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On the Theory of Order-Disorder (OD) Structures

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OD-structures consisting of equivalent layers are first characterized as having pairs of adjacent layers which are all equivalent. Then a slightly more general condition—the '*vicinity condition*'—is formulated which is satisfied not only by all ordered structures but also by all **OD**-structures. Partial operations (**PO**s) are seen to be of fundamental importance for characterizing the symmetry properties of **OD**-structures and the set of **PO**s of a certain structure is called an **OD**-groupoid. **OD**-structures of the same substance, built of the same kind of layers with the same kinds of pairs of adjacent layers are said to belong to the same family, the corresponding **OD**-groupoids to the same **OD**-groupoid family. Twins of one particular type are described as special members of families of **OD**-structures. A report on the deduction of a complete list of **OD**-groupoid families is given, and the resulting numbers of such families with different symmetry characteristics are listed in tables. There are 333 in all.

1. Introduction

In earlier papers (Dornberger-Schiff, 1956, 1957, 1959*c*) one of us has described some examples of what we propose to call **OD**-*structures*. In such structures equivalent parts lie in equivalent vicinities but there need not be perfect long-range order.

It is the aim of this paper to report on results of theoretical investigations—to be published in full elsewhere—concerning one particular class of **OD**-structures—structures which consist of *equivalent** *layers* with two-fold periodicity, piled on top of one another in such a way that they all have two linearly independent translational vectors **a** and **b** in common which correspond to this periodicity. Apart from these translations and their linear combinations $m\mathbf{a}+n\mathbf{b}$ an **OD**-structure need not possess any (total) symmetry operation. Structures with one-dimensional position disorder also belong to this class.

In these introductory remarks we shall refer to structures in which all pairs of adjacent layers are equivalent. In part 3 of this paper we shall see however, that the discussion of ordered structures suggests a somewhat wider definition of what we shall call the 'vicinity condition'. This will then be used to trace out the concept of an **OD**-structure.

As all layers of the structures discussed are equivalent, there must exist partial repeating operations† which transform any one of these layers either into itself or into any other layer. Such partial operations will be called **PO**s for short.

We shall not consider any partial operations referring to parts of a layer (or of layers) only. Thus any repeating operation under consideration may be described by a **PO** or by combinations of **PO**s.

A **PO** is fully characterized by

(*a*) the transformation of space, and
(*b*) the layer which is to be transformed.

The transformation need not bring any other layer into coincidence with any part of the structure.

Amongst the structures consisting of equivalent layers with equivalent pairs of adjacent layers we may distinguish between

(α) *fully ordered structures*, i.e. structures in which any transformation characterizing a **PO** is itself a (total) symmetry operation of the structure, and
(β) **OD**-*structures* in which proper **PO**s exist, i.e. **PO**s characterized by transformations which are not themselves (total) symmetry operations of the structure.

It is convenient to number the layers according to their position: $\ldots, L_{\bar{2}}, L_{\bar{1}}, L_0, L_1, L_2, L_3, \ldots$. To denote **PO**s we shall use small letters with the numbers of the layer transformed and of the resulting layer as prefixes. The symbol ${}_{p,q}a$ would thus denote a **PO** transforming L_p into L_q. To each **PO** ${}_{p,q}a$ there exists an inverse operation which is given the symbol ${}_{q,p}a^{-1}$.

In accordance with an earlier suggestion (Dornberger-Schiff, 1956) to call the plane space group of the single layer the Λ-symmetry of the structure, **PO**s ${}_{p,p}a$, transforming any layer L_p into itself are to be called λ-**PO**s. The set of ${}_{p,p}a$ for a particular layer L_p forms a group, namely one of the 80 plane space groups in three dimensions (see also Holser, 1958). A **PO** ${}_{p,p+1}a$ or ${}_{p,p-1}a$ transforming a layer L_p into an adjacent layer (L_{p+1} or L_{p-1}) will be called a σ-**PO**.

* Here and in the following the term 'equivalent' stands for 'congruent or enantiomorphous'.

† For a discussion of the term 'repeating operation' see M. J. Buerger (1956) p. 3 ff.

The complete set of **PO**s does not form a group (in the mathematical sense), as two **PO**s $_{p,q}a$ and $_{r,s}b$ may not be combined in this order, unless $q=r$, that is unless the layer L_q into which the original layer is transformed by the first **PO** is identical with the layer L_r to be transformed by the second **PO**. The **PO**s do, however, form a groupoid as defined by Brandt (1927).* (A fuller mathematical treatment is to be given by the authors in a paper in preparation.)

Obviously the complete set of **PO**s of a structure may be generated from all λ- and σ-**PO**s. For example, any **PO** $_{1,3}a$ may be generated as combination or 'product' of arbitrary σ-**PO**s $_{1,2}b$ and $_{2,3}c$, multiplied by a suitable λ-**PO** $_{3,3}d$.

As we know, an ordered structure is completely determined by the coordinates x_j, y_j, z_j of the atoms of an asymmetric unit, together with all symmetry operations. Similarly, an **OD**-structure is completely determined by the coordinates x_j, y_j, z_j of the atoms of an asymmetric unit of a layer together with all **PO**s.

In the case of an **OD**-structure it is, however, not only extremely difficult but also—for many purposes—quite unnecessary to carry out a complete structure determination. Practically all questions of chemistry—atomic distances, coordination numbers and usually coordination polyhedra and bond angles—may be answered, if the structure of a single layer and the relative position of two adjacent layers are known, provided that not only all layers but also all pairs of adjacent layers are equivalent. With these data a whole set of geometrically possible structures is compatible, unless they define a fully ordered structure. Such a set is called a family of **OD**-structures or **OD**-family.

A well-known example of such an **OD**-family are the various (ordered and disordered) SiC-structures:

A single layer consists of

Si-atoms in (000) } and points equivalent with respect
C-atoms in $(00z_0)$ } to translations $m\mathbf{a}+n\mathbf{b}$.

Pairs of adjacent layers are equivalent to a pair consisting of the layer just described and the layer with

Si-atoms in $(\frac{1}{3}, \frac{2}{3}, 1)$ }
C-atoms in $(\frac{1}{3}, \frac{2}{3}, 1+z_0)$ } and equivalent points .

(All coordinates referred to hexagonal axes, with the unit in the **c**-direction taken as c/n (for ordered structures) where c is the lattice constant and n the number of layers per repeat in the **c**-direction.)

For the determination of an **OD**-family it is sufficient to determine

(i) all λ-**PO**s $_{p,p}a$ transforming one particular layer, L_p say, into itself,

(ii) one particular σ-**PO** $_{p,p+1}b$ transforming L_p into L_{p+1},

(iii) the coordinates x_j, y_j, z_j of the atoms of the asymmetric unit.

The set of **OD**-groupoids corresponding to an **OD**-family is called a family of **OD**-groupoids.

It is the aim of the present investigations, to put at the disposal of the crystallographer the means—corresponding in many ways to the main tables of the *International Tables for X-ray Crystallography*—for determining the family of **OD**-groupoids of a structure from its X-ray data.

Other authors have been interested in questions of the statistical characterization of samples of disordered **OD**-structures within their particular family. (See e.g. Hendricks & Teller, 1942; Jagodzinski, 1949*a*, *b*, *c*, 1954; Wilson, 1942). Such questions are, however, outside the scope of this paper.

2. Remarks on POs

The fact that the layers transformed by **PO**s are periodic in two dimensions only, limits the range of transformations which may characterize **PO**s to those given in Table 1.

In this table a distinction has been made between the so called τ-**PO**s, which transform the side of a layer facing upwards into a side facing upwards, and the so called ϱ-**PO**s which transform a side of a layer facing upwards into one facing downwards.

Table 1. *Transformations compatible with* **OD** *layer structures*

Transformations characterizing τ-**PO**s	Transformations characterizing ϱ-**PO**s
translations	centre of inversion
rotations and screw movements (axes perpendicular to layer plane)	inversion axes (axes perpendicular to layer plane)
	mirror and glide planes (parallel to layer plane)
mirror and glide planes (perpendicular to layer plane)	2-fold rotations and screw movements (parallel to layer plane)

Thus in symbols (with the layer plane parallel to x and y):

τ-**PO**s convert x, y, z into $x', y', \mathrm{C}+z$
ϱ-**PO**s convert x, y, z into $x', y', \mathrm{C}-z$

where x' and y' are functions of x and y only; C may be any constant.

Thus the rules for the combination ('multiplication') of τ- and ϱ-**PO**s are given by the following

Multiplication table

	τ	ϱ
τ	τ	ϱ
ϱ	ϱ	τ

* Our thanks are due to Prof. H. Wielandt for drawing our attention to this mathematical concept.

If two pairs of adjacent layers, e.g. L_p, L_{p+1} and L_q, L_{q+1} are equivalent then there exists

either a **PO** ${}_{p,q}a$ characterized by the same transformation as a **PO** ${}_{p+1,q+1}a$
or a **PO** ${}_{p+1,q}b$ characterized by the same transformation as a **PO** ${}_{p,q+1}b$.

This rather involved statement may be expressed in a more concise form with the help of the term *continuation*: If ${}_{p,q}a$ and ${}_{r,s}b$ are characterized by the same transformation and differ only by the layers to which they apply, we call ${}_{p,q}a$ a continuation of ${}_{r,s}b$ and vice versa; in symbols

$$ {}_{p,q}a \longleftrightarrow {}_{r,s}b $$

or

$$ {}_{r,s}b \longleftrightarrow {}_{p,q}a \,. $$

We shall frequently use the same main letter for different **PO**s which are continuations of one another, e.g.

$$ {}_{p,q}a \longleftrightarrow {}_{r,s}a \,. $$

From the definition of τ- and ϱ-**PO**s follows:

The continuation of a τ-**PO** is a τ-**PO**, the continuation of a ϱ-**PO** is a ϱ-**PO**;

if ${}_{p,q}\tau \longleftrightarrow {}_{r,s}\tau$ then $r-p=s-q$ (see Fig. 1(a))
if ${}_{p,q}\varrho \longleftrightarrow {}_{r,s}\varrho$ then $r-p=q-s$ (see Fig. 1(b)).

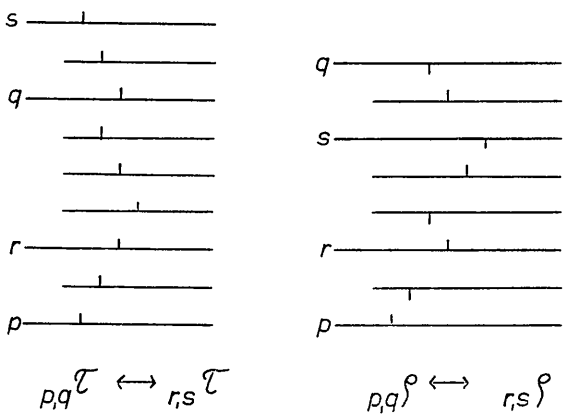


Fig. 1(a) and (b) τ- and ϱ-**PO**s and their continuations.

Thus the pairs L_p, L_{p+1} and L_q, L_{q+1} are equivalent, if there exists either a **PO**

$$ {}_{p,q}\tau \longleftrightarrow {}_{p+1,q+1}\tau $$

and/or a **PO**

$$ {}_{p+1,q}\varrho \longleftrightarrow {}_{p,q+1}\varrho \,. $$

In particular, for $p=1$ and $q=2$ follows: the pairs L_1L_2 and L_2L_3 are equivalent, if there exists either a **PO**

$$ {}_{1,2}\tau \longleftrightarrow {}_{2,3}\tau $$

and/or a **PO**

$$ {}_{2,2}\varrho \longleftrightarrow {}_{1,3}\varrho \,. $$

3. The vicinity condition as generalization from fully ordered structures

Fully ordered structures are necessarily periodic in three dimensions. The reverse is also true: Any structure periodic in three dimensions may be thought of as a fully ordered structure consisting of equivalent layers, piled on top of one another in a certain way. Actually, this manner of looking at a fully ordered structure is more in keeping with the physical causes of the existence of such structures than the description making use of periodicity, as the periodicity—a long range property of the structure—results from short-range forces of interaction.

The layers themselves can be thought of as consisting of rods periodic in one dimension only, arranged according to forces of interaction between them, and the rods as consisting of bricks limited in all directions. This will certainly be useful when treating structures of higher degree of disorder. Then the term **PO** will have to be defined in a more general way. For the present purposes it is sufficient to treat the single layers as prefabricated elements out of which the structure is to be built.

Actually we can understand the formation of a fully ordered structure from equivalent layers, even if the range of the forces of interaction is so limited that the energy of interaction between layers which are not immediate neighbours is small in comparison with the energy of interaction between adjacent layers.

Then equivalent pairs of layers will probably be formed in different parts of the structure, as a certain relative arrangement of two adjacent layers which is energetically favourable in one part of the structure will be equally favourable in any other part of the structure.

Further, we have to expect the relative arrangement of adjacent layers to be such that translationally equivalent asymmetric units of one layer have translationally equivalent vicinities in an adjacent layer. This would then lead necessarily to an arrangement of layers with common translations $m\mathbf{a}+n\mathbf{b}$.

These conditions to be expected are met by any fully ordered structure built of equivalent layers. They are also met by structures not fully ordered, which we named **OD**-structures (order–disorder structures). Before formulating them more precisely, it is convenient to look at them with the help of practical examples. To do so, we take the schematic representation of a fully ordered structure of space group, $Pnc2$. It may be considered as built of equivalent layers and with all pairs of adjacent layers equivalent according to Fig. 2(a), with the layer planes parallel to **ab**, or according to Figs. 3(a) and 4(a) with the layer planes parallel to **ac**.

In each of the Figures the layers are indicated as L_1, L_2, ...

There is only one possibility—that indicated in Fig. 2(a)—of splitting this structure into equivalent

Figs. 2–5. Representation of corresponding fully ordered (*a*) and **OD**-structures (*b*).
Black triangles correspond to $x=x_0$, white triangles to $x=\bar{x}_0$.

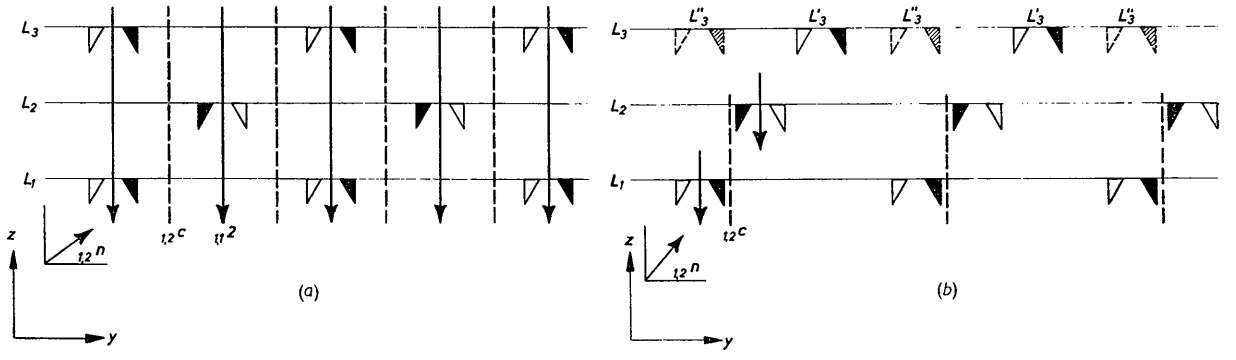


Fig. 2(*a*). Space group *Pnc*2, split into layers parallel to **ab**.

Fig. 2(*b*). **OD**-groupoid-family $\begin{matrix} P\ 1 & 1\ (2) \\ \{n_{s,2} & c_2\ (1)\} \end{matrix}$
corresponding to Fig. 2(*a*).

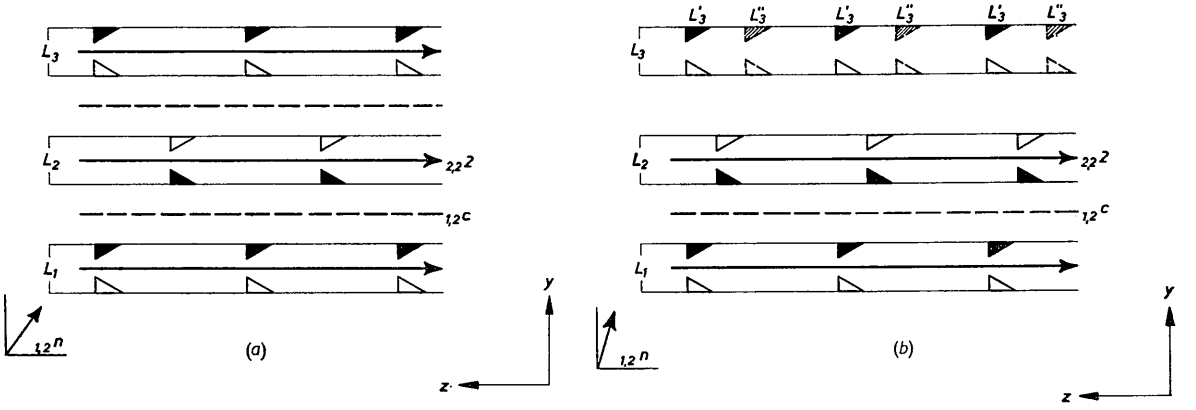


Fig. 3(*a*). Space group *Pnc*2, split into layers parallel **ac**.

Fig. 3(*b*). **OD**-groupoid-family $\begin{matrix} P\ 1 & (1)\ 2 \\ \{n_{2,s} & (c_s)\ 1\} \end{matrix}$
corresponding to Fig. 3(*a*).

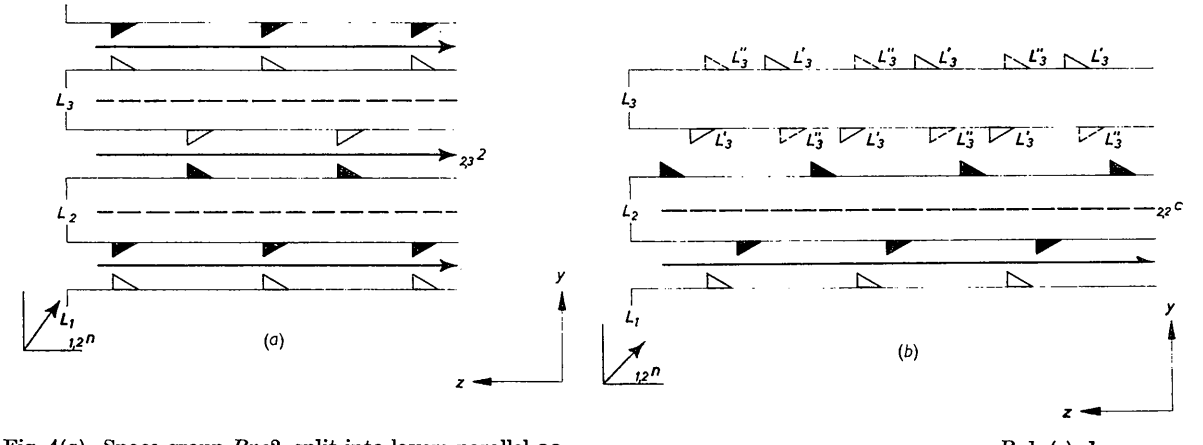


Fig. 4(*a*). Space group *Pnc*2, split into layers parallel **ac**.

Fig. 4(*b*). **OD**-groupoid-family $\begin{matrix} P\ 1\ (c)\ 1 \\ \{1\ (1)\ 2_r\} \end{matrix}$
corresponding to Fig. 4(*a*).

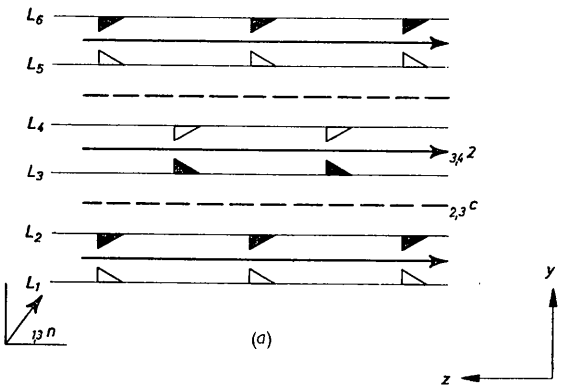


Fig. 5(*a*). Space group *Pnc*2, split into layers parallel **ac**.

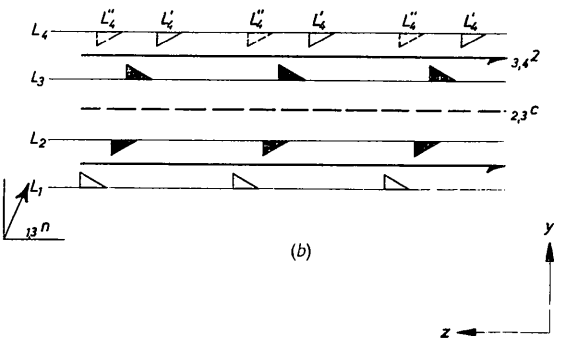


Fig. 5(*b*). **OD**-groupoid-family $\begin{matrix} P\ 1\ (1)\ 1 \\ \{1\ (1)\ 2_r\} \\ \{1\ (c_s)\ 1\} \end{matrix}$
corresponding to Fig. 5(*a*).

layers parallel to **ab** in such a way that each symmetry operation of the space group corresponds to a class of **POs**.

There is, however—besides those corresponding to Figs. 3(*a*) and 4(*a*)—one more possibility of splitting the structure into equivalent layers parallel to **ac**, so that each symmetry operation of the space group corresponds to a class of **POs**; namely that indicated in Fig. 5(*a*). Whereas, however, in all the other cases not only the layers but also all the *pairs of adjacent layers* are equivalent, in this case there are two classes of pairs of adjacent layers: the pairs L_{2n-1}, L_{2n} and the pairs L_{2n}, L_{2n+1}; only those pairs belonging to the same class are equivalent.

The reason for this difference is as follows. We have seen that the equivalence of two pairs of adjacent layers, e.g. of the pairs L_1, L_2 and L_2, L_3, results from the existence of either a **PO** $_{1,2}\tau$ or a **PO** $_{2,2}\varrho$ with a suitable continuation. Now looking at the various cases discussed above, we see that in those depicted in Figs. 2(*a*), 3(*a*) and 4(*a*) there exist **POs** $_{1,2}\tau$ (in the latter two cases as well as **POs** $_{2,2}\varrho$). Thus there exist **POs** which, by having a continuation, can give rise to the equivalence of the pairs. In the case depicted in Fig. 5(*a*), however, there exists neither a $_{1,2}\tau$ nor a $_{2,2}\varrho$. So, no matter how the layer L_3 is arranged, it cannot possibly lead to a pair L_2, L_3 equivalent to the pair L_1, L_2.

We can now proceed to formulate the vicinity condition which holds in fully ordered structures as well as in **OD**-structures. It refers to the vicinity of any one layer in any adjacent layer (whereas the region surrounding any atom within the same layer is bound to be equivalent to the region surrounding any equivalent atom, by reason of the plane space group of the layer and the equivalence of layers).

Vicinity condition

(Part 1) Asymmetric units of one layer which are translationally equivalent have translationally equivalent vicinities in any adjacent layer.*

(Part 2) The pairs of layers L_p, L_{p+1} and L_q, L_{q+1} are equivalent, i.e. there exist

either **POs**

$$_{p,q}\tau \longleftrightarrow {}_{p+1,q+1}\tau$$

or **POs**

$$_{p+1,q}\varrho \longleftrightarrow {}_{p,q+1}\varrho\ ,$$

if there is in the structure either a **PO** $_{p,q}\tau$ or a **PO** $_{p+1,q}\varrho$, i.e. if there exists a **PO** of the kind given on the left side of the $\longleftrightarrow$ signs at all.

The Figs. 2(*b*), 3(*b*), 4(*b*) and 5(*b*) indicate **OD**-structures corresponding to the fully ordered structures just described. Each of them consists of the same kind of layers as the corresponding ordered structure and the layers are linked by σ-**POs** differing only by their translational components or their arrangement from the σ-**POs** of the corresponding ordered structure.

For these **OD**-structures the vicinity condition holds just as it holds for fully ordered structures. In the case of a fully ordered structure we could, however, choose arbitrarily what we considered to be our single layer in a number of different ways. In the case of an **OD**-structure, the single layer may be defined as the biggest part of the structure which allows the

* The vicinity condition (part 1) may be weakened to read as follows: 'There exists a set of translations (not all collinear) so that asymmetric units of one layer which may be brought to coincidence by one of these translations have vicinities in any adjacent layer which are brought to coincidence by the same translation'. This weakened version may be of practical importance for structures consisting of more than one set of equivalent layers.

relevant* partial operations of the structure to be formulated as **PO**s or combinations of **PO**s. In many cases this definition determines uniquely the single layer. In some other cases of **OD**-structures this definition may be unique only when the orientation of the layers has been fixed, or there may even be two or more possibilities of defining the single layer in accordance with this definition. It ensures, that there is no relevant partial operation which would transform part of a particular layer into part of the same layer, except those operations the transformations of which transform the whole layer into itself.

We wish to note here in passing that this formulation of the vicinity condition allows a generalization of the concept of **OD**-structure: We may also call structures consisting of two or more sets of layers where only those layers belonging to the same set are equivalent, **OD**-structures, if the vicinity condition (given above) holds. A further generalization to cover structures with higher degree of (potential or actual) disorder—structures composed of rods or of bricks finite in all directions—is possible but requires a more general formulation of the vicinity condition.

In the case of structures consisting of periodic layers, the existence or non-existence of τ- and ϱ-**PO**s amongst σ-**PO**s decides which special form the vicinity condition (part 2) takes. Let all the σ-**PO**s ${}_{p,p+1}\sigma$ be known for a particular p. The ${}_{p,p}\lambda$ may then be deduced from them. As all layers are equivalent, at least one ${}_{p,p+1}\sigma$ is bound to exist. Thus we can distinguish 3 categories, depending on the τ- or ϱ-**PO**s amongst the ${}_{p,p+1}\sigma$.

Definition

Category I: There exists (at least) one ${}_{p,p+1}\tau$, as well as (at least) one ${}_{p,p+1}\varrho$. (See Figs. 3(*b*) and 4(*b*)).

Category II: There exists (at least) one ${}_{p,p+1}\tau$, but no ${}_{p,p+1}\varrho$. (See Figs. 2(*b*)).

Category III: There exists no ${}_{p,p+1}\tau$, but (at least) one ${}_{p,p+1}\varrho$. (See Fig. 5(*b*)).

Only in Category I are there ϱ-**PO**s amongst the λ-**PO**s. From the vicinity condition it follows for categories I and II that:

(*a*) all pairs of adjacent layers are equivalent;
(*b*) if there exist **PO**s ${}_{p,p+1}\tau$ and/but no ${}_{p,p+1}\varrho$ for one particular value p, then there exist ${}_{q,q+1}\tau$ and/but no ${}_{q,q+1}\varrho$ for any value q, respectively.

For category III it follows that the pairs L_pL_{p+1} and $L_{p+1}L_{p+2}$ cannot be equivalent. The existence of a ${}_{p+1,p+2}\tau$ would contradict the vicinity condition (part 2) so that the existence of a ${}_{p+1,p+2}\varrho$ follows.

From the vicinity condition it follows for category III that:

(*a*) there are two sets of pairs of adjacent layers: the pairs $L_{2n-1}L_{2n}$ and $L_{2n}L_{2n+1}$. Pairs belonging to the same set are equivalent;
(*b*) if there exists a **PO** ${}_{p,p+1}\varrho$, but no ${}_{p,p+1}\tau$ for one particular value p, then there exists a **PO** ${}_{q,q+1}\varrho$ but no ${}_{q,q+1}\tau$ for any value q.

The existence or non-existence of τ- and ϱ-**PO**s in structures of the 3 categories is summarized in Table 2.

Table 2. *τ- and ϱ-**PO**s in the 3 categories*

Category	${}_{pq}\tau$	${}_{pq}\varrho$
I	present	present
II	present	absent
III	present if $p-q=2n$	present if $p-q=2n+1$

Now, let a structure be built of equivalent layers (in the sense defined above) and let the vicinity condition hold. Then the question arises if it is possible to decide, from the knowledge of all **PO**s ${}_{p,p+1}\sigma$ (for one particular value p only), whether the corresponding structure is a fully ordered structure (i.e. any transformation characterizing a **PO** is a symmetry operation of the structure) or an **OD**-structure (i.e., there exist proper **PO**s, with characterizing transformations which are not symmetry operations of the structure).

From the ${}_{p,p+1}\sigma$ and their inverse **PO**s ${}_{p+1,p}\sigma^{-1}$ all **PO**s ${}_{p,p}\lambda$ and ${}_{p+1,p+1}\lambda$ may be deduced (${}_{p,p}\lambda = {}_{p,p+1}\sigma' \cdot {}_{p+1,p}\sigma^{-1}$ and ${}_{p+1,p+1}\lambda = {}_{p+1,p}\sigma^{-1} \cdot {}_{p,p+1}\sigma'$, where σ denotes one particular **PO** and σ' any one **PO** converting L_p into L_{p+1}). If there is either a ${}_{p,p}\tau$ amongst the ${}_{p,p}\lambda$ which doesn't posses a continuation ${}_{p+1,p+1}\tau$, or a ${}_{p,p+1}\varrho$ without a continuation ${}_{p+1,p}\varrho$, then the structure is an **OD**-structure (and at least one of these two possibilities is realized in any possible **OD**-structure either for the particular value p chosen or for $p'=p+1$). The category to which the **OD**-structure belongs may be found according to the definition of categories (see above) and depends on the existence or non-existence of τ- and ϱ-**PO**s amongst the ${}_{p,p+1}\sigma$, with one exception: If there exists a ${}_{p,p+1}\varrho$ but no ${}_{p,p+1}\tau$, then the **OD**-structure belongs either to category I or to category III, depending on whether there exists a continuation ${}_{p,p+1}\varrho \longleftrightarrow {}_{p+1,p}\varrho$ or not. In the former case the pair of adjacent 'layers' $L_{p-1}L_p$ ought to have been called one layer according to the rules. The structures indicated by Figs. 3(*b*) and 4(*b*) described by means of single layers as indicated in Fig. 5(*b*) are examples of that kind.

The vicinity condition (part 2) may now be specialized to read as given in Table 3 for the different categories of structures consisting of equivalent layers.

* Some partial operations will almost always be left out of our considerations as irrelevant. E.g. in many structures at least some of the atoms may be regarded as spherically symmetrical within the limits of accuracy. The corresponding partial rotations by arbitrary angles transforming only one particular atom into itself will be entirely irrelevant to the structure. Besides, partial operations referring to a part of a layer will always be considered as irrelevant, if there exists a **PO** referring to the same layer, and characterized by the same transformation.

Table 3. *Vicinity condition (part 2)*

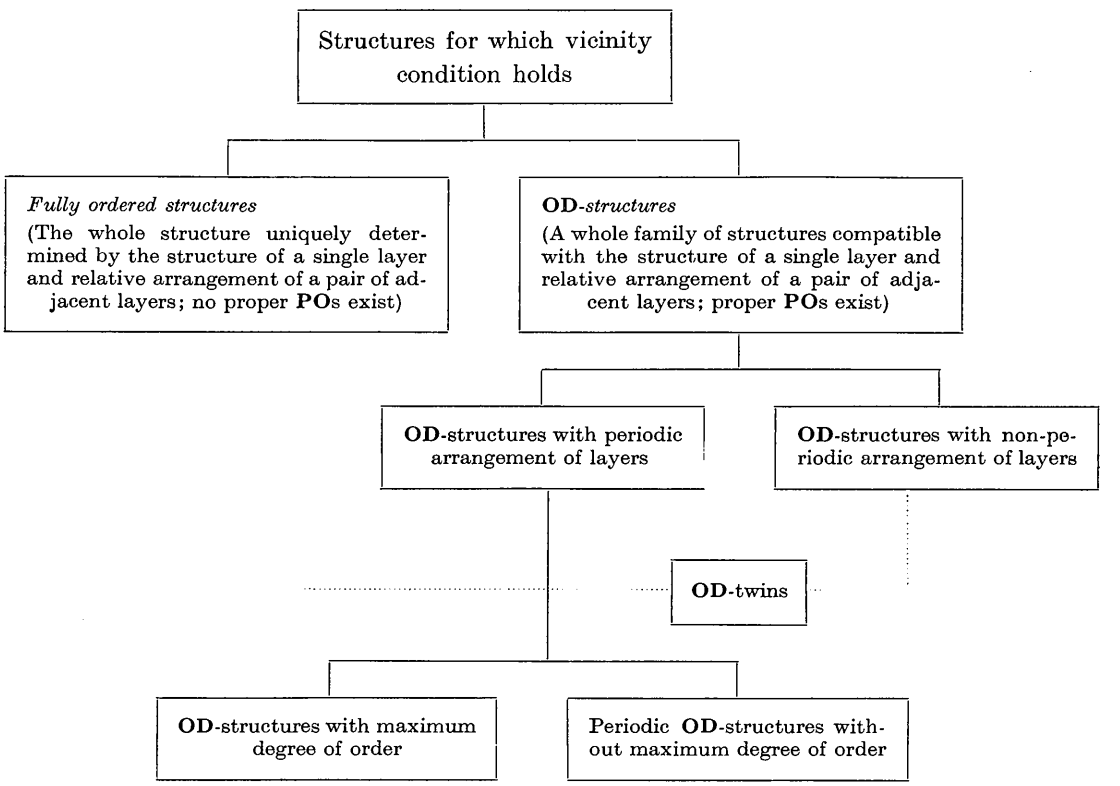
Category	(L_{p-1}, L_p) equivalent to (L_{q-1}, L_q)
I, II	for arbitrary values p, q
III	for p, q both odd or both even

4. Special ordered OD-structures. Twinning

Although not only the layers but also corresponding pairs of adjacent layers of the different structures of one family are equivalent, different structures in a family differ at least in some triples, i.e. sets of three adjacent layers. Obviously, there is (potentially) an infinite number of ordered (i.e. periodic) members of any **OD**-family, but only very few with the property that all triples are equivalent. These will be called **OD**-*structures with a maximum degree of order.*

We have to expect the formation of disordered **OD**-structures if, at the temperature of growth, differences in the energy of interaction between the outer layers of different kinds of triples are small compared with kT; if this energy is large compared with kT, we have to expect that ordered **OD**-structures be formed, especially structures with a maximum degree of order. Actually, in a number of cases of polymorphism the polymorphs are family members with a maximum degree of order; this is the case for the cubic face-centred and simple hexagonal structures of close-packed spheres, for zincblende and wurtzite, for the normal and the rhombohedral forms of graphite and others. Buerger (1945) has given a genetic explanation of the formation of twins, starting from energetic considerations very similar to those underlying the geometrical theory presented here. He has pointed out that a certain class of twinned structures may be described as consisting of two equivalent ordered parts which have one layer—the boundary layer—in common. Such twins we might call **OD**-*twins*. This name is justified, because any such **OD**-twin may be regarded as an **OD**-structure consisting either of layers all equivalent or of two kinds of layers. The 'boundary layer' is then a layer in the sense used in this paper. We would expect the twin individuals of such **OD**-twins to have **OD**-structures of maximum degree of order. The possibilities of twinning of this kind may then be deduced from the knowledge of possible **OD**-groupoids, consisting either of equivalent layers (i.e. the 333 referred to in this paper) or of two kinds of layers (which have not, so far, been deduced). This procedure seems to us more promising than the one proposed by Holser (1958). (See also Dornberger-Schiff, 1959(*b*)).

Particularly interesting are the polymorphic forms of SiC. They are members of the same **OD**-family but none of them is a structure with maximum degree of order. The many ordered, i.e. periodic, polymorphs, some of which have extraordinarily large periods, have been explained as consisting of a disordered (finite) stack of layers the sequence of which is repeated periodically because of the spiral growth of the structure. Other ordered (or nearly ordered) **OD**-structures



which do not possess maximum degree of order have been observed. They are likely to occur if there is a relatively high energy of interaction between layers more than one removed. An example of this kind seems to be the structure of samarium, a close-packed arrangement with a rhombohedral sequence of layers **ABCBCACAB ABC**.... (Daane, Rundle, Smith & Spedding, 1954). This sequence evidently does not correspond to maximum degree of order. Although the authors assume twinning this does not seem to us to be proved beyond doubt.

Amongst the structures for which the vicinity condition holds, we thus distinguish the types of structures given in the diagram p. 173.

OD-twins thus should be considered as **OD**-structures of maximum degree of order, as far as the structure of the twin-individual is concerned, but as non-periodic **OD**-structures inasmuch as the twinning violates the periodicity. Obviously, all the intermediate stages, from the single twin to multiple twinning, micro-twins and the entirely statistically disordered structures may be possible.

5. Possible POs in OD-structures and combinations of them. Possible OD-groupoid families

We have discussed above some limitations on the operations which may occur as **PO**s. Besides these we may state:

Only 'crystallographic' operations are possible as λ-**PO**s because the ${}_{pp}a$ for a given p form a plane space group. Only those combinations of λ-**PO**s known from space-group theory may occur. Thus only **PO**s corresponding to the symmetry elements present in the 80 plane space groups are admissible. They are listed in Table 5 according to the translational net. Translational components parallel to **c** cannot occur.

The possible σ-**PO**s are limited in a similar way by the periodicity of a pair of layers, postulated by the vicinity condition (part 1); those compatible with a given net may differ from the λ-**PO**s compatible with the same net only in their translational components, and that in two respects:

(1) The z-coordinate must be transformed by a σ-**PO** in such a way that one layer is transformed into the adjacent layer.

(2) Whereas in the case of λ-**PO**s the translational components in the x and y directions must have values 0 or $\frac{1}{2}$, arbitrary values of these components may occur in the case of σ-**PO**s. (Examples of glide planes with components ± 0 and $\pm\frac{1}{2}$ occurred in the **OD**-examples of categories I, II and III. See Figs. 2(*b*), 3(*b*), 4(*b*) and 5(*b*)).

Thus the relations given in Table 4 hold.

Table 4. *Relation between permissible λ- and σ-***PO***s*

	To any possible λ-**PO**	there are possible σ-**PO**s
τ-**PO**	$x, y, z \rightarrow x', y', z'$	$x, y, z \rightarrow x'+r, y'+r, z+1$
ϱ-**PO**	$x, y, z \rightarrow x', y', \bar{z}'$	$x, y, z \rightarrow x'+r, y'+s, 1-z$

where r and s denote fractions, and the unit in the **c**-direction is suitably chosen.

As symbols for such **PO**s generalizations of the international space-group symbols have been proposed (Dornberger-Schiff, 1956, 1959*a* and *c*).

As we know, the symbols $2_1, 3_1, 3_2$ denote screw axes with translational components which are $\frac{1}{2}, \frac{1}{3}, \frac{2}{3}$, respectively, of the cell length. Correspondingly, the symbols $2_r, 2_{\frac{1}{2}}, 3_3, 4_4$ denote screw movements with translational components $r/2, \frac{1}{4}, 1, 1$, respectively, of the repeat unit or of a unit defined as the distance between successive layers, measured in a direction perpendicular to the translational vectors, respectively.

Corresponding to the glide components $\frac{1}{2}$ or $(\frac{1}{2}, \frac{1}{2})$ of the glide planes a or n, respectively, a glide plane denoted by a_r or $n_{r,s}$ should have glide components $r/2$ or $(r/2, s/2)$, respectively.

Table 5 gives the **PO**s compatible with the different kinds of nets.

We may also note here a difference between the arrangement of operational elements* of **PO**s in **OD**-structures and that of symmetry elements in ordered structures: In ordered structures parallel symmetry elements occur in equidistant arrangements only. This rule no longer holds in **OD**-structures for operational elements which do not correspond to total symmetry elements. As an example we may take the structures shown in Figs. 2(*a*) and 2(*b*) where twofold axes alternate with glide planes.

The λ-**PO**s may occur in 80 different combinations called the plane groups in three dimensions. The 17 without ϱ-**PO**s may give rise to **OD**-groupoids of categories II and/or III; the 63 with ϱ-**PO**s give **OD**-groupoids of category I (see Tables 6, 7, 8). To

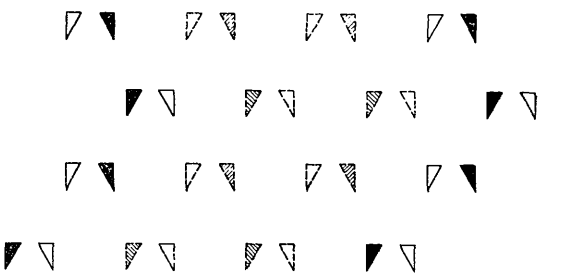


Fig. 6. **OD**-groupoid-family (see Fig. 2(*b*)) shown in full lines together with the superposition group (full lines and broken lines).

* We define the operational element of a **PO** in strict analogy to the definition of the operational element of a symmetry operation, i.e. the symmetry element.

Table 5. *λ- and σ-POs compatible with the different Bravais-nets of the single layer*

Net	λ τ	λ ρ	σ τ	σ ρ
General	1 1 (2)	T 1 1 (m) 1 1 (n)	$t_{r,s,1}$ 1 1 $\left(2_2\right)$	T 1 1 $\left(n_{r,s}\right)$
Rectangular Primitive or centred.*)	1 1 (2) m 1 (1) b 1 (1)	T 1 1 (m) 1 1 (n) 1 1 (a) 2 1 (1) 2_1 1 (1)	$t_{r,s,1}$ 1 1 $\left(2_2\right)$ $n_{s,2}$ 1 (1)	T 1 1 $\left(n_{r,s}\right)$ 2_r 1 (1)
Square Sequence of symbols: a, b, (c), u, v. u=a+b v=a-b *)	1 1 (2) 1 1 m 1 (1) 1 1 b 1 (1) 1 1 1 1 (1) m 1 1 1 (1) v 1 1 1 (4) 1 1	T 1 1 (m) 1 1 1 1 (a) 1 1 1 1 (u) 1 1 2 1 (1) 1 1 2_1 1 (1) 1 1 1 1 (1) 2 1 1 1 (1)2_1 1 1 1 (4) 1 1	$t_{r,s,1}$ 1 1 $\left(2_2\right)$ 1 1 $n_{s,2}$ 1 (1) 1 1 1 1 (1)$n_{r,2}$ 1 1 1 $\left(4_4\right)$ 1 1	T 1 1 $\left(n_{r,s}\right)$ 1 1 2_r 1 (1) 1 1 1 1 (1)2_u 1 1 1 (4) 1 1
Hexagonal Sequence of symbols: a, a', a'' (c), b, b', b''. a ⊥ b a' ⊥ b' a'' ⊥ b'' **)	1 1 1 (2) 1 1 1 m 1 1 (1) 1 1 1 b 1 1 (1) 1 1 1 1 1 1 (1) m 1 1 1 1 1 (1) a 1 1 1 1 1 (3) 1 1 1 1 1 1 (6) 1 1 1	T 1 1 1 (m) 1 1 1 1 1 1 (a) 1 1 1 1 1 1 (b) 1 1 1 2 1 1 (1) 1 1 1 2_1 1 1 (1) 1 1 1 1 1 1 (1) 2 1 1 1 1 1 (1)2_1 1 1 1 1 1 (3) 1 1 1 1 1 1 (6) 1 1 1	$t_{r,s,1}$ 1 1 1 (2_2)1 1 1 $n_{s,2}$ 1 1 (1) 1 1 1 1 1 1 (1)$n_{r,2}$ 1 1 1 1 1 $\left(3_3\right)$ 1 1 1 1 1 1 $\left(6_6\right)$ 1 1 1	T 1 1 1 $\left(n_{r,s}\right)$1 1 1 2_r 1 1 (1) 1 1 1 1 1 1 (1)2_s 1 1 1 1 1 (3) 1 1 1 1 1 1 (6) 1 1 1

*) In addition operations must be considered in which the a and b directions or – in case of the square net also the u and v – are reversed; e.g.
1 a (1) as well as b 1 (1) or 1 1 (1) 1 u as well as 1 1 (1) v 1

**) In addition operations must be considered in which the a, a', a'' directions and correspondingly b, b', b'' change places e.g.
b 1 1 (1) 1 1 1 as well as 1 b 1 (1) 1 1 1 and 1 1 b (1) 1 1 1.

The indices r, s indicating translational components of σ-POs may, in special cases, be equal to 0 or $\frac{1}{2}$. Thus $2_r 1(1)$ may become $21(1)$ or $2_1 1(1)$; not in all combinations of λ- and σ-POs (OD-groupoids) are such specializations possible without all POs becoming improper POs and the corresponding structure a fully ordered one.

obtain a complete list of all families of OD-groupoids, we have to take one plane space group after the other, and combine with it in turn each σ-PO compatible with the respective net. As net we have to take not only the net required by the particular plane space group, but also more specialized ones compatible with the plane space group. In this way all families of OD-groupoids have been obtained; most of them even more than once, because the composition of λ-POs with a chosen σ-PO results in further σ-POs. Those combinations which automatically lead to fully ordered structures have, of course, to be left out of account.

As symbol of a family of OD-groupoids, we use a notation which allows λ- and σ-POs to be recognized at a glance, in analogy to international space-group

Table 6. *Category I*

PSG \ S-OD	Monoclinic I	Monoclinic II	Orthorhombic	Tetragonal	Hexagonal	
Triclinic	1	2	—	1	2	6
Monoclinic I	4	—	10	4	6	24
Monoclinic II	—	8	11	11	6	36
Orthorhombic	—	—	40	30	8	78
Tetragonal	—	—	—	24	—	24
Hexagonal	—	—	—	—	29	29
	5	10	61	70	51	197

PSG = System of plane space group of the single layer.
S–OD = System of the **OD**-groupoid.

Table 7. *Category II*

PSG \ S-OD	Monoclinic I	Monoclinic II	Orthorhombic	Tetragonal	Hexagonal	
Monoclinic I	1	—	2	1	1	5
Monoclinic II	—	3	3	3	2	11
Orthorhombic	—	—	4	4	1	9
Tetragonal	—	—	—	4	—	4
Hexagonal	—	—	—	—	11	11
	1	3	9	12	15	40

PSG = System of plane space group of the single layer.
S–OD = System of the **OD**-groupoid.

Table 8. *Category III*

PSG \ S-OD	Monoclinic I	Monoclinic II	Orthorhombic	Tetragonal	Hexagonal	
Triclinic	1	2	4	4	9	20
Monoclinic I	1	—	4	4	3	12
Monoclinic II	—	3	6	9	7	25
Orthorhombic	—	—	4	8	2	14
Tetragonal	—	—	—	5	—	5
Hexagonal	—	—	—	—	20	20
	2	5	18	30	41	96

PSG = System of plane space group of the single layer.
S-OD = System of the **OD**-groupoid.

nomenclature. In the first line of the symbol, the symbol of the plane space group formed by the λ-**POs** of the **OD**-groupoid family is given, in the second line, in brackets $\{\}$ the symbols of a set of σ-**POs** ${}_{p,p+1}a$ are put down; only for families belonging to category III where the set of σ-**POs** ${}_{p+1,p+2}a$ may be of a kind different from the set ${}_{p,p+1}a$, a third line in brackets $\{\}$ contains the symbols of the set of ${}_{p+1,p+2}a$.

As we have already stated, arbitrary translational components of σ-**POs** (screw axes and glide planes) occur which are indicated by indices r, s, u, v etc. in the symbol of the groupoid family. In some of the groupoid families it is possible to give special values to one or the other of these translational components (e.g. 0 or 1 to the corresponding indices) without the **OD**-character being lost. Then the number of positions of L_{p+1} compatible with the positions of the L_q (with $q \leqq p$) and the vicinity condition is in general reduced as compared with the corresponding general case. As an example the groupoid family

$$\begin{matrix} P\,m & m & (2) \\ \{n_{s,2} & n_{2,r} & (2_2)\} \end{matrix}$$ and its special case $$\begin{matrix} P\,m & m & (2) \\ \{n_{s,2} & c_2 & (2_2)\} \end{matrix}$$

are shown in Figs. 7(*a*) and (*b*).

The complete list, without special cases (which is to be published elsewhere) shows that there are 333 essentially different **OD**-groupoid families all in all; 197 of category I, 40 of category II and 96 of category III. Tables 6, 7 and 8 give the numbers of the **OD**-groupoid families specified according to the various symmetry systems of categories I, II and III, respectively. At the beginning of each line the symmetry system of the plane space group of the single layer is given. To understand the classification which is given at the top of the columns, we assume to start with that the translational components of σ-**POs** are simple rational numbers. Under these circumstances a fully ordered structure may be obtained by superposing various members of the same family in such a way that any pair of superposed structures has at least one

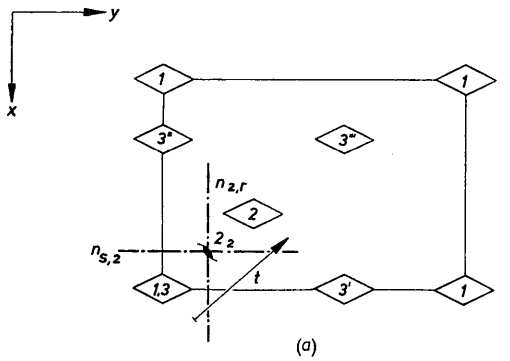


Fig. 7(*a*). **OD**-groupoid-family $\begin{matrix} Pm & m & (2) \\ \{n_{s,2} & n_{2,r} & (2_2)\} \end{matrix}$

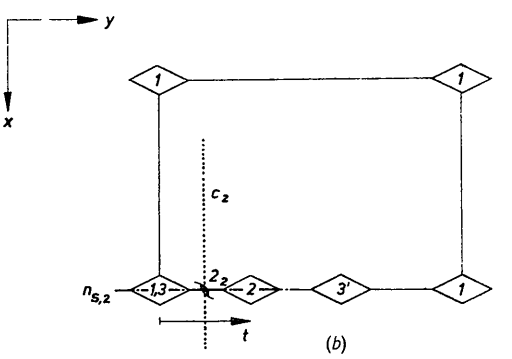


Fig. 7(*b*). **OD**-groupoid-family $\begin{matrix} Pm & m & (2) \\ \{n_{s,2} & c_2 & (2_2)\} \end{matrix}$

One unit cell is outlined; the **POs** $_{1,2}\sigma$ are shown.

Projections on to a layer plane. The figures inside the rhombs give the index of the respective layer.

layer in common (see Fig. 6). This 'superposition-structure' will have a space group which may depend on certain features of the indices characterizing the translational components—e.g. whether even or odd—but with a corresponding point group which is not dependent on the indices. The symmetry class of this point group is called the *System of the* **OD**-*groupoid.*

If the translational components of all σ-**POs** are rational, the Fourier transform plotted in reciprocal space will show sharp points identical in position and weight with the reciprocal-lattice points of the superposition structure just defined. These sharp points can in many cases be recognized in the X-ray pattern and the superposition structure (or at least its space group) deduced. They are a common feature of X-ray diagrams of different **OD**-structures belonging to the same family. The symmetry of an ordered member of an **OD**-family may, however, be far lower and even lower than the symmetry of the plane space group. Thus the observation made in some cases (see e.g. Dornberger-Schiff, 1957) that some classes of reflections—e.g. those of even layer lines—show higher symmetry than the others, can be explained.

The Fourier transforms of **OD**-structures generally, and in particular their characteristic features corresponding to the different **OD**-groupoid families, will be the subject of a later paper.

Furthermore, the theory of **OD**-structures consisting of two or more different kinds of layers, as well as the theory of **OD**-structures consisting of rods periodic in one dimension only (all equivalent, or of two or more different kinds) has still to be worked out.

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