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# Geometrical Properties of MDO Polytypes and Procedures for their Derivation. I. General Concept and Applications to Polytype Families Consisting of OD Layers All of the Same Kind

BY K. DORNBERGER-SCHIFF†

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

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## Abstract

The concept of MDO structures (structures of *m*aximum *d*egree of *o*rder) is explained in detail and defined. This concept corresponds closely to the concepts of standard, simple or regular polytypes; it seems, however, to be more adequate for complicated examples. MDO polytypes consisting of equivalent OD layers are treated in detail. For the six subcategories, simple tests showing whether a given polytype is an MDO polytype or not are given, and stepwise procedures for obtaining a complete list of all MDO polytypes of a polytypic substance are introduced. The approach is demonstrated by examples.

## Introduction

The determination of the structure of a polytype is usually more difficult than that of other crystalline bodies for a number of reasons: non-space-group systematic absences, symmetry enhancement and twinning may simulate a wrong space group and the latter even a multiple of the true unit cell. Therefore routine methods of structure determination may fail, even if single-crystal data are available. Besides, even the notion of a space group is problematic for disordered polytypes.

The knowledge of a suitably selected subset of a set of possible polytypes of a substance has turned out to be useful for structure determination. Jagodzinski (1949) has classified the periodic polytypes of close-packed layer structures such as silicon carbide using the concepts *Reichweite* and *Grenzfälle*. For quite a number of polytypic substances, certain polytypes have been singled out as simple (*e.g.* Takéuchi & Nowacki, 1964; Bailey, 1967, 1971). Zvyagin (1964, 1967) – generalizing an earlier statement (Zvyagin, 1962) – defines regular layer structures by the condition of uniformity. The concept of *n*-simple polytypes (Fichtner, 1980) is a generalization of the concept of regular polytypes, 1-simple corresponds to regular.

Another condition, singling out so-called MDO structures or MDO polytypes has actually been formulated independently (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff, 1964). The letters M, D, O here stand for *m*aximum *d*egree of *o*rder (in German M, O, G corresponding to m*aximaler* O*rdnungsgrad*). The MDO concept has been applied to a number of polytypic substances, such as $SrVO_3.4H_2O$ (Sedlacek & Dornberger-Schiff, 1965*a*,*b*), sapphirine, aenigmatite and related minerals (Dornberger-Schiff & Merlino, 1974), $\gamma$-$Hg_3S_2Cl_2$ (Ďurovič, 1968), $YCl(OH)_2$ (Dornberger-Schiff & Klevtsova, 1967), $K_4Mo(CN)_5NO$ (Svedung & Vannerberg, 1968), $WO_2Cl_2$ (Backhaus, 1979), $CuC_2O_4.nH_2O$ (Schmittler, 1968) and $K_4Si_8O_{18}$ (Ďurovič, 1974).

For many substances, the set of MDO polytypes coincides with the set of simple or regular polytypes. Differences occur for more complicated examples, especially in category III (see below) and for polytypes consisting of more than one kind of OD layer. In these cases, the MDO concept seems to be more adequate than the other existing concepts. Behind the OD theory and the concept of MDO polytypes, there is the basic idea of decreasing interatomic forces with increasing distance, thus leading to a preference of polytypes with a minimum number of layer pairs (principle of OD structures) or even a minimum number of kinds of *n*-tuples of layers, for any number *n* (principle of MDO structures).

OD theory is a geometrical approach to polytypism. The MDO concept presupposes a division of the structure into OD layers. For all polytypic structures which have come to my knowledge, the layers may be chosen in such a way that the conditions for OD structures are fulfilled, and thus the results of OD theory may be applied. How the choice of OD layers

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may be performed has been sketched recently (Dornberger-Schiff, 1980) and will be worked out in detail in a forthcoming paper. In the following, we suppose that the polytypes under consideration consist of one kind of OD layer. The notions OD structure and polytype are considered as synonyms.

A family of OD structures (Dornberger-Schiff, 1964, 1966; Dornberger-Schiff & Fichtner, 1972) is defined as the set of structures consisting of the same kind(s) of layer(s) and the same kind(s) of layer pair(s). The symmetry of any kind of layer and any kind of layer pair occurring in the structure is described by an OD groupoid family. A family of OD structures may be called a family of polytypes, if all polytypes with OD structures belonging to this family are taken into account, no matter whether ordered or disordered, whether occurring or only possibly occurring in nature.

In this paper, a general way is given of how to derive from the OD groupoid family, to which a polytypic substance may be referred, all possible MDO polytypes of this substance. The question how, in general, to recognize MDO polytypes has been answered by Ďurovič (private communication), but is also dealt with in this paper. Firstly, a generally applicable definition of MDO polytypes is given. Paper I of this series then is concerned with polytypes containing OD layers all of the same kind, and based on the results of paper I polytypes containing OD layers of more than one kind are treated in paper II (Dornberger-Schiff & Grell, 1982).

### Definition of MDO polytypes

In accordance with the definition of MDO structures (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff, 1964, 1966; Fichtner, 1965), MDO polytypes are defined as follows: a polytype $\pi_0$ is called an MDO polytype, if the following conditions apply.

MDO(i) For the chosen layers, the polytype is in keeping with the definition of an OD structure, *i.e.* the so-called vicinity condition applies.

MDO(ii) Amongst the whole family of polytypes, there is no polytype $\pi_1$ in which the kinds of $n$-tuples of consecutive layers for some numbers $n$ constitute only a selection of the kinds of $n$-tuples contained in $\pi_0$.

For recognition and deduction of MDO polytypes a more convenient form of this definition is necessary. The suitable tools are developed in the following paragraphs.

### Characterization of categories by sequences

OD theory is based on considerations of geometrical equivalence of layers and layer pairs to be brought about by coincidence operations. These coincidence operations are classified into those leaving layers and layer pairs upside up, to be called $\tau$ operations, and those turning them upside down, to be called $\rho$ operations.

By presence and/or absence of $\tau$ and $\rho$ operations for layers and layer pairs the categories and subcategories may be characterized and distinguished. For a characterization of these features the following conventions are made: A layer which is converted into itself by a $\rho$ operation (*i.e.* is non-polar with respect to the direction of missing periodicity) is in the following to be indicated by the symmetric letter $A$; a layer for which no such operation exists (*i.e.* the layer is polar with respect to the direction of missing periodicity) is to be indicated by a letter $b$ or $d$, where layers related by $\tau$ ($\rho$) operations are indicated by the same (different) letter. Non-specified layers are denoted by the letter $L$.

A sequence of layers may then be characterized by a sequence of such letters. Subscripts may be used to number the layers in the order of their occurrence in the polytype. In paper II superscripts are used to distinguish between layers of different kinds.

According to the vicinity condition (VC) (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff, 1964, 1966, 1979; Dornberger-Schiff & Fichtner, 1972), there are only three kinds of sequences of letters for families of OD structures containing equivalent layers and four kinds for families containing more than one kind of layer (Fichtner, 1977; Grell & Dornberger-Schiff, 1982). The kinds of sequences correspond to the respective categories: category I is represented by a sequence of letters $A$; category II by a sequence of letters $b$ (or, if the layers are otherwise indicated, by a sequence of letters $d$); category III by a sequence of letters $b$ and $d$ alternating (compare columns 1 to 4 of Table 1).

### Further classification of categories I and III into subcategories and their characterization by sequences

The classification of the families of OD structures into subcategories refers to polarity or non-polarity of layer pairs with respect to the direction of missing periodicity. Obviously, any layer pair of category II represented by $b$ $b$ (or $d$ $d$) is polar and no further indication is needed in this case. With respect to polarity or non-polarity of layer pairs of this category no further subdivision is possible.

Two equivalent non-polar layers indicated by $A$ are related by at least one $\rho$ operation and so are polar layers $b$ and $d$, and also $d$ and $b$. This does not mean, however, that the resulting pairs of layers are necessarily non-polar. Non-polar layers forming non-polar layer pairs are shown schematically in Fig. 1($a$): $A_1$ is transformed into $A_2$ by the same centre of symmetry transforming $A_2$ into $A_1$ as do the $2_1$ axes in the **b** direction. Non-polar layers forming polar layer pairs are shown schematically in Figs. 2($a$), ($b$) and ($c$).

There is no $\rho$ operation transforming $A_1$ into $A_2$ and $A_2$ into $A_1$. The twofold screw axis parallel to **a** transforming $A_1$ into $A_2$ does not transform $A_2$ into $A_1$ and the same is the case with the $n$-glide perpendicular to **c**. Indication of polarity of a layer pair (if not obvious as in the case of $b$ $b$) is given by small arrows above or below the pair of letters representing the layer pair, with absence of such an arrow indicating that the pair is non-polar. In this way, characteristic sequences of letters with and without arrows for any of the subcategories result (columns 5 to 8 of Table 1). A simple small line, so to speak an arrow without an arrow head, is used to indicate that the layer pair is polar without specifying the sense of polarity.

### Characterization of MDO polytypes by MDO sequences

The sequences representing MDO structures require obviously further specifications. All polytypes, that means also MDO polytypes of families belonging to subcategory I*a*, or III*a* or to category II, are represented by the same sequence, respectively. Polytypes belonging to families of the other subcategories may differ in the sense of polarity of their layer pairs as indicated in Table 1 column 8 by arrows without arrow heads.

Two $n$-tuples of layers which are $\tau$ equivalent are obviously represented by the same two sequences of $n$ letters and arrows, if any. Sequences of $n$ letters and arrows, if any, are to be called $n$-sequences for short. We call such sequences $\tau$ equivalent in analogy to the $\tau$ equivalence of the layer $n$-tuples represented by them. Layer $n$-tuples which are $\rho$ equivalent are represented

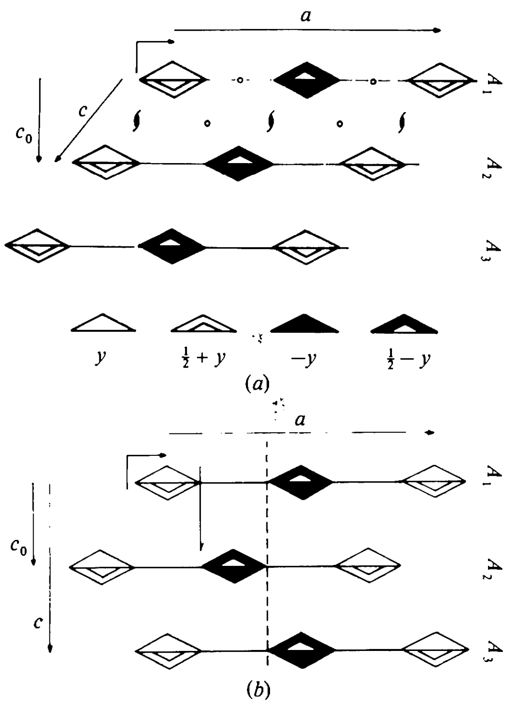


Fig. 1. Schematic representation of the symmetry and stacking in two MDO polytypes of OD groupoid family (1), projected along **b**.

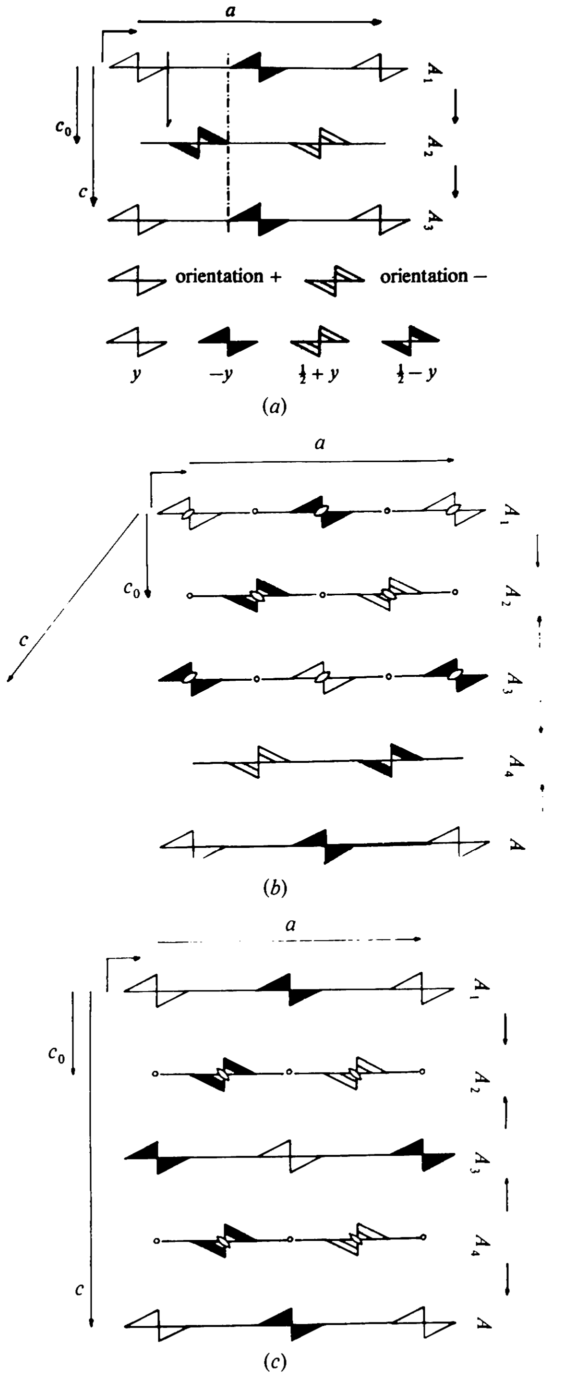


Fig. 2. Schematic representation of the symmetry and stacking in (*a*), (*b*) two MDO polytypes and (*c*) a periodic polytype of OD groupoid family (2), projected along **b**.

Table 1. *Characterization of categories, subcategories and MDO polytypes*

| 1 | 2 | 4 | 5 | 6 | 7 | 8 | 9 | | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Layer characterized by | | | | Layer pair characterized by | | | | | | |
| Category | operation(s) | letter | Layers of a pair linked by | Subcategory | operation(s) | letter pair (and arrow) | Sequence | Example | MDO sequence | Sequence period | Additional condition |
| I | $L_1{:}\rho{:}L_1$ | $A$ | $A_1{:}\tau{:}A_2$ and $A_1{:}\rho{:}A_2$ | I*a* | $A_1A_2{:}\rho{:}A_1A_2$ | $AA$ | $AAAAA\ldots$ | 1 | $AAAAA\ldots$ | 1 | – |
| | | | | I*b* | $A_1A_2{:}\text{no }\rho{:}A_1A_2$ | $A\,{}^{\cdot}A$ | $A\,{}^{\cdot}A\;A\;A^{\cdot}A\ldots$ | 2 | $A\,{}^{\cdot}A\,{}^{\cdot}A\,{}^{\cdot}A\,{}^{\cdot}A\ldots$ | 1 | – |
| | | | | | | | | | $A\,{}^{\cdot}A^{\cdot}\,A\,{}^{\cdot}A^{\cdot}\,A\ldots$ | 2 | $A_1A_2{:}\rho{:}A_2A_3$ |
| II | $L_1{:}\text{no }\rho{:}L_1$* | $b$ | $b_1{:}\tau{:}b_2$ | | $\rho$ | $bb$ | $bbbbb\ldots$ | | $bbbbb\ldots$ | 1 | – |
| III | $L_1{:}\text{no }\rho{:}L_1$ $L_2{:}\text{no }\rho{:}L_2$ | $b$ $d$ | $b_1{:}\rho{:}d_2$ $d_2{:}\rho{:}b_3$ | III*a* | $b_1d_2{:}\rho{:}b_1d_2$ $d_2b_3{:}\rho{:}d_2b_3$ | $bd$ $db$ | $bdbdb\ldots$ | 3 | $bdbdb\ldots$ | 2 | $b_1d_2b_3{:}\rho{:}d_2b_3d_4$ |
| | | | | III*b* | $b_1d_2{:}\text{no }\rho{:}b_1d_2$ $d_2b_3{:}\text{no }\rho{:}d_2b_3$ | $b\,{}^{\cdot}b$ $d\,{}_{\cdot}b$ | $b\,{}^{\cdot}d\,{}_{\cdot}b^{-}d\;b\ldots$ | | $b\,{}^{\cdot}d\,{}_{\cdot}b\,{}^{\cdot}d\,{}_{\cdot}b\ldots$ | 2 | – |
| | | | | III*c* | $b_1d_2{:}\text{no }\rho{:}b_1d_2$ $d_2b_3{:}\rho{:}d_2b_3$ | $b\,{}^{\cdot}d$ $d\;b$ | $b\,{}^{\cdot}d\;b\;d\;b\ldots$ | | $b\,{}^{\cdot}d\;b\,{}^{\cdot}d\;b\ldots$ | 2 | – |
| | | | | | | | | | $b\,{}^{\cdot}d\;b^{\cdot}\,d\;b\,{}^{\cdot}d\ldots$ | 4 | $b_1d_2b_3{:}\rho{:}d_2b_3d_4$ $b_3d_4b_5{:}\rho{:}d_4b_5d_6$ |

* $L_r{:}\text{no }\rho{:}L_r$ means there does not exist a $\rho$ operation transforming $L_r$ into itself, and a correspondiong statement holds for layer pairs.

by $\rho$-equivalent $n$-sequences, *i.e.* one of these sequences is obtained from the other by reversing the sequence of letters and arrows, reversing also the sense of any arrow and interchanging the letters $b$ and $d$. Thus, *e.g.* the 3-sequence $b\;d^{\rightarrow}b$ is $\rho$ equivalent to $d^{\leftarrow}b\;d$.

It may be shown that if an MDO polytype is represented by a sequence of letters (and arrows), then any two equivalent $n$-sequences represent equivalent layer $n$-tuples, where $\tau$-equivalent $n$-sequences correspond to $\tau$-equivalent layer $n$-tuples and an analogous statement holds for $\rho$ equivalence.

In most cases, indication of polarity and non-polarity of layers and layer pairs suffices for $n$-sequences to reflect this feature from layer $n$-tuples of MDO polytypes. There are, however, cases in which arrows indicating the relative polarity of triples or higher $n$-tuples are required to indicate that an $n$-tuple containing $\rho$ equivalent parts is polar. An example of this kind may be constructed (Fig. 3):

The OD groupoid family

$$\begin{array}{ccccc} P & 1\;1 & (\bar{4}) & 1\;1 \\ \Big\{ & 1\;1 & \left(\dfrac{4_4}{n_{r,s}}\right) & 1\;1 & \Big\} \end{array}$$

belongs to category I*a*. The single layer is non-polar and so is a pair of adjacent layers, as the layers are related by a centre of symmetry, but any triple of layers is polar and this is to be indicated by an arrow referring to a triple of layers, otherwise the one-to-one correspondence of $n$-sequences and layer $n$-tuples is violated.

Such cases seem to be rare, they presuppose the existence of a symmetry operation of higher order than two in the layer group, and even for stackings of layers with such symmetry operations these seem to be exceptional cases. No polytypic substance belonging to such an exceptional case has actually been found so far. Exceptional cases would require special considerations, and they are not included in this paper.

The connection between sequences of letters (and arrows) and MDO structures results in a condition for MDO sequences, similar to condition MDO(ii) for MDO polytypes:

A sequence of letters (and arrows) is to be called an MDO sequence, if there is no $n$ with the following property, a sequence may be constructed containing the same $m$-sequences with $m < n$ but only a selection of $n$-sequences.

From this condition the MDO sequences listed in column 10 (Table 1) result. (Note that there are only such sequences listed with notation of relative polarity of layers and layer pairs, the exceptional cases are not included here.)

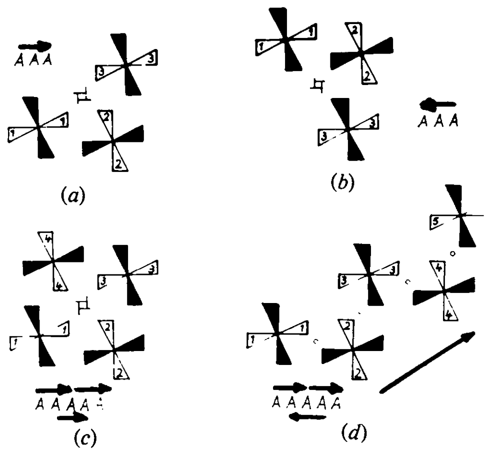


Fig. 3. Schematic representation of an exceptional case. (*a*), (*b*) Two layer triples $A_1A_2A_3$, where the position of $A_3$ in one triple is related to that in the other by the only $\tau$ operation of $A_2$, namely the twofold axis. The $\rho$ operation of $A_2$, the $\bar{4}$, converts, if applied to $A_1$ and $A_3$, one of the triples into the other, *i.e.* the triples are polar and are to be characterized by an arrow as indicated. (*c*), (*d*) MDO polytypes of OD groupoid family (4). (*c*) There is a total $\tau$ operation $A_x{:}\tau{:}A_{x+1}$, the $4_4$. (*d*) There is only one kind of triple but two kinds of quadruples, no polytype exists containing only one of these two kinds of quadruples. The total $\tau$ operation is in this case of the kind $A_x{:}\tau{:}A_{x+2}$, the indicated translation.

The last paragraphs may now be summarized for conditions equivalent to conditions MDO(i) and MDO(ii).

MDO(1) Any MDO polytype is represented by an MDO sequence;

MDO(2) the same $n$-sequence occurring in different parts of a sequence representing an MDO polytype stands for $\tau$-equivalent $n$-tuples of layers, $\rho$-equivalent $n$-sequences stand for $\rho$-equivalent $n$-tuples of layers.

As may be seen from column 10 of Table 1, the MDO sequences are periodic, this is indicated in column 11. MDO(2) requires that any two parts of an MDO structure which are represented by the same $n$ sequences are $\tau$ equivalent, therefore periodicity of sequences implies the existence of total $\tau$ operations for MDO structures represented by the sequences. These total operations transform any layer into that which follows with period distance of the sequence. The period of the corresponding MDO structure may be a multiple of the sequence period, depending on the order of the corresponding point group of the $\tau$ operation. For polytypes represented by one of the sequences with a hyphen in column 12 headed 'additional condition', the existence of such a $\tau$ operation suffices to ensure its MDO character. For other polytypes additional conditions ensure the validity of condition MDO(2) with respect to $\rho$ equivalence.

For compiling complete lists of MDO polytypes, Table 2 is to be used. For any subcategory, steps are given leading from given layer pairs (or in category III from a given triple of layers) with the help of procedures finally to MDO polytypes. For subcategories I$b$ and III$c$ two sorts of steps are given, namely those resulting in polytypes with letter sequence period $m = 1$ for category I$b$ and $m = 2$ for category III$c$ and those with twice the respective period, *i.e.* $m = 2$ for subcategory I$b$ and $m = 4$ for subcategory III$c$. For deriving the complete set of all polytypes of a given family, the knowledge of all $\tau$ and $\rho$ operations converting an OD layer into itself and those converting an OD layer into an adjacent OD layer is necessary. The number of these operations is closely connected with the order $G$ of the layer group.* For category I the number of $\tau$ operations converting an OD layer into itself is equal to the number of $\rho$ operations converting an OD layer into itself and therefore equal to $G/2 = g$. There are also $g$ $\tau$ operations as well as $g$ $\rho$ operations converting any $A$ layer into an adjacent layer.

For category II and category III there are only $\tau$ operations in the layer group, the order $G$ of the layer group is in these cases equal to $g$, the number of $\tau$ operations. In category II there are only $\tau$ operations converting a layer into an adjacent layer, whereas in category III this is done by $\rho$ operations only. In both cases, the number of the respective operations is equal to $g$. In Table 2 the superscripts in brackets of coincidence operations are always referred to the number $g$ as they denote $g$ operations to be carried out one after the other. The superscripts of letters denoting layers refer to one given or one resulting position of the respective layer.

Now some examples are given to show how to proceed with polytype families containing equivalent layers. Any OD groupoid family is indicated in the following by its symbol in accordance with the symbolism introduced earlier for families of OD

* Strictly speaking the factor group modulo the translations $m\mathbf{a} + n\mathbf{b}$ ($m,n$ integers) of the layer group is meant, otherwise the order of the layer group is infinite.

Table 2. *Procedures for compiling complete lists of MDO polytypes.*

| Subcategory | Step | Start | Procedure | Result (intermediate) | Result (final) |
|---|---|---|---|---|---|
| I$a$ | 1 | $A\ A$ | $A_1:\tau^{(j)}:A_2 \leftrightarrow A_x:\tau^{(j)}:A_{x+1}$ | | $A\ A\ A\ldots$ |
| I$b$ | 1 ($m=1$) | $A^{\rightarrow}A$ | $A_1:\tau^{(j)}:A_2 \leftrightarrow A_x:\tau^{(j)}:A_{x+1}$ | | $A^{\rightarrow}A^{\rightarrow}A\ldots$ |
| | 1 ($m=2$) | $A^{\rightarrow}A$ | $A_2:\rho^{(j)}:A_2 \leftrightarrow A_1:\rho^{(j)}:A_3$ | $A^{\rightarrow}A^{\leftarrow}A$ | |
| | 2 ($m=2$) | any $A^{\rightarrow}A^{\leftarrow}A$ | $A_1:\tau^{(j)}:A_2 \leftrightarrow A_x:\tau^{(j)}:A_{x+2}$ | | $A^{\rightarrow}A^{\leftarrow}A^{\rightarrow}A^{\leftarrow}A\ldots$ |
| II | 1 | $b\ b$ | $b_1:\tau^{(j)}:b_2 \leftrightarrow b_x:\tau^{(j)}:b_{x+1}$ | | $b\ b\ b\ldots$ |
| III$a$ | 1 | one $b\ d\ b^{(1)}$ | $d_2:\tau^{(j)}:d_2 \leftrightarrow b_3^{(1)}:\tau^{(j)}:b_3^{(j)}$ | all $b\ d\ b$ | |
| | 2 | any $b\ d\ b$ | $d_2b_3:\rho^{(j)}d_2b_3 \leftrightarrow b_1:\rho^{(j)}:d_4$ | $b\ d\ b\ d$ | |
| | 3 | any $b\ d\ b\ d$ | $b_1d_2:\tau^{(j)}:b_3d_4 \leftrightarrow L_x:\tau^{(j)}:L_{x+2}$ | | $b\ d\ b\ d\ldots$ |
| III$b$ | 1 (first part) | one $b^{\rightarrow}b_{\rightarrow}b^{(1)}$ | $d_2:\tau^{(j)}:d_2 \leftrightarrow b_3^{(1)}:\tau^{(j)}:b_3^{(j)}$ | all $b^{\rightarrow}d_{\rightarrow}b^{(j)}$ | |
| | 1 (second part) | one $b^{\rightarrow}b_{\rightarrow}b^{(1)}$ | $b_3:\rho^{(k)}:d_2 \leftrightarrow d_2:\rho^{(k)}:b_3^{(k)}$ | all $b^{\rightarrow}d_{\leftarrow}b^{(k)}$ | |
| | 2 | any $b^{\rightarrow}b_{\rightarrow}b$ <br> any $b^{\rightarrow}b_{\leftarrow}b$ | $b_1:\tau^{(j)}:b_3 \leftrightarrow L_x:\tau^{(j)}:L_{x+2}$ | | $b^{\rightarrow}d_{\rightarrow}b^{\rightarrow}d_{\rightarrow}b\ldots$ <br> $b^{\rightarrow}d_{\leftarrow}b^{\rightarrow}d_{\leftarrow}b\ldots$ |
| III$c$ | 1 | one $b^{\rightarrow}d\ b^{(1)}$ | $d_2:\tau^{(j)}:d_2 \leftrightarrow b_3^{(1)}:\tau^{(j)}:b_3^{(j)}$ | all $b^{\rightarrow}d\ b^{(j)}$ | |
| | 2 ($m=2$) | any $b^{\rightarrow}d\ b$ | $b_1:\tau^{(j)}:b_3 \leftrightarrow L_x:\tau^{(j)}:L_{x+2}$ | | $b^{\rightarrow}d\ b^{\rightarrow}d\ldots$ |
| | 2 ($m=4$) | any $b^{\rightarrow}d\ b$ | $d_2b_3:\rho^{(j)}:d_2b_3 \leftrightarrow b_1:\rho^{(j)}:d_4$ | $b^{\rightarrow}d\ b^{\leftarrow}d$ | |
| | 3 ($m=4$) | any $b^{\rightarrow}d\ b^{\leftarrow}d$ | $d_2:\tau^{(j)}:d_4 \leftrightarrow b_3:\tau^{(j)}:b_5$ | $b^{\rightarrow}d\ b^{\leftarrow}d\ b$ | |
| | 4 ($m=4$) | any $b^{\rightarrow}d\ b^{\leftarrow}d\ b$ | $d_4b_5:\rho^{(j)}:d_4b_5 \leftrightarrow b_3:\rho^{(j)}:d_4$ | $b^{\rightarrow}d\ b^{\leftarrow}d\ b^{\rightarrow}d$ | |
| | 5 ($m=4$) | any $b^{\rightarrow}d\ b^{\leftarrow}d\ b^{\rightarrow}d$ | $b_3d_4b_5d_6:\rho^{(j)}:b_3d_4b_5d_6 \leftrightarrow b_1d_2:\rho^{(j)}:b_7d_8$ | $b^{\rightarrow}d\ b^{\leftarrow}d\ b^{\rightarrow}d\ b^{\leftarrow}d$ | |
| | 6 ($m=4$) | any $b^{\rightarrow}d\ b^{\leftarrow}d\ b^{\rightarrow}d\ b^{\leftarrow}d$ | $b_1d_2b_3d_4:\tau^{(j)}:b_3d_4b_5d_6 \leftrightarrow L_x:\tau^{(j)}:L_{x+4}$ | | $b^{\rightarrow}d\ b^{\leftarrow}d\ b^{\rightarrow}d\ b^{\leftarrow}d\ldots$ |

structures containing layers all of the same kind (Dornberger-Schiff, 1964, 1966; Dornberger-Schiff & Fichtner, 1972). Any of these symbols gives the layer group of a single layer in its first line, and operations linking a layer into its successor, within curly brackets, in a second line, if all layer pairs are equivalent. If two kinds of layer pairs occur, the operations linking the pairs of either kind are given within two pairs of curly brackets, either both in the second line or in a second and a third line (see also Grell & Dornberger-Schiff, 1982). Operations referring to a direction perpendicular to the direction of the translational vectors **a**, **b** common to the layers are given in round brackets. Translational components are given as subscripts of the corresponding symbols for the respective symmetry operations, where an $n$-fold screw with translational component $t$ is symbolized by $n_{n.t}$, and a glide plane $g$ with components $k$ and $l$ by $g_{2k,2l}$.

## Examples

*Example* (1)

The polytypes of the mineral spurrite $Ca_5(SiO_4)_2CO_3$ (Smith, Karle, Hauptmann & Karle, 1960), $K_4Mo(CN)_5NO$ (Svedung & Vannerberg, 1968) and $K_4V(CN)_6$ (Jagner, 1975) are to be described as belonging to an OD groupoid family denoted by

$$\begin{array}{cccc} P & m & a & (b) \\ \{c_2 & n_{2,1/2} & (n_{\bar{1}/2,1}) & \}. \end{array} \qquad (1)$$

The structures are to be considered as being built of layers all of the same kind. The layers are non-polar, *i.e.* they are to be indicated by the letter $A$ and they are schematically represented in Figs. 1($a$) and ($b$) by strings of signs connected by a line and indicated by letters $A$ with subscripts. The layer pairs are non-polar as indicated by the twofold screw and the centres of symmetry between $A_1$ and $A_2$ in Fig. 1($a$). The polytypes whose relevant coincidence operations are described by the OD groupoid family (1) belong therefore to subcategory I$a$. From Table 1 it follows that the MDO structures of this category have a sequence period with one layer. That means there must exist a total $\tau$ operation converting any layer into its successor. Such a $\tau$ operation converts also $A_1$ into $A_2$. Corresponding to the order of the layer group of a single layer there are four $\tau$ operations transforming $A_1$ into $A_2$, namely a translation (indicated by **c** in Fig. 1$a$), an $n$ glide perpendicular to **b** with component 1 in the **c** direction and $\frac{1}{4}$ in the **a** direction, a twofold screw in the **c** direction (Fig. 1$b$) and a $c$ glide perpendicular to **a** (Fig. 1$b$). The first two $\tau$ operations lead to the same position of $A_3$, if applied to $A_2$ as indicated in Fig. 1($a$). Any of these $\tau$ operations leads, if it is made total by its continuations,* in signs

$$A_1{:}\tau{:}A_2 \leftrightarrow A_x{:}\tau{:}A_{x+1},$$

to the same stacking of layers, which constitutes an MDO structure with basic vectors **a**, **b**, **c** and space group $P2_1/a$ (Fig. 1$a$). An analogous statement holds for the second two $\tau$ operations, indicated in Fig. 1($b$). In this case an MDO structure results with basic vectors **a**, **b**, $\mathbf{c} = 2\mathbf{c}_0$ and space group $Pcab$. As there are no other $\tau$ operations transforming $A_1$ into $A_2$ all MDO structures of OD groupoid family (1) are obtained. The general method for proceeding with structures of this subcategory is given in Table 2. The predominant way in which the OD layers in the polytypes $Ca_5(SiO_4)_2CO_3$ and $K_4Mo(CN)_5NO$ are stacked corresponds to the monoclinic MDO structure $P2_1/a$ with $\mathbf{c} = \mathbf{c}_0 - \mathbf{a}/4$, polysynthetically twinned to a greater or lesser degree; in the case of $K_4V(CN)_6$ the orthorhombic MDO structure with space group $Pcab$ and $\mathbf{c} = 2\mathbf{c}_0$ is predominant.

*Example* (2)

Decaborane (Kasper, Lucht & Harker, 1950) is a polytypic substance with the OD groupoid family†

$$\begin{array}{cccc} P & 1 & 2/a & (1) \\ \left\{\dfrac{2_{1/2}}{n_{1,2}}\right. & 1 & \left(\dfrac{2_2}{n_{1/2,1}}\right) & \left.\right\}. \end{array} \qquad (2)$$

The decaborane molecules have the site symmetry 2 and thus lie on special positions of the layer group. They are represented in Figs. 2($a$), ($b$), ($c$) by any two triangles sharing a corner. The layers are indicated similarly to Fig. 1. They are also non-polar and therefore a letter $A$ is given for them. Pairs of adjacent layers are polar, as there is no $\rho$ operation transforming $A_1$ into $A_2$ and $A_2$ into $A_1$, therefore an arrow is given $A_1 \vec{} A_2$ stating the sense of polarity for any other pair of layers occurring in an arbitrary stacking. The structures of (2) belong to category I$b$ and for them two types of MDO sequences are given in Table 1. The sequence period of one layer requires a total $\tau$ operation

$$A_1{:}\tau{:}A_2 \leftrightarrow A_x{:}\tau{:}A_{x+1}.$$

There are two $\tau$ operations, the twofold screw and the glide plane indicated in Fig. 2($a$), transforming $A_1$ into $A_2$. Their continuations to a total operation lead both to the same MDO structure as indicated in Fig. 2($a$) with space group $Pna2_1$ and lattice parameters **a**, **b**, $\mathbf{c} = 2\mathbf{c}_0$. The second type of MDO sequences is of period two layers, with the additional condition $A_1 \vec{} A_2{:}\rho{:}A_2 \vec{} A_3$, *i.e.* the position of $A_3$ is given by a $\rho$ operation trans-

* That means the transformation characterizing the partial coincidence operation is applied to generate a whole structure.

† With cyclic interchange of axes compared with the quoted paper.

forming $A_2$ into itself and $A_1$ into one possible position of $A_3$. There are two $\rho$ operations of such a kind, as indicated in Fig. 2(*b*), a centre of symmetry and a twofold axis parallel to **b**. Both lead to the same position of $A_3$. A sequence period of two layers requires a $\tau$ operation transforming $A_1$ into $A_3$, and its continuations to a total operation

$$A_1{:}\tau{:}A_3 \leftrightarrow A_x{:}\tau{:}A_{x+2}$$

lead to an MDO structure. The *c* glide perpendicular to **b** and the translation $\mathbf{t} = 1/2\mathbf{a} + 2\mathbf{c}_0$ lead to the same MDO structure as indicated in Fig. 2(*b*) with space group $P2/a$ and $\mathbf{c} = 2\mathbf{c}_0 - \mathbf{a}/2$. The general way for deducing all MDO structures of this subcategory is given in Table 2.

The OD structure as represented in Fig. 2(*c*) is not an MDO structure, although this OD structure has a space group $P2/a$ with $\mathbf{c} = 4\mathbf{c}_0$. This may be proved in two ways: on the one hand, the sequence of letters and arrows indicated at the right of Fig. 2(*c*), representing the sequence of layers, is not an MDO sequence; on the other hand, there are two kinds of triples, whereas the OD structure shown in Fig. 2(*a*) contains triples of only one of these kinds and that of Fig. 2(*b*) contains triples of the other kind only.

The crystals of decaborane examined by the quoted authors were disordered but contained extended regions of the MDO structure represented in Fig. 2(*b*).

*Example* (3)

$\gamma$-$Hg_3S_2Cl_2$ (Ďurovič, 1968) is a polytypic substance with the OD groupoid family

$$\begin{array}{cccc} C & m & m & (2) \\ \{2_{1/2} & 2 & (a_{1/2})\} & \\ \{2_{1/2} & 2 & (a_{1/2})\} & \end{array} \qquad (3)$$

or

$$\begin{array}{c} C \quad m \quad m(2) \\ \{2_{1/2}\ 2\ (a_{1/2})\} \quad \{2_{1/2}\ 2\ (a_{1/2})\}. \end{array}$$

Fig. 4(*a*) shows the two kinds of layer pairs. They are non-polar, therefore the structures of this family belong to category III*a*. From Table 1 it follows that there is only one type of MDO sequence with a sequence period of two layers and the additional condition $b_1d_2b_3{:}\rho{:}d_2b_3d_4$. For deducing all MDO polytypes we proceed corresponding to Table 2. First, all triples $b_1d_2b_3$ are to be obtained. We start with one possible triple $b_1d_2b_3^{(1)}$ and apply all $\tau$ operations of $d_2$ to $b_3^{(1)}$. Thus all positions $b_3^{(j)}$, *i.e.* all possible triples, are obtained. For any of the triples all $\rho$ operations transforming $d_2$ into $b_3$ and $b_3$ into $d_2$ are to be applied to $b_1$. In this way, $b_1$ is transformed into $d_4$ in a position so that the additional condition of Table 1 is fulfilled. For any of the quadruples thus obtained, any of the $\tau$ operations transforming $b_1d_2$ into $b_3d_4$ are to be continued to total $\tau$ operations

$$b_1d_2{:}\tau{:}b_3d_4 \leftrightarrow L_x{:}\tau{:}L_{x+2}.$$

From this procedure all possible MDO polytypes are

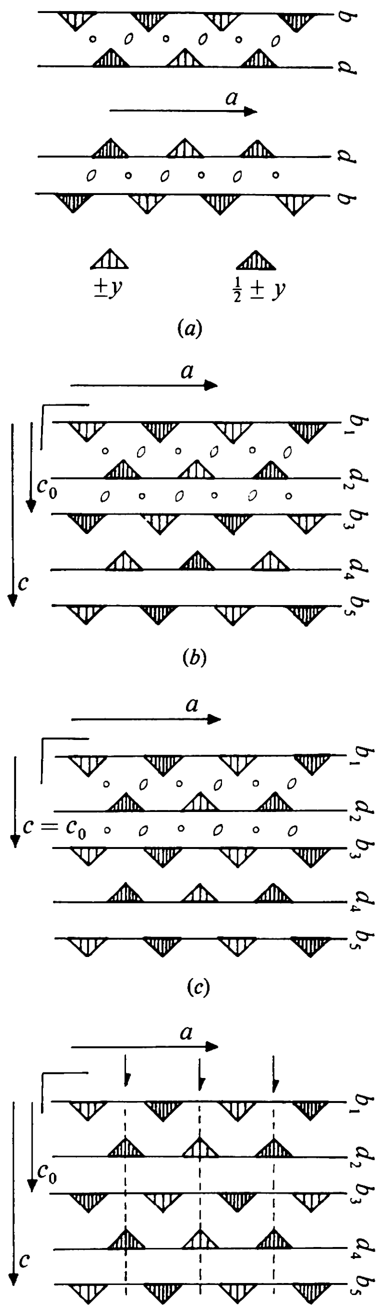


Fig. 4. Schematic representation of the symmetry and relative position of layers (*a*) in layer pairs, (*b*), (*c*) in two MDO polytypes, (*d*) in a periodic polytype of OD groupoid family (3), projected along **b**.

obtained, may be some of them more than once. The additional condition ensures the same result, if starting with a triple $d_2 b_3 d_4$.

Figs. 4(*b*) and (*c*) show schematically the two MDO polytypes belonging to OD groupoid family (3). There are only two different positions of $b_3$ relative to the pair $b_1 d_2$. One of these positions is obtained from the other by applying one of the $\tau$ operations of $d_2$ to $b_3$ in a given position. Corresponding to the order of the layer group there are eight $\tau$ operations, namely: (1) the identity, (2) $m \perp \mathbf{a}$, (3) $m \perp \mathbf{b}$, (4) $2 \parallel \mathbf{c}$ and from the $C$-centring follow (5) the translation $\mathbf{a}/2 + \mathbf{b}/2$, (6) $b \perp \mathbf{a}$, (7) $a \perp \mathbf{b}$ and (8) an additional twofold axis parallel to $\mathbf{c}_0$. The operations $m \perp \mathbf{a}$, $b \perp \mathbf{a}$ and both twofold axes change the position of $b_3$, whereas the other $\tau$ operations leave $b_3$ as it is. Therefore two kinds of triples and no more occur as represented in Figs. 4(*b*) and (*c*) by the layer triples $b_1 d_2 b_3$. For any of these triples the $\rho$ operations transforming $d_2$ into $b_3$ and $b_3$ into $d_2$ [they are centres of symmetry and twofold axes as indicated in Figs. 4(*b*) and (*c*)] lead to the same position of $d_4$. For any of the two quadruples thus obtained the $\tau$ operations transforming the pair $b_1 d_2$ into the pair $b_3 d_4$ lead to one MDO polytype, if continued to total $\tau$ operations:

$$b_1 d_2 : \tau : b_3 d_4 \leftrightarrow L_x : \tau : L_{x+2},$$

and that with space group $F2/m$ and lattice parameters $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c} = 2\mathbf{c}_0$ for the MDO polytype represented in Fig. 4(*b*), which may also be referred to space group $C2/m$ with $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c} = \mathbf{c}_0 - \mathbf{a}/2$.

The third polytype shown in Fig. 4(*d*) is not an MDO polytype, although there are total $\tau$ operations transforming any layer $L_x$ into a layer $L_{x+2}$. These operations are the twofold screw parallel to $\mathbf{c}$ and the $c$ glide perpendicular to $\mathbf{a}$. There are two kinds of triples: one of the kind as shown in Fig. 4(*b*), the other of the kind as shown in Fig. 4(*c*). This rests on the fact that the position of $d_4$ does not satisfy the additional condition.

The crystals of $\gamma$-$HgS_2Cl_2$ examined by Ďurovič (1968) were all disordered in various degrees, but all had extended regions corresponding to MDO polytypes; some corresponding to that of Fig. 4(*b*), others also to that of Fig. 4(*c*).

The other categories and subcategories are to be tackled accordingly with the help of Tables 1 and 2.

## Summary and conclusions

The effort seems to be fairly expensive as compared with the result of two MDO polytypes for any of the examples. And, indeed, no polytypic substance containing equivalent OD layers with more than three non-equivalent MDO polytypes has so far come to my knowledge. On the other hand, polytypic substances with $M > 1$ kinds of OD layers with a great number of non-equivalent MDO polytypes seem to be fairly frequent. The characterization and deduction of MDO polytypes for families with $M > 1$ are the subject of paper II of this series.

The statements made in this paper have been proved, but some of the proofs are still rather clumsy and would, if included in this paper, have taken up too much space. This is why I decided to publish the content matter without any proofs, and postpone publication of the proofs until they have been brought into a better form, perhaps with the help of a qualified mathematician. Even without the proofs, the content matter summarized in Table 1 seemed worth publishing, as well as the way in which it may be used to solve the two problems treated: to test whether a given polytype is an MDO polytype or not, and to compile a complete list of all MDO polytypes of a given polytypic substance.

My sincere thanks are due to my colleagues of the Abteilung Strukturforschung of our Institute as well as to Dr Ďurovič (Institute for Inorganic Chemistry of the Slovac Academy of Sciences, Bratislava) for a great number of helpful discussions, in particular, however, to Mrs H. Grell of the Abteilung, who untiringly helped by her critical remarks and suggestions to produce a text which – I hope – will be understandable for the reader. I have also to thank Dr sc. K. Fichtner of our Abteilung for carefully reading the manuscript and for drawing my attention to a mistake.

*Note added in final version:* In the present version of this paper, remarks of Professor B. B. Zvyagin have been taken into account. Mrs H. Grell has completed the revision of the paper according to notes of Professor K. Dornberger-Schiff after her sudden death.

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# Geometrical Properties of MDO Polytypes and Procedures for Their Derivation. II. OD Families Containing OD Layers of $M > 1$ Kinds and Their MDO Polytypes

BY K. DORNBERGER-SCHIFF† AND H. GRELL

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

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## Abstract

The condition for MDO polytypes formulated in paper I [Dornberger-Schiff (1982). *Acta Cryst.* A**38**, 483–491] is applied to OD structures containing OD layers of $M > 1$ kinds. Methods for ascertaining whether a certain polytype is an MDO polytype or not, and for deducing a complete list of MDO polytypes for any family of polytypes are given. These are applied to $YCl(OH)_2$ and some $MeX_2$ polytype families.

## Introduction

Amongst the polytypic substances whose structures turn out to be OD structures consisting of OD layers of more than one kind, there are some of great theoretical and practical importance, such as the various phyllosilicates, pyroxenes, sulfides, selenides and others. Compilation of a complete list of MDO polytypes for such polytypic substances is of particular importance because this may lead to a recognition of the structure, even if no single crystals are available (see *e.g.* Weiss & Ďurovič, 1980).

The definition of MDO polytypes for polytypic substances has been given in paper I of this series (Dornberger-Schiff, 1982). This and other notions – such as $\tau$ and $\rho$ operations – described there will also be used here. As already mentioned, layers of different kinds are to be given different superscripts. Four different categories of families of OD structures have been distinguished (Dornberger-Schiff, 1964; Grell & Dornberger-Schiff, 1982; Grell, 1980), of which category II contains only polar layers, with equivalent layers related exclusively by $\tau$ operations, so that no $\rho$

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