9.2. LAYER STACKING

Table 9.2.1.4. *Intrinsic fault configurations in the 9R ($A_0B_1A_2C_0A_1C_2B_0C_1B_2$, ...) structure*

Fault configuration *ABC* sequence	Subscript notation
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_0\ A\ C\ B\ C\ B\ A\ B\ A$ ...	$I_{0,0}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_1\ B\ A\ B\ A\ C\ A\ C\ B$ ...	$I_{0,1}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_2\ B\ C\ B\ A\ B\ A\ C\ A$ ...	$I_{0,2}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_{\bar{0}}\ B\ C\ A\ C\ A\ B\ A\ B$ ...	$I_{0,\bar{0}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_{\bar{1}}\ A\ B\ A\ B\ C\ B\ C\ A$ ...	$I_{0,\bar{1}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A_0 \mid C_{\bar{2}}\ A\ C\ A\ B\ A\ B\ C\ B$ ...	$I_{0,\bar{2}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_0\ A\ C\ B\ C\ B\ A\ B\ A$ ...	$I_{1,0}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_1\ B\ A\ B\ A\ C\ A\ C\ B$ ...	$I_{1,1}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_2\ B\ C\ B\ A\ B\ A\ C\ A$ ...	$I_{1,2}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_{\bar{0}}\ B\ C\ A\ C\ A\ B\ A\ B$ ...	$I_{1,\bar{0}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_{\bar{1}}\ A\ B\ A\ B\ C\ B\ C\ A$ ...	$I_{1,\bar{1}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B_1 \mid C_{\bar{2}}\ A\ C\ A\ B\ A\ B\ C\ B$ ...	$I_{1,\bar{2}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_0\ C\ B\ A\ B\ A\ C\ A\ C$ ...	$I_{2,0}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_1\ A\ C\ A\ C\ B\ C\ B\ A$ ...	$I_{2,1}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_2\ A\ B\ A\ C\ A\ C\ B\ C$ ...	$I_{2,2}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_{\bar{0}}\ A\ B\ C\ B\ C\ A\ C\ A$ ...	$I_{2,\bar{0}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_{\bar{1}}\ C\ A\ C\ A\ B\ A\ B\ C$ ...	$I_{2,\bar{1}}$
... $A\ B\ A\ C\ A\ C\ B\ C\ B\ A\ B\ A_2 \mid B_{\bar{2}}\ C\ B\ C\ A\ C\ A\ B\ A$ ...	$I_{2,\bar{2}}$

Note: $I_{0,\bar{0}}$ and $I_{1,\bar{1}}$, $I_{0,\bar{1}}$ and $I_{1,\bar{2}}$, $I_{0,\bar{2}}$ and $I_{2,\bar{1}}$, and $I_{1,2}$ and $I_{2,0}$ are crystallographically equivalent.

Reverse:

$$\begin{array}{ccccccccc} h & h & k & h & h & k & h & h & k \\ \dots\ A_{\bar{0}} & C_{\bar{1}} & A_{\bar{2}} & B_{\bar{0}} & A_{\bar{1}} & B_{\bar{2}} & C_{\bar{0}} & B_{\bar{1}} & C_{\bar{2}}\ \dots. \\ & -\mathbf{s} & +\mathbf{s} & +\mathbf{s} & -\mathbf{s} & +\mathbf{s} & +\mathbf{s} & -\mathbf{s} & +\mathbf{s} \end{array}$$

In the obverse setting, we choose the origin layer (0 type) in the h configuration such that the next layer is cyclically shifted whereas in the reverse setting the origin layer ($\bar{0}$ type) in the h configuration is related to the next layer through an anticyclic shift. Tables 9.2.1.3 and 9.2.1.4 list the crystallographically unique intrinsic fault configurations in the 6*H* and 9*R* structures.

9.2.1.8.1. *Structure determination of one-dimensionally disordered crystals*

Statistical distribution of stacking faults in close-packed structures introduces disorder along the stacking axis of the close-packed layers. As a result, one observes on a single-crystal diffraction pattern not only normal Bragg scattering near the nodes of the reciprocal lattice of the average structure but also continuous diffuse scattering between the nodes owing to the incomplete destructive interference of scattered rays. Just like the extra polytype reflections, the diffuse streaks are also confined to only those rows for which $h - k \neq 0 \bmod 3$. A complete description of the real structure of such one-dimensionally disordered polytypes requires knowledge of the average structure as well as a statistical specification of the fluctuations due to stacking faults in the electron-density distribution of the average structure. This cannot be accomplished by the usual consideration of the normal Bragg reflections alone but requires a careful analysis of the diffuse intensity distribution as well (Pandey, Kabra & Lele, 1986).

The first step in the structure determination of one-dimensionally disordered structures is the specification of the geometry of stacking faults and their distribution, both of which require postulation of the physical processes responsible for their formation. An entirely random distribution of faults may result during the layer-by-layer growth of a crystal (Wilson, 1942) or during plastic deformation (Paterson, 1952). On the other hand, when faults bring about the change in the stacking sequence of layers during solid-state transformations, their distribution is non-random (Pandey, Lele & Krishna, 1980*a,b,c*; Pandey & Lele, 1986*a,b*; Kabra, Pandey & Lele, 1986). Unlike growth faults, which are accidentally introduced in a sequential fashion from one end of the stack of layers to the other during the actual crystal growth, stacking faults involved in solid-state transformations are introduced in a random space and time sequence (Kabra, Pandey & Lele, 1988*b*). Since the pioneering work of Wilson (1942), several different techniques have been advanced for the calculation of intensity distributions along diffuse streaks making use of Markovian chains, random walk, stochastic matrices, and the Paterson function for random and non-random distributions of stacking faults on the assumption that these are introduced in a sequential fashion (Hendricks & Teller, 1942; Jagodzinski 1949*a,b*; Kakinoki & Komura, 1954; Johnson, 1963; Prasad & Lele, 1971; Cowley, 1976; Pandey, Lele & Krishna, 1980*a,b*). The limitations of these methods for situations where non-randomly distributed faults are introduced in the random space and time sequence have led to the use of Monte Carlo techniques for the numerical calculation of pair correlations whose Fourier transforms directly yield the intensity distributions (Kabra & Pandey, 1988).

The correctness of the proposed model for disorder can be verified by comparing the theoretically calculated intensity distributions with those experimentally observed. This step is in principle analogous to the comparison of the observed Bragg intensities with those calculated for a proposed structure in the structure determination of regularly ordered layer stackings. This comparison cannot, however, be performed in a straightforward manner for one-dimensionally disordered crystals due to special problems in the measurement of diffuse intensities using a single-crystal diffractometer, stemming from incident-beam divergence, finite size of the detector slit, and multiple scattering. The problems due to incident-beam divergence in the measurement of the diffuse intensity distributions were first

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pointed out by Pandey & Krishna (1977) and suitable correction factors have recently been derived by Pandey, Prasad, Lele & Gauthier (1987). A satisfactory solution to the problem of structure determination of one-dimensionally disordered stackings must await proper understanding of all other factors that may influence the true diffraction profiles.

9.2.2. Layer stacking in general polytypic structures
(By S. Ďurovič)

9.2.2.1. *The notion of polytypism*

The common property of the structures described in Section 9.2.1 was the stacking ambiguity of adjacent layer-like structural units. This has been explained by the geometrical properties of close packing of equal spheres, and the different modifications thus obtained have been called *polytypes*.

This phenomenon was first recognized by Baumhauer (1912, 1915) as a result of his investigations of many SiC single crystals by optical goniometry. Among these, he discovered three *types* and his observations were formulated in five statements:

(1) all three types originate simultaneously in the same melt and seemingly also under the same, or nearly the same, conditions;

(2) they can be related in a simple way to the same axial ratio (each within an individual primary series);

(3) any two types (I and II, II and III) have certain faces in common but, except the basal face, there is no face occurring simultaneously in all three types;

(4) the crystals belonging to different, but also to all three, types often form intergrowths with parallel axes;

(5) any of the three types exhibits a typical X-ray diffraction pattern and thus also an individual molecular or atomic structure.

Baumhauer recognized the special role of these *types* within modifications of the same substance and called this phenomenon *polytypism* – a special case of polymorphism. The later determination of the crystal structures of Baumhauer's three types indicated that his results can be interpreted by a family of structures consisting of identical layers with hexagonal symmetry and differing only in their stacking mode.

The stipulation that the individual polytypes grow from the same system and under (nearly) the same conditions influenced for years the investigation of polytypes because it logically led to the question of their growth mechanism.

In the following years, many new polytypic substances have been found. Their crystal structures revealed that polytypism is restricted neither to close packings nor to heterodesmic 'layered structures' (*e.g.* CdI$_2$ or GaSe; *cf.* homodesmic SiC or ZnS; see §§9.2.1.2.2 to 9.2.1.2.4), and that the reasons for a stacking ambiguity lie in the crystal chemistry – in all cases the geometric nearest-neighbour relations between adjacent layers are preserved. The preservation of the bulk chemical composition was not questioned.

Some discomfort has arisen from refinements of the structures of various phyllosilicates. Here especially the micas exhibit a large variety of isomorphous replacements and it turns out that a certain chemical composition stabilizes certain polytypes, excludes others, and that the layers constituting polytypic structures need not be of the same kind. But subsequently the opinion prevailed that the sequence of individual kinds of layers in polytypes of the same family should remain the same and that the relative positions of adjacent layers cannot be completely random (*e.g.* Zvyagin, 1988). The postulates declared mixed-layer and turbostratic structures as non-polytypic. All this led to certain controversies about the notion of polytypism. While

Thompson (1981) regards polytypes as 'arising through different ways of stacking structurally compatible tabular units ... [provided that this] ... should not alter the chemistry of the crystal as a whole', Angel (1986) demands that 'polytypism arises from different modes of stacking of one or more structurally compatible modules', dropping thus any chemical constraints and allowing also for rod- and block-like modules.

The present official definition (Guinier *et al.*, 1984) reads:

''An element or compound is *polytypic* if it occurs in several different structural modifications, each of which may be regarded as built up by stacking layers of (nearly) identical structure and composition, and if the modifications differ only in their stacking sequence. Polytypism is a special case of polymorphism: the two-dimensional translations within the layers are (essentially) preserved whereas the lattice spacings normal to the layers vary between polytypes and are indicative of the stacking period. No such restrictions apply to polymorphism.

Comment: The above definition is designed to be sufficiently general to make polytypism a useful concept. There is increasing evidence that some polytypic structures are characterized either by small deviations from stoichiometry or by small amounts of impurities. (In the case of certain minerals like clays, micas and ferrites, deviations in composition up to 0.25 atoms per formula unit are permitted within the same polytypic series: two layer structures that differ by more than this amount should not be called polytypic.) Likewise, layers in different polytypic structures may exhibit slight structural differences and may not be isomorphic in the strict crystallographic sense.

The *Ad-Hoc* Committee is aware that the definition of polytypism above is probably too wide since it includes, for example, the turbostatic form of graphite as well as mixed-layer phyllosilicates. However, the sequence and stacking of layers in a polytype are always subject to well-defined limitations. On the other hand, a more general definition of polytypism that includes 'rod' and 'block' polytypes may become necessary in the future.''

This definition was elaborated as a compromise between members of the IUCr *Ad-Hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures. It is a slightly modified definition proposed by the IMA/IUCr Joint Committee on Nomenclature (Bailey *et al.*, 1977), which was the target of Angel's (1986) objections.

The official definition has indeed its shortcomings, but not so much in its restrictiveness concerning the chemical composition and structural rigidity of layers, because this can be overcome by a proper degree of abstraction (see below). More critical is the fact that it is not 'geometric' enough. It specifies neither the 'layers' (except for their two-dimensional periodicity), nor the limitations concerning their sequence and stacking mode, and it does not state the conditions under which a polytype belongs to a family.

Very impressive evidence that even polytypes that are in keeping with the first Baumhauer's statement may not have exactly the same composition and the structure of their constituting layers *cannot* be identical has been provided by studies on SiC carried out at the Leningrad Electrotechnical Institute (Sorokin, Tairov, Tsvetkov & Chernov, 1982; Tsvetkov, 1982). They indicate also that each periodic polytype is *sensu stricto* an individual polymorph. Therefore, it appears that the question whether some *real* polytypes belong to the same

references