funden:

H(3)H(4) $\varphi=118°$ $\theta=$ 93,5° $H_{max}=19,7$ Gauss
H(1)H(2) $\varphi=164°$ $\theta=131,0°$ $H_{max}=19,7$ Gauss

Um mit dieser Information die Lage der H-Atome zu bestimmen, muss noch zusätzliche Information über mögliche H-Brückenbindungen vorhanden sein. Für O(2) wurden zwei kurze O–Cl-Abstände gefunden [zu Cl(6): 3,19 Å und zu Cl(8): 3,28 Å], die fast genau den H–O–H-Winkel des Wassers einschliessen. Nimmt man lineare H-Brücken zu diesen Cl-Atomen an, so sind die berechneten H-Lagen:

H(1) $x=0,5486$    $y=0,0528$    $z=0,8692$
H(2) $x=0,4780$    $y=0,2085$    $z=0,8721$

Die daraus resultierende HH-Richtung wird durch das Experiment bestätigt (Fig. 2).

Die Lage des zweiten Wassermoleküls ist wesentlich uncicherer zu bestimmen, da zu O(1) nur ein Cl-Atom einen besonders kurzen Abstand zeigt [Cl(6): 3,26 Å]. Da aber diese O–Cl-Richtung mit HH fast den theoretischen Winkel von 35,25° bildet, ist es sinnvoll, eine lineare H-Brücke in dieser Richtung anzunehmen. Mit dem experimentellen HH-Vektor berechnen sich so die H-Lagen:

H(3): $x=0,3020$    $y=0,2862$    $z=0,1288$
H(4): $x=0,2688$    $y=0,3799$    $z=0,2384$

Die O(1)–H(2)-Richtung zeigt etwa zwischen die beiden anderen Cl-Nachbarn von O(1) [Cl(5): 3,59 Å und Cl(8): 3,46 Å], was eine schwache gegabelte H-Brücke vermuten lässt.

Das Dreieck H(1)–O(2)–H(2) bildet mit der Cu(1)–O(2)-Richtung einen Winkel von 170,3°, während das Dreieck des zweiten H₂O-Moleküls mit der Cu(2)–O(1)-Richtung einen Winkel von 89° bildet.

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# An OD-Disordered Modification of the Calcium Monoborate Dihydrate Ca[B(OH)₄]₂ . 2H₂O

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The X-ray diagrams of the crystals under investigation show sharp reflexions and diffuse streaks with maxima on them. The corresponding distribution in reciprocal space is in keeping with the assumption of a disordered OD-structure consisting of two kinds of layers with OD-groupoid family

$$P(1) \frac{2}{c} 1[\cdot\frac{1}{4}\cdot]4(1) \frac{2}{m} 1$$

and translational periods $b=6·69$, $c=7·95$ Å, and a layer to layer vector $a=4·02$ Å with $\beta=104·9°$. This assumption is confirmed in good approximation by the structure as determined. The structure contains two kinds of ordered domains with space groups $P2/c$ and $I2/c$ and lattice constants $a=8·04$ and $a=16·08$ Å, respectively. The structure of these domains is described; atomic positions, bond distances and angles are given. The relation to the modifications previously described by other authors is discussed. The course of the structure determination is described.

### 1. Introduction

This investigation was undertaken in order to test the possibility of a complete structure determination of a disordered structure, basing the investigation on the theory of OD structures. The papers by Ozol, Wimba & Jevinsk (1964) and Kravchenko (1964) were not known to us at that time. The relation of the results

of these and other investigations on calcium borate dihydrate with our results are to be discussed at the end of this paper.

## 2. Interpretation of the symmetry

Weissenberg photographs were taken, one of which is shown in Fig. 1. Although at first glance it might be considered as a quite ordinary diagram, closer inspection shows that some of the reflexions are joined by diffuse streaks or have tails. Disregarding these faint lines and tails, the reflexions may be indexed with respect to a unit cell with dimensions $a = 16\cdot08$, $b = 6\cdot69$, $c = 7\cdot95$ Å, $\beta = 104\cdot9°$. Referred to this cell, diffuse streaks or tailed reflexions occur parallel to **a** for $k + l$ odd only, whereas the reflexions with $k + l$ even are sharp. The 'reflexions' with $k + l$ odd have thus to be considered as maxima on the diffuse streaks $(\xi kl)$. Along such a streak, strong and weak maxima alternate (the weak maxima are in many places too weak to be seen). The systematic absences and distribution of maxima are summarized in Table 1.

Table 1. *Summary of present and absent reflexions*

The Bragg indices refer to the apparent unit cell. $h, k, l$ indicate integral numbers; $\xi'$ may take on non-integral values.

| $\xi' kl$ | $\xi' \neq h$ | $\xi' = h = 2n$ | $\xi' = h = 2n + 1$ |
|---|---|---|---|
| $k + l = 2n$ | missing | sharp | missing |
| $k + l = 2n + 1$ | | weak maxima | strong maxima |

Table 1 (*cont.*)

$\xi' 0l$

| | | | |
|---|---|---|---|
| $l = 2n$ | (missing) | (sharp) | (missing) |
| $l = 2n + 1$ | missing | missing | missing |

Symmetry of intensities: monoclinic (*b* axis).

The sharp reflexions with $k + l = 2n$, taken by themselves, correspond to an ordered superposition structure (Dornberger-Schiff, 1964, 1966) with lattice constants $\hat{a} = a/2$, $b$, $c$. The systematic absences of these reflexions, an intensity statistic and the observed monoclinic symmetry indicate the space group $A1\frac{2}{m}1$ [Fig. 2(*b*)]. All reflexions and streaks $(\xi' 0l)$ with $l$ odd are absent. This indicates the presence of $c$ glides, either referring to the entire structure, or of different $c$ glides referring to all parts of the real structure. The fact that only the reflexions with $(k + l = 2n)$ are sharp shows the density of the superposition structure $\hat{\varrho}(x,y,z)$ to be related to the electron density of the real structure $\varrho(x,y,z)$ according to

$$\hat{\varrho}(x,y,z) = \tfrac{1}{2}[\varrho(x,y,z) + \varrho(x, y + \tfrac{1}{2}, z + \tfrac{1}{2})] . \quad (1)$$

Within the set of all reflexions, sharp and diffuse, reflexions with $k + l = 2n + 1$ also occur. Thus the translational periods of the real structure are **b, c** without the $A$ centring of the superposition structure. This $A$ centring can, therefore, only be the result of two alternative positions of any one layer, related by a translation $(\mathbf{b} + \mathbf{c})/2$. There exist three different plane space



*superposition structure*

z      1/2 + z

z̄      1/2 - z

*OD-structure consisting of 2 kinds of layers*

$L_{2n} \dots P (1) 2/c 1$

$L_{2n+1} \dots A (1) 2/m 1$
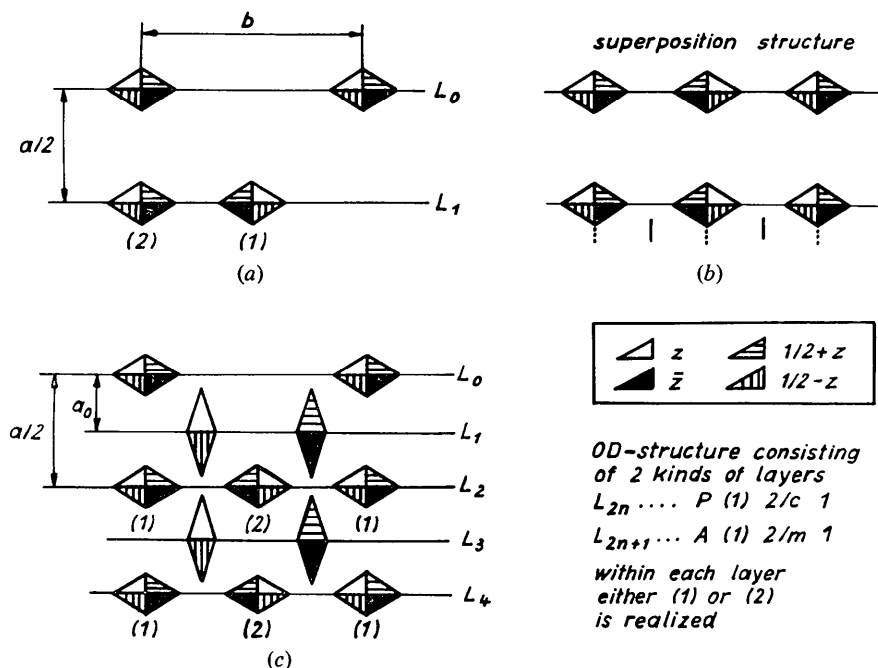
*within each layer either (1) or (2) is realized*

Fig. 2. (*a*) Symmetry of the two possible pairs of layers $(L_0, L_1^{(1)})$ and $(L_0, L_1^{(2)})$ under the assumption of layers of the same kind. (*b*) Superposition structure. (*c*) Symmetry and relative positions of the layers under the assumption of an OD structure of two kinds of layers.
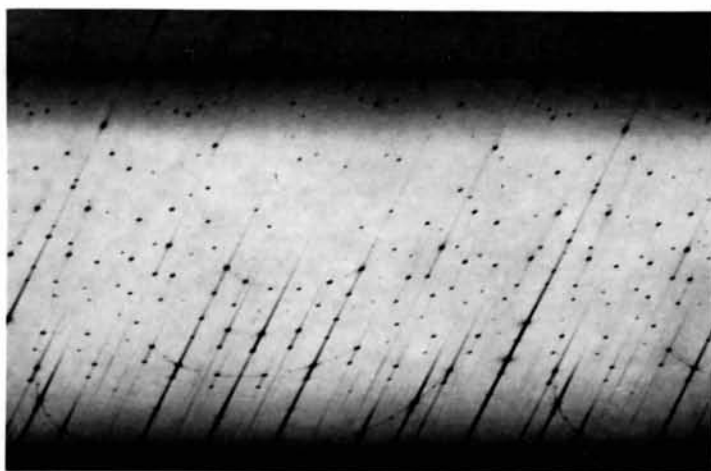
Fig. 1. Weissenberg photograph ($\xi k0$).

groups with primitive (two-dimensional) Bravais lattice which, together with the translation of the (three-dimensional) $A$ face-centred Bravais lattice, would give rise to the space group $A(1)\dfrac{2}{m}1$ of the superposition structure. Only one of them, $P(1)\dfrac{2}{c}1$ contains a $c$ glide, and this explains the missing reflexions ($\zeta'0l$) with $l=2n+1$ (Table 1). Thus a structure consisting of translationally equivalent layers of symmetry $P(1)\dfrac{2}{c}1$ with any one layer converted into the subsequent layer by a translation of either $\mathbf{a}/2$ or $(\mathbf{a}+\mathbf{b}+\mathbf{c})/2$ would give sharp reflexions and streaks corresponding exactly to Table 1. Such a structure would, however, possess pairs of adjacent layers $L_0L_1^{(1)}$ and $L_0L_1^{(2)}$, which are not geometrically equivalent [Fig. 2(a)]. A disorder as indicated by the X-ray diagram is therefore not to be expected, unless the energy of interaction between $L_0$ and $L_1^{(1)}$ happens to be approximately equal to that of $L_0$ and $L_1^{(2)}$, which is rather unlikely.

As no structure consisting of geometrically equivalent layers of other symmetry would give sharp reflexions and diffuse streaks distributed in reciprocal space as observed, it seemed worth while considering whether the structure could possibly be an OD structure consisting of two different kinds of layers, i.e. we ask the question which symmetry of the layers of the two kinds and relative arrangement of them (if any) would be in keeping with the observed facts. There is exactly one symmetry and relative arrangement that fulfils these requirements. One kind of layer ($L_{2n}$) has the symmetry $P(1)\dfrac{2}{c}1$, i.e. the symmetry deduced above for a single layer, the other kind of layer ($L_{2n+1}$) has the

symmetry $A(1)\dfrac{2}{m}1$, [Fig. 2(c)]. Both layers have lattice constants $\mathbf{b},\mathbf{c}$. For a given position of layer $L_0$ only one position of $L_1$ exists which leads to a pair as indicated schematically in Fig. 2(c). For a given position of $L_1$, however, two alternative positions $L_2$ (marked (1) and (2), respectively) exist, which lead to a pair ($L_1\,L_2$) geometrically equivalent to the pair ($L_0\,L_1$). Such a structure is thus an OD structure (Dornberger-Schiff, 1956, 1964, 1966). The symmetry of the superposition structure resulting from such an arrangement according to (1) is indeed $A(1)\dfrac{2}{m}1$.

A whole family of structures results whose members are built of the same two kinds of layers in alternation but which differ in the actual sequence of these layers. The symmetry of these structures is characterized by an OD-groupoid family which we may describe by the following symbol

$$P(1)\dfrac{2}{c}1\ [.\tfrac{1}{4}.]\ A(1)\dfrac{2}{m}1\ .$$

The symbol in square brackets indicates the relative position of the $c$ glide and mirror plane of the two plane space groups, respectively, given in this symbol.

### 3. Structures of maximum degree of order (MDO)

The plane space groups characterizing the symmetries of the layers of the two kinds, each contain symmetry elements, turning the layer upside down ($\bar{1}$ and 2, respectively). Thus the OD-groupoid family belongs to category IV (Dornberger-Schiff, 1964) and layers of the two kinds alternate. We shall, in the following, call the layers with primitive Bravais lattice '$P$ layers', those
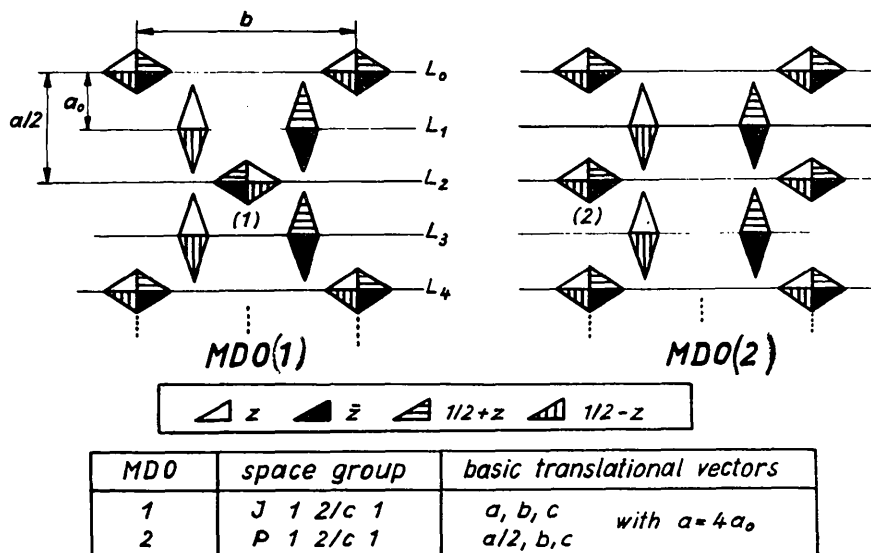


Fig. 3. Symmetry of the domains MDO (1) and MDO (2).

with $A$-centred lattice '$A$ layers', for short. If we take $L_0$ to be a $P$ layer, then the structure contains triples $(L_{2n}^{(P)}, L_{2n+1}^{(A)}, L_{2n+2}^{(P)})$ and triples $(L_{2n-1}^{(A)}, L_{2n}^{(P)}, L_{2n+1}^{(A)})$. There exists only one kind of triple $(L_{2n-1}^{(A)}, L_{2n}^{(P)}, L_{2n+1}^{(A)})$ because, assuming an arbitrary position of $L_{2n}^{(P)}$, the positions of the preceding and the subsequent layer ($L_{2n-1}^{(A)}$ and $L_{2n+1}^{(A)}$) are uniquely determined [Fig. 2(c)]. There are, however, two kinds of triples ($L_{2n}^{(P)}, L_{2n+1}^{(A)}, L_{2n+2}^{(P)}$). Assuming an arbitrary position of $L_{2n+1}^{(A)}$, there are two positions each for the preceding and the subsequent layer $L_{2n}^{(P)}$ and $L_{2n+2}^{(P)}$, respectively, and pairs of the 4 resulting triples are geometrically equivalent.

In the two kinds of triples $L_{2n}^{(P)}$ is transformed into $L_{2n+2}^{(P)}$ by a translation $\hat{a}$ or $\hat{a}+(b+c)/2$, respectively. A structure containing exclusively triples $L^{(P)} L^{(A)} L^{(P)}$ of one kind is to be called an MDO structure (Dornberger-Schiff, 1964); if the triples are of the first kind, MDO(1), if they are of the second kind, MDO(2). The MDO structures are periodic and have the following space groups and lattice constants

$$\begin{array}{lll} \text{MDO(2)} & I2_1/c & 2\hat{a}\,b\,c \\ \text{MDO(1)} & P2_1/c & \hat{a}\,b\,c \end{array}$$

A pure MDO(1) structure would give reflexions at the positions in reciprocal space corresponding to the observed sharp reflexions and the strong maxima, a pure MDO(2) structure at positions corresponding to the sharp reflexions and the weak maxima.

## Symmetry of the structure factors

Let the set of atomic coordinates of a layer $L_p$ referred to a common origin at a centre of symmetry of $L_0$ be symbolized by $[L_p]$.

Then the sets of coordinates of the odd numbered layers are

$$[L_{2m+1}] = [L_1] + (m, 0, 0), \tag{1}$$

whereas those of the even numbered layers are

$$[L_{2m}] = [L_0] + \left(m, \frac{\alpha_m}{2}, \frac{\alpha_m}{2}\right), \tag{2}$$

where $\alpha_m$ may be either 0 or 1, and the set of $\alpha_m$ values depends on the sequence of layers and characterizes it.

Thus the Fourier transform $F(\xi,k,l)$ of the real structure is related to the Fourier transform $F_0(\xi,k,l)$ and $F_1(\xi,k,l)$ of the zero ($P$) layer and the first ($A$) layer, respectively, by

$$F(\xi,k,l) = S_0(\xi,k,l)F_0(\xi,k,l) + S_1(\xi,k,l)F_1(\xi,k,l) \tag{3}$$

with

$$S_0(\xi,k,l) = \frac{1}{2M} \sum_{m=0}^{M-1} (-1)^{\alpha m(k+l)} \exp\{2\pi i 2m\xi\} \tag{4}$$

and

$$S_1(\xi,k,l) = \frac{1}{2m} \sum_{m=0}^{M-1} \exp\{2\pi i 2m\xi\}$$

$$\begin{cases} = 0 \text{ for } 2\xi \text{ non-integral} \\ = \frac{1}{2} \text{ for } 2\xi = \hat{h} \text{ integral}. \end{cases} \tag{5}$$

Therefore, for $k+l$ even

$$F(\xi,k,l) \begin{cases} = 0 \text{ for } 2\xi \text{ non-integral} \\ = \frac{1}{2} F_0(\xi,k,l) + F_1(\xi,k,l) \text{ for } 2\xi = \hat{h} \text{ integral}. \end{cases} \tag{6}$$

Thus for $k+l$ even we have to expect sharp reflexions, as observed, with a Fourier transform corresponding to the structure factors of the superposition structure. The unit to which we referred $\xi'$ was, however, chosen differently from that of $\xi$; for the sharp reflexions $\xi' = h = 2\hat{h} = 4\xi$. This corresponds in real space to the relation $4a_0 = a$ where $a$ is the apparent lattice constant obtained, if all maxima on the diffuse streaks as well as the sharp reflexions are treated as if they were ordinary reflexions of a preiodic crystal.

To the diffraction pattern corresponding to $k+l$ odd, the odd layers do not contribute and thus the intensity is equal to

$$|F(\xi,k,l)|^2 = |S_0(\xi,k,l)|^2 |F_0(\xi,k,l)|^2. \tag{7}$$

For $k+l$ odd the value of $S_0$ depends only on $\xi$. For the values of $\xi$ for which maxima have been observed i.e. for integral values of $4\xi = h$ one value of $S_0$ results for $h$ even, another value for $h$ odd, either of them independent of the particular values of $h,k,l$ (Table 2). Thus the distinction between 'strong' and 'weak' maxima originally made to account for observations finds its explanation in different $S_0$ values, i.e. in the particular stacking of the layers present in the investigated crystal.

## 5. Determination of the structure

The diffuse streaks at $k+l$ odd are very weak in comparison to the maxima on it. This is probably due to large ordered domains containing sequences corresponding to MDO(1) and MDO(2). This makes it easy to measure the intensities at just those positions of the diffuse streaks. We shall assume in the following that the values of $|F(\xi,k,l)|^2$ may be obtained in sufficient approximation for values $\xi = \xi'/4 = h/4$ with $h$ integral,

Table 2. *Characterization of the three sets of 'reflexions'*

| | $v$ | $k+l$ | $h$ | $S_0^{(v)}(h,k,l)$ | $S_1^{(v)}(h,k,l)$ |
|---|---|---|---|---|---|
| Sharp reflexions | 0 | even | even | $\frac{1}{2}$ | $\frac{1}{2}$ |
| Strong maxima | 1 | odd | odd | $\dfrac{1}{2M} \sum\limits_{m=0}^{M-1} (-1)^{\alpha m}$ | 0 |
| Weak maxima | 2 | odd | even | $\dfrac{1}{2M} \sum\limits_{m=0}^{M-1} (-1)^{\alpha m+m}$ | 0 |

but shall not make use of the assumption of ordered domains.

Let us denote by $\varrho_0$ and $\varrho_1$ the electron density of the layers $L_0$ and $L_1$, respectively. Let us characterize the three sets of reflexions by a superscript $v$ according to Table 2. Then the electron densities $\varrho^{(v)}$ of three fictitious structures correspond to the three sets of structure factors $F^{(v)}(h,k,l)$ (with $v=0,1,2$) each taken by itself. We have already discussed the structure for $v=0$ i.e. the superposition structure. In order to find the relation between the $\varrho^{(v)}$, and $\varrho_0$ and $\varrho_1$ (the electron density of layer $L_0$ and layer $L_1$, respectively) the following points have to be taken into account

(i) the translation or antitranslations resulting from the selection of $hkl$ values

(ii) the values of $S_0^{(v)}$ and $S_1^{(v)}$ as summarized in Table 2.

Thus the following relations result

$$4\varrho^{(0)} = \tfrac{1}{2}[\varrho_0(x,y,z) + \varrho_0(\tfrac{1}{2}+x,y,z) + \varrho_0(x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)$$
$$+ \varrho_0(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z) + \varrho_1(x,y,z)$$
$$+ \varrho_1(\tfrac{1}{2}+x,y,z) + \varrho_1(x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)$$
$$+ \varrho_1(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)] \tag{8}$$

$$4\varrho^{(1)} = |S_0^{(1)}|[\varrho_0(x,y,z) - \varrho_0(\tfrac{1}{2}+x,y,z)$$
$$- \varrho_0(x,\tfrac{1}{2}+y,\tfrac{1}{2}+z) + \varrho_0(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)] \tag{9}$$

$$4\varrho^{(2)} = |S_0^{(2)}|[\varrho_0(x,y,z) + \varrho_0(\tfrac{1}{2}+x,y,z)$$
$$- \varrho_0(x,\tfrac{1}{2}+y,\tfrac{1}{2}+z) - \varrho_0(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)] \tag{10}$$

The electron densities of the MDO structures $\varrho_{MDO(1)}$ and $\varrho_{MDO(2)}$ are closely related to the $\varrho^{(v)}$. The relations are obtained from (8), (9) and (10) taking into account that by definition

$$\varrho_{MDO(1)} = \tfrac{1}{4}[\varrho_0(x,y,z) + \varrho_1(x,y,z) + \varrho_0(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)$$
$$+ \varrho_1(\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}+z)] \tag{11}$$

and

$$\varrho_{MDO(2)} = \tfrac{1}{4}[\varrho_0(x,y,z) + \varrho_1(x,y,z) + \varrho_0(\tfrac{1}{2}+x,y,z)$$
$$+ \varrho_1(\tfrac{1}{2}+x,y,z)] . \tag{12}$$

Thus

$$\varrho_{MDO(1)} = \varrho^{(0)} + \frac{1}{2|S_0^{(1)}|} \varrho^{(1)} \tag{13}$$

and

$$\varrho_{MDO(2)} = \varrho^{(0)} + \frac{1}{2|S_0^{(2)}|} \varrho^{(2)} . \tag{14}$$

Because $S_0^{(1)}$ and $S_0^{(2)}$ are not known to start with, these relations can only be used at a later stage for refining the structure, and this has actually been done.

At the start of the structure determination the Patterson projection $P^{(1)}(u,v)$ corresponding to $\varrho^{(1)}$ was obtained which is shown in Fig. 4. It possesses antitranslations $a/2$ and $b/2$ and consists solely of contributions of the $P$ layers, because $S_1^{(1)}=0$ (Table 2). Thus the projection of the $P$ layers may be deduced from this Patterson projection by disregarding the negative maxima.

The density proves that two formula units Ca[B(OH)₄]₂.2H₂O are present within a repeat unit of a

pair of layers ($L^{(P)}$ plus $L^{(A)}$). Thus two Ca atoms are either at symmetry centres of the $A$ layers or they occupy a twofold position on the rotation diad of the $P$ layers. In the first case only boron, oxygen and hydrogen atoms could contribute to the diffuse streaks and the maxima on it; this seemed rather unlikely in view of the fact that on the average the observed maxima are not much weaker than the sharp reflexions although the $S$ value tends to weaken the maxima. In the second case, the distance $y_{Ca}$ of the Ca atoms from the $c$ glide plane cannot differ very much from 0 or $\tfrac{1}{4}$ because otherwise a Ca–Ca vector on the line $x=0$ ought to be visible outside the origin peak. $y_{Ca} \simeq \tfrac{1}{4}$ may be excluded for the same reason as case 1, thus case 2 was assumed with $y_{Ca} \simeq 0$. Thus the Patterson projection $P^{(1)}(u,v)$ resembles closely the corresponding electron density projection $\varrho^{(1)}(x,y)$ and this is born out by Fig. 4 in which the projections of the atomic positions obtained after refinement are also indicated. It shows Patterson peaks – apart from the origin peak corresponding to the two Ca atoms nearly coinciding in projection – indicating approximate positions of the oxygen atoms 1,2,4 and 5 as well as a small peak in the interior of the triangle formed by the oxygen atoms 1,2 and 4, which may be due to the boron atom. Thus only the oxygen atom O(3) and possibly the boron atom lie approximately on the *anti* mirror line of this projection and are thus converted by the $c$-glide plane into another atom related to it (within certain limits of error) by a translation $(b+c)/2$. These atoms are thus the only atoms (except possibly hydrogen atoms) which may belong to the $A$ layers.

With signs taken from structure factors $F^{(1)}(h,k)$ and $F^{(2)}(h,k)$ calculated from approximate atomic coordinates obtained from the Patterson projection as described, projections $\varrho^{(1)}(u,v)$ and $\varrho^{(2)}(u,v)$ were obtained.
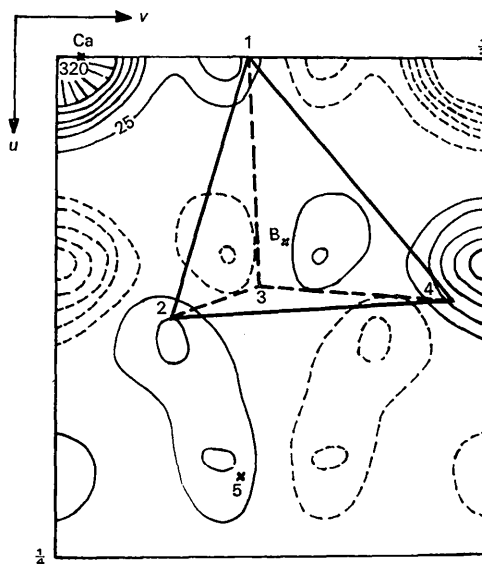


Fig. 4. Patterson projection calculated from the intensities of the reflexions $hk0$ with $h$ odd and $k$ odd.

Comparison of observed and calculated structure factors were also used to determine $S_0^{(1)}$ and $S_0^{(2)}$. The $z$ coordinates were determined from the $xz$ projection which is the same for all members of the family of OD structures and is the same as the projection of the superposition structure. Further refinement then proceeded for the structures MDO(1) and MDO(2) separately, according to (13) and (14) by structure factor calculations and difference projections as well as least-squares methods.

Refinement resulted in the coordinates given in Table 3 along with the atomic coordinates obtained by Kravchenko (1964) and Ozol, Wimba & Jevinsh (1964), referred to the same axes. The number of reflexions used and $R$ values obtained are summarized in Table 4.

Because the weak maxima corresponding to MDO(2) fade out at smaller sin $\theta$ values, sharp reflexions of only

a correspondingly smaller region of reciprocal space were included in the refinement of this structure. The results are also given in Table 4. The atomic coordinates obtained for MDO(1) and MDO(2) show differences which may be just outside the limits of error.

## 6. Description of the structure and discussion

In Figs. 5 and 6 the two structures MDO are shown schematically. The odd-numbered OD layers consist of O(3) atoms only, lying approximately in special positions ($y = \frac{1}{4}$) with the site symmetry $m$.

The $B(OH)_4$ tetrahedra belonging to the same layer, e.g. $L_0$, are held together by links Ca–O and bond between O atoms and water molecules.

The $B(OH)_4$ tetrahedra of $L_0$ and $L_2$ are bound together only by the water molecules. Water molecules

### Table 3. Atomic coordinates

| | | Sedlacek & Dornberger-Schiff | | Ozol, Wimba & Jevinsh (1964) | Kravchenko (1964) |
| | | MDO (1) | MDO (2) | MDO (2) | MDO (1) |
|---|---|---|---|---|---|
| Ca | $x$ | 0·000 | 0·000 | 0·000 | 0·000 |
| | $y$ | −0·029 | −0·030 | −0·025 | −0·020 |
| | $z$ | 0·250 | 0·250 | 0·250 | 0·250 |
| B | $x$ | 0·091 | 0·091 | 0·092 | 0·091 |
| | $y$ | 0·271 | 0·264 | 0·275 | 0·274 |
| | $z$ | 0·065 | 0·070 | 0·067 | 0·069 |
| O(1) | $x$ | −0·003 | −0·004 | 0·000 | −0·002 |
| | $y$ | 0·221 | 0·226 | 0·217 | 0·220 |
| | $z$ | 0·033 | 0·035 | 0·021 | 0·033 |
| O(2) | $x$ | 0·133 | 0·133 | 0·133 | 0·133 |
| | $y$ | 0·128 | 0·126 | 0·117 | 0·128 |
| | $z$ | 0·202 | 0·198 | 0·188 | 0·201 |
| O(3) | $x$ | 0·113 | 0·112 | 0·116 | 0 112 |
| | $y$ | 0·246 | 0·247 | 0·267 | 0·246 |
| | $z$ | −0·099 | −0·097 | −0·104 | −0·100 |
| O(4) | $x$ | 0·109 | 0·108 | 0·109 | 0·109 |
| | $y$ | 0·477 | 0·477 | 0·479 | 0·480 |
| | $z$ | 0·124 | 0·126 | 0·133 | 0·124 |
| O(5) | $x$ | 0·213 | 0·213 | 0·213 | 0·212 |
| | $y$ | 0·210 | 0·208 | 0·192 | 0·209 |
| | $z$ | 0·553 | 0·549 | 0·558 | 0·550 |

Coordinate standard deviations (present authors)

| MDO (1,2) | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|
| Ca | — | 0·001 | 0·001 |
| B | 0·001 | 0·002 | 0·002 |
| O | 0·001 | 0·001 | 0·001 |

### Table 4. Number of reflexions used and R values

| Type | Authors | $hkl$ | Sharp reflexions | Maxima on streaks | Reflexions plus maxima | $R(\%)$ |
|---|---|---|---|---|---|---|
| MDO (1) | Sedlacek Dornberger-Schiff | all | 211 | 230 | 441 | 10·7 |
| MDO (1) | Kravchenko (1964) | all | | | 490 | 13·8 |
| MDO (2) | Sedlacek Dornberger-Schiff | all | 159 | 122 | 281 | 10·8 |
| MDO (2) | Ozol, Wimba & Jevinsh (1964) | $hk0$ | | | 62 | 18·0 |
| MDO (2) | Ozol, Wimba & Jevinsh (1964) | $h0l$ | | | 64 | 21·0 |

of $L_0$ are bound to three oxygen atoms of the same layer (bonds $d,e,f$) and to an oxygen atom O(3) of layer $L_1$, which belongs to a B(OH)₄ tetrahedron of $L_2$. Similarly three oxygen atoms of $L_2$ are bound to a water molecule of $L_2$, which is bound to an atom O(3) of $L_1$ belonging to a B(OH)₄ tetrahedron of $L_0$. Thus $L_0$ is bound to $L_2$ only by means of atoms O(3) which form the $A$ layer $L_1$.

The two translationally non-equivalent O(3) atoms of $L_1$ which belong to B(OH)₄ tetrahedra of $L_0$ and of $L_2$, respectively, are linked by the symmetry operations (1) 2 1 and $\bar{1}$ of the $A$ layer $L_1$. In the structure MDO(1) the $\bar{1}$ is a total operation of the structure and (1) 2 1 is not; in the case of MDO(2) it is the other way round. Apart from the deviations from the ideal position of the O(3) atoms, the atomic distances and valency angles must thus be the same in the two MDO structures. Actually, refinement of the MDO structures resulted in a $y$ coordinate for O(3) which is significantly different from $\frac{1}{4}$ (0·247 and 0·246 respectively). The assumed symmetry for the odd-numbered layers is thus not exactly fulfilled.

The OD layers of the structure defined solely with respect to symmetry, are not to be confused with the layers which could be used to describe the structure from the chemists point of view. Also from this point of view two kinds of layers perpendicular to a could be defined. One kind consists of the Ca atoms and the B(OH)₄ tetrahedra, the other kind of the water molecules.

Each Ca atom is surrounded by 8 O atoms forming a distorted cube; these O atoms belong to 4 different B(OH)₄ tetrahedra. The O atoms of the water molecules have tetrahedral hydrogen bonds to 4 O atoms of 4 different B(OH)₄ tetrahedra. Each O atom of the B(OH)₄ tetrahedra is surrounded by 4 atoms with distorted tetrahedral valency angles (Fig. 5). The interatomic distances and valency angles are collected in Tables 5 to 7.

### Table 5. Ca–O distances ($\pm 0.03$ Å)

|  |  | MDO (1) |
|---|---|---|
| Ca'–O(1) | h | 2·60 Å |
| Ca –O(1) | j | 2·40 |
| Ca'–O(3) | k | 2·39 |
| Ca –O(2) | l | 2·50 |
| Mean value |  |  |
| Ca –O |  | 2·47 |

### Table 6. B–(OH)₄ tetrahedron

| Distances ($\pm 0.03$ Å) |  |  | Angles ($\pm 0.4°$) |  |
|---|---|---|---|---|
|  |  | MDO (1) |  | MDO (1) |
| B——O(1) | t | 1·50 Å | tu | 103·8° |
| B——O(2) | u | 1·48 | tv | 106·8 |
| B——O(3) | v | 1·45 | tw | 111·8 |
| B——O(4) | w | 1·46 | uv | 114·5 |
| Mean value |  |  |  |  |
| B——O |  | 1·47 | uw | 111·1 |

### Table 6 (cont.)

| O(1)–O(2) | m | 2·35 | vw | 108·7 |
|---|---|---|---|---|
| O(1)–O(3) | n | 2·37 | Mean value | 109·4 |
| O(1)–O(4) | o | 2·46 |  |  |
| O(2)–O(3) | p | 2·46 |  |  |
| O(2)–O(4) | r | 2·43 |  |  |
| O(3)–O(4) | s | 2·36 |  |  |
| Mean value |  |  |  |  |
| O——O |  | 2·40 |  |  |

From the deviation of the $y$ coordinate of O(3) from $\frac{1}{4}$, we would expect the values of the interatomic distances $d,e,f,g$ and the angles between these bonds to differ for the two MDO structures. They have, therefore, been given separately. As Table 7 shows, they cannot be stated to differ significantly. It seems likely to us that the O–O contacts given in Table 7 all correspond to asymmetric hydrogen bridges. Under this assumption there are 4 different ways to assign short and
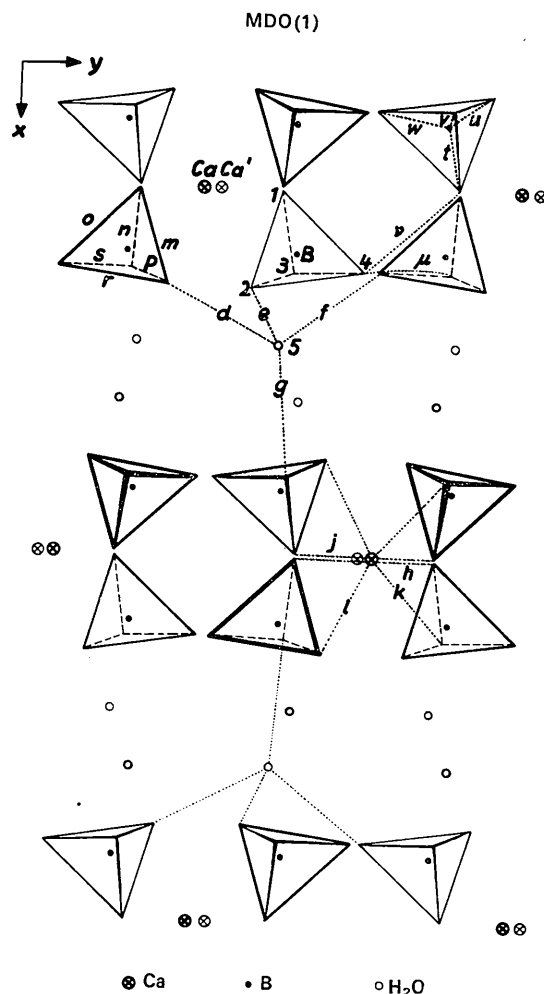


MDO(1)

Fig. 5. The structure MDO (1) projected onto the a, b plane. The oxygen atoms are numbered 1 to 5. The letters refer to Tables 5 to 7.

long ends to these bridges, which would assign to each oxygen atom two strong bonds (to a B atom or the short end of the bridge) and two weak bonds (to a Ca atom or the long end of the bridge).

These four possibilities are shown in Fig. 7. One pair of possibilities has hydrogen positions marked as dots combined with positions called '1' and '2', respectively, the other pair has positions marked as rings.

We think that most likely one of these possibilities or a resonating mixture of some or all four of them is present in the structure. This assumption is supported by the fact that a search in difference Fourier syntheses (projections and three-dimensional) for maxima which could be due to hydrogen atoms, only revealed a position near to O(1) which is common to all 4 possibilities.

It seems to us not unlikely that MDO(1) and MDO(2) might correspond to different possibilities (or perhaps pairs of possibilities) whereas in disordered structures these possibilities would occur in resonance.
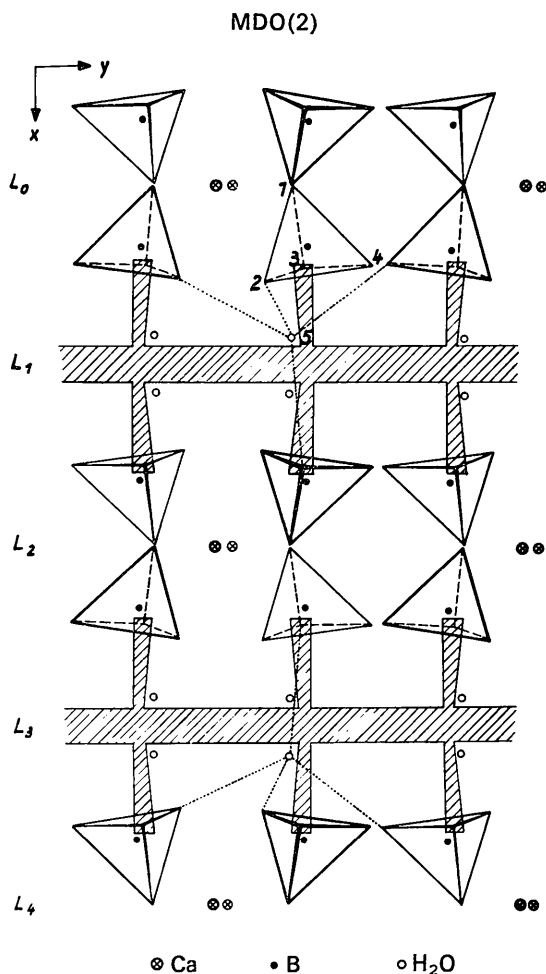
### 7. Relation of the results of this paper to those of other authors

Crystals of calcium diborate dihydrate have been investigated with X-ray methods by Peacock & Vigfusson (1939), Ghose (1963), Ozol, Wimba, & Jevinsh (1964), Kravchenko (1964) and by one of us (Sedlacek 1966). Although Peacock & Vigfusson and Ghose assumed that they had crystals of the hexahydrate there seems no doubt about the identity of the material with that studied by us, not only on account of the lattice constants, but also, because the samples for this study were kindly supplied by Ghose and taken from the same charge he had previously studied. Comparison with the results of these authors may be made only by comparison of the lattice constants, whereas Ozol et al. and Kravchenko determined the structure and thus comparison of atomic coordinates is also possible. Lattice constants $a, b, c, \beta$ as given by all these authors are collected in Table 8 and exhibit a striking similarity, $b$, $c$ and $\beta$ being almost equal in all cases, and $a$ either equal to approximately 8 Å or twice this length. The space group is given as monoclinic, and systematic absences corresponding to a $c$ glide were observed in all cases. Different Bravais lattices have, however, been found and it was not at all clear, to start with, how these evidently different modifications could be related. Actually the situation is obscured by the fact that for the $C$-face and the body-centred cell

$$c/a = -2 \cos \beta$$

so that the magnitude of $\mathbf{a} + \mathbf{c}$ is about equal to the magnitude of $a$, and the angle $\beta'$ between $\mathbf{a} + \mathbf{c}$ and $-\mathbf{c}$ is about equal to $\beta$. Thus the $C$-face-centred structures could equally well be described as body-centred structures with approximately the same lattice constants and vice versa. The lattice constants found by us differ up



Fig. 6. The structure MDO (2) projected onto the a,b plane. The layers are numbered $L_0, L_1 \ldots$, odd layers shown hatched.

Table 7. O-H-O bonds

| | O-O distances ($\pm 0.03$ Å) | | | Angles ($\pm 0.4°$) | |
| --- | --- | --- | --- | --- | --- |
| | | MDO (1) | MDO (2) | | MDO (1) | MDO (2) |
| O'(2) –O(5) | $d$ | 2·99 Å | 2·97 Å | $de$ | 96·5° | 96·6° |
| O(2)—O(5) | $e$ | 2·81 | 2·81 | $df$ | 98·2 | 97·4 |
| O'(4) –O(5) | $f$ | 2·83 | 2·86 | $dg$ | 123·8 | 123·2 |
| O''(3)-O(5) | $g$ | 2·74 | 2·75 | $ef$ | 101·6 | 102·2 |
| O(4)—O'(3) | $\mu$ | 2·87 | — | $eg$ | 110·1 | 110·2 |
| O(4)—O'''(1) | $v$ | 2·72 | — | $fg$ | 122·0 | 122·6 |
| O——O | Mean value | 2 83 | | Mean value | 108 6 | 108·6 |

Table 8. *Results of earlier authors*

| Modification and authors | Symmetry as described by the author | Lattice constants as given by the authors | | | | Transformed cell for comparison with this paper $\lvert a'\rvert=\lvert a+c\rvert$ | | Space group, if any | Interpretation as members of an OD-groupoid family |
|---|---|---|---|---|---|---|---|---|---|
| | | $a$ | $b$ | $c$ | $\beta$ | | $\beta'$ | | |
| I. Peacock & Vigfusson (1939) | $Pc$ | 7·98 | 6·61 | 7·97 | 104·42 | — | — | $P2/c$ | MDO (2) |
| II. Ghose (1963) | presumed $Pc$ or $P2/c$ | 15·96 | 6·61 | 7·97 | 104·42 | 15·97 7·98 | 104·5 104·5 | disordered $I2/c$ $P2/c$ | containing large domains of MDO (1) MDO (2) |
| III. Ghose (1963) | $C2/c$ for nearly all reflexions | 15·96 | 6·61 | 7·97 | 104·42 | 15·97 | 104·5 | probably disordered $I2/c$ | containing large domains of MDO (1) and far less of MDO (2) (see II) |
| IV. Ozol, Wimba & Jevinsh (1964) | $P2/c$ | 7·9997 | 6·726 | 7·9693 | 103·798 | (7·98) | (104·5) | ($P2/c$) | MDO (2) |
| V. Kravchenko (1964) | $C2/c$ | 16·02 | 6·70 | 7·94 | 104·0 | 16·07 | 104·7 | $P2/c$ $I2/c$ | MDO (2) MDO (1) |
| VI. Sedlacek (1966) | disordered; reflexions and maxima corresponding to $I2/c$ and $P2/c$ | 16·08 8·04 | 6·69 6·69 | 7·95 7·95 | 104·9 104·9 | | | disordered $I2/c$ $P2/c$ | containing large domains of MDO (1) MDO (2) |

to 0·1 Å and 0·4° from those obtained by Ghose (1963) from the same crystalline material.

In the last three columns of Table 8 the lattice constants of the transformed cell are given where such a transformation is necessary for comparison with the results of this paper, as well as the interpretation as members of the OD-groupoid family, and space group (if any). In the case of the data given by Peacock & Vigfusson (1939), either the original or the transformed primitive cell may correspond to the MDO(2) structure.

Table 3 gives the atomic coordinates obtained by Kravchenko referred to our unit cell, in comparison with our results for domain MDO(1) and those of Ozol with our results for domain MDO(2).

In Table 4 the numbers of reflexions of various kinds on which the structure determinations were based are given, together with the reliability indices.

In the discussion of the structure Kravchenko describes only one of the four possibilities for hydrogen bonds described above and in Fig. 7, namely the possibility marked as dots 1, whereas Ozol *et al.* assume that the water molecule is bound only by the three hydrogen bridges $d,f,g$ in analogy to the structure of KH$_2$(H$_3$O)$_2$B$_5$O$_{10}$ as given by Zachariasen (1938).

## 8. Summary

The X-ray diagrams (sharp reflexions and diffuse streaks with a systematic distribution of strong and weak maxima on it) have been explained by the assumption of an OD-structure consisting of two kinds of layers periodic with periods **b** and **c**.
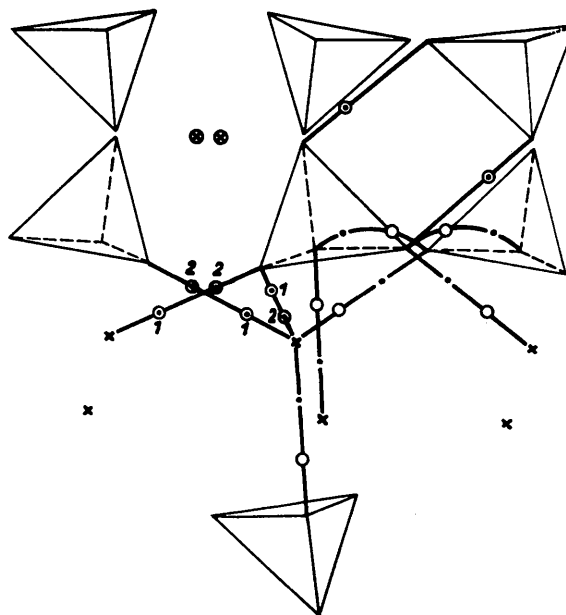


Fig. 7. Schematic drawing of 4 possibilities for the position of H atoms on hydrogen bridges. Dots or empty circles, respectively, may occur in conjunction with dotted circles marked '1' or '2', respectively.

The OD-groupoid family is

$$P(1)\frac{2}{c} 1 \ [.\tfrac{1}{4}.] \ A(1)\frac{2}{m} 1 \ .$$

The structure contains two kinds of large ordered domains with space group $I1\frac{2}{c}1$ and $P1\frac{2}{c}1$ corresponding to the strong maxima and the weak maxima respectively. Based on the OD theory, methods have been developed to determine the structures of the two kinds of layers (Figs. 5 and 6). The $A$ layers (each of them contains only one O atom in the asymmetric unit) with the higher symmetry lie ordered (periodic vector $a/2$). The $P$ layers may occupy either of two equivalent positions characterized by the vectors between the mirror planes of the $A$ layers and the $c$ glides of the adjacent $P$ layers ($.\tfrac{1}{4}.$).

The structures of domains MDO(1) and MDO(2) (Figs. 5 and 6) have been determined independently, one from the other, using sharp reflexions and strong maxima, or sharp reflexions and weak maxima, respectively. For both kinds of domains the result of the structure determination is practically the same in agreement with our assumption (Table 3).

The results of this paper show, that apparently different modifications of calcium monoborate dihydrate described by Kravchenko (1964), Ozol, Wimba & Jevinsh (1964) and by Sedlacek (1966) and such modifi-

cations which were assumed by mistake to be calcium diborate hexahydrate, described by Peacock & Vigfusson (1939) and Ghose (1963) belong to the same OD-structure family as described in this paper.

The different modifications are either members of this family with maximum degree of order (those described by Kravchenko and Ozol et al.) or one-dimensionally disordered members with different degrees of disorder (those described by the other authors quoted above). The structure determined by Kravchenko is in very good agreement with the structure of domains MDO(1) and that determined by Ozol et al. is obviously the same as MDO(2) (Table 3). Only the interpretation of the O–H–O bonds is rather different (§ 6).

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# The Crystal and Molecular Structure of Ethylenebisbiguanidenickel(II) Chloride Monohydrate, C6H16N10NiCl2.H2O

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Ethylenebisbiguanidenickel(II) chloride monohydrate, $C_6H_{16}N_{10}Ni.Cl_2H_2O$, crystallizes in the monoclinic system with $a=6\cdot905$ (5), $b=11\cdot680$ (4), $c=18\cdot038$ (23) Å, $\beta=101\cdot41$ (10)°, $D_m=1\cdot740$ g.cm$^{-3}$, $Z=4$, $D_x=1\cdot750$ g.cm$^{-3}$; the space group is $P2_1/c$. The structure was determined by using 1714 'observed' intensities collected on a General Electric XRD-5 diffractometer using Mo $K\alpha$ radiation and the parameters were refined by least-squares until $R=0\cdot031$. The nickel atom is in square planar configuration with an average Ni–N bond length of $1\cdot866$ Å. The tetradentate ethylenebisbiguanide ligand is essentially planar around the nickel. Through extensive hydrogen bonding involving the water of hydration and the two chloride ions, the molecules are formed into infinite sheets parallel to the (100) planes. Additional hydrogen bonds between the sheets create a rigidly bound structure. A particularly interesting feature of the hydrogen bonding is the discovery of five bonds involving the water of hydration. This report presents the third independent solution and refinement of the structure. A comparison with the structure reported by Holian & Marsh using the $\delta_p$ half-normal probability plot, indicates that most of the standard deviations derived in both studies are too small by a factor of about $1\cdot7$; some are too small by a considerably larger factor.

## Introduction

The X-ray crystal structure study of ethylenebisbiguanidenickel(II) chloride monohydrate was under-

taken owing to the interest in multidentate ligands and interest in organic compounds of transition metals. The present compound combines these qualities and is of special interest because of the tetradentate nature of the ethylenebisbiguanide ligand.

After this study was completed, it was discovered

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