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AN ATTEMPT AT AN ALGEBRAIC THEORY OF CRYSTAL STRUCTURE. PART 2.

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ABSTRACT

A modification of a previously established Diophantine equation enables the structure of further inclusion hydrates to be predicted, and points the way to a general algebraic theory of crystal structure.

Key words: crystal structure, algebraic theory, space-filling polyhedra.

INTRODUCTION

In the first part of this work (Aboav, 1997) an attempt was made to classify certain crystalline substances topologically, without invoking the concepts of length and angle. The substances chosen were inclusion hydrates, whose structure is commonly regarded as a periodic, 3-dimensional, 4-connected honeycomb, with an atom of oxygen at each vertex, with some or all of its cells enclosing molecules of various kinds. The elements of such a figure are vertices Π_0, edges Π_1, faces Π_2, and *cells* or polyhedra Π_3, whose number is here denoted by N_0, N_1, N_2, and N_3, respectively*. A *unit cell* comprises N_3 contiguous polyhedra, sharing N_0 vertices, N_1 edges, & N_2 faces.

Table 1. Topological structure of some inclusion hydrates.

hydrate	12	14	15	16	N_0	N_3	R
chlorine	2	6	...	...	46	8	11·50
chloroform	16	...	...	8	136	24	11·33
alkyl onium salt	6	4	4	...	80	14	11·43
bromine (tetragonal)	10	16	4	...	172	30	11·47
" (orthorhombic)	14	4	4	4	148	26	11·39

Table 1 shows for five such hydrates, the number of 12–, 14–, 15–, and 16–hedra (cols.2 through 5); N_0, the number of vertices (col.6); and N_3, the number of polyhedra (col.7) per unit cell. R, the ratio $2N_0/N_3$, is shown in col.8. [This corrects Table 1 of Part 1, which contained two errors].

*__Note:__ In Part 1, N_0 and N_3 were referred to as Π_0 and Π_3; but, following Coxeter (1973), we shall henceforth denote the number of elements Π_i by N_i (i =0,1,2,3).

In each case, excepting the tetragonal variety of bromine hydrate, N_0 and N_3 were found to be proportional to solutions of the Diophantine equation:

$$2^a x = 3^6 y + z \tag{1}$$

where x, y, and z are odd primes or unity, and z may be positive or negative. The factors of proportionality were found from the experimental data to be given by the equations:

$$N_0 = 2^\alpha x_a \tag{2}$$

and

$$N_3 = 2^\beta y_a \tag{3}$$

where x_a, y_a, and z_a are solutions of Eq.(1) for a given value of a; and α and β are positive integers, such that:

$$(\alpha - \beta + 1) = a - 6. \tag{4}$$

It was further established, as an empirical finding, that in those instances where Eq.(1) serves to classify a crystalline form, its first and second terms do not differ from each other by more than about 1 per cent, i.e. the quotient $z/2^a x$ does not exceed 1/100. The ratio R is consequently approximately expressible in each case as:

$$R \simeq (3/2)^6 \tag{5}$$

Doubtless as more data become available it will be possible to fix this apparent limit to the magnitude of $z/2^a x$ more precisely. Meanwhile we aim, by generalizing them, to extend the above relations to cover a wider range of hydrates, with the ultimate object of eliciting from the empirical data a universally applicable algebraic theory of crystal structure.

A MORE GENERAL ALGEBRAIC REPRESENTATION

As can be seen from Table 1, the factor y_a in Eq.(3) for the tetragonal variety of bromine hydrate is not prime, but is composite and equal to 3x5. To extend the proposed classification to include this and possibly other hydrates we now consider the more general Diophantine equation:

$$2^a x = 3^b y + z \tag{6}$$

where x, y, and z are as in Eq.(1), with the aforesaid limitation $z/2^a x < 1/100$; and b, like a , is a positive integer. To indicate their dependence on a and b the roots of this equation are denoted as x_{ab}, y_{ab}, and z_{ab}.

The experimental data show that, if the above variety of bromine hydrate is to be included in the classification, the ratio R (= $2N_0/N_3$), which as Eqs.(2) & (3) show is proportional to $2^{\alpha-\beta+1}$, must also be inversely proportional to 3^γ, i.e. that:

$$R = (2^{\alpha-\beta+1}/3^\gamma) x_{ab}/y_{ab}. \tag{7}$$

where

$$\gamma = b - 6. \tag{8}$$

Since $x_{ab}/y_{ab} \simeq 3^b/2^a$, R is in this case still expressible by the approximate relation (5); but the fact that neither N_0 nor N_3 may be fractional indicates that either:

$$\left.\begin{aligned} N_0 &= 2^{\alpha}3^{-\gamma}x_{ab} \\ N_3 &= 2^{\beta}y_{ab} \end{aligned}\right\} \qquad (9)$$

or

$$\left.\begin{aligned} N_0 &= 2^{\alpha}x_{ab} \\ N_3 &= 2^{\beta}3^{\gamma}y_{ab} \end{aligned}\right\} \qquad (9')$$

according as b is less than, or greater than 6. If as in Eq.(1) b = 6, γ from Eq.(8) is equal to zero; and N_0 and N_3 are consequently given as before by Eqs.(2, 3).

Odd-prime solutions of Eq.(6) for b = 4 through 8, and for which $z/2^a x < 1/100$, are shown in Table 2 where, as before, solutions beyond the smallest, as well as those for which any of the three numbers x_{ab} y_{ab} z_{ab} exceeds 100, are omitted. Those appertaining to the four hydrates dealt with in Part 1 of this work are shown in **bold type.**

Table 2: Smallest odd-prime solutions of Eq.(6) for which $z/2^a x < 1/100$

	b = 4			b = 5			b = 6			b = 7			b = 8		
a	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}
2	*61*	*3*	*1*												
3	*71*	*7*	*1*												
4	*97*	*19*	*13*												
5	*43*	*17*	*−1*				**23**	**1**	**7**						
6	*29*	*23*	*−7*	*19*	*5*	*1*									
7	*7*	*11*	*5*	*59*	*31*	*−19*	**17**	**3**	**−11**						
8	*13*	*41*	*7*	*41*	*43*	*−47*	**37**	**13**	**−5**	*43*	*5*	*73*			
9	*3*	*19*	*−3*	*11*	*23*	*43*	*67*	*47*	*41*	*47*	*11*	*7*			
10	*7*	*89*	*−41*	*23*	*97*	*−19*	**5**	**7**	**17**	*79*	*37*	*−23*			
11				*7*	*59*	*−1*	*11*	*31*	*−71*						
12							*13*	*73*	*31*						
....															
15													*1*	*5*	*−37*

For convenience, solutions of Eq.(6) are henceforth denoted by placing its indices a,b in square [ ], and its roots x_{ab} y_{ab} z_{ab} in curly { } brackets; so that, for example, [7 4]{7 11 5} denotes the solution $2^7.7 = 3^4.11 + 5$.

Table 2 shows that, subject to the above restriction on the magnitude of $z/2^a x$, the smallest odd-prime solutions of Eq.(6) for a = 8 and b = 7 are $x_{ab} = 43$, $y_{ab} = 5$; from which it follows by Eqs.(4, 8, 9') that $N_0(=2^2.43)= 172$ and N_3 (= 2.3.5) = 30. That these two numbers are the same as those found by experiment to characterize the tetragonal variety of bromine hydrate (Table 1), which as we saw was excluded from the initial classification, indicates that, if Eq.(1) is generalized as here suggested, the range of inclusion hydrates included in a classification based on the resulting equation is extended, and the structure of further, hitherto unidentified chemical compounds thus made predictable.

PREDICTED HYDRATE STRUCTURES

Five of the 26 solutions of Eq.(6) listed in Table 2 thus give, through Eqs.(9) & (9'), values of N_0 and N_3 equal to those found by experiment to characterize the hydrates of Table 1. These solutions, which lie in the range $5 \leq a \leq 10$, are shown separately in Table 3, from which it will be seen that for them y_{ab} in no case exceeds 13.

Table 3: Solutions of Eq.(6) for the hydrates of Table 1

	b = 4			b = 5			b = 6			b = 7			b = 8		
a	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}
5							**23**	**1**	**7**						
6															
7							**17**	**3**	**-11**						
8							**37**	**13**	**-5**	**43**	**5**	**73**			
9															
10							**5**	**7**	**17**						

Table 2 has, however, three further solutions of Eq.(6) which lie within the same range and for which y_{ab} does not exceed 13: [6 5]{19 5 1}, [7 4]{7 11 5}, and [9 7]{47 11 7}. These are shown in Table 4 in *italics*, together with the solutions of Table 3.

Table 4: Solutions of Eq.(6) for which $5 \leq a \leq 10$, and $y_{ab} \leq 13$.

	b = 4			b = 5			b = 6			b = 7			b = 8		
a	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}	x_{ab}	y_{ab}	z_{ab}
5							**23**	**1**	**7**						
6				*19*	*5*	*1*									
7	*7*	*11*	*5*				**17**	**3**	**-11**						
8							**37**	**13**	**-5**	**43**	**5**	**73**			
9										*47*	*11*	*7*			
10							**5**	**7**	**17**						

Since hydrates exist with a structure characterized by the first five of these eight solutions, it is reasonable to suppose there may be some with structure corresponding to the other three. Hence, as a first step, models of honeycombs corresponding to one of these solutions, [6 5]{19 5 1}, will now be made, with the object of discovering whether there exist inclusion hydrates of that structure.

The construction of such models is problematic, since there is no logical path from the solutions of Eq.(6) to the metrical properties of the figures they represent. Moreover Eqs.(9' & 9), which give the total number of polyhedra (N_3) and of vertices (N_0) in the unit cell of the honeycomb, do not specify their partition, that is, they do not indicate how these numbers are to be distributed among differently shaped polyhedra. Without that information therefore the models have to some extent to be constructed intuitively.

The way here chosen to set about that task depends on a method of Wells, who, in his study of the topological structure of crystalline inorganic compounds (Wells, 1984), held that "in this subject, models [of the three-dimensional polyhedra] are indispensable ...... [and] are constructed quite easily from strips of thin card" (Wells, 1977). That they might moreover be more easily distinguished, the polyhedra of different shape were in this case made from differently coloured strips of card, as shown in Plates 1 & 2.

Once their partition had been guessed it was not difficult to spot how such polyhedra should be put together to obtain the topological form of the desired unit cell and its resulting honeycomb. The geometrical characteristics of the honeycomb on the other hand, being not fixed by its topology, were taken as they chanced to turn out in the course of the construction, and were drawn only as accurately as the illustrations demanded. These characteristics can be subsequently modified as required by the phenomena, without affecting the topology.

Varieties of the [6 5]{19 5 1} honeycomb: ($2^6.19 = 3^5.5 + 1$).

From Eqs.(4), (7) & (8) it follows that N_0 and N_3 for these honeycombs are proportional to 3x19 and 2x5 , i.e. to 57 and 10, respectively. N_2, the number of faces of its unit cell, is therefore proportional to 2(57 + 10), or 134.

In the honeycombs now to be described, 268 (= 2x134) faces are distributed among 20 (= 2x10) variously shaped polyhedra as follows:

9	12-hedra (yellow) with a total of	108 faces
10	14-hedra (red) " " " "	140
1	20-hedron (blue) "	20
20	polyhedra with a total of	268 faces

These polyhedra have pentagonal and hexagonal faces only (Fig.1). Those with the same number of faces are topologically identical, but their metrical characteristics are not necessarily the same for each position in the unit cell.

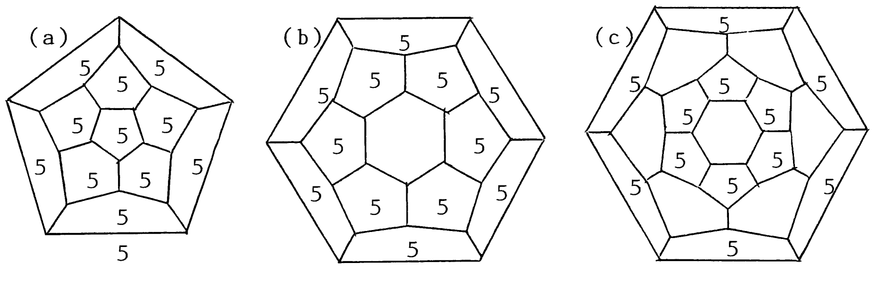

Fig.1. Schlegel diagrams of (a) 12-hedron, (b) 14-hedron, and (c) 20-hedron.

In Plates 1A and 1B the 20-hedron (blue) is viewed along its *c*-axis and *a*-axis, respectively. To it are added six 14-hedra (red) as shown in Plate 1C; and to these are added a further four 14-hedra as in Plates 1D and 1E. To the resulting assembly of 11 polyhedra are added six 12-hedra (yellow) (Plates 1F and 1H), and a further three 12-hedra as shown in Plates 1G and 1K. These 20 polyhedra constitute the unit cell, which has hexagonal symmetry.

As can be seen from these illustrations the 14-hedra are oriented in two ways: in one their axis of symmetry is parallel to the *a*-axis of the cell ('vertical'); in the other it lies along one of its *c*-axes ('horizontal'). These two kinds of 14-hedron are hereinafter designated as *14v* and *14h*, respectively. Although topologically equivalent they are not congruent.

In Plate 2A seven unit cells are joined to form, in the *c*-plane, part of a layer, which is shown without its 12-hedra in Plate 2B. These layers, as we shall now see, can be stacked to form a [6 5]{19 5 1} honeycomb in three different ways.

In the [6 5]{19 5 1} **honeycomb of the 1st type** the layers are stacked so as to form columns of 20-hedra, with accompanying pairs of columns of 14-hedra *(14v)* parallel to the *a*-axis. The columns are separated from one another along their whole length by pairs of 14-hedra *(14h)* ; and the remaining, intervening spaces are occupied by 12-hedra.

The three-dimensional arrangement of polyhedra in the resulting honeycomb is made evident in Plate 2C, which shows a vertical stacking of unit cells without their 12-hedra. A column of 20-hedra (on the left) and one of two columns of 14-hedra (on the right) are clearly discernible; while the remaining column of 14-hedra (at the back) is partly visible, through gaps in the unit cells left by the missing 12-hedra.

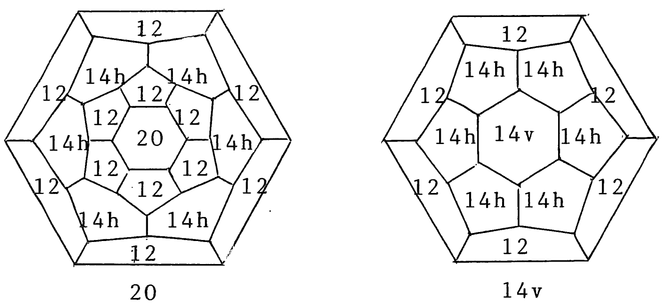

Fig.2. Polyhedra in contact with (a) 20-hedron, and (b) 14-hedron *(14v)*, in columns of [6 5]{19 5 1} honeycomb of the 1st type.

The polyhedra in contact with the 20- and 14-hedra *(14v)* in this variety of the [6 5]{19 5 1} honeycomb are shown schematically in Fig.2, where they are represented by Schlegel-type diagrams. A number shown inside a polygon here indicates the number of faces of the polyhedron that is in contact with the face represented by the polygon; and, as in the standard Schlegel diagram, the number that appears below the diagram refers to the face represented by its 'window'. One of the above three columns consists, as we have seen, of 20-hedra in contact with one another (Fig. 2a), while the other two are made up of contiguous 14-hedra only (Fig. 2b).

* * *

Two further types of honeycomb are obtained, if in the stacking each successive layer of cells is rotated through 120° about an *a*-axis.

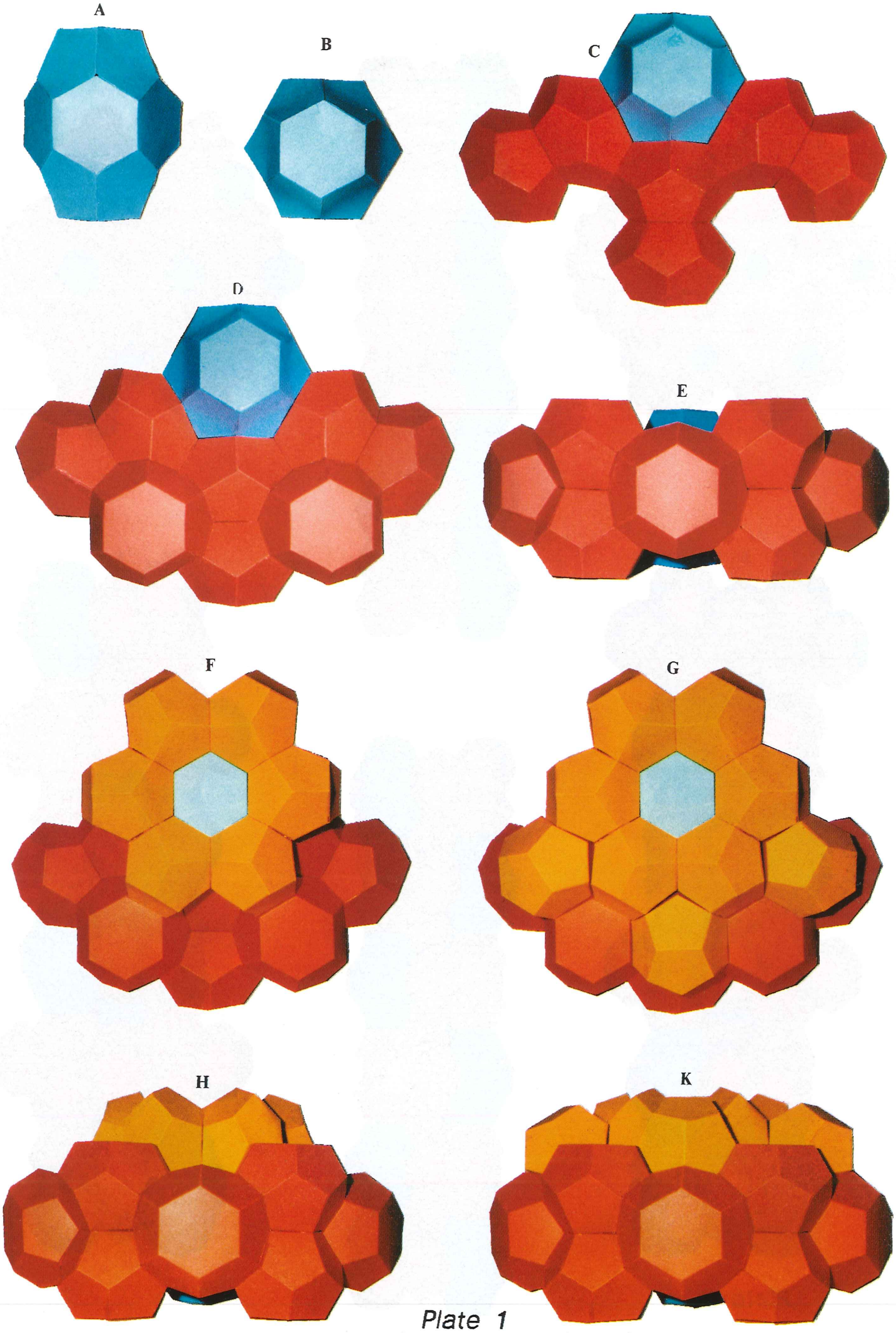

Plate 1

Honeycomb [6,5]{19 5 1}. Construction of unit cell.

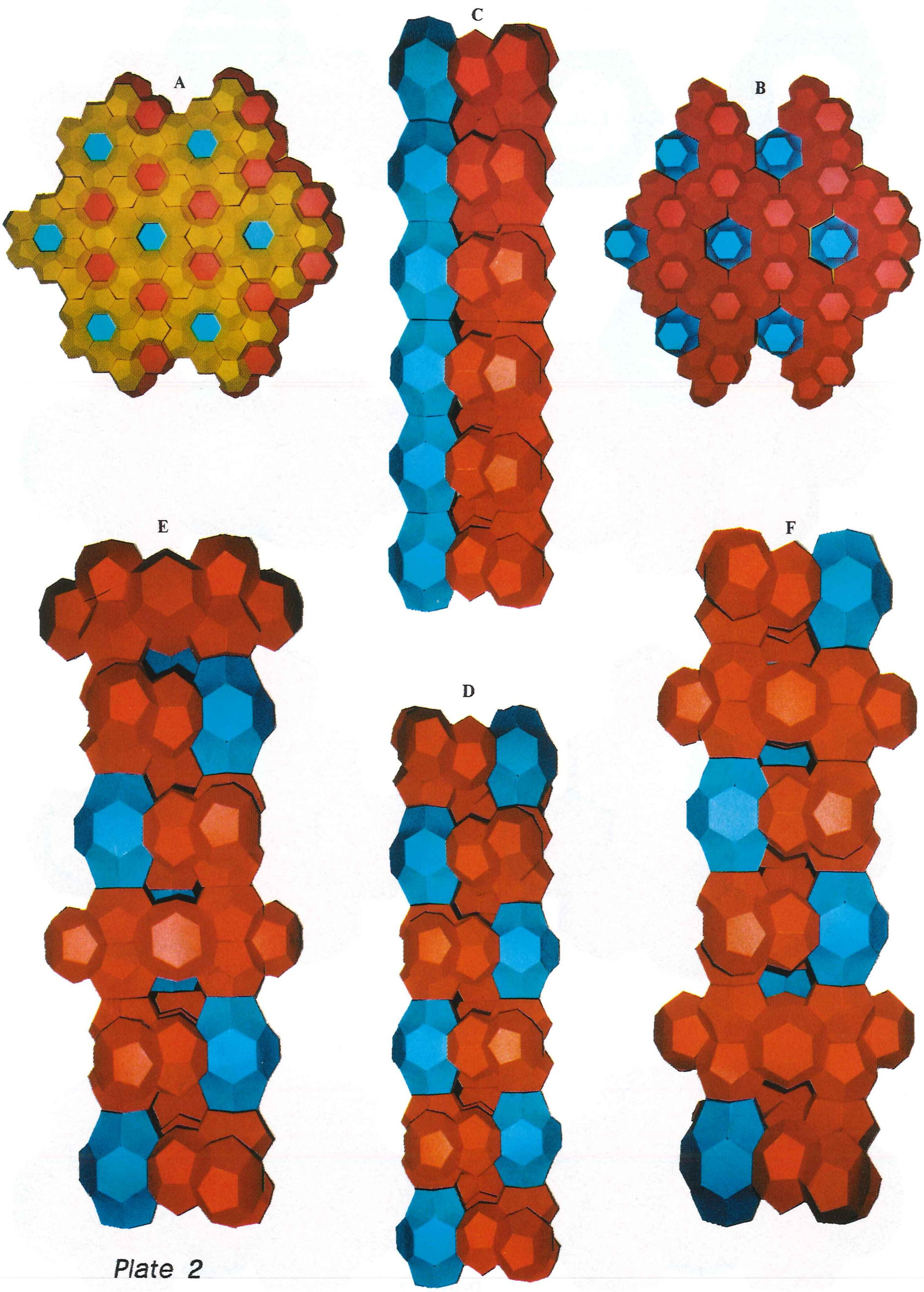

Plate 2

Honeycomb [6,5]{19 5 1}. Assembling of unit cells.

Plate 2D shows 6 unit cells, again without their 12-hedra, stacked as before, but with the cells rotated through 120°, *in opposite senses*, at each successive stage. This stacking again produces three columns of polyhedra: two consisting of pairs of alternating 20- and 14-hedra (as seen on the left and the right of Plate 2D), and one consisting of 14-hedra *(14v)* only (visible at the back through gaps in the cells left by the missing 12-hedra). New unit cells comprising *pairs* of the original ones are thus formed. Since these pairs of cells, too, 'fill' space, they may be used to construct another, or **second type** of [6 5]{19 5 1} honeycomb.

The polyhedra in contact with the 20- and the 14-hedra *(14v)* in these new columns of cells can again be represented by Schlegel-type diagrams. Two of the columns consist of pairs of alternating 20- and 14-hedra, as represented in Figs.3a and 3b; and the third column is made up of contiguous 14-hedra only, as represented in the previous figure (Fig.2b).

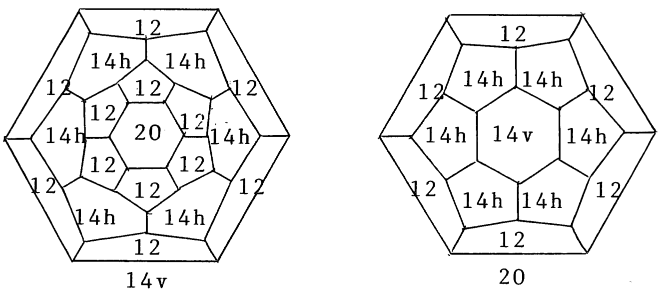

Fig.3 Polyhedra in contact with (a) 20-hedron and (b) 14-hedron *(14v)*, in [6 5]{19 5 1} honeycomb of 2nd type.

* * *

Finally, plates 2E and 2F show 6 of the unit cells of Plate 1G and 1K (without their 12-hedra) stacked with the cells rotated through 120° *in the same sense* at each successive stage, so as to form helical polyhedral arrangements, turning as a right-handed screw (Plate 2E) or a left-handed screw (Plate 2F). In either case a new unit cell, comprising in this case *three* of the original ones, is formed. As before, these trios of cells 'fill' space and so give rise to another, or **third type** of [6 5]{19 5 1} honeycomb; but unlike the first two types this one with its screw axis has a *laevo-* and a *dextro-*rotary isomeric form.

Here the arrangement of polyhedra is the same in each of the three columns, the 20-hedra being separated in each case by groups of four 14-hedra *(14v)* . The polyhedra in contact with two of these 14-hedra, the 'end' ones of the group, are as represented in Fig.3b, while those in contact with the other two, the 'middle' ones, are as represented in Fig.2b. The contiguous polyhedra of the 20-hedra are as in Fig.3a.

* * *

As to the 14-hedron *(14h)*, whose axis of symmetry is parallel to a *c*-axis of the unit cell (Plate 1C), the arrangement of its contiguous polyhedra, represented in Fig.4 by a Schlegel-type diagram, is the same in each of the three types of honeycomb.

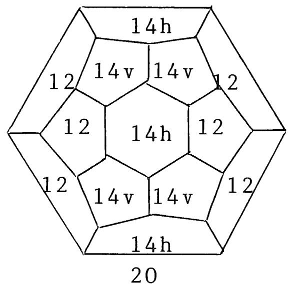

Fig.4 Polyhedra in contact with 14-hedra *(14h)*, in [6 5]{19 5 1} honeycombs of 1st, 2nd, & 3rd types.

It is tentatively suggested there may exist inclusion hydrates with the structure of the above honeycombs; and it seems that one or more of them may already have been identified (Ripmeester et al., 1987; Dyadin et al., 1991).

TOWARDS A MORE GENERAL THEORY

Since it may be objected that the theory at present applies only to inclusion hydrates, it is proposed in the next instalment to show how Eq.(6) can be extended to cover a wider range of compounds.

(to be continued)

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