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CURRENT STATUS AND PROSPECTS OF NANOSTRUCTURED THERMOELECTRIC MATERIALS

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- This paper analyzes peculiar to nanoobjects (quantum dots, quantum wires, etc.) imperfections that must be taken into account in the development of nanostructured material intended for use in microelectronics, thermoelectric converters of new generation, as well as in other fields of electronic engineering.

In a series of reports presented to previous ITA forums [1–3] and some international conferences [4–6] we tried to clarify the main difficulties encountered on the way to introduction of achievements of nanophysics and nanotechnologies in the development of thermoelectric converters of new generation based on nanoobjects. Under nanoobjects we meant nanoclusters, including quantum dots, quantum wires, thin and ultrathin layers, as well as heterostructures and superlattices created on their basis.

For practical applications in small-scale power engineering and other fields of technology it is preferable to use not isolated nanoobjects (like quantum dots or quantum wires), but their ensembles interacting in a certain array. Exactly these ensembles (together with the array) or superlattice will represent nanostructured materials suitable for practical applications.

Creating nanostructured materials based on nanoobjects, one should bear in mind that peculiar to nanoobjects defects and imperfections, naturally, will be transferred to the bulk of nanostructured materials. Therefore, we remind that the most typical (and practically nonremovable) imperfections of nanoobjects include:

- gigantic inhomogeneities both in chemical composition and internal mechanical stresses;
- principal absence of the long-range order, and two above-mentioned peculiarities of nanoobjects violate the constancy of interatomic distances in their bulk and, therefore, considerably deviate, if not exclude, translational symmetry in the bulk. These circumstances, in the general case, place the use of standard band theory, intended for description of kinetics of charge motion in nanoobjects, in special conditions. And ultimate small dimensions of nanoobjects ($\leq 1 - 2$ nm), comprising in their bulk not more than $10^1 \div 10^2$ atoms, make the use of standard band theory inadmissible;
- the fact of coexistence within a separate nanoobject of atoms with atomic interactions overlapping the entire range: from those typical of atoms being in the bulk of the crystal to typical of purely surface atoms;
- in thin layers of superlattices [7] and in case of other heterostructures [8, 9] the effective mass of current carriers m^* can differ considerably from that typical of the same substance in the form of a bulk crystal, and under certain conditions m^* also becomes coordinate-dependent, i.e. $m^* = m^*(\vec{r})$ [8];
- with a marked change in crystal potential at the distances of interatomic order the effective mass method becomes little substantiated, hence, little suitable for rigorous calculations [10].

As far back as 1990-s in experiments with nanoclusters of lead [11], and later on with the nanoclusters of other atoms [12], it was shown that they (i.e. nanoclusters comprising a very small number of atoms $\leq 10 - 20$) form a kind of dense packing that corresponds to minimum potential energy. With a larger number of atoms in nanoclusters, they demonstrate a rule known as “magic numbers” [13].

By example of studying fluorescent excitation spectra of separate atoms of krypton (*Kr*) and nanoclusters with different number of *Kr* atoms in their bulk, papers [13, 14] demonstrated exceptionally important role of interatomic interactions inside nanoclusters that cause structural rearrangement of nanoclusters depending on the number of particles they comprise, which serves as physical foundation for “magic numbers” effect.

Note two more specific features of nanoclusters that seem to be well known, but somehow have not attracted the attention of researchers they are worthy of. First of all, it is the shape of nanoclusters which, for simplicity, in many cases is taken to be spherical, though it is probably rarely the case. From Fig. 1, shown in paper [15] (and also discussed in paper [13]), it is seen that dependence of resonance cross-sections of absorption on E_{rad} for ellipsoidal Na_{11}^+ and spherical Na_9^+ clusters is qualitatively different. Therefore, studying such resonance, one can get information on the actual shape of nanocluster itself and, possibly, further information on its other properties. Of course, in the very recent past both home and foreign researchers in theoretical consideration of nanoclusters properties take into account their shape different from spherical – in the form of oblong and oblate ellipsoids, parallelepipeds, cylinders, etc.

However, all of them assume substance distribution and internal mechanical stresses in the bulk of these geometric figures of nanoclusters as homogeneous (at best consisting of two layers – the core and shell), which in actual practice (with regard to current nanoclusters manufacturing technique) cannot be realized.

Another interesting peculiarity of nanoclusters distinguishing them from the bulk crystals is a nonmonotonous change of magnetic moment (based on one nanocluster atom) with a reduced number of atoms in it, as was demonstrated by the authors of [16] by example of *Fe* nanocluster (Fig. 2 a) and, in addition to the above dependence, the appearance in nanocluster of a magnetic moment that is completely absent in the bulk ingot of the same material. The latter was convincingly shown by the authors of [17] by example of *Rh* nanocluster (Fig. 2 b).

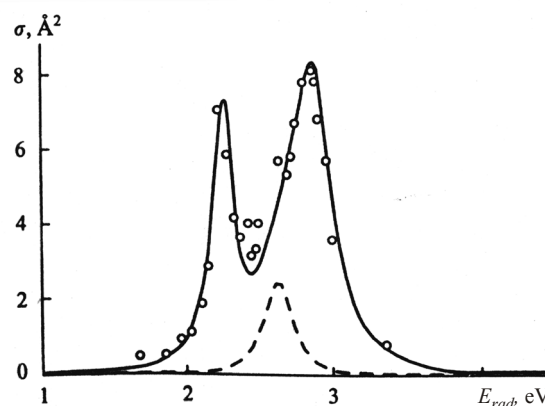


Fig. 1. Gigantic resonance for ellipsoidal Na_{11}^+ -clusters [15]. Lower energy peak corresponds to vibrations along the axis of ellipsoid, higher energy – to perpendicular vibrations. Dashed line corresponds to spherical Na_9^+ clusters.

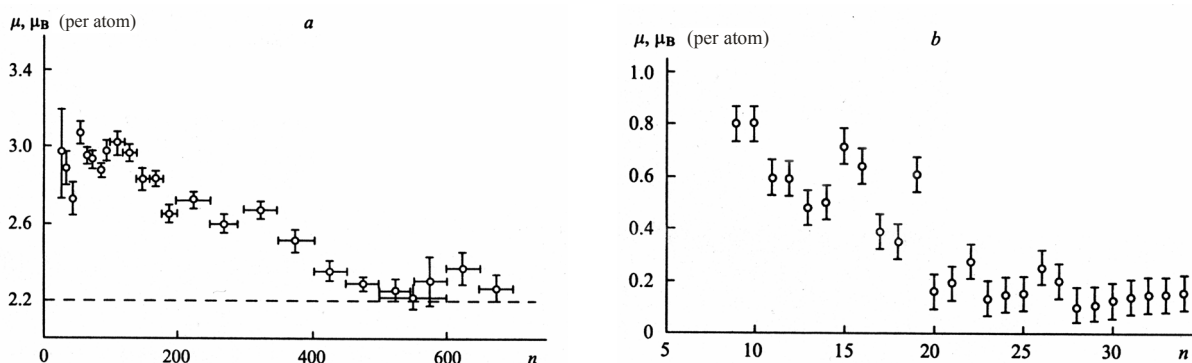


Fig. 2. Magnetic moments (based on atom) for clusters of *Fe* (a) [16] and *Rh* (b) [17] of different size. Dashed line corresponds to magnetic moment $\mu = 2.2 \mu_B$ of bulk *Fe*; n – the number of metal atoms in a cluster.

As long as the spectrum of defects introduced into an array of nanostructured materials with elementary nanoobjects (like quantum dots and quantum wires) can be only expanded due to intrinsic defects of the array and defects arising at its boundaries with nanoclustered inclusions, one should

dwell at least in brief on the defects peculiar to typical array and possible consequences of its interaction with conductive nanoinclusions. Moreover, the authors are inclined to think such consideration necessary due to the fact that nanoobjects have a well developed surface. This primarily accounts for their unusually high chemical activity. In view of the fact that semi-insulating (or isolating) array is actually a “supporting” component of nanostructured materials, considerations of the authors of [11] on the impossibility of all-round analysis of properties of nanoobjects without regard to their environment (array) are well founded.

Instead of considering the most typical defects of zeolite (or opal), we shall refer to the most popular in microelectronics isolating material SiO_2 that is quite capable of serving as an array surrounding nanoinclusions in created nanostructured materials. Intrinsic defects in SiO_2 can be divided into two classes. To the first class refer centres with oxygen vacancy (of the type $\equiv Si-Si \equiv$). To the second class refer nonbridge oxygen ($\equiv Si-O \bullet$) and $O-O$ complexes that can exist as a peroxide bridge ($\equiv Si-O-O-Si \equiv$), peroxide radical ($\equiv Si-O-O \bullet$) and even interstitial molecule O_2 . Oxygen-containing defects can localize charge carriers of both signs [18]. The structure $Si-SiO_2$ is characterized by the presence of mechanical stresses in it. It is primarily attributable to the difference (almost by an order) in linear expansion coefficients of respective materials (Si and SiO_2) with temperature. Besides, silicone oxide film is grown onto Si crystal at elevated temperature. On cooling, SiO_2 film becomes compressed, and the surface part of Si crystal - stretched [19]. A similar effect will also take place near the interface of SiO_2 array – nanoobjects embedded into its bulk (in the form of quantum dots or quantum wires), if these materials will have thermal expansion coefficients of different values. By means of analysis of TEM-images the authors of paper [20] discovered at SiO_2/Si interface an ultrathin (~ 1 nm) amorphous Si layer with compression strain ~ 2 GPa (i.e. $\sim 2 \cdot 10^4$ kgf/cm²).

Planning creation of nanostructured materials, for example, in the form of flat or bulk superlattices, suitable for application in various fields of technology, including creation of efficient thermoelectric converters, one should proceed from the fact that for such nanostructured materials typical (and basically nonremovable) is heterogeneity of its constituents, as well as extremely inhomogeneous distribution of internal mechanical stresses within each nanocluster inclusion or layer taken separately.

Taking into account the foregoing, one can formulate the most relevant problems related to developed nanotechnologies, namely:

1. Creation of quantum dots (and other nanoobjects) of given dimensions and shape, i.e. with a minimum spread in the above and other their related parameters.
2. Provision of high periodicity (ordering) level in arrangement of quantum dots (and other nanoobjects) on the plane or in the bulk of arrays.
3. Investigation of all forms of manifestation of gigantic inhomogeneities of quantum dots (and other nanoobjects) as regards structure, composition and internal mechanical stresses.
4. Detection and analysis of self-organization motives due to the necessity to improve the manufacturing technology of nanoobjects of different dimensions standardized in size and basic parameters.
5. It is not improbable that deep analysis of the results of studying self-organization processes of biomacromolecules can prove practically helpful for physicists searching for technologically perfect method for growing nanoobjects, standardized in size and shape and possessing other quite reproducible essential characteristics and properties.

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