

Atomic model for the growth of icosahedral quasicrystals

V. E. Dmitrienko and S. B. Astaf'ev

A. V. Shubnikov Institute of Crystallography, 117333 Moscow, Russia

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It is demonstrated how the binary alloys with a short-range oscillating atomic interaction can grow large, nearly perfect quasicrystal grains. The calculated Bragg peaks become narrower during the grain growth; nevertheless, they exhibit clear evidence for phasonic deformations. © 1995 American Institute of Physics.

Ten years after the discovery of quasicrystals¹ their atomic origin is still controversial. The modeling of the quasicrystal structure and growth usually includes either projection from high-dimensional spaces² (six-dimensional in the case of icosahedral quasicrystals) or special atomic clusters (the Ammann rhombohedra, the canonical cells,³ different units with icosahedral symmetry, etc.) which are attached according to some matching rules.^{4–6} These two methods are very powerful and mutually related (see Ref. 5 and the bibliography cited there). However, among those clusters only the 13-atom icosahedron seems to be reasonable from the atomistic point of view.

In this paper we propose a growth algorithm which uses neither the high-dimensional spaces nor the ready-made clusters. Atoms are assumed to be spherical (without directional bonds); only the interatomic distances are specifically chosen. First the growth model is postulated, then the physical and geometric reasons for the model are given and finally the properties of the grown grains are discussed.

The postulated feature of the model is the *dodecahedral local ordering* (DLO) of atoms as the basic structure motif of quasicrystals. The ideal DLO means that every atom has its closest neighbors positioned at the vertices of a regular pentagon-dodecahedron. Experimentally, the DLO was found both in the approximants and in the icosahedral quasicrystals of different compositions [Al–Mn–Si (Ref. 7), Al–Fe–Cu (Ref. 8), and Al–Pd–Mn (Ref. 9)]. In the six-dimensional projection scheme the same local ordering arises if the size of the acceptance domain is enlarged in comparison with the standard triacontahedron.^{10,11} A detailed discussion of the DLO in small and large approximants (including α -Al–Mn–Si and R -Al₅Li₃Cu crystals) is presented elsewhere.¹²

A possible physical reason for DLO is the close packing of the atoms of two different sizes, large (L) and small (S), with the special ratio of interatomic distances

$$r_{LS}/r_{LL} = \sqrt{3}/2. \quad (1)$$

The same distances are found in the CsCl crystals and approximately the same distances are found in the FeSi and Hg crystals.¹² In Al transition metal alloys, r_{LL} is a typical Al–Al distance (of about 2.9 Å), while r_{LS} can be attributed to Al transition metal distances (of about 2.5 Å, the minimal distance in the model). These distances are related to the quasilattice constant, a_R : $a_R = r_{LL}\sqrt{\tau+3/4}$, etc., where τ is the golden mean

$[\tau = (1 + \sqrt{5})/2]$. The r_{SS} distance seems to be of minor importance, because the proper positions of small atoms can be fixed by three or more LS bonds.

If we stack L and S atoms in a pile so that every new atom is in contact with at least three old atoms, a DLO structure can result. The golden mean τ , which is frequently found inside quasicrystalline structures, is therefore a corollary of Eq. (1). Unfortunately, wrong positions can also arise in this stacking. For example, the regular tetrahedron of four L atoms produces non-DLO positions. These and other disruptions can cause amorphization of DLO structures. At present, it is therefore not completely clear why the DLO occurs in the quasicrystalline and similar structures. A possible clue might be that in our growth process every new atom is fixed not by three old atoms but usually by five or six atoms; as a result, the non-DLO positions can be excluded. On the other hand, in the Hg crystal the DLO seems to be a result of the electronic properties (the Jones effect), rather than the result of different atomic sizes. Further work is needed here and we believe that our paper should stimulate such research. Another difficulty is that in real structures the DLO is usually imperfect for many reasons.¹² Nevertheless, in this model of quasicrystal growth the ideal DLO is assumed to be present.

The suggested growth algorithm includes the following steps:

- (i) The growth starts with a small initial DLO cluster of atoms (3–50 atoms).
- (ii) New trial positions are generated at all the vertices of the regular dodecahedron near every atom.
- (iii) Bad positions (see below) are excluded from the trial list.
- (iv) The trial position, which has the lowest energy, is stuck to the cluster; then the growth process is repeated during reasonable computer time. In our simplified model the negative energy of a trial position should be proportional to the number of neighboring atoms (i.e., the number of atoms at the LS and LL distances). If several positions have the lowest energy, then the first position of the trial list is stuck to the cluster; there were no attempts to randomize the growth process.

This algorithm is similar to the Eden model of alloy quenching, which was previously used for two-dimensional quasicrystals.¹³ Therefore, we discuss here only the most important features of the simulations.

The computer growth shows that the iii stage is crucial for the competition between crystalline and quasicrystalline structures: If only those trial positions which are too close (closer than r_{LS}) to the already existing atoms are excluded, then the CsCl-type crystal will grow. To suppress the crystalline structure, we assume that some interatomic distances, which are intrinsic to that structure, are forbidden. The physical reason is that the interatomic potential in metals is not of the Lenard–Jones form (with one minimum); it may be an oscillating function of the interatomic distances with several minima and maxima (the Friedel oscillations). The interatomic potentials of this type have been used in the studies of the quasicrystal stability.¹⁴ The distances corresponding to the maxima of the oscillations are energetically unfavorable. In our model some of them are totally forbidden (much larger forbidden distances were used for icosahedral clusters,⁶ but in the latter case the physical reason is not clear). Of course, in a more sophisticated theory a

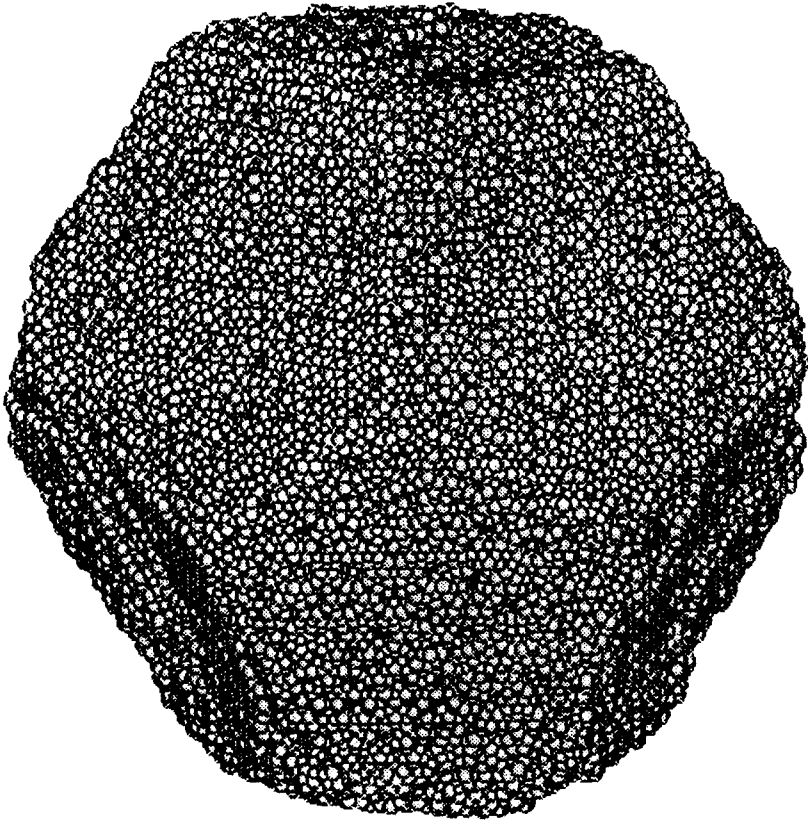


FIG. 1. The views along a threefold axis on the quasicrystalline dodecahedral cluster (more than 2×10^5 atoms) grown from the outer shell of the Mackay icosahedron (42 atoms); the fivefold facets of the cluster are quite evident.

realistic interatomic potential¹⁴ should be used and the iii and iv stages should be considered simultaneously.

In the computer simulations we assume that two distances, r_{LL}^* and r_{LS}^* , are forbidden: $r_{LL}^* = \sqrt{3}r_{LL}$ and $r_{LS}^* = \sqrt{11/3}r_{LS}$. These distances are intrinsic both to the CsCl and to the Hg structures (r_{LL}^* is the distance between diagonal vertices of the cubic unit cell of the CsCl structure, whereas r_{LS}^* is the distance from the vertex to the center of a neighboring cube). For reference, the forbidden distances are just after the outer shell of the Mackay icosahedron; for those distances a gap in the radial atomic distribution is observed in quasicrystalline structures. Our experience shows that more complex selection rules can improve the quality of growing clusters, but our aim here is only to demonstrate the idea.

An example of the grain grown with our algorithm is shown in Fig. 1. Different initial clusters were examined: the piece of the FeSi crystal, the twelve-atom empty icosahedron, the outer shell of the Mackay icosahedron (30+12 atoms), etc. It seems that

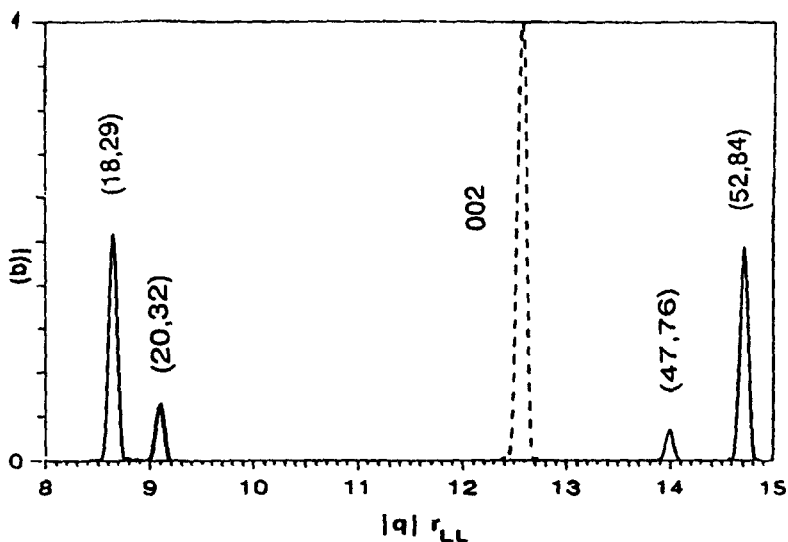


FIG. 2. Simulation of the Bragg reflections from the cluster of about 4×10^5 atoms ($f_L=1.3$, $f_S=0.7$). Longitudinal scans were made for the (20, 32) and (52, 84) peaks along all twofold axes and for the (18, 29) and (47, 76) peaks along all fivefold axes. The last peak vanishes if $f_L=f_S$. All the equivalent reflections are plotted; therefore, the thickness of the lines characterizes the scatter in the widths and in the positions of the icosahedrally equivalent reflections. For reference, the 002 reflection from the CsCl crystal of the same number of atoms is represented by the dashed line.

the coarse-grained structure and the faceting of large grown clusters are nearly independent of the initial cluster. The fivefold facets are highly pronounced. Therefore, the clusters are distorted dodecahedra.

It was found that the average coordination numbers for different interatomic distances, $N(r)$, are similar to (or larger than) those obtained for the Al-Cu-Fe quasicrystals from the six-dimensional approach:⁸ $N(r_{LS}) \approx N(r_{LL}) \approx 6$, $N(a_R) \approx 8$, and $N(\tau r_{LL}) \approx 14$. However, in comparison with the Mackay icosahedron, where $N(a_R) = 12$ and $N(\tau r_{LL}) = 30$, this coordination sphere is approximately half-populated; hence the large fragments of the outer shells of the Mackay icosahedra can be found near many atoms.

The number of L and S atoms in the clusters are almost equivalent and the quasilattice is face-centered (L and S atoms correspond to two sublattices). This results in the τ inflation for the fivefold reflection (Fig. 2). However, if the scattering amplitudes of L and S atoms are the same or if the L - S ordering is not long range, then the superstructure reflections vanish and the τ^3 inflation is restored. The normalized intensities of the reflections, $I(\mathbf{q})$, are calculated as $I(\mathbf{q}) = |\sum f_k \exp(i\mathbf{q}r_k)|^2/N^2$, where f_k and r_k are the atomic-scattering factor and the position of the k th atom, \mathbf{q} is the wave vector, and N is the total number of atoms in the cluster. The deviations of calculated reflections from their ideal icosahedral positions are much smaller than their widths (the widths are determined mainly by the finite sizes of the clusters). Nevertheless, those deviations and the slightly different widths of the reflections provide evidence for phasonic disorder in the

grown clusters. It is rather surprising that the widths of the reflections are so small, and that they are comparable to the widths observed in real quasicrystals. We found that until the number of atoms 2×10^6 is reached, the reflection widths decrease with increasing cluster size. It is therefore not clear yet whether the residual widths are induced by the disorder when the cluster grows *ad infinitum*.

We conclude that a simple growth algorithm can produce clusters with quasicrystal-line ordering and with sharp diffraction peaks. Geometrically, the suggested model is similar (with a factor τ^{-3}) to the icosahedral glass model,⁵ but instead of the ready-made clusters, it is constructed from the atoms of two sizes with rather realistic interatomic potentials. All the atoms have a unified ordering, and there is no need for "glue" atoms. The phasonic jumps along the twofold and fivefold directions are allowed for many atoms: hence the clusters can relax and improve their quality.

Among other things, our model explains the closeness of CsCl crystals and icosahedral quasicrystals on the phase diagrams of many alloys. It is also intriguing that the densely populated, fivefold layers and the distances between them in the grown clusters are very similar to the puckered and flat atomic layers observed in the decagonal quasicrystals.¹⁵ Perhaps a similar growth algorithm may be used for the real three-dimensional decagonal quasicrystals and for their approximants.

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