In all equations for $a_i(\mathbf{r})$, the set of coordinates is chosen as in *International Tables for X-ray Crystallography* (1952); if the tables give two alternative origins (of coordinates) then the first one is adopted.

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How to Choose OD Layers

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Abstract

A method for choosing OD layers in a structure is given. For any structure one of four cases is possible: 1. the structure cannot be interpreted as an OD structure consisting of layers; 2. the OD layers are uniquely determined; 3. the limits between OD layers may be changed with keeping the OD groupoid family; and 4. the limits may be changed with changing the OD groupoid family.

Introduction

Since OD theory has been developed it has proved its worth for the investigation of disordered structures and for the explanation of relations between polytypes (for some references see, for example, Table 1 in Dornberger-Schiff, 1979).

OD theory is based on the principle that interatomic forces decrease with increasing distance. A local arrangement of atoms occurring equivalently again and again in a structure does not necessarily enforce a three-dimensional periodicity of the total arrangement of all atoms in the structure. Because of the possible absence of three-dimensional periodicity, the symmetry relations within structures with (possible) disorder cannot be adequately described in the usual way by total symmetry operations which form space groups. The geometrical means used instead by Dornberger-Schiff are partial coincidence operations which in their turn form groupoids (Brandt, 1926; Ehresmann, 1957). The partial coincidence operations refer to parts of the structure occurring equivalently again and again in the structure. These parts may be aperiodic blocks, one-dimensionally periodic rods, or two-dimensionally periodic layers. In the case of polytypes which differ in layer stacking sequence (Bailey *et al.*, 1977) these parts are two-dimensionally periodic layers. OD theory is a geometrical approach and therefore these layers, called OD layers, are not identical with crystallochemical layers, although they often refer to the same region of the structure. OD layers reflect predominantly symmetry properties of two-dimensionally periodic parts. With the knowledge about the OD layers and about the pairs of adjacent OD layers all possible polytypes of a substance may be deduced, especially the MDO structures, called simple or regular by other authors, disordered and periodic polytypes of any length may be deduced as well. All these theoretically possible structures consisting of the same kinds of OD layers and the same kinds of layer pairs are said to belong to a family of OD structures (Dornberger-Schiff, 1964; Dornberger-Schiff & Ďurovič, 1975). Until now there have been no exact methods for choosing OD layers

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and it seemed there is only a method of trial and error to find them. Dornberger-Schiff (1980) sketched for the first time how to proceed in choosing OD layers. The present paper is based on these ideas.

Preliminary premise: the vicinity condition

OD structures are defined by the 'vicinity condition'. It relates parts of the structure fairly near to each other and it singles out from all possible types of structures those which show a certain kind of order. The vicinity condition is cited as formulated by Dornberger-Schiff (1980). In this form it defines OD structures consisting of layers and holds for all polytypic structures known to us.

The vicinity condition (VC) is said to hold for a structure (a set of structures) if and only if

(α) it (they) may be considered as consisting of disjunct parts periodic in two dimensions (layers) which are either of the same or of a small number of kinds;

(β) all layers of a crystal have a translational group $m\mathbf{a}+n\mathbf{b}$ in common ($\mathbf{a}, \mathbf{b}$ non-collinear);

(γ) equivalent sides of equivalent layers are in any and all considered structures faced by adjacent layers in such a way that the layer pairs thus formed are equivalent.

For our further considerations we presuppose the knowledge of the structure of at least two different polytypes belonging to one family of polytypic structures or the structure of a sample showing one-dimensional disorder is known. An example will serve to demonstrate how to proceed in principle. Equivalent regions play a fundamental role for determining OD layers. In the paragraph following, equivalent regions will be defined exactly. Then all cases occurring for equivalent regions and the consequences for the choice of OD layers are given and demonstrated by examples.

An example representing the procedure in a simple case
Example 1: tantalum pentaiodide $(TaI_5)_2$

In $(TaI_5)_2$ sheets of edge-sharing dimers are stacked as indicated in Fig. 1 (Müller, 1979). This structure shows one-dimensional disorder, which means that a splitting of the structure perpendicular to the direction of missing periodicity results in two-dimensionally periodic parts, all with common periodicity vectors, *i.e.* VCβ is fulfilled. For specifying such parts so that they fulfil also VCα and VCγ, maximal equivalent regions will be determined occurring again and again in the structure. All pairs of adjacent sheets of edge-sharing dimers are such maximal equivalent regions as required. These regions cover the structure in such a way that any sufficiently small part of the structure is contained in two such regions. All parts of the structure which are the intersection of any two overlapping equivalent regions fulfil VCα and VCγ. That means they are OD layers and $(TaI_5)_2$ is an OD structure.

There are two possible positions for any OD layer so that it forms with the preceding one a layer pair as required by VCγ. These possible positions differ by $\mathbf{a}/2$. Any stacking of these OD layers which results in layer pairs, any of them equivalent to the preceding one, leads to a structure with equivalent atomic arrangements within the layer pairs but not necessarily to a three-dimensionally periodic structure.

Equivalent regions

The procedure for choosing OD layers starts always in the same way. The maximal equivalent regions are to be determined. The notion 'equivalent region' is more precisely defined as follows:

Conditions for equivalent regions (ER)

*C*1. Equivalent regions are two-dimensionally periodic parts of the structure (two-dimensionally periodic in the same directions as the whole structure) occurring again and again equivalently (congruently or enantiomorphously) in the structure or in the structures to be compared.

*C*2. They are to be chosen in such a way that, wherever a part of an equivalent region occurs equivalently in the structure or in the structures to be compared, it must lie in a part equivalent to the complete equivalent region. (This equivalence of parts is to be regarded with respect to the immediate vicinity of these parts. Two atomic planes, for example, are not regarded as equivalent although the atoms are of

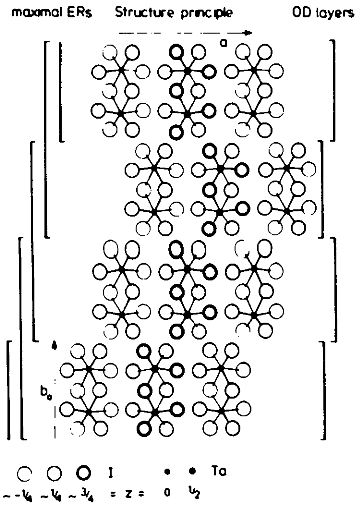


Fig. 1. Structure principle of $(TaI_5)_2$ projected along $\mathbf{z}$. Maximal equivalent regions (ER) and OD layers are indicated to the left and right, respectively.

the same kind and arranged in the same way, if the adjacent atomic planes of the one plane are different from the adjacent atomic planes of the other.)

*C*3. To any equivalent region there exist at least two different parts of the structure different from the equivalent region and equivalent to it.

In the following, parts of the structure fulfilling these conditions are called ERs for short. An ER is called maximal if it is not possible to enlarge it without violating these conditions. If there are maximal ERs, then any limit of the ERs means that the immediately following part of the structure does not have a uniquely determined position. If the limit lies within another ER, called ER′, then the position of the following part has only a limited number of possibilities for it must fit into ER′.

Covering a structure by ERs may occur in four variants:

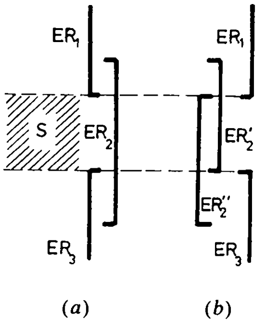
*V*0. There are parts of the structure covered by no maximal ER, or there are limits of maximal ERs which are not contained within another ER. In this case the structure cannot be interpreted as an OD structure.

*V*1. Any sufficiently small part of the structure is contained in exactly two maximal ERs (compare with example 1). In this case, any intersection of two overlapping ERs is an OD layer and the ERs are the pairs of adjacent OD layers.

*V*2. There are parts covered by only one maximal ER (Fig. 2).

*V*3. There are parts covered by more than two maximal ERs (example 3).

*V*2 is shown schematically in Fig. 2. Obviously, any two-dimensionally periodic part of an ER is also an ER. If ER_2 is replaced by ER_2' and ER_2'' in keeping with *C*1, *C*2 and *C*3, then part *S* is also covered by two ERs. This has to be done for all ERs equivalent to ER_2. Take note that the part covered only once belongs to one OD layer, although it may happen that adjacent atomic layers or atomic half-layers may be attached to it as we shall see in the next example. As such a part always belongs as a whole to an OD layer it is called the 'kernel' of an OD layer.



(*a*) (*b*)

Fig. 2. (*a*) Region *S* contained in ER_2 only. (*b*) ER_2 is replaced by ER_2' and ER_2''.

An example with parts covered only once by maximal ERs

Example 2: dioctahedral mica

In Fig. 3 the structure of a dioctahedral mica with equivalent 2:1 layers is shown with idealized symmetry according to the original Pauling (1930) model. The polytypes of this substance occur in a variety of ordered as well as disordered polytypes. On the basis of the OD interpretation of this substance all possible MDO polytypes (of mica and chlorites) have been deduced (Dornberger-Schiff, Backhaus & Ďurovič, 1982; Backhaus, Ďurovič & Weiss, 1984). As shown in Fig. 3, the planes of octahedrally coordinated cations are always covered once by maximal ERs. If the maximal ERs are replaced by modified ERs, then the octahedrally coordinated cations are covered twice by these ERs. This corresponds to *V*1 and OD layers and layer pairs are determined as in the first example. Two kinds of OD layers result as indicated under the heading A^i. But another replacement of the maximal ERs is also possible, and it is shown under the heading 'modified ER″'. New kinds of OD layers A'^j result then. Although attaching the atoms to the respective OD layers is different for the ERs and the ER′s, the layer groups of the resulting OD layers are the same and so are the OD groupoid families. The limits between the OD layers may vary within the indicated regions, *i.e.* the parts of the structure in which the regions of partial symmetry overlap (indicated to the left of Fig. 3). In any case of modifying the ERs, the conditions for ERs must be fulfilled.

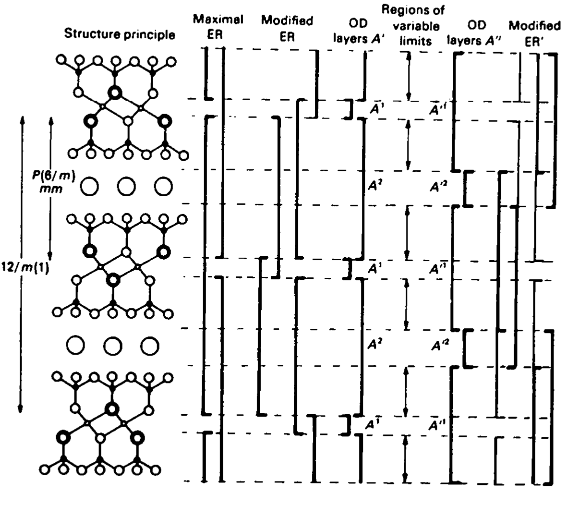


Fig. 3. Three arbitrarily stacked mica layers. Small open circles denote octahedrally coordinated cations, full circles Si atoms, medium-sized open circles O atoms, double circles OH groups and large circles interlayer cations. ER and ER′ are modifications of maximal ERs, where ER leads to the smallest OD layer A^1 and ER′ to the largest OD layer A'^1. ER′s are obtained from the maximal ERs by reducing twice the maximal ERs, indicated by the complete brackets (first step) and finally by the heavy part of the brackets (second step).

$V3$ seems rarely to occur. If a part of a structure is covered more than twice by maximal ERs, it may be regarded as an OD layer. But it is also possible that it does not occur as an OD layer at all, as we shall see in the next example. Consequently, the OD groupoid family is in such cases not uniquely determined. But there is only a limited number of OD groupoid families compatible with the symmetry relations of the structure to be investigated. Additional criteria (crystallochemical) may lead to an unequivocal decision for one of the OD groupoid families in question.

An example with parts covered more than twice by maximal ERs

Example 3: strontium germanate

As already shown by Dornberger-Schiff (1980), $Sr_3(GeO_3)_3$ is an example for $V3$. The structure consists of Sr atoms alternating with sheets of three-membered germanate rings (Fig. 4). If the sequence of the sheets of the three-membered germanate rings is as indicated in Fig. 4 (at the bottom), *i.e.* all triples of consecutive sheets are equivalent, then any of the maximal ERs contains three consecutive sheets including the Sr atoms attached to either side of these sheets. Any Sr plane is thus contained in four ERs and any sheet of germanate rings is contained in three ERs. The reduction of this case to $V1$ is done by shortening any ER in an equivalent way. Four different possibilities are shown, indicated by ER^1, ER^2, ER^3, ER^4, respectively. ER^1 and ER^2 originate from shortening any maximal ER to the beginning of the next but one maximal ER. This may be done in two directions resulting in ER^1s with OD layers A^1 or ER^2s with OD layers A^2. The aim is to describe the partial symmetry of the structure as well as possible. Any one of the two layer groups indicating the partial symmetry of the structure (Fig. 4, left) may be a layer group of OD layers. Which of them is realized depends on the modification of the maximal ERs. The two possibilities are indicated under ER^3 with layer group $P(\bar{6})2m$ of OD layers A^3 and under ER^4 with layer group $C12/m(1)$ of OD layers A^4, respectively. With ER^3s, for any ring sheet one position more is possible relative to the last but one sheet of rings compared with ER^4. This is the position which coincides in projection with the last but one germanate ring sheet. If this position is to be excluded, then ER^4 is to be preferred. If this position is to be taken into account, then any of the maximal ERs contains only two sheets of three-membered rings as shown under 'maximal ER'', *i.e.* $V1$ is present disregarding the Sr atoms which belong in this case to three ERs. Any of the Sr planes may constitute another kind of OD layer, but as they do not cause any disorder, they may be attached to the three-membered rings keeping their symmetry, *i.e.* the Sr half atoms may be attached to the respective neighbouring ring sheets.

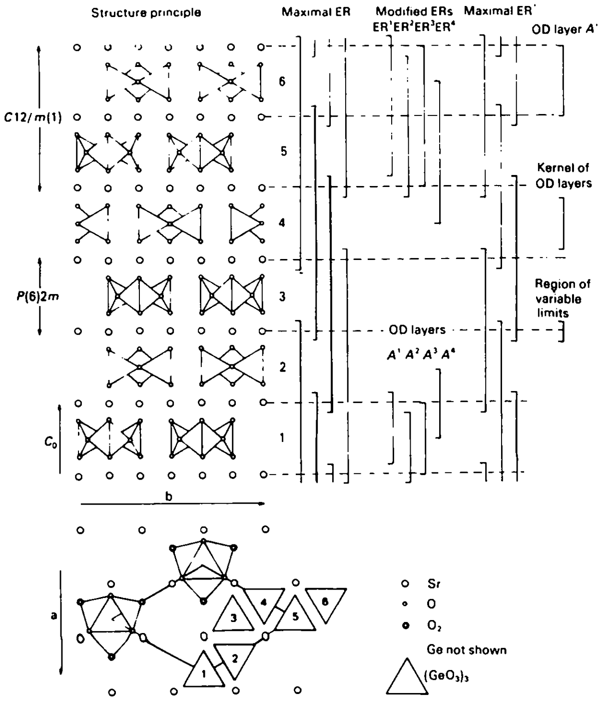


Fig. 4. At the bottom $Sr_3(GeO_3)_3$ projected along $\mathbf{c}_0$. Two $(GeO_3)_3$ rings of one sheet are shown with schematic representation given by an equilateral triangle with number 1. Further numbered triangles indicate a possible sequence of ring sheets in the $\mathbf{c}_0$ direction. Above it, this sequence projected along $\mathbf{a}$ is shown with partial layer symmetry indicated to the left. To the right, maximal ER's and corresponding OD layers A^i ($i = 1, \ldots, 4$) are shown. From maximal ER's, OD layers A^i may be deduced. The limits of OD layers may vary within the indicated region, whereas any region equivalent to that indicated by the kernel of OD layers is part of one OD layer.

This example shows that it sometimes may be very difficult to determine the OD layers. But, as already mentioned, there is only a limited number of possibilities if starting from maximal ERs. The OD groupoid family will, in general, not be changed if sufficiently small parts of the structure are covered either twice or once by maximal ERs (compare with example 2). In this case there are regions of variable limits, meaning that the attachment of the atoms contained in these regions is left to the taste of the user. For $V1$ the OD groupoid family as well as the OD layers are uniquely determined.

Application of the procedure for fully ordered structures results in $V3$ for them. Any part of such a structure is contained in an infinite number of ERs. Formally OD layers may be chosen perpendicular to each periodicity direction. The corresponding ERs contain two period lengths in such a direction. This shows fully ordered structures may be interpreted as OD structures but this is a formalism which does not make much sense.

Subfamilies

If for a polytypic substance the OD family and thus the OD layers are determined, it may occur that the investigation of another sample of the substance yields new maximal ERs. In this case the ERs chosen do not meet all sites of possible disorder, and at least one kind of ERs have to be replaced by new maximal ERs defining new additional limits for OD layers. This leads to a splitting of the original OD layers. Obviously, the structures of the original family are contained in the new family. Any of the new maximal ERs fulfils the conditions for ERs also in the original family.

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Determination of Anomalous Scattering Lengths of Samarium for Thermal Neutrons*

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Abstract

Anomalous scattering lengths of natural Sm for thermal neutrons with wavelengths between 0·827 and 1·300 Å have been determined by single-crystal diffraction from a Sm complex of known structure. 140 selected reflections were measured at a temperature of 37 K at each wavelength and b_0+b' and b'' refined in each case. The values obtained are in good agreement with values obtained from a Breit–Wigner calculation using tabulated absorption resonance parameters for ^{149}Sm. A value of $b_0=4\cdot3\pm0\cdot2$ fm is deduced from the diffraction experiments.

Introduction

Anomalous scattering of thermal neutrons by resonant nuclei has been exploited for crystal-structure determination – see, for example, Bartunik (1978), Flook, Freeman & Scudder (1977), Koetzle & Hamilton (1975), Schoenborn (1975), Sikka & Rajagopal (1975) and references cited therein.

For successful application of phase determination techniques the anomalous scattering lengths must be known at all wavelengths employed in an experiment. We report here the determination of the scattering lengths of natural Sm at a number of wavelengths from measurements of reflections from a single crystal of known structure. The refined values are compared with values calculated from absorption resonance parameters. A preliminary report of this work has been published by Engel & Koetzle (1982).

Table 1 gives a list of references to previous neutron diffraction determinations of scattering lengths of nuclei with large imaginary components.

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