

## Askhabov A.M. Cluster self-organization of a substance and its role in the formation of crystalline and non-crystalline materials

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Some crystal genetic, mineralogical, and material science consequences of the proposed theory of the cluster self-organization of substance on the nanolevel [1-3] are discussed.

A key suggestion of the new theory is an existence in non-equilibrium conditions of specific clusters of nonometer size, which follows from the formula for the energy of their formation

$$\Delta G = \frac{S\gamma_0}{3} \left( 1 - \frac{4\delta}{r} \right) \quad (1)$$

where  $S$  – surface area of a cluster,  $r$  – its radius,  $\gamma_0$  – specific surface energy on the flat boundary. Parameter  $\delta$  is an interphase thickness. Physically, it means a minimal distance, which can be established between the cluster atoms and surrounding media without formation of bonds between them. For inorganic compounds and minerals, the minimal  $\delta$  is usually varies from 0.22 to 0.36 nm. According to (1), a formation of clusters, whose radius is  $r \leq 4\delta$ , does not cause the energetic loss ( $\Delta G \leq 0$ ). Therefore, they can form spontaneously and exist in the crystal forming media (solutions, melts, etc.).

No suggestions on the nature of the forming clusters were made in deduction of (1). They are considered as a group of atoms and molecules connected by physical forces and chemical bonds. Such group can be transform into large molecule at the complete realization of valence, or into crystalline particle at three-dimensional ordering (atomic distribution by the rules of lattice). In this case, the potential centers for crystallization can be clusters, whose size is larger than  $4\delta$ . Clusters of smaller sizes can not be characterized as clusters of usual states of substance. They are interpreted as clusters of a "hidden phase" and called as quatarons, following to their characteristic quasi-spherical shape.

Conceptually, quatarons are a transition state of substance, which occurs in metastable state. This is a new form of atomic and molecular organization of substance on the nanolevel, which, however, does not have macroscopic analogies. Quatarons of sizes from  $r=\delta$  to  $r=4\delta$  are the basis for the formation of diverse forms of structural organization of substance on the nanolevel, from usual tetra- or octahedral complexes to well-known fullerenes, or dense dodecahedral or icosahedral clusters. In particular, the problem of the fullerene formation can be easily solved within the theory of the cluster self-organization of substance. Quatarons are clusters, precursors of fullerenes [4].

The most general approach to the geometrical interpretation of quatarons, suggested by us, can be summarized in terms of the Delone systems, or the  $(R, r)$  systems. A distribution of atoms in quatarons is not strongly fixed. However, atoms in such cluster can not move away from each other on significant distance (the distance  $R$  in the

Delone system) and approach to each other closer to some distance (the distance  $r$  in the Delone system). Thus, quatarons are finite portions of the Delone system, as well as crystalline nuclei are finite portions of infinite crystalline structure (regular systems). Crystals are known to be a particular case of the  $(R, r)$  systems. For their formation, the local regularity within the area, which is equal to sphere of radius  $4R$ , is necessary and sufficient (the local theorem) [5]. Since the parameter  $\delta$  (the thickness of the interphase region) is practically equal to the  $R$  distance in a cluster (the maximal distance, which can be achieved by atoms of the cluster, preserving the identity of the cluster), the value  $4\delta \approx 4R$  determines a region, in which the local regularity of the system is maximal. Then it occurs, the cluster turns to the crystalline nucleus. In this case, a probability of the cluster crystallization is very high. As the quataron radius becomes closer to  $4\delta$ , its structure becomes closer to the crystalline structure. Earlier or later, the dynamic and relatively flexible structure of the quataron will be trapped into the symmetrical "pitfall" of the crystal.

Evidently, if the significant part of substance in the crystal forming medium is connected to the above clusters, then they will participate in the crystal growth. Their attachment to the crystal is facilitated by their topological closeness to the structural modules of the crystal. The complete adaptation of the cluster structure to the crystal structure takes place on the growing face. As a result, a "two-dimensional" nucleus forms on the face, and this solves a problem of a source of a step during the layer-by-layer crystal growth. This is a general essence of the quataron mechanism of crystal growth. The theory of the cluster self-organization of substance can explain all fundamental regularities of crystal growth, i.e. kinetics of growth, outer morphology, formation of defects, entrapment of impurities. For the last process, the presence of impurities in endo- and exoquataron forms is significant.

The cluster particles in condensed state are able to form solid amorphous materials. Structural and textural features of such materials, evidently, depend on the nature, sizes, properties and the way of attachment of the condensed nanoparticles. The formation of a number of amorphous materials, from ordinary glasses to more or less ordered material, such as noble opal. Porous materials form at fractal orientation of the particles. As a result of accumulation of crystalline particles, nanocrystalline materials form. Probably, the formation of complex amorphous-crystalline materials is also possible. Especially, it is possible at precipitation of quatarons, whose size is close to the maximal ( $r=4\delta$ ), when some portion of them crystallizes, while another portion is amorphous. Sometimes, quatarons, fullerenes, or other cluster complexes in the condensed state are distributed by the rules of lattice, and we have objects of crystalline properties. For example, it is observed in fullerites-crystals composed of the clusters (fullerenes) of carbon. According to this principle, the term quatarite is proposed to describe ultra-disperse ordered materials with the discrete internal structure composed of separate quatarons or their aggregates. It is interesting that the amorphous quatarite compounds with some definite packing of the particles are able to form visually symmetrical objects of non-crystallographic form. An example of such objects for  $B_6O$  with icosahedral symmetry was described in [6]. Quatarons and their larger hierarchical structures provide conditions for the formation of di-

verse morphological forms of nonocrystals and non-crystalline nanoobjects [7]. Moreover, these ideas help to interpret the formation of aperiodical structures and quasicrystals as well.

Understanding of regularities of the formation of nonclusters in oversaturated (overcooled) media, their organization, and self-organization into nanostructures opens new ways to create materials with unique properties. There is a reliable basis to assume such properties in amorphous materials composed of clusters of radius  $2\delta$ , and nano-crystalline materials composed of particles (crystallites) of radius  $4\delta$ .

It should be noted in the conclusion, that according to the above features of structure and formation of non-crystalline materials, the term "mineral" can be expanded. As a result, a significant number of objects, which are considered as mineraloids, come under the mineral definition, and can be considered as new mineral types. Thus, minerals are not only natural objects (chemical compounds) of crystalline structure, but also x-ray amorphous solid compounds with organized structure (fullerites, quatarites, opals, etc.). In this sense, M.I. Novgorodova is right to consider fullerite as a new polymorphic modification of carbon, i.e. as a new mineral type.

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