Acta Cryst. (1982). A**38**, 49–54

Symbols for OD Groupoid Families Referring to OD Structures (Polytypes) Consisting of More Than One Kind of Layer

By H. Grell and K. Dornberger-Schiff†

Central Institute of Physical Chemistry, Academy of Sciences of the German Democratic Republic, Rudower Chaussee 5, 1199 *Berlin, German Democratic Republic*

(*Received* 27 *March* 1979; *accepted* 21 *May* 1981)

Abstract

Principles for the construction of such symbols are given and exemplified for any of the four categories. The symbols characterize the symmetry relations common to all OD structures or polytypes of a family. They consist, as a rule, of two lines – the first containing the layer group symbols of any of the constituting OD layers, the second indicating the positional and/or symmetry relations between adjacent OD layers. Symbols in use, referring to OD crystals containing equivalent OD layers, result from an application of these principles. The principles are discussed for schematic examples and applied to kaolinite-type minerals and yttrium hydroxychloride. Further examples: $Ca[B(OH)_4]_2.2H_2O$, mica, chlorites, vermiculites and pyroxenes are quoted.

Introduction

OD groupoid family symbols* for OD crystals consisting of equivalent OD layers have been in use for many years (Dornberger-Schiff, 1964; Dornberger-Schiff & Fichtner, 1972). For categories I and II the symbols describe coincidence operations in one pair of adjacent OD layers (called layer pair in the following); for category III the coincidence operations for layer pairs of two different kinds have to be indicated. Actually, in any OD structure consisting of equivalent OD layers there cannot be layer pairs of more than one kind, if the structure belongs to category I or II, of two different kinds and not more, if it belongs to category III (see *e.g.* Dornberger-Schiff, 1979). Correspondingly, the OD groupoid family symbols consist of two (categories I and II) or three lines (category III). For OD groupoid families of any category, the first line characterizes the layer group of the single OD layer. For categories I and II the second line contains coincidence operations linking the OD layers of a layer pair; for category III the coincidence operations linking the OD layers of each kind of layer pair have been given in a second and a third line, respectively.

A considerable number of crystals have, in the last decade, been found to be OD structures containing more than one kind of OD layer. This is why the introduction of symbols for their OD groupoid families seemed to us to be indicated. Such a symbol – although with slightly different arrangement of its characters – was proposed about ten years ago for $Ca[B(OH)_4]_2.2H_2O$ (Sedlacek & Dornberger-Schiff, 1971) and the information it contains used for structure analysis.

Terms and conventions

*P*artial coincidence *o*perations converting an OD layer into an OD layer have been called PO's. The PO's converting an OD layer into itself have been called λ-PO's, those converting an OD layer into the next following OD layer equivalent to it have been called σ-PO's. If it leaves the direction perpendicular to the translational vectors of an OD layer unchanged, it is called a τ-PO, if it inverts this direction, it is called a ρ-PO. Non-specified OD layers are denoted by the letter L; any non-polar OD layer, *i.e.* one for which there exists a ρ-λ-PO, by the symmetric letter A; any polar* OD layer, *i.e.* one for which no ρ-λ-PO exists, by a letter b or d.

All equivalent polar OD layers which are linked by τ-PO's are denoted by the same letter b or d. Two equivalent polar OD layers which are linked by a ρ-PO are denoted by different letters b, d. Superscripts (A^i, b^j, d^k) are used for characterizing the kind of A, b or d layer. Subscripts (A_k, b_l, d_m) are used to number the OD layers according to their sequence.

The *v*icinity *c*ondition (VC) is assumed to hold for any OD structure whether containing only one kind or

† Deceased 27 July 1981.

* Such a symbol indicates properties common to all crystals of a family, in contrast to a polytype symbol which characterizes the stacking of OD layers in one particular OD crystal.

* Any indication of polarity or non-polarity refers to the direction perpendicular to the translations of the single layers.

0567-7394/82/010049-06$01.00

$M > 1$ kinds of OD layers. The most important part of it, part VCγ (Dornberger-Schiff & Fichtner, 1972) may be formulated as follows: for any kind of OD layer A^j, all pairs of OD layers (L_{n-1}; A^j_n) and (A^j_m; L_{m+1}) are equivalent (for any number m and n for which an OD layer of kind A^j exists); similarly, for any kind of OD layer b^k all pairs (L_{n-1}; b^k_n) and (d^k_m; L_{m+1}) are equivalent and so are all pairs (b^k_n; L_{n+1}) and (L_{m-1}; d^k_m) (for any number n for which OD layers b^k exist and any number m for which OD layers d^k exist). The letters b and d for polar OD layers may and will be chosen in such a way that adjacent polar OD layers of different kinds are indicated by the same letter.

Sequence of OD layers in the polytypes of the four categories and their representative parts

There are four categories of OD structures consisting of $M > 1$ kinds of OD layers – one more than for OD structures consisting of equivalent OD layers. VCγ implies that the sequence of kinds of OD layers is the same for all members of a family, and is periodic, as indicated below for the respective categories; there are no other possibilities in keeping with VCγ (Dornberger-Schiff, 1964; Fichtner, 1977).

Category I

One kind of non-polar OD layer $L^1 = A^1$, and $M - 1$ kinds of polar OD layers $L^i = b^i$; $i = 2, 3, \ldots, M$. Sequence of OD layers:

$$\ldots A^1_1\, b^2_2 \ldots b^M_M\, d^M_{M+1} \ldots d^2_{2M-1}\, A^1_{2M} b^2_{2M+1} \ldots$$

Category II

All OD layers polar $L^i = b^i$, $i = 1, 2, \ldots, M$. No ρ-PO's. Sequence of OD layers:

$$\ldots b^M_0\, b^1_1\, b^2_2 \ldots b^M_M\, b^1_{M+1}\, b^2_{M+2} \ldots b^M_{2M} \ldots$$

Category III

All OD layers polar $L^i = b^i$, $i = 1, 2, \ldots, M$. Adjacent equivalent OD layers linked by ρ-PO's. Sequence of OD layers:

$$\ldots d^1_0\, b^1_1\, b^2_2 \ldots b^{M-1}_{M-1}\, b^M_M d^M_{M+1}\, d^{M-1}_{M+2} \ldots d^2_{2M-1}\, d^1_{2M} \ldots$$

Category IV

Two kinds of non-polar OD layers $L^1 = A^1$ and $L^M = A^M$; $M - 2$ kinds of polar OD layers b^i, $i = 2, 3, \ldots, M - 1$. Sequence of OD layers:

$$\ldots d^2_0\, A^1_1\, b^2_2 \ldots b^{M-1}_{M-1}\, A^M_M\, d^{M-1}_{M+1} \ldots d^2_{2M-2}\, A^1_{2M-1}\, b^2_{2M} \ldots$$

Each horizontal line underlines a part containing all kinds of OD layers of a polytype. Different possibilities for choosing such a part, if any, are indicated by lines at different heights. The symbols we need have to describe all relevant geometrical features of all pairs of adjacent OD layers, *i.e.* the layer groups of the layers of any kind, and the relative position of OD layers in any kind of layer pair. Any fork at an end of a line indicates that the pair of the last (first) OD layer of the underlined part and the succeeding (preceding) OD layer is of a kind different from any pair of adjacent OD layers within the underlined part. Thus, any of the underlined parts together with the OD layer preceding or succeeding it, if indicated by a fork, represents the symmetry relations common to all members of such a family, and is therefore called a representative part of the OD groupoid family.

General outline of the symbols

In analogy to the known symbols, the first line of any of the symbols to be constructed contains the layer group symbol of any of the M different kinds of OD layers. The sequence of these layer group symbols corresponds to the stacking sequence of the M different kinds of OD layers within the underlined part. As indicated above, the beginning of the sequence is unequivocal for category I, there are M possibilities for category II, and two possibilities for categories III and IV.

Layer groups induce directions of basic vectors. For any family of polytypes there exists a translational group $m\mathbf{a} + n\mathbf{b}$ ($m, n = 0, \pm 1, \pm 2, \ldots$) common to all layers of any crystal of a family. All layer groups of the OD layers of the underlined part have to be referred to this common translational group. This translational group is either identical with, or a subgroup of, the translational group of any single OD layer. If it is a subgroup, this is to be indicated by a – possibly unusual – Bravais letter, *e.g.* D, if the cell is doubled by the common translational group. Such letters have to be explained.

In order to indicate the orientation, layer group symbols with places in accordance with their system do not, in all cases, suffice. Thus, three-place symbols, for example, as used for orthorhombic groups, may have to be used for monoclinic layer groups in order to indicate the orientation of the monoclinic axis. Three-place symbols may not suffice, if the common translational group is tetragonal or hexagonal. In such cases five- or seven-place symbols, respectively, have to be used. These have already been introduced and used for the symbols of OD groupoid families with $M = 1$ (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff, 1964; Dornberger-Schiff & Fichtner, 1972; Fichtner, 1979).

The second line of symbols is used to indicate, for any kind of OD layer characterized in the first line, one of the possible positions relative to its predecessor. Within the underlined part all OD layers are of different kinds. The relative position of adjacent OD layers L_n^i and L_{n+1}^j, say, is indicated by the components of the projection onto the layer plane of the vector leading from the origin of L_n^i to that of L_{n+1}^j.

The components r, s of such a projection are to be referred to the basic vectors **a**, **b** of the common translational group (in the hexagonal case to $\mathbf{a}_3$, $\mathbf{b}_3$). They are written in brackets $[r,s]$ underneath the site between the layer group symbols of L_n^i and L_{n+1}^j. The origin of any of the kinds of OD layers is to be chosen in accordance with the rules of *International Tables for X-ray Crystallography* (1952).

Adjacent layers of the same kind are related by σ-PO's: they are indicated within curly brackets in the same way as in symbols for OD groupoid families with equivalent OD layers (Dornberger-Schiff, 1964; Dornberger-Schiff & Grell-Niemann, 1961). The site occupied by them is given below for the respective categories.

Symbols for the different categories and examples

In the following, symbols for the categories and simple schematic examples for them are given.

Category I

The first line of the symbols in this category starts off with the layer group symbol of the only kind of non-polar OD layer. Then the layer group symbols of the polar OD layers follow according to the order of their stacking. The second line contains items $[r,s]$ at the sites between the layer group symbols of the first line. The last item of the second line is the set of ρ-σ-PO's converting b_M^M into d_{M+1}^M within curly brackets, to the right of the last layer group.

Fig. 1 gives a schematic representation of the OD groupoid family

$$\begin{array}{ccc} Pmm(m) & Pmm(2) & \\ & [r,s] & \{2_{2r'}\ 2_{2s'}\ (n_{2r',2s'})\}, \end{array}$$

with $r = 3/8$; $s = 1/4$; $r' = 1/4$; $s' = 1/3$.

Remark. Owing to the symmetry of A^1 there are four different possibilities for the position of b^2, resulting in equivalent layer pairs (A^1; b^2). These possible positions are in this case characterized by the four combinations of signs of $r = \pm 3/8$; $s = \pm 1/4$. Similarly, the four combinations of signs for r' and s' characterize equivalent layer pairs (b^2; d^2). The different symbols resulting from different combinations of signs may easily be recognized as denoting the same OD groupoid family.

In a similar manner, different symbols may denote the same OD groupoid family in any of the categories. A test showing whether two symbols denote the same OD groupoid family has to check whether corresponding layer pairs are equivalent or not.

Category II

The first line contains the layer group symbols of the M different kinds of OD layers in the sequence of their stacking. The second line of the symbol contains M items $[r,s]$ between the respective layer group symbols of the first line. The last of these items is given to the right of the last layer group of the first line and indicates the position of the origin of b_{M+1}^1 relative to that of b_M^M.

In this category the layer b_{M+1}^1 may or may not have an orientation different from that of b_1^1. This is not indicated by the displacement $[r,s]$ from the origin of b_M^M to that of b_{M+1}^1. If there are no additional remarks, then the displacement $[r,s]$ is meant to lead to a position of b_{M+1}^1 translationally equivalent to that of b_1^1, and such a translationally equivalent position – if any – is to be preferred. If there is no possible position of b_{M+1}^1 translationally equivalent to b_1^1, then the PO's transforming the layer b_1^1 into one possible position of

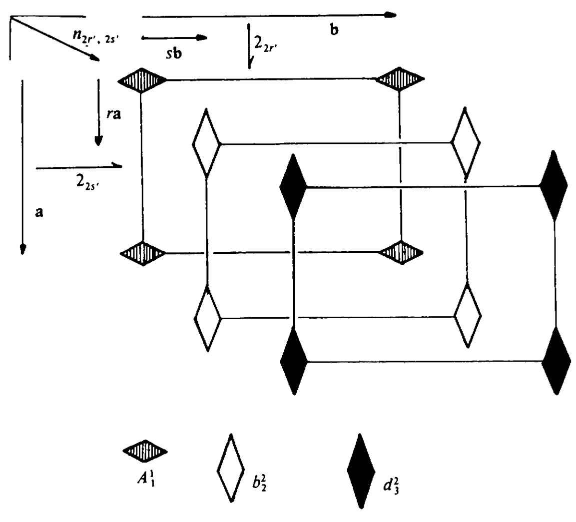


Fig. 1. Schematic representation of OD groupoid families exemplified by a sequence of consecutive OD layers containing layer pairs of all kinds occurring in polytypes of the respective family. Category I; $M = 2$.

b^1_{M+1} have to be given in curly brackets in a third line underneath the layer group symbol of b^1_1.

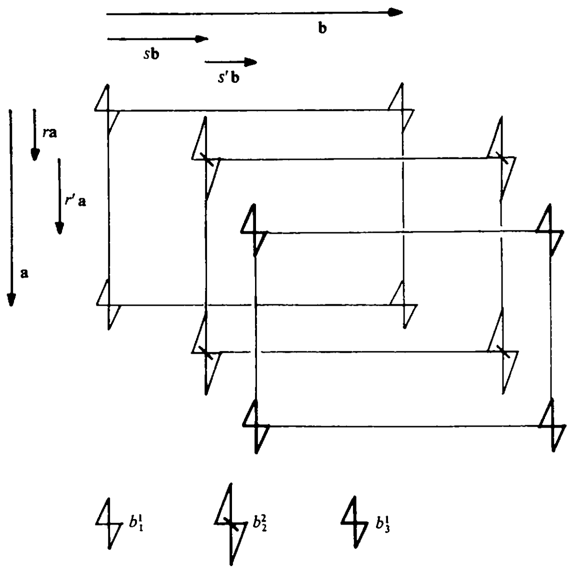
Figs. 2(*a*) and (*b*) are schematic representations of the OD groupoid families

$$P11(2) \underset{[r,s]}{} P11(2) \underset{[r',s']}{}$$

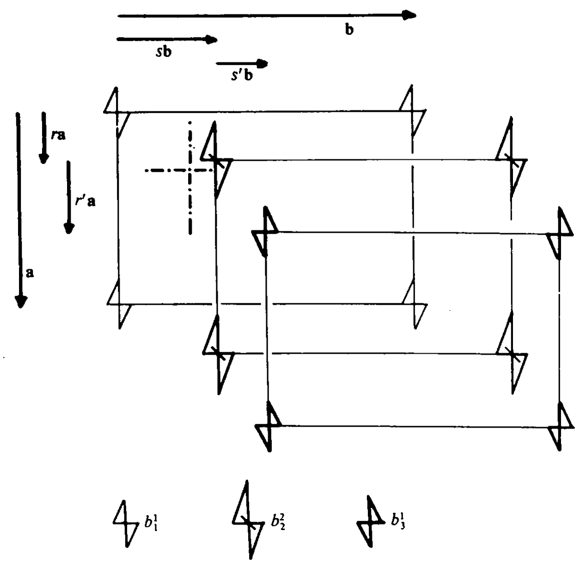
and

$$\begin{array}{l} P\;\;1\;\;\;1\;\;(2) \\ \{n_{2s'',4}\; n_{4,2r''}\;(1)\} \end{array} \underset{[r,s]}{} P11(2) \underset{[r',s']}{},$$

respectively, with $r'' = r + r'$ and $s'' = s + s'$.



(*a*)



(*b*)

Fig. 2. Schematic representation of OD groupoid families exemplified by a sequence of consecutive OD layers containing layer pairs of all kinds occurring in polytypes of the respective family. (*a*) Category II; $M = 2$, OD layer b^1_{M+2} translationally equivalent to OD layer b^1_1. (*b*) Category II; $M = 2$, OD layer b^1_{M+1} related to OD layer b^1_1 by glide operations as indicated.

Category III

The first line starts off with the layer group symbol of an OD layer which is related to the preceding OD layer by a ρ-σ-PO, and ends with the symbol of an OD layer which is related to the succeeding OD layer by a ρ-σ-PO. Correspondingly, the second line starts and ends with one set of ρ-σ-PO's within curly brackets, respectively, before the first and after the last layer group symbol of the first line. The first set of ρ-σ-PO's is meant to bring d^1_0 into coincidence with b^1_1. The components of the ρ-σ-PO's are again to be referred to the basic vectors of the common translational group. The sites in the second line, between the layer group symbols, are occupied by items $[r,s]$.

Fig. 3 gives a schematic representation of the OD groupoid family

$$\begin{array}{l} \phantom{\{2_{2r}}\; Pmm(2) \\ \{2_{2r}\, 2_{2s}(n_{2r,2s})\} \end{array} \underset{[r',s']}{} \begin{array}{r} P11(2)\phantom{\{2_{2r''}} \\ \{2_{2r''}\, 2_{2s''}(1)\} \end{array}$$

Category IV

The first line starts and ends with the layer group symbols of a non-polar layer. The second line contains items $[r,s]$ only.

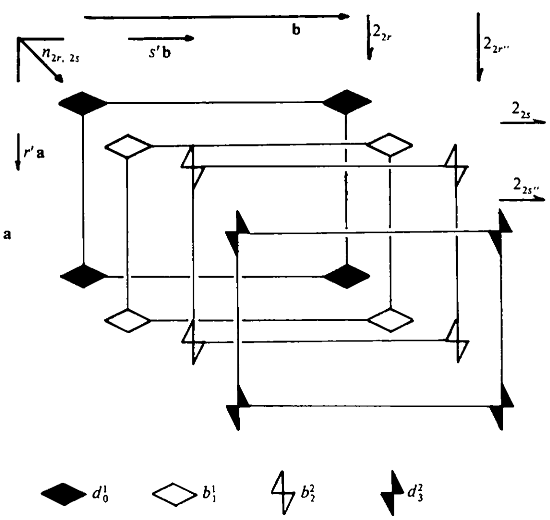


Fig. 3. Schematic representation of OD groupoid families exemplified by a sequence of consecutive OD layers containing layer pairs of all kinds occurring in polytypes of the respective family. Category III; $M = 2$.

Fig. 4 gives a schematic representation of the OD groupoid family

$$Pmm(m) \underset{[rs]}{\quad} Pmm(2) \underset{[r',s']}{\quad} P22(2).$$

Application of the principles: two examples

Example 1

The polytypes of kaolinite-type minerals, regarded from the point of view of the generalized Pauling model, have been shown to be members of families of OD structures belonging to category II, containing three kinds of polar OD layers (Dornberger-Schiff & Ďurovič, 1975*a*,*b*). Fig. 5 shows the projection along **b** of a representative part of a kaolinite-type structure; OD layers are indicated [with the boundary between the tetrahedral layer and the octahedral layer chosen in a way different from that chosen in the papers of Dornberger-Schiff & Ďurovič (1975*a*,*b*)].

The OD groupoid family of trioctahedral kaolinites may be indicated by the symbol

$$\begin{array}{ccccccc} b^1 & & b^2 & & b^3 & & \\ P(6)mm & & H(3)1m & & H(6)mm & & , \\ & [1/3,0] & & [1/3,0] & & [1/3,0] & \end{array}$$

and for dioctahedral kaolinites by

$$\begin{array}{ccccccc} b^1 & & b^2 & & b^3 & & \\ P(6)mm & & P(3)1m & & H(6)mm & & \\ & [1/3,0] & & [1/3,0] & & [1/3,0] & \end{array}$$

(Grell, 1981).

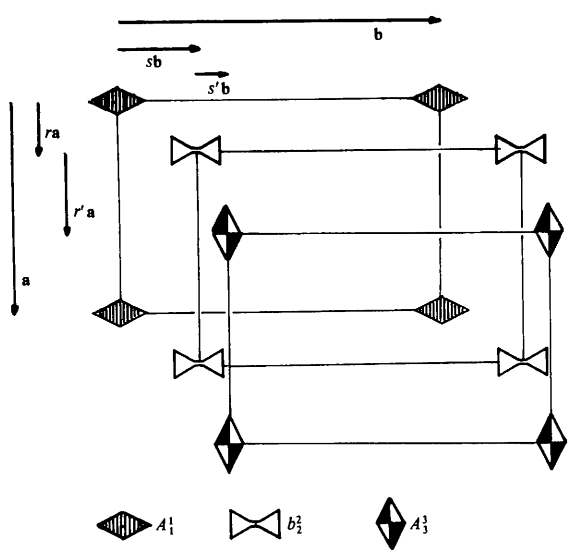


Fig. 4. Schematic representation of OD groupoid families exemplified by a sequence of consecutive OD layers containing layer pairs of all kinds occurring in polytypes of the respective family. Category IV; $M = 3$.

Example 2

$YCl(OH)_2$. The polytypes of $YCl(OH)_2$ belong to an OD family of category IV with two (non-polar) OD layers A^1 and A^2. The OD groupoid family symbol reads

$$\begin{array}{ccc} A^1 & & A^2 \\ P12_1/m(1) & & Pmm(m), \\ & [r,0] & \end{array}$$

where A^1 corresponds to the inner part $[Y(OH)_2]_n$ of a sheet while A^2 stands for the part consisting of the

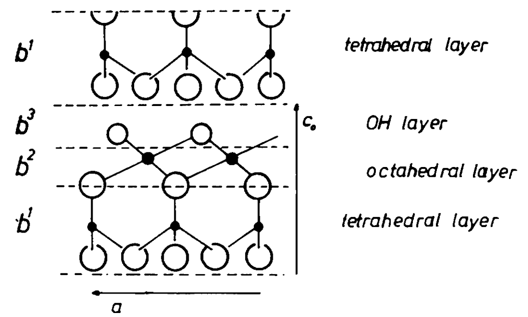


Fig. 5. Projection of a representative part of a kaolinite-type structure along **b**.

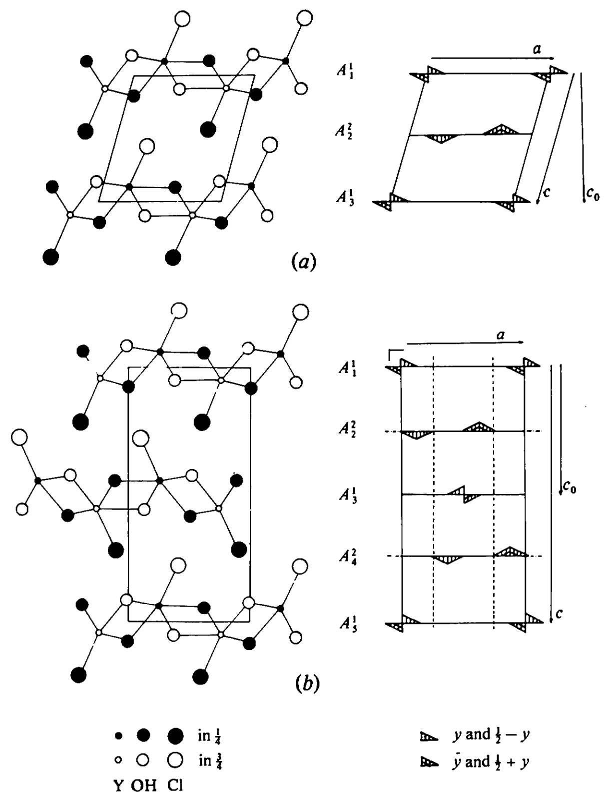


Fig. 6. Projection of $YCl(OH)_2$ along **b** (left) and schematic representation of symmetry relations (right). (*a*) Monoclinic, (*b*) orthorhombic polytype.

adjacent Cl atoms of two neighbouring sheets. Figs. 6(*a*) and (*b*) show the atomic arrangements (left) and their schematic OD interpretation (right) (Dornberger-Schiff & Klevtsova, 1967).

This is an example of a situation which seems to occur fairly frequently amongst polytypic substances: OD layers contain parts of different crystallochemical sheets with boundaries cutting across these sheets.

Summary and concluding remarks

The symbols for OD groupoid families constructed in accordance with the proposed principles give in a concise way the symmetry relations common to all polytypes of a family. The knowledge of the symmetry relations which the proposed symbols indicate may play for disordered structures a role similar to that played by space groups for fully ordered structures. Disregarding local symmetry relations of a crystal may lead to difficulties in its structure determination (see, for example, Kuban & Sedlacek, 1979; Freer & Kraut, 1965). The information conveyed by the OD groupoid family is also necessary for obtaining complete lists of polytypes of a given polytypic substance with particular features, such as polytypes with a given number of OD layers per repeat, or of MDO polytypes.

All MDO polytypes have been derived from such information for tri-, di-, and 'mon'octahedral kaolinite-type minerals (Dornberger-Schiff & Ďurovič, 1975*b*), for tri-, di-, and 'mon'octahedral mica (Dornberger-Schiff, Backhaus & Ďurovič, 1981*b*), for vermiculites (Weiss & Ďurovič, 1980), for high and low pyroxenes (Sedlacek, Zedler & Reinecke, 1979) as well as for a number of not so complicated families of OD crystals.

Obviously, polytypic substances which have to be treated as OD structures containing layers of more than one kind present more difficulties than those containing only equivalent OD layers. This explains, at least in part, why the symbols for OD groupoid families with equivalent OD layers have already proved their worth for more practical instances than those for families with $M > 1$ kinds of OD layers. Symbols for the families of vermiculites (Weiss & Ďurovič, 1980), of mica (Dornberger-Schiff, Backhaus & Ďurovič, 1981*a*) and for the chlorites (Ďurovič, Weiss & Dornberger-Schiff, 1981) have already been given and put to practical use. Polytypic substances with OD layers of more than one kind seem, however, to occur more frequently in nature than one might think, and also amongst substances of great practical importance, so that the development of the appropriate tools seemed worthwhile.

References

DORNBERGER-SCHIFF, K. (1964). *Grundzüge einer Theorie der OD Strukturen aus Schichten, Abh. Dtsch. Akad. Wiss. Berlin Kl. Chem. Geol. Biol.* No. 3.

DORNBERGER-SCHIFF, K. (1979). *Krist. Tech.* **14**, 1027–1045.

DORNBERGER-SCHIFF, K., BACKHAUS, K. O. & ĎUROVIČ, S. (1981*a*). *Clays Clay Miner.* Accepted for publication.

DORNBERGER-SCHIFF, K., BACKHAUS, K. O. & ĎUROVIČ, S. (1981*b*). In preparation.

DORNBERGER-SCHIFF, K. & ĎUROVIČ, S. (1975*a*). *Clays Clay Miner.* **23**, 219–229.

DORNBERGER-SCHIFF, K. & ĎUROVIČ, S. (1975*b*). *Clays Clay Miner.* **23**, 231–246.

DORNBERGER-SCHIFF, K. & FICHTNER, K. (1972). *Krist. Tech.* **7**, 1035–1065.

DORNBERGER-SCHIFF, K. & GRELL-NIEMANN, H. (1961). *Acta Cryst.* **14**, 167–177.

DORNBERGER-SCHIFF, K. & KLEVTSOVA, R. F. (1967). *Acta Cryst.* **22**, 435–436.

ĎUROVIČ, S., WEISS, Z. & DORNBERGER-SCHIFF, K. (1981). In preparation.

FICHTNER, K. (1977). *Beiträge Algebra Geom.* **6**, 71–99.

FICHTNER, K. (1979). *Krist. Tech.* **14**, 1073–1078.

FREER, S. T. & KRAUT, J. (1965). *Acta Cryst.* **19**, 992–1005.

GRELL, H. (1981). *Symposium on Special Topics of X-ray Crystal Structure Analysis, Hohengrün.* DDR Gesellschaft für geologische Wissenschaften der DDR.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

KUBAN, R.-J. & SEDLACEK, P. (1979). *Krist. Tech.* **14**, 1063–1072.

SEDLACEK, P. & DORNBERGER-SCHIFF, K. (1971). *Acta Cryst.* B**27**, 1532–1541.

SEDLACEK, P., ZEDLER, A. & REINECKE, K. (1979). *Krist. Tech.* **14**, 1055–1062.

WEISS, Z. & ĎUROVIČ, S. (1980). *Acta Cryst.* A**36**, 633–640.