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The structure model of a cubic aperiodic phase ('quasicrystal without forbidden symmetry axes')

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Abstract

A model structure of the aperiodic cubic phase (a cubic quasicrystal) has been constructed as a periodical packing of hierarchical octahedral clusters which were composed of truncated tetrahedra (Friauf–Laves polyhedra) and chains of Frank–Kasper polyhedra with 14 vertices. The construction of the hierarchical model for the cubic aperiodic phase became possible due to the discovery of a new space subdivision with equal edges and with vertices belonging to two orbits of the space group $Fm\bar{3}m$. The subdivision is characterized by unique values and unique relations between the coordinates of the starting points of two orbits. Calculated x-ray diffraction patterns for the proposed hierarchical model are in qualitative agreement with published experimental x-ray patterns for aperiodical phases observed in melt-quenched Mg–Al and Fe–Nb–B–Si alloys.

1. Introduction

Different theoretical models have been proposed for the description of the quasicrystal structure, i.e. the structure of objects exhibiting a forbidden point symmetry of their electron diffraction patterns. Some models use the formalism of spaces with higher dimensions, i.e. 4D-space [1], 6D-space, [2] and 8D-space [3]. Nevertheless, the question 'Where are the atoms?' is still unresolved, for example, this question is the title of one section in the monograph 'Quasicrystals' by Janot [4]. The situation became more complicated after the discovery of so-called quasicrystals without forbidden symmetry axes, now these objects are called, with some precautions, 'aperiodic phases'. Such phases have been discovered in different alloy systems: V–Ni–Si [5], Mg–Al [6], Fe–Nb–Cu–B–Si [7], Ti–Mn–Si [8]. These phases exhibit both the cubic point group 432 and aperiodicity of its electron diffraction patterns. In one case the aperiodical electron diffraction pattern has been successfully indexed using a projection method [9]. The present paper reports a

three-dimensional geometrical model for the structure of the aperiodic phase having the cubic symmetry.

2. Model

Some time ago the crystal structure of B₆O oxide has been deciphered as a hierarchical periodical packing of icosahedral boron clusters with oxygen atoms occupying the holes between boron clusters [10]. While commenting on this result, Mackay [11] put forward two important concepts: (1) clusters of clusters are an alternative to strict crystalline arrangements, and could form a new type of condensed matter; (2) true quasicrystals can probably also be described as icosahedral clusters, themselves clustered icosahedrally in hierarchical levels, the gaps being filled by the overlapping of these clusters.

Earlier a geometric model was proposed for the 3D-space structure of icosahedral and decagonal quasicrystals [12, 13] just in the spirit of these concepts by Mackay. In that model a building unit for the quasicrystal structure is the hierarchical dodecahedron assembled from atomic clusters of the two types shown in figure 1. Both clusters represent projections of the {3, 3, 5} polytope straightened onto 3D-Euclidean space, where

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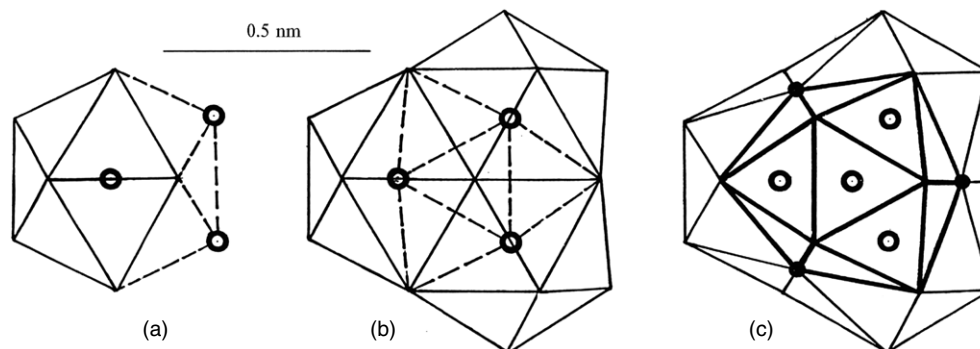


Figure 1. Clusters used for assembling the hierarchical icosahedron in the quasicrystal model: single icosahedron (a), intersections of three icosahedra with D_{3h} symmetry (b) and four icosahedra with T_d symmetry (c). All clusters have been observed experimentally (see the text). Dashed lines designate the edges of each individual icosahedron which became the inner ('invisible') edges of the cluster after the joining of icosahedra.

the $\{3, 3, 5\}$ polytope is the 4D-counterpart of the icosahedron containing a 600 regular tetrahedral cell with 120 vertices altogether [14].

Single icosahedron (figure 1(a)) is the projection started from a polytope vertex. A cluster with the D_{3h} symmetry is the projection started from a cell face (figure 1(b)) while the cluster with the T_d symmetry is the projection started from a tetrahedral cell (figure 1(c)). All clusters have been experimentally observed as fragments of the crystalline structures of certain intermetallic compounds [15]. For example, D_{3h} -cluster forms the hexagonal structures of $Al_{10}Mn_3$, Al_9Mn_2Si , Al_5Co_2 and $Al_{23}V_4$ compounds, T_d -cluster forms the cubic structures of Ti_2Ni , Cu_5Zn_8 , $Al_{13}Cr_4Si_4$, Th_6Mn_{23} and Fe_3W_3C compounds. The alternate joining of D_{3h} and T_d clusters along common hexacycles generates a hierarchical dodecahedron with an edge length of 0.7–0.75 nm (figure 2). Centers of the T_d -clusters form a dodecahedron, while centers of the D_{3h} clusters form an icosidodecahedron. Since the dodecahedron and icosidodecahedron are sections of the $\{3, 3, 5\}$ polytope, we can say that joining of these two sections of the $\{3, 3, 5\}$ polytope are determined also by the $\{3, 3, 5\}$ polytope. In other words for constructing the hierarchical dodecahedron one must cut off an icosahedral rod from the $\{3, 3, 5\}$ polytope along the 6_1 -symmetry axis of this polytope. In this rod icosahedra are joined together in the face-to-face mode. Both length and diameter of this rod are determined by the experiment, since we are joining together only clusters which have been observed experimentally. Distortions of tetrahedron edges are required for straightening of polytope substructures. Necessary distortions are effected by placing different atomic species in different vertices.

In turn, this hierarchical dodecahedron sticks together with similar ones along pentagonal faces (in the face-to-face mode) thus forming a 3D-projection of the $\{5, 3, 3\}$ polytope (a 4D-counterpart of the dodecahedron). This projection is straightened onto 3D-Euclidean space due to inserting the disclination network into the polytope space, as was described by Sadoc and Mosseri [16, 17]. The final hierarchical cluster has several shells with the hollow dodecahedron shown on figure 2 at the center. That giant hierarchical icosahedron (not

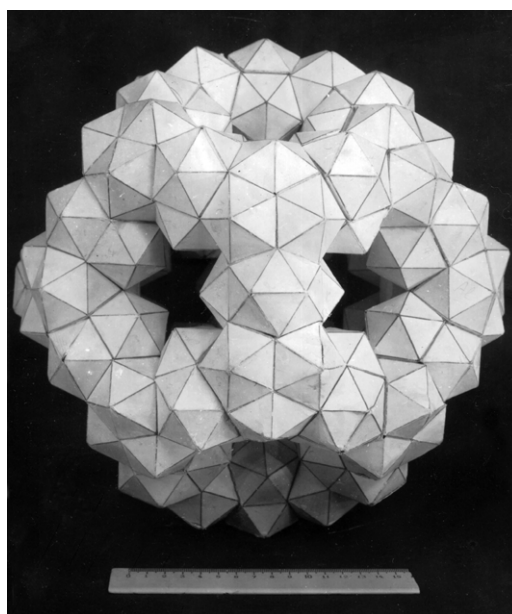


Figure 2. Cartoon model of the hierarchical dodecahedron assembled by alternate sticking of D_{3h} and T_d clusters (see figure 1) in the face-to-face mode. The photo is taken along a two-fold symmetry axis.

shown here) has a diameter of about 10 nm and contains several thousands of atoms. In general, the structure of this hyper-cluster ('a collective atom') is in accordance with the shell model of a 3D-quasicrystal by Sadoc and Mosseri constructed as sections of the 8D lattice E_8 [3].

Further space filling by such hyper-clusters is possible in different ways, a periodical packing being included [12, 13]. As distinct to ordinary atoms, these hierarchical cooperative (pseudo) atoms are packed with the mutual intersection as was proposed by Mackay [11]. Evidently, point diffraction patterns from the parallel arrangement of these giant clusters must exhibit icosahedral symmetry. To tell the truth, in the case of a periodical packing the lattice period is quite large (of about 32 nm [12]), so one cannot obtain unambiguous evidence for this model from the experimental diffraction patterns of

quasicrystals. Nevertheless this model cluster gives a correct description of the chemical composition of the quasicrystal and it is in good accordance with the angle positions of diffraction peaks on the x-ray patterns [13]. At any rate, this model gives us a key to construct a similar hierarchical model for the above mentioned aperiodical phases with cubic symmetry. Firstly, one must construct a hierarchical octahedron since the hierarchical principle for atomic packing does not impose any crystallographic restrictions on the symmetry of a condensed phase. Secondly, the hierarchical octahedron can be translated by the FCC lattice generating a 3D-periodical structure.

The unique space subdivision with equal edges has been used for assembling the hierarchical octahedron. Vertices of this subdivision belong to two regular point systems (orbits) of the space group $Fm\bar{3}m$. The first orbit is designated as the Wyckoff position 24(e) for this space group. (In accordance with the International tables for x-ray crystallography, Wyckoff positions designate the type of orbit for a given space group by letters (a, b, c, d,...). In our case the Wyckoff position 24(e) for the $Fm\bar{3}m$ group means that there are 24 points (e) in the unit cell: six points having coordinates (x_100) , $(0x_10)$, $(00x_1)$, $(-x_100)$, $(0-x_10)$, $(00-x_1)$, i.e. they are the vertices of an octahedron. The remaining 18 points are obtained from these six points by adding to each point translating vectors $(0, 1/2, 1/2)$, $(1/2, 0, 1/2)$ and $(1/2, 1/2, 0)$. In other words, the point $x_1, 0, 0$ generates points $x_1, 1/2, 1/2$; $1/2+x_1, 0, 1/2$; $1/2+x_1, 1/2, 0$ etc.)

The second orbit is the Wyckoff position 32(f). In this case there are 32 points (f) in the unit cell: eight points having coordinates (x_2, x_2, x_2) , $(-x_2, -x_2, x_2)$, $(-x_2, x_2, -x_2)$, $(x_2, -x_2, -x_2)$, $(x_2, x_2, -x_2)$, $(-x_2, -x_2, -x_2)$, $(x_2, -x_2, x_2)$, $(-x_2, x_2, x_2)$, i.e. they are the vertices of a cube. The remaining 24 points are obtained by adding to each of eight points the same translating vectors $0, 1/2, 1/2$; $1/2, 0, 1/2$; and $1/2, 1/2, 0$. The vertices of the octahedron and the cube will belong to one rhombic dodecahedron with equal edges if relations $x_1 = 2x_2$ and $x_2 = \frac{4-\sqrt{6}}{10}$ are fulfilled. Since the center of the rhombic dodecahedron occupies the point $(0, 0, 0)$, therefore centers of all rhombic dodecahedra form the FCC lattice. Rhombic dodecahedra are isolated from each other and are surrounded by octahedra, tetrahedra, trigonal prisms and parallelepipeds. The enumerated polyhedra form the first crown for the rhombic dodecahedron (see figure 3). (The first crown of a given polyhedron is the joining of all polyhedra having at any rate one vertex with it.) The center coordinates for the tetrahedron, octahedron and trigonal prism are respectively: $(1/4, 1/4, 1/4)$, $(1/2, 1/2, 1/2)$ and $(1/8, 1/8, 3/8)$.

This first crown can be used in our model as the so-called 'hierarchical octahedron'. In preceding works only the subdivisions with tetra-coordinated graphs were considered [18]. In our case more than four edges are meeting at one vertex.

In the ordinary crystallographic packing of individual atoms, the edge of this unique subdivision is equal to atomic diameter d . With typical metallic atom $d = 0.3$ nm the lattice period of the FCC structure composed from these hierarchical octahedra will be equal to 1.117 nm. Lack of a periodicity on the electron point diffraction pattern of the aperiodic phase

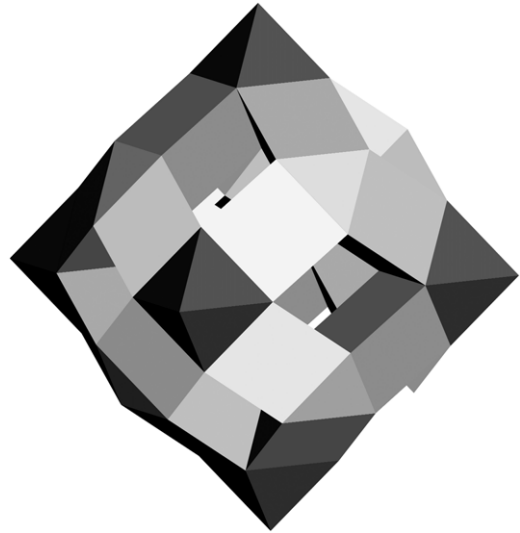


Figure 3. The face-to-face joining of octahedra, tetrahedra, trigonal prisms and parallelepipeds with equal edges forms this first crown of the rhombic dodecahedron. This first crown can be regarded as 'the hierarchical octahedron' with the rhombic dodecahedron in the interior of the 'the hierarchical octahedron'.

can be due to a larger value of the period of the hierarchical lattice. Hence, the next step for the model construction must be a decoration of the vertices belonging to the discovered subdivision by more complex atomic clusters and not by individual atoms.

It will be natural to decorate vertices by the clusters which are the main building units for the crystalline structures of the phases existing in a given alloy system. In the Mg–Al system there are many intermetallic compounds with complex crystal structures, and all these structures are composed from Frank–Kasper polyhedra (FK) with the coordination numbers $Z = 12, 14, 15$ and 16 [19]. In particular, there is the γ -Mg₁₇Al₁₂ phase which is isomorphic to the α -Mn structure. At the same time, the aperiodic phase with the same cubic symmetry 432 has been observed during the devitrification of some iron-based metallic glasses, and the aperiodic phase was obtained directly in the melt-quenched state in alloys with a certain chemical composition [7]. In many cases the aperiodic phase was observed together with the metastable phase of the α -Mn. Moreover, the intensity distribution on the x-ray diffraction patterns of the aperiodic phase and the α -Mn phase have very much in common [7]. This fact evidences the intimate structural similarity between phases in the Mg–Al alloys and in Fe–Nb–B–Si, Fe–Cr–P–C metallic glasses investigated in [6, 7]. The main building unit for the α -Mn structure and other phases in the Mg–Al alloys is the truncated tetrahedron (a Laves–Friauf polyhedron) [19]. We used some fragments of known intermetallic phases for the decoration of vertices in the discovered subdivision. Tetrahedral and octahedral complexes formed by Friauf–Laves polyhedra are shown in figure 4.

In our decoration, the center of a tetrahedral complex occupies the tetrahedron center at $(1/4, 1/4, 1/4)$, the center of an octahedral complex coincides with the octahedron center

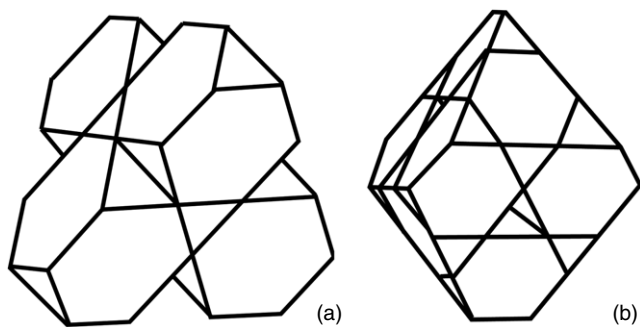


Figure 4. Tetrahedral (a) and octahedral (b) complexes formed by Friauf-Laves polyhedra (truncated tetrahedra).

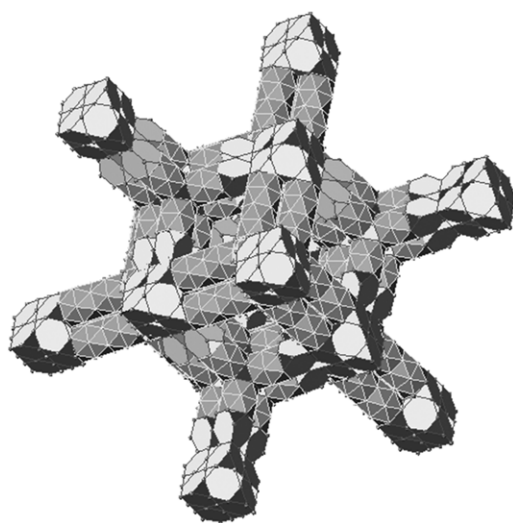


Figure 5. The hierarchical cluster obtained by the decoration of the hierarchical octahedron (see figure 3) by tetrahedral and octahedral complexes from figure 4. Connecting rods between complexes are decorated by chains of Frank-Kasper polyhedra with 14 vertices.

at $(1/2, 1/2, 1/2)$. The remaining edges of the trigonal prisms are decorated by rods of the Frank-Kasper polyhedra with 14 vertices, which are fragments of the structure of the Zr_4Al_3 phase [15]. The obtained giant hierarchical octahedron is shown in figure 5.

3. Comparison with experiment and discussion

In some sense our decoration is similar to the structure model of the Cu_4Cd_3 phase with the giant unit cell. Samson [20] has composed complexes with the tetrahedral and octahedral symmetry from the Laves-Friauf polyhedra, i.e. fragments of the cubic Laves phase (see figure 4) and constructed the cubic structure of Cu_4Cd_3 from these complexes. That Cu_4Cd_3 cubic phase has a lattice period of 2.5871 nm.

The giant octahedron shown in figure 5 generates the hierarchical FCC structure with the lattice period ranging from several up to tens of nanometers; it depends on the size of the tetrahedral and octahedral complexes (numbers of Laves-Friauf polyhedra in one complex), which can be varied in certain limits. In the case of the complexes shown

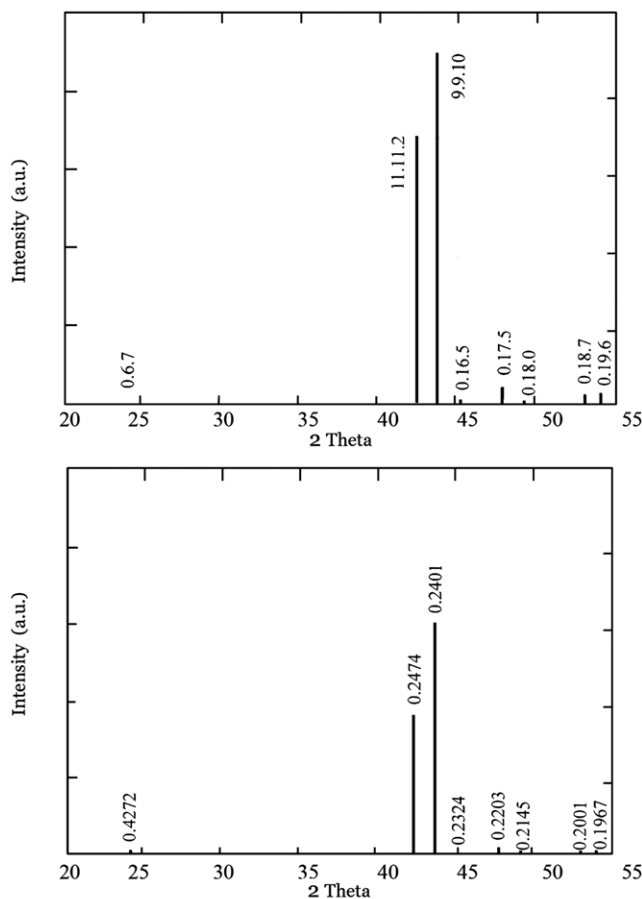


Figure 6. Calculated x-ray intensity distribution (a) for the cubic periodic lattice (Miller indices correspond to $a = 3.9$ nm) assembled from hierarchical clusters shown in figure 5 and experimental distribution for the aperiodic phase in the Mg-Al alloy from [6] (b) with interplanar spacing indicated at each line.

in figure 4 (two Friauf-Laves polyhedra along the edge of both tetrahedral and octahedral complexes) the period of the cubic lattice assembled from giant octahedra can be easily calculated as equal to about 3.9 nm. The calculated intensity distribution of the x-ray pattern is in qualitative agreement with experiment (see figures 6 and 7). These x-rays patterns can be indexed (as shown in figures) with cubic lattice parameters $a = 3.9$ nm for both Mg-Al and Fe-Nb-Si-B aperiodic phases. With increasing numbers of Friauf-Laves polyhedra in both tetrahedral and octahedral complexes, the numbers of atoms in the giant octahedron become quite large and fall beyond computational possibilities of the computer.

One must note also that our approach allows us to predict only the types of polyhedra and their sticking mode, but we can say nothing about the occupation of different vertices by different atomic species. The actual site occupations influence the intensity distribution of the diffraction pattern. While constructing this hierarchical model we simply state that a larger atom (magnesium in the Mg-Al alloy and niobium in the Fe-Nb-B-Si alloy) is positioned in the center of the Friauf-Laves polyhedron. Due to this, one can speak only about the qualitative agreement of the calculated intensity distribution with the experimental diffraction pattern, mainly concerned

Table 1. Calculated and experimental intensity (in arbitrary units) of the x-ray reflections for the cubic aperiodic phase in the Mg–Al alloy.

Reflection	1	2	3	4	5	6	7	8
Diffraction angle (deg)	24	42.5	43.5	45.5	46	48	53	54
Calculated intensity (the hierarchical model)	0.5	63	77	1	5	0.3	3	4
Experimental intensity from [6]	0.5	31	51	1	3	0.5	0.3	0.3

Table 2. Calculated and experimental intensity (in arbitrary units) of the x-ray reflections for the cubic aperiodic phase in the Fe–Nb–B–Si alloy.

Reflection	1	2	3	4	5	6	7	8
Diffraction angle (deg)	50	51	56	58.5	63	87.5	92.5	95.5
Calculated intensity (the hierarchical model)	43	84	10	3	1	—	0.2	—
Experimental intensity from [7]	30	58	7	1	1	—	—	—

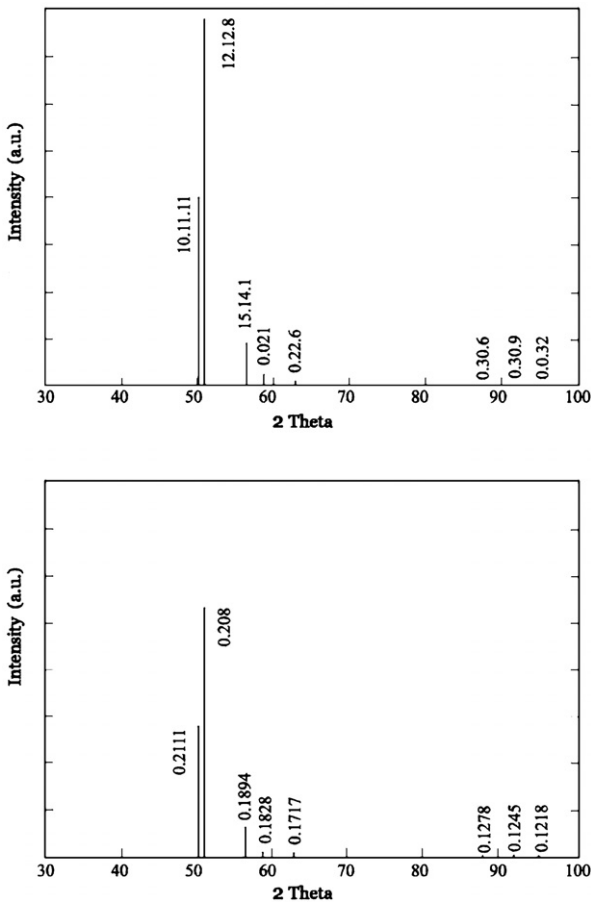


Figure 7. The same calculated (a) and experimental [7] (b) x-ray intensity distributions as in figure 6 for the Fe–Nb–B–Si alloy. Miller indices at (a) correspond to the cubic periodic lattice with $a = 3.9$ nm.

only with the two strongest reflections. A comparison of the calculated and measured intensities of the x-ray reflections (in arbitrary units) is shown in table 1 for the Mg–Al alloy and in table 2 for the Fe–Nb–B–Si alloy.

The suggested model is conceptually similar to the hierarchical models of icosahedral and decagonal quasicrystals proposed in [12, 13]. In any case, the assembling of the structure from giant hierarchical clusters coincides with the

Mackay principle for the organization of ordered (not only crystalline) structures. Also one must note that Sadoc and Mosseri [3] have considered the existence of ‘a tetrahedral quasicrystal’ as projected from the eight-dimensional E_8 lattice.

4. Conclusion

- (1) A model structure of the aperiodic cubic phase (‘a cubic quasicrystal’) can be constructed as a periodical packing of hierarchical clusters with 432 symmetry. These cluster were composed of truncated tetrahedra (Laves–Friauf polyhedra) and rod chains of Frank–Kasper polyhedra with 14 vertices.
- (2) The calculated x-ray diffraction patterns for the proposed hierarchical model are in qualitative agreement with the experimental x-ray patterns for the aperiodical phases observed in the melt-quenched Mg–Al and Fe–Nb–B–Si alloys.
- (3) The assembling of the structure of the aperiodic cubic phase from giant hierarchical octahedral clusters coincides with the concept of the assembling of icosahedral and decagonal quasicrystals from hierarchical icosahedral clusters, both models are a realization of the Mackay principle for the hierarchical organization of ordered (not only crystalline) structures.
- (4) The construction of the hierarchical model for the cubic aperiodic phase became possible due to the discovery of a new space subdivision with equal edges. The vertices of this subdivision belong to two orbits of the space group $Fm\bar{3}m$. The subdivision is characterized by unique values of the coordinates of starting points of two orbits and the unique relationship between coordinates.

Acknowledgments

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