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The Combinatorics of Cation-Deficient Close-Packed Structures

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Pólya's enumeration theorem is used to derive an algorithm for counting all hexagonal close-packed structures with a unit cell of given size, having composition MX_2, where X is an hcp anion, M is an octahedrally coordinated cation, and no face sharing is permitted between octahedra. Generalizations of this algorithm to enumerate ordered derivatives of these structures, hcp structures with tetrahedral instead of octahedral cations, and similar structures having different stacking sequences among the close-packed layers are sketched.

Introduction

Mathematical counting problems are important in crystallography. The 14 Bravais lattices, 32 crystallographic point groups, and 230 Fedorov space groups are well known, and the 1651 Shubnikov two-colored symmetry groups and their extensions by Belov and others are becoming increasingly familiar as space groups of ferromagnetic materials. Readable derivations of these symmetry groups can be found in (*1–3*), to name only three.

The work of Smith and Rinaldi (*4*) on feldspars and zeolites, Ross *et al.* (*5*) on micas, and Moore (*6*, *7*) on complex oxides has shown the success of straightforward combinatorial methods in developing structural hierarchies. Despite these successes, the number of families of structures which have been provided with a careful enumerative classifications remains very small.

I present a combinatorial algorithm for the enumeration of all hexagonal close-packed structures with cations ordered over the octahedral sites, and suggest related applications. The primary mathematical tool used here is Pólya's enumeration theorem, a method for counting colorings of a set under the action of a given symmetry group (see the original account by Pólya (*8*), or the treatment by de Bruijn (*9*), whose explanation the following paragraphs summarize).

If G is a group of symmetries acting on a finite set D containing k elements then each element g of G can be decomposed into a collection of cyclic permutations. If there are t_1 cycles of length 1, t_2 cycles of length 2, and so on, the cycle structure of g is the monomial $x_1^{t_1}x_2^{t_2}\ldots x_k^{t_k}$, where no cycle has length greater than k and where the x_i's are dummy variables. The cycle index of G is defined as the average $Z(G; x_1, x_2, \ldots)$ of the cycle structures of the elements of G. Let R be a set in which each element $r \in R$ is assigned a weight $w(r)$. Then each function f from D to R can be given a weight $w(f) = \prod_{d\in D} w(f(d))$. Let two functions f and h be considered equivalent if an element $g \in G$ exists such that $f(g(d)) = h(d)$ for every $d \in D$. Then Pólya's theorem says that the number of equivalence classes of these functions (called patterns) counted according to their weights is

$$\sum_f w(f) = Z\left(G; \sum_{r\in R} w(r), \sum_{r\in R} [w(r)]^2, \sum_{r\in R} [w(r)]^3, \ldots\right).$$

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As a simple example, let D be the set of vertices of an octahedron, let G be the group of proper rotations of the octahedron, let R = {black, white} and let w(black) = w(white) = 1. Then the patterns are the discrete ways of coloring the octahedral vertices in the two colors, and every pattern has weight 1. Two colorings are regarded as different if one cannot be taken to the other by a proper rotation. $\sum w(f)$ counts the number of colorings. The group G contains the identity, having cycle structure x_1^6; six 90° rotations, having cycle structures $x_1^2x_4$; eight 120° rotations, having cycle structures x_3^2; three 180° rotations about lines connecting two vertices, having cycle structures $x_1^2x_2^2$; and six 180° rotations about lines joining the midpoints of two edges, having cycle structures x_2^3. The cycle index of G is therefore $(1/24)(x_1^6 + 6x_1^2x_4 + 8x_3^2 + 3x_1^2x_2^2 + 6x_2^3)$ and the number of G-distinct two-colorings of the vertices of an octahedron is $(1/24)(2^6 + 6\cdot 2^2\cdot 2 + 8\cdot 2^2 + 3\cdot 2^2\cdot 2^2 + 6\cdot 2^3) = 10$.

Enumerating hcp Structures

Consider the question of how many hcp structures exist having stoichiometric composition MX_2 in which the octahedral sites stacked perpendicular to the close-packed layers are alternately filled and empty with respect to M cations. This number depends upon the unit cell chosen. Let R be the radius of an X ion. We shall assume that the cell is orthorhombic with c perpendicular to the close-packed layers, $c = 4R\,6^{1/2}/3$ (a two-layer repeat), b parallel to the vector between two nearest-neighbor X ions in one layer, $b = 2nR$, and $a = 2(3)^{1/2}mR$. The cell origin is chosen to lie at the center of an octahedral void. This cell and its two-dimensional image under projection parallel to c we call an $m \times n$ cell. The compounds rutile ($m = n = 1$), α-PbO_2 ($m = 1, n = 2$), ξ-Nb_2C ($m = 2, n = 1$), ε-Fe_2N ($m = 1, n = 3$) can all be referred to such a cell (Wells (*10*)), and other cell geometries pose no additional difficulties.

In a hexagonal close packing the octahedral sites between two adjacent layers share edges to form a configuration which, when projected along c, becomes a hexagonal net. All other octahedral sites are stacked directly above or below these through face sharing (*10*). Hence, each of the structures we wish to count can be uniquely represented by a colored hexagonal net showing the projection of one layer of octahedra, in which the hexagons are colored black or white according as the corresponding octahedra are filled or vacant. The hexagons of the two-dimensional $m \times n$ cell are labeled as in Fig. 1.

Two hcp structures MX_2 are considered equivalent if one is the image of the other under the action of some element of $P6_3/m\,mc$, the symmetry group of the anion framework. The symmetry group induced by $P6_3/m\,mc$ on the space of colored nets is $p6m \oplus \{1, 1'\}$ (see Appendix for definition), where $1'$ is the anti-identification map interchanging the two colors. Since two hcp structures MX_2 are related by $P6_3/m\,mc$ exactly if the corresponding colored nets are related by $p6m \oplus \{1, 1'\}$,

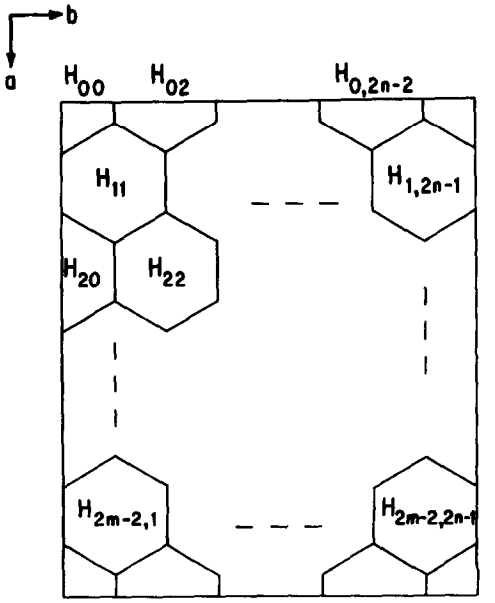

FIG. 1. The labeling of the hexagons in the m × n unit cell.

the problem of counting structures reduces to the problem of counting equivalence classes of colored nets under the action of $p6m \oplus \{1, 1'\}$.

This problem must be treated in three steps, each of which is reducible to a problem in graph theory solved using Pólya's theorem (see (*11*) or (*12*) for an account of graphical enumeration theory).

The first step is to count the number of equivalence classes under the action of the group *cmm* of symmetries of four types: translations, glide reflections normal to *b*, glides normal to *a*, and twofold rotations parallel to *c* (if in the cell shown in Fig. 1 either *m* or *n* is 1, some of these classes are the same). This is equivalent to counting equivalence classes of two-colorings of a graph whose vertices are the centers of the hexagons in one unit cell and whose edges connect the centers of adjacent hexagons. Thus H_{00} is connected to H_{02}, H_{11}, $H_{0,2n-2}$, $H_{1,2n-1}$, $H_{2m-1,1}$, and $H_{2m-1,2n-1}$. The symmetry group S of this graph is *cmm* modulo unit cell translations.

To determine the cycle structure of a translation τ, we note that the number of cycles of length k in τ is $1/k$ times the number of hexagons H_{ij} such that $\tau^k(H_{ij}) = H_{ij}$, and such that if $0 < p < k$, $\tau^p(H_{ij}) \neq H_{ij}$. The action of any translation can be written $\tau(H_{ij}) = H_{i+s,j+t}$, where $0 \leq s < 2m$, $0 \leq t < 2n$, and $s \equiv t \pmod 2$. Consequently, $\tau^r(H_{ij}) = H_{rs+i,rt+j}$; so that $\tau^r(H_{ij}) = H_{ij}$ if and only if both $rs + i \equiv i \pmod{2m}$ and $rt + j \equiv j \pmod{2n}$, i.e., if and only if both $2m|rs$ and $2n|rt$. This in turn is equivalent to the two conditions that both $(2m/(2m,s))|r$ and $(2n/(2n,t))|r$, or to the single condition that $[2m/(2m,s), 2n/(2n,t)]|r$.

The smallest positive r satisfying this condition is $[2m/(2m,s), 2n/(2n,t)]$ itself. Further, this condition is independent of i and j so that if $\tau^r(H_{ij}) = H_{ij}$ then for any k and l, $\tau^r(H_{kl}) = H_{kl}$. Therefore, if τ is the translation given by $\tau(H_{ij}) = H_{i+s,j+t}$, then all of the cyclic permutations into which τ can be decomposed have length $[2m/(2m,s)\ 2n/(2n,t)]$. Since τ permutes $2mn$ different hexagons, the number of these cycles is $2mn/[2m/(2m,s),\ 2n/(2n,t)]$. The sum of the cycle structures of the pure translations in S is thus

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

Glides normal to *b*, i.e., translations following a reflection in a mirror plane normal to *b*, act by $\sigma(H_{ij}) = H_{i+s,-j+t}$, with the restrictions above on s and t. Thus, $\sigma^r(H_{ij}) = H_{ij}$ if and only if both $i + sr \equiv i \pmod{2m}$ and either r is even or r is odd and $-j + t \equiv j \pmod{2n}$. If $\sigma^r(H_{ij}) = H_{ij}$ and r is odd, then $2j \equiv t \pmod{2n}$, so t is even and can be written $t = 2t'$. Since s and t have the same parity, $s = 2s'$. Further, $j \equiv t' \pmod n$, so j is either t' or $t' + n$; and $2m|sr$, so $m|s'r$. For an odd r satisfying this condition to exist, it is necessary and sufficient that the smallest r satisfying this condition, $m/(m,s')$, be odd. Thus, $\sigma^r(H_{ij})$ occurs with r odd if, and only if, $s = 2s'$, $t = 2t'$, $m/(m,s')$ is odd and j equals t' or $t' + n$. In this case, the $2m$ hexagons with these values of j are permuted by σ in cycles of length $m/(m,s')$, and all other hexagons are permuted in cycles whose length is the smallest even number r' divisible by $m/(m,s')$, i.e., $2m/(m,s')$. In the other case where $\sigma^r(H_{ij}) = H_{ij}$ implies that r is even, all the disjoint cycles of σ have length $2m/(2m,s)$. Thus, the sum of the cycle structures of all glides normal to *b* is

$$\sum_{\substack{0\leq 2t'<2n\\ 0\leq 2s'<2m\\ m/(m,s')\text{ is odd}}} x_{m/(m,s')}^{2m/(m/(m,s'))}\, x_{2m/(m,s')}^{(2mn-2m)/(2m/(m,s'))}$$

$$+ \sum_{\substack{\text{all other } s,t\\ 0\leq s<2m\\ 0\leq t<2n\\ s\equiv t\,(\mathrm{mod}\,2)}} x_{2m/(2m,s)}^{2mn/(2m/(2m,s))}$$

$$= \sum_{\substack{0<s<m\\ m/(m,s')\text{ odd}}} nx_{m/(m,s')}^{2(m,s')}\, x_{2m/(m,s')}^{(n-1)(m,s')}$$

$$+ \sum_{\substack{\text{all other } s\\ 0\leq s<2m}} nx_{2m/(2m,s)}^{n(2m,s)}$$

$$= \sum_{d\mid\mu} n\phi(d)\, x_d^{2^{a+1}\mu/d}\, x_{2d}^{2^a(n-1)\mu/d}$$

$$+ \sum_{\substack{0<k\leq a+1\\ d\mid\mu}} n\phi(2^k d)\, x_{2^k d}^{2^{a+1-k}\mu/d},$$

where $m = 2^a\mu$, μ is odd, and ϕ is the Euler ϕ function (see Appendix). The last equality arises because if $k|l$ then $\phi(l/k)$ is the number of integers x with $0 \leq x < l$ satisfying $(x,l) = k$.

Exactly the same formulas with s and t interchanged and m and n interchanged give the sum of the cycle structures of all glides normal to a.

Finally, twofold rotations parallel to c act by $\psi(H_{ij}) = H_{s-i,\,t-j}$. For all these operations $\psi^2(H_{ij}) = H_{ij}$. If $\psi(H_{ij}) = H_{ij}$ then $s - i \equiv i \pmod{2m}$ and $t - j \equiv j \pmod{2n}$. As shown above, this forces $s = 2s'$, $t = 2t'$, $i \equiv s' \pmod{m}$, and $j \equiv t' \pmod{n}$. Since i and j, like s and t, must have the same parity, these congruences have four solutions i, j with $0 \leq i < 2m$ and $0 \leq j < 2n$ if both $s' \equiv t' \pmod 2$ and $m \equiv n \equiv 0 \pmod 2$, they have no solutions if both $s' \not\equiv t' \pmod 2$ and $m \equiv n \equiv 0 \pmod 2$, and they have two solutions if one or both of m and n are odd. Counting the number of times each of these conditions is met we see that the sum of the cycle structure of this last set of symmetries is $mn(x_1^2x_2^{mn-1} + x_2^{mn})$ if either m or n is odd, and is $mn_1^4x_2^{mn-2}/2 + 3mnx_2^{mn}/2$ if both m and n are even.

The total number of symmetries considered is $8mn$, so the cycle index of the symmetry group S is $1/8mn$ times the sum of the four terms derived above. Call this cycle index $Z(m,n;\, x_1,\, x_2,\, x_3,\, \ldots)$. By Pólya's theorem, the number of S-distinct two-colorings of the $m \times n$ cell is $Z(m,n;\, 2,\, 2,\, 2,\, \ldots)$.

The second step of the solution is to expand S by including in it $1'$, the anti-identification map, and to count the two-colorings of the $m \times n$ cell under the action of the new symmetry group $S \oplus \{1, 1'\}$. According to a generalization of Pólya's theorem found in (*9*), this number is $(Z(m,n;\, 2,\, 2,\, \ldots) + Z(m,n;\, 0,\, 2,\, 0,\, 2,\, \ldots))/2$.

The third step is to extend the symmetry group *cmm* to include three- and six-fold rotations. This is more difficult because in general when a pattern having an $m \times n$ planar unit cell is rotated 60 or 120° the orthogonal unit cell of the rotated pattern with edges parallel to the unrotated axes is no longer an $m \times n$ cell. Since a threefold rotation together with *cmm* generates a sixfold rotation, we may confine ourselves to the latter and ask which $m \times n$ patterns are transformed into others by such a rotation. We shall call such patterns *rotation consistent* patterns.

A sixfold rotation ρ about the center of the H_{00} acts by taking H_{ij} to $H_{(i+j)/2,\,(j-3i)/2}$. In any $m \times n$ pattern, the color of H_{ij} is the same color of $H_{i+2mx,\,j+2ny}$, and $\rho(H_{i+2mx,\,j+2ny}) = H_{(i+j)/2+mx+ny,\,(j-3i)/2+ny-3mx}$; so for any $m \times n$ pattern related to another by a sixfold rotation it must be that for any i, j, x, and y, $H_{(i+j)/2,\,(j-3i)/2}$ has the same color as $H_{(i+j)/2+mx+ny,\,(j-3i)/2+ny-3mx}$. A straightforward analysis of this condition using elementary number theory shows that it forces the pattern to have as a unit cell a subcell of that generated by the vectors $H_{0,\,(2n,\,6m)}$ and $H_{(m,\,n),\,\mu}$, where μ is any number of the form $(m,n) - 4mx - (2n,6m)z$, z is arbitrary and x is a fixed integer such that for some y, $mx + ny = (m,n)$. We may choose μ such that the unit cell has $\gamma = 60°$ or $\gamma = 30°$ by making $\mu = (n,3m)$. If $(n,3m) = (n,m)$ this is the most convenient set of basis vectors and results in a unit cell having one edge going from H_{00} to $H_{0,\,2(n,\,m)}$ and another of equal length at a 60° angle to it. If $(n,3m) = 3(n,m)$, a better choice of basis vectors is $H_{(2n,\,2m),\,0}$ and $H_{(n,m),\,(n,\,3m)}$, so that the unit cell is a 60° rhombus having $H_{(2n,\,2m),\,0}$ as one edge. Any $m \times n$ pattern having as a unit cell a subcell of this will be carried by a three- or sixfold rotation to another $m \times n$ pattern, and any pattern not having such a unit cell will not.

An algorithm to complete the solution now proceeds as follows. Let $T(m,n) = (Z(m,n;\, 2,\, 2,\, \ldots) + Z(m,n;\, 0,\, 2,\, 0,\, 2,\, \ldots))/2$. Use the formulas in the paragraph above to choose a unit cell which is shared by all rotation consistent $m \times n$ patterns, and compute the cycle index Z' of S', the symmetry group of the smaller cell generated by translations and mirror planes normal to the original

orthogonal axes, i.e., by *cmm* modulo the translation group of the new cell. Let $T'(m,n) = (Z'(m,n; 2, 2, \ldots) + Z'(m,n; 0, 2, \ldots))/2$. This is the number of $S \oplus \{1,1'\}$-distinct patterns which, after a three- or sixfold rotation still possess an $m \times n$ unit cell with respect to unrotated axes. Finally, compute the cycle index Z'' of the new cell under the symmetry group S'' generated by translations, mirror planes normal to the axes of the old cell, and sixfold rotations around H_{00}, i.e., by *p6m* modulo unit cell translations. $T''(m,n) = (Z''(m,n; 2, 2, \ldots) + Z''(m,n; 0, 2, \ldots))/2$ is the number of $S'' \oplus \{1,1'\}$-distinct two-colorings of the new cell. The original enumeration by Z counts $T'(m,n)$ distinct rotation consistent $m \times n$ patterns. In reality there are only $T''(m,n)$ such patterns under the action of $p6m \oplus \{1,1'\}$. Hence, the total number of distinct $m \times n$ hexagonally close-packed structures MX_2 with two-layer repeat perpendicular to the close-packed layers is $N(m,n) = T(m,n) - T'(m,n) + T''(m,n)$. This completes the algorithm, and with it the original problem.

Observe that the new cell can be made into a graph just as the old $m \times n$ cell was, and that the groups S' and S'' act naturally on this graph. The cycle indices Z' and Z'' could be written down explicitly as was Z; however, the explicit formulas are not as compact as those for Z, and thus they add little clarity. Further,

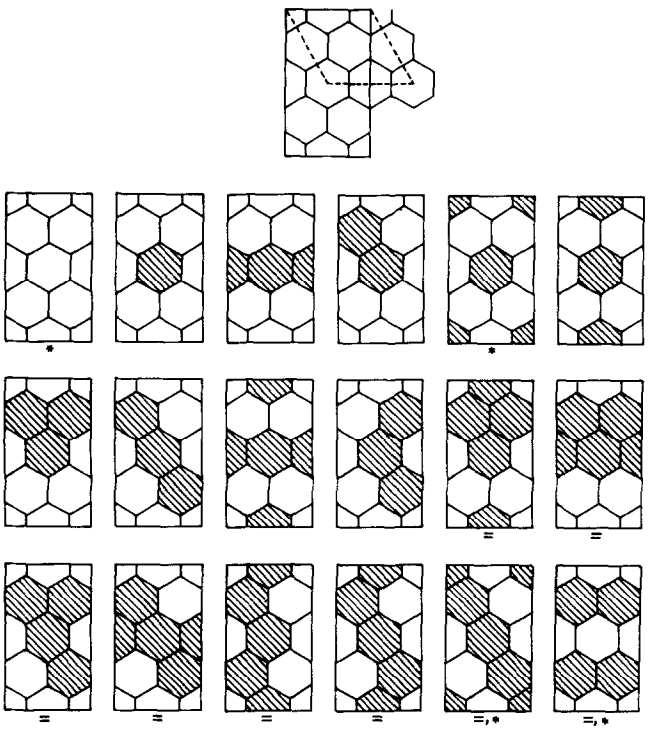

FIG. 2. The orthorhombic cell in the top row is the 2×2 cell. The hexagonal subcell is that common to all 2×2 patterns taken to other such patterns by a three- or sixfold rotation. The remaining rows show the 18 $S \oplus \{1,1'\}$-distinct 2×2 patterns. Self-complementary patterns are marked =, and patterns having the hexagonal cell above as a unit are marked *. The last two patterns are $S \oplus \{1,1'\}$-distinct, but are related by a 60° rotation and are, therefore, $S'' \oplus \{1,1'\}$-equivalent and represent the same structure. Physically, these are projections showing the occupied octahedra in one layer of each of the 18 hcp structures MX_2 sharing the 2×2 "olivine" cell, where two structures are regarded as identical only if they are related by an element of $C\,2/c\,2/m\,2_1/m$, the maximal orthorhombic subgroup of $P6_3/m\,mc$. Only the first 17 of these actually represent distinct structures; the last two patterns are different settings of the rutile structure related by a symmetry in $P6_3/mmc$ but not in $C\,2/c\,2/m\,2_1/m$.

the new unit cell is often much smaller than the old; and unless m and n are both multiples of some fairly large number, it is easier to determine Z' and Z'' by constructing all elements of S' and S'' than by the use of these formulas.

Some Examples

Let us show how the arguments above work in some special cases. Consider the 2×2 orthorhombic cell which is the unit cell of the well-known olivine structure type. For this unit cell, $Z(2,2;\ x_1,\ x_2,\ x_3,\ \ldots) = (1/32)(x_1^8 + 6x_1^4x_2^2 + 13x_2^4 + 12x_4^2)$, $Z'(2,2;\ x_1, x_2, x_3, \ldots) = (1/8)(x_1^4 + 2x_1^2x_2 + 3x_2^2 + 2x_4)$, and $Z''(2,2;\ x_1, x_2, x_3, \ldots) = (1/24)(x_1^4 + 6x_1^2x_2 + 8x_1x_3 + 3x_2^2 + 6x_4)$. Thus, $T(2,2) = 18$, $T'(2,2) = 4$, $T''(2,2) = 3$, and $N(2,2) = 18 - 4 + 3 = 17$. There are, therefore, eighteen $S \oplus \{1,1'\}$-distinct 2×2 patterns, four of which are still 2×2 patterns after a sixfold rotation. These four collapse to three under the action of $S'' \oplus \{1,1'\}$, so that $N(2,2) = 17$. Figure 2 shows the 2×2 cell and these patterns.

Table I lists the values of $T(m,n)$ and $N(m,n)$ for $m + n \leq 8$. The formulas used to compute $T(m,n)$ are symmetric in m and n so that $T(m,n) = T(n,m)$. The unit cell common to all rotation consistent $m \times n$ patterns is selected by formulas not symmetric in m and n, so that in general $N(m,n) \neq N(n,m)$. In particular, $N(2,6) \neq N(6,2)$.

For $m + n \leq 8$, $T(m,n)$ is always very nearly equal to $N(m,n)$ and is considerably easier to compute. Indeed, this is true in general, and as $mn \to \infty$, $N(m,n)/T(m,n) \to 1$. The proof of this assertion is as follows. The leading term in $Z(m,n;\ x_1,\ x_2,\ \ldots)$ is $x_1^{2mn}/8mn$, so $T(m,n) \geq 2^{2mn}/16mn$. Further, the cell common to all rotation consistent $m \times n$ patterns is always smaller than the

TABLE I

VALUES OF $T(m,n)$ AND $N(m,n)$ FOR $m + n \leqslant 8$[a]

$N(m,n)$ / $T(m,n)$	n = 1	2	3	4	5	6	7
m = 1	2	4	8	18	44	122	362
	2	4	8	18	44	122	362
2	4	17	88	728	7456	92352	
	4	18	88	729	7456	92393	
3	8	88	2170	90466	4503160		
	8	88	2176	90466	4503160		
4	18	728	90466	16835760			
	18	729	90466	16836158			
5	44	7456	4503160				
	44	7456	4503160				
6	122	92392					
	122	92393					
7	362						
	362						

[a] The number $T(m,n)$ of $S \oplus \{1,1'\}$-distinct 2-colorings of an $m \times n$ cell and the actual number $N(m,n)$ of $p6m \oplus \{1,1'\}$-distinct 2-colorings of the same cell. $T(m,n)$ is the number of hcp structures MX_2 with the $m \times n$ cell if two structures related by an element of $C\ 2/c\ 2/m\ 2_1/m$ are regarded as identical. $N(m,n)$ is the number of these structures under the action of $P6_3/mmc$.

$m \times n$ cell itself. If it were not, the areas of the two cells would be equal. If $(3m,n) = 3(m,n)$, this implies that $4mn3^{1/2}R^2 = 6(m,n)^2 3^{1/2}R^2$, so that $2(3m)n = (3m,n)^2$. This is impossible since $(3m,n) \leq \min\{3m,n\} \leq ((3m)n)^{1/2}$. A similar contradiction arises if $(3m,n) = (m,n)$.

The smaller hexagonal cell therefore contains at most mn hexagons, so each of the numbers whose average is $Z'(m,n; 2, 2, \ldots)$ is at most 2^{mn}, and $T'(m,n) \leq Z'(m,n; 2, 2, \ldots) \leq 2^{mn}$. Also, $Z''(m,n; x_1, x_2, \ldots) = Z'(m,n; x_1, x_2, \ldots)/3 + P(x_1, x_2, \ldots)$, where P is a polynomial all of whose coefficients are positive, so $T''(m,n) \geq T'(m,n)/3$. Thus, $T(m,n) - N(m,n) = T'(m,n) - T''(m,n) \leq 2T'(m,n)/3 \leq 2^{mn+1}/3$, so $(T(m,n) - N(m,n))/T(m,n) \leq 16mn2^{mn+1}/(3 \cdot 2^{2mn}) = mn/(3 \cdot 2mn^{mn-5})$, which approaches zero as $mn \to \infty$. For all pairs of m and n except those with $m = 1$ or $n = 1$ (for which $N(m,n) = T(m,n)$) and those in Table I, $mn \geq 14$, so $|1 - N(m,n)/T(m,n)| \leq 7/768$. For most m and n, these bounds can be refined considerably.

The cycle indices produced here can also be employed to calculate the number of (2×2)-ordered derivatives of the seventeen 2×2 structures in Fig. 2. Indeed, Pólya's theorem implies that if $Z(2,2; 1 + z_1 + z_2 + \ldots + z_7, 1 + z_1^2 + z_2^2 + \ldots + z_7^2, \ldots)$ is expanded using multinominal coefficients, then the coefficient of the $1^{i_0}z_1^{i_1}z_2^{i_2} \ldots z_7^{i_7}$ term in the expansion will be the number of S-invariant patterns in which i_0 hexagons are colored with color c_0, i_1 hexagons are colored c_1, etc. For example, the coefficient of $z_1^5 z_2^2 z_3$, 9, represents the number of S-distinct ways to color five of the hexagons red, two of them white, and one of them blue. The actual number of $p6m$-distinct $m \times n$ patterns in which i_j hexagons are colored c_j will be, by the same reasoning used in our earlier algorithm, the coefficient of $1^{i_0}z_1^{i_1} \ldots z_7^{i_7}$ in $Z(2,2; 1 + z_1 + \ldots + z_7, 1 + z_1^2 + \ldots + z_7^2, \ldots) - Z(2,2; 1 + z_1^2 + \ldots + z_7^2, 1 + z_1^4 + \ldots + z_7^4, \ldots) + Z''(2,2; 1 + z_1^2 + \ldots + z_7^2, 1 + z_1^4 + \ldots + z_7^4, \ldots)$, where the exponents in the arguments of Z' and Z'' are doubled because there are two of the hexagonal unit cells derived in the third part of the basic algorithm in each of the original orthorhombic cells (see (9)).

Colored patterns may be used to represent ordered derivatives of the structures represented by black and white patterns. The three-colored patterns, for example, could be used to represent derivatives of the MX_2 structures in which the M atoms are replaced by A and B atoms, the A atoms can occupy octahedra in either of the nonequivalent layers, and all the B atoms are constrained to occupy octahedra in the layer $c = 0$. The four-colored patterns might then represent all derivatives $A_aB_bX_{2(a+b)}$ of the MX_2 structures, with A and B atoms constrained only by the requirements that the repeat distance parallel to c be two close-packed layers and that occupied octahedra not share faces. If this representation is to be used to enumerate such structures, some account must be taken of the fact that there are two nonequivalent layers of octahedra, either of which may be chosen as the layer at $c = 0$ and projected to form a colored net. In the case of two-colorings, this was done by implicitly imposing a symmetry group on the set of colors and using a theorem of de Bruijn (9). This was described as extending the groups S, S', and S'' to include the anti-identification. Here, also, it can be done by imposing upon the colors c_1, c_2, c_3, and c_4 a symmetry group H consisting of the identity and an element interchanging c_1 and c_2 and interchanging c_3 and c_4 (if c_1 and c_2 represent an A atom in layers 1 and 2, respectively, and c_3 and c_4 represent a B atom in these layers). Two patterns P and P' are now regarded as identical if for some symmetries $g \in p6m$ of the hexagonal net and $h \in H$, $Pg = hP'$. Theorem 5.4 of de Bruijn (9) can be used to count all such patterns, which represent all orderings of two atomic species over the occupied octahedral sites in the structures enumerated by $N(m,n)$. This number is $M(m,n) = (Z(m,n; 4, 4, \ldots) + Z(m, n; 0, 4, 0, 4, \ldots))/2 - (Z'(m,n; 4, 4, \ldots) + Z'(m,n; 0, 4, \ldots))/2 + (Z''(m,n; 4, 4, \ldots) + Z''(m,n; 0, 4,$

. . .))/2. For the olivine cell, $m = n = 2$, $M(2,2) = 1506$.

In Table II, the numbers of colorings of different types have been listed assuming symmetry group $\{1\}$ on the space of colors. Note that this table gives additional information about the two-colorings of the 2×2 cell by telling how many distinct colorings have k hexagons white and 8-k hexagons black. This information could have been obtained more easily by considering the two-colorings where w(black) = 1, w(white) = x.

TABLE II

NUMBERS OF COLORINGS OF DIFFERENT TYPES ASSUMING SYMMETRY GROUP $\{1\}$ ON THE SPACE OF COLORS[a]

Representative term	S-Distinct patterns	Actual patterns
x_1^8	1	1
$x_1^7 x_2$	1	1
$x_1^6 x_2^2$	4	4
$x_1^6 x_2 x_3$	4	4
$x_1^5 x_2^3$	4	4
$x_1^5 x_2^2 x_3$	9	9
$x_1^5 x_2 x_3 x_4$	15	15
$x_1^4 x_2^4$	8	7
$x_1^4 x_2^3 x_3$	14	14
$x_1^4 x_2^2 x_3^2$	24	23
$x_1^4 x_2^2 x_3 x_4$	33	33
$x_1^4 x_2 x_3 x_4 x_5$	57	57
$x_1^3 x_2^3 x_3^2$	25	25
$x_1^3 x_2^3 x_3 x_4$	44	44
$x_1^3 x_2^2 x_3^2 x_4$	63	63
$x_1^3 x_2^2 x_3 x_4 x_5$	114	114
$x_1^3 x_2 x_3 x_4 x_5 x_6$	210	210
$x_1^2 x_2^2 x_3^2 x_4^2$	102	100
$x_1^2 x_2^2 x_3^2 x_4 x_5$	171	171
$x_1^2 x_2^2 x_3 x_4 x_5 x_6$	324	324
$x_1^2 x_2 x_3 x_4 x_5 x_6 x_7$	630	630
$1x_1 x_2 x_3 x_4 x_5 x_6 x_7$	1260	1260
Total	3117	3113

[a] Column 1 shows a representative term $1^{n_0} x_1^{n_1} \ldots x_t^{n_t}$ indicating that n_0 hexagons are colored c_0, etc. Column 2 shows how many S-distinct patterns satisfy this coloring scheme, and column 3 shows how many patterns exist satisfying this coloring scheme distinct under all symmetries of the hexagonal net. The unit cell is the 2×2 "olivine" cell.

By Pólya's theorem such colorings are enumerated according to their weights by $Z(2,2; 1 + x, 1 + x^2, \ldots)$ and the corresponding Z' and Z''.

Related Problems

The approach used here lends itself to a large number of related problems of possible importance to crystallographers. The requirements that no face-sharing octahedra be permitted and that the repeat distance parallel to c be two close-packed layers can be relaxed using either of two techniques. S, S', and S'' may be enlarged to symmetries of the actual three-dimensional octahedral framework instead of symmetries of a two-dimensional projection. Alternatively, S, S', and S'' may be left unchanged; all the desired stackings of different atomic species, plus vacancies in vertical columns with given vertical repeat, may be represented as colors on the hexagon net; and de Bruijn's (*9*) generalization of Pólya's theorem may be used just as in the example above of four-colorings to impose on the set of colors a group of symmetries corresponding to translations parallel to c and three-dimensional inversions. The problem in which all the octahedral holes are empty but the tetrahedral holes are partially occupied is similar to the situation considered here and can be treated using identical methods. The problem of enumerating structures with given unit cells possessing r-occupied octahedral sites and s-occupied tetrahedral sites can also be solved using a generalization of Pólya's theorem stated by Sheehan (*13*). This enumeration, however, counts a large number of physically improbable structures containing face-sharing polyhedra. There does not seem to be a straightforward generalization of the methods used here which eliminates this drawback, although in practice for fairly small cells with fairly large octahedral populations (for example, in the case of the olivine structure type itself), the pattern of occupancy of octahedral holes along with Pauling's (*14*) electro-

static rules more or less dictates the location of tetrahedrally coordinated cations.

The problem of enumerating hcp structures MX_2 with a hexagonal unit cell is less complex than the case treated here in which the cell is orthorhombic in that three- and sixfold rotations always preserve the two-dimensional hexagonal unit cell with regard to unrotated axes. Thus, *p6m* can act directly on the graph constructed from the hexagonal cell, while it could not do so in the orthorhombic case, forcing us to construct a smaller cell on which it could act via S''. The number of $P6_3/mmc$-distinct hcp structures MX_2 with a given hexagonal unit cell is thus $\frac{1}{2}(Z(G; 2, 2, \ldots) + Z(G; 0, 2, 0, 2, \ldots))$, where G is *p6m* modulo two-dimensional cell translations, and G acts on equivalence classes of hexagons.

Most other enumeration problems involving close packings with a given unit cell will most closely resemble the problem of counting hcp structures MX_2 with an orthorhombic cell, in that the symmetry group G_a of the anion framework (in our original problem $G_a = P6_3/mmc$) will properly contain the maximal subgroup G_a' (above, $G_a' = C2/c\ 2/m\ 2_1/m$) having the unit cell translations as a normal subgroup. To evaluate the number of G_a-equivalence classes of structures it will be necessary in these cases also to choose subcells whose translation groups are normal in groups H_a, $G_a' \subset H_a \subseteq G_a$, and to evaluate quantities analogous to T' and T'' above. Indeed, if G_a' is not a maximal subgroup of G_a (as $C\ 2/c\ 2/m\ 2_1/m$ was of $P6_3/mmc$) it will be necessary to construct such cells for several groups H_a.

Consider, for example, the problem of counting cubic close-packed structures with several atomic species, plus vacancies ordered over the octahedral (or tetrahedral) sites. This means enumerating derivatives of the NaCl structure where earlier we enumerated derivatives of the NiAs structure. If the unit cell is given to be isometric the enumeration can be carried out using de Bruijn's (*9*) theorem and the cycle index of $Fm3m$ modulo cell translations, where $Fm3m$ is regarded as acting on octahedra (or tetrahedra). If, however, the unit cell has lower symmetry than cubic, then the cell translation group will not be normal in $Fm3m$. As an example, let the unit cell be orthorhombic, have edges parallel to the edges of the usual cubic unit cell generated by $\{a_0 = b_0 = c_0\}$ of the ccp framework and let it have $a = a_0$, $b = 2b_0$, $c = 3c_0$. Let $N(1 \times 2 \times 3; \text{orth})$ be the number of ccp structures having this cell with ordered occupancy of the octahedral holes and no tetrahedrally coordinated cations, where two structures are regarded as identical if one is related to the other by some element of the maximal orthorhombic subgroup of $Fm3m$ having axes parallel to $\{a,b,c\}$. If all other symbols are defined similarly, then it will be seen that the number of structures possessing this cell and not related to one another by any element of $Fm3m$ is $N(1 \times 2 \times 3; \text{orth}) + (N(1 \times 1 \times 3; \text{tet}) - N(1 \times 1 \times 3; \text{orth})) + (N(1 \times 2 \times 1; \text{tet}) - N(1 \times 2 \times 1; \text{orth})) + (N(1 \times 1 \times 1; \text{cub}) - N(1 \times 1 \times 1; \text{tet}_b) - N(1 \times 1 \times 1; \text{tet}_c) + N(1 \times 1 \times 1; \text{orth}))$. Here tet_b (tet_c, resp.) is the maximal tetragonal subgroup of $Fm3m$ with four-fold axis parallel to b (c, resp.).

The double hexagonal and other close packings are subject to the same analysis used here on the hexagonal and cubic close packings.

Conclusion

The examples sketched here may serve to illustrate some of the range of applications of elementary combinatorial techniques to crystallographic problems. Combinatorial mathematics provides many valuable tools for constructing algorithms enumerating classes of crystal structures. The classifications produced by these algorithms must then be evaluated on the basis of their usefulness in other aspects of crystal chemistry. It must be determined, for example, whether any type of simple stability calculation applied to all members of a family

of structure types suffices to discriminate between real structures and those seemingly not found in nature. Future problems in crystallographic enumeration may address still other questions in structure analysis, crystal chemistry, and structure systematics.

Appendix: Mathematical Notation

$d \in D$	d is an element of the set D
$\prod_{d \in D} g(d)$	The product of all $g(d)$ such that $d \in D$
$a \equiv b \pmod{c}$	c divides $a - b$; a and b have the same remainder on division by c
$a \mid b$	a divides b; b is an integral multiple of a
(m,n)	The greatest common divisor of m and n
$[m,n]$	The least common multiple of m and n.
$\phi(n)$	The number of positive integers less than or equal to n having no common divisors with n except ± 1.
$G \oplus \{1, 1'\}$	The direct sum of G and $\{1, 1'\}$; the group consisting of all elements $g \cdot 1$ and $g \cdot 1'$, where g is in G.
$A \subseteq B$	A is a subset of B; all elements of A are elements of B.
$A \subset B$	A is a proper subset of B; $A \subseteq B$ and $A \neq B$.

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