

1.6. Relating crystal structures by group–subgroup relations

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1.6.1. Introduction

Symmetry relations using crystallographic group–subgroup relations have proved to be a valuable tool in crystal chemistry and crystal physics. Some important applications include:

- (1) Structural relations between crystal-structure types can be worked out in a clear and concise manner by setting up family trees of group–subgroup relations (see following sections).
- (2) Elucidation of problems concerning twinned crystals and antiphase domains (see Section 1.6.6).
- (3) Changes of structures and physical properties taking place during phase transitions; applications of Landau theory (Aizu, 1970; Aroyo & Perez-Mato, 1998; Birman, 1966*a,b*, 1978; Cracknell, 1975; Howard & Stokes, 2005; Igartua *et al.*, 1996; Izyumov & Syromyatnikov, 1990; Landau & Lifshitz, 1980; Lyubarskii, 1960; Salje, 1990; Stokes & Hatch, 1988; Tolédano & Tolédano, 1987).
- (4) Prediction of crystal-structure types and calculation of the numbers of possible structure types (see Section 1.6.4.7).
- (5) Solution of the phase problem in the crystal structure analysis of proteins (Di Costanzo *et al.*, 2003).

Bärnighausen (1975, 1980) presented a standardized procedure to set forth structural relations between crystal structures with the aid of symmetry relations between their space groups. For a review on this subject see Müller (2004). Short descriptions are given by Chapuis (1992) and Müller (2006). The main concept is to start from a simple, highly symmetrical crystal structure and to derive more and more complicated structures by distortions and/or substitutions of atoms. Similar to the ‘diagrams of lattices of subgroups’ used in mathematics, a tree of group–subgroup relations between the space groups involved, now called a *Bärnighausen tree*, serves as the main guideline. The highly symmetrical starting structure is called the *aristotype* after Megaw (1973) or *basic structure* after Buerger (1947, 1951); other terms used in the literature on phase transitions in physics are *prototype* or *parent structure*. The derived structures are the *hettotypes* or *derivative structures*. In Megaw’s (1973) terminology, the structures mentioned in the tree form a *family of structures*.

The structure type to be chosen as the aristotype depends on the specific problem and, therefore, the term aristotype cannot be defined in a strict manner. For example, a body-centred packing of spheres (space group $Im\bar{3}m$) can be chosen as the aristotype for certain intermetallic structures. By symmetry reduction due to a loss of the centring, the CsCl type (space group $Pm\bar{3}m$) can be derived. However, if all the structures considered are ionic, there is no point in starting from the body-centred packing of spheres and one can choose the CsCl type as the aristotype.

1.6.2. The symmetry principle in crystal chemistry

The usefulness of symmetry relations is intimately related to the symmetry principle in crystal chemistry. This is an old principle based on experience which has been worded during its long history in rather different ways. Bärnighausen (1980) summarized it in the following way:

- (1) In crystal structures the arrangement of atoms reveals a pronounced tendency towards the highest possible symmetry.
- (2) Counteracting factors due to special properties of the atoms or atom aggregates may prevent the attainment of the highest possible symmetry. However, in most cases the deviations from the ideal symmetry are only small (key word: pseudosymmetry).
- (3) During phase transitions and solid-state reactions which result in products of lower symmetry, the higher symmetry of the starting material is often indirectly preserved by the formation of oriented domains.

Aspect (1) is due to the tendency of atoms of the same kind to occupy equivalent positions, as stated by Brunner (1971). This has physical reasons: depending on chemical composition, the kind of chemical bonding, electron configuration of the atoms, relative sizes of the atoms, pressure, temperature *etc.*, there exists *one* energetically most favourable surrounding for atoms of a given species which all of these atoms strive to attain.

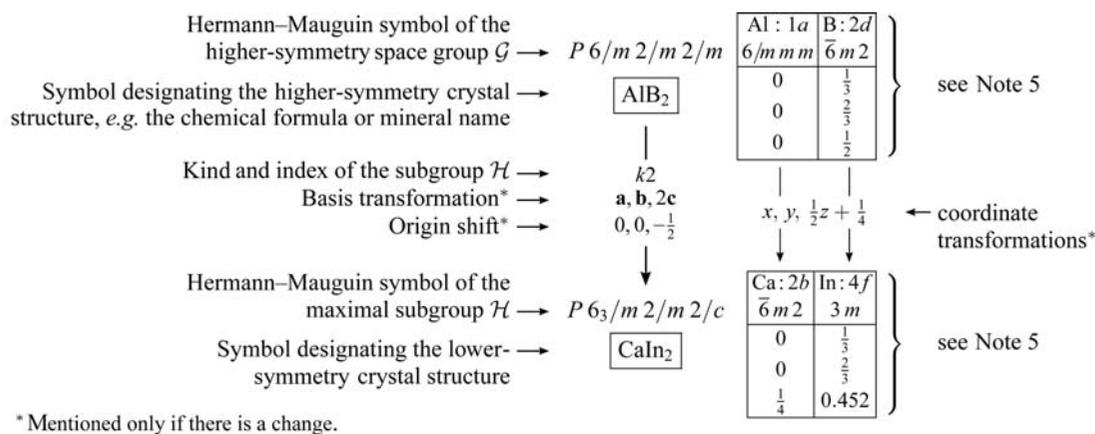
Aspect (2) of the symmetry principle is exploited in the following sections. Factors that counteract the attainment of the highest symmetry include: (1) stereochemically active lone electron pairs; (2) Jahn–Teller distortions; (3) covalent bonds; (4) Peierls distortions; (5) ordered occupation of originally equivalent sites by different atomic species (substitution derivatives); (6) partial occupation of voids in a packing of atoms; (7) partial vacation of atomic positions; (8) freezing (condensation) of lattice vibrations (soft modes) giving rise to phase transitions; and (9) ordering of atoms in a disordered structure.

Aspect (3) of the symmetry principle has its origin in an observation by Bernal (1938). He noted that in the solid state reaction $Mn(OH)_2 \rightarrow MnOOH \rightarrow MnO_2$ the starting and the product crystal had the same orientation. Such reactions are called *topotactic reactions* after Lotgering (1959) (for a more exact definition see Giovanoli & Leuenberger, 1969). In a paper by Bernal & Mackay (1965) we find the sentence: ‘One of the controlling factors of topotactic reactions is, of course, symmetry. This can be treated at various levels of sophistication, ranging from Lyubarskii’s to ours, where we find that the simple concept of Buridan’s ass illumines most cases.’ According to the metaphor of Buridan (French philosopher, died *circa* 1358), the ass starves to death between two equal and equidistant bundles of hay because it cannot decide between them. Referred to crystals, such an asinine behaviour would correspond to an absence of phase transitions or solid-state reactions if there are two or more energetically equivalent orientations of the domains of the product. Crystals, of course, do not behave like the ass; they take both.

1.6.3. Bärnighausen trees

To represent symmetry relations between different crystal structures in a concise manner, we construct a tree of group–subgroup relations in a modular design, beginning with the space group of the aristotype at its top. Each module represents one

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Explanatory Notes

(1) Possible kinds of maximal subgroups \mathcal{H} of a given space group \mathcal{G} :

Symbol	Term	Meaning
t	<i>translationengleiche</i>	\mathcal{G} and \mathcal{H} have the same translations; the crystal class of \mathcal{H} is of lower symmetry than that of \mathcal{G}
k	<i>klassengleiche</i>	\mathcal{G} and \mathcal{H} belong to the same crystal class; \mathcal{H} has lost translational symmetry, its primitive unit cell is larger than that of \mathcal{G}
i	isomorphic	\mathcal{G} and \mathcal{H} belong to the same or the enantiomorphic space-group type; \mathcal{H} has lost translational symmetry, its unit cell is larger than that of \mathcal{G}

(2) The index i of a subgroup is the number of cosets of \mathcal{H} in \mathcal{G} . The number of symmetry operations of \mathcal{H} is $1/i$ of those of \mathcal{G} (in the same way as the amount of even numbers is half the amount of all integer numbers).

(3) Basis transformation: The three basis vectors of \mathcal{H} are expressed as linear combinations of the basis vectors \mathbf{a} , \mathbf{b} , \mathbf{c} of \mathcal{G} . Never omit this information if there is a change of the basis vectors.

(4) Origin shift: The coordinate triplet of the origin of \mathcal{H} is given in the coordinate system of \mathcal{G} . Never omit this information if there is an origin shift.

(5) Additional information (only if there is enough space; otherwise this information must be listed in a separate table): The atomic positions are given in a box next to the space-group symbol in the following way:

element symbol: Wyckoff label site symmetry
x
y
z

The coordinates are given for one atom in the asymmetric unit. If a numeric value is fixed by symmetry, it is stated as 0 or as a fraction, e.g. 0 , $\frac{1}{4}$, $\frac{1}{2}$. Free parameters are stated as decimal numbers, e.g. 0.0 , 0.25 , 0.53 . If possible, align the site-symmetry symbols in one line with the space-group symbol.

Fig. 1.6.3.1. Scheme of the formulation of the smallest step of symmetry reduction connecting two related crystal structures.

step of symmetry reduction to a *maximal* subgroup. Therefore, we have to discuss only one of these modules in detail.

For two structures we want to interrelate, we place their space-group symbols one below the other and indicate the direction of the symmetry reduction by an arrow pointing downwards (Fig. 1.6.3.1). Since they are more informative, it is advisable to use only the full Hermann–Mauguin symbols. In the middle of the arrow we insert the kind of maximal subgroup and the index of symmetry reduction, using the abbreviations t for *translationengleiche*, k for *klassengleiche* and i for isomorphic. If the unit cell changes, we also insert the new basis vectors expressed as vector sums of the basis vectors of the higher-symmetry cell. If there is an origin shift, we enter this as a triplet of numbers which express the coordinates of the new origin referred to the coordinate system of the higher-symmetry cell. This is a shorthand notation for the transformation matrices. *Any change of the basis vectors and the origin is essential information that should never be omitted.*

If the atomic coordinates of two related crystal structures differ because of different settings of their unit cells, the similarities of the structures become less clear and may even be obscured. Therefore, it is recommended to *avoid cell transformations whenever possible*. If necessary, it is much better to fully

exploit the possibilities offered by the Hermann–Mauguin symbolism and to choose nonconventional space-group settings [see Chapter 4.3 of *International Tables for Crystallography* Volume A (2005) and Section 3.1.4 of this volume].

Origin shifts also tend to obscure relations. However, they often cannot be avoided. There is no point in deviating from the standard origin settings, because otherwise much additional information would be required for an unequivocal description. *Note:* The coordinate triplet specifying the origin shift in the group–subgroup arrow refers to the *coordinate system of the higher-symmetry space group*, whilst the corresponding changes of the atomic coordinates refer to the coordinate system of the subgroup and therefore are different. Details are given in Section 3.1.3. Also note that in the tables of Parts 2 and 3 of this volume the origin shifts are given in different ways. In Part 2 they refer to the higher-symmetry space group. In Part 3 (relations of the Wyckoff positions) they are given only as parts of the coordinate transformations, *i.e.* in the coordinate systems of the subgroups. As explained in the Appendix, the chosen origin shifts themselves also differ in Parts 2 and 3; an origin transformation taken from Part 3 may be different from the one given in Part 2 for the same group–subgroup relation. If needed, one has to calculate the corresponding values with the formulae given in Section 3.1.3.

1. SPACE GROUPS AND THEIR SUBGROUPS

The calculation of coordinate changes due to cell transformations and origin shifts is prone to errors. Some useful hints are given in Section 1.6.5.

For space groups with two possible choices of origin ('origin choice 1' and 'origin choice 2'), the choice is specified by a superscript (1) or (2) after the space-group symbol, for example $P4/n^{(2)}$. The setting of rhombohedral space groups is specified, if necessary, by superscript (rh) or (hex). Occasionally it may be useful to use a nonconventional rhombohedral 'reverse' setting, *i.e.* with the centring vectors $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{3})$ instead of 'obverse' with $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$; this is specified by superscript (rev), for example $R\bar{3}^{(rev)}$.

In a Bärnighausen tree containing several group–subgroup relations, it is recommended that the vertical distances between the space-group symbols are kept proportional to the logarithms of the corresponding indices. This way all subgroups that are at the same hierarchical distance, *i.e.* at the same index, from the aristotype appear on the same line.

If several paths can be constructed from one space group to a general subgroup, *via* different intermediate groups, usually there is no point in depicting all of them. There is no general recipe indicating which of several possible paths should be preferred. However, crystal-chemical and physical aspects should be used as a guide. First of all, the chosen intermediate groups should be:

- (1) Space groups having actually known representatives.
- (2) Space groups that disclose a physically realizable path for the symmetry reduction. Observed phase transitions should be given high priority. For phase transitions that are driven by certain lattice vibrations, those intermediate space groups should be considered that are compatible with these lattice modes (*i.e.* irreducible representations; Stokes & Hatch, 1988).
- (3) In the case of substitution derivatives: Space groups showing a splitting of the relevant Wyckoff position(s). These intermediate groups allow for substitution derivatives, even if no representative is yet known.

Bärnighausen trees sometimes contain intermediate space groups which, in Howard & Stokes' (2005) opinion, 'have no physical significance'. As an example, they cite the phase transition induced by the displacement of the octahedrally coordinated cations in a cubic perovskite along the $+z$ axis. This lowers the symmetry directly from $Pm\bar{3}m$ to the non-maximal subgroup $P4mm$, skipping the intermediate space group $P4/mmm$. In this particular case, $P4/mmm$ 'has no physical significance' in the sense that it cannot actually occur in this kind of phase transition. However, the intermediate space group $P4/mmm$ can occur in other instances (*e.g.* in order–disorder transitions) and it has been found among several perovskites. In addition, we are not dealing merely with phase transitions. Intermediate space groups do have significance for several reasons: (1) Any step of symmetry reduction reduces the restrictions for every Wyckoff position (either the site symmetry is reduced or the position splits into independent positions, or both happen); every intermediate space group offers new scope for effects with physical significance, even if none have yet been observed. (2) Skipping intermediate space groups in the tree of group–subgroup relations reduces the informative value of the symmetry relations. For example, it is no longer directly evident how many *translationengleiche* and *klassengleiche* steps are involved; this is useful to decide how many and what kind of twin domains may appear in a phase transition or topotactic reaction (see Sections 1.2.7 and 1.6.6).

Group–subgroup relations are of little value if the usual crystallographic data are not given for every structure. The mere mention of the space groups is insufficient. The atomic coordinates are of special importance. It is also important to present all structures in such a way that their relations become clearly visible. In particular, all atoms of the asymmetric units should exhibit strict correspondence, so that their positional parameters can immediately be compared.

For all structures, the same coordinate setting and among several symmetry-equivalent positions for an atom the same location in the unit cell should be chosen, if possible. For all space groups, except $Im\bar{3}m$ and $Ia\bar{3}d$, one can choose several different equivalent sets of coordinates describing one and the same structure in the same space-group setting. It is by no means a simple matter to recognize whether two differently documented structures are alike or not (the literature abounds with examples of 'new' structures that really had been well known). One is often forced to transform coordinates from one set to another to attain the necessary correspondence. In Section 15.3 of Volume A (editions 1987–2005) and in a paper by Koch & Fischer (2006) one can find a procedure for and examples of how to interconvert equivalent coordinate sets with the aid of the Euclidean normalizers of the space groups. *Note:* For enantiomorphic (chiral) space groups like $P3_1$ this procedure will yield equivalent sets of coordinates without a change of chirality; for chiral structures in non-enantiomorphic (non-chiral) space groups like $P2_12_12_1$ the sets of coordinates include the enantiomorphic pairs [for the distinction between chiral and non-chiral space groups see Flack (2003)].

If space permits, it is useful to list the site symmetries and the coordinates of the atoms next to the space-group symbols in the Bärnighausen tree, as shown in Fig. 1.6.3.1 and in the following examples. If there is not enough space, this information must be provided in a separate table.

1.6.4. The different kinds of symmetry relations among related crystal structures

In this section, using a few simple examples, we point out the different kinds of group–subgroup relations that are important among related (homeotypic) crystal structures.

The crystal structures of two compounds are *isotypic* if their atoms are arranged in the same way and if they have the same or the enantiomorphic space group. The absolute values of the lattice dimensions and interatomic distances may differ, and small deviations are permitted for non-fixed coordinates of corresponding atoms. The axial ratios and interaxial angles must be similar. Two structures are *homeotypic* if the conditions for isotypism are relaxed because: (1) their space groups differ, allowing for a group–subgroup relation; (2) the geometric conditions differ (axial ratios, interaxial angles, atomic coordinates); or (3) corresponding atomic positions are occupied by various atomic species (substitution derivatives). (Lima-de-Faria *et al.*, 1990.)

1.6.4.1. Translationengleiche maximal subgroups

The space group $Pbca$ of PdS_2 is a *translationengleiche* maximal subgroup of $Pa\bar{3}$, the space group of pyrite (FeS_2 ; Bärnighausen, 1980). The threefold axes of the cubic space group have been lost, the index of the symmetry reduction is 3. As shown in Fig. 1.6.4.1, the atomic coordinates have not changed