

Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. I. Perpendicular linkage from simple hexagonal net

JOSEPH V. SMITH

Department of the Geophysical Sciences
University of Chicago, Chicago, Illinois 60637

Abstract

Systematic enumeration of 4-connected 3D nets permits classification of and discovery of new structure types relevant to framework silicates and other materials. Addition of a perpendicular branch to each node of a simple 2D hexagonal net yields an important subset. There are 8 possible sequences of branches around a hexagon: *CCCCCC*, *SCCSCC*, *SCSCCC*, *SSCCCC*, *SSCSCC*, *SSSCSC*, *SSSSCC*, and *SSSSSS*, where *S* and *C* specify whether adjacent branches have the same or changed directions. When all hexagons have the same sequence, the 2D nets can be linked into the following 3D nets: *CCCCCC* (tridymite, cristobalite, and polytypes), *SCCSCC* (monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$), *SCSCCC* (monoclinic CaGa_2O_4), *SSCCCC* (two unknown types with polytypism), *SSCSCC* [Li-A(BW) zeolite], *SSSCSC* (paracelsian), and *SSSSCC* (two unknown types with polytypism). Sequence *SSSSSS* (hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$) gives double sheets only. Of the many theoretical frameworks containing more than one sequence, one with *SCSCSC* rings separated by *SCSCCC* rings occurs in beryllonite and trimerite.

Introduction

In a long series of papers and several books, A. F. Wells has explored many topological and geometrical aspects of structural inorganic chemistry (e.g. Wells, 1975). The second paper (Wells, 1954) outlined derivation of three-dimensional 4-connected nets, and considered nets with a small unit-cell.

Many important silicates, such as molecular-sieve zeolites, contain $(\text{Si,Al})\text{O}_4$ tetrahedra whose shared oxygens lead to a framework structure. Each framework can be described topologically by its tetrahedral nodes whose linkages form a 4-connected 3D net. Other materials, including diamond, have atoms lying on the nodes of this kind of net. Although an infinity of topologies exists, it is important to enumerate those in which simple rules relate subunits. This leads to rational classification, and allows prediction of new structure types, some of which might be matched by cell dimensions and space-group symmetry against materials of known composition. For example, attachment of a double-crankshaft chain to a 2D net composed of alternating 4- and 8-rings, as initially demonstrated in Wells (1954, Fig. 14), yielded by simple enumeration 17 flexible and 13

inflexible structures (Smith and Rinaldi, 1962; Smith, 1968). Three of these were already represented by feldspar, harmotome, and paracelsian, and three others turned out to be the then unknown structures of banalsite and of the zeolites gismondine and merlinoite (see Part II). Predicted structures with no natural or synthetic counterpart present a target for synthesis, especially if the predicted geometry appears to promise novel properties, for example in molecular sieving.

Wells (1954) concentrated on nets with high symmetry and with small Z_t , where Z_t is the number of nodes in the smallest possible unit cell. ("Smallest possible" means that the geometry of the framework is adjusted to give the highest possible symmetry, and the smallest repeating parallelepiped is chosen for the unit cell even if it has lower symmetry than the conventional unit cell.) Odd-numbered Z_t is impossible, and Wells (1954, Fig. 2) ended up with the diamond net ($Z_t = 2$), the wurtzite net ($Z_t = 4$), and two more nets with $Z_t = 4$, then not represented by known materials, but now recognized here as the topology of monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Takéuchi *et al.*, 1973) and Li-AB(W) zeolite (Kerr, 1974). All four frameworks

are based on up-down linkage of the simple hexagonal net. Wells (1954, Fig. 15) also described some 3D nets based on other 2D nets, including those found in feldspar and paracelsian.

The pioneering study of Wells is here extended to systematic enumeration of 4-connected 3D nets according to selected building schemes, followed by classification of known structures of framework silicates. This first paper considers addition of a perpendicular linkage to nodes of a simple hexagonal net, as suggested in several earlier papers (e.g. Dollase, 1968).

Enumeration of 3D networks from a 6³ net

The simple hexagonal net has only one type of 3-connected node, and because each node lies between three circuits of 6 nodes, this net is described by the Schläfli symbol 6³.

For any node in a simple hexagonal net in horizontal position, an additional perpendicular linkage can point either upward or downward. This linkage is then joined to a node of another simple hexagonal net lying either above or below the first hexagonal net. Two adjacent nodes of a horizontal hexagon can have the additional linkages pointing in either the same (*S*) or changed direction (*C*). The 8 ways in which the sequence of *C* and *S* can occur are enumerated as follows: *CCCCCC*, *SCCSCC*, *SCSCCC*, *SSCCCC*, *SSCSSC*, *SSSCSC*, *SSSSCC*, *SSSSSS*. The numbers of each symbol must be even, and either 0, 2, 4, or 6, in order to close the circuit. There is only one choice for 0 and 6, while there are three each for 2 and 4, differentiated by the run length of the symbols.

An infinity of frameworks can be produced if more than one sequence occurs in the hexagons of a 6³ net. Restriction to only one kind of sequence yields the 3D nets whose projections are shown in Figures 1 and 2.

Sequence *CCCCCC* allows only one type of horizontal 3-connected 2D net, but an infinity of 3D nets is possible, because there are two choices for relative position of adjacent horizontal nets, as depicted by the continuous and dashed lines. When all branches project downwards onto the continuous lines, the topology of the nodes of the mineral wurtzite is produced (actually Zn and S atoms occupy alternate nodes), and when horizontal branches are rotated 180° about the connecting vertical branch, the topology of diamond is produced. The silicate tridymite has Si atoms at the nodes of the wurtzite structure type and O atoms near the midpoints of the branches. Similarly cristobalite is related to diamond. Whereas

the wurtzite structure type has hexagonal symmetry in its most symmetrical configuration, the diamond type has isometric symmetry with *CCCCCC* 2D nets lying in all four {111} planes. An infinity of more complex arrangements (polytypes) can occur (e.g. Verma and Krishna, 1966).

Sequence *SCCSCC* yields only one net, because there is only one way of arranging it in three adjoining hexagons, and because adjacent 2D nets can fit in only one position. The *SCCSCC* net also occurs in a second plane of the 3D net; the second one cannot be seen easily in Figure 1, but is revealed immediately by looking east-west in a 3D model. Furthermore upon looking north-south, the nodes are seen to fall on a 4.8² 2D net to be described in a later paper. The *SCCSCC* sequence is found in the synthetic material originally called orthorhombic CaAl₂Si₂O₈, but now denoted monoclinic CaAl₂Si₂O₈ (Takéuchi *et al.*, 1973). Although the highest symmetry of the theoretical 3D net is tetragonal, monoclinic CaAl₂Si₂O₈ has lower symmetry because of Si,Al alternation on the tetrahedral nodes coupled with geometrical distortion involving the Ca atoms.

Sequence *SCSCCC* produces only one 3D net because there is only one way of arranging it on adjoining hexagons, and because adjacent 2D nets fit in only one position. This 3D net is the basis of monoclinic CaGa₂O₄ (Deiseroth, 1973), but has not yet been reported in a silicate.

Sequence *SSCCCC* does not yield a unique net. Net *SSCCCC*₁ (Fig. 1) consists of *C* chains (dot and circle) alternating with *S* chains (either all dots or all circles). Adjacent *S* chains must change from dots to circles because of the intervening *C* operation. Net *SSSSCC*₂ contains trigonal stars in projection (heavy lines in Fig. 2), which contrast with the *S* chains in Figure 1. In projection the net consists of slabs separated by arrows marked "choice." Each slab is three hexagons wide, and no choice is allowed in the sequences of each slab. However, at the boundaries the *C* operator between two trigonal stars can tilt either north-east or south-east. If all arrows point the same way, the unit cell is oblique (continuous lines); if they zig-zag, the unit cell is rectangular with doubled area (dashed lines). Polytypic modifications can be derived from these two basic units, analogous to the polytypism in pyroxene. Furthermore the *SSCCCC*₁ and *SSCCCC*₂ 2D nets can be intermixed within a layer, because the *C* chain of the first type occurs along the lines marked "choice" in the second type.

Sequence *SSCSCC* produces only one 3D net, which is the basis of NH₄LiSO₄ (Dollase, 1968), the

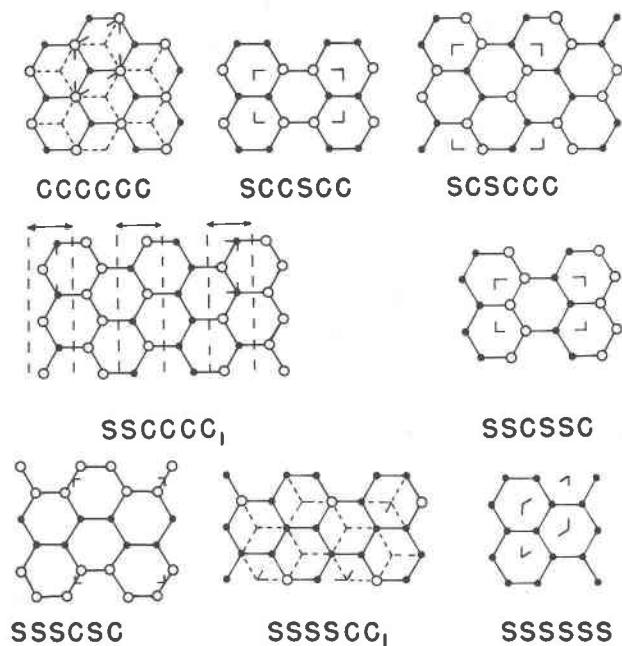


Fig. 1. Simple ways of adding a vertical linkage to each node of a simple hexagonal net to give a 4-connected 3D-network. Only part of one hexagonal net is shown in each diagram, and the unit cell is marked by corner symbols. Dots and circles, respectively, show opposite directions of vertical linkage. Dashes in CCCCCC and SSSSCC₁ show alternate positions for adjacent hexagonal nets.

zeolite Li-A(BW) described by Kerr (1974), and orthorhombic RbAlSiO₄ (Klaska and Jarchow, 1975). When a 3D model is viewed north-south with respect to Figure 1, the nodes fall on a 2D net of alternating 8- and 4-rings to be described later. Although the highest symmetry of the theoretical pattern is orthorhombic, Si,Al ordering and geometrical distortion reduce the symmetry of Li-A(BW) to monoclinic.

Sequence SSSCSC produces only the topology of paracelsian (Smith, 1953) which can also be obtained by attaching double-crankshaft chains to a 4.8² 2D net (Wells, 1954). Although the highest symmetry of the SSSCSC pattern is *Cmcm*, Si,Al ordering and framework crumpling lower the symmetry of paracelsian to monoclinic *P2₁/a* (Craig *et al.*, 1973).

Sequence SSSSSC produces infinite sets of nets. The simplest 2D net, SSSSCC₁ (Fig. 1), has hexagonal symmetry, and all nodes marked by circles are separated by three nodes marked by dots. Just as for CCCCCC, the hexagonal symmetry of the circled nodes allows polytypism by 180° rotation about a vertical axis of adjacent layers (shown in projection by dashed lines). This is the only pattern in which all nodes marked by circles are separated by three nodes

marked by dots. The SSSSCC₂ net (Fig. 2) can be decomposed into alternating single chains (all dots) and double chains. In the double chains the circles must be placed as shown to avoid placing two circles in one 6-ring. However, each double chain can occupy either of two positions related by a translation vector shown by the double-headed arrow. An infinite number of polytypes is possible, and the smallest unit cell is shown in Figure 2. Nodes marked by circles are separated by either 2,3, or 4 nodes marked by dots.

Sequence SSSSSS produces a double sheet and not a framework. This sheet occurs in hexagonal BaAl₂Si₂O₈ (Takéuchi, 1958), hexagonal CaAl₂Si₂O₈ (Takéuchi and Donnay, 1959), and cymrite (Kashayev, 1966), in all three of which cross-linkage is provided by bonding from oxygens to either Ba or Ca.

Table 1 utilizes *Z_i*, the Schläfli symbol of the nodes, the space group of the most symmetrical con-

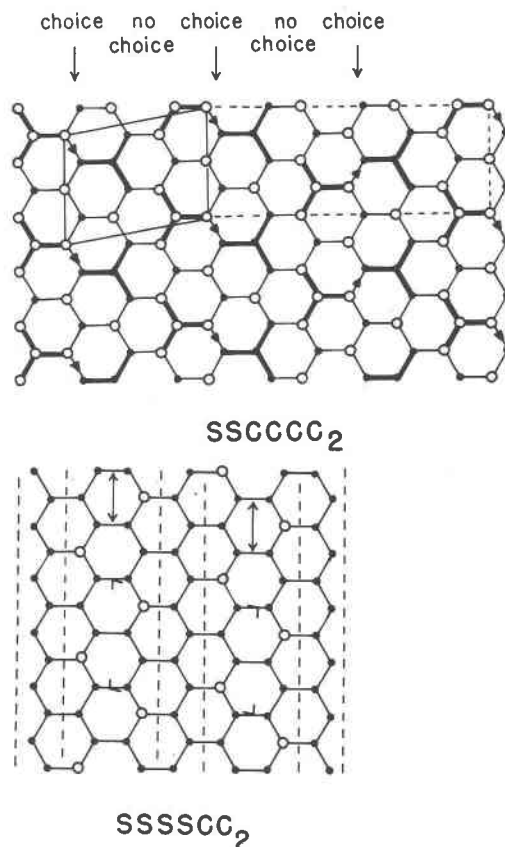


Fig. 2. Two complex ways of adding a vertical linkage to each node of a simple hexagonal net. The two unit cells in the upper diagram correspond to different choices of nodes shown by the arrows. See text for explanation of lower diagram.

Table 1

(a) CLASSIFICATION AND DESCRIPTION OF SOME THEORETICAL FRAMEWORKS								
Arbitrary number	Sequence in 6^3	Z_t	Schläfli symbol(s)	Highest space group	Z_c	a	b	c
1	CCCCC	2	6^6	Fd3m	8	7.16	-	-
2	do.	4	6^6	$P6_3/mmc$	4	~5.06	-	~8.27
3	SCCSCC	4	4.6^5	I4/mmm	8	~8.3	-	~5.1
4	SSCSCC	4	$4^2.6^3.8$	Imam	8	~8.8	~8.8	~5.1
5	SCSCCC	8	4.6^5	Cmca	16	~8.3	~10.1	~8.3
6	SSSCSC	8	$4^2.6^3.8$	Cmcm	16	~9.3	~10.0	~8.5
7	SSCCCC ₁	8	$(4^2.6^4)(6^5.8)$	Cm2m	16	~8.3	~17	~5.1
8	SSSSCC ₁	12	$(4^2.6^4)_3(4^3.6^3)_2(6^3.10^3)$	$P6_2m$	12	~9.2	-	~8.3
9	CCCCC; SCSCCC	12	$(4.6^5)_2(6^6)_1$	Ibmm	24	~9.2	~15	~8.3
10	CCCCC; SCSCCC	36	$(4.6^5)_2(6^6)_1$	$P6_3/mmc$	36	~15	-	~8.3

Cell dimensions based on internodal distance 3.1A.

(b) DATA FOR SILICATES AND SELECTED OTHER MATERIALS.								
Type	Name	Z_t	Reference	Actual space group	a	b	c	
1	high cristobalite	2	Wyckoff (1963)	Fd3m	7.16	-	-	
1	low cristobalite	2	Dollase (1965)	$P4_12_1$	4.98	-	6.95	
1	high carnegieite	2	Smith and Tuttle (1957)	$P2_13$	7.38	-	-	
2	high tridymite	4	Wyckoff (1963)	$P6_3/mmc$	5.03	-	8.22	
2	high tridymite ^a	4	Dollase (1967)	$C222_1$	8.74	5.04	8.24	
2	low tridymite ^b	4	Hoffmann (1967)	C2/c or Cc	18.54	5.01	25.79 ^c	
2	kalsilite	4	Perrotta and Smith (1965)	$P6_3$	5.16	-	8.69	
2	nepheline	4	Footnote d	$P6_3$	10.05	-	8.38	
3	mono-CaAl ₂ Si ₂ O ₈	4	Takéuchi <i>et al.</i> (1973)	$P12_11$	8.23	8.62	4.83 ^e	
4	NH ₄ LiSO ₄	4	Dollase (1968)	$Pna2_1$	8.786	9.140	5.280	
4	Li-A(BW)	4	Kerr (1974)	$Pna2_1$	10.31	8.18	5.00	
4	RbAlSiO ₄	4	Klaska and Jarchow (1975)	Imam	9.23	8.74	5.34 ^f	
5	monoclinic CaGa ₂ O ₄	8	Deiseroth (1973)	$P2_1/c$	7.992	8.883	10.58 ^g	
6	paracelsian	8	Craig <i>et al.</i> (1973)	$P2_1/a$	9.06	9.57	8.57 ^e	
6	hurlbutite	8	Lindbloom <i>et al.</i> (1974)	$P2_1/a$	8.30	8.78	7.80 ^e	
6	danburite	8	Phillips <i>et al.</i> (1974)	Pnam	8.04	8.75	7.73	
9	beryllonite	12	Giuseppetti and Tadini (1973)	$P2_1/n$	8.178	7.819	14.11 ^e	
9	trimerite	12	Moore and Ribbe (1965)	$P2_1/n$ (subcell)	16.1	7.62	27.9 ^h	
?	esperite	?	Moore and Ribbe (1965)	$P2_1/n$ (subcell)	17.6	8.27	30.5 ^e	
?	O1-KAlSiO ₄	?	Smith and Tuttle (1957)	orthorhombic ?	9.01	15.67	8.57 ⁱ	
?	O2-KAlSiO ₄	?	do.	orthorhombic ?	8.89	10.47	8.55	
?	kaliophilite	?	do.	hexagonal ?	26.94	-	8.55	
?	syn-kaliophilite	?	do.	hexagonal ?	5.18	-	8.56	
?	NaAlSiO ₄ ·1/2H ₂ O	?	Edgar (1966)	orthorhombic ?	7.50	8.20	5.22	

^aat 220°C; ^bat 25°C; ^c β 117.67°; ^dcomplex polymorphism occurs; Dollase and Peacor (1971); Foreman and Peacor (1970); Ghélis and Gasperin (1972); Parker (1972); Simmons and Peacor (1972); ^e β 90.00°; ^faxes relabeled; ^g β 94.72; ^h β 90.15°; ⁱKunze (1954) proposed unverified trial structure.

figuration, and the number of nodes in the conventional crystallographic cell (Z_c) to give an orderly classification. For convenience of cross-reference, an arbitrary number is assigned. Six nets have nodes of

only one kind (congruent nodes), but $SSCCCC_1$ and $SSSSCC_1$ have two and three kinds of nodes, respectively. In the two $CCCCC$ nets, the six shortest circuits associated with the internodal angles at each

tetrahedral node are all 6-fold, whereas *SCCSCC* and *SCSCCC* have one 4-fold circuit and five 6-fold ones. One 8-fold circuit occurs in *SSCSSC*, *SSSCSC*, and *SSCCCC₁*, and 10-fold ones in one-sixth of the nodes in *SSSSCC₁*.

The first six sequences shown in Figure 1 have equal numbers of up (*U*) and down (*D*) nodes in every layer, and the corresponding 3D nets can be derived therefore from 2D nets by simple translation of adjacent nets such that *U* of a lower net is below *D* of the adjacent higher net. Hence Z_t of the 3D net is the same as for its component 3D net. The *SSSSCC* and *SSSSSS* layers have different numbers of *U* and *D* nodes, and can be extended only by linkage through a horizontal mirror plane to the next layer. This doubles the value of Z_t from 6 to 12 in going from the 2D to 3D net for *SSSSCC₁*.

Unfortunately there is an infinite number of frameworks based on more than one type of up-down sequence in a 2D hexagonal net, and it is not feasible to enumerate them without placing arbitrary limits on the size of the unit cell. So far, only one framework type has been discovered with more than one type of up-down sequence in a 2D hexagonal net. Beryllonite, NaBePO_4 , (Golovastikov, 1962; Guiseppetti and Tadini, 1973) and trimerite, $\text{CaMn}_2\text{Be}_2\text{Si}_2\text{O}_8$, (Klaska and Jarchow, 1974) have alternating *CCCCCC* and *SCSCCC* rings (Fig. 3), and esperite, $(\text{Ca,Pb})\text{ZnSiO}_4$, (Moore and Ribbe, 1965) may be isostructural with them. Figure 3 shows another arrangement of alternating *CCCCCC* and *SCSCCC* rings which differs in the orientations of the *CCCCCC* rings (denoted *A* and *B*): its maximum symmetry is hexagonal (Table 1), and polytypism is possible, as explained in the figure legend. Other structural types with mixed sequences may be awaiting discovery, and the polymorphs of KAlSiO_4 should be worth investigation (e.g. Kunze, 1954).

Conclusion

Apart from the beryllonite group, all materials with structures in the present topological group have only one Schläfli symbol (Table 1). Most observed structures have simple subunits; thus *CCCCCC* has strict alternation of up and down in a hexagonal sheet, *SCCSCC* can be assembled from chains with alternating pairs of tetrahedra pointing in opposite directions, *SSCSSC* can be built from chains with tetrahedra pointing the same way, and *SSSCSC* from double-crankshaft chains. Perhaps simple subunits are actually assembled during the growth process, as has been suggested many times (e.g. for zeolites; Breck, 1974).

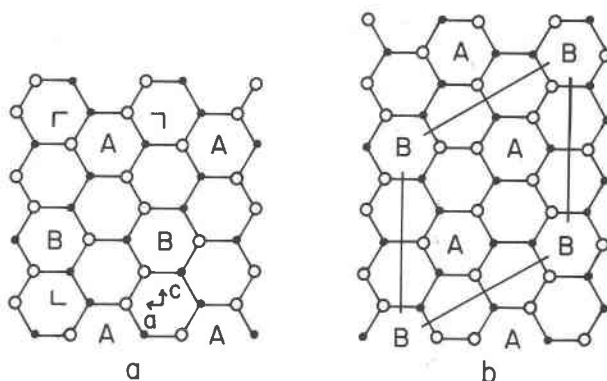


Fig. 3. Two simple ways of arranging *CCCCCC* and *SCSCCC* sequences in a simple hexagonal net. The patterns differ in the relative orientations of the *CCCCCC* rings as denoted by *A* and *B*. In diagram a (Table 1, no. 9) the orthorhombic unit-cell contains one *A* and one *B*, while in diagram b (Table 1, no. 10) the hexagonal cell contains two *A* and one *B*. Polytypism is possible by changing the horizontal sequence of vertical slabs of *A* and *B*.

From the viewpoint of molecular sieving, most of the theoretical structures have small pores and windows. The largest ring in *CCCCCC* has only 6 tetrahedra, and the pores of the corresponding silicates are large enough only for cations (as in kalsilite and nepheline derivatives of tridymite and the carnegieite derivative of cristobalite), or perhaps a single water molecule. Net *SCCSCC* has channels limited by boat-shaped 8-rings interconnected by boat-shaped 6-rings which outline small pores; the framework of monoclinic- $\text{CaAl}_2\text{Si}_2\text{O}_8$ is collapsed around the small Ca cations, though that of orthorhombic RbAlSiO_4 is not so strongly collapsed because of the larger Rb cations. Net *SCSCCC* has 8-rings across the waist of ellipsoidal cavities, but access is limited by 6-rings. Nonintersecting channels spanned by elliptical 8-rings occur in *SSCCCC₁*. Net *SSSCSC* has channels spanned by irregular 8-rings, and cross-linked through 6-rings. Although elliptical pores bounded by 10-rings occur in *SSCCCC₂*, diffusion in 3-dimensions is limited by 6-rings. Net *SSCSSC* has nonintersecting channels spanned by elliptical 8-rings and walled by 4- and 6-rings. Net *SSSSCC₁* consists of tightly-bonded layers (dots in Fig. 1) linked only at wide distances (circles in Fig. 1). Access to the inter-layer volume is through flattened 10-rings. A silicate with this structure might have rather unusual sorption properties. The more irregular net *SSSSCC₂* also has strongly-bonded sheets, but the cross-links yield 8-, 10-, and 12-rings.

From the topologic viewpoint, the geometry and symmetry of the framework are irrelevant. For simplicity, all patterns in Figures 1 and 2 are drawn with

respect to a 6^3 net with rotational 6-fold symmetry; such a net, of course, outlines a tessellation composed of regular hexagonal tiles. In actual crystal structures, the hexagonal net may be distorted in response to chemical bonds or to occupancy of the nodes by different elements (e.g. Si and Al). The net may be distorted vertically as well as horizontally, and indeed when models are built of tetrahedral stars linked by plastic spaghetti each vertical link pulls its two tetrahedral nodes away from their hexagonal nets. For each net, the concept of highest symmetry can be developed by (a) equalizing the distance between all adjacent nodes, and (b) varying the internodal angles to get the highest symmetry. Thus the cristobalite modification of $CCCCC$ has isometric symmetry when all the internodal distances and angles are equal, but would have only hexagonal symmetry if one of the hexagonal nets were planar instead of puckered. Although high-cristobalite and high-tridymite (Wyckoff, 1963) actually have the same symmetry as the highest symmetry of the corresponding theoretical frameworks (i.e. $Fd3m$ and $P6_3/mmc$), other varieties at lower temperatures have lower symmetry (Table 1) because of angular distortion of the framework. A detailed review of distortions in cristobalite-type structures is given by O'Keefe and Hyde (1976). Although the highest symmetry of $SCCSCC$ is $I4/mmm$, the actual symmetry of monoclinic $CaAl_2Si_2O_8$ is $P2_1$ because of alternate occupancy of tetrahedral nodes by Si and Al, coupled with framework distortion and movement of Ca (Takéuchi *et al.*, 1973). Similarly, the actual symmetry of LiA-(BW) is $Pna2_1$ instead of the highest symmetry of $Imam$ for $SSCSCC$. Two types of ordering for the $SSCSCC$ topology occur; strict alternation of Si and Al in paracelsian and of Be and P in hurlbutite (Lindbloom *et al.*, 1974) give space group $P2_1/a$, whereas alternation of pairs of Si and B in danburite (Phillips *et al.*, 1974) gives $Pnam$. When such a reduction of symmetry occurs, it may be difficult to match the cell dimensions and observed symmetry of a material of unknown structure against those for a theoretical net. However, the space group for the unknown must be a possible subgroup of the highest space group for the theoretical net, and there should be a pseudosymmetry in the unknown as well as a fairly close match in the cell dimensions. This is illustrated in Table 1, which lists the *highest symmetry* and related geometry for the theoretical nets in Figure 1 together with corresponding parameters for some actual structures. In determining the cell dimensions for the theoretical nets, an internodal distance of 3.1Å was used to give

an approximate match to all framework silicates. Only one possible geometry satisfies the highest symmetry of $CCCCC$ (cristobalite), but for all the other theoretical nets some angles between tetrahedral nodes can be flexed without violating the symmetry. For the latter networks, distances were estimated for near-equal angles.

In addition to the symmetry reduction caused by Si,Al ordering and framework puckering, one or more cell edges may be multiplied. This occurs for nepheline which has a doubled a parameter over that for the tridymite pseudostructure (Smith and Tuttle, 1957).

The cell dimensions for nepheline hydrate (Table 1, last row) may result from very strong distortion of the $SCCSCC$ structure type, but a full structure analysis is needed to test this idea.

The preceding four rows in Table 1 list cell dimensions of four materials with composition near $KAlSiO_4$ whose structure has not been determined. Although the cell dimensions have near-integral relations to those expected for structures with up-down links from hexagonal sheets (note that $a = 26.94\text{Å}$ for natural kaliophilite is related to $a = 5.18\text{Å}$ for synthetic kaliophilite by $3\sqrt{3}$, and that $\sqrt{3}$ merely means 30° rotation in a hexagonal lattice), framework puckering, Si,Al ordering, possible existence of more than one sequence type, and perhaps twinning may cause difficulty in determining the type of framework topology is crystal structure analysis.

Although the main emphasis of this paper is on framework silicates, other types of materials can be classified in the present scheme. Wurtzite, sphalerite, and chalcopyrite are examples of sulfides. Hahn *et al.* (1969) described synthetic sulfates and fluoroberyllates with structure type 4, and there are many non-silicates with frameworks like those of paracelsian and tridymite (e.g. Dinh and Bertaut, 1965; Deiseroth and Müller-Buschbaum, 1973a,b).

Acknowledgments

I am extremely grateful to A. F. Wells for prolonged discussion and guidance in improvement of the paper, P. B. Moore for exciting my interest in enumeration methods, W. A. Dollase for improvement of the manuscript, J. R. Clark for hospitality while building models, Union Carbide Corporation (Linde Division) for a grant-in-aid, and NSF for grants CHE-75-22451 and MRL DMR76-00697.

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Manuscript received, November 12, 1976; accepted for publication, March 2, 1977.