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Filling three-dimensional space with tetrahedra: A geometric and crystallographic problem

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Exact, nonperiodic, close-packed structures with randomness that can fill three-dimensional space are found. We find many solutions for distances between atoms that satisfy the necessary conditions of filling three-dimensional space with tetrahedra formed with two kinds of atoms. Only three solutions that also satisfy the sufficient condition of filling three-dimensional space are discussed. They all involve periodic as well as nonperiodic structures resulting from the random stacking of layers. One solution corresponds to the NaCl structure. Another solution exhibits both tetragonal and hexagonal symmetry, which violates crystallography. A third solution has a unit cell whose surface exhibits distorted pentagonal symmetry and whose elementary unit is a 44-face polyhedron. Suggestions for a possible growth model in three dimensions with tetrahedra are discussed.

I. INTRODUCTION

It is well known that regular tetrahedra cannot fill three-dimensional space[1,2] since the dihedral angle of a regular tetrahedra is $\gamma_0=\cos^{-1}(\frac{1}{3})\simeq 70.5°$, which is not a submultiple of 2π. This geometric property has important crystallographic consequences, for instance, concerning the number and nature of close-packed networks of identical atoms (or hard spheres). While in two dimensions the triangular lattice is the only close-packed network, in three dimensions there are many close-packed lattices (periodic or not) which can be obtained by stacking successive two-dimensional triangular arrays. In all cases each atom not at the surface has twelve neighbors, and this guarantees that no denser packing of an *infinite* number of hard spheres can be found. Another consequence of the impossibility of filling space with regular tetrahedra is that the closest packing (defined here as the packing which minimizes the number of nearest-neighbor pairs) of a *finite* number of hard spheres is not always a piece of an infinite close-packed lattice. An example is the packing of six hard spheres. The closest packing is obtained with three regular tetrahedra and has twelve bonds. The three tetrahedra have two common vertices. If one continues the addition of hard spheres, then not all of the spheres can have twelve neighbors. But in a close-packed lattice, a set of six atoms never forms more than 11 bonds. This effect has consequences on the growth of crystals (formation of stacking faults) and aggregates (magic numbers[3]).

The problem addressed in this paper is whether three-dimensional space can be filled by tetrahedra, the vertices of which belong to two classes A and B, the three distances d_{AA}, d_{BB}, and d_{AB} being the same for all tetrahedra. The condition $2d_{AB}=d_{AA}+d_{BB}$ (valid for true hard spheres) is not imposed but we would like it to be approximately satisfied.

One motivation of our work comes from the existence of quasicrystalline solutions[4] with a five-fold symmetry in the analogous two-dimensional problem. In the simple crystal-growth models such as the Eden model[5] or the solid on solid (SOS) model,[6] one assumes that each atom goes to a given predefined place. One way to realize that is to form successive tetrahedra: at least one tetrahedron for each new atom. A second motivation is to investigate if the close packing of spheres of two different sizes can fill three-dimensional space. The gaps or defects found in the packing of regular tetrahedra may be avoided if we introduce a second species of "filler" atoms. From a practical point of view, this introduction of a second species of atoms addresses the structure of alloy. From a theoretical point of view, we would like to see the positions of atoms in three-dimensional Euclidean space, rather than in curved space.[7] This necessitates the introduction of a second kind of atoms. A third motivation is to look for possible random structures. This has implication in the studies of amorphous[8] and quasicrystalline materials.[9]

Our investigation of filling three-dimensional space with tetrahedra formed from two species of atoms therefore proceeds with the following sequence of questions. (1) Can the local arrangement of atoms satisfy the conditions of filling three-dimensional Euclidean space? (2) Is there a random space-filling structure? (3) What are *all* the possible forms of random space-filling structures? We will answer all these questions.

To highlight our results, we briefly describe the three solutions here. First of all, if our problem of filling three-dimensional space with tetrahedra has solutions, then special values of $x=d_{AA}/d_{AB}$ and $y=d_{BB}/d_{AB}$ are expected. We find several solutions, the simplest one is shown in Fig. 1. It corresponds to $y=\sqrt{2}$. It is a face-centered lattice where the B atoms occupy the corners of the cubic unit cells and the centers of the faces while A atoms occupy the centers of the unit cells and the middles of the edges. This is the NaCl structure.

Another solution corresponds to $x=\sqrt{4/7}$ and $y=\sqrt{12/7}$ and has the chemical formula A_2B (Fig. 2). It has hexagonal symmetry and a projection on the hexagonal plane is shown by Fig. 2. The B atoms are at heights

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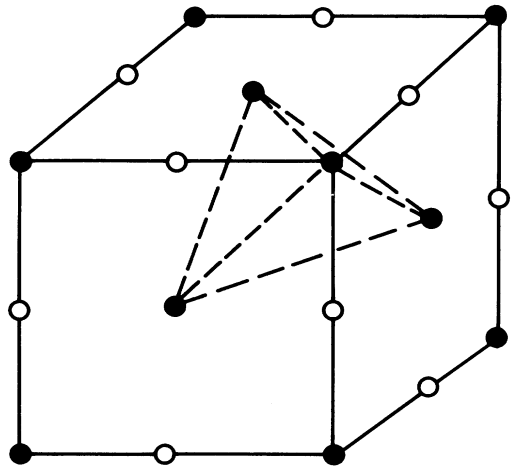

FIG. 1. Unit cell for the $y=\sqrt{2}$ solution. (Open circles for A, solid circles for B.)

ny and the A atoms are at heights $(n+\frac{1}{2})y$. Lines joining two A neighbors are seen to be fourfold axes. Thus, this solution is both tetragonal and hexagonal. This accidental violation of crystallography would be corrected by any perturbation (introducing some elasticity for instance).

More complicated solutions will be found in this paper, which is organized as follows. In Sec. II we write the necessary conditions to be satisfied in order to put tetrahedra around the three kinds (AA,BB, AB) of bonds. In Sec. III it is shown that these conditions have only a finite number of solutions, at least in the physically more realistic range $0\le x\le 1\le y<\sqrt{3}$, and these solutions are enumerated. These necessary conditions guarantee one can build the surroundings of isolated pairs, but not that one can assemble them to fill space. In Sec. IV additional compatibility conditions are used and allow one to eliminate most of the solutions found in Sec. III. In Sec. V the remaining solutions are described. They involve periodic structures and nonperiodic structures resulting from the random stackings of layers. Finally, we discuss possible growth models[10,11] associated with these exact solutions.

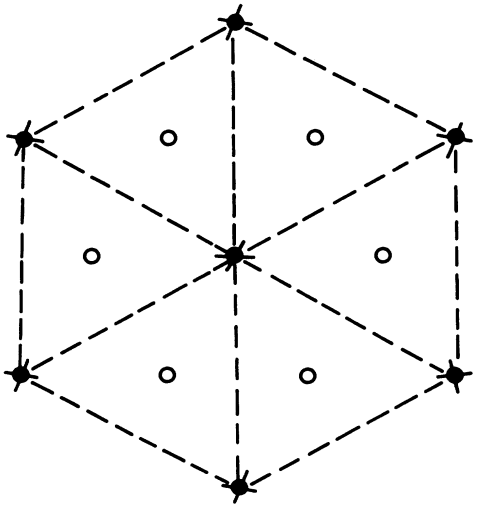

FIG. 2. Unit cell for the $(x,y)=(\sqrt{4/7},\sqrt{12/7})$ solution. (Open circles for A, solid circles for BB bonds.)

II. MATCHING CONDITIONS OF THE DIHEDRAL ANGLES

We consider the following problems: (a) Is it possible to fill space with tetrahedra, the corners of which belong to either one of two species A and B, so that the minimal distances $d_{\mu\nu}$ between a μ atom and ν atom have fixed values? (b) Is it possible to generate nonperiodic structure in this way? For two types of atoms, there are three distances $d_{\mu\nu}$. Since one of them (d_{AB}) sets the distance scale, there remain two ratios $x\equiv d_{AA}/d_{AB}$ and $y\equiv d_{BB}/d_{AB}$. There are five types of tetrahedra, $AAAA$, $AAAB$, $ABAB$, $ABBB$, and $BBBB$, two of which are regular with dihedral angle $\gamma_0=\arccos(\frac{1}{3})$. The remaining three tetrahedra are shown in Fig. 3, with the seven dihedral angles expressible in the variables x and y by the following equations, where $t_x=1-x^2/4$ and $t_y=1-y^2/4$:

$$\cos\phi_1=1-y^2/2t_x\ , \tag{1a}$$

$$\cos\phi_2=\left[\frac{x^2}{12t_x}\right]^{1/2}\ , \tag{1b}$$

$$\cos\theta_1=1-x^2/2t_y\ , \tag{1c}$$

$$\cos\theta_2=\left[\frac{y^2}{12t_y}\right]^{1/2}\ , \tag{1d}$$

$$\cos\psi_1=1-\frac{1}{2t_x}\ , \tag{1e}$$

$$\cos\psi_2=1-\frac{1}{2t_y}\ , \tag{1f}$$

$$\cos\psi_3=\left[\frac{x^2y^2}{16t_xt_y}\right]^{1/2}\ . \tag{1g}$$

There are three kinds of bonds, $A-A$, $B-B$, and $A-B$. The *necessary* condition that a bond be completely surrounded by tetrahedra of these five types is that the sum of the dihedral angles around the given bond is 2π, resulting in the following three "dihedral equations" for the $A-A$, $B-B$, and $A-B$ bonds, respectively:

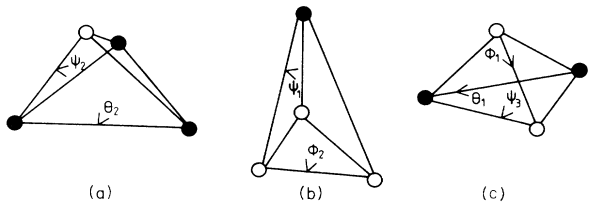

FIG. 3. Three types of tetrahedra: $ABBB$, $AAAB$, and $AABB$, and their dihedral angles. (Open circles for A, solid circles for B.)

$$p_1\phi_1+2p_2\phi_2+p_3\gamma_0=2\pi\ , \tag{2a}$$

$$q_1\theta_1+2q_2\theta_2+q_3\gamma_0=2\pi\ , \tag{2b}$$

$$r_1\psi_1+r_2\psi_2+2r_3\psi_3=2\pi\ , \tag{2c}$$

and in the special case where the $A-A$ bond is absent, the dihedral equations simplify to

$$2q_2\theta_2+q_3\gamma_0=2\pi\ , \tag{2d}$$

$$r_2\psi_2=2\pi\ . \tag{2e}$$

Equation (2a) expresses the fact that there are p_1 $ABAB$ tetrahedra, $2p_2$ $AAAB$ tetrahedra, and p_3 $AAAA$ tetrahedra around an $A-A$ bond. We denote the set of integers $(p_1p_2p_3)$ by P. Similar notation and meaning for $Q\equiv(q_1q_2q_3)$ and $R\equiv(r_1r_2r_3)$ for the $B-B$ and $A-B$ bonds.

From the definitions of the dihedral angles in Eqs. (1), we have several restrictions on x and y. In order that $\cos\phi_2\le 1$, Eq. (1b) implies $x^2\le 3$. Similarly, Eq. (1d) implies $y^2\le 3$. In order that $\cos\psi_3\le 1$, Eq. (1g) implies $x^2+y^2\le 4$. The dihedral equations (2a)–2(c) should be satisfied by two unknowns x and y in the physical domain, and Eqs. (2d) and (2e) should be satisfied by the single unknown y. Thus if the sets of integer coefficients P, Q, and R of these equations were randomly chosen, no solution for x and y would be expected. It turns out, however, that there are many sets of P, Q, and R such that there are solutions in x and y for the dihedral equations. We do not want to enumerate them all, as many of them do not fill space or are topologically impossible solutions, as discussed in the next two sections.

We focus our attention to those solutions shown in Table I that lie in the range $0<x\le 1\le y<\sqrt{3}$. This is the range of x and y that allows us to interpret A as a small atom and B as a big one. The hard-sphere constraint, $x+y=2$, is not imposed on our solutions, although solutions close to the hard-sphere solution are found.

For the range $0<x\le 1\le y<\sqrt{3}$ we can deduce the following ranges for the dihedral angles using Eqs. (1):

$$\pi/3\le\phi_1<\pi,\quad \gamma_0\le\phi_2<\pi/2\ ; \tag{3a}$$

$$0\le\theta_1<\pi,\quad 0\le\theta_2\le\gamma_0\ , \tag{3b}$$

and

$$\pi/3\le\psi_1<\gamma_0,\quad \pi/3\le\psi_2<\pi,\quad 0<\psi_3<\pi/2\ . \tag{3c}$$

The last inequality in Eq. (3c) requires some explanation. Since $\psi_3=0$ only at $(x,y)=(1,\sqrt{3})$ and that corresponds to $\phi_1=\pi$ and $\phi_2=\gamma_0$, we can check that Eq. (2a) cannot be satisfied for all possible P. Therefore $\psi_3>0$. These ranges of the dihedral angles can be used to

TABLE I. Solutions to dihedral equations for $0<x\le 1\le y<\sqrt{3}$.

x	y	P	Q	R	Fills three-dimensional space?
Unspecified	$\sqrt{2}$	None	022	040	Yes (Sec. V A), no $A-A$ bond
$\sqrt{4/7}$	$\sqrt{12/7}$	400	600 410 220	012	Yes (Sec. V B)
$\sqrt{8/11}$	$\sqrt{12/11}$	310 211 112	600	102	Yes (Sec. V C)
1	$\sqrt{2}$	210	022 211 400 022 211 400 022 211 400	040 040 040 121 121 121 202 202 202	No
$\sqrt{8/11}$	$\sqrt{2}$	013	022	040	No
$[\frac{7}{4}-(\frac{3}{2})^{1/2}]^{1/2}$	1	112	311	121	No
$\sqrt{8/11}$	$\sqrt{32/11}$	013 111	113	302 211	No
$2\left[\frac{\sqrt{2}-1}{3\sqrt{2}+1}\right]^{1/2}$	$2\left[\frac{\sqrt{2}+1}{3\sqrt{2}+1}\right]^{1/2}$	400	800	211 102	No
1/2	$\sqrt{5/2}$	202	420	021	No

deduce upper limits on the p's and r's, so that there is only a finite number of sets of P and R. This is the subject of the next section.

III. NUMBER OF SOLUTIONS OF THE DIHEDRAL EQUATIONS

We argue in this section that the number of solutions in the range $0<x\le 1\le y<\sqrt{3}$ is finite. The argument for the other values of x and y is similar. First we show that the number of sets of P and R is finite. From Eqs. (3) we can immediately write down the upper limit of P_1 as $[2\pi/\phi_{1l}]$, where $[z]$ denotes the integer part of z and ϕ_{1l} is the lower limit of ϕ_1, which is $\pi/3$ in Eq. (3a). [This is because for $p_1>[2\pi/\phi_{1l}]=6$, Eq. (2a) cannot be satisfied.] Similarly, the range for the other coefficients can be deduced to be $0\le p_1\le 6$, $0\le p_2\le 2$, $0\le p_3\le 5$, $0\le r_1\le 6$, and $0\le r_2\le 6$. Since $\psi_3>0$, there exists an upper limit for r_3. We consider two cases. First consider two tetrahedra $AABB'$ and $AABB''$ with a common face AAB. The distance between B' and B'' must be ≥ 1, implying $\psi_3\ge\pi/6$, or $r_3\le 6$. Next, consider $\psi_3<\pi/6$. In this case, it is impossible to put $AABB'$ and $AABB''$ together with a common face, as B' and B'' will overlap. This overlap should be prevented by separating any pair of $AABB$ tetrahedra by at least one $AAAB$ tetrahedron, implying that $r_3\le r_1$, where $2r_3$ is the number of $AABB$ tetrahedra around an AB edge and r_1 is the number of $AAAB$ tetrahedron around the AB edge. Since $r_1\le 6$, therefore in both cases $r_3\le 6$. This completes the proof that there are at most $\max(p_1)\max(p_2)\max(p_3)\max(r_1)\times\max(r_2)\max(r_3)=6\times 2\times 5\times 6^3$ sets of possible coefficients of P and R. One can further reduce considerably the number of sets of P and R using the following constraints:

$$p_1\phi_{1u}+2p_2\phi_{2u}+p_3\gamma_0\ge 2\pi\ , \tag{4a}$$

$$p_1\phi_{1l}+2p_2\phi_{2l}+p_3\gamma_0\le 2\pi\ , \tag{4b}$$

$$r_1\psi_{1u}+r_2\psi_{2u}+2r_3\psi_{3u}\ge 2\pi\ , \tag{4c}$$

$$r_1\psi_{1l}+r_2\psi_{2l}+2r_3\psi_{3l}\le 2\pi\ . \tag{4d}$$

Here the indices u and l on the dihedral angles indicate the upper and lower limits.

For a given set of P and R, we look for solutions x and y of the dihedral equations (2a) and (2c). For a given solution (x,y) of Eqs. (2a) and (2c) we work out the dihedral angles θ_1 and θ_2 in Eq. (2b), as well as $\max(q_2)=[2\pi/\theta_1]$ and $\max(q_1)=[\pi/\theta_2]$. Then we test if there is a set of $Q=(q_1,q_2,q_3)$ for $0\le q_1\le\max(q_1)$, $0\le q_2\le\max(q_2)$, and $0\le q_3\le 5$ that satisfies also Eq. (2b). In this way we obtain a simultaneous solution of all three dihedral equations (2a)–(2c). The method of solving Eqs. (2d) and (2e) is similar, and in Appendix A we briefly describe the trick of finding simultaneous solutions to Eqs. (2a) and (2c) for a given set of P and R.

These numerical procedures of solving the dihedral equation give approximate values of x and y. But once the integers P, Q, and R are known, one can work out x and y analytically. In this way we find many exact solutions (of the order of hundreds). We also find that as the number of intervals N for the binary search of roots of the dihedral equations increases, the number of solutions also increases, despite the finite number of possible P and R. However, we observe that the increase in the number of solutions all comes from the set with $P=(111)$, and the number of solutions that do not have $P=(111)$ remain constant as N increases beyond 10^3. Indeed, we can show analytically that for $P=(111)$, $Q=(n00)$, and $R=(111)$, we have solutions for all $n\ge 6$ (refer to Appendix B). This means that there are *infinitely* many solutions to the dihedral equations. However, these solutions are not acceptable, as discussed in the next section. Apart from these forbidden configurations, the number of solutions generated by the numerical search is constant for $N>10^3$. Unless there are two roots the separation of which is smaller than 10^{-5} (we carry out the search up to $N=10^5$), we can say that the number of solutions to the dihedral equations is finite. In the next section we will discuss some simple topological considerations that eliminate as many solutions found for the dihedral equations as possible, as well as a computer-assisted method of eliminating solutions.

IV. COMPATIBILITY CONDITIONS

As already mentioned, the dihedral equations (2), even completed by the inequalities (3) and (4), have many solutions. However, most of them can be discarded by the simple compatibility arguments given below.

A first rule is that $P=(p_10p_3)$ is forbidden if $p_1p_3\neq 0$. Indeed, the hypothesis $p_1p_3\neq 0$ implies that there are $AABB$ and $AAAA$ tetrahedra with a common AA edge, and in that case there should be some $AAAB$ tetrahedron separating $AABB$ from $AAAA$ tetrahedra; therefore $p_2\neq 0$. The same argument shows that $Q=(q_10q_3)$ for $q_1q_3\neq 0$ and $R=(r_1r_20)$ for $r_1r_3\neq 0$ are forbidden. This rule eliminates for instance the solution $x=\frac{1}{2}$, $y=\sqrt{5/2}$ in Table I because it has the configuration $P=(202)$.

The compatibility of P,Q,R can sometimes readily be checked by simple arguments. For instance, $r_3\neq 0$ implies the existence of $AABB$ tetrahedra and therefore $q_1\neq 0$ and $p_1\neq 0$. This rule therefore eliminates the $P=(210)$, $Q=(022)$, $R=(202)$ configuration in the $x=1$, $y=\sqrt{2}$ solution.

When these simple methods fail, the compatibility of a given solution of (2) should be tested by the following procedure. One starts with one tetrahedron and one adds one atom after the other trying to keep the cluster as spherical as possible. This requires the use of a computer. After a certain cluster size (in practice, not more than 50 atoms) (i) either it becomes impossible to build the environment of some atom, proving that the considered values of x and y are not acceptable, or (ii) it becomes possible to form a periodic lattice. Then the values of x and y are acceptable. Examples of case (ii) are given in the next section. An example of case (i) is $P=(111)$, $Q=(n00)$, $R=(111)$. One can start with two B neighbors and their n A neighbors. The surroundings of the n A atoms are completed by $2n$ other A atoms, and if one now wants to complete the surroundings of these A atoms, this turns out to be impossible.

Other cases are more complicated (for instance $x=1$, $y=\sqrt{2}$) because the surroundings of some pairs may be

completed in many ways. The rule in this case is to choose whenever possible pairs which do not leave any choice. Most of the solutions of (2) can thus be eliminated. The remaining solutions (listed in the first three rows of Table I) are discussed in the next section.

V. SPACE-FILLING SOLUTIONS

Our simple compatibility conditions eliminate all but three solutions, which we now show to fill space. We first prove the space-filling property of a solution by giving its unit cell for a crystalline arrangement of the tetrahedra. We then show by construction modifications of the crystalline arrangement of the tetrahedra that exhibit randomness. Finally, we investigate *all* the possible random structures associated with a given solution.

A. Arrangements of regular tetrahedra and octrahedra

The $y=\sqrt{2}$ solution has $Q=(022)$ and $R=(040)$ and no $A-A$ bonds. The top-view diagrams of Q and R are shown in Figs. 4(a) and 4(b). $R=(040)$ is the deterministic part of this solution, in the sense that there is a unique arrangement of tetrahedra around the $A-B$ bond. There are two possibilities associated with $Q=(022)$ and they provide the randomness in this solution. [Refer to Figs. 4(b) and 4(c).]

We have shown in the introduction the unit cell of this solution to be the NaCl structure. (Refer to Fig. 1.) Therefore it fills space. The unit cell shown in Fig. 1 is arrived at by using the deterministic part of the solution, $R=(040)$, to obtain a regular octahedron with B atoms at the vertices and an A atom at its center. The other unit needed for filling space is the regular tetrahedra of B atoms. According to the $Q=(022)$ configurations shown in Fig. 4(b), we get the NaCl structure.

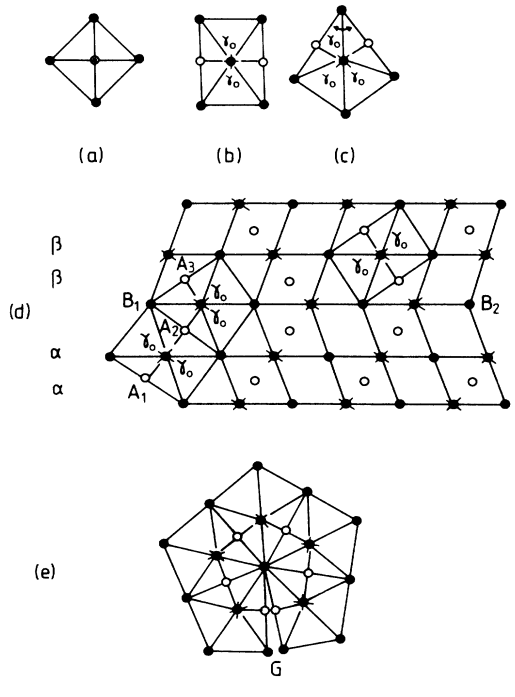

FIG. 4. (a) Projection (or top-view) diagram of the $y=\sqrt{2}$ solution for $R=(040)$. (b) and (c) are two different configurations of tetrahedra around a BB bond for $Q=(022)$. γ_0 is $\arccos(\frac{1}{3})$. (d) Random stacking of planes ($\alpha\alpha\beta\beta$). The boundary of the α and β phases is B_1B_2. (Open circles for A, solid circles for B.) (e) Successive rotations of the octahedron lead to a gap G.

To see that there is randomness in this solution, we refer to Fig. 4(d) where a stacking of planes in the NaCl structure is shown. In this figure, the location of A atoms, being at the center of an octahedron, is marked with an empty circle. The two octahedra centered around A_2 and A_3 are connected by sharing a fact using the $Q=(022)$ configuration shown in Fig. 4(c). If we call the arrangements of atoms below the line B_1B_2 the α phase and above B_1B_2 the β phase, then Fig. 4(d) shows an $\alpha\alpha\beta\beta$ stacking of planes. In general, one can have any sequence of $\alpha\ldots\alpha$ and $\beta\ldots\beta$, thereby a random structure of this solution.

To see that random stacking of planes is the only possible randomness in this structure, we consider all possible mixing of the two configurations of $Q=(022)$. Figure 4(b) corresponds to a translation of the octahedron, while Fig. 4(c) corresponds to a rotation of the octahedron by γ_0. Because γ_0 is not a submultiple of π, we can have at most one rotation by γ_0. Successive rotations around a point will lead to a gap G [Fig. 4(e)]. Can a combination of rotation and translation of the octahedron [a mixture of Fig. 4(b) and 4(c)] lead to other random structure? Let us start with a translation from octahedron A_1 to A_2. A third octahedron A_3 can relate to A_2 either by translation or rotation. If it is rotation then a fourth octahedron A_4 that is a common neighbor to A_3, and either A_1 or A_2, must be related to A_3 by a translation. [This can be seen with the help of Fig. 4(d)]. If it is a translation, then we can repeat the arguments above applied to A_2 and A_3. In both cases, one obtains a stacking of α and β planes. This proves the uniqueness of the type of the random structure possible in the $y=\sqrt{2}$ solution.

B. Random stacking of hexagonal layers

The solution $(x,y)=(\sqrt{4/7},\sqrt{12/7})$ has $P=(400)$, $R=(012)$, and three possible Q's: (600), (410), and (220). The arrangements of tetrahedra around the respectives bonds are shown in Fig. 5(a).

The P and R determine the prism, shown in Fig. 5(b). (This is obtained by applying R to the AB, AB', and AB'' edges of the $ABB'B''$ tetrahedron, which must exist because $r_2=1$.) By applying $Q_{II}=(220)$ along the BB', $B'B''$, and BB'' edges, we have two prisms stacked together on their common triangular face $BB'B''$. Continued application of Q_{II} yields a tube with a triangular cross section, and application of $P=(400)$ to the tube of prisms yields a hexagonal lattice, the unit cell of which has been shown in Fig. 2 in the Introduction. Thus, this solution can fill space.

There is a random structure, shown in Fig. 5(c), where the boundary between the α and β phases has the two prisms connected in the way shown in Fig. 5(d). [Note

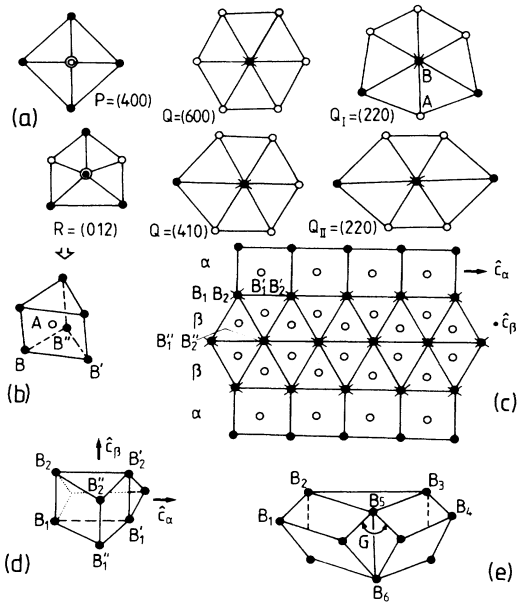

FIG. 5. (a) Top-view diagrams of the $(\sqrt{4/7},\sqrt{12/7})$ solution. Note that there are two configurations for $Q=(220)$. (b) The regular prism determined by P and R. (c) A random stacking of hexagonal layers ($\alpha\beta\beta\alpha$). (d) Phase boundary between α and β. (e) Successive rotations of prisms lead to a gap G.

that the $B_1''B_2''$ edge has $Q=(600)$, B_1B_2, $B_1'B_2'$, B_1B_1', and B_2B_2' edges all have $Q=(410)$.] The $\hat{c}$ axis of the hexagonal lattice in the α phase is along $\hat{c}_\alpha$, which is perpendicular to the $\hat{c}_\beta$ axis in the β phase.

Is there another possible random structure? If we do not stack the prisms together to form a tube using Q_{II}, then we have the configuration illustrated in Fig. 5(d). Continued rotation of the prism to avoid stacking leads to a gap G shown in Fig. 5(e). Although this gap can be completed using Q_I for the B_5B_6 edge, the subsequent application of R to the A—B bond leads to a defect. Therefore, stacking of prisms using Q_{II} is necessary to avoid defect. Once we accept this conclusion, the random stacking of a hexagonal lattice shown in Fig. 5(c) is inevitable, proving that this is the only form of random structure.

C. Random stacking of the 44-face polyhedral

The solution $(\sqrt{8/11},\sqrt{12/11})$ had $R=(102)$, $Q=(600)$, and three possible P's: (310), (211), and (112), shown in Fig. 6(a). If we follow the procedure of analysis in Sec. V B we find instead of a prism a deterministic structure (using R and Q): a 44-face polyhedron with 24 surface atoms (18 A and 6 B) around a B—B bond. (Refer to Appendix C.) Stacking of this polyhedron leads to a tube, and the random structure obtained is again a stacking of planes of atoms. In the following discussion, however, we present a different method of analysis which may be more illuminating in showing the uniqueness of the type of random structure allowed in this solution.

Instead of starting with the deterministic structure R and Q we start with one of the three possible P configurations and try to determine all positions of atoms, using all possible P, Q, and R. In *all* three possible initial P arrangements of atoms around the A—A bond we find that the fully determined part of the positions of atoms form layers, with a unit cell whose projection is shown in Fig. 6(b) for $P=(310)$, (211), and (112). Layers can be generated by translating the projection of the unit cell shown in Fig. 6(c) in the xz plane. In Fig. 6(c) we show the projection on the xy plane of a stacking of layer along the y axis.

First of all, the existence of a unit cell for the layer and the possibility of stacking layers as shown in Fig. 6(e) indicate that this solution is space filling. To see the randomness in this solution, we see from Fig. 6(e) the random choice of A and B along the line indicated by the arrow. At the bottom of the figure we have B_1, and if we repeat the unit cell containing B_1 along $\hat{y}$, we put a B_2 at the translated site. However, we can also have an A atom at B_2. The choices of atoms shown in Fig. 6(e) correspond to a stacking of a $\beta\beta\alpha$ sequence of layers, with α denoting the choice of an A atom and β a B atom.

The uniqueness of the type of random structure in this solution is proved by the fact that in *all* three possible initial configurations of atoms around the A—A bond, we invariably arrive at a layer structure and the only possibility of randomness is in the stacking sequence of layers. In Appendix III, this randomness is manifested in the two possible senses of orientation which the 44-face polyhedron can take with the same positions of the B—B bond inside the polyhedron.

VI. DISCUSSION

We have discussed three solutions, $y=\sqrt{2}$, $(x,y)=(\sqrt{4/7},\sqrt{12/7})$ and $(\sqrt{8/11},\sqrt{12/11})$, that can fill three dimensional space with tetrahedra formed from two kinds of atoms. Furthermore, these solutions can fill space with some degree of randomness, which always correspond to a random stacking of layers. Therefore, the diffraction pattern for these structures can be computed using the theory of Hendricks and Teller.[12] A more surprising result is the conclusion that the random stacking of layers is the only form of randomness permissible in these solutions, if we do not introduce defects.

These solutions have the chemical formula AB, for $y=\sqrt{2}$ and A_2B for $(x,y)=(\sqrt{4/7},\sqrt{12/7})$ and $(\sqrt{8/11},\sqrt{12/11})$. The first solution, AB, is the NaCl structure. If we introduce the A—A bond in this solution, then the NaCl structure, shown in Fig. 1, suggest a value of $x=\sqrt{2}$. Therefore, this solution is certainly not a hard-sphere solution as $x+y=2\sqrt{2}$. On the other hand, the $(\sqrt{4/7},\sqrt{12/7})$ solution has $x+y\simeq 2.065$ and the $(\sqrt{8/11},\sqrt{12/11})$ solution has $x+y\simeq 1.987$. These two more interesting solutions satisfy the hard-sphere condition ($x+y=2$) approximately.

Since we fill space only with tetrahedra, the structure we obtained is close packed. If the bonding energy for A—A A—B, and B—B bonds are the same, then the close-packed structures from our geometric analysis also

have the lowest energy. On the other hand, if we use a general set of bonding energies, we do not know if our close-packed structure is the ground-state structure. It will be interesting to investigate a crystal growth model[10,11] in which the A and B atoms have the distance $d_{\mu\nu}$ given by our geometric analysis and a set of bonding energies $E_{\mu\nu}$ and see if one can generate the close-packed structure. In the spirit of the quenched growth model of Ref. 12, it will be interesting to grow three-dimensional crystals "surface after surface," and forbid the atoms to move once they stick to the initial cluster. Since the $(\sqrt{8/11},\sqrt{12/11})$ solution has a distorted pentagon on the surface of its unit cell, shown in Fig. 6, a quenched growth model may yield a structure intermediate between crystalline and amorphous material. In particular, if we grow the cluster with groups of atoms at a time, such as those specified by the $R=(1,0,2)$ environment of an A—B bond, we may preserve the distorted pentagonal symmetry.

The remaining solutions exhibited in Table I are exact, but they do not fill space. Thus they yield finite clusters. If we want to fill space with these solutions, we must

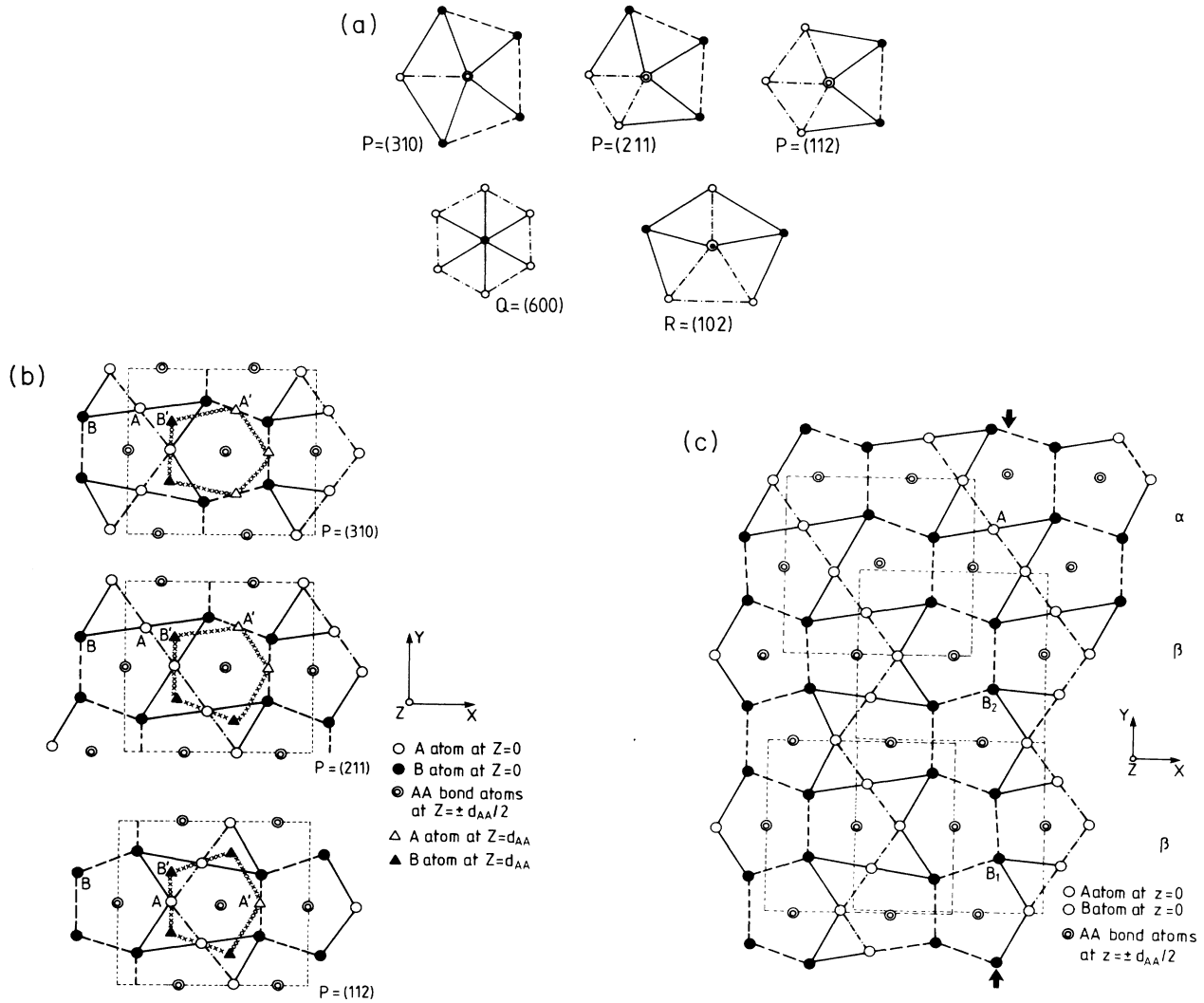

FIG. 6. (a) Top-view diagram of the solution $(x,y)=(\sqrt{8/11},\sqrt{12/11})$. (b) Projection on the xy plane of the unit cell for $P=(310)$, (211), and (112). The single circles are A and B atoms at $z=0$, the double circles are the top view of an A—A bond, with A atoms at $z=\pm d_{AA}/2$. The open triangles and solid triangles are A and B atoms at $z=d_{AA}$. The atoms with $z=0$ can be translated on the xz plane to form a three-dimensional unit cell. Some of the translated atoms are shown, with A to A' and B to B'. The unit cell has dimension shown by the dotted line on the xy plane and height d_{AA} along the z direction. The atoms indicated by solid and open circles have $z=2nd_{AA}$ and those indicated by solid and open triangles (only some of them are shown in the figure) form a plane at $z=(2n+1)d_{AA}$. The double circle shows A atoms at $z=(2n\pm\frac{1}{2})d_{AA}$. Here n is an integer. (c) Projection on the xy plane of a stacking sequence of $\beta\beta\alpha$ layers. The unit cells are indicated by the dotted rectangle and the arrows indicate the line of atoms which can be randomly chosen to be A or B. The choice shown is a B_1B_2A sequence, corresponding to a stacking of $\beta\beta\alpha$ layers.

supplement the finite clusters, built from tetrahedra, with other polyhedra not as closely packed as tetrahedron. The possible number of "crystal" structures resulted from such an extended geometric investigation is enormous, and study along this direction with special attention to n-fold symmetry structure is underway. One notices that our geometric approach to crystal structure does not impose translational invariance, although in our proof that the structure is space-filling we find it useful to construct a periodic structure from the microscopic structure specified by P, Q, and R. Our approach is therefore completely different from the projection method,[14–16] from higher-dimensional space to three dimensions, used in the discussion of quasicrystals. The projection method *a priori* assumes a space-filling structure. It is our hope that the microscopic approach taken here can supplement some of the missing information in the projection method.

Finally, we also find many approximate solutions to the dihedral equations. Suppose that the x and y values yield dihedral angles, whose sum around the corresponding bond differs from 2π by 10^{-n}, then one can say that the given solution yield a finite cluster containing on the order of 10^n atoms. These may be relevant in experimental studies.[3]

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APPENDIX A: SIMULTANEOUS SOLUTION OF EQS. (2a) AND (2c)

For a given P and R, we consider two cases: (i) $p_1=0$ and (ii) $p_1\neq 0$.

If $p_1=0$, then Eq. (2a) involves only the variable x, and one can use binary search for the root of x in Eq. (2a) for the range $0<x\leq 1$. Assuming a solution is found, then Eq. (2c) becomes an equation of y only and a binary search for a root in the range of $1\leq y\leq\sqrt{3}$ can be used to solve Eq. (2c).

If $p_1\neq 0$, we can rewrite Eq. (2a) as

$$y^2=2\left[1-\frac{x^2}{4}\right]\left[1-\cos\left[\frac{2\pi-2p_2\phi_2-p_3\gamma_0}{p_1}\right]\right]. \tag{A1}$$

Since ϕ_2 is a function of x alone, this equation expresses y in terms of x and can be inserted into Eq. (2c). Then a binary search for the root x in Eq. (2c) can be carried out.

In both cases a binary search for roots is used implying that the probability of missing a root is proportional to N^{-1}, where N is the number of intervals that divide the range of the search. We have used $N=10^5$.

APPENDIX B: SOLUTIONS OF THE FORM $P=(111)$, $Q=(n00)$, $R=(111)$

It will be checked here that the system (2) has such solutions for $P=(111)$, $Q=(n00)$, and $R=(111)$, i.e.,

$$\phi_1+2\phi_2+\gamma_0=2\pi\ , \tag{B1a}$$

$$\theta_1=2\pi/n\ , \tag{B1b}$$

$$\psi_1+2\psi_3+\psi_2=2\pi\ . \tag{B1c}$$

Equation (B1a) is equivalent to

$$\cos(2\phi_2)=\cos(\gamma_0+\phi_1)=\tfrac{1}{3}\cos\phi_1-\frac{2\sqrt{2}}{3}\sin\phi_1$$

or (B2)

$$\tfrac{8}{9}\sin^2\phi_1=[\tfrac{1}{3}\cos\phi_1-\cos(2\phi_2)]^2\ .$$

Using (B1b) and (B1c), $\cos\phi_1$ can be expressed as a function of x:

$$\cos\phi_1=1-\frac{2}{t_x}+\frac{2}{t_x}\frac{x^2}{4\sin^2(\theta_1/2)}\quad\text{with } t_x=1-x^2/4\ .$$

Since $\cos(2\phi_2)$ is also a function of x according to (1b), (B2) can be written as an equation for x which turns out to be biquadratic in x^2, namely

$$\left[x^2-\tfrac{4}{3}-\frac{x^2}{3\sin^2(\theta_1/2)}\right]^2 =\tfrac{8}{9}x^2\left[\frac{1}{\sin^2(\theta_1/2)}-1\right]\left[4-\frac{x^2}{\sin^2(\theta_1/2)}\right]. \tag{B3}$$

It should now be checked that this is consistent with (B1c). The latter equation may be written as

$$\cos(2\psi_3)=\cos\psi_1\cos\psi_2-\sin\psi_1\sin\psi_2$$

or (B4)

$$\sin^2\psi_1\sin^2\psi_2=[\cos\psi_1\cos\psi_2-\cos(2\psi_3)]^2\ .$$

The cosines of ψ_i $(i=1,2,3)$ can be expressed as functions of x and y using (1e)–(1g) and then as functions of only x and n using (1c). Insertion into (B4) yields unexpectedly a biquadratic equation again, which is in fact identical with (B3).

The solution (x,y) can be written as

$$x=\sqrt{12t/(2+3t)},\quad y=2(1-x^2/k)^{1/2}\ , \tag{B5}$$

with

$$k=4\sin^2\pi/n,\quad t=[-\mathcal{B}-(\mathcal{B}^2-4\mathcal{A}\mathcal{C})^{1/2}]/2\mathcal{A}\ ,$$

$$\mathcal{A}=a^2-\frac{2a}{3}+1,\quad \mathcal{B}=-\tfrac{4}{3}(a+1)\ ,$$

$$\mathcal{C}=\tfrac{4}{9},\quad a=(12-3k)/k\ .$$

These values of (x,y) yield dihedral angles that satisfy the dihedral equation (2) only when $n\geq 6$.

APPENDIX C: 44-FACE POLYHEDRON

Starting with a B atom and using the deterministic configuration $R=(102)$, we can construct the surrounding of the B_0A_1, B_0A_2, and B_0A_3 edges [coordinate system is shown in Fig. 7(a)], and we obtain an elementary unit called u, the top view of which is shown in Fig.

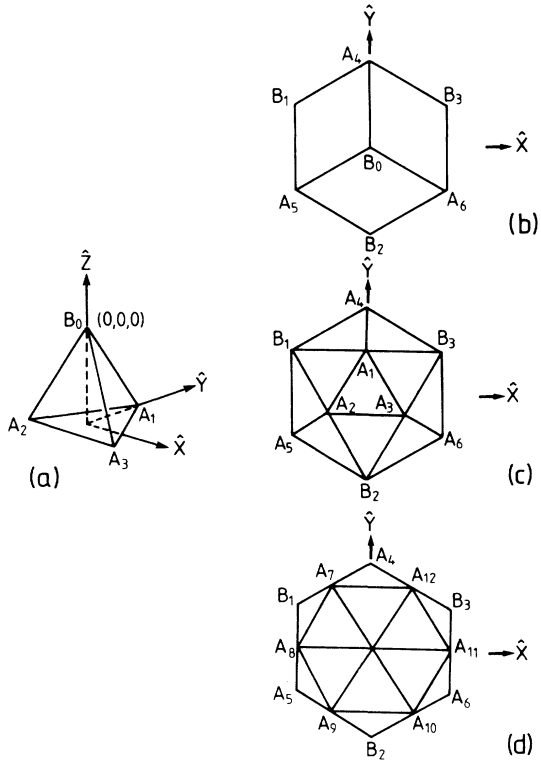

FIG. 7. (a) Coordinate systems. (b) Top view of u or v' or bottom view of v. (c) Top view of u' or bottom view of u. (d) Top view of v or bottom view of v'.

7(b), and the bottom view of which in Fig. 7(c). By considering a B_0' atom at $(0,0,\sqrt{12/11})$ with $d_{AB}=1$ as scale, we construct the elementary unit ω using the prescription of $Q=(600)$ for the B_0—B_0' bond, with the six A atoms chosen at $A_7, A_8, \ldots, A_{11}, A_{12}$. The top view of ω, shown in Fig. 7(d), is identical to its bottom view if we omit the points A_4, A_5, A_6, B_1, B_2, and B_3 in that figure. With these choices of A's and B's, the u and ω units thus constructed determine the v unit, whose constituent atoms are $B_0, B_1, B_2, B_3, A_4, A_5, A_6, \ldots, A_{11}, A_{12}$. Figure 7(d) shows the top view of v. This construction gives 16 nearest neighbors of B_0 at the origin with the following coordinates:

$$
\begin{aligned}
A_1&=(0,\sqrt{8},-5)/\sqrt{33}\ ,\\
A_2&=(-\sqrt{6},-\sqrt{2},-\sqrt{5})/\sqrt{33}\ ,\\
A_3&=(\sqrt{6},-\sqrt{2},-\sqrt{5})/\sqrt{33}\ ,\\
A_4&=(0,\sqrt{32},-1)/\sqrt{33}\ ,\\
A_5&=(-\sqrt{24},-\sqrt{8},-1)/\sqrt{33}\ ,\\
A_6&=(-\sqrt{24},\sqrt{18},-1)/\sqrt{33}\ ,\\
A_7&=(-\sqrt{6},0,3)/\sqrt{33}\ ,\\
A_8&=(-\sqrt{21},0,3)/\sqrt{33}\ ,\\
A_9&=(-\sqrt{6},-\sqrt{18},3)/\sqrt{33}\ ,\\
A_{10}&=(\sqrt{6},-\sqrt{18},3)/\sqrt{33}\ ,\\
A_{11}&=(\sqrt{21},0,3)/\sqrt{33}\ ,\\
A_{12}&=(\sqrt{6},\sqrt{18},3)/\sqrt{33}\ ,\\
B_0'&=(0,0,\sqrt{36})/\sqrt{33}\ ,\\
B_1&=(-\sqrt{24},\sqrt{8},-2)/\sqrt{33}\ ,\\
B_2&=(0,-\sqrt{32},-2)/\sqrt{33}\ ,\\
B_3&=(\sqrt{24},\sqrt{8},-2)/\sqrt{33})\ .
\end{aligned}
\tag{C1}
$$

These 16 nearest neighbors of B_0 at the origin are a fixed-stacking of $uv\omega$ units along $\hat{\mathbf{z}}$ once we fix the positions of the initial tetrahedron $B_0A_1A_2A_3$. There are also 16 nearest neighbors of B_0', with $\hat{\mathbf{z}}$ reflected by π and the corresponding stacking of elementary units is $\omega v'u'$. There are therefore $16+16-6-2=24$ atoms that are the vertices of a 44-face polyhedron. This 44-face polyhedron is a stacking of elementary units $(uvwv'u')$ along $\hat{\mathbf{z}}$ and contains inside it a B_0B_0' bond along $\hat{\mathbf{z}}$. Also, the bottom and top face of a 44-face polyhedron are regular triangles of A atoms, with the same orientation and separated along $\hat{\mathbf{z}}$ by $16/\sqrt{33}$. By stacking the 44-face polyhedron along the $\hat{\mathbf{z}}$ axis, sharing a common triangular face $A_1A_2A_3$, we have a chain of 44-face polyhedra. To show that this solution fills space, we look at the tiling of the xy plane by the hexagons $A_4A_5A_6B_1B_2B_3$. Once we are given the 44-face polyhedron unit constructed as the stacking of $(uv\omega v'u')$, the hexagons on the xy plane are fixed for that 44-face polyhedron, thereby also fixing its neighboring 44-face polyhedra on the xy plane. Therefore, such chains of 44-face polyhedra forming a tube along $\hat{\mathbf{z}}$ can be "glued" together to fill space. Also, from the threefold symmetry of the u unit shown in Fig. 7(b), and the sixfold symmetry of the ω unit shown in Fig. 7(d), we observe that there is a twofold degeneracy of stacking $v'u'$ onto ω. This intrinsic randomness of 44-face polyhedra in the stacking of $(uv\omega v'u')$ along $\hat{\mathbf{z}}$ can be considered as a random stacking of (uv) planes. Thus there is a random structure that fills space.

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