Pis'ma v ZhETF, vol.61, iss.4, pp.316 - 320 © 1995 February 25

ATOMIC MODEL FOR THE GROWTH OF ICOSAHEDRAL QUASICRYSTALS

V.E. Dmitrienko, S.B.Astaf'ev
A.V.Shubnikov Institute of Crystallography
117333 Moscow, Russia

Submitted 19 January, 1995

It is demonstrated how the binary alloys with 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.

Even ten years after the discovery of quasicrystals [1] their atomic origin is controversial. The modeling of quasicrystal structure and growth usually includes either projection from high-dimensional spaces [2] (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 some matching rules [4-6]. These two methods are very powerful and mutually related (see [5] where further references may be found). However, among those clusters only the 13-atom icosahedron seems to be reasonable from the atomistic point of view.

In this paper a growth algorithm is suggested which uses neither high-dimensional spaces nor ready-made clusters. Atoms are supposed to be spherical (without directional bonds); only the interatomic distances are specifically chosen. In the beginning, the growth model is postulated, then the physical and geometrical reasons for the model are presented and 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 composition (Al-Mn-Si [7], Al-Fe-Cu [8], Al-Pd-Mn [9]). Within the six-dim projection scheme, the same local ordering arises if the size of the acceptance domain is enlarged in comparison with the standard triacontahedron [10, 11]. The detailed discussion of the DLO in small and large approximants (including α-Al-Mn-Si and R-Al_5Li_3Cu 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:

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

Just the same distances occur in the CsCl-type crystals and, approximately, in the FeSi- and Hg-type crystals [12]. In Al-transition metal alloys, r_{LL} is a typical Al-Al distance (of about 2.9 Å) whereas r_{LS} may be attributed to Al-transition metal distances (of about 2.5 Å, the minimal distance in the model). These distances are simply related with 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 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; thus the golden mean τ, frequently found inside quasicrystalline structures, is really a consequence of equation 1. Unfortunately, wrong positions can also arise in this stacking: for instance, the regular tetrahedron of four L-atoms produces non-DLO positions. Such and other disruptions can cause amorphisation of DLO-structures. Therefore, at the moment it is not completely clear why the DLO occurs in the quasicrystalline and related structures. A possible clue to the clearance is that in our growth process every new atom is really fixed not by three old atoms but usually by 5–6 atoms; as a result, the non-DLO positions could 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 of the different atomic sizes. Further work is needed here and we believe that our paper should attract the researchers to this. Another difficulty is that in real structures the DLO is usually imperfect for many reasons [12]. Nevertheless, in the present model of quasicrystal growth the ideal DLO is supposed.

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 around 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 is supposed to be proportional to the number of neighboring atoms (that is, to 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, 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 already existing atoms, are excluded then the CsCl-type crystal grows. To suppress the crystalline structure we suppose that some interatomic distances, 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 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 also used for icosahedral clusters [6] but in the latter case the physical reason is not clear). Of course, in more sophisticated theory a realistic interatomic potential [14] should be used and the iii and iv stages should be considered simultaneously.

In the computer simulations we suppose that two distances, r^*_{LL} and r^*_{LS}, are forbidden: $r^*_{LL} = \sqrt{3}r_{LL}$ and $r^*_{LS} = \sqrt{11/3}r_{LS}$. Those 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 a 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 is only to demonstrate the idea.

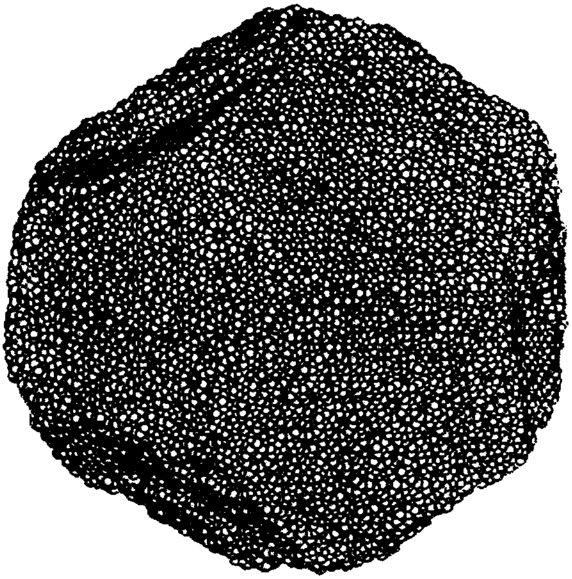

Fig.1.The views along a threefold axis on the quasicrystalline dodecahedral cluster (more than $2 \cdot 10^5$ atoms) grown from the outer shell of the Mackay icosahedron (42 atoms); the fivefold facets of the cluster are rather evident

An example of the grain, grown with our algorithm, is shown in Fig.1. Different initial clusters were examined: the piece of the FeSi-type crystal, the twelve-atom empty icosahedron, the outer shell of the Mackay icosahedron (30+12 atoms), *etc.* It seems that the coarse-grain structure and faceting of large grown clusters are almost independent on the initial cluster. The fivefold facets are well pronounced, therefore the clusters are distorted dodecahedra.

It is found that the average coordination numbers for different interatomic distances, $N(r)$, are similar to (and even larger than) those obtained for the Al−Cu−Fe quasicrystals from the 6-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 large fragments of the outer shells of the Mackay icosahedra can be found around many atoms.

The numbers 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 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 restores. The normalized intensities of reflections, $I(q)$, are calculated as $I(q) = |\sum f_k \exp(iqr_k)|^2/N^2$ where f_k and r_k are the atomic scattering factor and the

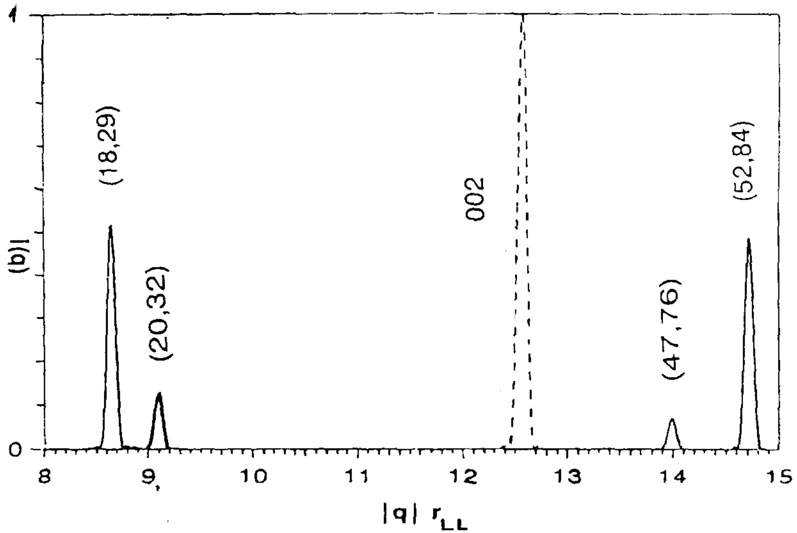

Fig.2. Simulation of the Bragg reflections from the cluster of about $4 \cdot 10^5$ atoms ($f_L = 1.3$, $f_S = 0.7$). Longitudial scans were made for the (20,32) and (52,84) peaks along all twofold axes and for the (18,29) and (47,76) peaks along all fivefold axes. The last peak vanishes if $f_L = f_S$.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

position of k-th atom, 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 slightly different widths of the reflections provide an evidence for phasonic disorder in the grown clusters. It was rather surprising that the widths of reflections are so small and comparable with the widths observed in real quasicrystals. We found that until $2 \cdot 10^6$ atoms the reflection widths decrease in accordance with the cluster size increasing; therefore it is not clear yet are there residual widths induced by the disorder when the cluster grows *ad infinitum.*

We conclude that simple growth algorithm can produce the clusters with the quasicrystalline ordering and with sharp diffraction peaks. Geometrically the suggested model is similar (with 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 the unified ordering and there is no need of "glue" atoms. The phasonic jumps along 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 the CsCl-type crystals and the icosahedral quasicrystals on the phase diagrams of many alloys. It is also intriguing that the dense-populated fivefold layers and distances between them in the grown clusters are very similar to the puckered and flat atomic layers observed in decagonal quasicrystals [15]; perhaps, similar growth algorithm may be used for the real three-dimensional decagonal quasicrystals and for their approximants.

We would like to thank L.Pauling for encouraging advice and A.A.Chernov, M.A.Fradkin, V.L.Indenbom and M.Kléman for critical discussions. This work was supported by the International Science Foundation (the emergency grant and the long-term grant N M5B000) and by Université Pierre et Marie Curie (Paris VI). The 486DX2/66 computer, donated by Alexander von Humboldt-Foundation, was used in the simulations.

1. D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
2. P.A.Kalugin, A.Yu.Kitaev and L.S.Levitov. Pis'ma Zh. Eksp. Teor. Fiz. **41**, 119 (1985); Engl. Transl.: JETP Lett. **41**, 145 (1985).
3. C. L. Henley, Phys. Rev. **B43**, 993 (1991).
4. P.W.Stephens, In Aperiodicity and Order. Vol. 3. Extended Icosahedral Structures (eds. M.Jaric, and D.Gratias) 37-104 (Academic Press, San Diego, 1989).
5. V.Elser, In Aperiodicity and Order. Vol. 3. Extended Icosahedral Structures (eds M.Jaric, and D.Gratias.) 105-136 (Academic Press, San Diego, 1989).
6. J.L.Robertson and S.C.Moss, Phys. Rev. Lett. **66**, 353 (1991); Z. Phys. B - Condensed Matter **83**, 391 (1991).
7. C.Janot, J.M.Dubois, J.Pannetier et al., in Quasicrystalline Materials (eds. Ch. Janot and J. M. Dubois) 107-125 (World Scientific, Singapore, 1988).
8. M. Cornier-Quiquandon, A.Quivy, S.Lefebre et al., Phys. Rev. **B44**, 2071 (1991).
9. M.Boudard, M. de Boissieu, C.Janot et al., J. Phys.: Condens. Matter **4**, 10149 (1992).
10. C.L.Henley, Phys. Rev. **B34**, 797 (1986).
11. M.Duneau and C.Oguey, J. Phys. France **50**, 135 (1989);
12. V.E.Dmitrienko, (a) J. Phys. France **51**, 2717 (1990); (b) JETP Lett. **55**, 391 (1992); (c) J. Non-Cryst. Solids **153&154**, 150-154 (1993); (d) Acta Cryst. **A50**, 515 (1994).
13. B.Minchau, K.Y.Szeto, and J.Villain, Phys. Rev. Lett. **58**, 1960 (1987); K.Y.Szeto and Z.M.Wang Phys. Rev. **B41**, 1347 (1990).
14. J.Hafner and M.Krajčí, Europhys. Lett. **13**, 335 (1990); J.Hafner and M.Krajčí, J. Non-Cryst. Solids **150**, 337 (1992); M.Krajčí and J.Hafner, Phys. Rev. **B46**, 10669 (1992).
15. V.E.Dmitrienko and V.G.Kamensky (in press).