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N-Dimensional Diamond, Sodalite and Rare Sphere Packings

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Abstract

The diamond, lonsdaleite and sodalite structures are generalized to N dimensions and described. Ring counts and coordination sequences for the $N+1$-connected nets are given for $N\le 6$. Simple analytic expressions are given for coordination sequences for diamonds, sodalites and the primitive hypercubic lattice. Replacing the vertices of diamonds and sodalites by regular simplices produces rare (open) stable sphere packings; general expressions for the density of these are given.

Introduction

Recent developments in the theory of quasicrystals and incommensurate structures have led to an increased interest in crystallography in more than three dimensions (*e.g.* Janssen, 1986); this is an area that has also been of enormous stimulation to pure and applied mathematics although there the emphasis has been mainly on dense lattices and sphere packings (Conway & Sloane, 1988).

In three-dimensional crystal chemistry the four-connected nets are of particular importance being, among many other things, the basis of some elemental structures and of the framework silicates and hydrates. The diamond structure has a special place among these as it is the only such net with all vertices (atoms), edges (bonds) and angles equivalent. Such a net I term *regular* (it is noted that graph theorists usually employ this term in a much less restrictive sense). In this paper some properties of the N-dimensional analogs of diamond and its simplest polytype (in three dimensions, lonsdaleite) are described. Another important net is that of sodalite; it has all vertices and edges equivalent (*quasiregular*). Generalizations of this net are also described. Some reasons why the properties of these structures might be of interest are given below after some necessary basic definitions.

Recent discussions of nets (Stixrude & Bukowinski, 1990; O'Keeffe, 1991*a*) have focused particular attention on coordination sequences (Brunner, 1979; Meier & Moeck, 1979) and ring statistics (Marians & Hobbs, 1990). A coordination sequence consists of the numbers, n_k, of kth neighbors of a vertex, a kth neighbor being one for which the shortest path to the reference vertex consists of k edges. One can define (O'Keeffe, 1991*a*) a dimensionless local topological density

$$\rho_k=\sum_{i=1}^{k} n_i/k^3. \qquad (1)$$

The limit as $k\to\infty$ is called the global topological density ρ_∞. The generalization to N dimensions is obvious. The number of neighbors n_{Nk} for an N-dimensional structure can sometimes be fit to a polynomial

$$n_{Nk}=\sum_{i=0}^{N-1} a_{Ni}k^i. \qquad (2)$$

In that event $\rho_\infty=a_{N,N-1}/N$. In this work the coefficients have been empirically determined from a count of a large number of neighbors, the number of shells counted being at least twice the number of coefficients.

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The primitive rhombohedral cell of diamond contains two atoms (C1 and C2) and four bonds. The topology of the structure is completely determined once the bonds are specified. Let the reference unit cell be 000 and adjacent unit cells 100 *etc.* Atom C1 is bonded to four C2 atoms in unit cells 000, 100, 010 and 001. (It follows at once that C2 is bonded to C1 in 000, $\bar{1}00$, $0\bar{1}0$, $00\bar{1}$.) N-dimensional diamond is defined topologically as forming $N+1$ bonds from C1 to C2 in 0000..., 1000..., 0100....... The two-dimensional analog is the familiar honeycomb structure, 6^3; primitive unit cells of this and the diamond structure are shown in Fig. 1.

From a geometric point of view, in its most symmetric form, the N nearest neighbors of an atom in the generalized diamond structure are at the vertices of a regular simplex (the N-dimensional solid with $N+1$ vertices, each of which is joined to the N others by an edge). The $N(N+1)/2$ bond angles are $\cos^{-1}(-1/N)$ and, for unit edge length, the next-nearest distance (the simplex edge length) is $(2+2/N)^{1/2}$. In three dimensions the diamond structure can be described as the structure obtained from a lattice sphere packing (cubic closest packing) combined with one half of the tetrahedral interstices. The analogous N-dimensional lattice sphere packing with simplicial interstices that is designated A_n (Conway & Sloane, 1988) can be similarly used to derive the N-dimensional diamond structure.

The vertices of the sodalite net form the lattice complex labeled W^* (Fischer & Koch, 1985). They consist of all the (irregular) tetrahedral interstices of the b.c.c. lattice (the lattice reciprocal to f.c.c.); these are the only interstices in this lattice. The sodalite net also arises as a space-filling packing of truncated octahedra. The vertices of the N-dimensional analog of sodalite are taken to be the simplicial interstices of the corresponding lattice reciprocal to A_N, *viz* A_N^* (Conway & Sloane, 1988). It is likewise a space filling by polytopes.

Nets are frequently (partially) characterized by the nature of the shortest circuits contained in the angles (pairs of edges) of a vertex. In so doing it is desirable (Marians & Hobbs, 1990) to identify *fundamental* circuits or *rings*, which are those in which the path between any pair of vertices on the circuit is a shortest path. There is a finite number of such rings per vertex; for example in the diamond and lonsdaleite structures there are two 6-rings at every angle for a total of twelve meeting at each vertex. As each 6-ring is shared with six vertices there are two 6-rings per vertex. In the sodalite structure there are two 4-rings and four 6-rings at each vertex (1/2 a 4-ring and 2/3 a 6-ring per vertex). The sodalite net also has 32 12-rings meeting at each vertex. In contrast to the other rings mentioned in this paragraph, the 12-rings can be decomposed into a sum of smaller rings; in the terminology of Goetzke & Klein (1991) they are not *strong* rings. It is shown below that the N-dimensional nets can be similarly chracterized.

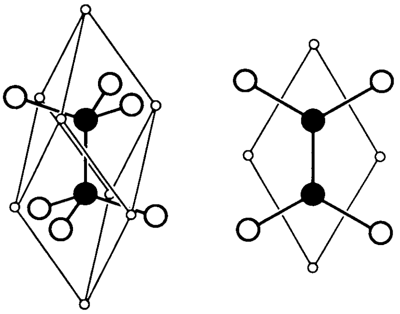

Fig. 1. Primitive units for diamond (left) and 6^3. Small circles and light lines represent the vertices and edges of a primitive unit cell.

One of the fundamental unsolved questions concerning nets is the nature of the constraints on the number and sizes of rings (Goetzke & Klein, 1991) and their influence on other properties such as density (Stixrude & Bukowinski, 1990). In two dimensions simple constraints on ring sizes are well known (O'Keeffe & Hyde, 1980). Three-dimensional nets can be divided into two classes. In the first class the net is derived from the edges and vertices of a space filling by polyhedra in which three polyhedra meet at an edge and four at a corner (the sodalite net is the simplest example). For such nets, constraints on the number and size of strong rings can be derived (O'Keeffe, to be published). The second class of three-dimensional net is that in which at least some of the angles contain more than one strong ring (this is not possible in two dimensions for topologically planar nets). For such nets (diamond is a simple example) constraints on ring sizes and numbers are much more difficult to derive, although useful empirical observations can be made (Stixrude & Bukowinski, 1990). It might be expected that investigation of these topics in higher dimensions will eventually lead to insights in the more practical three-dimensional world.

The diamond and sodalite structures are also of interest as the parents of rare (low-density) three-dimensional sphere packings (O'Keeffe, 1991*a*). The term 'sphere packing' is used here to refer to an arrangement of equivalent (symmetry-related) spheres in contact, with not all contacts on the same hemisphere. The latter condition ensures that the sphere packing is stable. Here the analogous N-dimensional structures are described.

The lattices A_N and diamond

Consider the N-dimensional lattice defined by a unit cell (a parallelotope) with all equal edges, a, and with all angles between the unit-cell vectors equal to $\pi/3$. This is the N-dimensional generalization of a rhombus (2D) and rhombohedron (3D), here called a rhombotope. The two-dimensional case is the familiar hexagonal lattice described with $\gamma = 60°$ rather than the more usual $\gamma = 120°$. The lattice is the well known A_N described using a primitive cell. The following properties of the structure may readily be verified.

(1) The lattice points A $(0, 0, \ldots)$ have $N(N+1)$ equidistant neighbors. For $N \leq 3$, this is the densest lattice packing, but for $N > 3$ denser packings are known (Conway & Sloane, 1988).

(2) Sites B at $\pm(x, x, \ldots)$ with $x = 1/(N+1)$ have $N+1$ lattice points as nearest neighbors with $d(A-B) = a[N/(2N+2)]^{1/2}$ and at the vertices of a regular simplex. These are the simplicial interstices of the structure.

(3) The site C at $\frac{1}{2}, \frac{1}{2}, \ldots$ is in an interstice with Z neighbors at a distance d away. For an $(N-1)$ or N-dimensional structure, $Z = N!/[(N/2)!(N/2)!]$ and $d = a(N/8)^{1/2}$. Note that for seven and eight dimensions $d(A\text{-}A) = d(A\text{-}C) = d(C\text{-}C)$ and the coordination number for C by A (and *vice versa*) is 70. For $N = 7$ each atom has $70 + 7 \times 8 = 126$ equidistant neighbors; this is known to be the maximum number of equal spheres that can contact a central one in seven dimensions.

(4) The unit-cell content ('volume') is $a^N(N+1)^{1/2}/2^{N/2}$.

N-dimensional diamond (or Si) can now be described in crystallographic terms in terms of the same unit cell with a shift of origin to a center of symmetry. For unit bond lengths, the unit-cell parameter is $a = [(2N+2)/N]^{1/2}$. The atoms are in $\pm(x, x, \ldots, x)$ with $x = N/(2N+2)$. The number of vertices per unit content is, for unit edge length, $r = 2N^{N/2}(N+1)^{-(N+1)/2}$. The N-dimensional (ideal) cristobalite structure, SiO_2, is obtained by combining these positions with O at the centers of the edges at $(\frac{1}{2}, \frac{1}{2}, \ldots, \frac{1}{2})$ and the N permutations of $(\frac{1}{2}, \frac{1}{2}, \ldots, \frac{1}{2}, 0)$. The O-atom packing (with $2N$ neighbors) is now an N-dimensional array of vertex-sharing simplices with the remaining space being comprised of truncated simplices. In three dimensions the O atoms are on the T lattice complex, and in two dimensions the structure is the familiar kagomé pattern (tessellation 3.6.3.6).

The number of neighbors n_{Nk} for the diamond net are empirically found to be given by a polynomial, (2), but with coefficients that depend on the parity of k and which are given in Table 1.

It is also found that at each vertex there are $N-1$ 6-rings, for a total of $(N+1)N(N-1)/2$ 6-rings meeting at each vertex. For $N > 3$, 10-rings also appear (Table 2). Counting circuits is easy, but with my computer algorithm it is tedious to check whether they are fundamental (*i.e.* rings); accordingly, as the number of n-circuits increases rapidly with both n and N, no search for n-rings wth $n > 12$ was made.

Table 1. *Coefficients a_{Ni} in the polynomial for n_{Nk}, equation* (2), *for diamonds, even and odd refer to the parity of k*

N	a_{N0}	a_{N1}	a_{N2}	a_{N3}	a_{N4}	a_{N5}
3 even	2	0	5/2			
3 odd	3/2	0	5/2			
4 even	0	35/6	0	35/24		
4 odd	0	85/24	0	35/24		
5 even	2	0	35/8	0	21/32	
5 odd	45/32	0	63/16	0	21/32	
6 even	0	49/10	0	49/16	0	77/320
6 odd	0	1253/320	0	91/32	0	77/320

Table 2. *Ring statistics for N-dimensional diamond* (*Nd*) *and lonsdaleite* (*Nl*)

The numbers are the number of rings containing each angle with total number of n-circuits per angle in parentheses. Angles is the number of angles per vertex. For the lonsdaleites the first set of angles contains an edge along **c**.

N	Angles	6	8	10	12
2	3	1 (1)	0 (0)	0 (3)	0 (1)
3*d*	6	2 (2)	0 (4)	0 (24)	0 (56)
3*l*	3	2 (2)	0 (4)	0 (24)	0 (44)
	3	2 (2)	0 (4)	0 (20)	0 (73)
4*d*	10	3 (3)	0 (12)	6 (111)	0 (507)
4*l*	4	3 (3)	0 (12)	0 (111)	0 (447)
	6	3 (3)	0 (12)	0 (101)	0 (549)
5*d*	15	4 (4)	0 (24)	24 (312)	0 (2416)
5*l*	5	4 (4)	0 (24)	0 (312)	0 (2248)
	10	4 (4)	0 (24)	6 (294)	0 (2449)
6*d*	21	5 (5)	0 (40)	60 (675)	(7565)
6*l*	6	5 (5)	0 (40)	0 (675)	
	15	5 (5)	0 (40)	24 (647)	

It is noted in passing that filling all the simplicial interstices of A with B produces stoichiometry AB_2: 'N-dimensional fluorite'. The B structure is a sphere packing with $N(N+1)/2$ neighbors with $B \ldots B$ distance $[(2N-2)/N]^{1/2}$ times the $A\text{-}B$ distance. For $N = 3$, the B structure is just the primitive cubic lattice.

A two-layer sphere packing and lonsdaleite

Hexagonal closest packing $(N = 3)$ can be derived from the two-dimensional packing by stacking layers along a direction, **c**, perpendicular to the layers in a familiar way. In N dimensions we can analogously stack $(N-1)$-dimensional layers in an orthogonal direction, which is still labeled **c** for convenience, to obtain an N-dimensional sphere packing with the same density and coordination number as A_N. The unit-cell vectors $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_{N-1}$ are of unit length and mutually at 60° to each other and the Nth lattice vector **c** is at right angles to all these with $c = [(2N+2)/N]^{1/2}$. Centers of spheres are at $\pm(x, x, \ldots, \frac{1}{4})$ with $x = (N-1)/2N$. The N-dimensional lonsdaleite structure is now obtained by combining the lattice positions with those of one-half of the simplicial interstices. If the origin is shifted to a center of symmetry of this new structure, it is formally described for unit edge length as $a = [(2N+2)/N]^{1/2}$, $c = (2N+2)/N$ and atoms at

Table 3. *Numbers of kth neighbors, n_{Nk}, for N-dimensional lonsdaleite*

N	n_{N2}	n_{N3}	n_{N4}	n_{N5}	n_{N6}	n_{N7}	n_{N8}	n_{N9}	n_{N10}
3	12	25	44	67	96	130	170	214	264
4	20	53	116	213	360	561	832	1171	1600
5	30	96	252	546	1070	1901	3172	4971	7490
6	42	157	482	1207	2702	5417	10 092	17 505	28 860

$\pm(x, x, \ldots, z;\ x, x, \ldots, \frac{1}{2}-z)$ with $x=(N-1)/2N$, $z=1/(4N+4)$.

The coordination sequences for lonsdaleites for the first ten shells are given in Table 3. They do not fit such simple polynomials as do those for diamonds although a simple expression for $N=3$ has been given (O'Keeffe, 1991*b*). The topological density ρ_k is always greater for lonsdaleites than for diamonds for $k \geq 3$.

Sodalites

The rhombotopical lattice with $a=1$, $\alpha=\cos^{-1}(-1/N)$ is a sphere packing with $2N+2$ spheres in contact and is body-centered cubic for $N=3$. It is the lattice reciprocal to A_N and is designated A_N^*. The unit-cell volume is $a^N(N+1)^{(N-1)/2}N^{-N/2}$. There are $N!$ simplicial interstices with coordinates which are all the permutations of $1/(N+1)$, $2/(N+1)$, $\ldots$, $N/(N+1)$. The distance from a lattice point to an interstice is $a[(N+2)/12]^{1/2}$ and each interstice has N nearest neighbors at a distance of $a[2/N(N+1)]^{1/2}$. The net obtained by connecting each simplicial interstice to its nearest neighbors is considered to be the N-dimensional analog of sodalite. For a net of unit edge length the number of points per unit content is $r=N!\,2^{N/2}(N+1)^{1/2-N}$.

The structure is now a tessellation of space by congruent polytopes with $(N+1)!$ vertices whose centers are lattice points; alternatively the polytopes are the Voronoi polyhedra of the lattice. The vertices in the unit cell are those of the $(N-1)$-dimensional polytope in the $(11\ldots1)$ hyperplane. The three-dimensional structure is the familiar tessellation of space by truncated octahedra.

The number of kth neighbors in N dimensions n_{Nk} is given by (2) with the values of the coefficients given in Table 4. The coefficient of k^{N-1} is $(N+1)/(N-1)!$; if that should be the case in general, the topological density would be $\rho_\infty=(N+1)/N!$

The shortest ring at an angle is either a square or a regular plane hexagon; these are the only strong rings in the structure. At $N+1$ angles the rings are hexagons and at the remaining $(N+1)(N-2)/2$ angles they are squares. There are also larger rings; for example, the three-dimensional structure has 32 12-rings. Numbers of n-circuits and n-rings for $n \leq 12$ are given in Table 5. The higher-dimensional structures have even larger rings which have not been enumerated. It might be noted that all edges are equivalent and are common to two hexagons and $N-2$ squares. The $N=2$ case is just 6^3 again. The local topology of a net of congruent vertices is best appreciated by mapping the vertex onto a graph (let's call it the vertex graph) in which vertices of the graph represent edges of the net that meet at one vertex of the net and in which the edges of the vertex graph represent angles of the net. For an n-connected net, the vertex graph is the complete graph K_{n+1}. Fig. 2 shows how the three kinds of angle in the five-dimensional net map onto K_6 and also illustrates that the edges of the net (vertices of the graph) are equivalent.

Table 4. *Coefficients a_{Ni} in the polynomial for n_{Nk}, equation (2), for sodalites*

N	a_{N0}	a_{N1}	a_{N2}	a_{N3}	a_{N4}	a_{N5}
2	0	3				
3	2	0	2			
4	0	25/6	0	5/6		
5	2	0	15/4	0	1/4	
6	0	49/10	0	49/24	0	7/120

Table 5. *Ring statistics for sodalites*

The entry under Angles is the number of angles of each kind and the remaining entries in the row are the numbers of rings (all circuits in parentheses) containing one angle.

N	Angles	4	6	8	10	12
3	2	1 (1)	0 (0)	0 (6)	0 (18)	4 (90)
	4	0 (0)	1 (1)	0 (4)	0 (17)	6 (87)
4	5	1 (1)	0 (2)	2 (20)	0 (92)	2 (522)
	5	0 (0)	1 (2)	2 (15)	0 (70)	6 (452)
5	3	1 (1)	0 (4)	4 (50)	0 (356)	12 (3500)
	6	1 (1)	1 (6)	2 (38)	0 (412)	8 (3140)
	6	0 (0)	1 (3)	4 (35)	0 (283)	14 (2432)
6	7	1 (1)	2 (10)			
	7	1 (1)	1 (8)			
	7	0 (0)	1 (4)			

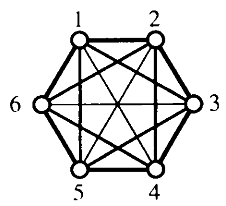

Fig. 2. The vertex graph for five-dimensional sodalite. The vertices of the graph represent six edges meeting at a vertex of the sodalite net and edges of the graph represent angles of the net. Heavy lines represent angles containing only one 6-ring, medium lines represent angles containing both a 4- and a 6-ring and light lines represent angles containing only a 4-ring.

Rare sphere packings

One can replace each vertex of the diamond structure by a regular simplex centered on the original vertex and with new vertices on the old edges. I call this process *decoration* (O'Keeffe, 1991*a*). In this way one obtains a new sphere packing with $N+1$ times as many vertices per cell and with cell edge increased by a factor $1+[2N/(N+1)]^{1/2}$. The structure produced in two dimensions is shown in Fig. 3; it is the familiar $3\,.\,12^2$ tessellation which is also well known to arise as the rarest two-dimensional sphere packing. The three-dimensional analog (with regular tetrahedra decorating the vertices of the diamond structure) was long thought to be the rarest sphere packing, but a rarer packing is now known (see below). The density is given by

$$r=2[N^N/(N+1)^{N-1}]^{1/2}\{1+[2N/(N+1)]^{1/2}\}^{-N}. \tag{3}$$

One can get a rarer packing by decorating the sodalite net similarly with simplices. The new vertices do not fall on the old edges but the squares are converted to regular octagons. The new density is then (for $N>2$)

$$r=\frac{(N+1)!2^{N/2}}{(N+1)^{N-1/2}} \times\left\{1+\left[\frac{N+(N^2-1)^{1/2}}{N+1}\right]^{1/2}\right\}^{-N}. \tag{4}$$

This is possibly the rarest stable sphere packing in three dimensions (O'Keeffe, 1991*a*). It is unwise to speculate about higher dimensions as each new dimension seems to have surprises in store; however, in the absence of anything better, (4) can serve as an upper bound to the density of rarest sphere packings. Fig. 4 shows the density of the structures discussed and of densest lattice sphere packings (Conway & Sloane, 1988) as a function of dimensionality. The increasing range of densities hints at the richness of structures awaiting exploration in higher dimensions.

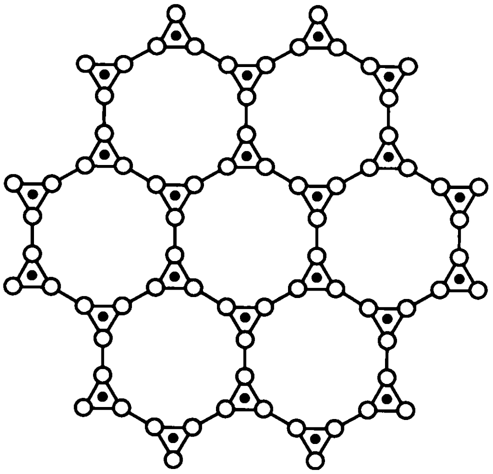

Fig. 3. Production of $3\,.\,12^2$ (open circles) by decoration of 6^3 (filled circles) with triangles.

Coordination sequences for primitive hypercubic lattices

It is of some interest to compare the number of kth neighbors for primitive hypercubic lattices, Z^N, with those given for the nets above. n_{Nk} is found to be given by expressions similar to those for sodalites. In this case, n_{Nk} is just the number of distinct solutions of

$$\sum_{i=1}^{N}|m_i|=k \tag{5}$$

where m_i is any integer (including 0). It is almost trivial to find n_{Nk} by direct enumeration using pencil and paper, although it is not entirely obvious to me that it should be given by a simple polynomial in k. Coefficients for (2) are given for the first ten dimensions in Table 6. The coefficient of k^{N-1} is $2^N/(N-1)!$. If that were the case in general, the topological density would be $\rho_\infty=2^N/N!$, *i.e.* $2^N/(N+1)$ times that conjectured for sodalite. It is worth calling attention to the fact that n_{Nk} rapidly gets rather large; $n_{10,10}=4\,780\,008$. This makes empirical evaluation of coordination sequences by

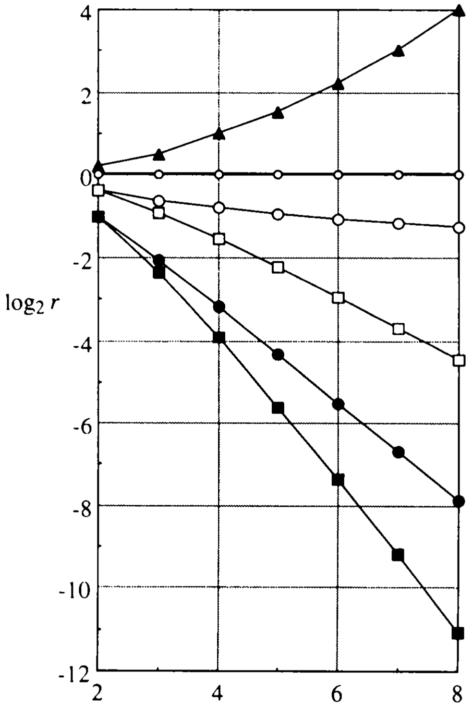

Fig. 4. The density (plotted as $\log_2 r$) as a function of dimensionality, N, for densest sphere packings (filled triangles), primitive hybercubic, Z^N (small open circles), diamonds (open circles), sodalites (open squares), decorated diamonds (filled circles) and decorated sodalites (filled squares). The lines serve merely to guide the eye.

Table 6. *Coefficients a_{Ni} in the polynomial for n_{Nk}, equation* (2), *for primitive hypercubic lattices* (Z^N)

N	a_{N0}	a_{N1}	a_{N2}	a_{N3}	a_{N4}	a_{N5}	a_{N6}	a_{N7}	a_{N8}	a_{N9}
1	2									
2	0	4								
3	2	0	4							
4	0	16/3	0	8/3						
5	2	0	20/3	0	4/3					
6	0	92/15	0	16/5	0	8/15				
7	2	0	392/45	0	28/9	0	8/45			
8	0	704/205	0	352/45	0	64/45	0	16/315		
9	2	0	3272/315	0	76/15	0	8/15	0	4/315	
10	0	2252/315	0	5744/567	0	2408/945	0	160/945	0	4/1575

computer difficult for more-complicated higher-dimensional structures.

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Methodology Employed for the Structure Determination of Tumour Necrosis Factor, a Case of High Non-Crystallographic Symmetry

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Abstract

The structure of the protein tumour necrosis factor (TNF) was determined from crystals of space group $P3_121$ which contain six copies of the TNF monomer per crystallographic asymmetric unit [Jones, Stuart & Walker (1989). *Nature* (*London*), **338**, 225-228]. The nature of these crystals (relatively high crystallographic symmetry coupled with multiple copies of the protein in the asymmetric unit) led to some peculiarly challenging problems at several points in the structure determination. In particular, (1) self-rotation function calculations failed to yield clearly interpretable solutions, (2) the analysis of difference Patterson maps for heavy-atom derivatives required the development of a Patterson search program suite *GROPAT*. The redundancy in the asymmetric unit allowed refinement of poor-quality isomorphous phases at 4 Å resolution and phase extension from 4 to 2·9 Å resolution using real-space symmetry

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