

9. BASIC STRUCTURAL FEATURES

possible positions indicated by the superposition structure. An analysis of the Fourier transform relevant to the above OD groupoid family showed that the Patterson function calculated with coefficients $|\Delta(hkl)|^2 = |F(hkl)|^2 + |F(\bar{h}kl)|^2$ shows interatomic vectors *within* any single OD layer, and it turned out that even a first generalized projection of the function yields the necessary ‘yes/no’ answer.

The structural principle is shown in Fig. 9.2.2.20.

There are two MDO polytypes in this family. Both are monoclinic (*c* axis unique) and consist of equivalent triples of OD layers. The first, MDO₁, is periodic after two layers and has symmetry $A2/m$. The second, MDO₂, is periodic after four layers, has symmetry $F2/m$ and basis vectors $2\mathbf{a}$, \mathbf{b} , \mathbf{c} . Domains of MDO₁ were present in all crystals (the system of diffuse maxima, mentioned above), but some of them also contained small proportions of MDO₂.

Later, single crystals of pure periodic MDO₁ were also found in specimens prepared hydrothermally (Rabenau, private communication). The results of a structure analysis confirmed the previous results but indicated desymmetrization (Đurovič,

1979). The atomic coordinates deviated significantly from the ideal OD model; the monoclinic angle became 90.5° . Even the family diffractions, which in the disordered crystals exhibited an orthorhombic symmetry, deviated significantly from it in their positions and intensities.

9.2.2.3.4. Remarks for authors

When encountering a polytypic substance showing disorder, many investigators try to find in their specimens a periodic single crystal suitable for a structure analysis by current methods. So far, no objections. But a common failing is that they often neglect to publish a detailed account of the disorder phenomena observed on their diffraction photographs: presence or absence of diffuse streaks, their position in reciprocal space, positions of diffuse maxima, suspicious twinning, non-space-group absences, higher symmetry of certain subsets of diffractions, *etc.* These data should always be published, even if the author does not interpret them: otherwise they will inevitably be lost. Similarly, preliminary diffraction photographs (even of poor quality) showing these phenomena and the crystals themselves should be preserved – they may be useful for someone in the future.

9.2.2.4. List of some polytypic structures

A few examples of some less-common polytypic structures published up to 1994 are listed below:

Minerals: McGillite (Iijima, 1982), tridymite (Wennemer & Thompson, 1984), pyrosmalite (Takéuchi, Ozawa & Takahata, 1983), zirconolite (White, Segall, Hutchison & Barry, 1984), Ti-biotite (Zhukhlistov, Zvyagin & Pavlishin, 1990), diamond (Phelps, Howard & Smith, 1993), scholzite (Taxer, 1992), fiedlerite (Merlino, Pasero & Perchiazzi, 1994), penkvilskite (Merlino, Pasero, Artioli & Khomyakov, 1994), lengebachite – non-commensurate structure (Makovický, Leonardsen & Moelo, 1994).

Inorganic compounds: Borates with general formula $RAI_3(BO_3)_4$, where $R = Y, Nd, Gd$ (Belokoneva & Timchenko,

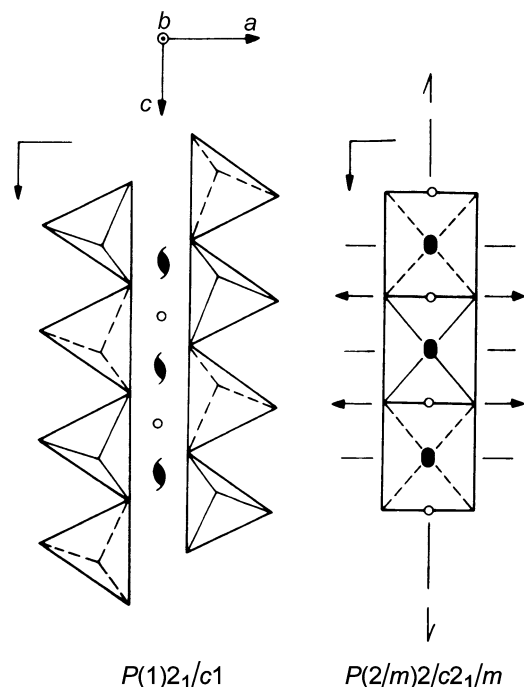


Fig. 9.2.2.18. The two kinds of OD layers in the stibivanite family (after Merlino *et al.*, 1989).

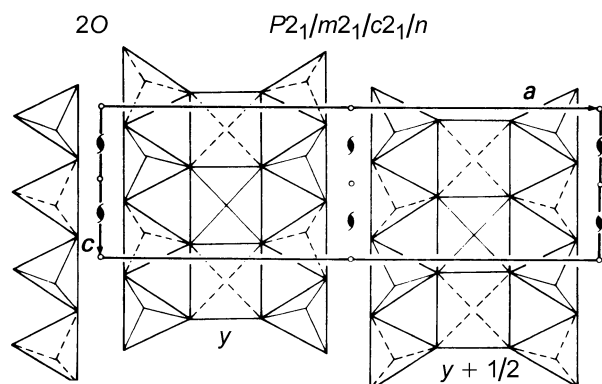


Fig. 9.2.2.19. The structure of stibivanite-2O (after Merlino *et al.*, 1989).

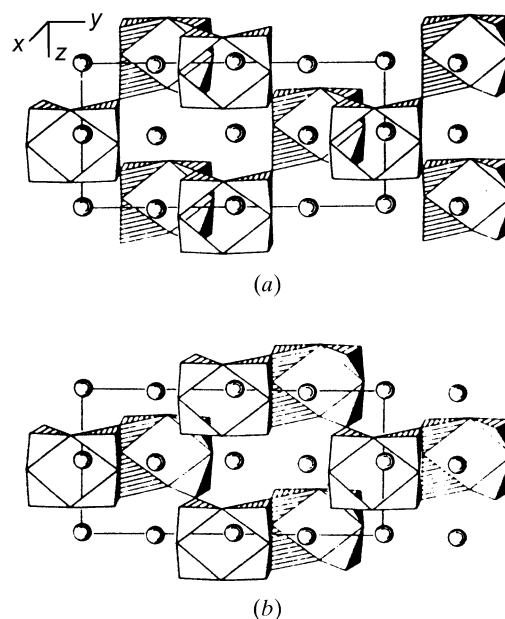


Fig. 9.2.2.20. The structural principle of $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$. The shared corners of the pyramids are occupied by the Hg atoms; unshared corners are occupied by the S atoms. A pair of layers, but only the Cl atoms at their common boundary, are drawn. The two geometrically equivalent arrangements (a) and (b) are shown.

9.2. LAYER STACKING

1983), BaCrO₃ (Chamberland, 1983), hexacyanocomplexes of transition metals (Jagner, 1985), chromium iron carbides (Kowalski, 1985), Fe_{1-x}S (Kuban, 1985), hexagonal copper(I) ferrite (Effenberger, 1991), PbS · 18TiS₂ – a modulated structure (van Smaalen & de Boer, 1992), α-LiNH₄SO₄ (Tomaszewski, 1992), fullerene C₆₀ (de Boer, van Smaalen, Petříček, Dušek, Verheijen & Meijer, 1994).

Organic compounds: Oxalates (Fichtner-Schmittler, 1979), primetine (Jarchow & Schmalte, 1985), 2-hydroxy-4-methoxy-2*H*-1,4-benzoxazin-3-one, C₉H₉NO₄ (Kutschabsky, Kretschmer, Schrauber, Dathe & Schneider, 1986), carbamazepine dihydrate (Reck & Dietz, 1986), piroxicam (Reck, Dietz, Laban, Günther, Bannier & Höhne, 1988), *E*-octadecanoic acid (Kaneko, Sakashita, Kobayashi, Kitagawa, Matsuura & Suzuki, 1994).

Metals, intermetallic compounds and alloys: Alloys are treated in a monograph by Nikolin (1984); a lecture note by Amelinckx (1986) gives details of high-resolution electron microscopy and

examples of the investigation of some alloys but also of other polytypic structures. Special papers: Li metal (Schwarz & Blaschko, 1990), Zr(FeCr)₂ Laves phases (Burany & Northwood, 1991), doped Co–W and Co–Mo alloys (Nikolin, Babkevich, Izdkovskaya & Petrova, 1993).

Further data are given in articles by Bailey *et al.* (1977), Dornberger-Schiff (1979), Zvyagin (1988), Baronnet (1992) and Zorkii & Nesterova (1993).

High-resolution electron microscopy (HREM) applied in the structure analysis of (also disordered) polytypic substances: orientite (Mellini, Merlino & Pasero, 1986), ardennite (Pasero & Reinecke, 1991), pseudowollastonite (Ingrin, 1993), laurionite and paralaurionite (Merlino, Pasero & Perchiazzi, 1993), perovskites in the system La₄Ti₃O₁₂–LaTiO₃ (Bontchev, Darriet, Darriet, Weill, Van Tendeloo & Amelinckx, 1993), baumhauerite (Pring & Graeser, 1994), bementite (Heinrich, Eggleton & Guggenheim, 1994), parsettensite (Eggleton & Guggenheim, 1994).