomposes $\mathcal{G}$ into left or right cosets with respect to $\mathcal{H}$.

Input to *COSETS*:

The data that are needed are the group $\mathcal{G}$, the subgroup $\mathcal{H}$ and the transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$ that relates the default settings of $\mathcal{G}$ and $\mathcal{H}$. The user can choose between right- or left-coset decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$.

Output of *COSETS*:

The output data consist of the list of the cosets of the decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$. The first coset corresponds to the subgroup $\mathcal{H}$ represented by the set of its general-position triplets, $\{h_\nu, \nu = 1, \ldots, f|\mathcal{P}_{\mathcal{H}}|\}$, where $|\mathcal{P}_{\mathcal{H}}|$ is the order of the point group $\mathcal{P}_{\mathcal{H}}$ and f is the so-called centring factor that equals the number of lattice points per cell. The triplets of the rest of the cosets are of the form $(g_s h_\nu)$ for the left-coset decomposition or $(h_\nu g_r)$ for the right-coset decomposition, with $s, r = 1, \ldots, |\mathcal{G} : \mathcal{H}|$.

Example 1.7.3.1.3

Consider the group–subgroup pair $R\bar{3}m$ (No. 166) > $P2_1/c$ (No. 14) of index 6, with the transformation matrix

$$\boldsymbol{P} = \begin{pmatrix} \frac{2}{3} & 0 & -2 \\ \frac{1}{3} & 1 & -1 \\ \frac{1}{3} & 0 & 0 \end{pmatrix}, \quad \boldsymbol{P}^{-1} = \begin{pmatrix} 0 & 0 & 3 \\ -\frac{1}{2} & 1 & 0 \\ -\frac{1}{2} & 0 & 1 \end{pmatrix}$$

relating the bases defined for the default settings of the group and the subgroup (hexagonal axes setting for $R\bar{3}m$, and the unique axis b setting for $P2_1/c$). The decomposition of $P2_1/c$ with respect to $\mathcal{T}_{\mathcal{H}}$ consists of four cosets. (For P space groups, $\mathcal{T}'_{\mathcal{H}}$ coincides with $\mathcal{T}_{\mathcal{H}}$.) There are 36 coset representatives of $\mathcal{G} : \mathcal{T}'_{\mathcal{G}}$, with $\mathcal{T}'_{\mathcal{G}}$ consisting of integer translations only. From the determinant of the transformation matrix it follows that there are $\frac{2}{3} \times 36 = 24$ cosets in the decomposition of $\mathcal{G} : \mathcal{T}_{\mathcal{H}}$, *i.e.* some of the coset representatives of $\mathcal{T}'_{\mathcal{G}}$ belong to the same cosets with respect to $\mathcal{T}_{\mathcal{H}}$. The distribution of the coset representatives of $\mathcal{G} : \mathcal{T}'_{\mathcal{G}}$ into cosets of $\mathcal{G}$ with respect to $\mathcal{T}_{\mathcal{H}}$ is different for the right- and left-coset decomposition. Consider the three coset representatives of $\mathcal{G} : \mathcal{T}'_{\mathcal{G}}$ corresponding to the threefold rotation, namely $(\boldsymbol{3}^+, 000)$, $(\boldsymbol{3}^+, \frac{2}{3}\frac{1}{3}\frac{1}{3})$ and $(\boldsymbol{3}^+, \frac{1}{3}\frac{2}{3}\frac{2}{3})$. In the basis of the subgroup, the rotational part

$$(\boldsymbol{3}^+) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

is transformed by $\boldsymbol{P}^{-1}(\boldsymbol{3}^+)\boldsymbol{P}$ to

$$(\boldsymbol{3}^+) = \begin{pmatrix} 1 & 0 & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{pmatrix}$$

and the translational parts by $\boldsymbol{P}^{-1}\boldsymbol{t}_j$ to (000), (100) and $(2\frac{1}{2}\frac{1}{2})$, correspondingly. The elements with translational parts (000), (100) belong to the same coset $\mathcal{T}_{\mathcal{H}}(\boldsymbol{3}^+, 000)$ in the case of right-coset decomposition, and $(\boldsymbol{3}^+, 2\frac{1}{2}\frac{1}{2})$ can be taken as a representative of a different coset [the program chooses the element $(\boldsymbol{3}^+, 0\frac{1}{2}\frac{1}{2})$ as a coset representative]. In the case of left-coset decomposition, the coset representatives are $(\boldsymbol{3}^+, 000)$ and $(\boldsymbol{3}^+, 100)$: the elements $(\boldsymbol{3}^+, 100)$ and $(\boldsymbol{3}^+, 2\frac{1}{2}\frac{1}{2})$ belong to the same coset $(\boldsymbol{3}^+, 100)\mathcal{T}_{\mathcal{H}}$ as the difference in their translational parts $\Delta_q = (1, \frac{1}{2}, \frac{1}{2})$ satisfies the condition $\Delta_q = \boldsymbol{W}_q t_{\mathcal{H}}$, with $\boldsymbol{W}_q = \boldsymbol{3}^+$ and $t_{\mathcal{H}} = (1, 0, 0)$.

The output of *COSETS* gives the distribution of the 24 coset representatives of $\mathcal{G} : \mathcal{T}_{\mathcal{H}}$ into the six cosets of the decomposition of $R\bar{3}m$ with respect to $P2_1/c$. In the case of right-coset decomposition, the elements $\{(\boldsymbol{1}, 000)$, $(\boldsymbol{1}, 0\frac{1}{2}\frac{1}{2})$, $(\boldsymbol{3}^+, 000)$, $(\boldsymbol{3}^+, 0\frac{1}{2}\frac{1}{2})$, $(\boldsymbol{3}^-, 000)$, $(\boldsymbol{3}^-, 0\frac{1}{2}\frac{1}{2})\}$ can be selected as coset representatives. The elements $\{(\boldsymbol{1}, 000)$, $(\boldsymbol{1}, 0\frac{1}{2}\frac{1}{2})$, $(\boldsymbol{3}^+, 000)$, $(\boldsymbol{3}^-, 000)\}$ are valid coset representatives also for the left-coset decomposition of $R\bar{3}m$ with respect to $P2_1/c$, while $(\boldsymbol{3}^+, 0\frac{1}{2}\frac{1}{2})$, $(\boldsymbol{3}^-, 0\frac{1}{2}\frac{1}{2})$ have to be substituted by $(\boldsymbol{3}^+, 100)$, $(\boldsymbol{3}^-, 100)$.

1.7.3.1.4. The program CELLSUB

For several applications, it is of interest to determine the subgroups of a space group for a specific multiple of the cell, *i.e.* for a given $[i_L]$ index. This happens, for example, in the search for possible low-symmetry phases after a phase transition from a known high-symmetry phase with experimental data indicating the reduction of translational symmetry. The program *CELLSUB* calculates the different subgroups of a space group $\mathcal{G}$ for a given maximal index $[(i_L)_{\max}]$ in two steps:

(i) It determines all possible space-group types $\mathcal{H}$ which form group–subgroup pairs with $\mathcal{G}$, $\mathcal{G} > \mathcal{H}$ of index $[i] = [i_P] \cdot [i_L]$, such that the index $[i_L]$ is equal to or smaller than a given value $[(i_L)_{\max}]$.

(ii) For each pair of space-group types $\mathcal{G} > \mathcal{H}$ and their index $[i]$ satisfying the above condition, *CELLSUB* finds all possible subgroups $\mathcal{H}_j$ specified by the matrix–column pairs $(\boldsymbol{P}, \boldsymbol{p})_j$ and classifies them into classes of conjugate subgroups.

The method for obtaining the different subgroup types and indices of a given space group $\mathcal{G}$ is similar to that used in the *SUBGROUPGRAPH* module. It is also based on the data for maximal subgroups of the space groups in *IT* A1. Given the

group $\mathcal{G}$, the program constructs a graph of maximal subgroups, imposing the additional condition $[i_L] \leq [(i_L)_{\max}]$.

Input to *CELLSUB*:

(i) The space group $\mathcal{G}$. It can be specified either by its sequential *IT* A number or by its Hermann–Mauguin symbol.

(ii) The (maximal) $[(i_L)_{\max}]$ index. By default (full-list option), all subgroups with an index $[i_L]$ smaller than the given $[(i_L)_{\max}]$ are shown. As an option, it is possible to choose only the subgroups with a specified $[(i_L)_{\max}]$ index.

Output of *CELLSUB*:

(i) A list of the space–group types of the subgroups $\mathcal{H}$ with the corresponding index $[i]$, the index $[i_P]$ and the index $[i_L]$. The subgroups are further classified into *k*-subgroups, *t*-subgroups (for the special case of $[i_L] = 1$) or general subgroups.

(ii) For every space-group type $\mathcal{H}$ of the list, a link to the *SUBGROUPGRAPH* module provides the following data: the chains of maximal subgroups relating $\mathcal{G}$ and $\mathcal{H}$ with the given index, the classification of the different subgroups $\mathcal{H}_j$ of $\mathcal{G}$ in classes of conjugate subgroups, the graphical representations and all the benefits of the program *SUBGROUPGRAPH*.

1.7.3.1.5. The program COMMONSUBS

Two space groups $\mathcal{G}_1$ and $\mathcal{G}_2$ which are not in a group–subgroup relation may be related by common subgroups $\mathcal{H}_j$ with $\mathcal{G}_1 > \mathcal{H}_j < \mathcal{G}_2$. Given $\mathcal{G}_1$ and $\mathcal{G}_2$, the program *COMMONSUBS* determines these groups $\mathcal{H}_j$. Such group–subgroup relations have a subjective component: in general the lattices of both space groups do not fit ideally. There will be some misfit between the lattice parameters of $\mathcal{H}_1$, a subgroup of $\mathcal{G}_1$ and those of $\mathcal{H}_2$, a subgroup of $\mathcal{G}_2$. The decision as to how much misfit could be tolerated depends on the specific structural criteria applicable to the problem studied.

The higher the proportion of common symmetry between $\mathcal{G}_1$ and $\mathcal{G}_2$, *i.e.* the smaller the indices $[i_1] = |\mathcal{G}_1 : \mathcal{H}|$ and $[i_2] = |\mathcal{G}_2 : \mathcal{H}|$ are, the more promising is the search for a relation between the two crystal structures. Owing to the theorem of Hermann both the indices $[i_1]$ and $[i_2]$ may be split into the point-group index $[(i_P)_m]$ and the lattice index $[(i_L)_m]$, such that $[i_m] = [(i_P)_m] \cdot [(i_L)_m]$, $m = 1, 2$. The point-group indices are finite, $[(i_P)_m] \leq 48$; the lattice index may have any value in principle. Large indices, however, mean little common symmetry and thus low probability of structural relevance. Therefore, it is reasonable to limit the value of $[(i_L)_m]$ and thus of $[i_1]$ and $[i_2]$ by introducing a maximal value $[(i_L)_{\max}]$.

If two structures with space groups $\mathcal{G}_1$ and $\mathcal{G}_2$ can be compared within a common subgroup $\mathcal{H}$, then the number of formula units $Z_{\mathcal{H}}$ of a primitive unit cell of $\mathcal{H}$ should be the same for both structures. This means that $Z_{\mathcal{H}} = Z_1 \cdot [(i_L)_1] = Z_2 \cdot [(i_L)_2]$, where Z_1 and Z_2 are the numbers of the formula units of the primitive unit cells of the crystal structures 1 (with space group $\mathcal{G}_1$) and 2 (with space group $\mathcal{G}_2$). It follows that $[i_2] = [i_1] \cdot (Z_1/Z_2) \cdot ([(i_P)_2]/[(i_P)_1])$ or

$$[i_2] = [i_1] \cdot \frac{Z_1}{Z_2} \cdot \frac{|\mathcal{P}_{\mathcal{G}_2}|}{|\mathcal{P}_{\mathcal{G}_1}|}, \qquad (1.7.3.1)$$

where $|\mathcal{P}|$ is the order of the point group $\mathcal{P}$.

Given the space groups $\mathcal{G}_1$ and $\mathcal{G}_2$, the formula units per primitive cells Z_1 and Z_2, and $[(i_L)_{\max}]$, the program *COMMONSUBS* calculates the common subgroups in several steps:

(i) A dedicated module of the program *CELLSUB* (*cf.* Section 1.7.3.1.4) calculates the sets of subgroups $\{\mathcal{H}_{1,r}, i_{1,r}\}$ of $\mathcal{G}_1$ and $\{\mathcal{H}_{2,s}, i_{2,s}\}$ of $\mathcal{G}_2$ with $[(i_L)_m] \leq [(i_L)_{\max}]$. Here, the indices r and s distinguish the different space-group types of the subgroups $\mathcal{H}_1$ and $\mathcal{H}_2$.

(ii) The intersection of the sets $\{\mathcal{H}_{1,r}, i_{1,r}\}$ and $\{\mathcal{H}_{2,s}, i_{2,s}\}$ for $\mathcal{H}_{1,r} \cong \mathcal{H}_{2,s} \cong \mathcal{H}$ then gives the set of the space-group types of the common subgroups $\{\mathcal{H}\}$ of $\mathcal{G}_1$ and $\mathcal{G}_2$ with $[(i_L)_m] \leq [(i_L)_{\max}]$, $m = 1, 2$.

(iii) The program *COMMONSUBS* selects and lists those subgroups of the set $\{\mathcal{H}\}$ whose indices $[i_1]$ and $[i_2]$ in $\mathcal{G}_1$ and $\mathcal{G}_2$ satisfy the condition given by equation (1.7.3.1).

The generalization of the procedure for the case of common subgroups of three groups $\mathcal{G}$ is straightforward and has been also implemented in the program *COMMONSUBS*.

Input to *COMMONSUBS*:

The necessary data include the specification of the space-group types $\mathcal{G}$, the index $[(i_L)_{\max}]$ and the number of formula units per conventional unit cell[1] (or the ratio of the two $[i_L]$ indices for the special case of common subgroups of two space groups). The search for common subgroups can be further restricted by specifying the point group, the crystal class or the type of centring desired for the common subgroup.

Output of *COMMONSUBS*:

(i) A list of common subgroups $\mathcal{H}$ specified by their Hermann–Mauguin symbols, the point groups $\mathcal{P}_{\mathcal{H}}$, the indices $[i]$ of $\mathcal{H}$ in the space groups $\mathcal{G}$, and the corresponding factors $[(i_P)]$ and $[(i_L)]$. Optional links to the databases give access to additional information related to $\mathcal{H}_m$, its maximal subgroups or the point group $\mathcal{P}_{\mathcal{H}}$.

(ii) The output for the case of common subgroups of two space groups gives more details on the group–subgroup relations for the two branches $\mathcal{G}_1 > \mathcal{H}$ and $\mathcal{G}_2 > \mathcal{H}$. Apart from the specification of the common subgroups $\mathcal{H}$ and their indices $[(i_1)]$ and $[(i_2)]$ in $\mathcal{G}_1$ and $\mathcal{G}_2$, one obtains a list of representatives of the conjugacy classes of the subgroups $\mathcal{H}$ with respect to $\mathcal{G}_1$ and $\mathcal{G}_2$. There are also links to the programs *WYCKSPLIT* (for the splittings of the Wyckoff positions for $\mathcal{G} > \mathcal{H}$, *cf.* Section 1.7.4.1) and *SYMMODES* (Capillas *et al.*, 2003) (for the group-theoretical study of the possible phase-transition mechanism related to the symmetry break $\mathcal{G} > \mathcal{H}$). A list of all subgroups of a conjugacy class and the corresponding transformation matrices are obtained *via* links to the programs *HERMANN* (*cf.* Section 1.7.3.1.2) and *SUBGROUPGRAPH* (*cf.* Section 1.7.3.1.1).

The existence of a common subgroup does not automatically mean the existence of a structural relation between the corresponding crystal structures. In general, the existence of a common supergroup of two space groups is mostly taken as more indicative of a structural relation than that of a common subgroup, provided the indices of the common supergroup are comparable with those of the common subgroup. However, the following example shows the utility of the common-subgroup approach in the search for the possible symmetry of an intermediate phase between two phases with no group–subgroup relation between their space groups.

[1] The number of formula units per conventional unit cell Z_c is simply related to the number Z of formula units per primitive unit cell *via* the centring factor f, $Z = Z_c/f$, with $f = 1$ for primitive lattices, 2 for *I*-, *C*-, *B*- or *A*-centred lattices, 3 for *R*-centred lattices and 4 for *F*-centred lattices.

Example 1.7.3.1.4

The perovskite-like ferroelectric compounds $PbZr_{1-x}Ti_xO_3$ exhibit a morphotropic[2] phase boundary around $x = 0.45$–0.50. At compositions with $x < 0.47$ they are rhombohedral, at $x > 0.47$ tetragonal. For $x = 0.48$ a tetragonal-to-monoclinic phase transition has been observed at ~300 K, the space group changing from *P*4*mm*, No. 99, to *Cm*, No. 8 (Noheda *et al.*, 1999, 2000). The monoclinic structure results from the tetragonal one by shifts of the Pb and Zr/Ti atoms along the tetragonal [110] direction. The monoclinic structure can also be envisaged as a distorted variant of the rhombohedral phase, space group *R*3*m*, No. 160. There is no group–subgroup relation between *P*4*mm* and *R*3*m*, but *Cm* is a common subgroup of both. In this way, the monoclinic structure can be considered as providing a 'bridge' between the rhombohedral and tetragonal regions of the morphotropic phase boundary. The application of *COMMONSUBS* for $\mathcal{G}_1 = P4mm$ with $Z_{c,1} = 1$, $\mathcal{G}_2 = R3m$ with $Z_{c,2} = 3$, and $i_L = 1$ (*i.e.* no cell multiplication) yields exactly *Cm* as the common monoclinic subgroup.

Structural relations established through a common subgroup are also being used to model first-order transformations between phases with no group–subgroup relation between their symmetry groups. The local symmetry of a common subgroup of the two end symmetries is supposed to describe approximately the symmetry constraints of the local transient states taking place during the transformation [see *e.g.* Capillas *et al.* (2007) and the references therein].

In some cases these intermediate configurations can even be stabilized and appear as stable intermediate phases in the phase diagram. The program *COMMONSUBS* can be useful in both types of searches.

1.7.3.2. Supergroups of space groups

The problem of the determination of the supergroups of a given space group is of rather general interest. For several applications it is not sufficient to know only the space-group types of the supergroups of a given group; it is instead necessary to have available all different supergroups $\mathcal{G}_r > \mathcal{H}$ that are isomorphic to $\mathcal{G}$ and are of the same index [*i*]. In the literature there are few papers treating the supergroups of space groups in detail (Koch, 1984; Wondratschek & Aroyo, 2001). In *IT* A one finds only listings of minimal supergroups of space groups which, in addition, are not explicit: they only provide for each space group $\mathcal{H}$ the list of those space-group types in which $\mathcal{H}$ occurs as a maximal subgroup (*cf.* Section 2.1.6). It is not trivial to determine all supergroups $\mathcal{G}_r > \mathcal{H}$ if only the types of the minimal supergroups are known. The Bilbao Crystallographic Server offers two basic programs that solve this problem for a given finite index [*i*] (Ivantchev *et al.*, 2002): (i) *MINSUP*, which gives all minimal supergroups of index 2, 3 and 4 of a given space group, and (ii) *SUPERGROUPS*, which calculates all different supergroups of a given space-group type and a given index.

As in the case of subgroups, we have developed two complementary programs that involve the calculation of supergroups of space groups: (i) the program *CELLSUPER*, for calculating the supergroups of a space group for a given [i_L] index, and (ii) *COMMONSUPER* for the computation of common supergroups of two or more space groups.

1.7.3.2.1. The programs MINSUP and SUPERGROUPS

In analogy to the case of minimal supergroups (*cf.* Section 2.1.7), the determination of all supergroups $\mathcal{G}_r$ of a given space-group type $\mathcal{G}$ and index [*i*] of a space group $\mathcal{H}$ can be done by inverting the data for the subgroups $\mathcal{H}_s$ of $\mathcal{G}$ of index [*i*]. In the following we outline the basic arguments of this procedure.

Let $\mathcal{G}$ be a space group and $\mathcal{H} < \mathcal{G}$ be one of its subgroups of index [*i*]. Then all subgroups $\mathcal{H}_s$ of $\mathcal{G}$ of the same index [*i*] and isomorphic to $\mathcal{H}$ can be calculated by a dedicated module of *SUBGROUPGRAPH* (*cf.* Section 1.7.3.1.1). The number of subgroups with index [*i*] is finite for any space group. Therefore, such a list is always finite. Let $\mathcal{H} < \mathcal{G}$ be a member of this list. We are looking for all supergroups $\mathcal{G}_r > \mathcal{H}$ of index [*i*] that are isomorphic to $\mathcal{G}$, $\mathcal{G}_r \cong \mathcal{G}$. Then the supergroups $\mathcal{G}_r$ are also affine equivalent to $\mathcal{G}$, *i.e.* there must be a mapping $\mathsf{a}_r \in \mathcal{A}$ such that $\mathsf{a}_r^{-1}\,\mathcal{G}\,\mathsf{a}_r = \mathcal{G}_r$, where $\mathcal{A}$ is the group of all reversible affine mappings. Different supergroups $\mathcal{G}_r$ are obtained if $\mathsf{a}_r \notin \mathcal{N}_{\mathcal{A}}(\mathcal{G})$.

As in the case of minimal supergroups (*cf.* Section 2.1.7), there are two cases to be distinguished:

(1) The first candidates for the mapping a_r are the elements of the affine normalizer of $\mathcal{H}$, *i.e.* $\mathsf{a}_r \in \mathcal{N}_{\mathcal{A}}(\mathcal{H})$. Following Koch (1984) (see also Lemma 2.1.7.4.1), other supergroups $\mathcal{G}_r$ will be obtained by the transformation of $\mathcal{G}$ with the representatives of the cosets in the decomposition of the group $\mathcal{N}_{\mathcal{A}}(\mathcal{H})$ relative to the group $\mathcal{D} = \mathcal{N}_{\mathcal{A}}(\mathcal{H}) \cap \mathcal{N}_{\mathcal{A}}(\mathcal{G})$.

(2) There could exist further supergroups $\mathcal{G}_r > \mathcal{H}$, $\mathcal{G}_r \cong \mathcal{G}$ of the same index [*i*] with $\mathsf{a}_r \notin \mathcal{N}_{\mathcal{A}}(\mathcal{H})$, *i.e.* a_r is not an element of the affine normalizer of the group $\mathcal{H}$.

Summarizing: Any supergroup of $\mathcal{H}$, $\mathcal{G}_r > \mathcal{H}$, $\mathcal{G}_r \cong \mathcal{G}$ may be found by the following procedure: (i) determine all subgroups $\mathcal{H}_s < \mathcal{G}$ of the same index and distribute them into classes of conjugate subgroups with respect to $\mathcal{G}$. From each class of conjugate subgroups, choose a representative $\mathcal{H}_r$, specified by $(\boldsymbol{P}, \boldsymbol{p})_r$;[3] (ii) apply $(\boldsymbol{P}, \boldsymbol{p})_r^{-1}$ to the group $\mathcal{G}$ in order to obtain the group $\mathcal{G}_r$; and (iii) test whether $\mathcal{G}_r$ is already among the determined supergroups of $\mathcal{H}$. If it is not, then $\mathcal{G}_r$ is a new supergroup of $\mathcal{H}$ and further supergroups may be generated by the coset representatives of the decomposition of $\mathcal{N}_{\mathcal{A}}(\mathcal{H})$ relative to $(\mathcal{N}_{\mathcal{A}}(\mathcal{H}) \cap \mathcal{N}_{\mathcal{A}}(\mathcal{G}))$ as explained above.

The procedure described above for the determination of supergroups is also applied to the determination of minimal supergroups $\mathcal{G}$ of $\mathcal{H}$ (*cf.* Section 2.1.7). In this case, the distinct maximal subgroups $\mathcal{H}_r$, representatives of the classes of conjugate subgroups $\mathcal{H}_s$ with respect to $\mathcal{G}$, are retrieved directly from the maximal-subgroup database of the server.

Input to *MINSUP* and *SUPERGROUPS*:

(i) The program *MINSUP* needs as input the *IT* A number (or the Hermann–Mauguin symbol) of the group for which the minimal supergroups have to be determined. The type of supergroup is chosen from a table (returned by the program) which contains the *IT* A number of the minimal supergroup, its Hermann–Mauguin symbol and the index of the group in the supergroup. There is also a link to a list of the transformation matrices that relate the basis of the supergroup with that of the subgroup.

(ii) For the determination of all supergroups of a given type, it is necessary to select the type of the normalizers of the group and the supergroup. By default the Euclidean normalizers of general cell metrics are used as listed in Tables 15.2.1.3 and

[2] A morphotropic transition is an abrupt change in the structure of a solid solution with variation in composition.

[3] To simplify the algorithm, the condition $\mathsf{a}_r \notin \mathcal{N}_{\mathcal{A}}(\mathcal{G})$ is substituted by $\mathsf{a}_r \notin \mathcal{G}$.

15.2.1.4 of *IT* A. The affine normalizers of the space groups (except triclinic and monoclinic) are also accessible. For a translation lattice with metrics of apparent higher symmetry, the users may themselves provide the set of additional generators for the specific Euclidean normalizer (*cf.* Table 15.2.1.3 of *IT* A and Koch & Müller, 1990).

(iii) The program *SUPERGROUPS* takes as input the *IT* A numbers of the space groups $\mathcal{G}$ and $\mathcal{H}$ and the index of $\mathcal{H}$ in $\mathcal{G}$. The transformation matrices relating the bases of $\mathcal{G}$ and $\mathcal{H}$ necessary for the determination of the supergroups $\mathcal{G}_r$ are retrieved from the *IT* A1 database. In case of a non-minimal supergroup, the program *SUBGROUPGRAPH* determines the transformation matrix (or matrices) for the corresponding chains of maximal subgroups that relate $\mathcal{G}$ and $\mathcal{H}$. As in the case of *MINSUP*, the space-group normalizers used by default are the Euclidean normalizers. It is also possible for the user to use the affine normalizers given in *IT* A or to provide a specific one.

Output of *MINSUP* and *SUPERGROUPS*:

For the two supergroup programs the results contain:

(i) The transformation matrix $(\boldsymbol{P}, \boldsymbol{p})_r$ that relates the basis of the supergroup with that of the subgroup.

(ii) One representative from each coset in the decomposition of the supergroup $\mathcal{G}_r$ with respect to the group $\mathcal{H}$. The full cosets of the decomposition $\mathcal{G}_r : \mathcal{H}$ are also accessible. The elements of $\mathcal{G}_r$ are listed with respect to the basis of the subgroup $\mathcal{H}$.

From the considerations given above it should have become clear that the aim of the presented procedure and the supergroup programs is to solve the following 'purely' group-theoretical problem: Given a group–subgroup pair of space groups $\mathcal{G} > \mathcal{H}$, determine all supergroups $\mathcal{G}_r$ of $\mathcal{H}$ isomorphic to $\mathcal{G}$. The procedure does not include any preliminary checks on the compatibility of the metric of the studied space group with that of a supergroup. Depending on the particular case some of the supergroups obtained are not space groups but just affine groups isomorphic to space groups (see Koch, 1984). As an example consider the cubic supergroups of $P2_12_12_1$, No. 19: only if the three basis vectors of $P2_12_12_1$ have equal length can one speak of supergroups of the cubic space-group type $P2_13$, No. 198. However, for each group $P2_12_12_1$ there exist affine analogues of $P2_13$ as supergroups.

Example 1.7.3.2.1

Here we consider supergroups $\mathcal{G}_r = a_r^{-1}\,\mathcal{G}\,a_r$ of $\mathcal{H}$ with $a_r \in \mathcal{N}_{\mathcal{A}}(\mathcal{H})$. As an example we consider the group–supergroup pair $\mathcal{H} < \mathcal{G}$ with $\mathcal{H} = P222$, No. 16, and the supergroup $\mathcal{G} = P422$, No. 89, of index $[i] = 2$. Further, we suppose that the group $P222$ has specialized cell metrics specified as $a = b = c$. In the subgroup data of $P422$ there is only one entry for the subgroup $P222$ of index 2. We are interested in all $P422$ supergroups of index 2 of the group $P222$. The affine normalizer of $P422$ coincides with its Euclidean normalizer and it has the translations $(x+\frac{1}{2}, y+\frac{1}{2}, z)$, $(x, y, z+\frac{1}{2})$ and the inversion as additional generators (*cf. IT* A, Table 15.2.1.4). The Euclidean normalizer of $P222$ with $a = b = c$ coincides with its affine normalizer. It corresponds to the cubic group $Pm\bar{3}m$ with the additional generating translations $(x+\frac{1}{2}, y, z)$, $(x, y+\frac{1}{2}, z)$ and $(x, y, z+\frac{1}{2})$ (*cf. IT* A, Table 15.2.1.3). The decomposition of $\mathcal{N}(\mathcal{H})$ with respect to the intersection of the two normalizers contains six cosets, *i.e.* the group $P222$ has six supergroups $P422$ isomorphic to each other. The different supergroups, as calculated by *MINSUP*, are listed in Table 1.7.3.2. They are distinguished by their transformation matrix–column pairs $(\boldsymbol{P}, \boldsymbol{p})_r$ and the coset representatives of the decomposition of $\mathcal{G}_r$ with respect to $\mathcal{H}$. The existence of the six different supergroups becomes obvious if we consider the type and location of the symmetry elements corresponding to the listed coset representatives of the different supergroups (Table 1.7.3.2). Owing to the specialized metrics of $P222$, the fourfold axis of $P422$ can be chosen along any of the three orthorhombic axes. Accordingly, the six supergroups are distributed into three pairs. Comparison of the space-group diagrams of $P422$ and $P222$ (Fig. 1.7.3.5) shows that the two supergroups for each orientation of the fourfold axis correspond exactly to the two possible locations of the fourfold axis in the orthorhombic cell.

Table 1.7.3.2. *P422, No. 89, supergroups of P222, No. 16 (a = b = c), index 2, as determined by MINSUP*

The different supergroups are distinguished by the transformation matrices $(\boldsymbol{P}, \boldsymbol{p})_r$ and the coset representatives of the decomposition of $(P422)_r$ with respect to $\mathcal{H}$. (The unit element is taken as a coset representative in all cases and is not listed). The locations of the axes 4 are referred to the orthorhombic cell.

Supergroup	$(\boldsymbol{P}, \boldsymbol{p})_j$	Coset representative	Location of 4
$(P422)_1$	$\mathbf{a}, \mathbf{b}, \mathbf{c}; 0\,0\,0$	$(4_z \mid 0\,0\,0)$	$0\,0\,z$
$(P422)_2$	$\mathbf{a}, \mathbf{b}, \mathbf{c}; \frac{1}{2}\,0\,0$	$(4_z \mid \bar{\frac{1}{2}}\,\frac{1}{2}\,0)$	$\bar{\frac{1}{2}}\,0\,z$
$(P422)_3$	$\mathbf{b}, \mathbf{c}, \mathbf{a}; 0\,0\,0$	$(4_y \mid 0\,0\,0)$	$0\,y\,0$
$(P422)_4$	$\mathbf{b}, \mathbf{c}, \mathbf{a}; 0\,\frac{1}{2}\,0$	$(4_y \mid \bar{\frac{1}{2}}\,0\,\bar{\frac{1}{2}})$	$\bar{\frac{1}{2}}\,y\,0$
$(P422)_5$	$\mathbf{c}, \mathbf{a}, \mathbf{b}; 0\,0\,0$	$(4_x \mid 0\,0\,0)$	$x\,0\,0$
$(P422)_6$	$\mathbf{c}, \mathbf{a}, \mathbf{b}; \frac{1}{2}\,0\,0$	$(4_x \mid 0\,\bar{\frac{1}{2}}\,\frac{1}{2})$	$x\,\bar{\frac{1}{2}}\,0$

Example 1.7.3.2.2

Here we consider the supergroups $\mathcal{G}_r = a_r^{-1}\,\mathcal{G}\,a_r$ of $\mathcal{H}$ with $a_r \notin \mathcal{N}_{\mathcal{A}}(\mathcal{H})$. Consider the group *Pnma*, No. 62, and its minimal supergroups of type *Cmcm*, No. 63, of index 2. The group *Cmcm* has two maximal *Pnma* subgroups: $(Pnma)_1$ specified by $(\boldsymbol{P}, \boldsymbol{p})_1 = (\mathbf{b}, \mathbf{c}, \mathbf{a})$, and $(Pnma)_2$ with $(\boldsymbol{P}, \boldsymbol{p})_2 = (\mathbf{c}, \mathbf{a}, \mathbf{b}; \frac{1}{4}, \frac{1}{4}, 0)$. The Euclidean and affine normalizers of *Cmcm* and *Pnma* are identical and correspond to the group *Pmmm* with the additional translations $(x+\frac{1}{2}, y, z)$, $(x, y+\frac{1}{2}, z)$ and $(x, y, z+\frac{1}{2})$. Accordingly, the application of the normalizer procedure to any of the two group–subgroup pairs will not generate further equivalent supergroups. The first pair $Cmcm > (Pnma)_1$ gives rise to the minimal supergroup *Bbmm* (*Cmcm*, **b**, **c**, **a**). The second supergroup *Amma* (*Cmcm*, **c**, **a**, **b**) can only be obtained considering the second group–subgroup pair. Both supergroups are related by a cyclic

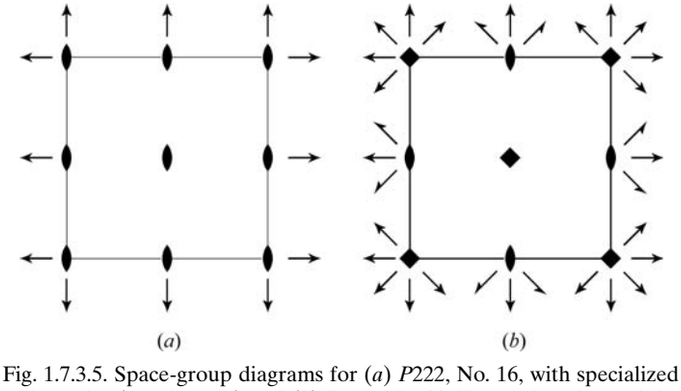

Fig. 1.7.3.5. Space-group diagrams for (*a*) *P222*, No. 16, with specialized cell metrics (see the text) and (*b*) *P422*, No. 89. For explanations of the space-group diagrams, see *IT* A Chapter 1.4.

rotation of the three axes which is not in the normalizer of $\mathcal{H}$ (or $\mathcal{G}$).

The number of supergroups of a space group $\mathcal{H}$ of a finite index is not always finite. This is the case of a space group $\mathcal{H}$ whose normalizer $\mathcal{N}(\mathcal{H})$ contains continuous translations in one, two or three independent directions (see *IT* A, Part 15). As typical examples one can consider the infinitely many centrosymmetric supergroups of the polar groups: there are no restrictions on the location of the additional inversion centre on the polar axis. For such group–supergroup pairs there could be up to three parameters *r*, *s* and *t* in the origin-shift column of the transformation matrix and in the translational part of the coset representatives. The parameters can have any value and each value corresponds to a different supergroup of the same space-group type.

1.7.3.2.2. The program CELLSUPER

The program *CELLSUPER* is an application similar to *CELLSUB* (*cf.* Section 1.7.3.1.4): in this case, the search is for the space-group types of supergroups $\mathcal{G}_s$ of $\mathcal{H}$ of a given maximum lattice index $[(i_L)_{\max}]$. The algorithm is similar to that of *CELLSUB*: using the data for the index and space-group types of minimal supergroups, the program constructs a tree of minimal supergroups starting from $\mathcal{H}$ and imposing the condition $[i_L] \leq [(i_L)_{\max}]$. The input data of *CELLSUPER* coincide with those of *CELLSUB* with the only difference being that they are referred to the low-symmetry group $\mathcal{H}$. The output data include:

(i) The space-group types of the supergroups $\mathcal{G}_s$ of $\mathcal{H}$ with the corresponding indices $[i]$, $[i_P]$ and $[i_L]$. The supergroups are classified into *t*-supergroups, *k*-supergroups and *general* supergroups.

(ii) A link to the *SUPERGROUPS* module (*cf.* Section 1.7.3.2.1) enables the calculation of all different supergroups $(\mathcal{G}_s)_r$ of $\mathcal{H}$ of the space-group type $\mathcal{G}_s$ and index $[i]$. Each supergroup $(\mathcal{G}_s)_r$ is specified by the corresponding transformation matrix relating the conventional bases of the supergroup and the group, and the representatives of the coset decomposition $(\mathcal{G}_s)_r : \mathcal{H}$.

1.7.3.2.3. The program COMMONSUPER

The program *COMMONSUPER* calculates the space-group types of common supergroups $\mathcal{G}$ of two space groups $\mathcal{H}_1$ and $\mathcal{H}_2$ for a given maximal lattice index $[(i_L)_{\max}]$. The procedure used is analogous to the one implemented in the program *COMMONSUBS* (*cf.* Section 1.7.3.1.5). The two sets of supergroups of $\mathcal{H}_1$ and of $\mathcal{H}_2$ are determined by the program *CELLSUPER*. The intersection of the sets of supergroups gives the set of the space-group types of the common supergroups $\{\mathcal{G}\}$ of $\mathcal{H}_1$ and $\mathcal{H}_2$ with $[i_L] \leq [(i_L)_{\max}]$. A relation between the indices $[i_1] = |\mathcal{G}|/|\mathcal{H}_1|$ and $[i_2] = |\mathcal{G}|/|\mathcal{H}_2|$ is obtained by imposing the structural requirement of equal numbers of formula units in the (primitive) unit cell of the common supergroup $\mathcal{G}$ obtained from the numbers of the formula units Z_1 and Z_2 of $\mathcal{H}_1$ and $\mathcal{H}_2$:

$$[i_2] = [i_1] \cdot \frac{Z_2}{Z_1} \cdot \frac{|\mathcal{P}_{\mathcal{H}_1}|}{|\mathcal{P}_{\mathcal{H}_2}|}. \qquad (1.7.3.2)$$

The program *COMMONSUPER* selects and lists those supergroups of the set $\{\mathcal{G}\}$ whose indices $[i_1] = |\mathcal{G}|/|\mathcal{H}_1|$ and $[i_2] = |\mathcal{G}|/|\mathcal{H}_2|$ satisfy the above condition.

The input data for *COMMONSUPER* include the specification of $\mathcal{H}_1$ and $\mathcal{H}_2$, the numbers of formula units per conventional unit cell, and the maximum lattice index $[(i_L)_{\max}]$. The output data of *COMMONSUPER* are:

(i) The space-group types of the common supergroups $\mathcal{G}$ of $\mathcal{H}_1$ and $\mathcal{H}_2$ with the indices $[i_1]$ and $[i_2]$, $[(i_L)_1]$ and $[(i_L)_2]$, and $[(i_P)_1]$ and $[(i_P)_2]$. Optional links to the programs *POINT* and *GENPOS* give access to data for the point group $\mathcal{P}_{\mathcal{G}}$ and the general positions of the supergroup $\mathcal{G}$.

(ii) A link to the *SUPERGROUPS* module (see Section 1.7.3.2.1) enables the calculation of all different supergroups $\mathcal{G}_r$ of $\mathcal{H}_1$ and $\mathcal{H}_2$ of a space-group type $\mathcal{G}$ and indices $[i_1]$ and $[i_2]$. Each supergroup $\mathcal{G}_r$ is specified by the corresponding transformation matrix relating the conventional bases of the supergroup and the group, and the representatives of the coset decomposition of $\mathcal{G}_r$ relative to $\mathcal{H}_1$ or $\mathcal{H}_2$.

Example 1.7.3.2.3

The program *COMMONSUPER* is useful in the search for structural relationships between structures whose symmetry groups $\mathcal{H}_1$ and $\mathcal{H}_2$ are not group–subgroup related. The derivation of the two structures as different distortions from a basic structure is a clear manifestation of such relationships. The symmetry group of the basic structure is a common supergroup of $\mathcal{H}_1$ and $\mathcal{H}_2$. Consider the ternary intermetallic compound CeAuGe. At 8.7 GPa a first-order phase transition is observed from a hexagonal arrangement (space group $P6_3mc$, No. 186, two formula units per unit cell, $Z_1 = 2$) into an orthorhombic high-pressure modification of symmetry *Pnma*, No. 62, $Z_2 = 4$ (Brouskov *et al.*, 2005). There is no group–subgroup relation between the symmetry groups of the high- and low-pressure structures. For $[(i_L)_{\max}] = 4$ the program finds two common supergroups of $\mathcal{H}_1 = P6_3mc$, $Z_1 = 2$ and $\mathcal{H}_2 = Pnma$, $Z_2 = 4$: (i) the group $P6_3/mmc$ with $[i_1] = 2$ and $[i_2] = 6$, and (ii) $P6/mmm$, with $[i_1] = 4$ and $[i_2] = 12$. The common basic structure of the AlB_2 type, proposed by Brouskov *et al.* (2005), corresponds to the common supergroup $P6/mmm$ found by *COMMONSUPER*.

1.7.4. Relations of Wyckoff positions for a group–subgroup pair of space groups

Consider two group–subgroup-related space groups $\mathcal{G} > \mathcal{H}$. Atoms that are symmetrically equivalent under $\mathcal{G}$, *i.e.* belong to the same orbit of $\mathcal{G}$, may become non-equivalent under $\mathcal{H}$, (*i.e.* the orbit splits) and/or their site symmetries may be reduced. The orbit relations induced by the symmetry reduction are the same for all orbits belonging to a Wyckoff position, so one can speak of Wyckoff-position relations or splitting of Wyckoff positions. Theoretical aspects of the relations of the Wyckoff positions for a group–subgroup pair of space groups $\mathcal{G} > \mathcal{H}$ have been treated in detail by Wondratschek (1993) (see also Section 1.5.3). A compilation of the Wyckoff-position splittings for all space groups and all their maximal subgroups is published as Part 3 of this volume. However, for certain applications it is easier to have the appropriate computer tools for the calculations of the Wyckoff-position splittings for $\mathcal{G} > \mathcal{H}$: for example, when $\mathcal{H}$ is not a maximal subgroup of $\mathcal{G}$, or when the space groups $\mathcal{G} > \mathcal{H}$ are related by transformation matrices different from those listed in the tables of Part 3. The program *WYCKSPLIT* (Kroumova, Perez-Mato & Aroyo, 1998) calculates the Wyckoff-position splittings for any group–subgroup pair. In addition, the program

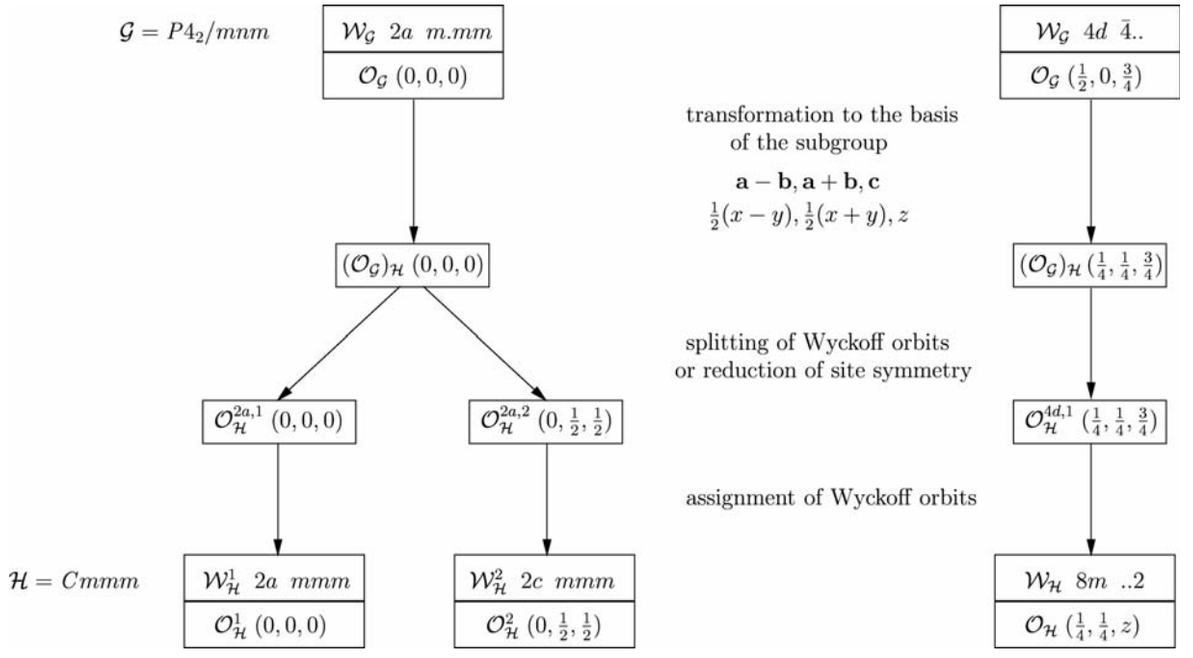

Fig. 1.7.4.1. Sequence of calculations of *WYCKSPLIT* for the splitting of the Wyckoff positions 2*a m.mm* (0, 0, 0) and 4*d* $\bar{4}$.. $(\frac{1}{2}, 0, \frac{3}{4})$ of $P4_2/mnm$, No. 136, with respect to its subgroup *Cmmm*, No. 65, of index 2. $(\mathcal{O}_\mathcal{G})_\mathcal{H}$ are the orbits of $P4_2/mnm$ in the basis of *Cmmm*.

provides further information on Wyckoff-position splittings that is not listed in Part 3, namely the relations between the representatives of the orbit of $\mathcal{G}$ and the corresponding representatives of the suborbits of $\mathcal{H}$.

1.7.4.1. The program WYCKSPLIT

To simplify the notation, we assume in the following that the group $\mathcal{G}$, its Wyckoff-position representatives and the points of the orbits are referred to the basis of the subgroup $\mathcal{H}$.

(1) *Splitting of the general position*. Consider the group–subgroup chain of space groups $\mathcal{G} > \mathcal{H}$ of an index [i]. The general-position orbits $\mathcal{O}_\mathcal{G}(X_0)$ have unique splitting schemes: they are split into [i] suborbits $\mathcal{O}_\mathcal{H}(X_{0,j})$ of the general position of the subgroup, *i.e.* they all are of the same multiplicity:

$$\mathcal{O}_\mathcal{G}(X_0) = \mathcal{O}_\mathcal{H}(X_{0,1}) \cup \ldots \cup \mathcal{O}_\mathcal{H}(X_{0,i}). \qquad (1.7.4.1)$$

This property is a direct corollary of the relation between the index [i] and the so-called reduction factors of the site-symmetry groups $\mathcal{S}_\mathcal{G}(X)$ and $\mathcal{S}_\mathcal{H}(X)$ of a point X in $\mathcal{G}$ and $\mathcal{H}$ (Wondratschek, 1993; see also Section 1.5.3).

The determination of the splitting of the general-position orbit $\mathcal{O}_\mathcal{G}(X_0)$ is then reduced to the selection of the [i] points $(X_{0,j})$ belonging to the [i] independent suborbits $\mathcal{O}_\mathcal{H}(X_{0,j})$ of $\mathcal{H}$, equation (1.7.4.1). Owing to the one-to-one mapping between the general-position points of $\mathcal{O}_\mathcal{G}(X_0)$ and the elements g of $\mathcal{G}$, the right cosets $\mathcal{H}g_j$ of the decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$ (*cf.* Definition 1.2.4.2.1) correspond to the suborbits $\mathcal{O}_\mathcal{H}(X_{0,j})$. In this way, the representatives of these cosets can be chosen as the [i] points $X_{0,j}$ in the decomposition of $\mathcal{O}_\mathcal{G}(X_0)$.

(2) *Splitting of a special position*. The calculation of the splitting of a special Wyckoff position $\mathcal{W}_\mathcal{G}$ involves the following steps:

(i) the determination of the suborbits $\mathcal{O}_\mathcal{H}(X_j)$ into which the special-Wyckoff-position orbit $\mathcal{O}_\mathcal{G}(X)$ has split;

(ii) the assignment of the orbits $\mathcal{O}_\mathcal{H}(X_j)$ to the Wyckoff positions $\mathcal{W}_\mathcal{H}^l$ of $\mathcal{H}$;

(iii) the determination of the correspondence between the points X_j^m of the suborbits $\mathcal{O}_\mathcal{H}(X_j)$ and the representatives of $\mathcal{W}_\mathcal{H}^l$.

The direct determination of the suborbits $\mathcal{O}_\mathcal{H}(X_j)$ is not an easy task. The restrictions on the site-symmetry groups $\mathcal{S}_\mathcal{H}(X_j)$ which follow from the reduction-factor lemma (*cf.* Section 1.5.3) are helpful but in many cases not sufficient for the determination of the suborbits. The solution used in our approach is based on the general-position decomposition, equation (1.7.4.1). It is important to note that each of the suborbits of the general position gives exactly one suborbit $\mathcal{O}_\mathcal{H}(X_j)$ when the variable parameters of $\mathcal{O}_\mathcal{H}(X_{0,j})$ are substituted by the corresponding parameters (fixed or variable) of the special position. The assignment of the suborbits to the Wyckoff positions of $\mathcal{H}$ is done by comparing the multiplicities of the orbits, the number of the variable parameters [the number of the variable parameters of $\mathcal{W}_\mathcal{H}^l$ is equal to or greater than that of $\mathcal{O}_\mathcal{H}(X_j)$] and the values of the fixed parameters. If there is more than one Wyckoff position

Table 1.7.4.1. *Wyckoff positions of Cmmm (No. 65) with multiplicities 2 and 8*

Each Wyckoff position is specified by its multiplicity and Wyckoff letter, site symmetry and a coordinate triplet of a representative element.

Wyckoff multiplicity and letter	Site symmetry	Representative element
2*d*	*mmm*	$(0, 0, \frac{1}{2})$
2*c*	*mmm*	$(\frac{1}{2}, 0, \frac{1}{2})$
2*b*	*mmm*	$(\frac{1}{2}, 0, 0)$
2*a*	*mmm*	(0, 0, 0)
8*q*	*..m*	$(x, y, \frac{1}{2})$
8*p*	*..m*	$(x, y, 0)$
8*o*	*.m.*	$(x, 0, z)$
8*n*	*m..*	$(0, y, z)$
8*m*	*..2*	$(\frac{1}{4}, \frac{1}{4}, z)$

of $\mathcal{H}$ satisfying these conditions, then the assignment is done by a direct comparison of the points of the suborbit $\mathcal{O}_{\mathcal{H}}(X_j)$ with those of a special $\mathcal{W}^l_{\mathcal{H}}$ orbit obtained by substitution of the variable parameters by arbitrary numbers. The determination of the explicit correspondences between the points of $\mathcal{O}_{\mathcal{H}}(X_j)$ and the representatives of $\mathcal{W}^l_{\mathcal{H}}$ is done by comparing the values of the fixed parameters and the variable-parameter relations in both sets.

The program *WYCKSPLIT* calculates the splitting of the Wyckoff positions for a group–subgroup pair $\mathcal{G} > \mathcal{H}$ given the corresponding transformation relating the coordinate systems of $\mathcal{G}$ and $\mathcal{H}$.

Input to *WYCKSPLIT*:

The program needs as input the following information:

(i) The specification of the space-group types $\mathcal{G}$ and $\mathcal{H}$ by their *IT* A numbers.

(ii) The transformation matrix–column pair $(\boldsymbol{P}, \boldsymbol{p})$ that relates the basis of $\mathcal{G}$ to that of $\mathcal{H}$. The user can input a specific transformation or follow a link to the *IT* A1 database for the maximal subgroups of $\mathcal{G}$. In the case of a non-maximal subgroup, the program *SUBGROUPGRAPH* provides the transformation matrix (or matrices) for a specified index of $\mathcal{H}$ in $\mathcal{G}$. The transformations are checked for consistency with the default settings of $\mathcal{G}$ and $\mathcal{H}$ used by the program.

The Wyckoff positions $\mathcal{W}_{\mathcal{G}}$ to be split can be selected from a list. In addition, it is possible to calculate the splitting of any orbit $O_{\mathcal{G}}(X)$ specified by the coordinate triplet of one of its points.

Output of *WYCKSPLIT*:

(i) Splittings of the selected Wyckoff positions $\mathcal{W}_{\mathcal{G}}$ into Wyckoff positions $\mathcal{W}^l_{\mathcal{H}}$ of the subgroup, specified by their multiplicities and Wyckoff letters.

(ii) The correspondence between the representatives of the Wyckoff position and the representatives of its suborbits is presented in a table where the coordinate triplets of the representatives of $\mathcal{W}_{\mathcal{G}}$ are referred to the bases of the group and of the subgroup.

WYCKSPLIT can treat group or subgroup data in unconventional settings if the transformation matrices to the corresponding conventional settings are given.

Example 1.7.4.1.1

To illustrate the calculation of the Wyckoff-position splitting we consider the group–subgroup pair $P4_2/mnm$ (No. 136) > *Cmmm* (No. 65) of index 2, see Fig. 1.7.4.1. The relation between the conventional bases $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ of the group and of the subgroup $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ is retrieved by the program *MAXSUB* and is given by $\mathbf{a}' = \mathbf{a} - \mathbf{b}$, $\mathbf{b}' = \mathbf{a} + \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$. The general position of $P4_2/mnm$ splits into two suborbits of the general position of *Cmmm*:

$$16k\ 1\ (x, y, z) \rightarrow 16r\ 1\ (x_1, y_1, z_1) \cup 16r\ 1\ (x_2, y_2, z_2).$$

This splitting is directly related to the coset decomposition of $P4_2/mnm$ with respect to *Cmmm*. As coset representatives, *i.e.* as points which determine the splitting of the general position, one can choose $X_{0,1} = (x_1, y_1, z_1)$ and $X_{0,2} = (x_2, y_2, z_2) = (y, x + \frac{1}{2}, z + \frac{1}{2})$) (referred to the basis of the subgroup).

The splitting of any special Wyckoff position is obtained from the splitting of the general position. The consecutive steps of the splittings of the special positions $4d\ \bar{4}..\ (\frac{1}{2}, 0, \frac{3}{4})$ and $2a\ m.mm\ (0, 0, 0)$ are shown in Fig. 1.7.4.1. First it is necessary to transform the representatives of $\mathcal{W}_{\mathcal{G}}$ to the basis of $\mathcal{H}$, which gives the orbits $(\mathcal{O}_{\mathcal{G}})_{\mathcal{H}}(0, 0, 0)$ and $(\mathcal{O}_{\mathcal{G}})_{\mathcal{H}}(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$. The substitution of the values $x = 0$, $y = 0$, $z = 0$ in the coordinate triplets of the decomposed general position of $\mathcal{G}$ (*cf.* the corresponding output of *WYCKSPLIT*) gives two suborbits of multiplicity 2 for the $2a$ position: $\mathcal{O}^{2a,1}_{\mathcal{H}}(0, 0, 0)$ and $\mathcal{O}^{2a,2}_{\mathcal{H}}(0, \frac{1}{2}, \frac{1}{2})$. The assignment of the suborbits $\mathcal{O}^{2a,j}_{\mathcal{H}}$ to the Wyckoff positions of $\mathcal{H}$ (*cf.* Table 1.7.4.1) is straightforward. Summarizing: the Wyckoff position $2a\ m.mm\ (0, 0, 0)$ splits into two independent positions of *Cmmm* with no site-symmetry reduction:

$$2a\ m.mm\ (0, 0, 0) \rightarrow 2a\ mmm\ (0, 0, 0) \cup 2c\ mmm\ (0, \tfrac{1}{2}, \tfrac{1}{2}).$$

No splitting occurs for the case of the special $4d$ position orbit: the result is one orbit of multiplicity 8, $\mathcal{O}^{4d,1}_{\mathcal{H}}(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$. The assignment of $\mathcal{O}^{4d,1}_{\mathcal{H}}(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ is also obvious: there are five Wyckoff positions of *Cmmm* of multiplicity 8 but four of them are discarded as they have fixed parameters 0 or $\frac{1}{2}$ (Table 1.7.4.1). The orbit $\mathcal{O}^{4d,1}_{\mathcal{H}}$ belongs to the Wyckoff position $8m\ ..2\ (\frac{1}{4}, \frac{1}{4}, z)$.

As expected, the sum of the site-symmetry reduction factors equals the index of *Cmmm* in $P4_2/mnm$ for both cases (*cf.* Section 1.5.3). The loss of the fourfold inversion axis results in the appearance of an additional degree of freedom corresponding to the variable parameter of $8m\ ..2\ (\frac{1}{4}, \frac{1}{4}, z)$.

References

Aroyo, M. I., Kirov, A., Capillas, C., Perez-Mato, J. M. & Wondratschek, H. (2006). *Bilbao Crystallographic Server. II. Representations of crystallographic point groups and space groups. Acta Cryst.* A**62**, 115–128.

Aroyo, M. I., Perez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A. & Wondratschek, H. (2006). *Bilbao Crystallographic Server: I. Databases and crystallographic computing programs*. *Z. Kristallogr.* **221**, 15–27.

Brouskov, V., Hanfland, M., Pöttgen, R. & Schwarz, U. (2005). *Structural phase transitions of CeAuGe at high pressure*. *Z. Kristallogr.* **220**, 122–127.

Capillas, C. (2006). *Métodos de la cristalografía computacional en el análisis de transiciones de fase estructurales*. PhD thesis, Universidad del País Vasco, Spain.

Capillas, C., Kroumova, E., Aroyo, M. I., Perez-Mato, J. M., Stokes, H. T. & Hatch, D. M. (2003). *SYMMODES: a software package for group-theoretical analysis of structural phase transitions*. *J. Appl. Cryst.* **36**, 953–954.

Capillas, C., Perez-Mato, J. M. & Aroyo, M. I. (2007). *Maximal symmetry transition paths for reconstructive phase transitions. J. Phys. Condens. Matter*, **19**, 275203.

International Tables for Crystallography (2005). Vol. A, *Space-Group Symmetry*, edited by Th. Hahn, 5th ed. Dordrecht: Kluwer Academic Publishers.

International Tables for Crystallography (2002). Vol. E, *Subperiodic Groups*, edited by V. Kopský & D. B. Litvin. Dordrecht: Kluwer Academic Publishers.

Ivantchev, S., Kroumova, E., Aroyo, M. I., Perez-Mato, J. M., Igartua, J. M., Madariaga, G. & Wondratschek, H. (2002). *SUPERGROUPS – a computer program for the determination of the supergroups of space groups*. *J. Appl. Cryst.* **35**, 511–512.

Ivantchev, S., Kroumova, E., Madariaga, G., Pérez-Mato, J. M & Aroyo, M. I. (2000). *SUBGROUPGRAPH: a computer program for analysis of group–subgroup relations between space groups*. *J. Appl. Cryst.* **33**, 1190–1191.

Koch, E. (1984). *The implications of normalizers on group–subgroup relations between space groups*. *Acta Cryst.* A**40**, 593–600.

Koch, E. & Müller, U. (1990). *Euklidische Normalisatoren für trikline und monokline Raumgruppen bei spezieller Metrik des Translationengitters*. *Acta Cryst.* A**46**, 826–831.

Kroumova, E., Perez-Mato, J. M. & Aroyo, M. I. (1998). *WYCKSPLIT: a computer program for determination of the relations of Wyckoff positions for a group–subgroup pair*. *J. Appl. Cryst.* **31**, 646.

Kroumova, E., Perez-Mato, J. M., Aroyo, M. I., Ivantchev, S., Madariaga, G. & Wondratschek, H. (1998). *The Bilbao Crystallographic Server: a web site with crystallographic tools using the International Tables for Crystallography*. *Abstracts of the 18th European Crystallographic Meeting*, Prague, Czech Republic.

Noheda, B., Cox, D. E., Shirane, G., Gonzalo, J. A., Cross, L. E. & Park, S.-E. (1999). *A monoclinic ferroelectric phase in the* $Pb(Zr_{1-x}Ti_x)O_3$ *solid solutions*. *Appl. Phys. Lett.* **74**, 2059.

Noheda, B., Gonzalo, J. A., Cross, L. E, Guo, R., Park, S.-E., Cox, D. E. & Shirane, G. (2000). *Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of* $Pb(Zr_{0.52}Ti_{0.48})O_3$. *Phys. Rev. B*, **61**, 8687–8695.

Wondratschek, H. (1993). *Splitting of Wyckoff positions (orbits)*. *Mineral. Petrol.* **48**, 87–96.

Wondratschek, H. & Aroyo, M. I. (2001). *The application of Hermann's group* $\mathcal{M}$ *in group–subgroup relations between space groups*. *Acta Cryst.* A**57**, 311–320.