

Summary and Comments

There has been a number of recognized cases in which complicated structures in a chemical system in fact consist of building units having a simple structure type; seeming complications of the structures basically lie in the manner of combination of the units. A majority of those structures form a series of structures referred to by Magnéli (1953) as homologous series. Twinning on the unit cell level has been recognized to be a useful crystallographic operation for understanding such a series of complex structures as forming a homologous series, provided that crystallographic slip is considered to be one of the cell-twin operations. Discussion on the class of inorganic structures based on crystallographic slips, known as CS structures, however, was beyond the scope of this book.

The term '*tropochemical cell-twinning*' has been introduced, after the suggestion made by Martin J. Buerger, to denote a specific class of cell-twinning which assumes a vehicle of changing chemical composition to yield the series of structures of the phases in a chemical system. Any phase of the structural series is neither a polymorphic form nor a polytypic variant of another but is a distinct phase because a specific range of chemical composition, though generally very small, is essentially associated with each phase. The cell-twinning, we are interested in here, is never concerned with such a chemical deviation as being due to impurities. One of the notable features shown by those chemical series is that their distinct (or distinct range of) chemical compositions can be explicable as a function of the breadth of the unit slab (cell-twin unit). This situation may be rephrased in such a way that the difference in chemical composition between phases is related to the difference in frequency of cell-twinning.

The chemical series based on tropochemical cell-twinning (TCT) known to date share the following features:

1. The scheme of cation substitution that yields the chemical series, now considered, in most cases falls in the category which may be called *heterovalent vacancy coupled* (HVVC) substitution. Namely, a cation species, Me' , that substitutes for Me of parent structure has a valence state which is different from that of Me .

Two cases may arise for Me' ; in one case Me' has ionic radius which is slightly larger than Me , or in the other Me' assumes such an electron configuration that gives rise to a steric distortion in the manner of the anion arrangement about it. Thus, the substitutions of Y^{3+} for Mn^{2+} and Sc^{3+} for Mg^{2+} that characterize $xMnS \cdot Y_2S_3$ and $EnIV-N$ series, respectively, fall in the former case, while those of Sb^{3+} for Pb^{2+} and Bi^{3+} for Pb^{2+} that characterize the TCT series in the $PbS-Sb_2S_3$ and $PbS-Bi_2S_3$ systems, respectively, fall in the latter. The substitution of Mn^{3+} for Fe^{3+} which characterize the pinakiolite homologous series may also be related to the latter case although it is not of the HVVC kind, exceptionally.

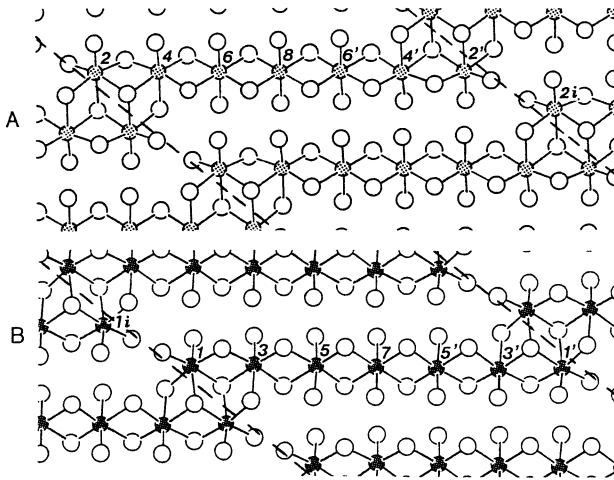
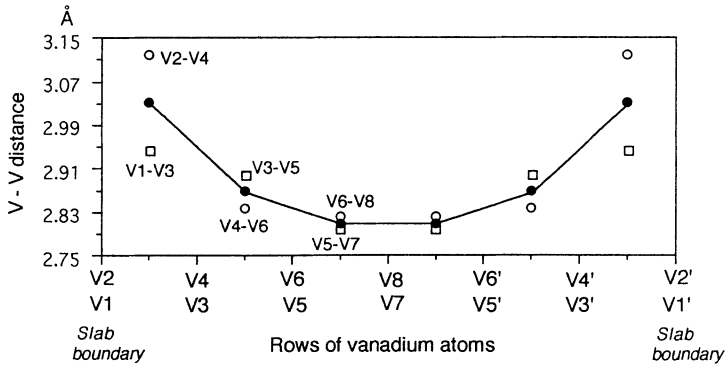


Fig. 1. The V-V distances in the two symmetrically independent types of chains of VO_6 octahedra, seven octahedra long, spanning the rutile-like slabs in the structure of V_7O_{13} . The vanadium atoms in each chain are indicated, along the horizontal axis, successively from that at one end of the row of vanadium atoms to that at the other end. Open circles indicate the V-V distances in the chain of the A layer and squares indicate those in the chain of the layer B. Each solid circle represents the mean of the V-V distance indicated by an open circle and that by a square in the same column. The slab boundaries in the A and B layers are indicated by broken lines (the data of V-V distances are taken from Horiuchi *et al.*, 1976).

develop her theory of order-disorder (OD) structures (Dornberger-Schiff, 1964) based on the theory of Brandt's groupoids. More generally, Sadanaga (*loc. cit.*) has shown that a set of local operations and symmetry operations of the space group of a complex structure form a groupoid defined by Brandt (1926), thus, developing his theory of *space groupoids*. Then, the fact that we have encountered the specific cell-twin operation in the case of the pinakolite group, may lead to the following

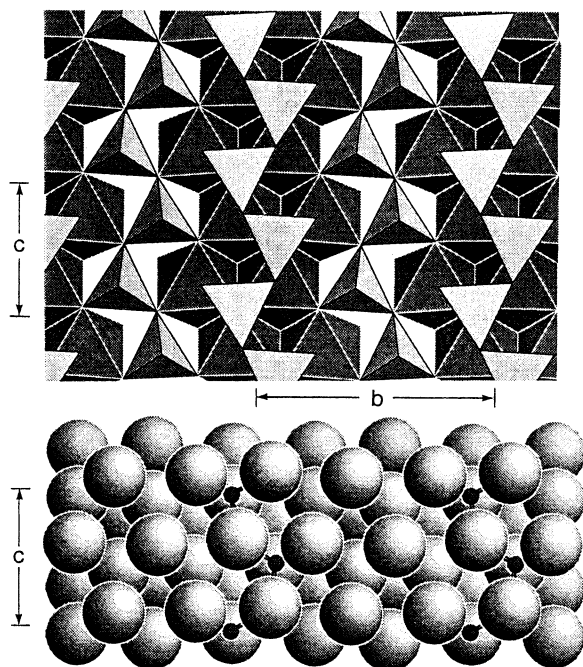


Fig. 2. (Top) The structure of monoclinic ($C2/c$) $MgGeO_3$ projected onto (100), showing the polyhedral arrangement in a (100) slab, 6 Å thick, which consists of a layer of tetrahedral chains placed on a layer of octahedral bands. (Bottom) A packing diagram of the same projection of the structure. The large spheres denote oxygen atoms and small spheres germanium atoms.

expression: *cell-twin operation may be such a symmetry operation that is characteristic of the elements of space groupoids.*

As a possible physical process underlying such a geometrical aspect of cell-twin operations, an atomic model has been suggested for the formation of plane defects during the crystal growth of pinakiolite (Chapter 6). Regarding the structures of pinakiolite related oxyborates, one should note the quite recent study reported by Norrestam *et al.* (1994). They have shown that the general structural scheme of the ludwigite type, characterized by alternate layers of high-valent cations and of low-valent cations, is supported by some empirical extended Hückel electronic band calculations performed on Fe-ludwigite $Fe_3O_2BO_3$ and Co-ludwigite $Co_3O_2BO_3$.

Observations by means of high resolution electron microscopy (HREM) of the chemical phases, here considered, have made substantial contributions to the progress of study of those chemical phases. Among them, HREM observation on the mechanism of transformations of $Pb_6Bi_2S_9$ and $Pb_3Bi_2S_6$ to PbS (Colaitis *et al.*, 1982; Skowron and Tilley, 1986) and the crystal growth model of pinakiolite related oxyborates suggested by Bovin and Norrestam (1990) based on their HREM observation are

notable. These results in addition to the various structural features mentioned above seem to suggest that topochemical cell-twinning might have genetic significance as suggested for the Pb-rich members of the lillianite homologous series.

In any case, the concept of topochemical cell-twinning, only elementarily discussed in this book, is not only useful for better understanding of complex structures, including their chemical intricacies, but also in predicting structures or the existence of new crystalline phases.

REFERENCES

- Andersson, S. and Hyde, B. G. (1974): vid. Chapter 1.
Bovin, J.-O. and Norrestam, R. (1990): vid. Chapter 6.
Brandt, H. (1926): vid. Chapter 1.
Colaïtis *et al.* (1982): vid. Chapter 3.
Dornberger-Schiff, K.: On order-disorder structures (OD-structures). *Acta Cryst.* **9** (1956) 593–601.
Dornberger-Schiff, K. (1964): vid. Chapter 1.
Horiuchi, H., Morimoto, N., and Tokonami, M. (1976): vid. Chapter 1.
Ito, T. and Sadanaga, R.: On the crystallographic space groupoid. *Proc. Japan Acad.* **52** (1976) 119–121.
Magnéli, A. (1953): vid. Chapter 1.
Norrestam, R., Kritikos, M., Nielsen, K., Sjøtofte, I., and Thorup, N.: Structural characterizations of two synthetic Ni-ludwigites, and some semiempirical EHTB calculations on the ludwigite structure type. *J. Solid State Chem.* **111** (1994) 217–223.
Sadanaga, R.: Extension of the theory of space groups, II. Two ways of extension. *J. Cryst. Soc. Japan* **5** (1963) 10–20 (in Japanese).
Sadanaga, R. (1978): vid. Chapter 1.
Skowron, A. and Tilley, R. J. D. (1986): vid. Chapter 3.
Thompson, J. B. (1970): vid. Chapter 5.
Yamanaka, T., Hirano, M., and Takéuchi, Y.: A high temperature transition in MgGeO₃ from clinopyroxene (*C2/c*) type to orthopyroxene (*Pbca*) type. *Am. Mineral.* **70** (1985) 365–374.