JOURNAL OF SOLID STATE CHEMISTRY 42, 300–321 (1982)

Observed Wurtzite Derivatives and Related Dipolar Tetrahedral Structures

W. H. BAUR

Department of Geological Sciences, University of Illinois,
Chicago, Illinois, 60680

AND T. J. McLARNAN

Department of Chemistry, The University of Chicago,
Chicago, Illinois, 60637

Received December 11, 1981

Eight lower-symmetry ordered derivatives of the wurtzite type and an additional six related dipolar tetrahedral structure types were observed. All these structures are based on hexagonal closest packing of anions. Their mutual symmetry relationships can be summarized in a Bärnighausen diagram. Dipolar tetrahedral structures are characterized by centrosymmetric space groups, thus resulting in a dipolar distribution of the coordination tetrahedra. Dipolar tetrahedral structures often exhibit disorder and random statistical occupations and several good ionic conductors are found among them. The wurtzite-type derivatives are characterized by polar space groups and all coordination tetrahedra in them are pointing in the same direction. Some simple, geometrically possible wurtzite derivatives have never been observed. Their absence can be rationalized on the basis of a poor geometrical fit between tetrahedral chains as demonstrated by computer simulations of their hypothetical structures. The ratio ϵ (quotient of the thickness of one hexagonal layer in [001] over one measure of the mean diameter of one atom within this layer) is useful for ordering the wurtzite derivatives on the basis of their chemical composition, since ϵ increases from the oxides, over the nitrides to the sulfides. The ϵ ratio also distinguishes clearly between the oxidic wurtzite types (0.79) and the tetrahedral rutile types or β-BeO derivatives (0.86), while the dipolar tetrahedral types have ϵ values around 0.82, that is, close to the value expected for hexagonal closest packing.

Introduction

The crystal structure of zinkite, ZnO, was solved by the Braggs (*1*). It is based on a hexagonally closest-packed (hcp) arrangement of atoms in which both the cations and the anions are tetrahedrally coordinated by each other. This structure type is usually referred to as the wurtzite type, after wurtzite, the dimorph of cubic ZnS, zinc blende, or sphalerite. Since it was determined, eight binary, ternary, and quaternary structures have been described, which are ordered, lower-symmetry derivatives of the wurtzite type. Four more closely related structures are known, in which the coordination tetrahedra are distributed in a dipolar fashion, pointing both up and down the hexagonal direction of the hcp. An additional two related types have been established in which some of the cations are located in octahedral interstices of the hcp array of anions. Five of these fourteen derivatives have been found since 1978.

0022-4596/82/060300-22$02.00/0

A review of all the then known tetrahedral structures, including both the wurtzite and the zinc blende derivatives, was given by Parthé (*2*). West and collaborators prepared many of the oxide compounds belonging to this class and reviewed both their work and related efforts (*3, 4*). O'Keeffe and Hyde explored the topological relation of the wurtzite type to the cristobalite type (*5*) and studied the nonbonded interactions between the cations in the wurtzite-type structures (*6*). The present review limits itself to the structure types based on hcp. This means that we are ignoring all zinc blende-related structures, which are based on a face-centered cubic arrangement of anions or cations. We also are not reviewing here the tetrahedral structures based on rutile close packing of anions, such as β-BeO, γ-$LiAlO_2$, γ-Li_2BeSiO_4, Li_4GeO_4, and Li_4PbO_4. These structures have occasionally been referred to as distorted hcp arrays. Actually, the anion packing in them is based on an 11 coordination of spheres around each other (*7*). The spatial relationship of the tetrahedral coordination polyhedra to each other is consequently fundamentally different from what is observed in hcp-based structures. The present review shows which of the potentially possible wurtzite derivatives enumerated in the companion paper (*8*) have been observed so far in nature.

The Wurtzite Type

A wurtzite-type structure, *AX*, can be viewed as a hexagonal closest packing of *X* in which one-half of the tetrahedral interstices are occupied by *A*. Conversely, it can be taken as an hcp of *A* in which the *X* atoms are arranged in the tetrahedral holes. All coordination tetrahedra are pointing in the same direction parallel to the *c* axis. The space group is $P6_3mc$ with both atoms located at sites of symmetry $3m$ with coordinates of equivalent positions of $\frac{1}{3}\frac{2}{3}z$, $\frac{2}{3}\frac{1}{3}z + \frac{1}{2}$, where $z_A = 0$ and $z_X \approx 0.375 = \frac{3}{8}$ (*1*). Each atom is surrounded tetrahedrally by four atoms of another kind: one at a distance of zc along the 6_3 axis, and three more at a distance of $[a^2/3 + (\frac{1}{2} - z)^2c^2]^{1/2}$. In addition, there is a fifth atom of the other kind at a distance of $(1 - z)c$. This fifth atom, together with the atoms at the base of the coordination tetrahedron, forms the second tetrahedral environment of hcp. This tetrahedral site, however, is not occupied in wurtzite because it shares a face with the occupied site, and one edge each with three neighboring tetrahedra. In addition, there are two empty octahedral sites per unit cell which each share three faces with occupied tetrahedral sites, three faces with empty tetrahedral sites, and two faces (along the *c* direction) with neighboring octahedral sites.

A large number of binary compounds *AX* crystallize in this structure type. Examples are: ZnS, ZnO, BeO, AlN, CuH, MgSe, MgTe, etc. Listings of the more than two dozen compounds of this type were provided previously (*2, 6*). The c/a ratio of an ideally hcp wurtzite-type structure should be $1.63299\,[=(8/3)^{1/2}]$. The actual measured values of c/a range from 1.600 (for AlN) to 1.656 (for BP). It has been shown (*9*) that wurtzite-type compounds with $c/a < 1.633$ tend to be stable relative to the zinc blende modification of *AX*, while those with $c/a > 1.633$ are unstable.

Ordered Wurtzite Derivatives

The wurtzite type proper is of hexagonal symmetry. Its derivative structures are of orthorhombic and monoclinic symmetry, but even the monoclinic varieties can be described in unit cells with approximately orthorhombic metric. In the smallest orthorhombic cell, (1,1), *a* corresponds to the unit distance from one closest-packed atom to its neighbor within the plane hexagonally closest-packed layer, *b* is the direction normal to a and its length is a multiplied by $3^{1/2}$, while c is twice the distance from one plane closest-packed layer to the next one. The ratio $\epsilon = 2c/(a/2 + b/3^{1/2})$ is the quotient of the thickness of one hexagonal layer in [001] over one measure of the mean diameter of one atom within this layer. For an ideal hcp the numerical value of the quotient ϵ is 0.8165 $[=(2/3)^{1/2}]$, that is, half the value of the customarily given c/a ratio of hcp.

The cell contents of one (2,1) cell are listed in Table I with their idealized coordinates. The setting of this reference cell does not correspond to any of the space groups assumed by various wurtzite derivatives, since no single setting could be used to describe conveniently all wurtzite variants in their conventional settings. Instead, one tetrahedrally coordinated cation in the up position is arbitrarily put in the origin of the unit cell. Subsequently, in order to compare the various ordering variants in the (2,1) and (2,2) cells with each other, the tetrahedral cation with the highest formal charge and in up position is located in the U000 site. For some of the structure types in Table II, two distinct ways of transforming the structure to the reference arrangement are possible. In such cases, the pattern chosen is the one which emphasizes the similarity to the other types. Because of their stoichiometry, one cannot use the analogous convention for the (3,1) cells in a meaningful way (Table III).

W-Pbn2_1*(2,1) or NaFeO*$_2$ *Type* (ABX_2)

The simplest way to obtain an ordered derivative of the wurtzite type for a composition ABX_2 would be a structure with the same cell constants as wurtzite itself but in space group $P3m1$ (a subgroup of $P6_3mc$). In such a structure, the cation sites at $z = 0$ would be occupied by A atoms, and those at $z = \frac{1}{2}$, by B atoms. However, Pauling's rule would not be satisfied if the formal charges of A and B are different. For the composition $NaFeO_2$, the sums of the bond

TABLE I

CONTENTS OF A REFERENCE UNIT CELL (2,1) WITH ORTHORHOMBIC METRIC

Symbol	x	y	z	Symbol	x	y	z
U000	0	0	0	X003	0	0	$\frac{3}{8}$
U044	0	$\frac{2}{3}$	$\frac{1}{2}$	X047	0	$\frac{2}{3}$	$\frac{7}{8}$
U114	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{2}$	X117	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{7}{8}$
U130	$\frac{1}{4}$	$\frac{1}{2}$	0	X133	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{8}$
U200	$\frac{1}{2}$	0	0	X203	$\frac{1}{2}$	0	$\frac{3}{8}$
U244	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	X247	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{7}{8}$
U314	$\frac{3}{4}$	$\frac{1}{6}$	$\frac{1}{2}$	X317	$\frac{3}{4}$	$\frac{1}{6}$	$\frac{7}{8}$
U330	$\frac{3}{4}$	$\frac{1}{2}$	0	X333	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{3}{8}$
D006	0	0	$\frac{3}{4}$	O021	0	$\frac{1}{3}$	$\frac{1}{8}$
D042	0	$\frac{2}{3}$	$\frac{1}{4}$	O025	0	$\frac{1}{3}$	$\frac{5}{8}$
D112	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{4}$	O151	$\frac{1}{4}$	$\frac{5}{6}$	$\frac{1}{8}$
D136	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	O155	$\frac{1}{4}$	$\frac{5}{6}$	$\frac{5}{8}$
D206	$\frac{1}{2}$	0	$\frac{3}{4}$	O221	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{8}$
D242	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{4}$	O225	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{5}{8}$
D312	$\frac{3}{4}$	$\frac{1}{6}$	$\frac{1}{4}$	O351	$\frac{3}{4}$	$\frac{5}{6}$	$\frac{1}{8}$
D336	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	O355	$\frac{3}{4}$	$\frac{5}{6}$	$\frac{5}{8}$

Note. The closest-packed anions are X, the tetrahedral interstices in a tetrahedron pointing up are U, pointing down D, while the octahedral interstices are called O. The three digits after the symbol refer to the coordinates counted in multiples of $\frac{1}{4}$ in x, of $\frac{1}{6}$ in y, and of $\frac{1}{8}$ in z.

TABLE II

ORDERING OF THE CATIONS INTO TETRAHEDRAL SITES IN (A) (2,1) AND (B) (2,2) CELLS FOR THE MAIN TYPES DISCUSSED IN THE TEXT

A

xy	$Cmc2_1$ ($=P6_3mc$) ZnO	$Pbn2_1$ β-$NaFeO_2$	$P1n1$ Li_2BeSiO_4	$P1n1$ reversed Li_2BeSiO_4	$Pmn2_1$ LT-Li_3PO_4	$Pbc2_1$ α-LiSiON	$P2_1/m11$ disordered Li_4SiO_4
00	Zn,U	Fe,U	Si,U	Si,U	P,U	Si,U	Si,U
04	Zn,U	Na,U	Li1,U	Li1,U	Li2,U	Si,U	Li2,3;U,D
11	Zn,U	Fe,U	Be,U	Li2,U	Li1,U	Li,U	Li1,4;U,D
13	Zn,U	Na,U	Li2,U	Be,U	Li1,U	Li,U	Li1,4;U,D
20	Zn,U	Na,U	Li1,U	Li1,U	Li2,U	Li,U	Li2,3;U,D
24	Zn,U	Fe,U	Si,U	Si,U	P,U	Li,U	Si,U
31	Zn,U	Na,U	Li2,U	Be,U	Li1,U	Si,U	Li1,4;U,D
33	Zn,U	Fe,U	Be,U	Li2,U	Li1,U	Si,U	Li1,4;U,D

B

	$Pbn2_1$ Li_2CoSiO_4		$Pmnb$ HT-Li_3PO_4		$P12_1/n1$ Li_2ZnSiO_4		$P112_1/b$ Na_2BeSiO_4	
xy	L	R	L	R	L	R	L	R
00	Si,U	Si,U	P,U	P,D	Si,U	Si,D	Si,U	Si,D
04	Li2,U	Li2,U	Li2,D	Li2,U	Li2,D	Li2,U	Na2,D	Na2,U
11	Li1,U	Co,U	Li1,U	Li1,D	Li1,U	Zn,D	Be,U	Be,D
13	Co,U	Li1,U	Li1,U	Li1,D	Zn,U	Li1,D	Be,D	Be,U
20	Li2,U	Li2,U	Li2,D	Li2,U	Li2,D	Li2,U	Na2,U	Na2,D
24	Si,U	Si,U	P,U	P,D	Si,U	Si,D	Si,D	Si,U
31	Co,U	Li1,U	Li1,U	Li1,D	Zn,U	Li1,D	Na1,U	Na1,D
33	Li1,U	Co,U	Li1,U	Li1,D	Li1,U	Zn,D	Na1,D	Na1,U

Note. The x and y coordinates are indicated in the left column. The z coordinate depends on the position of the cation (U or D) and can be read from Table I. The (2,2) cells are divided into a left and a right half, where the y coordinate of the right half is larger by one-half than in the left-half cell. The y coordinates for the (2,2) cells are in multiples of $\frac{1}{12}$. Thus, for example, the point in the left half of a (2,2) cell listed with $xy = 11$ has $y = \frac{1}{12}$, while the corresponding point in the right half of the cell has $y = \frac{7}{12}$.

strengths [p(O)] would be 1.5 and 2.5 valence units (v.u.) for the two crystallographically distinct oxygen atoms (*10, 11*). Furthermore, size mismatch between the A- and B-containing layers would tend to destabilize the $P3m1$ structure (see below). The structure actually adopted by many ABX_2 compounds is the β-$NaFeO_2$ type first described in 1954 (*12*). It crystallizes in a (2,1) cell and has space group $Pbn2_1$. Since it is a wurtzite-type derivative, it is called here a W-$Pbn2_1$(2,1) type, where the W stands for wurtzite, $Pbn2_1$ is the space group of the structure in the setting used here, and (2,1) is the size of the unit cell. Thirteen oxides, nitrides, and sulfides are reported to crystallize in this pattern (Table IV). Both the A and B cations form chains of corner-sharing coordination tetrahedra parallel to the [001] direction. Each A cation chain is surrounded by four B cation chains and vice versa. Another set of such

TABLE III

ORDERING OF CATIONS INTO TETRAHEDRAL SITES IN (3,1) CELLS

x	y	z(U)	z(D)	$Cmc2_1$ Na_2SiO_3	$Cmc2_1$ $Si_2\square N_2O$	$Pcmn$ $CuFe_2S_3$
0	0	0	6	Si,U		Cu,U
0	4	4	2	Si,U		Cu,U
1	1	4	2	Na,U	Si,U	Fe,U
1	3	0	6	Na,U	Si,U	Fe,U
2	0	0	6	Na,U	Si,U	Fe,D
2	4	4	2	Na,U	Si,U	Fe,D
3	1	4	2	Si,U		Cu,D
3	3	0	6	Si,U		Cu,D
4	0	0	6	Na,U	Si,U	Fe,D
4	4	4	2	Na,U	Si,U	Fe,D
5	1	4	2	Na,U	Si,U	Fe,U
5	3	0	6	Na,U	Si,U	Fe,U

Note. The x, y, and z coordinates are in units of $\frac{1}{6}$, $\frac{1}{8}$, and $\frac{1}{8}$, respectively.

chains runs parallel to the [010] direction. The sets of chains are interconnected to form three-dimensional frameworks of FeO_2 (or NaO_2) composition.

The ABX_2 compounds crystallizing in the W-$Pbn2_1$(2,1) type could adopt a structure in space group $Pmc2_1$ [(*8*) Table VIII] with a smaller unit cell, (1,1). Such arrangement would satisfy Pauling's postulate for an $A^{+}B^{3+}O_4$ stoichiometry, while those in Cm(1,1) and $Pmn2_1$(1,1) would not. However, all well-characterized ABX_2 wurtzite derivatives crystallize in the structure with the larger unit cell, in the W-$Pbn2_1$(2,1) or β-$NaFeO_2$ type. In addition to meeting the requirements of Pauling's valence rule, in the $Pmc2_1$ structure each cation has the same numbers of second nearest neighbors as in the observed W-$Pbn2_1$(2,1) structure type. Also, both cations form tetrahedral chains in this hypothetical structure, except that the chain directions are [001] and [100]. In both cases each chain is surrounded by four chains of the other kind, but the geometry differs slightly for the two types (Fig. 1). Therefore, the energy difference between these two types must be small. It is conceivable that this arrangement might be found in nature, provided the size difference between the A and B cations is small (see below).

W-$Pmn2_1$(2,1) or Enargite Type (AB_3X_4 and ABC_2X_4)

The first-ordered derivative of the wurtzite type to be described was the enargite type, Cu_3AsS_4 (*28*), crystallizing in space group $Pmn2_1$. Since the B atoms are distributed here over two crystallographically nonequivalent sites, the structure can also be adopted by ABC_2X_4 stoichiometries (Ta-

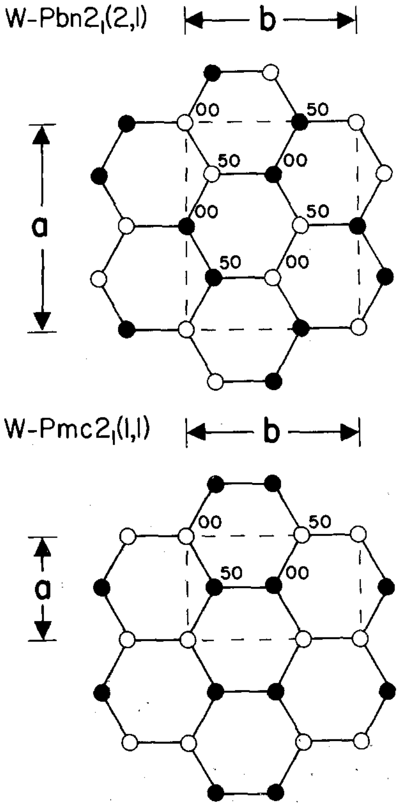

FIG. 1. Observed $NaFeO_2$ type [W-$Pbn2_1$(2,1)] and hypothetical ABO_2 type [W-$Pmc2_1$(1,1)], projected onto a plane normal to c. Each point in the net corresponds to a tetrahedrally coordinated cation position. The heights in c are given in 100× the fractional coordinate. Open circles correspond to Fe, solid circles to Na.

TABLE IV

CELL CONSTANTS (Å) AND ϵ VALUES OF ORDERED (2,1), (2,2), AND (3,1) WURTZITES IN THE ORTHORHOMBIC SPACE GROUPS $Pbn2_1$, $Pmn2_1$, $Pbc2_1$, AND $Cmc2_1$ AND IN THE MONOCLINIC SPACE GROUP Cc

Compound	*a*	*b*	*c*	ϵ	Reference
1. W-$Pbn2_1$(2,1)					
$LiGaO_2$	6.372(1)	5.402(1)	5.007(1)	0.794	*(13)*
$NaAlO_2$	7.075	5.376	5.216	0.785	*(14)*
$NaFeO_2$	7.136	5.672	5.377	0.786	*(12)*
$NaGaO_2$	7.201	5.519	5.301	0.781	*(15)*
$BeSiN_2$	5.747(6)	4.977(5)	4.674	0.813	*(16)*
$MgSiN_2$	6.476	5.279	4.992	0.794	*(17, 18)*
$MnSiN_2$	6.511(9)	5.248(5)	5.070(4)	0.807	*(19, 20)*
$MgGeN_2$	6.611	5.494	5.166	0.798	*(18)*
$MnGeN_2$	6.675(10)	5.486(6)	5.246(5)	0.806	*(20, 21)*
$ZnGeN_2$	6.441	5.454	5.194	0.815	*(22)*
$LiAlS_2$	7.875	6.484	6.188	0.806	*(81)*
$LiGaS_2$	7.864	6.513	6.217	0.808	*(23)*
$LiInS_2$	8.066	6.883	6.54	0.817	*(23)*
2. W-$Pmn2_1$(2,1)					
Li_3PO_4	6.1150(10)	5.2394(11)	4.8554(10)	0.798	*(24)*
Li_3VO_4	6.3259(12)	5.4460(8)	4.9469(9)	0.784	*(25)*
Li_3AsO_4	6.276	5.386	4.955	0.793	*(26)*
Cu_3PS_4	7.43(2)	6.46(2)	6.18(2)	0.830	*(27)*
$CuAsS_4$	7.407(1)	6.436(1)	6.154(1)	0.829	*(28, 29)*
Cu_2CdSiS_4	7.60	6.48	6.25	0.829	*(30)*
Cu_2CdGeS_4	7.692(2)	6.555(2)	6.299(2)	0.825	*(31)*
Cu_2MnGeS_4	7.61	6.50	6.18	0.818	*(32)*
3. W-$Pbc2_1$(2,1)					
LiSiON	6.395(2)	5.200(1)	4.728(2)	0.763	*(33)*
ZnAlON	7.006	5.332	5.109	0.776	*(93)*
MgAlON	6.937	5.361	5.079	0.774	*(93)*
4. W-$Pbn2_1$(2,2)					
Li_2CoSiO_4	6.253(5)	10.685(9)	4.929(9)	0.794	*(34)*
$Al_2Zn\square S_4$	7.500	12.825	6.099	0.818	*(35)*
5. W-$Cmc2_1$(3,1)					
Li_2SiO_3	9.396(1)	5.396(1)	4.661(1)	0.746	*(36)*
Li_2GeO_3	9.634(2)	5.481(2)	4.843(1)	0.760	*(36)*
Na_2SiO_3	10.482	6.064	4.826	0.689	*(37, 38)*
Na_2GeO_3	10.845(3)	6.224(3)	4.918(1)	0.682	*(39)*
Cu_2SiS_3	10.981(3)	6.416(2)	6.046(2)	0.821	*(40)*
$B_2\square O_3$	7.803(2)	4.613(1)	4.129(1)	0.784	*(41)*
Si_2LiN_3	9.186(3)	5.302(2)	4.776(2)	0.780	*(42)*
$Si_2\square N_2O$	8.843(5)	5.473(5)	4.835(5)	0.792	*(43)*
$Ge_2\square N_2O$	9.312(1)	5.755(1)	5.105(1)	0.794	*(44)*
β-LiSiOn[a]	9.097(18)	5.406(12)	4.778(8)	0.776	*(45)*
6. W-Cc(3,1)					
$Ga_2\square S_3$	11.094(2)	6.395(1)	6.008(2)[b]	0.813	*(46, 82)*
$Al_2\square Se_3$	11.680	6.733	6.274[b]	0.806	*(47)*

[a] Space group unknown.

[b] Angle $\beta = 121°$; the value given here for cell constant c is actually $c \sin \beta$.

ble IV). A number of sulfides, as well as the low-temperature forms of Li_3MO_4 (M = P, V, or As), crystallize in this type. Most of the other theoretically possible space groups and unit cells for AB_2X_4 and ABC_2X_4 stoichiometries result in structures in which the $p(X)$ received by the various anions deviate significantly from Pauling's postulate.

In terms of tetrahedral connections, this structure is characterized by sheets parallel to (010) formed by the coordination tetrahedra around the cations in the general set of equivalent positions [Cu(2) in Cu_3AsS_4; Li(1) in Li_3PO_4; and Cu in Cu_2CdGeS_4]. These sheets are arranged around the *n* glide; therefore, they are also connected by the 2_1 axes. They alternate with analogous sheets formed by the tetrahedra around the two other cations located in the two special sets of equipoints. In these other sheets formed by As and Cu, P and Li(2), or Cd and Ge in the three compounds mentioned above, each cation is surrounded by neighbors of the other kind. Any tetrahedral chains one wishes to isolate there are composed of alternating cation tetrahedra. If it were otherwise, Pauling's rule would not be satisfied.

In addition to the compounds listed in Table IV, a number of other obviously wurtzite-related compounds have been thought to belong to the W-$Pmn2_1$(2,1) or enargite type (Table V). Since the assignments are based only on X-ray powder diffraction data, they cannot be accepted as proven. The crystal structure of one of the oxide phases (Li_2ZnGeO_4) has been determined recently and found to be monoclinic (*48*). However, Li_2ZnGeO_4 could be dimorphic within essentially the same size unit cell (see the discussion below).

W-*P*1*n*1(2,1) or Liberite Type (ABC_2X_4)

The mineral liberite, Li_2BeSiO_4, the structure of which was determined by Chang (*49*), has a different arrangement of atoms (Fig. 2). It crystallizes in space group $P1n1$. This type is similar to the W-$Pmn2_1$(2,1) type insofar as the unit cell size is essentially the same, the number of second-neighbor cations around each cation is the same, and Pauling's postulate is fulfilled as well. However, the sheets of connected univalent cation coordination tetrahedra do not occur here. Instead, the Li tetrahedra form corner-sharing chains parallel to [001] and another set parallel to [010], exactly as the Na atoms do in β-$NaFeO_2$. These chains are interconnected to form a three-dimensional network interlaced by analogous interconnected chains composed of alternating di- and tetravalent cations. This network may be responsible for the good ionic conductivities reported for structures derived from Na_2MgSiO_4, a structure closely related to this type (*50, 51*). The W-$P1n1$(2,1) type has been reported for several Li and Na silicates and germanates of Be, Mg, Co, and Zn (Table VI). In view of the structural similarities between the W-

TABLE V

CELL CONSTANTS (Å) AND ϵ VALUES OF COMPOUNDS IN (2,1) CELLS WHICH CANNOT BE ASSIGNED TO A PARTICULAR WURTZITE-TYPE DERIVATIVE

Compound	a	b	c	ϵ	Reference
Li_2FeSiO_4	6.26	5.32	5.01	0.808	(*52*)
Li_2CoSiO_4	6.17	5.36	4.93	0.798	(*52*)
Li_2ZnSiO_4	6.13	5.37	4.94	0.801	(*52*)
Li_2CdSiO_4	6.47	5.35	5.10	0.806	(*52*)
Li_2MgGeO_4	6.39	5.48	4.99	0.785	(*52*)
Li_2MnGeO_4	6.45	5.48	5.05	0.790	(*52*)
Li_2FeGeO_4	6.41	5.44	5.01	0.790	(*52*)
Li_2CoGeO_4	6.37	5.46	5.01	0.791	(*52*)
Li_2ZnGeO_4	6.36	5.43	5.02	0.795	(*52*)
Li_2CdGeO_4	6.64	5.47	5.13	0.792	(*52*)
Cu_2FeSiS_4	7.43	6.43	6.16	0.829	(*53*)
Cu_2ZnSiS_4	7.40	6.40	6.08	0.822	(*53*)
$Cu_2ZnSiSe_4$	7.80	6.70	6.46	0.832	(*53*)
Cu_2ZnGeS_4	7.47	6.45	6.12	0.820	(*53*)
Ag_2CdGeS_4	8.044	6.849	6.593	0.827	(*31*)

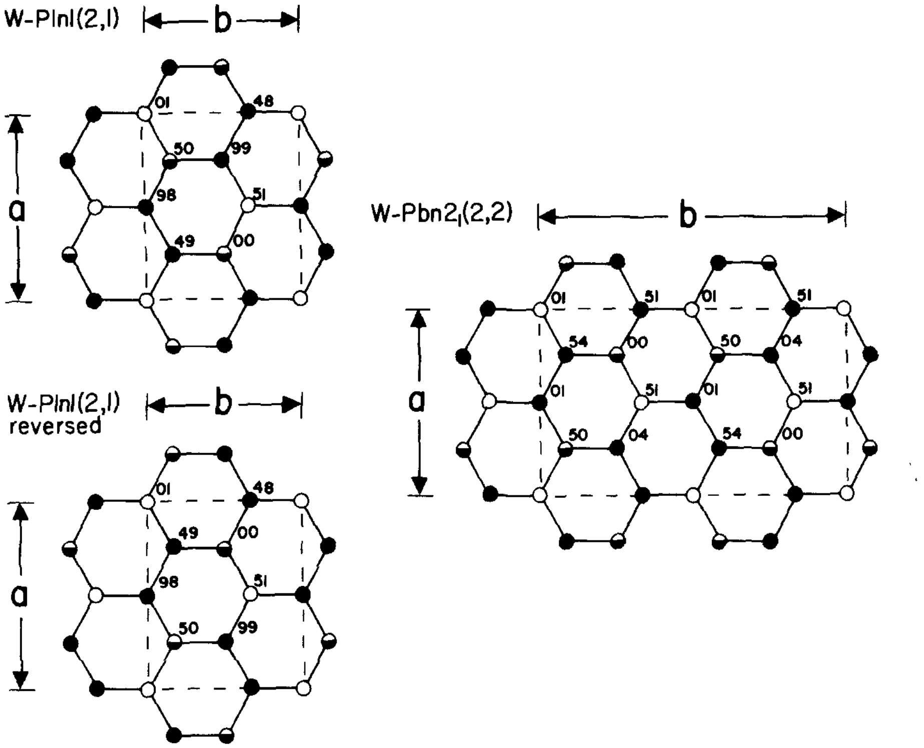

FIG. 2. Liberite type [W-$P1n1$(2,1)] shown in normal and reversed positions. The Li_2CoSiO_4 type [W-$Pbn2_1$(2,1)] shown as a twinning of the two liberite-type orientations. Open circles correspond to Si, solid circles to Li, half-filled circles to Be.

$Pmn2_1$(2,1) and the W-$P1n1$(2,1) types, it is expected that their lattice energies are similar.

W-$Pbn2_1$(2,2) or Li_2CoSiO_4 Type (ABC_2X_4)

An alternative way of reducing the symmetry of the W-$Pbn2_1$(2,1) type in order to accommodate a stoichiometry ABC_2X_4 is provided by a doubling of the b cell constant while retaining the space group. This arrangement is realized in Li_2CoSiO_4 (*34*). The right side of the unit cell in this W-$Pbn2_1$(2,2) type has the same pattern of distribution of mono-, di-, and tetravalent atoms as the liberite type (Table II). The left side of the unit cell of Li_2CoSiO_4 corresponds also to the liberite array, but in its reversed position. Therefore, the W-$Pbn2_1$(2,2) type can be described as an intimate twinning on unit cell scale of slices parallel (010) of the W-$P1n1$(2,1) type with the images of the same slices reflected normal to a. Obviously, the energetic differences between the two orientations must be small, which makes disorder between the two types possible. This is exactly what has been observed by Takaki and Yamaguchi (*58*), who describe one-dimensional disorder along b in Li_2CoSiO_4. Their detailed interpretation of diffuse X-ray reflections broadened along b^* involves disorder of half cells with $b' = b/2$. This is equivalent to saying that the disorder is between the liberite and the Li_2CoSiO_4 type.

In this structure type there are, as in the W-$Pbn2_1$(2,1) type, chains of univalent corner-sharing tetrahedra parallel to [001], but their relative orientation is different from the liberite type. The corresponding chains

TABLE VI

CELL EDGES (Å), ANGLES β (°), AND ϵ VALUES FOR WURTZITE TYPES W-$P1n1$(2,1) AND W-$P1n1$(2,2)

Compound	*a*	*b*	*c*	β	ϵ	Reference
			1. W-$P1n1$(2,1)			
Li_2BeSiO_4	6.104(5)	4.942(5)	4.698(5)	90.00(8)	0.796	(*49, 54*)
Li_2BeGeO_4	6.194(5)	5.064(5)	4.790(5)	90.25(8)	0.796	(*54*)
Li_2ZnGeO_4	6.40	5.45	5.04	90.2	0.794	(*48*)
Na_2CoSiO_4	7.07	5.46	5.22	90.0	0.781	(*55*)
Na_2ZnSiO_4	7.025	5.445	5.248	89.77	0.788	(*56*)
Na_2MgGeO_4	7.15	5.60	5.35	90.0	0.786	(*57*)
Na_2CoGeO_4	7.12	5.56	5.28	90.0	0.775	(*55*)
Na_2ZnGeO_4	7.17	5.56	5.32	90.0	0.783	(*57*)
			2. W-$P1n1$(2,2)			
Na_2MgSiO_4	7.015(2)	10.968(2)	5.260(1)	89.97(1)	0.788	(*51*)

parallel [010] are also present, but they are more kinked than in the liberite type. Presently, no other well-documented representative of this type is known.

W-$Pbc2_1$(2,1) or α-LiSiON Type (ABXY)

An ABX_2 compound in space group $Pbc2_1$ in a (2,1) cell would not obey Pauling's postulate [the values of p(O) would be 1.5 and 2.5 v.u. for an oxide like $NaFeO_2$]. However, for a composition such as Li SiON, there is a better agreement between the sum of bond strengths and the formal charge, even though it is not perfect. The value of $p(N)$ is 3.25 v.u., while the value of p(O) is 1.75 v.u. It is arithmetically impossible to obtain a valence-balanced arrangement for the composition LiSiON in a tetrahedral structure. However, the compound exists, and its structure has been recently determined (*33*). This shows us that hypothetical structures, which are unlikely for compounds with one anion, can, nevertheless, occur for compositions including anions with differing formal charges, if these formal charges approximately balance the $p(X)$ received. Furthermore, it demonstrates that while Pauling's rules are a very useful guide, they are not infallible. It has previously been shown (*11*) that the $p(X)$ received by anions can deviate from Pauling's postulate even in stable structures, provided the bond lengths are shortened in case of underbonding [$p(X) < -$charge of X] and lengthened in case of overbonding [$p(X) > -$charge of X]. In accordance with that, the Si–O bond length in α-Li SiON is significantly shorter than the expected value. Two more recently synthesized compounds, ZnAlON and MgAlON, also probably belong to this type (*93*). The values of p(O) and p(N) would be 2.25 and 2.75 v.u., respectively, in these compounds.

A second, high-temperature polymorph with a (3,1) cell has been reported for Li SiON. The space group of this β-LiSiON modification is not known, but it is likely to be of lower symmetry than the most common space group ($Cmc2_1$) of the (3,1) compounds listed in Tables III and IV. Only if it has a lower symmetry can all the O and N atoms be ordered over separate sets of equivalent sites. Inspection of all possible ordered LiSiON structures with (3,1) cells shows, however, that no such structure satisfies Pauling's postulate as well as LiSiON(LT). In particular all such structures have some anion sites with $p(X) = 2.5$ v.u. Because the valence sum mismatch is equal for O and N atoms in these sites the possibility of a disordered structure cannot be ruled out.

W-Cmc2$_1$*(3,1) or* Na_2SiO_3 *Type* (AB_2X_3, $A_2\square X_2Y$, $A_2\square X_3$)

The structures of this type give a second example of the possibility of $p(X)$ deviations in stable structures. Of the four different bond strength distributions observed (Table VII), only one results in valence-balanced anions ($Si_2\square N_2O$). This is similar to the case of α-LiSiON, where the presence of two different anions also enhances the valence balance. In the other cases of the W-*Cmc*2$_1$(3,1) type, the bond lengths are appropriately distorted, thus achieving an effective valence balance and the compounds are stable despite their failure to comply with Pauling's original postulate. Of interest is the difference in bond strength distributions between Li_2SiO_3 and Na_2SiO_3 (Table VII). The sodium atoms have moved in Na_2SiO_3 into the base of the tetrahedron, thus forming a trigonal bipyramidal five coordination. This change in coordination improves the p(O) distribution in Na_2SiO_3 as compared with Li_2SiO_3, where the smaller Li atom stays in four coordination.

TABLE VII

SUMS OF BOND STRENGTHS, $p(X)$, AT ANION SITES IN COMPOUNDS OF W-*Cmc*2$_1$(3,1) TYPE (IN VALENCE UNITS)

Compound	Anion	Bond strength	$p(X)$
Li_2SiO_3	O(1)	$3 \times \frac{1}{4} + \frac{4}{4}$	1.75
	O(2)	$2 \times \frac{1}{4} + 2 \times \frac{4}{4}$	2.50
Na_2SiO_3	O(1)	$4 \times \frac{1}{5} + \frac{4}{4}$	1.80
	O(2)	$2 \times \frac{1}{5} + 2 \times \frac{4}{4}$	2.40
Si_2LiN_3	N(1)	$3 \times \frac{4}{4} + \frac{1}{4}$	3.25
	N(2)	$2 \times \frac{4}{4} + 2 \times \frac{1}{4}$	2.50
$B_2\square O_3$	O(1)	$3 \times \frac{3}{4}$	2.25
	O(2)	$2 \times \frac{3}{4}$	1.50
$Si_2\square N_2O$	N	$3 \times \frac{4}{4}$	3.00
	O	$2 \times \frac{4}{4}$	2.00

There are two crystallographically distinct cation sites in this structure: *A* and *B*. Cations *A* form chains parallel [001] (SiO_3, GeO_3, SiS_3, LiN_3), while cations *B* form layers of tetrahedra parallel (100). These layers have a different geometry and symmetry from the layers present in the W-*Pmn*2$_1$(2,1) type. There is a *b* glide parallel to the layers in their center. The compositions of these layers are NaO_2 (in Na_2SiO_3), SiN_2 (in $LiSi_2N_3$), SiNO (in Si_2N_2O), or BO_2 (in B_2O_3).

W-Cc(3,1) or Ga_2S_3 *Type* ($A_2\square X_3$)

Closely related to the W-*Cmc*2$_1$(3,1) type are the structures of $Ga_2\square S_3$ and $Al_2\square Se_3$ of W-*Cc*(3,1) type. They are true wurtzite derivatives, since the tetrahedra all have the same orientation. The two types differ in their arrangement of vacancies. The layers present in the Na_2SiO_3 type are not observed in the Ga_2S_3 type.

W-P1n1(2,2) or Na_2MgSiO_4 *Type* (ABC_2X_4)

The wurtzite derivative with the lowest symmetry has been observed for Na_2MgSiO_4 (*51*). The topology of this structure is identical to the liberite type, but the *b* axis is doubled compared to it. Complete ordering would be possible in the (2,1) cell. There is no obvious reason why *b* should double. The superstructure with the doubled edge may be due to an ordering of the Na vacancies caused by the small OH content of Na_2MgSiO_4.

Dipolar Tetrahedral Structures

The crystal structure of olivine, Mg_2SiO_4, was determined by Bragg and Brown (*59*) on the basis of the similarity of its packing of oxygen atoms to a hexagonal closest packing. The Mg atoms in olivine occupy the octahedral interstices of this packing; therefore, most of the tetrahedral sites cannot be populated in order to avoid face sharing of polyhedra. The structure has a (2,2) cell with space group *Pmnb*, which is centric. Therefore, the orientation of the tetrahedral apices varies. In the left half-cell, both point up; in the right half-cell, both point down.

The structure of the high-temperature form of Li_3PO_4 (*60, 61*) is closely related: it also has a (2,2) cell and the same space group as olivine itself. The PO_4 tetrahedra in HT-Li_3PO_4 are distributed as the SiO_4 tetrahedra are in olivine. However, the Li atoms here are in tetrahedral coordination. Since all the cations are tetrahedral, one can refer to this as a tetrahedral olivine type. There are several other structures closely related to the olivine types, which all crystallize in centric space groups, and, therefore, can be simply distinguished from the wurtzite types, which all have polar space groups. A common feature of them is the dipolar orientation of the coordination tetrahedra.

D-Pmnb(2,2) or HT-Li_3PO_4 Type [AB_3X_4, $A(B,C)_3X_4$, and Defect Structures]

In analogy to the symbol W used to indicate the wurtzite derivatives, the dipolar structures are labeled D. The projection parallel [001] of one half-cell of HT-Li_3PO_4 is identical to the projection parallel [001] of LT-Li_3PO_4. The difference lies in the heights *z* of the tetrahedral cations (Table II). Because some of the coordination tetrahedra are in up, and some in down, position, shared edges between some of the Li tetrahedra do occur. This could not happen in the wurtzite type proper. The up–down distribution does not affect the valence balancing. The HT-Li_3PO_4 type satisfies Pauling's postulate just as the LT-Li_3PO_4 type does. However, the shared tetrahedral edges cause some of the Li atoms to come relatively close to each other; thus, the lattice energy of the HT type is less advantageous than for the LT type (*8*). The sheets of coordination tetrahedra parallel (010) around the cations in the general position in the W-*Pmn*2_1(2,1) type are present in the D-*Pmnb*(2,2) type as well, except that now they are alternately composed of layers of up tetrahedra in the left half-cells and of down tetrahedra in the right half-cells. The connecting layers in between them, composed of the tetrahedra around the cations in special positions, are now mixed in a double sense, since their tetrahedra are now not only mixed chemically, but also mixed by containing up and down tetrahedra within the same layer.

The LT-Li_3PO_4 and HT-Li_3PO_4 structures can be related formally to each other in the same way as were the W-*P*1*n*1(2,1) and the W-*Pbn*2_1(2,2) types. The latter type was described as a unit cell scale twinning of the former with itself after a reflection in the *a* direction, which preserved the orientation of the tetrahedra. the D-*Pmnb*(2,2) type can be taken as a unit cell scale twinning of the W-*Pmn*2_1(2,1) type with itself after reflection in the *c* direction, which, of course, changes the orientation of the tetrahedra in a systematic fashion. The other difference is that the reflected layer is not a clean straight slice but is instead a corrugated sheet (Fig. 3).

The compounds crystallizing in this type are high-temperature Li_3PO_4, Li_3VO_4, Li_3CrO_4, and Li_3AsO_4 and a number of partly disordered Li silicates and germanates with divalent cations like Mg and Zn (Table VIII), some of which have high ionic conductivities. In these disordered structures Li and Zn (or Mg) occupy statistically sites corresponding to both the general eightfold and the special fourfold Li positions of HT-Li_3PO_4. The overall stoichiometry can range from $(A,B,C)_2CO_4$ to $(A,B)_{3.75}CO_4$, that is, from having fewer tetrahedral cations than necessary to fill 50% of the tetrahedral interstices (the number filled in all the ordered structures we have considered so far), to having more cations

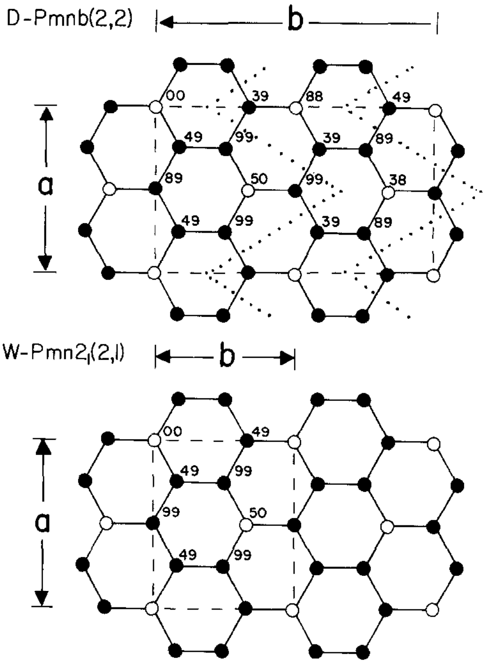

FIG. 3. The HT-Li_3PO_4 type]D-*Pmn*2_1(2,1)] as a twinning of corrugated sheets of the LT-Li_3PO_4 type [W-*Pmn*2_1(2,1)] after reversal in the *c* direction. Open circles correspond to P, solid circles to Li. Cations with $z \sim 0, \frac{1}{2}$ are in upward-pointing tetrahedra; those with $z \sim \frac{3}{8}, \frac{7}{8}$ point down.

than can be accommodated in tetrahedral coordination sites. In the latter case some of the cations have to move into octahedral interstices. This group includes solid electrolytes of the LiSiCON type (*75*). These can be formally understood to be solid solutions between the tetrahedral and the octahedral olivine types (*61*).

D-P$12_1/n1$*(2,2) or* Li_2ZnSiO_4 *Type (*ABC_2X_4 *and Defect Structures)*

A composition such as Li_2ZnSiO_4 could crystallize in the D-*Pmnb*(2,2) type if the Zn atoms would occupy the special Li(2) set of positions. Instead the Zn atoms are located in an ordered way in one-half of the original general eightfold set of D-*Pmnb*(2,2) thus breaking the *Pmnb* symmetry (*62*). The symmetry of space group $P2_1/m2_1/n2_1/b$ is reduced now to $P12_1/n1$. The mirror plane is lost, but otherwise the two types are identical (Table II). This is different from what happens when we go from Cu_3AsS_4 (enargite) to Cu_2CdGeS_4. There the Cd occupies the special Cu position and the W-*Pmn*2_1(2,1) type is maintained. This Zn substitution destroys the layers of Li coordination tetrahedra which can be identified in HT-Li_3PO_4. What remains are tetrahedral Li chains parallel [001]. The same structure is adopted by the low-temperature form of $Zn_{1.1}Li_{0.6}Si_{0.3}SiO_4$ (*63*).

D-P$112_1/b$*(2,2) or* Na_2BeSiO_4 *Type (*ABC_2X_4*)*

Formally this type can also be derived from the D-*Pmnb*(2,2) type. In this case we go from $P2_1/m2_1/n2_1/b$ to $P112_1/b$. However, in addition to removing the mirror plane by substituting Na(2) and Be in an ordered way into the general eightfold set of *Pmnb*, the up–down pattern is changed as well. One each of the substituting Be and Na atoms is flipped into down position in the left half-cell. Also, the pattern of the Si arrangement is different. Now in each half-cell they are pointing both ways (Table II). This structure is also different from the other types considered so far in having shared edges between tetrahedra occupied by the divalent Be ions. Furthermore, the geometry is distorted in such a way that the Na atoms have a tetrahedral coordination complemented by two additional oxygen atoms. This is the only known compound crystallizing in this type.

D-Pmcn(3,1) or Cubanite Type (AB_2X_3*)*

This type is related to the W-*Cmc*1_1(3,1) type. Part of the tetrahedra are flipped into the down position in such a way that three tetrahedra-wide slices of the structure parallel (100) alternate with three tetrahedra-wide slices in the up position. There are chains of Cu tetrahedra parallel [001], as there are chains of Si tetrahedra in

TABLE VIII

CELL EDGES (Å), ANGLES (°), AND ϵ VALUES OF DIPOLAR TETRAHEDRAL STRUCTURES

Compound	*a*	*b*	*c*	Angle	ϵ	Reference
1. D-*Pmnb*(2,2)						
Li_3PO_4	6.1147(5)	10.475(1)	4.9228(5)	90	0.810	(*60, 61, 69*)
Li_3VO_4	6.40	10.90	4.97	90	0.783	(*70*)
Li_3CrO_4	6.309	10.851	4.952	90	0.788	(*71*)
Li_3AsO_4	6.280	10.764	5.056	90	0.809	(*72*)
$Zn(Zn_{0.1}Li_{0.6}Si_{0.3})SiO_4$	6.406(3)	10.520(8)	5.043	90	0.808	(*63*)
Li_2MgGeO_4	6.224(3)	10.796(3)	5.123(3)	90	0.823	(*73*)
Li_2CaGeO_4	6.28(1)	10.85(1)	5.16(1)	90	0.823	(*73*)
Li_2FeGeO_4	6.28(1)	10.60(1)	5.10(1)	90	0.828	(*73*)
Li_2CoGeO_4	6.20(1)	10.85(1)	5.17(1)	90	0.830	(*73*)
Li_2NiGeO_4	6.17(1)	10.65(1)	5.11(1)	90	0.830	(*73*)
Li_2ZnGeO_4	6.26(1)	10.81(1)	5.14(1)	90	0.822	(*73*)
Li_2CdGeO_4	6.23(1)	10.90(1)	5.18(1)	90	0.827	(*73*)
$Li_3Zn_{0.5}GeO_4$	6.29	10.74	5.17	90	0.828	(*74*)
$Li_{3.5}Zn_{0.25}GeO_4$	6.25(1)	10.828(2)	5.140(1)	90	0.822	(*75*)
2. D-$P12_1/n1$(2,2)				β		
Li_2ZnSiO_4	6.262(3)	10.602(4)	5.021(4)	90.51(5)	0.811	(*62*)
$Zn(Zn_{0.1}Li_{0.6}Si_{0.3})SiO_4$	6.340(1)	10.516(2)	5.011(1)	90.50(2)	0.807	(*63*)
3. D-$P112_1/b$(2,2)				γ		
Na_2BeSiO_4	7.022(2)	9.933(3)	4.960(1)	90.03(2)	0.778	(*56*)
4. D-*Pmcn*(3,1)						
$CuFe_2S_3$	11.1201(8)	6.4679(5)	6.2336(4)	90	0.838	(*64, 76*)
$AgFe_2S_3$[a]	11.47	6.64	6.45	90	0.842	(*65*)
5. D-$P2_1/m11$(2,1)				α		
Li_4SiO_4	6.10	5.30	5.14	90.5	0.843	(*66*)
$Li_{3.75}Si_{0.75}P_{0.25}O_4$	6.1162(9)	5.3088(8)	5.1157(6)	90.40(1)	0.835	(*67*)
Li_4CoO_4	6.16	5.34	5.18	90.4	0.840	(*77*)
6. D-$P2_1/m11$(7×)				α		
Li_4SiO_4	6.090(2)	11.546(3)	16.645(3)	99.5(1)	0.843	(*68*)

[a] The reported space group is *Pmmn*.

Na_2SiO_3. There are also layers of Fe tetrahedra parallel (100), but they are different from the layers of Na tetrahedra in Na_2SiO_3, because in each layer half the Fe tetrahedra are flipped, resulting in shared edges between them. These shared edges are believed to be connected with the ferromagnetic properties of cubanite (*64*). Cubanite is the only structure known to crystallize in this type. Argentopyrite, $AgFe_2S_3$, has very similar cell constants, but apparently a different space group, *Pmmn* (*65*).

D-$P2_1/m11$(2,1) or Disordered Li_4SiO_4 Type (A_4BX_4 and Defect Structures)

The D-$P12_1/n1$(2,2) type retains the *n* glide of *Pmnb*, while the D-$P112_1/b$(2,2) type retains its *b* glide plane. Similarly, the D-$P2_1/m11$(2,1) type preserves the mirror normal to *a*. The analogy is incomplete, however, in two different but related ways: first the *b* cell edge in the D-$P2_1/m11(2,1)$ type is half as long as that in the D-$Pmnb(2,2)$ type, and second, some of the symmetry of this arrangement is only statistical. Most of the tetrahedra related by the mirror plane are too close to each other to be occupied simultaneously. The stoichiometry is such that some of the cations in Li_4SiO_4 (*66*) and in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (*67*) must occupy octahedral interstices. The solid solutions between Li_4SiO_4 and Li_3PO_4 are good ionic conductors, as are solid solutions of Li_4SiO_4 with Li_2SO_4, $LiAlO_2$, and Li_4GeO_4 (*78, 79, 80*).

D-$P2_1/m11(7x)$ or Ordered Li_4SiO_4 Type (A_4BX_4)

The true structure of the low-temperature form of Li_4SiO_4 is also monoclinic with space group $P2_1/m$, but has a unit cell with a volume seven times larger than the subcell of the D-$P2_1/m11(2,1)$ type (*68*). The disordered Li_4SiO_4 structure may be a quenched high-temperature form. In ordered Li_4SiO_4 there are no statistical occupations of closely adjoining sites. However, because of the stoichiometry of the compound, some of the Li atoms are in octahedral interstices. Ordered Li_4SiO_4 is not a good ionic conductor.

Discussion

Bärnighausen Tree

The relationships among the structure types presented above can be summarized concisely following Bärnighausen's procedure (*83*). One diagram (Fig. 4) contains the complete information on the group–subgroup connections and on the translational relations among the 15 structure types presented above. All of them can be formally derived from hexagonal closest packing. In this diagram the nomenclature and the definitions introduced by Bärnighausen are used. The symbol t signifies that both the subgroup U and the higher symmetric group G are lattice equivalent (translationengleich). The number after t (or k or e) indicates the index of the symmetry change, where the index of a subgroup U is the number of cosets of U in G. If G and U belong to the same crystal class the symbol k is used (for klassengleich). If G and U belong to the same space group type with a larger unit cell for U than for G the symbol e is employed to indicate that they are crystallographically equivalent. Thus e is a special case of k. Where necessary the unit cell transformations are given by listing the basis vectors of the unit cell of U as linear combinations of the basis vectors characterizing the unit cell of G. In all cases for which a representative structure has been observed the chemical composition of the first described example is given in a box (Fig. 4). Of the fourteen derivative tetrahedral types three are derived from the wurtzite type, one from an unobserved $C\ 2/m\ 2/c\ 2/m(3,1)$ structure type, and five from another hypothetical $P\ 2_1/m\ 2/n\ 2_1/m(2,1)$ type. Four types can be viewed as lower-symmetry derivatives of either wurtzite or the $P\,2_1/m\,2/n\,2_1/m$ type, while one derives from either wurtzite or the $C\ 2/m\ 2/c\ 2/m(3,1)$ type. The least symmetric of all the presently known derivatives is the W-$P1n1(2,2)$ type represented by Na_2MgSiO_4.

The most highly symmetrical structure in Fig. 4 is the hexagonally closest-packed arrangement. This maximum symmetry can be reduced either by ordered substitutions, where a vacancy is treated as an atomic species, or else by distortions of the geometry of the structure. The wurtzite type proper derives from hcp by an ordered distribution of tetrahedral cations and tetrahedral voids over the symmetrically equivalent tetrahedral sites of hcp. The $Cmc2_1(1,1)$ structure, which is simply the orthohexagonal equivalent of the W-$P6_3mc$

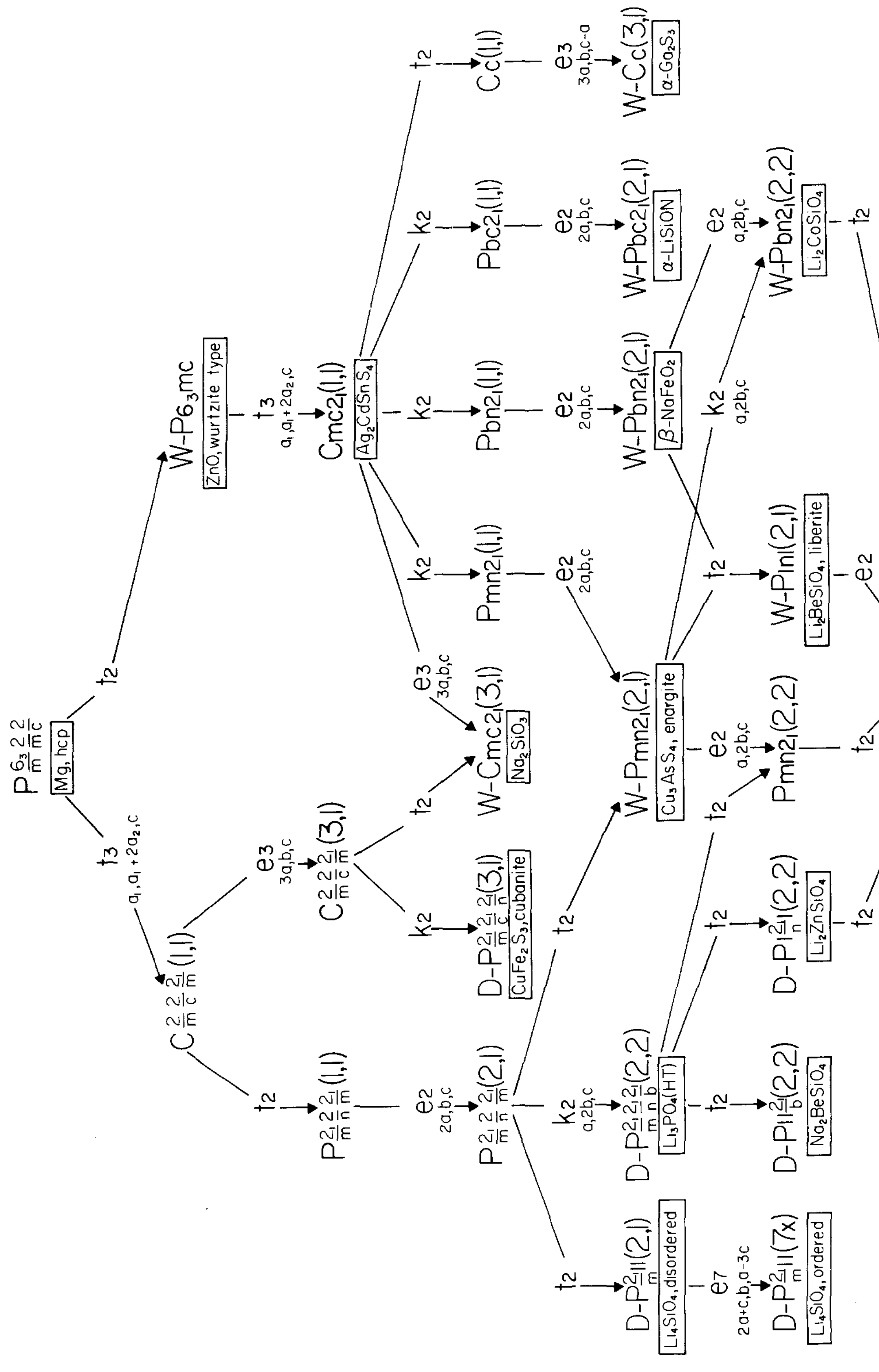

FIG. 4. Bärnighausen tree of all group–subgroup relationships between hcp, wurtzite type, and the fourteen presently known derivative structures.

type, can lower its symmetry to $Pmn2_1(1,1)$ by ordered substitution, or else to $Pbn2_1(1,1)$, $Pbc2_1(1,1)$, or $Cc(1,1)$ by distortion. The corresponding (2,1) cells can be obtained by ordered substitutions.

Disorder in Tetrahedral Structures

The common feature of all these structures is the hexagonally closest-packed arrangement of the anions. The actual symmetries of the derivatives are orthorhombic and monoclinic, however, their pseudohexagonal character surfaces in several ways. For one, it can confuse the investigator, because the diffraction patterns are pseudohexagonal as well. Second, the crystal growth can become confused, that is, disordered, because the energy differences between different stuffings of the hcp anion array must be slight. This can result in the development of twinning. Diffraction evidence for triplets around the pseudohexagonal axis has been observed for Cu_3AsS_4 (*28*), $AgFe_2S_3$ (*65*), $ZnAl_2S_4$ (*35*), and $BeSiN_2$ (*16*). Twinning by mirror planes and twofold axes is reported for LT-Li_3PO_4 (*24*), LT-Li_3VO_4 (*25*), β-Li_2BeSiO_4 (*54*), Li_2ZnSiO_4 (*62*), Na_2MgSiO_4 (*51*), and $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (*67*).

Another manifestation of this tendency to exhibit disorder is provided by statistical occupation of one site by two or three elements. A number of ternary and quaternary compounds have been reported with hexagonal symmetry or with space group $Cmc2_1$ in a (1,1) cell (Table IX). In the case of Al_2CO (*84*) it is C and O which occupy one site. This is the only instance among the compounds listed in Table IX where the random statistical occupation is supported by a single-crystal study. In all the other cases investigated so far by X-ray powder diffraction, study of single crystals, if they became available, might show that the true symmetry is lower. Several of the wurtzite derivatives discussed in the previous section were originally described as hexagonal.

Statistical occupations, however, are reported for related tetrahedral structures, which have been studied by single-crystal methods. Examples are provided exclusively by dipolar structures: Li_2MgGeO_4 (*73*), $Li_{0.6}Zn_{1.1}Si_{1.3}O_4$ (*63*), $Li_{3.5}Zn_{0.25}GeO_4$ (*75*), $Li_3Zn_{0.5}GeO_4$ (*74*), and $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (*67*). In most of these cases it is the Li atom which participates in the random occupation of a set of sites. Another kind of disorder was identified in single-

TABLE IX

CELL CONSTANTS (Å) AND ϵ VALUES OF WURTZITE-TYPE COMPOUNDS WITH APPARENTLY RANDOM OCCUPATION OF SETS OF SITES BY TWO OR THREE ELEMENTS

Compound	Space group	*a*	*b*	*c*	ϵ	Reference
Al_2CO	$P6_3mc$	3.17	—	5.06	0.798	(*84*)
$AgInS_2$	$P6_3mc$	4.121	—	6.674(5)	0.810	(*85*)
$CuCd_2AlSe_4$	$P6_3mc$	4.106(5)	—	6.752(5)	0.822	(*31*)
$CuCd_2InS_4$	$P6_3mc$	4.047(5)	—	6.617(5)	0.818	(*31*)
$AgZn_2AlS_4$	$P6_3mc$	3.846(5)	—	6.313(5)	0.821	(*31*)
$AgZn_2InS_4$	$P6_3mc$	3.944(5)	—	6.459(5)	0.819	(*31*)
$AgCd_2AlS_4$	$P6_3mc$	4.134(5)	—	6.723(5)	0.813	(*31*)
$AgCd_2GaSe_4$	$P6_3mc$	4.251(5)	—	6.956(5)	0.818	(*31*)
$AgCd_2InS_4$	$P6_3mc$	4.112(5)	—	6.709(5)	0.816	(*31*)
$AgCd_2InSe_4$	$P6_3mc$	4.277(5)	—	6.988(5)	0.817	(*31*)
Ag_2CdSnS_4	$Cmc2_1$	4.111(5)	7.038(5)	6.685(5)	0.818	(*31*)
$Ag_2CdSnSe_4$	$Cmc2_1$	4.262(5)	7.314(5)	6.979(5)	0.823	(*31*)

crystal studies of Li_4SiO_4 (*66*), $Li_{3.5}Zn_{0.25}GeO_4$ (*75*), $Li_3Zn_{0.25}GeO_4$ (*74*), and $Li_{3.75}Si_{0.75}P_{0.25}$ (*67*). It is the partial occupation of one or more sites by one atomic species (Li, in all these cases). It can be viewed formally as random occupation by atoms and vacancies. Such partial occupations by monovalent atoms often contribute to good ionic conductivity. Since Li_4SiO_4 itself is a relatively poor ionic conductor, this prompted a reinvestigation of its crystal structure (*68*).

Yet another kind of disorder manifests itself in diffuse diffraction peaks. One such case was discussed above when the disorder between the liberite and the W-$Pbn2_1(2,2)$ type of Li_2CoSiO_4 (*58*) was described. Here the disorder of the twinned components still maintains the polar wurtzite-type arrangement. In another example provided by Al_2CO the disordered components are reflected about a mirror normal to the hexagonal axis. This means that the disorder aims toward a dipolar arrangement, as observed, for instance, in cubanite (*64, 84*).

Superstructures

Some of the reported cases of random occupations and disorder might involve unrecognized instances of twinning or overlooked diffraction evidence for superstructures. Of course it can also happen that closely related phases can occur both in the disordered state and in lower-symmetry superstructures, as reported for Li_2CoSiO_4 (*34, 58*). This might also be true in the case of Li_4SiO_4 for which a substructure (*66*) and a superstructure (*68*) have been described, and it is unclear whether the two different groups of investigators studied really different or essentially similar samples. The superstructure of ordered Li_4SiO_4 is interesting as the only case in which a tetrahedral structure was determined with an increase in the multiplicity of the translation parallel to the pseudohexagonal axis. Idrestedt and Brosset (*43*) reported the occurrence of a (3,2,4) supercell of Si_2N_2O, but they did not determine its structure [the normal form, see Table IV, has a (3,1,1) cell]. We see that superstructures with multiplicities in the *c* direction are possible, but obviously they are rare.

Chemical Composition, Structure Type, and Ratio ϵ

Histograms of the ϵ values of tetrahedral compounds taken from Tables IV, V, VI, and VIII are plotted separately for wurtzite-type and dipolar oxides, nitrides, and sulfides. Added to it, for comparison, are the values of tetrahedral rutile close-packed structures (*7*), of lithiated transition metal rutile-type dioxides (*86*), and of Zn_2NF (*87*). For the confirmed wurtzite-type derivatives with oxygen anions the ϵ values range from 0.68 to 0.80. For the corresponding dipolar types the range is from 0.77 to 0.85, and for the oxidic tetrahedral rutile types it is from 0.82 to 0.88. The ϵ ratio thus discriminates cleanly between the oxides having the polar wurtzite-type structures and those with the tetrahedral rutile-type structures (that is, the superstructures of β-BeO). The dipolar types cluster in between and cannot be separated well from the other types.

The ϵ ratios of the tetrahedral rutile types are close to 0.860, which is the value for the ideal rutile close packing, and the ϵ ratios of the dipolar types are close to 0.817, that is, to the value for ideal hexagonal closest packing. There is no ready explanation for the fact that ϵ ratios of the wurtzite derivative oxides cluster around 0.79. The outliers among the wurtzite oxides, Na_2SiO_3 and Na_2GeO_3, however, can be correlated with the previously mentioned five coordination of Na in these compounds. The discussions of the *c*/*a* ratios in hexagonal binary wurtzites as given by Fleet (*9*), O'Keeffe and Hyde (*6*), and Burdett (*88*) are not applicable to the case of ternary and quaternary compounds which are displayed in Fig. 5. The trend, according to chemistry (that is, as a function of the anion being O, N, or S, which is shown by the wurtzite derivatives), is not observed for the binary hexagonal wurtzites entered for comparison in Fig. 5.

This diagram can be used to make tentative assignments of compounds to the different classes on the basis of known ϵ ratios. It appears that the oxides and sulfides listed in Table V are wurtzite-type derivatives, even though we do not know the space groups in which they crystallize. Furthermore, the lithiated rutile-type oxides prepared by Murphy *et al.* (*86*) are likely to contain tetrahedrally coordinated Li. Since NF is on average isoelectronic with O_2, it is appropriate to plot it with the oxides. Marchand and Lang (*87*) already recognized the similarity of the β-Zn_2NF prepared by them with γ-$LiAlO_2$, which crystallizes in a tetrahedral rutile structure. The ϵ ratio of β-Zn_2NF is 0.881. Since α-Zn_2NF, also prepared by them, has an ϵ value of 0.866, it likewise should belong to the tetrahedral rutile type.

Computer Simulation of Hypothetical Structures

Comparative studies of observed and corresponding hypothetical structures can help in deriving selection rules for stable structures, that is, in establishing crystal chemical principles. The geometric factors influencing structural arrangements can be explored by computer simulation of the observed and hypothetical structures. The

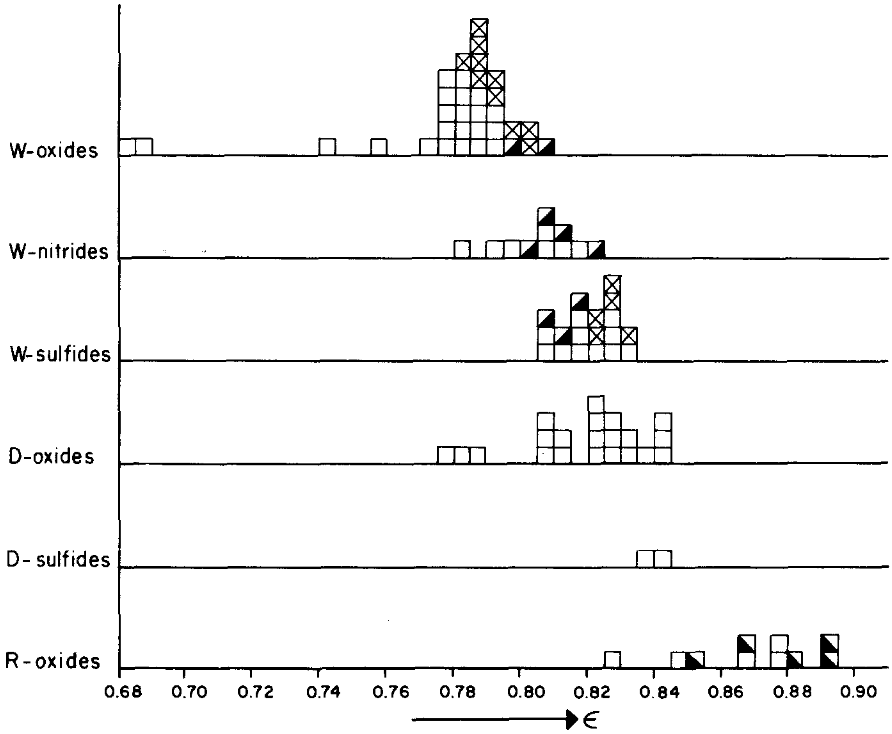

FIG. 5. Histogram of ϵ values of tetrahedral compounds of oxides, nitrides, and sulfides of the wurtzite type (W), the dipolar type (D), and the rutile-related type (R). Open squares correspond to confirmed derivative tetrahedral compounds, and apparent wurtzite types from Table V are identified by crossed squares. Wurtzite-type structures proper (*AB* compounds) are denoted by lower-right half-filled squares. Apparent tetrahedral rutile types are shown as lower-left half-filled squares.

method has been described by Baur (*89*), and an application to observed and hypothetical forms of Mg_2SiO_4 was given previously (*90*). In the simulations described below we used as observations the cation–anion distances [taken from effective ionic radii (*91*)], the edges of the anion coordination tetrahedra (calculated for ideal tetrahedra from the cation–anion distances), and the mean cation–cation distances appropriate for the volume of the unit cell. As weights we took the Pauling bond strengths (*10*) for the cation–anion distances, while the weights of the anion–anion and the cation–cation distances were chosen uniformly as 0.07 (*89*).

A simulation of $NaFeO_2$ in the observed W-$Pbn2_1(2,1)$ type and in the hypothetical W-$Pmc2_1(1,1)$ structure showed that in the hypothetical arrangement the coordination tetrahedra are severely distorted around Na and Fe. The largest angle O–Fe–O measured 144°, and the smallest angle O–Na–O is 100°. Both cation polyhedra have an identical tetrahedral edge length, corresponding to the length of the cell edge *a*. The point is that the W-$Pbn2_1(2,1)$ structure allows an alternation of Na and Fe along the *a* direction. In a (1,1) structure with half the *a* cell edge length the dimension of the chains of tetrahedra around Fe and Na must be equal in the [100] direction, even though the cations are of very different size (Fig. 1). This is apparently the reason why the smallest unit cells of the derivative tetrahedral structures are of a (2,1) type and not of the (1,1) size. If the W-$Pmc2_1(1,1)$ structure is found in nature, it would have to be for a chemical composition in which the different cations are of similar size. An obvious candidate would be a polymorph of $BeSiN_2$. The known structure of $BeSiN_2$ is isostructural with $NaFeO_2$ (*16*). Because of this size constraint it is unlikely that many of the other hypothetical (1,1) structures listed in Fig. 4 will be found.

Li_2BeSiO_4 crystallizes in the W-$P1n1(2,1)$ type. Theoretically it might crystallize just as well in the W-$Pmn2_1(2,1)$ type the way Cu_2CdSiS_4 does. A simulation of Li_2BeSiO_4 in the $Pmn2_1$ structure shows that both the BeO_4 and the SiO_4 tetrahedra would be strongly distorted there with O–Be–O and O–Si–O angles of about 136°, that is, they would be similar to the FeO_4 tetrahedra in the $Pmc2_1$ structure. The reasons for these distortions are analogous in both cases. If Li_2BeSiO_4 were to crystallize in the W-$Pmn2_1(2,1)$ type there would be chains of Be–Si tetrahedra parallel to chains of Li–Li coordination tetrahedra in the [100] direction. In the W-$P1n1(2,1)$ type we observe instead chains of Si–Li and Be–Li tetrahedra, which have a good dimensional fit to each other. Since the length of a tetrahedral edge is $(8/3)^{1/2}$ times the cation–anion distance, we can calculate the dimensions of various chains easily from the known effective ionic radii (*91, 92*). All but one of the ABC_2X_4 compounds of the W-$Pmn2_1(2,1)$ and W-$P1n1$ types listed in Tables IV and VI crystallize in the structure type which has the better dimensional fit (Table X). The exception is Li_2ZnGeO_4, where, however, the ratios between the dimensions of the short over the longer chains are very close to each other. Among the unassigned compounds listed in Table V there are nine for which the chain length ratios are similar for both structure types. For six of them, however, a clear choice on the basis of this ratio can be made (Table X).

Conclusion

The number of observed wurtzite derivatives and related dipolar tetrahedral structures is minute compared with the numbers enumerated in the preceding paper (*8*). Since five of the fourteen derivative types have been described in the last three years, it can be expected that additional related structures will be characterized in the future. The discrepancy between realized

TABLE X

Calculated Chain Dimensions (in Å) for Alternative Tetrahedral Chains in W-$Pmn2_1$(2,1) and W-$P1n1$ Types of ABC_2X_4 Compounds

Compound	AB chain	C_2 chain	Ratio	AC chain	BC chain	Ratio	Observed space group
$SiCdCu_2S_4$	7.62	7.63	0.964	7.28	7.96	0.915	$Pmn2_1$
$GeCdCu_2S_4$	7.76	7.63	0.983	7.42	7.96	0.932	$Pmn2_1$
$GeMnCu_2S_4$	7.57	7.63	0.992	7.42	7.77	0.955	$Pmn2_1$
$SiBeLi_2O_4$	5.37	6.43	0.835	5.90	5.91	0.998	Pn
$BeGeLi_2O_4$	5.59	6.43	0.869	5.91	6.11	0.967	Pn
$GeZnLi_2O_4$	6.12	6.43	0.952	6.11	6.45	0.947	Pn
$SiCoNa_2O_4$	5.88	7.74	0.760	6.55	7.07	0.926	Pn
$SiZnNa_2O_4$	5.91	7.74	0.764	6.55	7.10	0.923	Pn
$GeMgNa_2O_4$	6.08	7.74	0.786	6.76	7.06	0.958	Pn
$GeCoNa_2O_4$	6.09	7.74	0.787	6.76	7.07	0.956	Pn
$GeZnNa_2O_4$	6.12	7.74	0.791	6.76	7.10	0.952	Pn
$SiMgNa_2O_4$	5.86	7.74	0.757	6.55	7.06	0.928	Pn
							Proposed space group
$SiFeLi_2O_4$	5.96	6.43	0.927	5.90	6.50	0.908	$Pmn2_1$
$SiCdLi_2O_4$	6.21	6.43	0.966	5.90	6.74	0.875	$Pmn2_1$
$GeMnLi_2O_4$	6.22	6.43	0.967	6.11	6.55	0.933	$Pmn2_1$
$GeFeLi_2O_4$	6.17	6.43	0.960	6.11	6.50	0.940	$Pmn2_1$
$GeCdLi_2O_4$	6.42	6.43	0.998	6.11	6.74	0.907	$Pmn2_1$
$GeCdAg_2S_4$	7.76	8.56	0.907	7.89	8.43	0.936	Pn

structures and hypothetical structures will not be affected materially by such new observations. The ratio between observed and hypothetical types can be improved, however, by reducing the numbers of hypothetical structures by the application of empirical crystal chemical rules. Examples of this are Pauling's bond strength rule [see Li_3PO_4 in (*8*)] or the dimensional fit discussed above for the wurtzite derivatives. The hypothetical structures remaining after the chemically implausible examples have been removed are good candidates for further theoretical studies employing electrostatic energy calculations, computer simulations, EHMO, or other quantum chemical approaches.

Acknowledgments

We thank the National Science Foundation (DMR80-19017 and DMR80-19741) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and the Computer Center of the University of Illinois for computer time. We thank R. D. Shannon for an advance copy of Ref. (*92*).

References

1. W. H. Bragg and W. L. Bragg, "X Rays and Crystal Structure," Bell, London (1915).
2. E. Parthé, "Cristallochimie des structures tétraédriques," Gordon & Breach, Paris (1972).
3. A. R. West and F. P. Glasser, *J. Solid State Chem.* **4,** 20 (1972).
4. A. R. West, *Z. Kristallogr.* **141,** 422 (1975).
5. M. O'Keeffe and B. G. Hyde, *Acta Crystallogr. Sect. B* **32,** 2923 (1976).
6. M. O'Keeffe and B. G. Hyde, *Acta Crystallogr. Sect. B* **34,** 3519 (1978).
7. W. H. Baur, *Mater. Res. Bull.* **16,** 339 (1981).
8. T. J. McLarnan and W. H. Baur, *J. Solid State Chem.* **42,** 283 (1982).
9. M. E. Fleet, *Mater. Res. Bull.* **11,** 1179 (1976).
10. L. Pauling, "The Nature of the Chemical

Bond," 3rd ed., Chap. 13, Cornell Univ. Press, Ithaca, New York (1960).

11. W. H. Baur, *Trans. Amer. Crystallogr. Assoc.* **6,** 129 (1970).
12. F. Bertaut and P. Blum, *C. R. Acad. Sci. Paris* **239,** 429 (1954).
13. M. Marezio, *Acta Crystallogr.* **18,** 481 (1965).
14. J. Thery, A.-M. Lejus, D. Briançon, and R. Collongues, *Bull. Soc. Chim. Fr.,* 973 (1961).
15. E. Vielhaber and R. Hoppe, *Z. Anorg. Allg. Chem.* **369,** 14 (1969).
16. P. Eckerlin, *Z. Anorg. Allg. Chem.* **353,** 225 (1967).
17. M. Wintenberger, F. Tcheou, J. David, and J. Lang, *Z. Naturforsch.* B **35,** 604 (1980).
18. J. David, Y. Laurent, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **93,** 153 (1970).
19. M. Wintenberger, R. Marchand, and M. Maunaye, *Solid State Commun.* **21,** 733 (1977).
20. M. Maunaye, R. Marchand, J. Guyader, Y. Laurent, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **94,** 561 (1971).
21. M. Wintenberger, J. Guyader, and M. Maunaye, *Solid State Commun.* **11,** 1485 (1972).
22. M. Wintenberger, M. Maunaye, and Y. Laurent, *Mater. Res. Bull.* **8,** 1049 (1973).
23. R. Hoppe, *Chem. Zvesti* **19,** 172 (1965).
24. C. Keffer, A. Mighell, F. Mauer, H. Swanson, and S. Block, *Inorg. Chem.* **6,** 119 (1967).
25. R. D. Shannon and C. Calvo, *J. Solid State Chem.* **6,** 538 (1973).
26. P. Tarte, *J. Inorg. Nucl. Chem.* **29,** 915 (1967).
27. A. Ferrari and L. Cavalca, *Gazz. Chim. Ital.* **78,** 283 (1948).
28. L. Pauling and S. Weinbaum, *Z. Kristallogr.* **88,** 48 (1934).
29. G. Adiwidjaja and J. Löhn, *Acta Crystallogr. Sect. B* **26,** 1878 (1970).
30. G. Chapuis and A. Niggli, *Naturwissenschaften* **55,** 441 (1968).
31. E. Parthé, K. Yvon, and R. H. Deitch, *Acta Crystallogr. Sect. B* **25,** 1164 (1969).
32. J. Allemand and M. Wintenberger, *Bull. Soc. Fr. Mineral Cristallogr.* **93,** 14 (1970).
33. Y. Laurent, F. F. Grekov, J. David, and J. Guyader, *Ann. Chim. Fr.* **5,** 647 (1980).
34. H. Yamaguchi, K. Akatsuka, M. Setoguchi, and Y. Takaki, *Acta Crystallogr. Sect. B* **35,** 2680 (1979).
35. G. A. Steigmann, *Acta Crystallogr.* **23,** 142 (1967).
36. H. Völlenkle, *Z. Kristallogr.* **154,** 77 (1981).
37. A. Grund and M. Pizy, *Acta Crystallogr.* **5,** 837 (1952).
38. W. S. McDonald and D. W. J. Cruickshank, *Acta Crystallogr.* **22,** 37 (1967).
39. D. W. J. Cruickshank, A. Kálman, and J. S. Stephens, *Acta Crystallogr. Sect. B* **34,** 1333 (1978).
40. E. Parthé and J. Garin, *Monatsh. Chem.* **102,** 1197 (1971).
41. C. T. Prewitt and R. D. Shannon, *Acta Crystallogr. Sect. B* **24,** 869 (1968).
42. J. David, Y. Laurent, J.-P. Charlot, and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.* **96,** 21 (1973).
43. I. Idrestedt and C. Brosset, *Acta Chem. Scand.* **18,** 1879 (1964).
44. J. D. Jorgensen, S. R. Srinivasa, J. C. Labbe, and G. Roult, *Acta Crystallogr. Sect. B* **35,** 141 (1979).
45. F. F. Grekov, J. David, J. Guyader, and J. Lang, *C.R. Acad. Sci. Paris Ser. C* **286,** 373 (1978).
46. J. Goodyear and G. A. Steigmann, *Acta Crystallogr.* **16,** 946 (1963).
47. G. A. Steigmann and J. Goodyear, *Acta Crystallogr.* **20,** 617 (1966).
48. E. Plattner, H. Völlenkle, and A. Wittmann, *Monatsh. Chem.* **107,** 921 (1976).
49. H.-C. Chang, *Acta Geol. Sin.* **46,** 76 (1966).
50. R. D. Shannon, *Phys. Chem. Mineral.* **4,** 139 (1979).
51. W. H. Baur, T. Ohta, and R. D. Shannon, *Acta Crystallogr. Sect. B* **37,** 1483 (1981).
52. P. Tarte and R. Cahay, *C.R. Acad. Sci. Paris Ser. C* **271,** 777 (1970).
53. R. Nitsche, D. F. Sargent, and P. Wild, *J. Cryst. Growth* **1,** 52 (1967).
54. A. R. West, *Bull. Soc. Fr. Mineral Cristallogr.* **98,** 6 (1975).
55. M. Wintenberger, *C.R. Acad. Sci. Paris Ser. B* **271,** 669 (1970).
56. G. F. Plakhov and N. V. Belov, *Sov. Phys. Crystallogr.* **24,** 674 (1979).
57. C. A. Joubert-Bettan, R. Lachenal, E. F. Bertaut, and E. Parthé, *J. Solid State Chem.* **1,** 1 (1969).
58. Y. Takaki and H. Yamaguchi, *Acta Crystallogr. Sect. B* **36,** 234 (1980).
59. W. L. Bragg and G. B. Brown, *Z. Kristallogr.* **63,** 528 (1926).
60. J. Zemann, *Acta Crystallogr.* **13,** 863 (1960).
61. W. H. Baur, *Inorg. Nucl. Chem. Lett.* **16,** 525 (1980).
62. H. Yamaguchi, K. Akatsuka, and M. Setoguchi, *Acta Crystallogr. Sect. B* **35,** 2678 (1979).
63. S.-C. Yu, D. K. Smith, and S. B. Austerman, *Amer. Mineral.* **63,** 1241 (1978).
64. M. J. Buerger, *Amer. Mineral.* **32,** 415 (1947).
65. J. Murdoch and L. G. Berry, *Amer. Mineral.* **39,** 475 (1954).

66. H. Völlenkle, A. Wittmann, and H. Nowotny, *Monatsh. Chem.* **99,** 1360 (1968).
67. W. H. Baur and T. Ohta, *J. Solid State Chem.*, in press (1982).
68. D. Tranqui, R. D. Shannon, H.-Y. Chen, S. Iijima, and W. H. Baur, *Acta Crystallogr. Sect. B* **35,** 2479 (1979).
69. H. E. Swanson, M. C. Morris, E. H. Evans, and L. Ulmer, National Bureau of Standards Monograph 25, Sect. 3, 39 (1964).
70. G. Blasse, *Z. Anorg. Allg. Chem.* **331,** 44 (1964).
71. G. Meyer, D. Paus, and R. Hoppe, *Z. Anorg. Allg. Chem.* **408,** 15 (1974).
72. P. Tarte, *J. Inorg. Nucl. Chem.* **29,** 915 (1967).
73. B. Monnaye, *Rev. Chim. Mineral.* **13,** 422 (1976).
74. E. Plattner and H. Völlenkle, *Monatsh. Chem.* **110,** 693 (1979).
75. H. Y.-P. Hong, *Mater. Res. Bull.* **13,** 117 (1978).
76. M. E. Fleet, *Z. Kristallogr.* **132,** 276 (1970).
77. M. Jansen and R. Hoppe, *Naturwissenschaften* **60,** 104 (1973).
78. R. D. Shannon, B. E. Taylor, A. D. English, and T. Berzins, *Electrochim. Acta* **22,** 783 (1977).
79. I. M. Hodge, M. D. Ingram, and A. R. West, *J. Amer. Ceram. Soc.* **59,** 360 (1976).
80. Y-W. Hu, I. D. Raistrick, and R. A. Huggins, *J. Electrochem. Soc.* **124,** 1240 (1977).
81. E. E. Hellstrom and R. A. Huggins, *Mater. Res. Bull.* **14,** 881 (1979).
82. G. Collin, J. Flahaut, M. Guittard, and A.-M. Loireau-Lozach, *Mater. Res. Bull.* **11,** 285 (1976).
83. H. Bärnighausen, *Match,* No. 9, 139 (1980).
84. E. L. Amma and G. A. Jeffrey, *J. Chem. Phys.* **34,** 252 (1961).
85. H. Hahn, G. Frank, W. Klingler, A.-D. Meyer, and G. Störger, *Z. Anorg. Allg. Chem.* **271,** 153 (1953).
86. D. W. Murphy, F. J. DiSalvo, J. N. Carides, and J. V. Waszczak, *Mater. Res. Bull.* **13,** 395 (1978).
87. R. Marchand and J. Lang, *Mater. Res. Bull.* **6,** 845 (1971).
88. J. K. Burdett, *J. Amer. Chem. Soc.* **102,** 450 (1980).
89. W. H. Baur, *Phys. Chem. Mineral.* **2,** 3 (1977).
90. W. H. Baur, *Amer. Mineral.* **57,** 709 (1972).
91. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
92. R. D. Shannon, *in* "Structure and Bonding in Crystals" (M. O'Keeffe and A. Navrotsky, Eds.), Academic Press, New York (1981).
93. M. O'Keeffe, C. L. Shavers, and B. G. Hyde, *J. Solid State Chem.* **39,** 265 (1981).