That such bonding occurs in a large group of related compounds, which are in turn related to the nucleic acids and nucleo-proteins, is of considerable interest and importance since it is usually assumed that these latter compounds are held together in biological systems by hydrogen bonding between the neighbouring groups. Indeed, Watson & Crick (1953) have suggested that the macromolecule of deoxyribonucleic acids consists of a double helix, in which two helical chains are coiled round the same axis into the pyrimidine and purine bases on the inside of the helix. The two helical chains are held together by hydrogen bonds between the pyrimidine and purine bases. These hydrogen bonds must be of the type found in the simpler compounds.

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On Order–Disorder Structures (OD-Structures)

By K. Dornberger-Schiff

Deutsche Akademie der Wissenschaften zu Berlin, An der Rudower Chaussee, Berlin-Adlershof, Germany

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Certain features common to structures with one-dimensional position disorder and to related ordered layer structures (OD-structures) are discussed, the corresponding concepts are introduced by examples and the corresponding features of Fourier transforms are deduced. OD-structures are systematized and a glossary of terms is added. In an Appendix a nomenclature for plane space groups in three dimensions, which corresponds to the international nomenclature for three-dimensional space groups, is suggested.

Introduction

In the course of investigating the disorder phenomena exhibited by β-wollastonite (Jeffery, 1953) and Maddrell's salt (Dornberger-Schiff, Liebau & Thilo, 1955), it became evident that an adequate description of these and kindred structures cannot be expressed simply in terms of the current language of 'classical' crystallography, which, by its very nature, can be applied to fully ordered structures only. I have thus been led to attempt a generalization of these classical concepts wide enough to cover what I propose to call 'OD-structures' (order–disorder structures).

This term should—according to my proposal—embrace structures with stacking disorder (1-*dimensionale Lagefehlordnung*) if the lack of order in the stacking results (as usual) from the fact that there are two or more geometrically—and hence energetically—equivalent ways in which neighbouring layers may be placed with respect to one another. It should embrace also such structures which differ from these disordered structures only by the regularity of their stacking.

Before an attempt at the development of a general theory is made I propose to discuss in the present paper some well known examples of OD-structures in order to familiarize the reader both with the kind of problems to be tackled and with some concepts to be used for that purpose. In particular, we shall arrive at certain conclusions with regard to the distribution of structure amplitudes in reciprocal space which can be used to help in the structure analysis of OD-structures. The new terms will be introduced and defined in the course of the discussion of examples; a list of these definitions is also given in Appendix II for convenience.

Examples of OD-structures of type *A*

1st example: arrangements of close-packed spheres (e.g. cobalt)

These OD-structures can be characterized in the following way: The structure consists of identical layers, the symmetry of each of these layers, taken by itself, corresponds to the space group $P6/mmm$, except for the fact that there is no periodicity in the direction of the hexad. According to the notation proposed in Appendix I we shall denote this symmetry by $P(6/m)mm$.

Any pair of successive layers of a close packed structure is, however, of lower symmetry, namely $P(\bar{3})2/m1$.

The relation between two successive layers is such that a parallel displacement of the one by either of the vectors $\mathbf{s}_1$ or $\mathbf{s}_2$ would make that layer coincide with the other, where

$$\mathbf{s}_1 = \tfrac{1}{3}\mathbf{a}+\tfrac{2}{3}\mathbf{b}+\mathbf{e};\quad \mathbf{s}_2 = -(\tfrac{1}{3}\mathbf{a}+\tfrac{2}{3}\mathbf{b})+\mathbf{e} \qquad (1)$$

and **a** and **b** denote hexagonal basic translational vectors within the layer and **e** is a vector perpendicular to **a** and **b**.

The succession of vectors $\mathbf{s}_i$ may be used to characterize the stacking of layers; therefore I propose to call these vectors *stacking vectors*. Obviously, other vectors differing from those given by $m\mathbf{a}+n\mathbf{b}$ (with m, n integers) could have been chosen equally well. But we shall agree to call in each case the shortest (or one of the shortest) vectors of a set of equivalent vectors the stacking vector.

A set of layers which—like the layers of a close-packed structure—may be brought into coincidence by parallel displacement with a given layer shall be called a set of *translatable layers*.

The two stacking vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ are related to one another by the hexad axis of the single layer. Thus two pairs of layers characterized by the stacking vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ respectively differ only by their orientation, and are thus equivalent.

As we know, there exist whole 'families' of close-packed structures. The structures of each family consist of the same kind of layers, and the relative position of two given successive layers is characterized by one or the other of the stacking vectors $\mathbf{s}_1$ or $\mathbf{s}_2$. The different members of such a family differ in the sequence of stacking vectors and can hence be characterized by this sequence. The cubic close-packed structures have stacking vectors $\mathbf{s}_1$ throughout the structure, (or $\mathbf{s}_2$ throughout, if in different orientation); the normal hexagonal close packed structure has an alternation of $\mathbf{s}_1$ and $\mathbf{s}_2$; irregular sequences are characteristic of disordered structures.

I propose to denote, quite generally, by the term *OD-structures of type A*, structures consisting of a set of equal translatable layers, with successive layers related by one of several stacking vectors $\mathbf{s}_i$, which are derived from one another or from the inverse of the other by the symmetry elements of a single layer.

Although in some respects the stacking vectors $\mathbf{s}_i$ play a similar role to that of the translational vectors of an ordered structure, they must not be mistaken for translations: parallel displacement of the whole structure by $\mathbf{s}_i$ will, in general, not bring it into coincidence with itself.

By the term *family of OD-structures of type A* I mean a set of such structures consisting of the same kind of layers with the same set of stacking vectors $\mathbf{s}_i$ and differing only by the sequence of stacking vectors $\mathbf{s}_i$ which, therefore, is characteristic for a particular member of the family.

Although, in our example, as we have mentioned above, the symmetry of a pair of layers is $P(\bar{3})2/m1$, the symmetry of a structure belonging to this family may be even lower. The minimum symmetry which a member may possess is always characteristic of the whole family; in the case considered it is $P(3)m1$. I propose to call the symmetry of the layer (in our example, $P(6/m)mm$) the *Λ-symmetry*; the minimum symmetry in the family (in our example, $P(3)m1$) *φ-symmetry*. In referring to elements of Λ-symmetry which are not at the same time symmetry elements of the whole structure we shall put the corresponding symbols in $\langle\,\rangle$ brackets—in our example $\langle 6\rangle$ and $\langle m\rangle$ perpendicular to the c axis—to distinguish them from symmetry elements of the whole structure—in our example m perpendicular to the a axis.

As the concept of a *unit cell* is applicable only to the fully ordered members of a family, it is not suitable for the description of the general member of a family. It is possible, however, to define a term which refers to a single layer only and is the analogue to the term 'unit cell'. Such a unit cell of an individual layer we shall call *structural unit*. The structural unit is bounded by two pairs of parallel planes containing the basic translational vectors $\mathbf{a}'$ and $\mathbf{b}'$ of the periodic arrangement within the layer, respectively. The electron-density distribution $\varrho_\Lambda(\mathbf{r})$ of a single layer is the sum of the electron-density distributions $\varrho_{0'}(\mathbf{r}-m\mathbf{a}'-n\mathbf{b}')$ of the structural units:

$$\varrho_\Lambda(\mathbf{r}) = \sum_m \sum_n \varrho_{0'}(\mathbf{r}-m\mathbf{a}'-n\mathbf{b}') \qquad (3)$$

where

$$\varrho_{0'}(\mathbf{r}) = \varrho_{0'}(x'\mathbf{a}'+y'\mathbf{b}'+z'\mathbf{e}') = 0 \ \text{unless} \ \begin{array}{l} 0 \le x' < 1 \\ 0 \le y' < 1 \end{array} \qquad (4)$$

and $\mathbf{e}'$ is a vector not co-planar with $\mathbf{a}'$ and $\mathbf{b}'$, or not parallel to the *layer plane*, i.e. a plane containing the translations $\mathbf{a}'$ and $\mathbf{b}'$.

It is convenient to choose the vectors $\mathbf{a}', \mathbf{b}', \mathbf{e}'$ according to the following general rules, which correspond to the rules (I)–(III) given by Donnay & Nowacki (1954):

(I) wherever possible, the vectors $\mathbf{a}', \mathbf{b}', \mathbf{e}'$, should coincide with symmetry directions;
(II) the plane cell defined by $\mathbf{a}'$ and $\mathbf{b}'$ should have the same point-group symmetry as the plane lattice of a single layer;
(III) the plane cell should be the smallest possible cell that obeys (I) and (II);

besides, the length of $\mathbf{e}'$ should be chosen so as to make the component w_1 of the stacking vector $\mathbf{s}_1$, defined by

$$\mathbf{s}_1 = u_1'\mathbf{a}' + v_1'\mathbf{b}' + w_1'\mathbf{e}' \,, \tag{5}$$

equal to 1. A vector triple $\mathbf{a}', \mathbf{b}', \mathbf{e}'$ chosen in this way and the corresponding components will be denoted by letters without dashes. As can easily be shown, the traditional choice of axes according to the above-mentioned rules ensures that the components w_i of all stacking vectors related to each other by Λ-symmetry, i.e. of the vectors

$$\mathbf{s}_i = u_i\mathbf{a} + v_i\mathbf{b} + w_i\mathbf{e} \,, \tag{6}$$

are equal and thus equal to 1, and that all vectors $u_i\mathbf{a} + v_i\mathbf{b}$ have the same length.

These conventions enable us to make statements about OD-structures that correspond to statements about numbers of atoms in the unit cell in the case of fully ordered structures.

In our example, the structural unit contains one atom only. All atoms are, therefore, in positions equivalent to one another with respect to the translations $\mathbf{a}$ and $\mathbf{b}$. From this it follows that the number of closest neighbours, not only in the same layer but also in the preceding or succeeding layer, and thus the coordination number, is the same for all atoms; this number is thus independent of the particular sequence of stacking vectors $\mathbf{s}_i$, i.e. it is the same for all atoms and for all members of this family. The coordination polyhedron, however, is not the same for atoms of a layer between like, and a layer between unlike, stacking vectors; this is due to the fact that in our example the coordination polyhedron contains atoms not of one but of both neighbouring layers and that the relative position of these depends on the sequence of the $\mathbf{s}_i$.

2nd example: *graphite* (*hexagonal, rhombohedral, turbostratic*)

The Λ-symmetry is $P(6/m)mm$, the φ-symmetry $P(3)m1$, and also the stacking vectors are related to $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{e}$ in the same way as in the first example. There are, however, two carbon atoms in the structural unit, occupying positions which are equivalent with respect to the Λ-symmetry, but not equivalent with respect to the translations or the φ-symmetry. The stacking vectors and atomic positions are such that only one atom of each structural unit has a closest neighbour in the preceding layer. Therefore the number of closest neighbours is not independent of the sequence of stacking vectors. If one of the stacking vectors is repeated (rhombohedral structure), each atom has exactly one closest neighbour either in the preceding or in the succeeding layer; if the two stacking vectors alternate, half the atoms have one closest neighbour in the succeeding as well as in the preceding layer, and the other half have neither.

Thus, in this example, the coordination number does depend on the sequence of stacking vectors.

3rd example: SiC, *zincblende–wurtzite*

These families of OD-structures are very closely related to the first example. Their Λ-symmetry is $P(6)mm$, however, instead of $P(6/m)mm$. The φ-symmetry is $P(3)m$, as in the first example, and also the stacking vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ are related in the same way to $\mathbf{a}$ and $\mathbf{b}$ as in the examples already given.

The structural unit consists of one carbon and one silicon atom, with coordinates $(0, 0, z_1)$ and $(0, 0, z_2)$ respectively ($z_1 = 0$, $z_2 \approx \frac{3}{4}$). All C atoms are thus in positions equivalent with respect to the translations, and so are all Si atoms. The closest Si neighbours of a C atom belong partly to the same layer as the C atom, partly to the preceding layer; the closest C neighbours of a Si atom partly to the same, partly to the succeeding layer (or vice versa). Therefore, not only atomic distances, and coordination numbers, but also the coordination polyhedra, are independent of the sequence of stacking vectors.

There is a considerable number of compounds crystallizing in structures which belong to this family, e.g. crystals with a zincblende or wurtzite arrangement. Some of them, e.g. CdS and ZnS, exist in both forms, and of the latter, crystals with stacking disorder are known to exist (Jagodzinski, 1949; Krumbiegel & Jost, 1955). X-ray diagrams of such crystals show distinct maxima on the diffuse reciprocal-lattice rods corresponding to reciprocal-lattice points of the simpler ordered arrangements: the wurtzite and zincblende arrangements and an arrangement with a four-layer periodicity. From these maxima it is possible to judge whether the sequence can be regarded as consisting of ordered parts with occasional mistakes and, if so, what the character of these ordered parts is; or whether there is a repetition of one of the stacking vectors or a more complicated sequence.

Care has to be taken not to misjudge such maxima as reflexions of an ordered crystal. If this mistake is made, the attempt to index the 'reflexions' will, in general, lead to fictitious systematic non-space-group absences; if the real cause of these is not recognized the determination of space group and of the structure will be erroneous, as was the case with β-wollastonite (Barnick, 1936) and with Currol's salt (Plieth & Wurster, 1951).

4th example: orthoboric acid

The fully ordered structure of boric acid prepared from solution was first given by Zachariasen (1934), and has been further refined by the same author (1954). It is triclinic, space group $P\bar{1}$, and can be described as consisting of equal layers with a Λ-symmetry $P(6/m)mm$ and an alternation of two of the 12 Λ-symmetrical stacking vectors the components of which cannot be approximated to by the ratios of small integers. Cowley (1953), using electron-diffraction methods, has found that boric acid prepared from the vapour phase is in a disordered state and has an apparent hexagonal symmetry—as is to be expected if the sequence of stacking vectors is assumed to be statistical.

The stacking vectors found by Cowley for the disordered structure differ from those in the triclinic ordered structure. This may, however, be due to mistakes in the choice of the phases of the coefficients of his Fourier series (see below).

The diffraction phenomena of OD-structures of type Λ

Naturally, our knowledge of these and other families of OD-structures is based on the interpretation of X-ray diagrams of these structures. For this interpretation we may use the concept of the Fourier transform (F-transform for short) $F(\mathbf{r}^*)$ of the electron-density distribution within the crystal, which is proportional (with the usual correction factors) to the amplitude of the diffracted waves. We shall refer reciprocal vectors to a basic vector triple $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{e}^*$ reciprocal to the triple $\mathbf{a}$, $\mathbf{b}$, $\mathbf{e}$, defined above.

As follows from well known theorems, this F-transform may be obtained as the product of the F-transform $F_0(\mathbf{r}^*)$ of the structural unit, with two functions $G_\Lambda(\mathbf{r}^*)$ and $G_s(\mathbf{r}^*)$:

$$F(\mathbf{r}^*) = G_\Lambda(\mathbf{r}^*).G_s(\mathbf{r}^*).F_0(\mathbf{r}^*) = G(r^*).F_0(r^*)\,, \quad (7)$$

where $G_\Lambda(\mathbf{r}^*)$ depends only on the distribution of structural units within the layer, $G_s(\mathbf{r}^*)$ on the distribution of layers within the structure and $G(\mathbf{r}^*)$ on the distribution of structural units within the structure. They are defined as

$$G_\Lambda(\mathbf{r}^*) = \sum_m \sum_n \exp\,[2\pi i(\mathbf{r}^*, m\mathbf{a}+n\mathbf{b})] = \sum_m \sum_n \exp\,[2\pi i(m\xi+n\eta)]\,, \quad (8)$$

$$G_s(\mathbf{r}^*) = \sum_p \exp\,[2\pi i(\mathbf{r}^*, \mathbf{t}_p)] = \sum_p \exp\,[2\pi i(U_p\xi+V_p\eta+p\zeta)]\,, \quad (9)$$

where $\mathbf{t}_p$ is the sum of the first p stacking vectors (in the sequence present in the structure), and U_p and V_p are the sums of the components u_i and v_i, respectively, of these vectors.

$G_\Lambda(\mathbf{r}^*)$, $G_s(\mathbf{r}^*)$ and $G(\mathbf{r}^*)$ are the F-transforms of $D_\Lambda(\mathbf{r})$, $D_s(\mathbf{r})$ and $D(\mathbf{r})$, respectively, i.e. the distribution functions of structural units within the single layer, of layers within the structure and of structural units within the structure. These distribution functions are defined as

$$\left.\begin{aligned} D_\Lambda(\mathbf{r}) &= \sum_m \sum_n \delta(\mathbf{r}-m\mathbf{a}-n\mathbf{b}) \\ D_s(\mathbf{r}) &= \sum_p \delta(\mathbf{r}-\mathbf{t}_p) \\ D(\mathbf{r}) &= \sum_m \sum_n \sum_p \delta(\mathbf{r}-m\mathbf{a}.n\mathbf{b}-\mathbf{t}_p) \\ &= \sum_m \sum_n \sum_p \delta(\mathbf{r}-\mathbf{t}_{mnp}) \end{aligned}\right\} \quad (10)$$

with

$$\delta(\mathbf{r}) = \int \exp\,[-2\pi i(\mathbf{r}, \mathbf{r}^*)]d\tau^*\,, \quad (11)$$

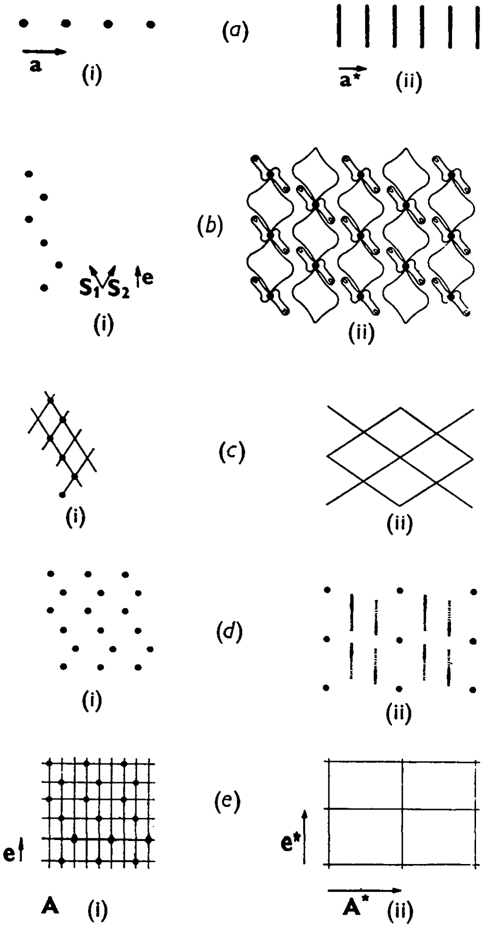

Fig. 1. (*a*) (i) Representative points within a layer $D_\Lambda(\mathbf{r})$. (ii) Absolute value of corresponding reciprocal distribution $|G_\Lambda(\mathbf{r}^*)|$.

(*b*) (i) Representative points of stacking $D_s(\mathbf{r})$. (ii) $|G_s(\mathbf{r}^*)|$.

(*c*) (i) Stacking lattice. (ii) Reciprocal stacking lattice.

(*d*) (i) Representative points of the distribution $D(\mathbf{r})$. (ii) $|G(\mathbf{r}^*)|$.

(*e*) (i) Distribution lattice. (ii) Reciprocal distribution lattice.

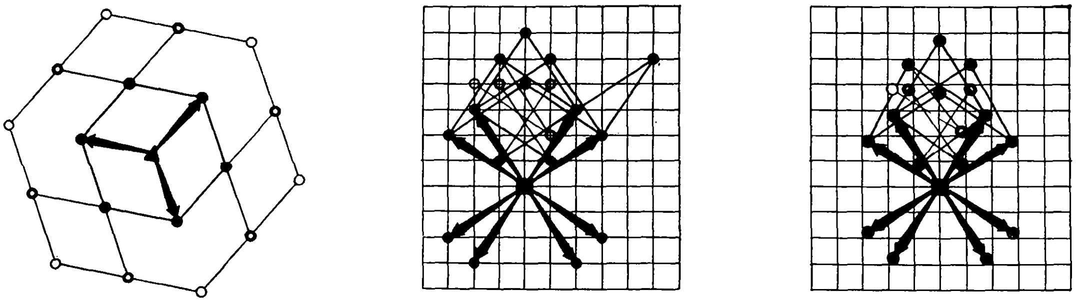
(a) (b) (c)

Fig. 2. Basal projection of points resulting from an addition of stacking vectors. (a) $P(3)$, all points lie on a lattice. (b) $P(4)mm$, with u_i and v_i rational numbers, all points lie on a lattice. (c) $P(4)mm$, with u_i and v_i only approximately rational, all points lie near the points of a lattice.

where the integral has to be taken over all reciprocal space and is zero except for $\mathbf{r} = 0$.

Thus $D_A(\mathbf{r}) \neq 0$ on the points $\mathbf{r} = m\mathbf{a}+n\mathbf{b}$, $D_s(\mathbf{r}) \neq 0$ on the points $\mathbf{r} = \mathbf{t}_p$ to be called *representative points of the stacking*, and $D(\mathbf{r}) \neq 0$ on the points $\mathbf{r} = m\mathbf{a}+n\mathbf{b}+\mathbf{t}_p = \mathbf{t}_{mnp}$, to be called *representative points of the distribution.*

In Fig. 1 these functions are shown schematically on a section parallel to $\mathbf{b}$ and $\mathbf{e}$ of real and of reciprocal space for $u_i = 0$ and $v_i = \pm\frac{1}{3}$. It can thus be taken to refer to the first three examples given above, if the vectors $\mathbf{s}_1 = \frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}+\mathbf{e} = \frac{1}{3}\mathbf{b}'+\mathbf{e}$ and $\mathbf{s}_2 = -(\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b})+\mathbf{e} = -\frac{1}{3}\mathbf{b}'+\mathbf{e}$ are chosen as stacking vectors and the section is chosen parallel to these vectors.

Fig. 1(*a*) (i) gives the distribution within the single layer $D_A(\mathbf{r})$ and Fig. 1(*a*) (ii) its F-transform $G_A(\mathbf{r}^*)$. In Fig. 1(*b*) (i) the representative points of a particular stacking are shown, which, as can be seen from Fig. 1(*c*) (i), are bound to lie on a lattice, to be called the *stacking lattice.* Therefore $G_s(\mathbf{r}^*)$ must necessarily be periodic, with periods corresponding to a lattice reciprocal to the stacking lattice and called the *reciprocal stacking lattice* (Fig. 1(*c*) (ii)). In Fig. 1(*d*)(i) the representative points of the distribution are shown. They lie, as can be seen in Fig. 1(*e*) (i), on a sublattice of the stacking lattice, called the *distribution lattice*, and $G(\mathbf{r}^*)$ is therefore (Fig. 1(*e*) (ii) and Fig. 1(*d*) (ii)) periodic with periods corresponding to the lattice reciprocal to the distribution lattice and called the *reciprocal distribution lattice.* This periodicity is independent of the sequence of stacking vectors.

The functions $G_s(\mathbf{r}^*)$ corresponding to various possible stackings have one more feature in common: they assume their maximum values on points $\mathbf{r}^* = l\mathbf{e}^*$ (where l is an integer) and are equal to zero on points $\mathbf{r}^* = \zeta\mathbf{e}^*$ for which ζ is not integral or very nearly so. This follows from the fact that the projection of the representative stacking points along $\mathbf{a}$ and $\mathbf{b}$ on to a line parallel to $\mathbf{e}$ results in a row of equidistant points at $p\mathbf{e}$ whatever the stacking may be.

It is easy to see that $G_A(\mathbf{r}^*) \neq 0$ for $\mathbf{r}^* = h\mathbf{a}^*+k\mathbf{b}^*+\zeta\mathbf{e}^*$ only (or for values of $\mathbf{r}^*$ very near to those), i.e. on a system of parallel rods—to be called *reciprocal-lattice rods.*

As a result of these features, there are in our example some reciprocal-lattice rods, to be exact one-third of the total, on which $G(\mathbf{r}^*) = G(h, k, \zeta) = 0$, except for $\zeta = l$ where $|G(\mathbf{r}^*)|$ assumes its maximum value. These points in reciprocal space correspond to sharp reflexions and will be called *sharp points.* Other reciprocal-lattice rods will be called *diffuse rods.*

The reciprocal-lattice rods are a result of the two-dimensional periodicity of the layers, and are thus a feature of all OD-structures built of such layers. Sharp points on the reciprocal-lattice rod through the origin result from the symmetry relations obtaining between the different stacking vectors, and are thus a feature of all OD-structures of type A (and also of some of the other types).

A periodicity of $G_s(\mathbf{r}^*)$, however, results—as can easily be shown—in general only for OD-structures of type A with not more than four different representative stacking vectors $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, $\mathbf{s}_4$, or with six representative stacking vectors related by a hexad; this is so because in these cases the representative stacking vectors define a stacking lattice on which all the representative points of the stacking are bound to lie (see Fig. 2). The representative points of the stacking must lie on a stacking lattice (and thus there results a corresponding periodicity of $G_s(\mathbf{r}^*)$) even if there are six or more different stacking vectors, provided the components u_i and v_i of the stacking vectors are rational numbers:

$$u_i = \mu_i/q_a, \quad v_i = \nu_i/q_b \tag{12}$$

(q_a, q_b, μ_i, ν_i integers).

Equation (12) is also the condition for the representative points of the distribution to lie on a lattice—the distribution lattice—and thus for $G(\mathbf{r}^*)$ to be periodic. If condition (12) holds, there are sharp points on reciprocal-lattice rods not passing through the origin and the recognition of these sharp points provides the easiest way to detect the periodicity of $G(\mathbf{r}^*)$ in disordered structures.

As the value of $G(\mathbf{r}^*)$ is the same for all sharp points, the intensities of these reflect the symmetry of $|F_0(\mathbf{r}^*)|^2$, i.e. the Laue symmetry corresponding to Λ-symmetry—to be called *Λ^*-symmetry*.

This Λ^*-symmetry may reveal even fully ordered structures as members of a family of OD-structures, although there are no diffuse rods in these cases. This will be the case, if the Λ^*-symmetry is higher than the Laue symmetry of the ordered structure, as, for example, in triclinic β-wollastonite (Jeffery, 1953). Then the Λ^*-symmetry will be a property of part of the reflexions only: of the sharp points, i.e. the points which are sharp for all members of the family. From the distribution of these Λ^*-symmetrical reflexions or sharp points the reciprocal distribution lattice, and hence the (real) distribution lattice, may be deduced. This and the Λ^*-symmetry itself may be of use in solving even an ordered structure.

The $G(\mathbf{r}^*)$ will, in general, be complex quantities. If they were known for all points in reciprocal space the distribution of representative points could be deduced. An attempt to deduce a basal projection of such a distribution was made by Cowley (1953) for the disordered form of orthoboric acid. His deduction, however, does not seem justifiable as he assumed the $G(hk0)$ to be real and positive.

OD-structures of type *B*

There exist structures built of layers which have very much in common with the structures discussed above but do not consist of one set of equal translatable layers only. We shall now discuss an example of such a structure and, in the course of this discussion, arrive at a definition of what I propose to call *OD-structures of type B*.

Example: *decaborane*, $B_{10}H_{14}$

The F-transform of this structure consists, as Kasper, Lucht & Harker (1950) observed, of a system of reciprocal-lattice rods $(h\eta l)$ parallel to the $\mathbf{b}^*$ axis†. The rods with h even bear sharp points at $\eta = k = 2n$, whereas the rods with h odd are diffuse and have their maxima at $\eta = k$ odd and almost vanish at $\eta = k$ even (Fig. 3). This disposition of diffuse rods and sharp points could not be the result of an OD-structure of type A. This becomes evident if we start with the discussion along the lines given above. Obviously, the structure must consist of layers with periodicity corresponding to the translations $\mathbf{a}$ and $\mathbf{c}$. The sharp points form an orthorhombic reciprocal distribution lattice with the constants

$$\mathbf{A}^* = 2\mathbf{a}^*,\quad \mathbf{B}^* = 2\mathbf{b}^*,\quad \mathbf{C}^* = \mathbf{c}^*\,.$$

Thus we arrive at a distribution lattice on which all representative points of the distribution would have to lie with the constants

$$\mathbf{A} = \tfrac{1}{2}\mathbf{a},\quad \mathbf{B} = \tfrac{1}{2}\mathbf{b},\quad \mathbf{C} = \mathbf{c}\,.$$

$\mathbf{B}$ obviously corresponds to the vector denoted by $\mathbf{e}$ above. The points of this distribution lattice cannot be reached by an addition of stacking vectors related by any symmetry element, but only by the vectors $\mathbf{a}$, $\mathbf{b}$ and

$$\mathbf{s}_1 = \mathbf{B} = \tfrac{1}{2}\mathbf{b},\quad \mathbf{s}_2 = \mathbf{B}+\mathbf{A} = \tfrac{1}{2}\mathbf{b}+\tfrac{1}{2}\mathbf{a}\,,$$

or vectors differing from the latter by $m\mathbf{a}+n\mathbf{c}$. Thus the explanation of this structure as OD-structure of type A fails.

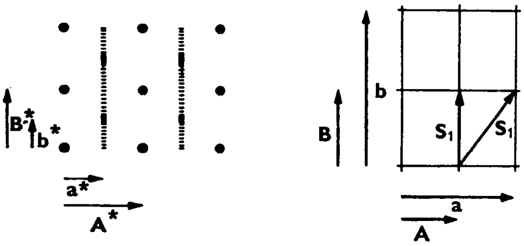

Fig. 3. Decaborane: position of sharp points and diffuse rods in reciprocal space and corresponding distribution lattice in real space.

The following systematic absences of diffuse rods and sharp points were observed by the authors:

(i) The diffuse rods $(h\eta 0)$ with h odd are missing.
(ii) The sharp points $(h0l)$ with h even and $\tfrac{1}{2}h+l$ odd are missing.
(iii) The sharp points $(0kl)$ with $\tfrac{1}{2}k+l$ odd are missing.

Rule (i) shows the presence of an $\mathbf{a}$ glide perpendicular to $\mathbf{c}$ in the structure and thus—as the glide direction is parallel to the layer plane—in the single layer. This glide is thus to be denoted by $\langle a\rangle$.

Rule (ii) would result from an n glide perpendicular to $\mathbf{b}$ with a glide component of either $\tfrac{1}{2}\mathbf{c}+\tfrac{1}{4}\mathbf{a}$ or $\tfrac{1}{2}\mathbf{c}-\tfrac{1}{4}\mathbf{a}$. We shall denote these operations by $\{n_{1,\frac{1}{2}}\}$ and $\{n_{1,\bar{\frac{1}{2}}}\}$, respectively. Neither of these can, however, by present as symmetry element in the proper sense of the word as their repetition would in either case lead to a translation $\mathbf{c}+\tfrac{1}{2}\mathbf{a}$, which is not present. Rule (ii) would, however, also result, if the points of any given layer, say the layer number p, were related to the $(p+1)$st layer by either $\{n_{1,\frac{1}{2}}\}$ or $\{n_{1,\bar{\frac{1}{2}}}\}$ and thus the $(p+1)$st layer to the pth layer by either $\{n_{1,\bar{\frac{1}{2}}}\}$ or $\{n_{1,\frac{1}{2}}\}$. We propose to call such operations relating a certain part of space to another part of space *σ-operations* and denote them by { }-brackets. The limited range of the σ-operations $\{n_{1,\frac{1}{2}}\}$ and $\{n_{1,\bar{\frac{1}{2}}}\}$ present in decaborane actually gives the clue to the disorder effect which manifests itself in the diffuse reciprocal-lattice rods.

A pair of layers consisting of a layer p related to the $(p+1)$st layer through the σ-operation $\{n_{1,\frac{1}{2}}\}$ is clearly geometrically (and hence energetically) equivalent to a similar pair with $\{n_{1,\frac{1}{2}}\}$ replaced by $\{n_{1,\bar{\frac{1}{2}}}\}$. This is

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† Choice of axes as given by the authors quoted.

Table 1. *σ-Operations in decaborane*

Glide plane		Screw dyad			Glide plane		Screw dyad	
In position* $y' = \frac{1}{2}(2p-1)$	Glide component	In position* $y' = \frac{1}{2}(2p-1)$ $z = \pm\frac{1}{4}$	Screw component		Glide component $\frac{1}{2}(\mathbf{e}+\mathbf{c})$	In position	Screw component $\frac{1}{2}\mathbf{e}$	In position $z = \pm\frac{1}{4}$
$\{n_{1,\frac{1}{2}}\}$	$\frac{1}{2}\mathbf{c}+\frac{1}{4}\mathbf{a}$	$\{2_{\bar{\frac{1}{2}}}\}$	$-\frac{1}{4}\mathbf{a}$	⟶ ⇢↘	$\{n\}$	$x = \frac{1}{8}, \frac{5}{8}$	$\{2_1\}$	$x = \frac{3}{8}, \frac{7}{8}$
$\{n_{1,\bar{\frac{1}{2}}}\}$	$\frac{1}{2}\mathbf{c}-\frac{1}{4}\mathbf{a}$	$\{2_{\frac{1}{2}}\}$	$\frac{1}{4}\mathbf{a}$	⟶ ⇢↗	$\{n\}'$	$x = \frac{3}{8}, \frac{7}{8}$	$\{2_1\}'$	$x = \frac{5}{8}, \frac{1}{8}$

——→ for p odd
- - -→ for p even

* For transition from pth layer to $(p+1)$st layer; y' in fractions of **e**.

obvious, if we note that the opposite is true for the sequence of layers $(p+1)$st to pth.

Now the most simple assumption is that the layers of such a pair are also related by an n glide σ-operation $\{n\}$ corresponding to rule (iii), i.e. a σ-glide plane perpendicular to **a** with glide component $\frac{1}{4}\mathbf{b}+\frac{1}{2}\mathbf{c} = \frac{1}{2}\mathbf{e}+\frac{1}{2}\mathbf{c}$. This assumption implies that the single layers possess rotation dyads $\langle 2\rangle$ parallel to **c** alternating with symmetry centres $\langle\bar{1}\rangle$ (see Fig. 4). Thus the Λ-symmetry $P1(1)2/a$ results from this assumption. Both sides of the single layer are thus equivalent and the relation between the second and the third layer may be either $\{n_{1,\frac{1}{2}}\}$ or $\{n_{1,\bar{\frac{1}{2}}}\}$. If $\{n_{1,\frac{1}{2}}\}$ is followed by $\{n_{1,\frac{1}{2}}\}$, the σ-operation $\{n\}$ leading from the first to the second layer is not continued from the second to the third layer, but transposed by $\frac{1}{4}\mathbf{a}$. If $\{n_{1,\frac{1}{2}}\}$ is followed by $\{n_{1,\bar{\frac{1}{2}}}\}$, the σ-operation $\{n\}$ is continued. The equivalence of the transposed σ-operation $\{n\}'$ with $\{n\}$ also results from the fact that these operations are related by the rotation dyads and symmetry centres of Λ-symmetry. Table 1 gives the full list of relations obtaining between neighbouring layers: the σ-operations described already as well as the resulting σ-screw dyads with half the normal screw component $\{2_{\frac{1}{2}}\}$ parallel to **a**, and σ-screw dyads $\{2_1\}$ with screw component $\frac{1}{2}\mathbf{e}$ parallel to **b**.

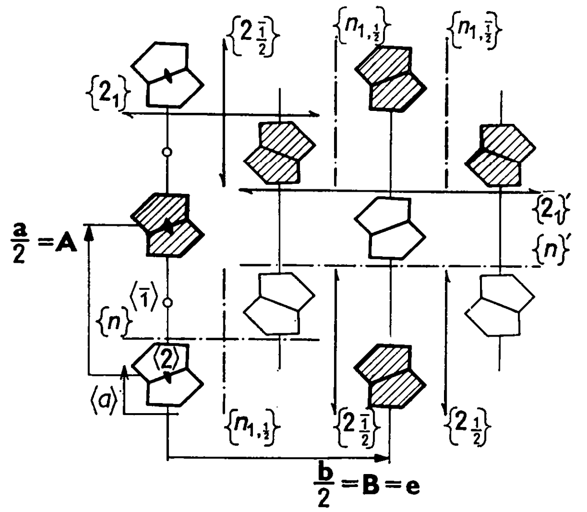

Fig. 4. Distribution of molecules, Λ-symmetry and σ-operations in decaborane. The molecules in $z = \frac{1}{2}$ are drawn in thin lines, those in $z = 0$ in thick lines. Shaded molecules are seen lying with the convex side upwards, unshaded with the convex side downwards. Λ-symmetry elements in $\langle\ \rangle$-brackets, σ-operations in $\{\ \}$-brackets.

The layers of the structure do not all belong to one set of translatable layers, but all even-numbered layers belong to one such set and so do all odd-numbered layers. OD-structures of that kind—i.e. consisting of substantially equal layers which, however, do not all belong to one set of translatable layers but to two or more such sets—we propose to call *OD-structures of type B*, provided neighbouring layers are related by one of a set of related σ-operations.

The vectors giving the displacement necessary to bring a layer into coincidence with the next translatable layer—in our case the next-but-one layer—are to be called (*composite*) *stacking vectors*. They can be obtained from the σ-operations and are listed for decaborane in Table 2.

Table 2. *Stacking vector resulting from σ-operations in decaborane*

(The operations given on the left side of Table 1 only are given)

σ-Operations;		
transition pth → $(p+1)$st layer	transition $(p+1)$st → $(p+2)$nd layer	Stacking vector; transition pth → $(p+2)$nd layer
$\{n_{1,\frac{1}{2}}\}\ \{2_{\bar{\frac{1}{2}}}\}$	$\{n_{1,\bar{\frac{1}{2}}}\}\ \{2_{\frac{1}{2}}\}$	$\frac{1}{2}\mathbf{b} = \mathbf{s}_1$
$\{n_{1,\frac{1}{2}}\}\ \{2_{\bar{\frac{1}{2}}}\}$	$\{n_{1,\frac{1}{2}}\}\ \{2_{\bar{\frac{1}{2}}}\}$	$\frac{1}{2}(\mathbf{a}+\mathbf{b}) = \mathbf{s}_2$
$\{n_{1,\bar{\frac{1}{2}}}\}\ \{2_{\frac{1}{2}}\}$	$\{n_{1,\frac{1}{2}}\}\ \{2_{\bar{\frac{1}{2}}}\}$	$\frac{1}{2}\mathbf{b} = \mathbf{s}_1$
$\{n_{1,\bar{\frac{1}{2}}}\}\ \{2_{\frac{1}{2}}\}$	$\{n_{1,\bar{\frac{1}{2}}}\}\ \{2_{\frac{1}{2}}\}$	$\frac{1}{2}(\mathbf{a}+\mathbf{b}) = \mathbf{s}_2$

As we see, the stacking vectors for each of the sets of translatable layers are just the vectors we had already deduced from the reciprocal distribution lattice. Thus each set taken separately gives a distribution of diffuse rods and sharp spots in reciprocal space, as observed, and the contributions of the two sets superimpose.

A thorough discussion shows that the assumptions made above are not only the most simple but also the only assumptions compatible with the observed distribution of sharp points and diffuse rods in reciprocal space and leading to geometrically equivalent operations transforming one layer into the neighbouring one.

Λ-symmetry and σ-operations deduced here are in entire agreement with the result of the full structure analysis carried out by Kasper *et al.* (1950), as Fig. 4 shows; this gives a succession of layers possible according to their paper, with the symbols of Λ-symmetry and σ-operations added.

It is not likely that the deduction of Λ-symmetry and σ-operations will in all cases be unique, as in the example just discussed. It is, however, very probable that much may be learned in all cases from a thorough discussion.

More examples of OD-structures of type B will have to be discussed before a systematic theory of such structures can be attempted.

We may, however, note in passing that type A structures may be considered as special cases of type B structures: the stacking vectors of an OD-structure of type A may be regarded as special kinds of σ-operations. Further σ-operations follow from Λ-symmetry and the stacking vectors; in our first example, in the close-packed structures, there are σ-glide planes perpendicular to $\mathbf{e}$ in position $z = p+\frac{1}{2}$ with glide component $\pm(\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b})$, σ-screw dyads $\{2_1\}$ parallel to $\mathbf{a}$ in position $y = \pm\frac{1}{6}$, $z = p+\frac{1}{2}$ and σ-screw dyads $\{2_2\}$ parallel to $\mathbf{e}$ in positions $x = \frac{1}{3}$, $y = \frac{1}{6}$ or $x = \frac{1}{6}$, $y = \frac{1}{3}$. As the Λ-symmetry and the stacking vectors in the graphite structures are the same as in the close-packed structures the σ-operations are also the same. In the SiC structures, of these σ-operations only the σ-screw dyads $\{2_2\}$ are present.

In spite of this close relation between type A and type B structures it seems advisable to me to distinguish between them.

OD-structures of type *C*

Another type of structures—to be called *OD-structures of type C*—seems to be present in the chlorites (Brindley, Oughton & Robinson. 1950). These consist of two or more sets of translatable layers, some of which differ also in substance. These may again—thanks to their Λ-symmetry—be placed in two or more ways relative to one another.

OD-structures of the second kind

Obviously structures consisting of rods with one-dimensional periodicity may show similar order–disorder effects. I propose to call such rod-structures *OD-structures of the second kind* to distinguish them from the layer structures (type A, B and C) discussed above (to be called *OD-structures of the first kind*).

For the treatment of OD-structures of the second kind, which promise to be rather more complicated that those of the first kind, some preliminary work would have to be carried through. It is difficult to say whether OD-structures of the second kind are indeed of lesser importance or whether such structures, though existing, have frequently escaped recognition as such.

Classification of OD-structures of the first kind

We may now attempt a rough classification of OD-structures of the first kind. These consist of layers with layer planes parallel to each other, which either form one set of translatable layers or belong to several such layers.

Type A: All layers belong to one set of translatable layers. Examples: cobalt, graphite, zincblende, wurtzite, silicon carbide.

Type B: All layers are substantially equal, but belong to two or more different interleaved sets of translatable layers. Successive layers belong to different sets and are related by σ-operations.

Type C: There are several sets of translatable layers some of which differ in substance.

I wish to thank Dr W. A. Wooster, who read two versions of the manuscript and made some valuable suggestions concerning the mode of presentation and nomenclature. I also had the opportunity to discuss the content of this paper with a number of workers in the field. I wish to express my thanks to them.

APPENDIX I

Proposal for international symbols for the 80 plane groups in three dimensions

As has been stated in the *International Tables for X-ray Crystallography* (1952, p. 56), the 80 plane groups can easily be deduced from the 230 space groups. In view of this and the fact that the international symbols for the latter are familiar to all crystallographers I propose the following nomenclature:

The symbols $P, C, 2, 2_1, a, b, n$ etc. retain their well known meaning. The sequence of symbols is exactly as in space-group notation, except for the necessity to add in certain cases (e.g. in the monoclinic groups) 'monad axes' 1. The direction in which there is no periodicity is noted by putting the corresponding symmetry symbols in round brackets. The direction of missing periodicity is preferably chosen as the c axis. Monoclinic groups with the monoclinic axis perpendicular to the layer plane (thus corresponding to oblique two-dimensional lattices) are to be called 'monoclinic I', monoclinic groups with the monoclinic axis parallel to the layer plane (corresponding to rectangular two-dimensional lattices) are to be called 'monoclinic II'. If the axis of missing periodicity is called the c axis, monoclinic I groups are describable with the 1st setting (see *International Tables*), and monoclinic II groups with the 2nd setting.

APPENDIX II

Glossary of terms

Composite stacking vectors: see stacking vectors.

Diffuse (reciprocal lattice) rods: reciprocal-lattice rods on which there are no sharp points.

Distribution function of a layer:

$$D_A(\mathbf{r}) = \sum_m \sum_n \delta(\mathbf{r} - m\mathbf{a} - n\mathbf{b})$$

characteristic of the distribution of structural units within a layer.

Distribution function of the stacking:

$$D_s(\mathbf{r}) = \sum_p \delta(\mathbf{r} - \mathbf{t}_p)$$

characteristic of the distribution of layers within the structure.

Distribution function of the structure:

$$D(\mathbf{r}) = \sum_m \sum_n \sum_p \delta(\mathbf{r} - m\mathbf{a} - n\mathbf{b} - \mathbf{t}_p)$$

characteristic of the distribution of structural units within the structure.

Distribution lattice: lattice on which the representative points of the distribution must necessarily lie whatever the sequence of stacking vectors.

Family of OD-structures: a set of OD-structures consisting of the same kind of layers in an arrangement governed by the same set of stacking vectors (for structures of type *A*) or σ-operations (for structures of type *B*). Different members of a family differ by the sequence of stacking vectors or the sequence of σ-operations, respectively. Periodic sequences are present in fully ordered members of a family.

Layer plane: plane defined by the translations **a** and **b** of the single layer.

OD-structures: for classification see text.

σ-operations: operations bringing a certain part of space (e.g. one layer) into coincidence with another part of space (another layer).

Reciprocal distribution lattice: lattice reciprocal to the distribution lattice, thus corresponding to the periodicity of $G(\mathbf{r}^*)$.

Reciprocal-lattice rods: rods in reciprocal space on which $G_A(\mathbf{r}^*) \neq 0$.

Reciprocal stacking lattice: lattice reciprocal to the stacking lattice, thus corresponding to the periodicity of $G_s(\mathbf{r}^*)$.

Representative points of the distribution: the points $\mathbf{t}_{mnp} = \mathbf{t}_p + m\mathbf{a} + n\mathbf{b}$.

Representative points of the stacking: the points t_p = sum of the first p stacking vectors (in the sequence actually present in the structure).

Set of translatable layers: set of layers which may be brought into coincidence with each other by parallel displacement.

Sharp points: lattice points of the reciprocal distribution lattice leading to sharp reflexions on X-ray photographs whatever the sequence of stacking vectors may be.

Stacking lattice: lattice on which the representative points of the stacking must necessarily lie whatever the sequence of stacking vectors may be.

Stacking vector, $\mathbf{s}_i$: vector giving the parallel displacement necessary to bring a certain layer of an OD-structure of type *A* into coincidence with the neighbouring layer. OD-structures of type *A* are characterized by the fact that there are at least two stacking vectors related to each other or the inverse of the other by Λ-symmetry.

Composite stacking vector, $\mathbf{s}_i$: vector giving the parallel displacement necessary to bring a certain layer of an OD-structure of type *B* or *C* into coincidence with the next layer belonging to the same set of translatable layers. The composite stacking vectors are the result of successive σ-operations.

Structural unit of an OD-structure: part of a single layer of the structure, by the twofold periodic repetition of which the whole layer may be built. The structural unit is bounded by two pairs of parallel planes so that the electron density $\varrho_0(\mathbf{r})$ of the structural unit is equal to zero outside a region

$$0 < x < 1,\quad 0 < y < 1\,,$$

where

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{e}\,;$$

a and **b** are translations of the periodicity of the layer and **a**, **b** and **e** are chosen corresponding to the symmetry of the single layer.

φ-symmetry: minimum symmetry which a member of a given family of OD-structures must necessarily possess.

Λ-symmetry: symmetry group (one of the 80 plane groups in 3 dimensions, see Appendix I) of a single layer of the structure.

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