remain unsolved. Such discussions may be difficult at the present stage because even the structural defects in original β''-alumina have so far not been satisfactorily clarified. It is, however, our opinion that the essential points of our results deduced from the idealized crystal structure of β''-alumina may hold substantially unchanged even for real, non-stoichiometric β''-alumina.

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Stacking Variants for Doubly-Connected Systems Arranged According to the Percentages of Hexagonal Stacking

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Abstract

As an extension of Table 7.1.5*B* of *International Tables for X-ray Crystallography* [(1967), Vol. II. Birmingham: Kynoch Press], the possible stacking variants up to ten layers are arranged according to the percentage of hexagonal stacking. A method is given which allows one to calculate the number of possible stacking variants for any number of layers.

Introduction

Over the last few years several relations have been found between certain physical or structural properties and the percentage of hexagonal stacking of the layers or sheets for compounds which have close-packed or derivative structures.

The following examples can be mentioned:

(*a*) The change in the percentage of hexagonal stacking of close-packed rare-earth metals, R, or of rare-earth–aluminium alloys, RAl_3, with increasing pressure (Gschneidner & Pearson, 1968).

(*b*) The change of the birefringence of ZnS variants with a change of the percentage of hexagonal stacking (Brafman & Steinberger, 1966; Parthé, 1972).

(*c*) The change of the percentage of hexagonal stacking of ternary Laves phases with valence electron concentration (Parthé, 1974; Komura & Kitano, 1977).

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(*d*) The change of the percentage of hexagonal stacking of CrB–FeB stacking variants in quasibinary rare-earth–nickel systems $R_{1-x}R'_xNi$ upon changing the R/R' ratio (Klepp & Parthé, 1980).

For a study of these relations it is desirable to have available a table of possible stacking variants arranged according to the percentage of hexagonal stacking. Unfortunately, neither in *International Tables for X-ray Crystallography* (1967) nor in Beck (1967) is such a table to be found.

Arrangement of stacking variants according to percentage of hexagonal stacking

In Table 1 all possible stacking variants up to ten layers ($N = 10$) are listed, arranged according to the percentage of hexagonal stacking. This table is applicable to all doubly-connected systems which, following Beck (1967), are characterized by the availability of only two stacking operations. For a given number of layers the entries are subdivided according to the difference between the number of positive (p) and negative (n) sideways displacements of the layers. A change of sign of the sideways displacement occurs with every new digit in the Zhdanov symbols. Table 1 serves also to obtain the cyclicity value of a stacking variant, which after Mardix, Steinberger & Kalman (1970) is defined as $|p - n|/N$. The total number of possible stacking variants for a given number of layers, $\sum(N)$, is given on the bottom line. In agreement with Table 7.1.5*B* of *International Tables for X-ray Crystallography* (1967) the extended Zhdanov notation has been applied to denote the stacking variants. Because we deal with a doubly-connected system the number of Zhdanov digits must be even. The mirror symmetry in the sequence of the Zhdanov succession numbers is shown in two ways according to whether the signs of the stacking sequence are alike or opposite. For like signs, parentheses are placed around the succession number in the mirror plane, whilst a vertical bar is placed between two succession numbers for a mirror symmetry relating opposite signs of identical succession numbers. The symmetry and particularly the space group of the stacking variant depend on the individual symmetry of the layer or sheet and on the symmetry of the Zhdanov symbol.* In each field the Zhdanov symbols are, where possible, arranged according to the symmetry of the stacking period. The percentage of hexagonal stacking is given by

$$\frac{\text{number of digits}}{\text{sum of numbers}} \times 100$$

of the corresponding Zhdanov symbol [except for the cubic stacking (1)(0) with 0% hexagonal stacking].

The possible values of the percentage of hexagonal stacking for different numbers of layers N are displayed graphically in Fig. 1. They correspond to the intersections of two families of hyperbolae with formulae

$$\% \text{ hexagonal stacking} = 100 \times \frac{N^* - N_c}{N^*}$$

and

$$\% \text{ hexagonal stacking} = 100 \times \frac{N_h}{N^*}$$

where N^* is a continuous positive variable and N_c and N_h are positive integers, the latter having only even values. At an intersection of two hyperbolae we find

$$N^* = N_c + N_h \equiv N.$$

For a given value of $N > 2$ the possible percentages of hexagonal stacking are given by $100 \times N_h/N$ where $N_h = 2, 4, 6, \ldots$ with $N_h < N$. N_h represents the number of digits in the Zhdanov formula or, expressed differently, the number of h symbols in the corresponding Jagodzinski formula which for doubly-connected systems has to be even. N_c corresponds to the number of c symbols in the Jagodzinski formula.

In the circles at the intersections of the hyperbolae the number of possible stacking variants is indicated. To the right of the figure is shown the total number of stacking variants $\sum(N)$ for a given number of layers.

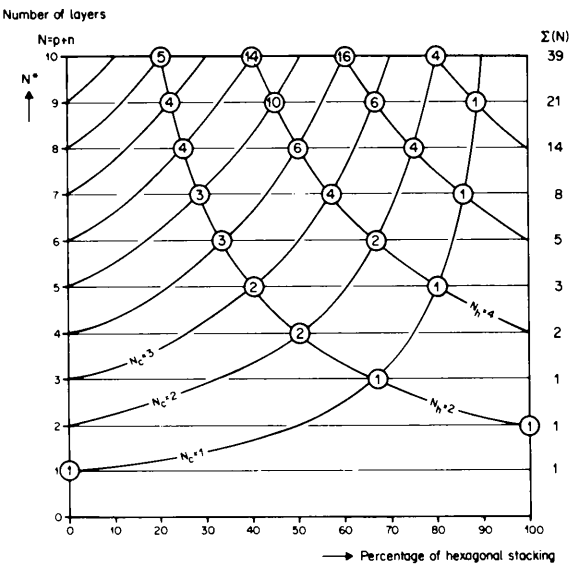


Fig. 1. Hyperbola construction displaying the possible values of the percentage of hexagonal stacking for up to ten layers.

* There are additional symmetry properties to be considered if the amount of sideways displacement is a fraction of the translation period in that direction (for example the rhombohedral symmetry in close-packed structures when the sideways displacement is one third of the translation period).

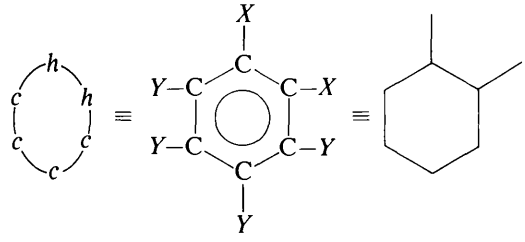
Table 1. *List of possible stacking variants up to ten layers arranged according to the percentage of hexagonal stacking*

Number of layers N and difference of the number of positive (p) and negative (n) sideways displacements of layers

Percentage of hexagonal stacking	$N = p + n$	1	2	3	4		5		6			7			8				9				10				
	$\lvert p - n \rvert$	1	0	1	0	2	1	3	0	2	4	1	3	5	0	2	4	6	1	3	5	7	0	2	4	6	8
0		(1)(0)																									
20																							|(5)|(5)|	(6)(4)	(7)(3)	(8)(2)	(9)(1)
22·2																			(5)(4)	(6)(3)	(7)(2)	(8)(1)					
25															|(4)|(4)|	(5)(3)	(6)(2)	(7)(1)								
28·6												(4)(3)	(5)(2)	(6)(1)													
33·3									|(3)|(3)|	(4)(2)	(5)(1)														
40							(3)(2)	(4)(1)															|4||4| |32|23| 4312	(5)2(1)2 (4)2(2)2 (3)3(1)3 5311 4321	6211 5221 4231	(7)1(1)1 (6)1(2)1 (5)1(3)1	
44·4																			(4)2(1)2 (3)2(2)2 4311 3321	(2)3(1)3 5211 4221	(6)1(1)1 (5)1(2)1 (4)1(3)1						
50					|(2)|(2)|	(3)(1)									|31|13| (3)2(1)2	4211 3221	(5)1(1)1 (4)1(2)1									
57·1												(2)2(1)2 3211	(4)1(1)1 (3)1(2)1													
60																							|1(3)1|1(3)1| |2(1)2|2(1)2| |311|113| |221|122| (3)21(1)12 321211	(4)11(2)11 (2)21(2)12 421111 322111 312211 321121	(5)11(1)11 (3)12(1)21 (1)31(1)13 412111		
66·7				(2)(1)					|21|12|	(3)1(1)1									(3)11(2)11 (2)21(1)12 321111 221211	(4)11(1)11 312111							
75															|1(2)1|1(2)1| |211|112|	(3)11(1)11 (1)21(1)12											
80							(2)1(1)1																|2111|1112| |1211|11211|	(3)111(1)111 (1)211(1)112			
85·7												(2)111(1)111															
88·9																			(2)111(1)111								
100			|(1)|(1)|																								
$\Sigma(N)$		1	1	1	2		3		5			8			14				21				39				

Calculation of the number of stacking variants for an arbitrary number of stacked layers

Since stacking is an infinite periodic operation, all layers of the stacking period are formally equivalent as possible starting points of the period. This fact can be expressed by writing down the corresponding stacking symbol in the form of a closed cycle. It is especially useful to apply this concept to the Jagodzinski notation since then only two different symbols are required (h and c) and the total number of symbols equals the number of layers. From the point of view of graph theory, the cyclic Jagodzinski symbol of a stacking sequence is equivalent to the molecular formula of an organic ring system with two different substituents (say X and Y). One substitution position is available on each C atom. Both cyclic Jagodzinski formulae and organic molecular formulae can be presented by the same graph as shown by the following example.



Except for two restrictions, to be discussed later, the problem of enumerating the number of possible stacking variants corresponds to the problem of calculating the number of substituted ring compounds. This problem has been solved by Pólya (1937).

The number of different solutions for substituted N-membered rings is given by the generating function

$$A(N) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots + a_N x^N, \quad (1)$$

where the exponents indicate the numbers of substituents of one kind and the coefficient a_i indicates the number of different arrangements for a given number i of substituents of one kind. According to Pólya's (1937) *Hauptsatz* the coefficients a_i can be obtained by calculation from the polynomial expressions

$$A(N) = \frac{1}{2N}\left[\sum_K \varphi(K)(1 + x^K)^{N/K} + N(1 + x)(1 + x^2)^{(N-1)/2}\right] \quad (2)$$

for N odd, and

$$A(N) = \frac{1}{2N}\left\{\sum_K \varphi(K)(1 + x^K)^{N/K} + \frac{N}{2}\left[(1 + x)^2 (1 + x^2)^{N/2-1} + (1 + x^2)^{N/2}\right]\right\} \quad (3)$$

for N even. The summation is to be made over all divisors, K, of N (including 1 and N) and $\varphi(K)$ is Euler's totient function which for $K = 1$ assumes the value 1 and is otherwise given by

$$\varphi(K) = K \prod_P \left(1 - \frac{1}{P}\right) \quad (4)$$

where P are the prime factors of K. Note that

$$\sum_K \varphi(K) = N. \quad (5)$$

The number of different stacking variants is a partial set of the number of solutions for the ring systems given above because the infinite nature of the lattice imposes two restrictions:

(1) The number of hexagonal stacking steps must be even. Thus in (1) only coefficients a_i with even index are of interest, the index corresponding to N_h.

(2) A stacking period containing identical subperiods with an even number of hexagonal stacking steps does not constitute a new stacking variant (for example h_2ch_2c corresponds to h_2c). Thus the numbers of stacking variants of the divisors of N at the corresponding values of the percentage of hexagonal stacking have to be subtracted.

Example: $N = 12$. Equation (3) can be written

$$A(12) = \tfrac{1}{24}\{(1 + x)^{12} + (1 + x^2)^6 + 2(1 + x^3)^4 + 2(1 + x^6)^2 + 4(1 + x^{12})^1 + 6[(1 + x)^2 (1 + x^2)^5 + (1 + x^2)^6]\} \quad (6)$$

$$= 1 + x + 6x^2 + 12x^3 + 29x^4 + 38x^5 + 50x^6 + 38x^7 + 29x^8 + 12x^9 + 6x^{10} + x^{11} + x^{12}. \quad (7)$$

The coefficients a_i corresponding to even exponents of x are listed in the second row of Table 2. From these values have to be subtracted, at the corresponding values of the percentage of hexagonal stacking, the number of stacking variants for $N = 6$, 4, 3, 2 and 1 written into the circles in Fig. 1. There are altogether 112 different stacking variants for $N = 12$ in agreement with Table 7.1.5*B* of *International Tables for X-ray Crystallography* (1967).

For the special case that N_h and N have no common divisor and $N_h \neq 0$ and N odd and >1, it is possible to obtain the coefficients a_{N_h} directly without solving (2) by

$$a_{N_h}(N) = \frac{1}{2}\frac{(N-1)(N-3)\ldots(N-N_h+1)}{1 \times 2 \times 3 \times \ldots \times N_h} \times [N(N-2)(N-4)\ldots(N-N_h+2)/N + 1 \times 3 \times \ldots \times (N_h - 1)] \quad (8)$$

Table 2. *Enumeration of the number of stacking variants for* $N = 12$

Percentage of hexagonal stacking	0	16·67	33·33	50	66·67	83·33	100	
Number of solutions obtained from Pólya's (1937) *Hauptsatz*	1	6	29	50	29	6	1	
Number of solutions for divisors of 12 to be subtracted								
$N = 6$			3		2			
$N = 4$				2				
$N = 3$					1			
$N = 2$							1	
$N = 1$	1							
Number of stacking variants for $N = 12$	0	6	26	48	26	6	0	$\sum(12) = 112$

with the special solutions

$$a_2(N) = (N-1)/2 \quad \text{and} \quad a_{N-1}(N) = 1.$$

For example, for $N = 11$ one obtains for $N_h = 2, 4, 6, 8$ and 10 the values 5, 20, 26, 10 and 1. The sum $\sum(11) = 62$ is again in agreement with *International Tables for X-ray Crystallography* (1967).

If N is a prime number and $N \geq 3$ the total number of stacking variants is given by

$$\sum(N) = \frac{2^{(N-1)/2}(2^{(N-1)/2} + N) - (N+1)}{2N}. \qquad (9)$$

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Solving Structures by Constrained Least-Squares Refinement

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Abstract

A systematic convergence test for constrained rigid-body least-squares refinement shows good possibility of convergence towards the right solution, even starting from strongly misplaced molecular models (translations of about 1·5 Å and rotations of about 30°), if an appropriate sequence of reflections and strategy is used. Consequently, a routine for solving structures with a known molecular model by *ab initio* least-squares refinement has been written, and successfully tested with three unknown structures: inclusion of second derivatives has also been tested, with a view to improving the method. In all cases so far examined, the routine is very fast, simple to use and competitive with usual methods, even when the model is only approximately known. The inclusion of second derivatives as such is not convenient, at least if precautions are not taken to reach a true minimum: a possible way of further improvement is discussed.

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