

## Possible 4-connected frameworks with 4-4-1 unit found in heulandite, stilbite, brewsterite, and scapolite

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### Abstract

A systematic enumeration of all chains, sheets, and frameworks obtainable by the interconnection of the SBU (secondary building unit) formed by ten tetrahedra with four 5-rings and two 4-rings of tetrahedra is given. Six chains, 23 sheets, and 45 4-connected 3D nets were found. Out of these nets, four are represented by the heulandite, stilbite, brewsterite, and scapolite structure types.

### Introduction

Following Wells (1954, 1977) the topology of a 4-connected 3D net may be represented by its tetrahedral centers (nodes) and by the oxygen bridges (linkages). Smith (1977, 1978) enumerated all possible 4-connected 3-dimensional nets which may be obtained by cross-linking simple 3-connected 2-dimensional nets. This kind of description allows the classification of many natural and synthetic minerals with framework structures.

The subject of this paper is the enumeration and classification of all possible structures which may be obtained by connecting a structural unit (or cage) formed by four 5-rings and two 4-rings (Fig. 1) which is present in some common framework silicates (*i.e.* zeolites of the heulandite group and scapolites). Meier (1968) named this unit SBU 4-4-1. These SBU's are linked in chains which are laterally joined to form sheets, which in turn connect to form tri-dimensional frameworks.

### Features of the structural unit

The highest symmetry of the 4-4-1-1 cage is  $2/m2/m2/m$ , which will be used throughout the paper. Chemical substitutions or geometrical distortions could lower the symmetry.

The positions and codes of the mirror planes, diads, and inversion center are also shown in Figure 1 (the diad  $2'$  will also be called "cage axis"). There are three nodes (coded A, B and C) which are non-equivalent from the symmetrical point of view. The internodal distances in Figure 1 were calculated by

assuming that the distance between two adjacent nodes is  $3.0A$  (the common Si-Si distance in a framework silicate). Other distances, periods, and parameters follow therefrom.

Twelve oxygen bridges can bind this unit to other units, 2 for each A node and 1 for each B or C node. Because the high number of available linkages leads to many possible connections in a infinite number of theoretically possible structures, some limitations must be placed on the enumeration of the possible topologies. A restriction is that each pair of adjacent units must share at least one node. The number of frameworks obtainable from units with no common nodes is too large for convenient description, and to date, none have been found in existing phases.

Consider now the general rules under which two adjacent units may share a node, or two or more adjacent nodes (a branch).

Nodes of type B and C, having three linkages within the cage (Fig. 1), have only one free linkage, whereas node A has two linkages within the cage and two free. Hence, if two units share only one node, this node should be the junction of 6 linkages if of type B or C (it has three linkages in one unit and three in the other); it should be the junction of 5 linkages if the node is node A in the one unit and node B (or C) in the other; finally it should be the junction of 4 linkages if the shared node is node A in both units.

If the two cages share a branch (two linked nodes), then the number of linkages reaching the nodes which define the edge is reduced by one with respect to the number given in the preceding paragraph, because the linkage is part of both units. If a node is

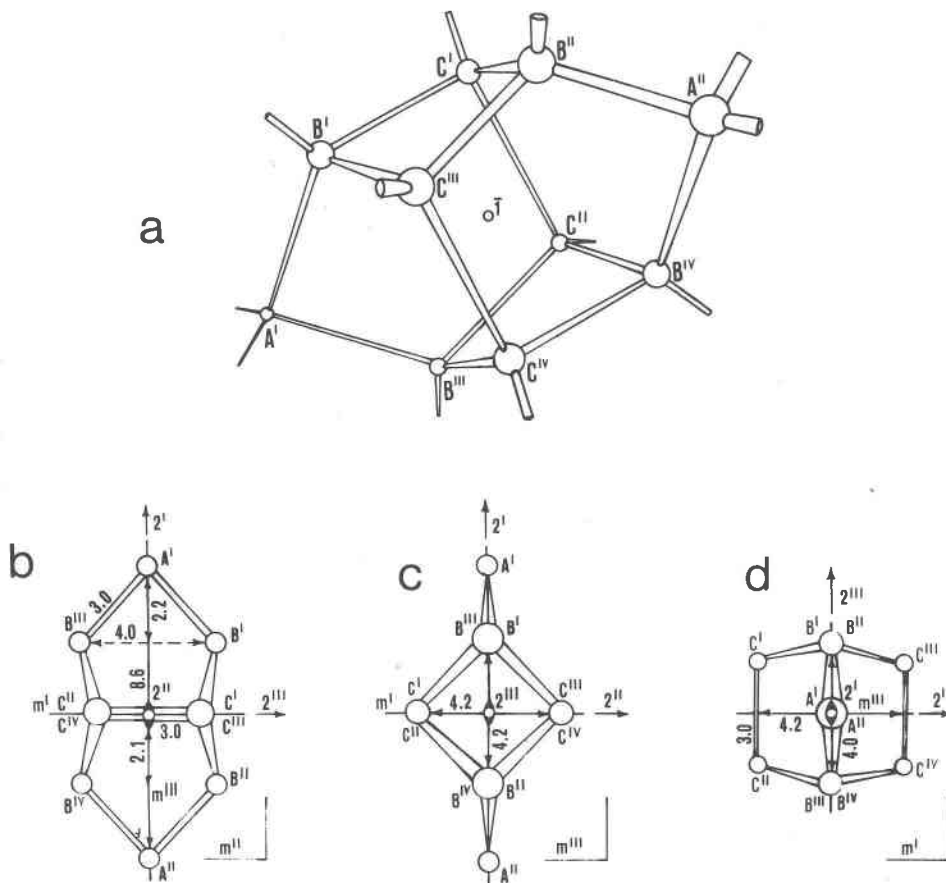


Fig. 1. The 4-4-1-1 structural unit with symmetry elements and approximate dimensions viewed from different directions.

part of two adjacent shared branches, the number of its linkages must be reduced by two. This second case also obviously applies to all shared nodes when two units share the four nodes of a square ring.

In what follows I assume that the linkages must yield a 4-connected net, not a 5-connected or 6-connected net. Therefore the balance of linkages for every node must be 4.

Table 1 summarizes the possible ways two units may be joined by sharing nodes or branches, on the basis of the above rules.

#### The possible chains

By restricting a "chain" to a 1-dimensional infinite set of units all connected in the same way (*i.e.* one of the ways listed in Table 1), possible chains with periodicity not larger than two units are listed and described crystallographically in Table 2 and represented in Figure 2. The length of the chain is always taken as the *a* axis.

Although chains have a 1-dimensional periodicity

and sheets a 2-dimensional periodicity, the symmetry of the chains in Table 2, as well as the symmetry of the sheets in Table 3, has been described by using the standard code for space-group symmetry. This code is useful when assembling chains into sheets (and sheets into frameworks), because new symmetry elements may appear between the chains (or the sheets), but never within each individual chain (or sheet). Therefore the symmetry elements in the isolated chain (or sheet) are always equal or greater in number than the symmetry elements in the chain (or sheet), when combined as part of a sheet (or of a framework).

*Chain of type e.* The units share only A nodes. As every unit has only two A nodes, only one type of chain is possible. The tetrahedral geometry enforces a 90° rotation of adjacent units.

*Chain of type f.* The units share a branch. As each unit may be connected by sharing either the A<sup>II</sup>B<sup>II</sup> or A<sup>II</sup>B<sup>IV</sup> edge, two kinds of chain are possible. Chain f<sub>1</sub>: each unit always shares the same branch

Table 1. Possible connections of two units by sharing nodes or branches

Set of nodes shared	Nodes in the 1st unit	Nodes in the 2nd unit	Balance of linkages	Relative orientation of the cages
1 node	A	A	2 + 2	The second rotated by 90° around 2'
1 branch	A	B	2 + 3 - 1	Isoorientated
	B	A	3 + 2 - 1	
2 branches	A	C	2 + 3 - 1	The second rotated by 90° around 2' and shifted laterally
	B	B	3 + 3 - 2	
	C	A	3 + 2 - 1	
4-ring	B	C	3 + 3 - 2	The second rotated by 90° around 2'''
	C	B	3 + 3 - 2	
	B	C	3 + 3 - 2	
	C	B	3 + 3 - 2	

(indifferently, either  $A''B^{IV}$  or  $A''B''$ ) with the adjacent unit.

Chain  $f_2$ : the units in the chain alternately share the  $A''B''$  and  $A''B^{IV}$  branches; the units have parallel orientation, and the chain features a zig-zag pattern.

Chain of type  $g$ . In view of the geometry of the cage, each unit may be connected in four different ways with the preceding one (shared nodes may be:  $A^I B^I C^I$ ,  $A^I B^I C^{III}$ ,  $A^I B^{III} C^{II}$ , or  $A^I B^{III} C^{IV}$ ) and with the subsequent unit ( $A'' B'' C^I$ ,  $A'' B'' C^{III}$ ,  $A'' B^{IV} C^{II}$ , and  $A'' B^{IV} C^{IV}$ ). This leads to 16 possible combinations, which are firstly reduced to 12 because the C node which is shared with preceding unit cannot be shared with the subsequent one. Furthermore, as the triplet  $A'' B^{IV} C^{II}$  is equivalent by rotation to the triplet  $A'' B'' C^{III}$ , and the triplet  $A'' B'' C^I$  to  $A'' B^{IV} C^{IV}$ , it is

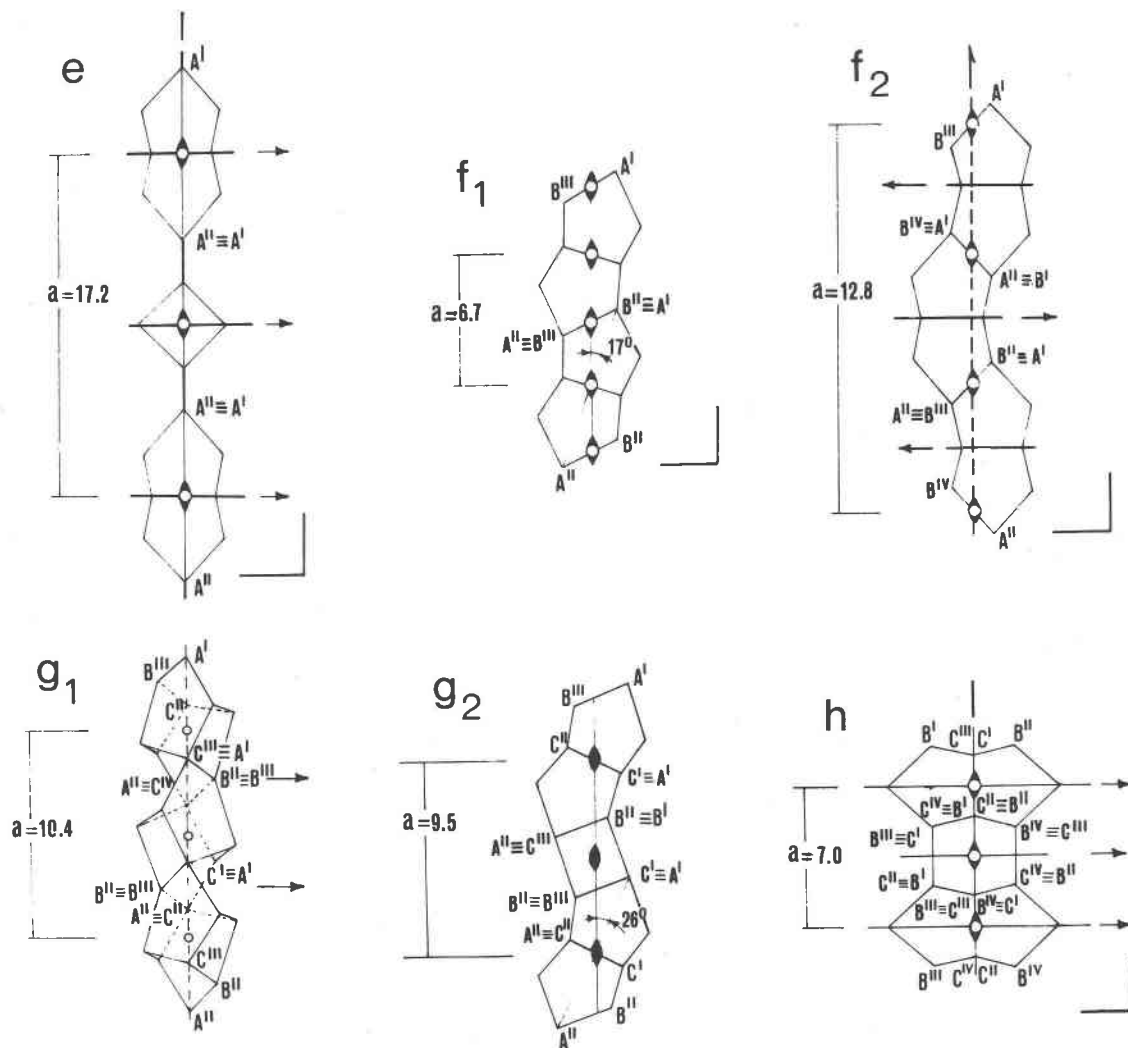


Fig. 2. Possible chains with a period repeated not more than every two units, and approximate parameters.

Table 2. Crystallographic properties of the chains with a period not more than two units

Set of nodes shared	Axis of the chain	no. of units in the period	Period (Å)	Symmetry of the chains	Origin	Free linkages		Code of the chain
						1st unit	2nd unit	
1 node	2 <sup>i</sup>	2	17.2	P 2/m 2/m 2/m	At the center of the unit	8 (4B+4C)	8 (4B+4C)	e
1 branch	Angle of 17° with 2 <sup>i</sup> , 73° with 2 <sup>iii</sup>	1	6.7	P 1 2/m 1	At the center of the unit	6 (2B+4C)		f <sub>1</sub>
1 branch	// 2 <sup>i</sup>	2	12.8	P 2 <sub>1</sub> /m 2/m 2/a	At the center of the shared edges	6 (2B+4C)	6 (2B+4C)	f <sub>2</sub>
2 branches	Angle of 34° with 2 <sup>i</sup> , 67° with 2 <sup>ii</sup> , 67° with 2 <sup>iii</sup>	2	10.4	P 1 1 2/a	At the center of the unit	4 (2B+2C)	4 (2B+2C)	g <sub>1</sub>
2 branches	Angle of 26° with 2 <sup>i</sup> , // m <sup>ii</sup> (or m <sup>iii</sup> )	2	9.5	P 1 2 1	At the center of the unit	4 (2B+2C) of the same 4-ring in alternate units	4 (2B+2C)	g <sub>2</sub>
4-ring	2 <sup>iii</sup>	2	7.0	P 4 <sub>2</sub> /m 2/m 2/c	At the center of the unit	4 (2A)	4 (2A)	h

sufficient to inspect only in detail the chains obtained by sharing nodes A<sup>ii</sup>B<sup>iv</sup>C<sup>ii</sup> and A<sup>ii</sup>B<sup>ii</sup>C<sup>i</sup>.

As shown before (Table 1), each unit is rotated by 90° around the cage-axis 2<sup>i</sup> with respect to the adjacent units. If one assumes that clockwise rotations are possible, then, given three nodes in one unit, the other three nodes are uniquely determined in the subsequent one. For instance, if the first unit shares nodes A<sup>ii</sup>B<sup>ii</sup>C<sup>i</sup>, they become A<sup>i</sup>B<sup>ii</sup>C<sup>ii</sup> in the second one.

Finally, in view of the rotational symmetry of the cage-axis 2<sup>i</sup> and of the 90° angle between two successive units, the periodicity along the chain must obviously be equal to an even number of cages (2, 4, . . .).

If we consider only the chains with a period of two units (the period is never higher than two units in all other chains), on the basis of the above stated rules the number of possible chains reduces to only two.

Chain g<sub>1</sub>: each unit shares nodes which are equivalent by inversion with the preceding and the succeeding units (for instance A<sup>i</sup>B<sup>i</sup>C<sup>iii</sup> and A<sup>ii</sup>B<sup>iv</sup>C<sup>ii</sup>).

Chain g<sub>2</sub>: each unit shares nodes which are equivalent by rotation around 2<sup>ii</sup> or 2<sup>iii</sup> with the preceding and succeeding units (for instance A<sup>i</sup>B<sup>i</sup>C<sup>iii</sup> and A<sup>ii</sup>B<sup>iv</sup>C<sup>iv</sup>, or A<sup>i</sup>B<sup>i</sup>C<sup>iii</sup> and A<sup>ii</sup>B<sup>ii</sup>C<sup>i</sup>).

There are two enantiomorphs of g<sub>2</sub> chains, whereas the other chains do not have enantiomorphic equivalents.

*Chain of type h.* The units share the four nodes of the 4-ring. Only one type of chain is possible, the axis of which coincides with axis 2<sup>iii</sup>; the units are alternately rotated by 90° around 2<sup>iii</sup>. From a topological

point of view, the sharing of the 4-ring by two iso-oriented units is possible, but impossible if the real dimensions of the unit are taken into consideration.

### Possible sheets

The possible 1-dimensional chains listed in Table 2 may be connected to form 2-dimensional sheets. The number of sheets formed by only one kind of chain, when juxtaposed according to one rule, is finite and small. The sheets have been classified on the basis of the building chains. Each sheet is characterized by the number of linkages per unit left free for connection with the other sheets. Each sheet is coded with a capital letter. This letter is the same for all sheets obtained by assembling the same type of chain, and with the same number of interlayer linkages. The capital letter coding the sheet is followed by a subscript which is a symbol for the symmetry element between the chains of the sheet.

The subscripts are:

*t* (translation). Each chain is equivalent to the adjacent one by translation. Remembering that the *a* parameter coincides with the period of the chain, let *c* be the second parameter in the sheet where  $c = t$ .

*m* (mirror). Each chain is equivalent to the adjacent one by reflection across a mirror plane; in this case the *c* period is twice the distance between two adjacent chains, as in the following two cases (*r* and *i*).

*r* (rotation). Each chain is equivalent to the adjacent one by 180° rotation around an axis outside the chain normal to *a* and *c*, which will be called [010] being [010] || *b*\* for all the sheets *r*.

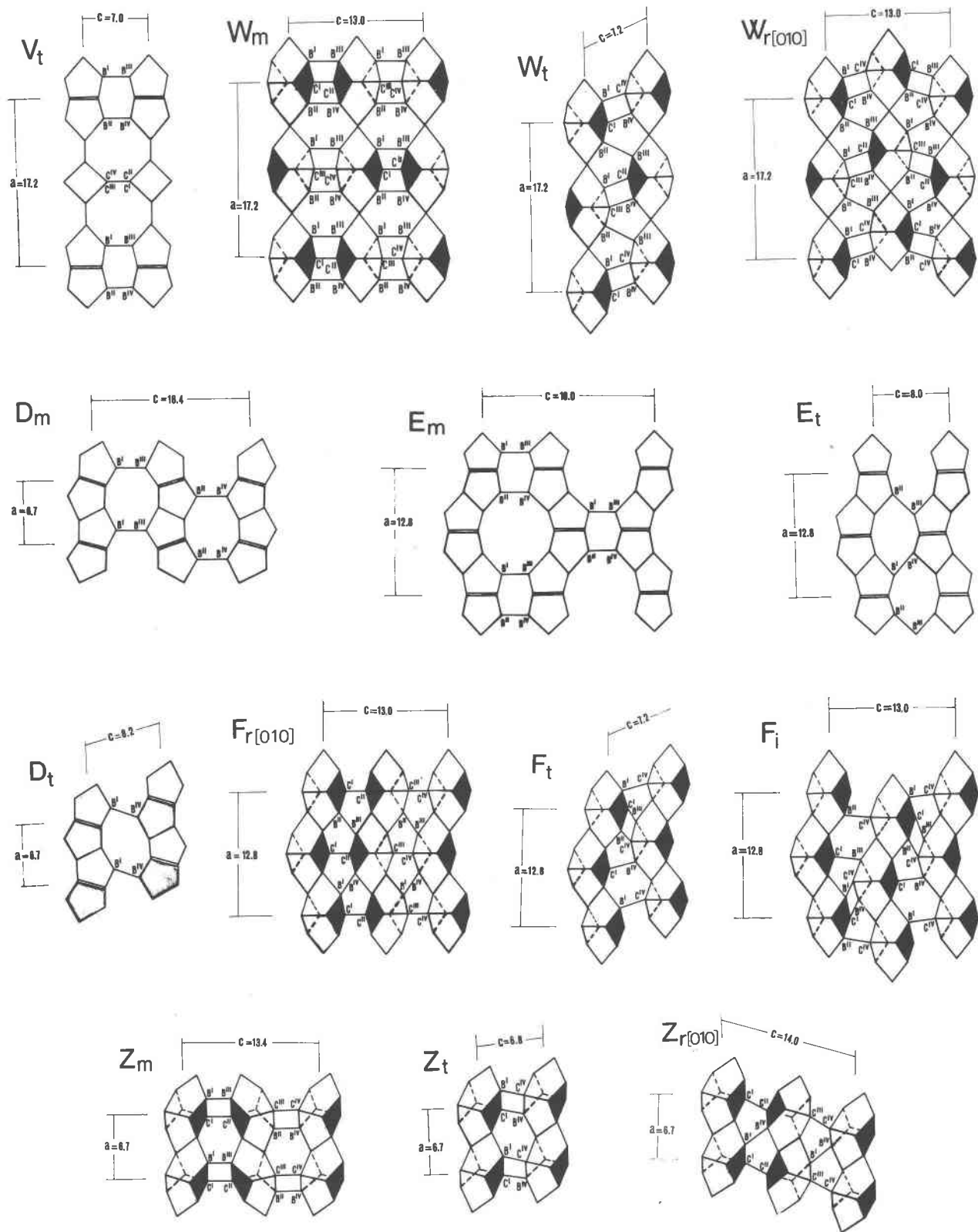


Fig. 3. Possible sheets with a period repeated not more than every two chains, and approximate parameters.

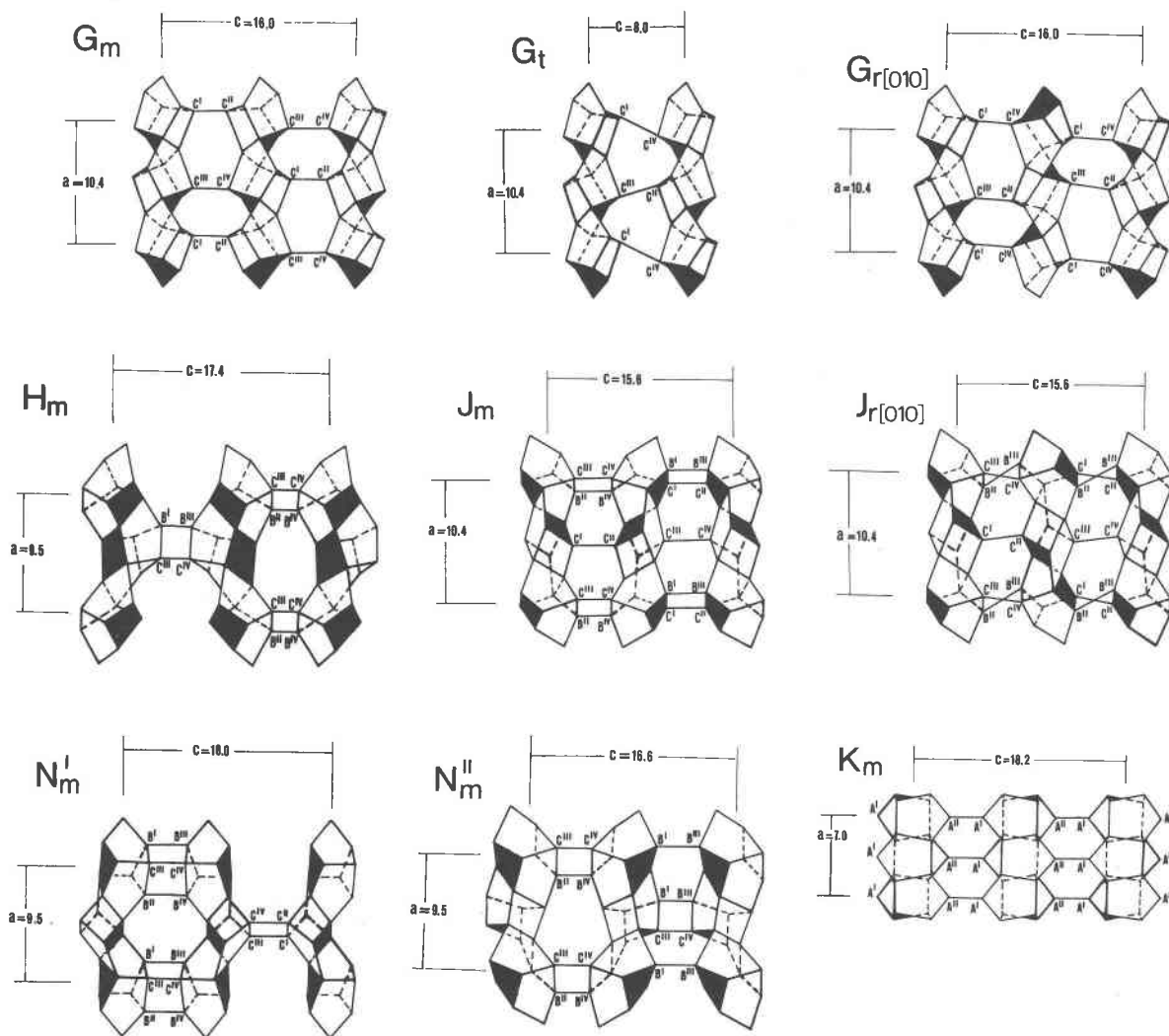


Fig. 3. (continued)

$i$  (inversion). Each chain is equivalent to the adjacent one by inversion across a center between (not inside) the chains.

If more than one of the listed symmetry elements are present between the chains of a sheet, the symbol will be chosen following a hierarchy of  $t \rightarrow m \rightarrow r \rightarrow i$ .

The resulting sheets (Table 3, Fig. 3) are now briefly described:

**Sheets with connected  $e$  chains.** Such sheets have either four interlayer linkages (V sheets) or two interlayer linkages (W sheets). For W sheets, the chains are distorted by alternately rotating the units clockwise and counterclockwise by  $15^\circ$  around the  $2^I$  axis, thereby reducing the symmetry of the chain to  $P2/m2/a2/a$ .

**Sheets with connected  $f_1$  and  $f_2$  chains.** For both chains, sheets are possible either with four interlayer

linkages (D sheets and E sheets respectively) or with only two interlayer linkages (Z sheets and F sheets). In the second case, the chain, whether  $f_1$  or  $f_2$ , is compelled to rotate by about  $30^\circ$  around its axis. Therefore the mirror plane (010) disappears, and the symmetry of chains  $f_1$  and  $f_2$  falls respectively to  $P\bar{1}$  and  $P2_1/m$  in these sheets.

**Sheets with connected  $g_1$  and  $g_2$  chains.** Two different types of sheets are possible for both chains. G and H sheets are obtained with two interlayer linkages respectively. Sheet J is obtained with one interlayer linkage and chain  $g_1$ . Sheet N is made of  $g_2$  chains, and each alternate unit has 1 or 2 interlayer linkages. The rotation of chain  $g_1$  around its axis in sheet type J implies the loss of the diad parallel to  $c$  and the lowering of the symmetry of the chain in the sheet to  $P\bar{1}$ . The rotation of chains  $g_2$  in both H and

Table 3. Crystallographic data on the sheets obtained by assembling the chains of Table 2

Code of the chain	no. of interlayer linkages per unit	Parameters of the sheet a(Å) c(Å)		$\beta$ (°)	Symmetry of the sheet	Origin	Code of the sheet
e	2	17.2	7.0		P 2/m 2/m 2/m	At the center of the unit	V <sub>t</sub>
e	1	17.2	7.2	115	P 1 2/a 1	At the center of the unit	W <sub>t</sub>
e	1	17.2	13.0		B 2/m 2/a 2 <sub>1</sub> /m	At the center of the unit	W <sub>m</sub>
e	1	17.2	13.0		P 2/c 2/a 2 <sub>1</sub> /a	At the center of the 4-ring between units of different chains	W <sub>r</sub> [010]
f <sub>1</sub>	2	6.7	8.2	105	P 1 2/m 1	At the center of the unit	D <sub>t</sub>
f <sub>1</sub>	2	6.7	16.4		P 2/c 2/m 2 <sub>1</sub> /m	At the center of the unit	D <sub>m</sub>
f <sub>1</sub>	1	6.7	6.8	95	P 1	At the center of the unit	Z <sub>t</sub>
f <sub>1</sub>	1	6.7	13.4	$\gamma \neq 90$	P 1 1 2 <sub>1</sub> /m	At the center of the unit	Z <sub>m</sub>
f <sub>1</sub>	1	6.7	14.0	75	P 1 2/c 1	At the center of the unit	Z <sub>r</sub> [010]
f <sub>2</sub>	2	12.8	8.0		P 2 <sub>1</sub> /m 2/m 2/a	At the center of the shared edges between units of the same chain	E <sub>t</sub>
f <sub>2</sub>	2	12.8	18.0		B 2/m 2/m 2/m	At the center of the 4-ring between units of different chains	E <sub>m</sub>
f <sub>2</sub>	1	12.8	7.2	115	P 1	At the center of the shared edges between units of the same chain	F <sub>t</sub>
f <sub>2</sub>	1	12.8	13.0		P 2 <sub>1</sub> /m 2/c 2 <sub>1</sub> /a	At the center of the shared edges between units of the same chain	F <sub>r</sub> [010]
f <sub>2</sub>	1	12.8	13.0	$\alpha \neq 90$	P 2 <sub>1</sub> /c 1 1	At the center of the 4-ring between units of different chains	F <sub>i</sub>
g <sub>1</sub>	1	10.4	8.0	$\gamma \neq 90$	P 1 1 2/a	At the center of the unit	G <sub>t</sub>
g <sub>1</sub>	1	10.4	16.0	$\gamma \neq 90$	B 1 1 2/m	At the center of the unit	G <sub>m</sub>
g <sub>1</sub>	1	10.4	16.0		P 2/c 2/n 2/a	At the center of the unit	G <sub>r</sub> [010]
g <sub>1</sub>	1/2	10.4	15.6	$\gamma \neq 90$	P 1 1 2 <sub>1</sub> /m	At the center of the unit	J <sub>m</sub>
g <sub>1</sub>	1/2	10.4	15.6	90	P 1 2/c 1	At the center of the linkages between different chains	J <sub>r</sub> [010]
g <sub>2</sub>	1	9.5	17.4	$\gamma \neq 90$	P 1 1 m	At the center of the 4-ring between units of different chains	H <sub>m</sub>
g <sub>2</sub>	3/4	9.5	18.0	$\gamma \neq 90$	P 1 1 m	At the center of the 4-ring between units of different chains	N <sup>'</sup> <sub>m</sub>
g <sub>2</sub>	3/4	9.5	16.6	$\gamma \neq 90$	P 1 1 m	At the center of the 4-ring between units of different chains	N <sup>''</sup> <sub>m</sub>
h	1	7.0	18.2		P 2/m 2/a 2 <sub>1</sub> /m	At the center of the unit	K <sub>m</sub>

N sheets implies the loss of the only diad of the chain. There are two kinds of N sheets, both with mirror planes between the chains, but with a different type of linkage. All the sheets with connected  $g_2$  chains ( $H_m$ ,  $N_m^l$ ,  $N_m^r$ ) consist of the regular alternation of a  $g_2$  chain and its enantiomorph. It is not possible to cross-link  $g_2$  chains by rotation or translation.

*Sheets with connected h chains.* Only one kind of sheet (K) with two interlayer linkages is formed. The h chains in the layer are alternately rotated  $45^\circ$  in the two directions. Destruction of the mirror planes parallel to  $a$  results in  $P2/m11$  symmetry of the h chain in the K sheet. A mirror plane, normal to  $c$ , between the chains restores the symmetry of the whole sheet to  $P2/m2/a_2/m$ .

### Possible frameworks

The above-described sheets are connected by the interlayer linkages to build 3-dimensional tetrahedral frameworks.

The following symbolism has been devised in order to compress information: each framework is coded by the sheet code preceded by a capital letter corresponding to the symmetry operation relating two superposed sheets: T: if the sheet is superposed by translation; M: if the sheet is superposed by reflection; R: if the sheet is superposed by rotation of  $180^\circ$ ; G: if the sheet is superposed by a glide-reflection.

The symbol is followed by the symbol of the edge corresponding to the translation (T-nets or G-nets) or to the rotation axis (R-nets) or it is followed by the symbol of the plane (010) which defines the reflection, with the assumption that these symbols refer to a cell whose parameters are  $a$ , parallel to the axis of the chain;  $c$ , the other parameter in the sheet as previously defined;  $b$ , normal to the plane of the sheet and equal in length to the interlayer distance. These parameters however are not generally the parameters of the structure described with this symbolism.

If there is more than one symmetry element between sheets, the symbol of the structure will obey the hierarchy  $T \rightarrow M \rightarrow R \rightarrow G$ . These frameworks are described in an abbreviated form and their crystallographic features are listed in Table 4. As nets containing chains of type  $g$  have not been found to date in natural or synthetic materials, they are not described here, in order to avoid excessive enumeration. Finally the description is limited to frameworks in which only two layers repeat. This choice is consistent with that of the maximum number of units in a chain and that of the maximum number of chains in a layer. Moreover, nets with a repeat after more than

two layers have not been found to date in natural and synthetic materials.

### Frameworks with V sheets

In the only possible structure of this kind, the (010) and (001) planes are topologically equivalent, so that the framework is metrically tetragonal, but with orthorhombic symmetry.

### Frameworks with W sheets

These are the frameworks of some of the most common zeolites, like heulandite and clinoptilolite with the framework  $M_{(010)}W_v$ , and stellerite, stilbite, and barrerite with the framework  $M_{(010)}W_m$ .

In the framework  $R_{[102]}W_v$ , each sheet can be superimposed on the preceding sheet by rotation around [102]; this fact implies a problem of nomenclature. So far,  $a$  has been considered a code for the axis of the chain and also an axis for the sheet and/or for the framework. This is not possible when considering a framework like  $R_{[102]}W_v$ , in which not all chains are parallel; in this case the directions of the  $a$  and  $c$  axes in one sheet are reversed in the subsequent sheet, and this results in  $a \approx 2c \approx 15.8A$ ,  $\beta$  being nearly  $115^\circ$ . In this diamond-shaped supercell, the [101] and  $[10\bar{1}]$  diagonals are diads and are the most appropriate orthorhombic cell edges, as given in Table 4.

In the framework  $R_{[102]}W_r$ , where each sheet can be superimposed on the preceding sheet by rotation around [102], the axis of the chain in a sheet coincides with the direction  $a-2c$  of the preceding (or succeeding) one. This results in a supercell with dimensions  $2a$  and  $a-2c$ ; the [101] and  $[10\bar{1}]$  diagonals of this supercell, which are equivalent to the [102] and  $[30\bar{2}]$  edges of the sheet, are diads, and they are chosen as crystallographic axes for the whole framework in Table 4. It is worth noting that the alternating orientation of the units in the chains seems to imply two different frameworks both for  $R_{[102]}W_v$  and  $R_{[102]}W_r$ . As a matter of fact in both cases the two structures are topologically equal, and they differ only in the choice of the origin.

### Frameworks with D sheets

The connections of the D sheets forming T-type structures do not occur only in the obvious [010] direction but also in the [121] and [021] directions for the  $TD_l$  structures, and in the [041] direction for the  $TD_m$  structures. In the structure  $T_{[101]}D_v$ , the unconventional space group  $I2/m$  has been introduced to make the parameters of the sheet coincide with the parameters of the whole framework.



Table 4. Crystallographic data of the structures obtained by assembling the sheets of Table 3

Code of the structure	no. of sheets in the period	Parameters of the structure						Space group	Origin
		a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$		
$T_{[010]}^V t$	1	17.2	7.0	7.0				P 2/m 2/m 2/m	At the center of the unit
$T_{[010]}^W t$	1	17.2	8.1	7.2		115		P 1 2/a 1	At the center of the unit
$aM_{(010)}^W t$	2	17.2	16.2	7.2		115		C 1 2/m 1	At the center of the unit
$R_{[102]}^W t$	2	17.0	16.2	26.6	a and c are parallel to the [102] and [10 $\bar{2}$ ] edges of the sheet			B 2/b 2/a 2/b	At the center of the unit on the center of symmetry
$bM_{(010)}^W m$	2	17.2	16.2	13.0				F 2/m 2/m 2/m	At the center of the 8-ring between sheets
$T_{[010]}^W r$	1	17.2	8.1	13.0				P 2/c 2/a 2 $_1/a$	At the center of the 4-ring between units of different chains
$M_{(010)}^W r$	2	17.2	16.2	13.0				C 2/c 2/m 2 $_1/a$	At the intersection of the mirror plane between the sheets and the [010] axis through the single linkage between chains
$R_{[102]}^W r$	2	32.8	16.2	56.8	a and c are parallel to the [102] and [30 $\bar{2}$ ] edges of the sheet			B 2/b 2/a 2/b	On the center of symmetry at the center of the 4-ring between units of different chains
$T_{[010]}^D t$	1	6.7	7.0	8.2		105		P 1 2/m 1	At the center of the unit
$T_{[121]}^D t$	2	6.7	12.6	8.2		105		I 1 2/m 1	At the center of the unit
$T_{[021]}^D t$	2	6.7	12.6	8.2	the $\beta$ angle of the sheet is rather distorted			A 1 2/m 1	At the center of the unit
$T_{[010]}^D m$	1	6.7	7.0	16.4				P 2/c 2/m 2 $_1/m$	At the center of the unit
$T_{[041]}^D m$	1	6.7	8.1	16.4		120		P 2/c 1 1	At the center of the unit
$R_{[100]}^D m$	2	6.7	14.0	16.4				P 2/c 2 $_1/m$ 2 $_1/b$	At the center of the interlayer linkage between isooriented units
$T_{[010]}^Z t$	1	6.7	8.1	6.8	95	95	90	P $\bar{1}$	At the center of the unit
$cM_{(010)}^Z t$	2	6.7	16.2	6.8		95		P 1 2 $_1/m$ 1	At the center of the unit
$R_{[100]}^Z t$	2	6.7	16.2	6.8		90		P 2/b 1 1	At the center of the unit
$R_{[001]}^Z t$	2	6.7	16.2	6.8			95	P 1 1 2/b	At the center of the unit
$R_{[101]}^Z t$	2	9.1	16.2	10.0		95		B 2/b 1 1	At the center of the unit
$R_{[10\bar{1}]}^Z t$	2	9.1	16.2	10.0	a and c are parallel to the [101] and [10 $\bar{1}$ ] edges of the sheet			B 1 1 2/b	At the center of the unit
$R_{[010]}^Z t$	2	6.8	16.2	6.8	95	95	90	P $\bar{1}$	At the center of the unit rotation around [010] axis $\sim 90^{\circ}$
$T_{[010]}^Z m$	1	6.7	8.1	13.4			100	P 1 1 2 $_1/m$	At the center of the unit
$M_{(010)}^Z m$	2	6.7	16.2	13.4				P 2/n 2 $_1/m$ 2 $_1/m$	At the center of the unit on the center of symmetry
$R_{[100]}^Z m$	2	6.7	16.2	13.4				P 2/b 2 $_1/c$ 2 $_1/m$	At the center of the unit
$R_{[001]}^Z m$	2	6.7	16.2	13.4			100	A 1 1 2/m	Between sheets at the center of the 8-ring

Table 4. (continued)

$R_{[201]}^Z m$	2	18.9	16.2	18.9	90		B 2/b 1 1	At the center of the unit	
		a and c are parallel to the [201] and [20 $\bar{1}$ ] edges of the sheet							
$R_{[20\bar{1}]}^Z m$	2	18.9	16.2	18.9	90		B 1 1 2/b	At the center of the unit	
		a and c are parallel to the [201] and [20 $\bar{1}$ ] edges of the sheet							
$T_{[010]}^Z r$	1	6.7	8.1	14.0	75		P 1 2/c 1	At the center of the unit	
$M_{(010)}^Z r$	2	6.7	16.2	14.0	75		A 1 2/m 1	At the center of the unit	
$R_{[201]}^Z r$	2	16.7	16.2	21.7			B 2/b 2/a 2/b	At the center of the unit on the center of symmetry	
		a and c are parallel to the [201] and [20 $\bar{1}$ ] edges of the sheet							
$T_{[010]}^E t$	1	12.8	7.0	8.0			P 2 $_1$ /m 2/m 2/a	At the center of the shared edges between units of the same chain	
$T_{[021]}^E t$	2	12.8	12.6	8.0			A 2 $_1$ /m 2/m 2/a	At the center of the shared edges between units of the same chain	
$R_{[100]}^E t$	2	12.8	14.0	8.0			P 2/m 2 $_1$ /m 2/b	At the center of the 4-ring between sheets	
$T_{[010]}^E m$	1	12.8	7.0	18.0			B 2/m 2/m 2/m	In the sheet at the center of the 4-ring between units of different chains	
$T_{[010]}^F t$	1	12.8	8.1	7.2	90	115	90	P $\bar{1}$	At the center of the shared edges between units of the same chain
$M_{(010)}^F t$	2	12.8	16.2	7.2	115		P 1 2 $_1$ /m 1	At the center of the shared edges between units of the same chain	
$G_{[100]}^F t$	2	12.8	16.2	7.2	115		P 1 2 $_1$ /a 1	At the center of the shared edges between units of the same chain	
$R_{[102]}^F t$	2	15.6	16.2	22.9	90		B 2/b 1 1	In the sheet at the center of the 4-ring between units of different chains	
		a and c are parallel to the [102] and [10 $\bar{2}$ ] edges of the sheet							
$R_{[10\bar{2}]}^F t$	2	15.6	16.2	22.9	90		B 1 1 2/b	In the sheet at the center of the 4-ring between units of different chains	
		a and c are parallel to the [102] and [10 $\bar{2}$ ] edges of the sheet							
$T_{[010]}^F r$	1	12.8	8.1	13.0			P 2 $_1$ /m 2/c 2 $_1$ /a	At the center of the shared edges between units of the same chain	
$M_{(010)}^F r$	2	12.8	16.2	13.0			A 2 $_1$ /m 2/m 2/a	At the intersection of the mirror plane between the sheets and the [010] axis through the B-B linkage between chains	
$T_{[010]}^F i$	1	12.8	8.1	13.0	90		P 2 $_1$ /c 1 1	At the center of the 4-ring between units of different chains	
$M_{(010)}^F i$	2	12.8	16.2	13.0			P 2 $_1$ /c 2 $_1$ /m 2 $_1$ /n	At the center of the 4-ring between units of different chains	
$R_{[100]}^F i$	2	12.8	16.2	13.0	90		C 2/c 1 1	On the glide plane between sheets at the center of the 8-ring	
$^d M_{(010)}^K m$	2	7.0	18.2	18.2			I 4/m 2/m 2/m	At the center of the 4-ring between sheets	

<sup>a</sup>Heulandite (space group C 2/m) and clinoptilolite (C 2/m) crystallize with this topology

<sup>b</sup>Stellerite (F m m m), barrerite (A m m a) and stilbite (F 2/m) crystallize with this topology

<sup>c</sup>Brewsterite (P 2 $_1$ /m) crystallizes with this topology

<sup>d</sup>Scapolites (P 4 $_2$ /n) crystallize with this topology

### Frameworks with Z sheets

The particular value of the ratio  $a/c$  in sheets  $Z$  ( $\approx 1$  in  $Z_t$ ,  $\approx 0.5$  in  $Z_m$  and  $Z_r$ ) and the low symmetry of these sheets permit the existence of many nets of type R. Therefore nets  $R_{1100}Z_t$  and  $R_{1001}Z_t$  and also  $R_{1101}Z_t$  and  $R_{110\bar{1}}Z_t$  are possible with sheet  $Z_t$ , the latter two both having symmetry  $B2/b$ , the unique axis being  $a$  in the first and  $c$  in the second ( $a$  and  $c$  of the framework, which are parallel to  $[101]$  and  $[10\bar{1}]$  in the sheets). The difference between the last two nets is the different angle between the units of adjacent sheets.

The net  $R_{1010}Z_t$  is somewhat anomalous, because each sheet is obtained by translation  $b$  (as described at the beginning of the present section) along  $[010]$  and by a rotation of  $90^\circ$  around  $[010]$ , clockwise and counterclockwise alternately in respect to the preceding sheet; this does not correspond to any conventional crystallographic symmetry operation (or it is the first step of a 4 screw-tetrad, performed alternately in the two directions).

In the case of  $Z_m$  sheet both  $R_{1201}Z_m$  and  $R_{120\bar{1}}Z_m$  are possible; the new parameters of the framework are the diagonals of a diamond-shaped supercell, the edges of which are  $\approx 2a \approx c$  ( $a$  and  $c$  of the sheet). Both frameworks are monoclinic  $B2/m$ , the unique axis being  $a$  (framework) in the first and  $c$  (framework) in the second.

In the case of  $Z_r$  the only possible framework is  $R_{1201}Z_r$ , because  $R_{120\bar{1}}Z_r$  is equivalent. The parameters in the framework have a relation with the parameters of the sheets identical to the one found in  $R_{1201}Z_m$ .

Brewsterite has a framework of this group, namely  $M_{1101}Z_t$ , with symmetry  $P1\ 2_1/m1$ .

### Frameworks with E sheets

The presence of a mirror plane in the sheet excludes the existence of type M frameworks. The fact that all axes of the sheets are diads excludes the existence of type R frameworks: there is one exception, due to the fact that the  $a$  axis is not a diad in sheet  $E_t$ , so that the only possible R-framework is  $R_{1100}E_t$ .

### Frameworks with F sheets

As mentioned in the preceding cases, the parameters  $a$  and  $c$  of the framework  $R_{1102}F_t$  and  $R_{110\bar{2}}F_t$  are given by the diagonals of a diamond-shaped supercell, the edges of which are  $\approx a \approx 2c$  ( $a$  and  $c$  of the sheet). The framework  $G_{1100}F_t$  is the only one generated by a glide plane in Table 4. RF<sub>t</sub>-type structures are not possible because the strong rigidity of the sheet prevents any distortion.

### Frameworks with K sheets

The high symmetry of sheet  $K_m$  allows the building of only one framework,  $M_{(010)}K_m$ , which is tetragonal with the tetrad parallel to the axis of the chains.

Scapolites have this framework.

### Conclusions

The systematic enumeration of all frameworks (45) which may be obtained by the interconnection of the secondary building unit made of ten tetrahedra, with four 5-rings and two 4-rings, is quite long and complex; only a few of these frameworks (4) really exist, and these are not necessarily the simplest.

When Smith and Rinaldi (1962) enumerated all possible ways (17) to connect the double crankshafts only two (paracelsian and phillipsite) corresponded to existing phases, but at a later date others were found (gismondine, merlinoite). In my opinion, more structures of the kind dealt with in this paper will probably be found. Moreover, it is worth noting that the same framework may be present in more minerals, with different symmetries, due to a different deformation of the framework caused by the extra-framework cations: a typical example is stellerite ( $Fmmm$ ), barrerite ( $Amma$ ), stilbite ( $C2/m$ ), all of which have the same framework,  $M_{(010)}W_m$ .

### Acknowledgments

I thank Glauco Gottardi for useful suggestions and critical reading of the manuscript and William Lugli for the drawings. This work was supported by the Consiglio Nazionale delle Ricerche, Roma.

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