

## 1. SPACE GROUPS AND THEIR SUBGROUPS

$$\begin{aligned} \mathbf{x}_{mn} &= \mathbb{P}_2^{-1} \mathbb{P}_1^{-1} \mathbf{x}_{cb} \\ \begin{pmatrix} x_{mn} \\ y_{mn} \\ z_{mn} \\ 1 \end{pmatrix} &= \begin{pmatrix} \frac{1}{2} & 0 & -1 & \frac{1}{4} \\ -\frac{1}{2} & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & -\frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{4} \\ 1 & 1 & 1 & -\frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ 1 \end{pmatrix}, \end{aligned}$$

which is the same as

$$\begin{aligned} x_{mn} &= -\frac{1}{2}y_{cb} - \frac{1}{2}z_{cb} + \frac{1}{2}, & y_{mn} &= \frac{1}{2}y_{cb} - \frac{1}{2}z_{cb} + \frac{1}{4}, \\ z_{mn} &= x_{cb} + y_{cb} + z_{cb} - \frac{3}{4}. \end{aligned}$$

**1.6.6. Comments concerning phase transitions and twin domains**

When a compound forms several polymorphic forms, a Bärnighausen tree can serve to show whether second-order phase transitions are feasible between them and what kinds of twin domains may be formed during such a transition. The possible kinds of domains can also be deduced for first-order phase transitions involving a group–subgroup relation and for topotactic reactions.

Second-order (continuous) phase transitions are only possible if there is a direct (not necessarily maximal) group–subgroup relation between the space groups of the two phases. If there is no such relation, for example, if two polymorphic forms can be related only by a common supergroup, the phase transformation can only be of first order. The condition of a direct group–subgroup relation is a necessary but not a sufficient condition; the phase transition can still be of first order.

The domain structure of crystalline phases that often results at solid-state phase transitions and during topotactic reactions can be transparently interpreted with the aid of symmetry considerations (Section 1.2.7; Bärnighausen, 1980; Janovec & Přívratká, 2003; van Tendeloo & Amelinckx, 1974; Wondratschek & Jeitschko, 1976). A domain structure is the result of nucleation and growth processes. The orientational relations between the phases before and after the transformation, as a rule, are not the result of a homogeneous process involving a simultaneous motion of the atoms in a single crystal. The crystalline matrix of the substrate rather governs the preferred orientation adopted by the nuclei that are formed during the course of the nucleation process. The crystallites that result from the subsequent growth of the nuclei maintain their orientations. Under these circumstances, aspect 3 of the symmetry principle, as stated in Section 1.6.2, is fully effective. A phase transition that is connected with a symmetry reduction will result in new phases that consist of

- (i) *twin domains* if the formed phase belongs to a crystal class with reduced symmetry, or
- (ii) *antiphase domains* (translational domains) if translational symmetry is lost.

The total number of domains, of course, depends on the number of nucleation sites. The number of different domain kinds, however, is ruled by the index of the symmetry reduction. At a *translationengleiche* symmetry reduction of index 3 (*t*3

group–subgroup relation) we can expect twins with three kinds of domains, having three different orientations. An isomorphic subgroup of index 5 (*i*5 relation), since it is a *klassengleiche* symmetry reduction, will entail five kinds of antiphase domains. If the symmetry reduction includes several steps (in a chain of several maximal subgroups), the domain structure will become more complicated. With two *t*2 group–subgroup relations, we can expect twins of twins with two kinds of domains each. In the example of Fig. 1.2.7.1, we have a sequence of one *t*2 and one *k*2 step; therefore, as explained in a more rigorous manner in Example 1.2.7.3.4, we can expect two kinds of twin domains having two different orientations and, in addition, two kinds of antiphase domains. The actual number of observable domain kinds may be less than expected if a domain kind is not formed during nucleation. This can be controlled by the nucleation conditions; for example, an external electric field can suppress the formation of more than one kind of differently oriented ferroelectric domains.

In the physical literature, phase transitions between *translationengleiche* space groups are sometimes called *ferroic* transitions, those between *klassengleiche* space groups are *non-ferroic*.

As mentioned at the end of Section 1.6.4.5, a common subgroup of two space groups usually is not suitable for relating two crystal structures. Just so, a common crystallographic subgroup is unfit to explain the mechanism for a reconstructive, first-order phase transition. Such mechanisms have been proposed repeatedly (see, e.g., Capillas *et al.*, 2007, and references therein). Like in a second-order transition, continuous atomic movements have been assumed, leading first to a structure with the reduced symmetry of a common subgroup, followed by a symmetry increase to the space group of the second phase. However, a first-order transition always shows hysteresis, which means that the initial and the final phase coexist during the transition and that there is a phase boundary between them. The transition begins at a nucleation site, followed by the growth of the nucleus (see, e.g., Binder, 1987; Chaitkin & Lubensky, 1995; Chandra Shekar & Gavinda Rajan, 2001; Christian, 2002; Doherty, 1996; Gunton, 1984; Herbststein, 2006; Jena & Chaturvedi, 1992; Wayman & Bhadeshia, 1996). The reconstruction of the structure and the necessary atomic motions occur at the phase boundary between the receding old phase and the growing new phase. Any intermediate state is restricted to this interface between the two phases. *It is impossible to assign a three-dimensional space group to an interface.* In addition, while the interface advances through the crystal, the atoms at the interface do not linger in a static state. A space group can only be assigned to a static state (time-dependent phenomena are not covered by space-group theory).

**1.6.7. Exercising care in the use of group–subgroup relations**

Using the tables of this volume or from other sources or using computer programs as offered by the Bilbao Crystallographic Server (see Chapter 1.7), it may be easy to search for group–subgroup relations between space groups of crystal structures. This should only be done bearing in mind and explicitly stating a crystallographic, physical or chemical context. It is senseless to construct relations in a purely formal manner, ‘just for fun’, without a sound crystal-chemical or physical foundation. There exist no clear criteria to determine what is a ‘sound foundation’, but crystallographic, chemical and physical common sense and knowledge should always be taken into consideration.

## 1.6. RELATING CRYSTAL STRUCTURES BY GROUP-SUBGROUP RELATIONS

In addition, by experience we know that setting up trees of group-subgroup relations is susceptible to pitfalls. Some sources of errors are: not taking into account necessary origin shifts; wrong origin shifts; wrong basis and/or coordinate transformations; unnecessary basis transformations just for the sake of clinging on to standard space-group settings; lack of distinction between space groups and space-group types; lack of keeping track of the development of the atomic positions from group to subgroup; using different space-group or coordinate settings for like structures. If the group-subgroup relations are correct, but origin shifts or basis transformations have not been stated, this can cause subsequent errors and misunderstandings.

### References

- Aizu, K. (1970). Possible species of ferromagnetic, ferroelectric, and ferroelastic crystals. *Phys. Rev. B*, **2**, 754–772.
- Aroyo, M. I. & Perez-Mato, J. M. (1998). Symmetry-mode analysis of displacive phase transitions using *International Tables for Crystallography*. *Acta Cryst.* **A54**, 19–30.
- Bärnighausen, H. (1975). Group-subgroup relations between space groups as an ordering principle in crystal chemistry: the ‘family tree’ of perovskite-like structures. *Acta Cryst.* **A31**, part S3, 01.1–9.
- Bärnighausen, H. (1980). Group-subgroup relations between space groups: a useful tool in crystal chemistry. *MATCH Commun. Math. Chem.* **9**, 139–175.
- Baur, W. H. (1994). Rutile type derivatives. *Z. Kristallogr.* **209**, 143–150.
- Baur, W. H. (2007). The rutile type and its derivatives. *Crystallogr. Rev.* **13**, 65–113.
- Baur, W. H. & Fischer, R. X. (2000, 2002, 2006). Landolt-Börnstein, Numerical data and functional relationships in science and technology, New Series. Group IV, Vol. 14, Zeolite type crystal structures and their chemistry. Berlin: Springer.
- Baur, W. H. & McLarnan, T. J. (1982). Observed wurtzite derivatives and related tetrahedral structures. *J. Solid State Chem.* **42**, 300–321.
- Becht, H. Y. & Struikmans, R. (1976). A monoclinic high-temperature modification of potassium carbonate. *Acta Cryst.* **B32**, 3344–3346.
- Bernal, J. D. (1938). Conduction in solids and diffusion and chemical change in solids. Geometrical factors in reactions involving solids. *Trans. Faraday Soc.* **34**, 834–839.
- Bernal, J. D. & Mackay, A. L. (1965). Topotaxy. *Tschermaks mineralog. petrogr. Mitt., Reihe 3* (now *Mineral. Petrol.*), **10**, 331–340.
- Billiet, Y. (1973). Les sous-groupes isosymboliques des groupes spatiaux. *Bull. Soc. Fr. Minéral. Cristallogr.* **96**, 327–334.
- Binder, K. (1987). Theory of first-order phase transitions. *Rep. Prog. Phys.* **50**, 783–859.
- Birman, J. L. (1966a). Full group and subgroup methods in crystal physics. *Phys. Rev.* **150**, 771–782.
- Birman, J. L. (1966b). Simplified theory of symmetry change in second-order phase transitions: application to  $V_3Si$ . *Phys. Rev. Lett.* **17**, 1216–1219.
- Birman, J. L. (1978). *Group-theoretical methods in physics*, edited by P. Kramer & A. Rieckers, pp. 203–222. New York: Springer.
- Bock, O. & Müller, U. (2002a). Symmetrieverwandtschaften bei Varianten des Perowskit-Typs. *Acta Cryst.* **B58**, 594–606.
- Bock, O. & Müller, U. (2002b). Symmetrieverwandtschaften bei Varianten des  $ReO_3$ -Typs. *Z. Anorg. Allg. Chem.* **628**, 987–992.
- Brostigen, G. & Kjeskhus, G. A. (1969). Redetermined crystal structure of  $FeS_2$  (pyrite). *Acta Chem. Scand.* **23**, 2186–2188.
- Brunner, G. O. (1971). An unconventional view of the ‘closest sphere packings’. *Acta Cryst.* **A27**, 388–390.
- Buerger, M. J. (1947). Derivative crystal structures. *J. Chem. Phys.* **15**, 1–16.
- Buerger, M. J. (1951). *Phase transformations in solids*, ch. 6. New York: Wiley.
- Byström, A., Hök, B. & Mason, B. (1941). The crystal structure of zinc metaantimonate and similar compounds. *Ark. Kemi Mineral. Geol.* **15B**, 1–8.
- Capillas, C., Perez-Mato, J. M. & Aroyo, M. I. (2007). Maximal symmetry transition paths for reconstructive phase transitions. *J. Phys. Condens. Matter*, **19**, 275203.
- Chaitkin, P. M. & Lubensky, T. C. (1995). *Principles of Condensed Matter Physics* (reprints 2000, 2003). Cambridge University Press.
- Chandra Shekar, N. V. & Gavinda Rajan, K. (2001). Kinetics of pressure induced structural phase transitions – a review. *Bull. Mater. Sci.* **24**, 1–21.
- Chapuis, G. C. (1992). Symmetry relationships between crystal structures and their practical applications. *Modern Perspectives in Inorganic Chemistry*, edited by E. Parthé, pp. 1–16. Dordrecht: Kluwer Academic Publishers.
- Christian, J. W. (2002). *The Theory of Transformations in Metals and Alloys*, 3rd ed. Oxford: Pergamon.
- Cracknell, A. P. (1975). *Group Theory in Solid State Physics*. New York: Taylor and Francis Ltd/Pergamon.
- Di Costanzo, L., Forneris, F., Geremia, S. & Randaccio, L. (2003). Phasing protein structures using the group-subgroup relation. *Acta Cryst.* **D59**, 1435–1439.
- Doherty, R. D. (1996). Diffusive phase transformations. *Physical Metallurgy*, ch. 15. Amsterdam: Elsevier.
- Entner, P. & Parthé, E. (1973). PtGeSe with cobaltite structure, a ternary variant of the pyrite structure. *Acta Cryst.* **B29**, 1557–1560.
- Ercit, T. S., Foord, E. E. & Fitzpatrick, J. J. (2001). Ordoñezite from the Theodoso Soto mine, Mexico: new data and structure refinement. *Can. Mineral.* **40**, 1207–1210.
- Flack, H. D. (2003). Chiral and achiral structures. *Helv. Chim. Acta*, **86**, 905–921.
- Foecker, A. J. & Jeitschko, W. (2001). The atomic order of the pnictogen and chalcogen atoms in equiatomic ternary compounds  $TPnCh$  ( $T = Ni, Pd; Pn = P, As, Sb; Ch = S, Se, Te$ ). *J. Solid State Chem.* **162**, 69–78.
- Giovanoli, D. & Leuenberger, U. (1969). Über die Oxidation von Manganoxidhydroxid. *Helv. Chim. Acta*, **52**, 2333–2347.
- Grønqvold, F. & Røst, E. (1957). The crystal structure of  $PdSe_2$  and  $PdS_2$ . *Acta Cryst.* **10**, 329–331.
- Gunton, J. D. (1984). The dynamics of random interfaces in phase transitions. *J. Stat. Phys.* **34**, 1019–1037.
- Herbstein, F. H. (2006). On the mechanism of some first-order enantiotropic solid-state phase transitions: from Simon through Ubbelohde to Mnyukh. *Acta Cryst.* **B62**, 341–383.
- Hoffmann, W. & Jäniche, W. (1935). Der Strukturtyp von  $AlB_2$ . *Naturwissenschaften*, **23**, 851.
- Howard, C. J. & Stokes, H. T. (2005). Structures and phase transitions in perovskites – a group-theoretical approach. *Acta Cryst.* **A61**, 93–111.
- Iandelli, A. (1964).  $MX_2$ -Verbindungen der Erdalkali- und seltenen Erdmetalle mit Gallium, Indium und Thallium. *Z. Anorg. Allg. Chem.* **330**, 221–232.
- Igartua, J. M., Aroyo, M. I. & Perez-Mato, J. M. (1996). Systematic search of materials with high-temperature structural phase transitions: Application to space group  $P2_12_12_1$ . *Phys. Rev. B*, **54**, 12744–12752.
- International Tables for Crystallography* (2005). Vol. A, *Space-Group Symmetry*, edited by Th. Hahn, corrected reprint of 5th ed. Dordrecht: Kluwer Academic Publishers.
- Izumov, Y. A. & Syromyatnikov, V. N. (1990). *Phase Transitions and Crystal Symmetry*. Dordrecht: Kluwer Academic Publishers.
- Janovec, V. & Přívratská, J. (2003). Domain structures. *International Tables for Crystallography*, Vol. D, *Physical Properties of Crystals*, edited by A. Authier, ch. 3.4. Dordrecht: Kluwer Academic Publishers.
- Jansen, M. & Feldmann, C. (2000). Strukturverwandtschaften zwischen cis-Natriumhyponitrit und den Alkalimetallcarbonaten  $M_2CO_3$  dargestellt durch Gruppe-Untergruppe Beziehungen. *Z. Kristallogr.* **215**, 343–345.
- Jena, A. K. & Chaturvedi, M. C. (1992). *Phase Transformations in Materials*. Englewood Cliffs: Prentice Hall.
- Jørgenson, J.-E. & Smith, R. I. (2006). On the compression mechanism of  $FeF_3$ . *Acta Cryst.* **B62**, 987–992.
- Koch, E. & Fischer, W. (2006). Normalizers of space groups: a useful tool in crystal description, comparison and determination. *Z. Kristallogr.* **221**, 1–14.
- Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics*, 3rd ed., Part 1, pp. 459–471. London: Pergamon. (Russian: *Statisticheskaya Fizika*, chast 1. Moskva: Nauka, 1976; German: *Lehrbuch der theoretischen Physik*, 6. Aufl., Bd. 5, Teil 1, S. 436–447. Berlin: Akademie-Verlag, 1984.)