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LETTER TO THE EDITOR

Tetrahedral classification in Euclidean space

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Abstract. A new classification of local structures in three-dimensional Euclidean space is formulated using a set of topological codes describing tetrahedra formed by n species of atoms or vacancies. Some exact results in binary systems, the Frank–Kasper phases, the truncated icosahedron, and the truncated octahedron are presented.

Since all three-dimensional Euclidean space-filling structures can be described as the packing of polyhedra [1], and all polyhedra can be described as specific packing of tetrahedra, the problem of local structure in three-dimensional Euclidean space can be reduced to that of filling space with tetrahedra [2]. We present a new structure classification scheme based on the decoration of atoms chosen from n species at the vertices of tetrahedra. For n species of atoms, there are $B(n)$ ($= n + \binom{n}{2}$) number of bonds with *single-valued* bond length $d_{\alpha\beta}$, $\Delta(n)$ ($= n + 2\binom{n}{2} + \binom{n}{3}$) number of triangular faces and $T(n)$ ($= n + \binom{n}{2} + 2\binom{n}{2} + n\binom{n-1}{2} + \binom{n}{4}$) number of tetrahedra. For real systems with multi-valued bond lengths, we introduce a coding species γ to specify different bond lengths between α and β such that $d_{\alpha\beta} = d_{\alpha\gamma} + d_{\gamma\beta}$ and the distance of γ to all other species is negative to indicate that γ is not bonded to any other species except α and β . In this way, the metrical relation between species remains single-valued. Defects can also be incorporated by treating, for example, the δ species as vacancies rather than atoms. A necessary condition to fill space is that the sum of the dihedral angles around every bond is 2π

$$\sum_{(k,l)} P_{ij:kl} \Phi_{ij:kl} = 2\pi.$$

The set of integers $\{P_{ij:kl}\}$ is called the topological code for the ij bond. They specify the number of $(ijkl)$ tetrahedra with dihedral angles $\Phi_{ij:kl}$ (which are inverse trigonometric functions of bond lengths) that are wrapped around the ij bond. The sum is over all possible combinations of tetrahedra containing at least one ij bond. Note that the topological code can specify more than one topology, as the order of arrangements of atoms around the given bond is not specified (figure 5a of [2] illustrates this point). Once we know the topological code $\{P\}$, the bond lengths can be solved. This property of the topological codes compares favourably with the Voronoi classification, which has no simple way to extract bond lengths and which can always be dissected into tetrahedra and mapped into a set of topological codes. Another classification scheme for systems

Table 1. Topological code for the coordination polyhedral in Frank–Kasper phase.

	CN12	CN14	CN15	CN16
<i>n</i>	2	2	2	2
Species ^a	A, B	A, B	A, B	A, B
γ^b	1	2	2	2
Code	(1) $P_{AB:AA} = 5$	(1) $P_{BB:AA} = 6$ (2) $P_{AB:AA} = 3$ $P_{AB:AB} = 2$	(1) $P_{AB:AA} = 2$ $P_{AB:AB} = 4$ (2) $P_{BB:AA} = 2$ $P_{BB:AB} = 2$ $P_{BB:BB} = 1$	(1) $P_{BB:AA} = 6$ (2) $P_{AB:AA} = 1$ $P_{AB:AB} = 4$
Bond length	$d_{AA} = K$ $d_{AB} = 1$	$d_{AA} = [2(1 - 1/3^{1/2})]^{1/2}$ $d_{AB} = 1$ $d_{BB} = 2[2/3^{1/2} -]^{1/2}$	$d_{AA} = d_{AB} = 1$ $d_{BB} = 2^{1/2}$	$d_{AA} = (8/11)^{1/2}$ $d_{AB} = 1$ $d_{BB} = (12/11)^{1/2}$

^a B is assumed to be the central atom in all four cases.

^b β is the number of sets of codes needed.

^c d_{BB} in CN12 and CN15 are not specified.

described by nets [3] involves the idea that the sum of the spherical excess subtended by neighbours (as defined in the Frank–Kasper phase) of a given atom is 4π

$$\sum_{(jkl)} Q_{i;jkl} \Omega_{i;jkl} = 4\pi.$$

Here $Q_{i;jkl}$ specifies the number of $(ijkl)$ tetrahedra with spherical excess $\Omega_{i;jkl}$ around i . The coordination number Z_i of species i is the sum of the $Q_{i;jkl}$ over all (jkl) . Novel structures can again be obtained by the solutions of this equation with this set of code $\{Q\}$.

To keep the problem manageable, we introduce a subclassification of structure by restricting the topological sum M_{ij} , (the sum of the integers $P_{ij;kl}$ over all kl), for each bond (ij) to be between some range. For example, the Frank–Kasper phase [1] corresponds to $5 \leq M_{ij} \leq 6$. An icosahedron of 20 A atoms at the vertices and one B atom at the centre corresponds to the topological code $P_{AB:AA} = 5$. The bond lengths satisfy $d_{AA} = \kappa d_{AB}$, with $\kappa = [2(1 - 1/5^{1/2})]^{1/2} = 1.051462224 \dots$. We have tabulated the topological codes for the coordination polyhedra in table 1. The degeneracy γ is the number of sets of codes for the given bond lengths. An algorithm has been developed to solve these non-linear equations for n up to 7 and to obtain all the compatible topological codes for a given set of bond lengths.

The following results of the local structures are obtained [4]. (i) Only three solutions for binary alloys for bond lengths satisfying $d_{AA} \leq d_{AB} \leq d_{BB}$ exist in nature. They are the NaCl, the packing of regular prism, and the MgZn₂ Friauf–Laves structures [2, 5]. (ii) The minimum number of species of atoms required to arrive at a truncated icosahedron structure is three and the uniquely defined bond lengths are shown in table 2. For $n \geq 4$, a continuum of bond lengths can be found, since one can put two different species at the vertices of the triacontahedron before arriving at the truncated icosahedron [4]. (iii) There exist two constructions of the truncated octahedron from the truncated icosahedron, both of which involve well defined distortions. The first class of distortion

Table 2. An exact solution for the truncated icosahedron.

Bond	AA	AB	AC	BB	BC	CC
Length ^a	Kd_{AC}	1	$\{[5 + 3(5)^{1/2}]/[1 + 7(5)^{1/2}]\}^{1/2}$	Kd_{BC}	$\{8(5)^{1/2}/[1 + 7(5)^{1/2}]\}^{1/2}$	$[1 - (K^2/4) d_{BB}]^{1/2}$
Degeneracy γ	2	2	7	3	12	1

^a d_{BC} in CN12 and CN15 are not specified.

involves bonds of slightly different lengths on the truncated icosahedron. The second involves distorted penta-pyramids and distorted hexa-pyramids in the linkage of the regular truncated icosahedron and the regular truncated octahedron. (iv) The degeneracy involved in Penrose rhombohedra with a specific decoration [4] consistent with that of Elser and Henley [6] is in the order of hundreds, implying that a large class of the Penrose structure can be obtained by this method of coding. (v) Matching rules can be enforced by suitable assignment of species. [4] These results are important to the study of quasi-crystal growths.

To complete the solution of a structural problem, one must show that the solutions can actually fill space and are not just forming finite clusters [7]. One way to prove that a given solution can fill space is to look for a unit cell, starting from atomic arrangements specified by the codes. Another way is to embed the local structure in higher-dimensional space as a simpler unit cell of a periodic structure, and re-project back to three-dimensions to obtain a structure which can be quasiperiodic [8]. A third way is to use the induction method of growth. Let us begin with a local structure (the seed) specified by a set of codes and demand that the seed be grown surface after surface. If all local defects can be eliminated by a suitable sequence of addition of atoms to the $(N + 1)$ th surface, given that the N th surface is defect free, then by induction one can obtain a space-filling structure. (This is how equation (3) of reference [11] can be proved.) For crystal growth, this new classification scheme will facilitate the implementation of an algorithm using cellular automata. We can say that a crystal is a structure grown deterministically, in the sense that the local density ρ of atoms is a single-valued function of the neighbours. If a continuous spectrum of ρ exists, then an amorphous structure is expected. If ρ has a multitude of discrete choices, quasi-crystal [9], twinning [10], or specific kinds of random structure can result [2, 11].

Many physical constraints can be imposed on these topological codes. One constraint is symmetry. To specify S -fold symmetry, we can say that there are S number of α atoms around an ij bond. In real systems, S usually is less than 10. So an exhaustive program to classify structures with $M_{ij} \leq 10$ may be made. Note that if some species are vacancies or coding species for bonds of difference lengths, M can be greater. For a system described by nets, the bond angles are fixed by quantum chemistry. This then corresponds to a sub-classification of structures using tetrahedra with fixed face angles. Another interesting constraint is to impose the hard-sphere condition: $d_{\alpha\beta} = \frac{1}{2}(d_{\alpha\alpha} + d_{\beta\beta})$. This constraint reduces the number of bond length variables, allows sphere-packing experiments [12], and has applications in communications [13].

The following iterative procedure can generate new structures using topological codes. By dissecting a known structure, one can obtain the topological codes. Using these codes, one can work out the bond lengths. Using these bond lengths, one can find out all compatible topological codes. For example, in the icosahedral structure of

Table 3. Bond lengths and topological codes for a truncated octahedron.

Bond	Bond length	Degeneracy γ	Topological code
AB	1	1	(1) $P_{AB:CD} = 6$
AC	$(5/3)^{1/2}$	1	(1) $P_{AC:BC} = 4,$ $P_{AC:CD} = 2$
AD	$2/3^{1/2}$	1	(1) $P_{AD:CC} = 4$
BC	$(2/3)^{1/2}$	1	(1) $P_{BC:AC} = 4$
CC	$(2/3)^{1/2}$	3	(1) $P_{CC:AB} = 4,$ $P_{CC:AD} = 2$ (2) $P_{CC:CC} = 2,$ $P_{CC:CD} = 4$ (3) $P_{CC:AB} = 2,$ $P_{CC:AD} = 2,$ $P_{CC:CD} = 2$
CD	$1/3^{1/2}$	3	(1) $P_{CD:AC} = 4$ (2) $P_{CD:CC} = 4$ (3) $P_{CD:AC} = 2,$ $P_{CD:CC} = 2$

Bergman and co-workers [14], we find an infinite number of solutions for the arrival from an icosahedron to a truncated octahedron, which fills space by itself periodically. If we dissect the truncated octahedron, we get its topological codes in table 3. The truncated octahedron can be described as the packing of two tetrahedra: ABCC and ADCC, where A is the atom in the centre of the truncated octahedron, C the atom at the vertices, B the atom in the centre of the hexagonal face, and D the atom in the centre of the square face. The truncated octahedron is described by the first set of codes, the second and third sets are new consistent structures with the second set identified as the NaCl structure.

Together with a set of bond lengths for relevant local structures of quasi-crystals, a set of energies E_{ij} between species [15] can be introduced to simulate growths. Correlations [9, 16] can be incorporated by the assignment of a many-body energy parameter $E_{ijk\dots}$, thereby allowing a generalisation of Finney's experiment [12]. The Bernal polyhedra [17] can also be coded for the study of Bernal ideal liquid. For quasi-crystals, the questions of finding where the atoms are is partially answered (we need also to know the dynamics). Using a growth algorithm, the 'glued' atoms in the icosahedral glass [18] can be specified, thereby providing further insights into the relation between the glass description and the quasi-crystal description of Steinhardt and co-workers [19].

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