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Enumeration of Wurtzite Derivatives and Related Dipolar Tetrahedral Structures

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Pólya's theorem and related results are used to count and classify by space group all possible wurtzite derivatives with small unit cells having composition ABX_2, AB_2X_3, AB_3X_4, or ABC_2X_4. The same arguments are applied to the *dipolar tetrahedral* structures, which resemble wurtzite but have a different pattern of occupancy of the tetrahedral voids in the hcp anion framework. Covalent molecular orbital and electrostatic calculations are used to study the two real and eight hypothetical structures for Li_3PO_4. Both predict shared edges to be destabilizing, in keeping with Pauling's rules.

Introduction

A large part of crystal chemistry is devoted to the study of variations on a small number of structural themes. One such simple type underlying numerous more complex structures is that of wurtzite, the two-layer hexagonal polytype of ZnS. This well-known structure type, first determined for ZnO by the Braggs (*1*), is based on a hexagonal closest packing of anions in which cations occupy half the tetrahedral voids, all those pointing in the $+c$ direction. The simple, symmetrical wurtzite arrangement gives rise to other structure types in a number of ways. The hcp framework may be replaced by a close packing with a longer c repeat, as found in more than 160 observed polytypes of ZnS itself, and in a similar number of polytypes (often different from those of ZnS) in the isostructural compound SiC (*2*). A systematic enumeration of hypothetical polytypes is given in Ref. (*3*). Alternatively, in the wurtzite derivatives proper, the stacking sequence is left intact but two or more species of atoms are ordered over the cation, anion, or both positions. In some cases this ordering may be accompanied by a shift in the pattern of occupancy of the tetrahedral holes in the anion packing to produce *dipolar tetrahedral* structures having some occupied tetrahedra pointing up and some pointing down. Then there are shared edges between occupied tetrahedra.

In this paper we present a systematic enumeration of possible hypothetical wurtzite derivatives and dipolar tetrahedral structures with a variety of unit cells and compositions. We also make some remarks about how these lists, coupled with some theoretical calculations and some knowl-

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edge of which structures are observed, enable us to say something about bonding in these compounds. The companion paper (*4*) is a discussion of all structure types in the families which have so far been observed, with a particular emphasis on the geometric factors which may stabilize some of these types.

Counting Methods

The problem of enumerating geometrically possible wurtzite derivative and dipolar tetrahedral structures is very similar to one treated earlier by one of us (*5*) involving MX_2 structures with the X atoms hexagonally close-packed and the M atoms octahedrally coordinated. The resolution of this problem used some general counting principles which have found application in a number of other problems in crystallography involving structure enumeration. These have included questions concerning the alkali sulfates and calcium orthosilicates (*6*), fluorite derivatives (*7*), $LiFeO_2$ (*8*), polytypic materials (*3, 9, 10*), and distortions of the rock salt and CaC_2 types (*11–13*). A review of the methods employed in these investigations is contained in Ref. (*14*).

The basic strategy in answering all these questions is to phrase them as problems involving colorings of a set under the action of a group. The classic example of such a problem—and one of the simplest—is to count the number of ways to color the four vertices of a square using two colors, black and white. Any coloring is regarded as identical with every other coloring produced from it by the action of the symmetry operations in the square's two-dimensional point group $4m$. The classes of equivalent colorings are called patterns. Thus, a coloring and any of its images under rotations or reflections represent the same pattern. It is easy to see that in this case there are six patterns.

A general way to arrive at this result is provided by Pólya's theorem (*9, 15–17*). This theorem associates with every element of the symmetry group $4m$ a monomial called the cycle structure. The cycle structure of a four-fold rotation is x_4^1, since it permutes the four vertices in one cycle of length 4. A mirror passing through the midpoints of two opposite sides has cycle structure x_2^2, since it possesses two cycles of length 2; while the mirror passing through two opposite vertices has two cycles of length 1 and one cycle of length 2, and so has cycle structure $x_1^2x_2^1$. The identity, with four cycles of length 1, has cycle structure x_1^4. In general, a symmetry operation with c_i cycles of length i, $1 \leqq i \leqq n$, has cycle structure $x_1^{c_1}x_2^{c_2} \ldots x_n^{c_n}$. The cycle index polynomial is the average of the cycle structures of all the elements of the group. In the case of the square, the cycle index is $Z(4m; x_1, x_2, \ldots) = \frac{1}{8}\{x_1^4 + 2x_1^2x_2 + 3x_2^2 + 2x_4\}$.

Pólya's theorem now says that the number of patterns is the value of the cycle index if each variable x_i is given a value equal to the number of colors. For colorings of the vertices of a square using two colors, the number of patterns is $Z(4m; 2, 2, \ldots) = \frac{1}{8}\{2^4 + 2 \cdot 2^2 \cdot 2 + 3 \cdot 2^2 + 2 \cdot 2\} = 6$.

Two generalizations of Pólya's theorem should also be stated. Details are in Ref. (*14*) and the references cited therein. One often wishes to count patterns of colorings in which one does not care which color is called black and which white. For example, a coloring of the vertices of a square with three white vertices and one black vertex is regarded as identical with a coloring having three black vertices and one white vertex. The number of patterns in this case is $\frac{1}{2}\{Z(G; 2, 2, 2, 2, \ldots) + Z(G; 0, 2, 0, 2, \ldots)\}$. For $G = 4m$, this number is $\frac{1}{2}(6 + 2) = 4$. This observation is called de Bruijn's theorem (*17–20*).

It is also often useful to count the number of patterns with a given number of vertices white and a given number black. To do this, assign a variable, say, y, as a weight for the color white, and another variable, say, z, as the weight of black. The weight of a pattern is defined in the obvious way: a pattern with three white vertices and one black vertex has weight y^3z. Then the patterns are counted by weight by the value of the cycle index when each variable x_i is given the weight $y^i + z^i$. For the problem of the square, $Z(4m; y + z, y^2 + z^2, \ldots) = \frac{1}{8}\{(y + z)^4 + 2(y + z)^2(y^2 + z^2) + 3(y^2 + z^2)^2 + 2(y^4 + z^4)\} = y^4 + y^3z + 2y^2z^2 + yz^3 + z^4$, indicating that one pattern has weight y^4, one has weight y^3z, two have weight y^2z^2, and so on. This is called the weighted form of Pólya's theorem. de Bruijn's theorem also has a weighted form, and generalizations to more than two colors are straightforward.

Application to Wurtzite

We now show how the problem of counting wurtzite derivatives and dipolar tetrahedral structures with small unit cells can be phrased as a problem of counting colorings of a set under the action of a group. The cycle indices of the relevant groups are derived, and the numbers of possible structures are listed.

When projected onto a plane normal to c, the centers of the occupied tetrahedral sites in wurtzite form a hexagonal 6^3 net as shown in Fig. 1. In this projection, the points adjacent to a vertex representing a tetrahedron at $z = 0$ are tetrahedra at $z = \pm\frac{1}{2}$ and vice versa. Each tetrahedron shares vertices with the six tetrahedra (three above it and three below it) represented by the three adjacent points in the projection, and with the six tetrahedra at the same height represented by the second nearest-neighbor points in the projection. If, as in nearly all observed wurtzite derivatives, the c repeat is two close-packed layers (*4*), then all tetrahedra which project to the same point in the 6^3 net are occupied by atoms of the same species.

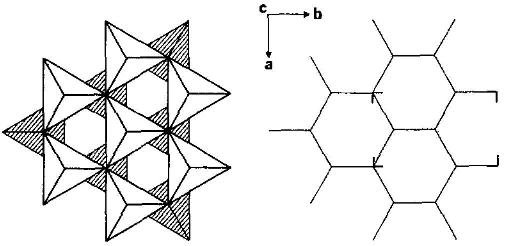

FIG. 1. The wurtzite structure, its projection on the plane to form a 6^3 net, and the orthohexagonal cell of that net.

The observed wurtzite derivatives can be referred to orthorhombic unit cells based on the orthohexagonal cell of the anion framework shown in Fig. 1. These cells vary in size, and the cell with $a = ma_{\text{orthohex}}$, $b = nb_{\text{orthohex}}$, and $c = c_{\text{orthohex}}$ will be called an (m,n) cell. This notation reverses a and b and m and n from those used by McLarnan (*5*) for a slightly different family of structures, but is more nearly in keeping with usual crystallographic convention.

A mathematical description of a wurtzite derivative in which two different species are ordered over the cation sites in an (m,n) unit cell while all the anion sites contain the same species is now easy to give. It is a coloring of the $4mn$ occupied tetrahedra in the (m,n) cell (or equivalently, of the $4mn$ points in the 6^3 net representing its projection in the plane) in two colors, representing the two species of cations. Derivatives with more than two ordered cation species can be described in the same way, only with more colors.

Two points about this description and the resulting enumeration should be made clear. First, a coloring having s white tetrahedra and $t = 4mn - s$ black tetrahedra leads to a stoichiometry which we shall write $A_sB_tX_{4mn}$. This formula does not imply that all the sites containing A atoms (or B or X atoms) are crystallographically equivalent, but merely that they contain the same type of atom. A real crystal of a compound we write as $A_sB_tX_{4mn}$ might contain several inequivalent sites $A(1)$, $A(2)$, $A(3)$, . . . containing primarily species A but differing slightly in geometry and minor element composition. Second, in the case of stoichiometries like ABX_2 or ABC_2X_4 we shall count the possible structures in such a way that a structure ABX_2 and the corresponding "antistructure" BAX_2 are considered to represent the same abstract structure type. That is, in our enumeration, we do not care which color represents A and which color represents B, only that the two colors represent different species. Obviously this is a consideration only for stoichiometries like ABX_2, not for those like AB_2X_3 in which the antistructure BA_2X_3 has a different composition. The alternative choice of regarding a structure and its antistructure as different is mathematically simpler.

After this description of the wurtzite derivatives as colorings of a set, it remains to find a group permuting that set which takes any coloring to an equivalent one. One might expect that this group would include every symmetry in the space group $P6_3mc$ of wurtzite. That is, a coloring should represent the same structure type as any translation, rotation, or mirror image of that coloring, or as the image of that coloring under any combined operation which takes one occupied tetrahedron to another. Unfortunately, the choice of an orthorhombic unit cell complicates this picture somewhat. This is because two points which are equivalent in the orthorhombic unit cell (say, 0,0,0 and 1,0,0) are in general not taken to equivalent points (that is, to points related by some translational symmetry of the unrotated unit cell) by symmetries of the anion framework including three- or six-fold rotations. Because of this, the group $P6_3mc$ cannot be regarded as a permutation group of the tetrahedra in one unit cell. The group $Cmc2_1$ (referred to the orthorhombic axes), the normalizer of $P1(m,n)$ in $P6_3mc(1,1)$, and a maximal orthorhombic subgroup of $P6_3mc$ does, however, take equivalent points to equivalent points, and is thus legitimately described as a group of permutations of the $4mn$ tetrahedra in one unit cell. For the moment, we therefore count patterns of colorings in which two colorings related by a symmetry in $Cmc2_1$ are regarded as identical. We shall see later how to incorporate the group $P6_3mc$.

To evaluate the cycle index of the group $Cmc2_1$ permuting the $4mn$ tetrahedra in an (m,n) unit cell, we observe that the elements of $Cmc2_1$ are of four types: (i) translations in the ab plane, (ii) 2_1 screw axes parallel to c, (iii) mirror planes normal to a, possibly followed by translations parallel to b, and (iv) c glide planes normal to b, possibly followed by translations along a. Any of these operations may be followed by a translation along c, but such translations take every tetrahedron to an equivalent tetrahedron, and so correspond to the identity permutation of the $4mn$ tetrahedra, and can be ignored. Each of these four sets of operations contains $2mn$ different permutations of the tetrahedra in an (m,n) cell. For example, there is a translation taking a given tetrahedron to each of the $2mn$ tetrahedra at the same height along c. There are thus $8mn$ symmetries whose cycle structures must be determined.

A slight conceptual simplification arises if we replace the (m,n) cell itself with the hexagonal net obtained by projecting it along c. The translations in $Cmc2_1$ correspond to translations of the hexagonal net, mirrors normal to a in $Cmc2_1$ become mirrors normal to a in the plane, 2_1 screws are simply two-fold rotations of the 6^3 net, and c glides normal to b go to mirrors normal to b. The result is a two-dimensional net whose vertices are permuted by the plane group $c2mm$.

As is easy to see from the fragment of the (m,n) unit cell shown in Fig. 2, every translation in this plane group takes the point (x,y) to some point whose fractional coordi-

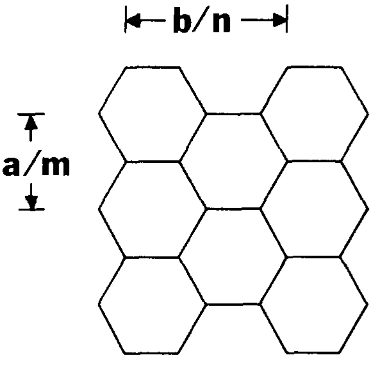

FIG. 2. A portion of an (m,n) unit cell in the 6^3 net.

nates are $[x + s/(2m), y + t/(2n)]$, where $s \equiv t (\mathrm{mod}\ 2)$, i.e., where s and t are either both even or both odd.[1] The ith power of such a translation takes (x,y) to $(x + si/(2m), y + ti/(2n))$. In order for this to equal (x,y), it must be that $2m|si$ and $2n|ti$. This happens if and only if $2m/(2m,s)|i$ and $2n/(2n,t)|i$, i.e., if and only if $[2m/(2m,s),2n/(2n,t)]|i$. Thus, every cycle in the permutation corresponding to this translation has length $[2m/(2m,s),2n/(2n,t)] = k$, and there are $4mn/k$ such cycles, so the cycle structure of this translation is $x_k^{4mn/k}$. The sum of the cycle structures of all translations is thus

$$\sum_{0 \leqq s < 2m} \sum_{\substack{0 \leqq t < 2n \\ s \equiv t (\mathrm{mod}\ 2)}} x_{[2m/(2m,s),2n/(2n,t)]}^{4mn/[2m/(2m,s),2n/(2n,t)]}.$$

Twofold rotors are rather simpler. No twofold rotation of the hexagonal net fixes any of its vertices, so every twofold rotation consists of $2mn$ cycles of length 2 and has cycle structure x_2^{2mn}. Since there are $2mn$ such distinct rotors in one unit cell, the sum of the cycle structures of all twofold axes of rotation is $2mnx_2^{2mn}$.

The cycle structures of mirror and glide planes can be evaluated with equal ease, as was shown for a related family of structures in (*5*). We state only the result of this analysis combined with the formulas above for translations and twofold axes. The average of the cycle structures of all the symmetry operations of $Cmc2_1$ permuting the occupied tetrahedra in an (m,n) unit cell is the cycle index polynomial $Z(m,n; x_1, x_2, \ldots) =$

$$\frac{1}{8mn}\left\{ \sum_{0 \leqq s < 2m} \sum_{\substack{0 \leqq t < 2n \\ s \equiv t(2)}} x_{[2m/(2m,s),2n/(2n,t)]}^{4mn/[2m/(2m,s),2n/(2n,t)]} + 2mnx_2^{2mn} \right.$$
$$+ m \sum_{\substack{0 \leqq t < 2n \\ 2|2n/(2n,t)}} x_{2n/(2n,t)}^{2m(2n,t)} + m \sum_{\substack{0 \leqq t < 2n \\ 2 \nmid 2n/(2n,t)}} x_{2n/(2n,t)}^{2(2n,t)} x_{4n/(2n,t)}^{(m-1)(2n,t)}$$
$$\left. + n \sum_{\substack{0 \leqq s < 2m \\ 2|2m/(2m,s)}} x_{2m/(2m,s)}^{2n(2m,s)} + n \sum_{\substack{0 \leqq s < 2m \\ 2 \nmid 2m/(2m,s)}} x_{4m/(2m,s)}^{n(2m,s)} \right\}.$$

Explicit cycle indices for some small values of m and n are listed in Table I.

Given these cycle indices, it is easy to compute the numbers of wurtzite derivatives with various unit cells and stoichiometries. We consider several stoichiometries in order of mathematical, rather than chemical, simplicity.

AB_3X_4 Structures

The number of AB_3X_4 structures having as unit cell a subcell of the (m,n) cell is found using the weighted form of Pólya's theorem by taking the cycle index $Z(m,n; x_1, x_2, \ldots)$, replacing x_i by $y^i + z^i$, and

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[1] Mathematical notation: $i|j$ means that i divides j, i.e., that j/i is an integer. $i \equiv j(\mathrm{mod}\ k)$ means that $k|(j - i)$. (i,j) is the greatest common divisor of i and j, and $[i,j]$ is their least common multiple.

TABLE I

THE CYCLE INDICES FOR THE GROUP $Cmc2_1$ PERMUTING THE OCCUPIED TETRAHEDRA IN SMALL (m,n) UNIT CELLS

(m,n)	$Z(m,n;\, x_1, x_2, \ldots)$
(1,1)	$\frac{1}{8}(2x_1^4 + 6x_2^2)$
(2,1)	$\frac{1}{16}(x_1^8 + 2x_1^4x_2^2 + 9x_2^4 + 4x_4^2)$
(3,1)	$\frac{1}{24}(x_1^{12} + 3x_1^4x_2^4 + 12x_2^6 + 2x_3^4 + 6x_6^2)$
(4,1)	$\frac{1}{32}(x_1^{16} + 4x_1^4x_2^6 + 15x_2^8 + 4x_4^4 + 8x_8^2)$
(5,1)	$\frac{1}{40}(x_1^{20} + 5x_1^4x_2^8 + 18x_2^{10} + 4x_5^4 + 12x_{10}^2)$
(1,2)	$\frac{1}{16}(2x_1^8 + 10x_2^4 + 4x_4^2)$
(2,2)	$\frac{1}{32}(x_1^{16} + 2x_1^8x_2^4 + 17x_2^8 + 12x_4^4)$
(3,2)	$\frac{1}{48}(x_1^{24} + 3x_1^8x_2^8 + 20x_2^{12} + 2x_3^8 + 8x_4^6 + 10x_6^4 + 4x_{12}^2)$
(4,2)	$\frac{1}{64}(x_1^{32} + 4x_1^8x_2^{12} + 27x_2^{16} + 16x_4^8 + 16x_8^4)$
(1,3)	$\frac{1}{24}(2x_1^{12} + 14x_2^6 + 4x_3^4 + 4x_6^2)$
(2,3)	$\frac{1}{48}(x_1^{24} + 2x_1^{12}x_2^6 + 21x_2^{12} + 2x_3^8 + 4x_3^4x_6^2 + 8x_4^6 + 6x_6^4 + 4x_{12}^2)$
(3,3)	$\frac{1}{72}(x_1^{36} + 3x_1^{12}x_2^{12} + 28x_2^{18} + 8x_3^{12} + 6x_3^4x_6^4 + 26x_6^6)$
(1,4)	$\frac{1}{32}(2x_1^{16} + 18x_2^8 + 4x_4^4 + 8x_8^2)$
(2,4)	$\frac{1}{64}(x_1^{32} + 2x_1^{16}x_2^8 + 29x_2^{16} + 16x_4^8 + 16x_8^4)$
(1,5)	$\frac{1}{40}(2x_1^{20} + 22x_2^{10} + 8x_5^4 + 8x_{10}^2)$

looking at the coefficient of the $y^{mn}z^{3mn}$ term in the resulting expression. Frequent use of the binomial theorem enables one to find this coefficient without actually multiplying out the whole polynomial, so that all the calculations reported below could be carried out on a hand calculator. For small unit cells, these numbers are listed in Table IIa.

These numbers count the patterns of colorings under the action of the group $Cmc2_1$, not $P6_3mc$. For only a few structures will this matter, since only rarely is a structure with an (m,n) unit cell taken to another such structure by a 3 or 6_3 operation. Structures which are so transformed, however, will not be counted correctly by the enumeration in Table IIa. For example, the two (2,2) structures of composition AB_3X_4 shown in projection in Fig. 3 are related to one another by a threefold rotation, but are not related by any symmetry in $Cmc2_1$. They are therefore counted as different structures in Table IIa when in fact one would normally regard them as identical. How can this error be corrected?

McLarnan (5) considered a problem

TABLE IIa

THE APPROXIMATE NUMBERS OF AB_3X_4 STRUCTURES WITH SMALL (m,n) UNIT CELLS, CALCULATED USING THE GROUP $Cmc2_1$ AND THE CYCLE INDICES IN TABLE I

	n				
m	1	2	3	4	5
1	1	6	19	130	776
2	5	85	3,107	169,390	
3	12	2,987	1,312,419		
4	77	165,850			
5	406				

TABLE IIb

THE EXACT NUMBERS OF AB_3X_4 STRUCTURES WITH SMALL (m,n) UNIT CELLS, OBTAINED FROM TABLE IIa BY INCLUDING THE GROUP $P6_3mc$ AND CORRECTING FOR SUBCELLS

	n				
m	1	2	3	4	5
1	1	5	18	124	775
2	4	73	3,084	169,181	
3	11	2,970	1,312,389		
4	72	165,693			
5	405				

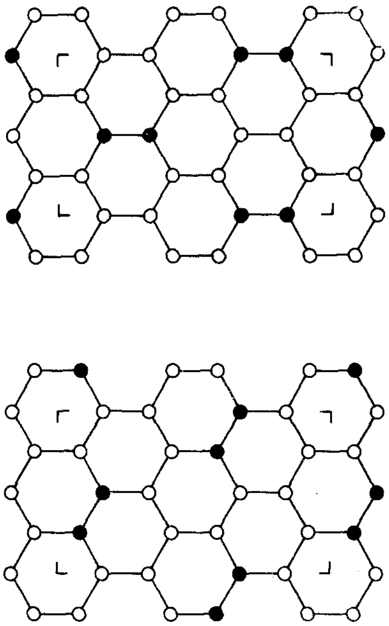

FIG. 3. Projections of two AB_3X_4 structures with (2,2) cells which are related by a threefold rotation around 00z but not by any operation in $Cmc2_1$. Black and white vertices represent A and B atoms, respectively.

mathematically identical to counting wurtzite derivatives except that in that paper not the vertices of the 6^3 net but its faces were to be colored. It was shown that for an (m,n) structure the property of being taken to another (m,n) structure by some symmetry involving a three- or sixfold rotor was equivalent to the property of possessing a unit cell of hexagonal geometry which is a subcell of the (m,n) orthorhombic cell. The size and shape of this subcell is shown in Table III and Fig. 4. Note that the structures in Fig. 3 have such a unit cell. Any (m,n) structure whose unit cell is not contained in this subcell is counted correctly in Table IIa. It remains, therefore, only to correctly count the structures having these metrically hexagonal cells.

TABLE III

THE HEXAGONAL SUBCELL OF THE (m,n) CELL SHARED BY EVERY (m,n) STRUCTURE WHICH IS CARRIED TO ANOTHER SUCH STRUCTURE BY SOME SYMMETRY OPERATION WHOSE ROTATIONAL PART IS A THREE- OR SIX-FOLD ROTOR

	n				
m	1	2	3	4	5
1	1	1	1	1	1
2	1	2_a	1	2_a	
3	2_b	2_b	3_a		
4	1	2_a			
5	1				

Note. These cells are shown in Fig. 4.

First we produce some cycle indices. The group $Cmc2_1$ can be regarded as a permutation group on the tetrahedra in the hexagonal unit cell instead of in the orthorhombic cell by forming, for example, the factor group $Cmc2_1(1,1)/P1(2_a)$ instead of $Cmc2_1(1,1)/P1(2,2)$. The cycle index of this new factor group with a hexagonal cell can then be computed just as with the orthorhombic cells. This is also true of the group $P6_3mc$ acting on the hexagonal unit cell, which was not the case with the orthorhombic cells. Rather than give gen-

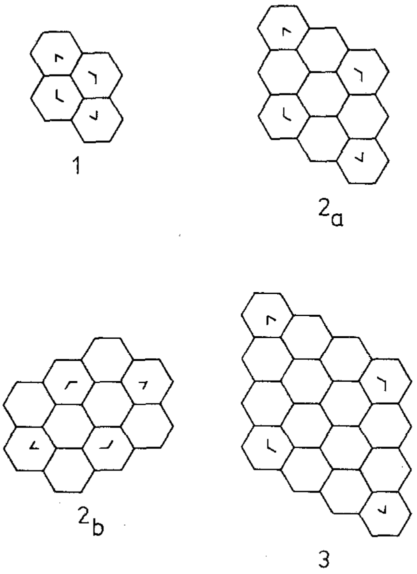

FIG. 4. The metrically hexagonal cells described in Table III.

eral formulas for these cycle indices, which are even more unwieldy than the general formula given for the orthorhombic case, we present only the results of direct calculations of a few of these polynomials. For cell 1, $Z(Cmc2_1; x_1, x_2, \ldots) = Z(P6_3mc; x_1, x_2, \ldots) = (1/2)(x_1^2 + x_2)$. For cell 2_b, $Z(Cmc2_1; x_1, x_2, \ldots) = Z(P6_3mc; x_1, x_2, \ldots) = (1/12)(x_1^6 + 3x_1^2x_2^2 + 4x_2^3 + 2x_3^2 + 2x_6)$. For cell 2_a, $Z(Cmc2_1; x_1, x_2, \ldots) = (1/16)(x_1^8 + 2x_1^4x_2^2 + 9x_2^4 + 4x_4^2)$; while $Z(P6_3mc; x_1, x_2, \ldots) = (1/48)(x_1^8 + 6x_1^4x_2^2 + 8x_1^2x_3^2 + 13x_2^4 + 8x_2x_6 + 12x_4^2)$. Finally, for cell 3_a, $Z(Cmc2_1; x_1, x_2, \ldots) = (1/36)(x_1^{18} + 3x_1^6x_2^6 + 12x_2^9 + 8x_3^6 + 6x_3^2x_6^2 + 6x_6^3)$ and $Z(P6_3mc; x_1, x_2, \ldots) = (1/108)(x_1^{18} + 9x_1^6x_2^6 + 18x_2^9 + 12x_1^3x_3^5 + 14x_3^6 + 18x_3^2x_6^2 + 36x_6^3)$.

The correct number of AB_3X_4 structures having a given hexagonal unit cell containing $4h$ tetrahedra is found by taking the cycle index of $P6_3mc$ permuting the tetrahedra in that cell, replacing x_i by $y^i + z^i$, and finding the coefficient k of the y^hz^{3h} term in the resulting expression. The number of these structures counted in Table IIa is the coefficient q of the same term in the cycle index of $Cmc2_1$. Hence, the appropriate correction term to add to the number in Table IIa for any (m,n) cell having the given hexagonal subcell is $k - q$. Among the small cells treated here, only cell 2_a has $k - q \neq 0$. For this cell, $k = 3$ and $q = 5$, so that to be correct, the numbers in Table IIa for the (2,2), (2,4), and (4,2) cells should all be reduced by 2.

One final change should be made in Table IIa in order that it agree with our usual notion of unit cell. The six structures listed in Table IIa as having a (1,2) unit cell include all those whose unit cells are subcells of the (1,2) cell. In particular, the structure with a (1,1) cell is included among these. Thus, there are really only five structures whose *smallest* orthorhombic cell is (1,2). Similarly, only four structures have a (2,1) cell as their minimal orthorhombic cell, and only 83 − 4 − 5 − 1 = 73 (remember the corrections in the above paragraph) really have a (2,2) cell. Proceeding through Table IIa from smaller to larger cells and subtracting off the numbers corresponding to all subcells of the given cell produces Table IIb. This final correction process could also be simply described in terms of generalized Möbius inversion (*21, 22*).

Table IIb is the final list of the number of AB_3X_4 structures with an (m,n) unit cell. No structure recorded as having an (m,n) cell possesses any smaller orthorhombic cell, though it may have a smaller cell of a different geometry. Any structure whose unit cell is geometrically hexagonal, like the structure shown twice in Fig. 3, is counted only once. In all the following counting problems we present only the analog of Table IIb, assuming that it is understood that corrections for the group $P6_3mc$ and for subcells have been made.

AB_2X_3 Structures

To count AB_2X_3 structures, we proceed exactly as with the AB_3X_4 structures, except that we look for the coefficient of the $y^{4mn/3}z^{8mn/3}$ term instead of the $y^{mn}z^{3mn}$ term in $Z(m,n; y + z, y^2 + z^2, \ldots)$. Obviously this term can be nonzero only if $3|mn$, which accords with the trivial fact that an AB_2X_3 structure must have a unit cell containing a multiple of three tetrahedra. The number of AB_2X_3 structures for small unit cells is shown in Table IV.

ABX_2 Structures

In counting ABX_2 structures a slight twist arises. We begin in the traditional way, putting $y^i + z^i$ into the cycle index for x_i and finding the coefficient, E, of the term $y^{2mn}z^{2mn}$. We wish, however, to regard every ABX_2 structure and its BAX_2 antistructure or *complement* as equivalent. The process used to obtain E counts them as distinct, except for the so-called self-com-

TABLE IV

THE NUMBERS OF AB_2X_3 STRUCTURES WITH SMALL (m,n) UNIT CELLS

	n				
m	1	2	3	4	5
1	0	0	50	0	0
2	0	0	16,158	0	
3	32	15,770	17,413,546		
4	0	0			
5	0				

plementary structures, those related to their complements by some symmetry in $Cmc2_1$. That is, E counts each self-complementary structure once and each non-self-complementary structure twice. From the proof of de Bruijn's theorem (*9, 17–20*) however, it is obvious that the self-complementary patterns are counted by $Z(m,n;\ 0, 2, 0, 2, \ldots) = S$. Thus, $S + E$ counts every structure twice, so $\frac{1}{2}(S + E)$ counts each once. These numbers, appropriately corrected for hexagonal cells and subcells, are listed in Table V.

ABC_2X_4 Structures

These structures can be counted just like those above except that now the tetrahedra are to be colored in three colors, A,B,C, instead of two. The weighted form of Pólya's theorem therefore says to replace x_i in the cycle index by $y^i + z^i + w^i$ and to find the coefficient E of the $y^{mn}z^{mn}w^{2mn}$ term in this expression. Since again we wish every pair of complementary structures ABC_2X_4 and BAC_2X_4 to be counted only once, we use the weighted form of de Bruijn's theorem (*9, 20*) to find the number S of self-complementary structures, which is the coefficient of $y^{mn}z^{mn}w^{2mn}$ in $Z(m,n;\ w,\ y^2 + z^2 + w^2,\ w^3,\ y^4 + z^4 + w^4, \ldots)$. The average $\frac{1}{2}(S + E)$ then counts each ABC_2X_4 structure once. The results of this calculation for small unit cells are in Table VI.

Dipolar Tetrahedral AX Structures

The last family of structures we consider are not wurtzite derivatives, but are closely structurally related to wurtzite. In the wurtzite structure, every occupied tetrahedron has its apex above (i.e., in the $+c$ direction with respect to) its three basal vertices, and shares its basal face with a downward-pointing empty tetrahedron. There are structures known (the high-temperature form of Li_3PO_4 is an example) which, instead of having 100% occupancy of the upward-pointing tetrahedra, have some of these downward-pointing tetrahedra occupied. The adjacent upward-pointing tetrahedron is always vacant in order to avoid face-sharing pairs of occupied tetrahedra. Every AX structure with some upward- and some downward-pointing tetrahedra must, however, contain some shared edges. We call such structures *dipolar tetrahedral* structures, and count the number of these types with an (m,n) cell assuming all cations to be of the same species.

This question is easily phrased as a coloring problem. The pairs of face-sharing tetrahedral sites project onto the plane to form a 6^3 net. The structures in question are colorings of an (m,n) unit cell in this net using two colors, U and D (up and down). Two such colorings will obviously be equivalent if one is taken to the other by some symmetry in $p6mm$ or its maximal orthorhombic

TABLE V

THE NUMBERS OF ABX_2 STRUCTURES WITH SMALL (m,n) UNIT CELLS

	n				
m	1	2	3	4	5
1	3	9	61	484	4,968
2	7	289	29,917	4,742,665	
3	41	29,425	63,117,162		
4	279	4,715,370			
5	2,628				

TABLE VI

THE NUMBERS OF ABC_2X_4 STRUCTURES WITH SMALL (m,n) UNIT CELLS

	n				
m	1	2	3	4	5
1	3	35	815	28,551	1,166,179
2	23	14,729	26,119,861	60,460,857,871	
3	436	26,047,359	3,064,146,632,213		
4	14,493	60,438,192,315			
5	584,305				

subgroup, *c2mm*. In addition, two structures related by a mirror normal to *c*, which correspond to colorings related by interchange of the two colors U and D, are to be regarded as identical. It is easy to see that every symmetry in $P6_3/mmc$, the space group of the anion framework, corresponds in projection to some symmetry in *p6mm* possibly followed by interchange of U and D, so no operations other than these need be considered.

We are therefore interested in colorings of the 6^3 net in two colors and do not care which color is called U and which is called D. This is exactly the situation to which de Bruijn's theorem applies. The number of dipolar *AX* structures with an (m,n) cell is therefore $\frac{1}{2}[Z(m,n;\ 2,\ 2,\ 2,\ 2,\ \ldots) + Z(m,n;\ 0,\ 2,\ 0,\ 2,\ \ldots)]$. These numbers, corrected in the usual ways, appear in Table VII.

Classification by Space Group

Obviously many additional counting problems could be treated in this way—larger unit cells, different stoichiometries, derivatives of the dipolar structures, compounds like LiSiON featuring ordering over both the cation and anion sites, and so on. Because very few of these structure types are observed, however, it is more valuable to consider in a bit more detail the numbers already produced.

A glance at Tables II–VII shows that the number of possible structures grows very rapidly as the unit cell increases in size. Indeed, it is easy to show that for the families we have considered the growth is always exponential in *mn*. The argument follows that given in (*5*).

To some degree this rapid growth is discouraging, but it is often possible to use simple chemical or crystallographic arguments to select from these enormous classes of hypothetical types a much smaller list of structures one reasonably believes to be the most stable. For example, there are 1286 dipolar *AX* structures with unit cell no larger than (2,2). Well over 10^6 derivatives of these structures exist with composition AB_3X_4. Yet we shall see below that only ten of these are plausible for Li_3PO_4 in that they satisfy the valence sum rule and have no PO_4 tetrahedra with shared edges. These ten include both ob-

TABLE VII

THE NUMBERS OF DIPOLAR TETRAHEDRAL *AX* STRUCTURES WITH SMALL (m,n) UNIT CELLS

	n				
m	1	2	3	4	5
1	5	22	209	2,168	26,775
2	17	1,242	181,806	33,842,878	
3	130	178,380	477,667,476		
4	1,189	33,612,433			
5	13,821				

served modifications of Li_3PO_4 and eight unknown types.

This enumeration does not take advantage of any counting theorems but merely proceeds geometrically in an ad hoc way. This is, however, not the only way to incorporate chemical hypotheses into the mathematics. In several of the problems treated in Refs. (*3, 10, 11*) chemical assumptions about local environments are made before structures are counted using general theorems. In the companion paper (*4*), we use a computer to generate explicitly all possible structures for β-LiSiON and to check at the same time how well they satisfy the valence sum rule. All these examples illustrate how one may "count after restrictions" in order to reduce the numbers dramatically while retaining the structures of chemical interest. Of course, the restrictions chosen may or may not be obeyed by all observed types.

Another way of focusing attention on a smaller family of atomic arrangements arises from the realization that in the limit of m and n large, nearly every possible structure will have space group $P1$ (in the sense that $\#\{(m,n)$ structures with space group $P1\}/\#\{$all (m,n) structures$\} \to 1$). By contrast, all the observed structures have at least monoclinic symmetry, and most have orthorhombic or higher. It is therefore interesting to see how many possible structures have each possible space group.

This question can be resolved using a result of White's (*23*) which is related to Pólya's theorem and has previously been employed for studying polytypic materials (*3, 9, 10*). Basically, this theorem proceeds by taking the permutation group G (in this case $Cmc2_1$ acting on the $4mn$ tetrahedra), listing all its subgroups $G_1, G_2, \ldots, G_N$, constructing an $N \times N$ lower triangular matrix based on the group–subgroup relations among them, inverting this matrix, and obtaining the number of structures with space group G_i by multiplying the ith row of the inverse matrix by a suitably chosen vector depending only on G. Unfortunately, the number N of possible subgroups grows steadily with the cell size and the process for producing the $N \times N$ matrix has not yet been computerized. We therefore consider only (1,1), (1,2), and (2,1) cells, which require no matrices larger than 43 × 43. Only a few hours of work by hand is needed to produce these matrices, which are rather sparse, and their inversion is the only use we have made of computers in this enumeration.

Table VIII lists the results of these calcu-

TABLE VIII

THE NUMBERS OF STRUCTURES WITH GIVEN COMPOSITION, UNIT CELL, AND SPACE GROUP FOR *m* AND *n* VERY SMALL

		Number of structures		
(m,n)	Space group	ABX_2	AB_3X_4	ABC_2X_4
(1,1)	$P3m1$	1	0	0
	$Pmc2_1^0$	1	0	0
	$Pmn2_1^n$	1	0	0
	$Pm11$	0	1	3
(1,2)	$Pmc2_1^0$	2	2	6(4)
	$Pmn2_1^n$	2	2	6(4)
	$Pm11$	6(5)	1	45(27)
(2,1)	$Pmc2_1^0$	0	1	1
	$Pmn2_1^0$	0	1	1
	$Pbc2_1^n$	1	0	0
	$Pbn2_1^n$	1	0	0
	$Pm11$	2	0	4(2)
	$Pb11$	0	1	3
	$P1c1$	0	0	1
	$P1n1$	0	0	1
	$P112_1^0$	1	0	2(1)
	$P112_1^n$	0	1	3
	$P1$	2	0	18(10)

Note. An ABX_2 or ABC_2X_4 structure and its antistructure are counted as distinct, unlike the enumeration in Tables V and VI. The numbers in parentheses show what changes occur when a structure and its antistructure are identified. The structure with space group $P3m1$ does not actually have the orthorhombic (1,1) cell but a hexagonal subcell, cell 1 of Fig. 4.

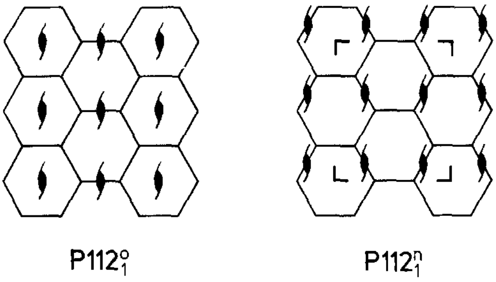

FIG. 5. 6^3 nets showing the space groups $P112_1^o$ and $P112_1^n$ for a (2,1) cell. Both groups have the same size unit cell.

lations; we refer to the references for details of the method. Not every imaginable space group for the cells in question is listed, but only the space groups actually possible for one of the stoichiometries considered. Some groups are listed twice because they can occur in two different settings, one having some of the 2_1 axes passing through the centers of the octahedral holes in the close packing (2_1^o), and another with none of the 2_1 axes in this position, but all midway between two octahedral centers (2_1^n). The groups $P112_1^o$ and $P112_1^n$ with the (2,1) cell, for example, are shown in Fig. 5.

The space group associated with each structure in Table VIII is the group of highest symmetry possible for the given composition and topology. It is possible that real structures may contain distortions which reduce their symmetry below that listed here. This explains the occurrence in Fig. 4 of the companion paper (*4*) of intermediate types with space groups not found in Table VIII. These represent distortions of more symmetrical structures with the same topology, and cannot be obtained from a symmetrical parent by cation ordering alone.

In the enumeration using White's theorem, unlike that of Tables V and VI, a structure and its complement are regarded as distinct. Consequently, the number of all ABX_2 or ABC_2X_4 structures with a given unit cell in Table VIII does not agree with that in Table V or VI. Because of the small total numbers, however, it is easy to list explicitly all the derivatives except those of minimal symmetry for each cell, and to note whether or not they are self-complementary. This allows us to count structures by space group, identifying any structure with its complement. Where these numbers differ from the results of White's theorem, they have been placed in parentheses in Table VIII. With these changes, the sums accord with the values in Tables V and VI. The enumeration of AB_3X_4 structures agrees with that in Table IIb.

Some Remarks on the Stability of Li_3PO_4 (HT)

These lists of possible structures and space groups will prove helpful in the companion paper (*4*), where they will be used to organize the observed structure types and to suggest possible alternatives to these arrangements or to demonstrate that none exist. Another use for structure enumeration, seen in Refs. (*11–13, 24*), is as a basis for energetic calculations which aim at producing some theoretical insight into bonding in a family of compounds. We shall not under-

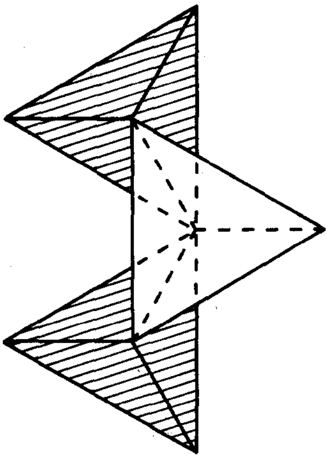

FIG. 6. The edge-sharing Li_3O_8 unit found in Li_3PO_4(HT).

take such a systematic study, but shall content ourselves with some preliminary remarks on one of the more interesting compounds with crystal structures derived from wurtzite, Li_3PO_4. This is known in a low-temperature modification with a wurtzite derivative structure with a (2,1) cell [the W-*Pmn*2_1 (2,1) structure]. It is also found in a high-temperature dipolar tetrahedral form with a (2,2) cell [the D-*Pmnb*(2,2) structure] containing the edge-sharing trimers of LiO_4 tetrahedra shown in Fig. 6. These two structures are shown in Fig. 7 and are further described in our following paper (*4*).

An interesting feature of these two structures is the presence in the high-temperature form of shared edges, in violation of Pauling's second rule. This situation should be contrasted with the violation of the electrostatic valence sum rule in such compounds as LiSiON. No wurtzite derivative or dipolar tetrahedral structure (in all of which every atom is four-coordinate) with composition LiSiON can exactly satisfy the valence sum rule, but the observed structure comes as close as possible. On the other hand, both polymorphs of Li_3PO_4 are based on the same anion packing and both satisfy the valence sum rule exactly, yet

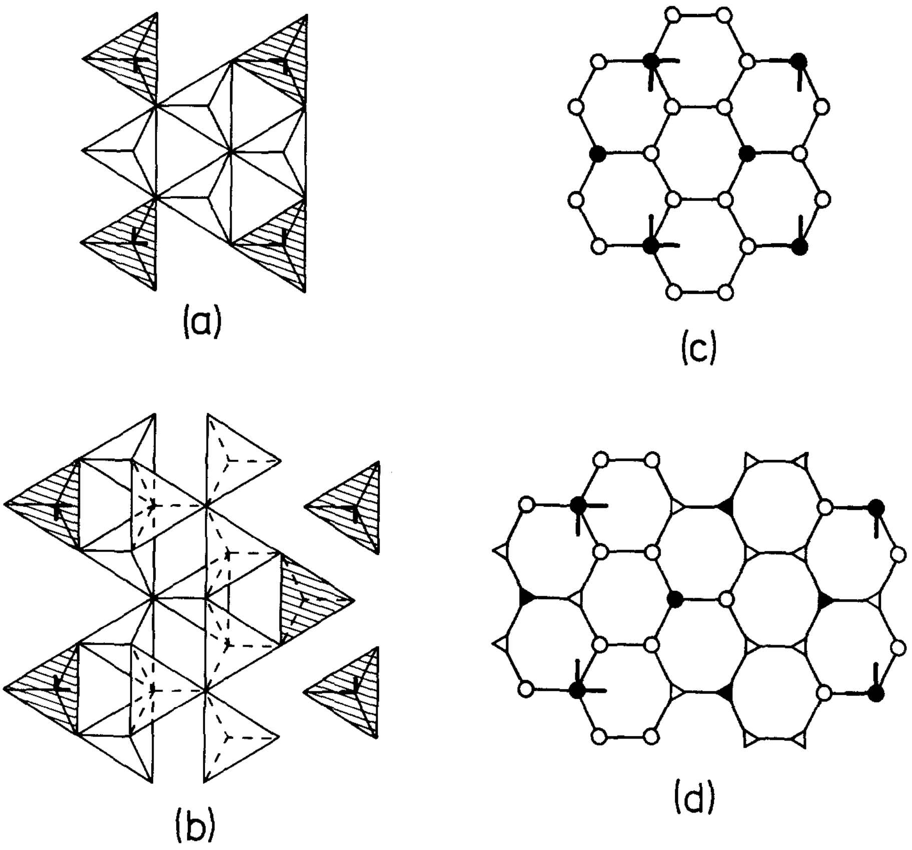

FIG. 7. Slabs of the structures of Li_3PO_4(LT) (a) and Li_3PO_4(HT) (b). Shaded tetrahedra contain P atoms; unshaded tetrahedra, Li. Both structures consist of two layers like those shown which are related by 2_1 screw operations normal to the plane of the paper and which share only vertices with one another. The colored 6^3 nets representing these structures are shown as (c) and (d). Open circles represent Li tetrahedra pointing up, solid circles are P tetrahedra pointing up, and open and solid triangles are Li and P tetrahedra, respectively, which point down.

one contains shared edges between LiO_4 tetrahedra, which should be destabilizing.

In an attempt to understand this, we first seek a reasonable collection of structures to compare with those observed. As mentioned above, the number of possible dipolar tetrahedral structures for Li_3PO_4 with at most a (2,2) cell is enormous unless additional constraints are imposed. Let us therefore consider only structures in which the valence sum rule is exactly satisfied. This requires that every oxygen atom be coordinated by one phosphorus atom and three lithiums. In particular, PO_4 groups cannot share vertices. Consider, therefore, a single layer of close-packed oxygen atoms and all the tetrahedra whose bases lie in that layer. There are only four possible arrangements of phosphate tetrahedra in such a layer which satisfy this "phosphorus avoidance rule," have at most a (2,2) cell, and contain enough P atoms that they can combine with other layers to produce the composition Li_3PO_4. They are shown in Fig. 8. The shaded tetrahedra in this figure contain lithium atoms, and at this stage can point either up or down.

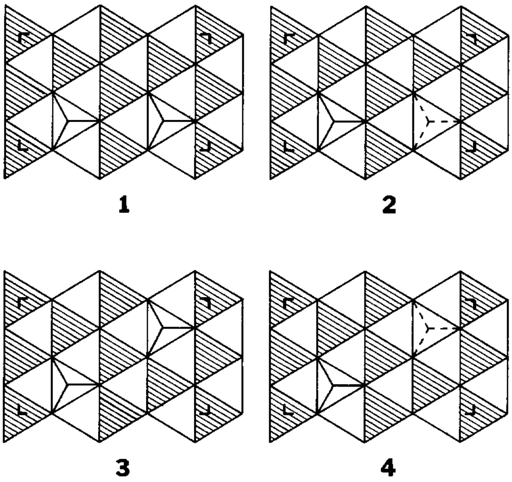

FIG. 8. The four possible Li_3PO_4 layers with (2,2) or (2,1) cells satisfying the "phosphorus avoidance rule." PO_4 groups are the light tetrahedra pointing up or down. The shaded triangles are LiO_4 tetrahedra, and point up or down depending on how two layers are combined to form a three-dimensional structure.

TABLE IX

THE TEN POSSIBLE WAYS OF COMBINING TWO OF THE LAYERS IN FIG. 8 TO PRODUCE A STRUCTURE SATISFYING THE "PHOSPHORUS AVOIDANCE RULE"

Structure	Bottom layer	Top layer	Translation of top layer	Shared edges	Space group
1 + 1	1	1	0,0,0	0	$Pmn2_1$
$1 + \bar{1}$	1	$\bar{1}$	0,0,0	2	$P2_1/m11$
$(2 + 2)_1$	2	2	0,0,0	$\frac{2}{3}$	$Pmnb$
$(2 + 2)_2$	2	2	$0,\frac{1}{2},0$	$\frac{4}{3}$	$Pmnb$
1 + 2	1	2	0,0,0	1	$Pm11$
3 + 3	3	3	0,0,0	0	$Cmc2_1$
$3 + \bar{3}$	3	$\bar{3}$	0,0,0	2	$C2/m11$
$(4 + 4)_1$	4	4	0,0,0	$\frac{2}{3}$	$Pmnn$
$(4 + 4)_2$	4	4	$0,\frac{1}{2},0$	$\frac{4}{3}$	$Pmcn$
3 + 4	3	4	0,0,0	1	$Pm11$

Note. To generate one of these structures, place the top layer directly above the bottom layer with the unit cells shown in Fig. 8 coinciding, rotate the top layer 180° about 00z, and translate it by the amount shown. Layers $\bar{1}$ and $\bar{3}$ are the reflections of layers 1 and 3, respectively, in the mirror at xy0. The last two columns list the average number of shared edges in a LiO_4 tetrahedron assuming Li and P tetrahedra do not share edges with one another, and the space group of the resulting structure. The two observed arrangements are 1 + 1, the Li_3PO_4(LT) or enargite type [W-$Pmn2_1$ (2,1)], and $(2 + 2)_2$, the Li_3PO_4(HT) type [D-$Pmnb$ (2,2)].

To produce a unit cell with c repeat equal to two close-packed layers, two of these layers must be stacked in a way which respects the phosphorus avoidance rule. There are ten ways to do this, which are listed in Table IX. In each of these ten arrangements the valence sum rule is satisfied whether the LiO_4 tetrahedra point is up or down. Another condition is therefore necessary in order to locate the lithium atoms. The high formal charge on P makes it unlikely that a PO_4 tetrahedron should share an edge with a LiO_4 tetrahedron, and no such configurations have been observed. Requiring that this be the case unambiguously determines the Li atom positions in all ten of the arrangements in Table IX, leaving us with ten hypothetical Li_3PO_4 structures.

The simplest way to assess the effect of lithium tetrahedral edge sharing on the energies of these structures is to compute their Madelung constants. This amounts to replacing each atom with a point charge q_i equal to its formal charge, and then evaluating the total electrostatic energy,

$$\frac{1}{2}\sum_{i\neq j}\frac{q_iq_j}{r_{ij}},$$

where i and j range over all atoms in the crystal. This is the energy of an ideal ionic crystal in which no account is taken of interatomic repulsion, van der Waals' forces, polarization, zero point energy, and so on. In general, however, all these terms account for only about 10% of the total energy (*25*), so as a first approximation in an ionic material the electrostatic energy may suffice. Figure 9 shows the electrostatic energy of the ten hypothetical structures as a function of the amount of edge sharing. The calculations were performed on structures with ideal hcp geometries and with cell volumes equal to the observed value, using a locally written program employing the Ewald method (*26*).

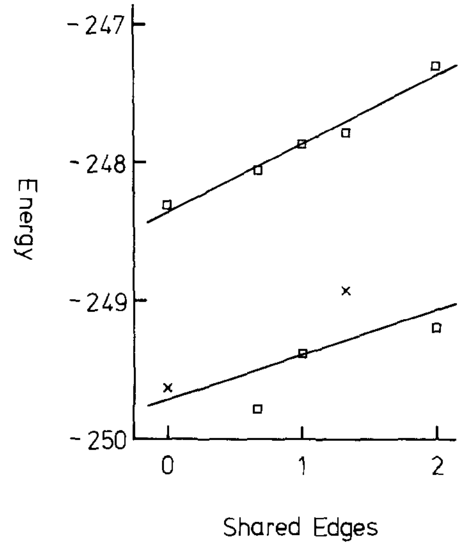

FIG. 9. The electrostatic energy (in eV/formula unit) of the 10 possible Li_3PO_4 structures, plotted as a function of the average number of edges shared by a LiO_4 tetrahedron. The five points at lower energy represent the first five structures in Table IX. The observed structures are marked by crosses.

The structures fall energetically into two families, those composed of sheets 1 and 2, and those made of sheets 3 and 4. These differ in energy by about 1.5 eV (1 eV ≐ 23.1 kcal/mole) because of different P atom site potentials in the two families. This is ultimately probably caused by P–P repulsions in view of both its independence on Li atom arrangement and the high formal charge on P. Within each of these classes, however, energy increases more or less linearly with the number of shared edges, in keeping with Pauling's second rule. Thus, the calculations support Pauling's rule for each of the individual families, but suggest that there may be large energetic effects not taken into account if one merely counts shared edges, even among very similar structure types. The two observed conformations are not predicted to be the two most stable, but they at least lie in the lower energy class. This provides a partial rationalization for the occurrence of the observed high temperature $(2 + 2)_2$ structure, which is lower in energy than 3 + 3, $(4 + 4)_1$, 3 + 4, or $(4 + 4)_2$ despite having as many or more shared edges.

It is interesting to compare these results with those of another set of computations based on extended Hückel (EHMO) theory, a basically covalent molecular orbital method which has proved very successful in calculating geometric and electronic properties of molecules, and which has also been used to explain bond angles and distances in crystals [(*27–31*) see, however, (*32, 33*)]. This approach can be combined with the band structure formalism to produce a method for evaluating the energy and "molecular orbitals" of a crystal [(*34,35*); for applications see (*11–13, 24*)]. Unfortunately, storage requirements of the program preclude consideration of a unit cell as large as (2,2), but the structures 3 + 3, 3 + $\bar{3}$, 1 + 1, and 1 + $\bar{1}$ have (2,1) cells

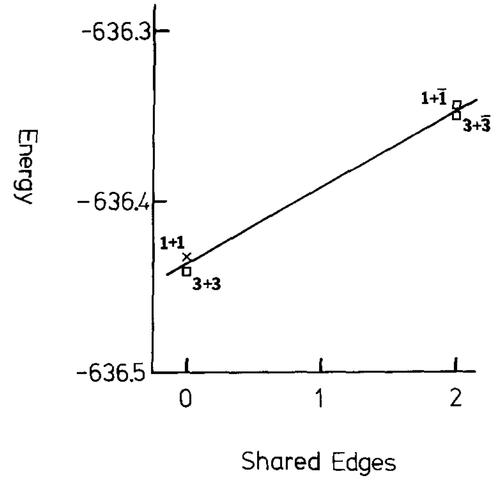

FIG. 10. The extended Hückel band energies of the four possible Li_3PO_4 structures with (2,1) cells, plotted as a function of the average number of edges shared by a LiO_4 tetrahedron. The observed structure is marked by a cross.

and are accessible. The energies of these structures[2] are plotted in Fig. 10. Because of a different assumed standard state, the magnitude of the energies in this figure differs from that in Fig. 9.

This time the separation of the structures into two classes has disappeared, presumably because P–P repulsion no longer plays a major role in the total energy. It is interesting, however, that these covalent calculations still show shared edges to be destabilizing. This is true in other families of structures as well, and is apparently related to the fact that shared edges force the anions to have distorted coordination environments, hindering effective orbital hybridization and bond formation at these sites (*36*). Thus, extended Hückel calculations do not appear to explain the occurrence of Li_3PO_4 (HT)—though no calculations on this structure itself were possible—but they do suggest that Pauling's second rule can be understood in covalent as well as ionic terms.

Though neither of these sets of calculations lets us completely understand the observed structures of Li_3PO_4, they should at least suggest the utility of structure enumeration in seeking this understanding.

Acknowledgments

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[2] Computational details: We use *s* and *p* valence orbitals only. Slater exponents are 0.650(Li), 2.275(O), and 1.600(P). The H_{ii} are −5.4 eV (Li *s*), −3.5 eV (Li *p*), −18.6 eV (P *s*), −14.0 eV (P *p*), −32.3 eV (O *s*), and −14.8 eV (O *p*). The Hamiltonian matrix is computed using the modified Wolfsberg–Helmholz formula. The energies reported are averages of the band energies at the special points at $k = \pm \frac{1}{4} \pm \frac{1}{4} \pm \frac{1}{4}$.

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