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, 1966a,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: pseudo-symmetry).
(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