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Influence of the size of iron nanoclusters on their magnetization

The size of iron nanocrystals significantly affects the value of their magnetization. However, an adequate model of the structure of nanocrystalline formations comprising different numbers of iron atoms still does not exist. In this work, spatial models of nanocrystalline iron clusters differing in configuration and the number of their constituent atoms are constructed. Tetrahedrally close-packed cluster assemblies of iron atoms are taken as the basis for the proposed structures of nanocrystals. The spectra of the density of electronic states for the proposed clusters are constructed using the theory of the electron density functional. The calculation was carried out by the method of scattered waves in accordance with the band theory of crystals. The appearance of magnetization in tetrahedral close-packed cluster formations is associated with excited electronic states of atoms located on the surface of the nanocluster. Excited atoms have an increased electron density, that is, electrons are able to transition to states with higher energy, approaching the Fermi energy. In this case, the Stoner criterion necessary for the occurrence of magnetization is fulfilled. The configurations of electrons with spin up and down differ, which is why uncompensated magnetic moments appear. It is shown that the proposed models of iron nanoclusters are in satisfactory agreement with the known experimental data.

Keywords: iron nanocluster, tetrahedrally tightly packed structures, magnetic properties.

Introduction

The nanocrystalline state changes not only the structure but also many physical characteristics of substances [1]. In [2], studies of the magnetic properties of cluster iron particles from different numbers of atoms are presented. It is shown that the ferromagnetic properties of iron clusters depend on the number of atoms in them. For clusters less than 50 atoms in size, the magnetic moments reach 3.1 Bohr magnetons. With an increase in the number of atoms to 500–700 atoms in the cluster, the magnetic moments approach the magnetization of bulk samples, which are 2.2 Bohr magnetons (Fig. 1).

The authors [3] found the presence of magnetization in cluster formations even in the absence of atoms of ferromagnetic substances in them. Hysteresis loops confirming magnetization were obtained for clusters CeO2, GaN, Al2O3, etc. Ferromagnetism is also observed in thin films of HfO2, TiO2, and ZnO [4, 5].

Cluster models are the most objective representation of the structure of metals with a small number of atoms [6]. In addition, structures corresponding to cluster structures also occur in the volume of metals, at interfaces, on fracture surfaces, etc. When modeling nanocluster formations, we use sets of dense tetrahedron packages that most adequately correspond to the nanocrystalline state [7].

The purpose of the work is to explain the nature of the increase in the magnetization of iron in nanocluster formations containing different numbers of atoms.

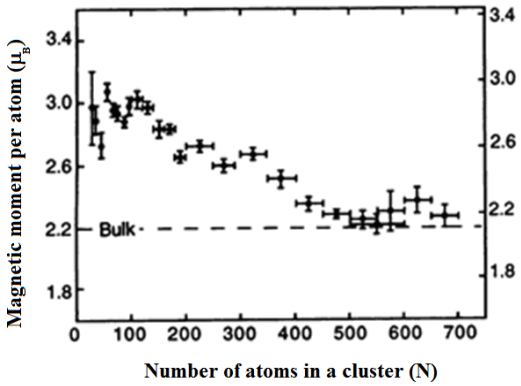


Figure 1. Dependence of the average magnetic moment per atom for iron clusters on the number of atoms in it at 120 K [2]

Tasks of the work:

1. Construction of three-dimensional cluster models of tetrahedral densely packed iron nanoclusters with different numbers of atoms.

2. Construction of density spectra of electronic states of nanoclusters under study.

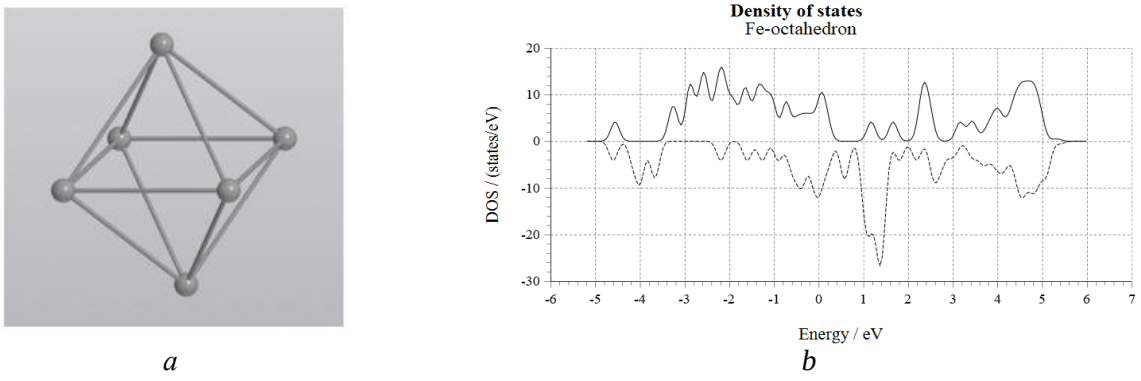
Experimental

To determine the coordinates of the atoms, spatial models of clusters were constructed using a three-dimensional modeling program. The program has the necessary tools to determine the coordinates of the atoms of the studied clusters. The cluster models were based on the theoretical values of the parameters of iron crystal lattices: a_{HCC} = 3.656 Å, a_{BCC} = 2.866 Å [8].

The electron state density spectra were constructed within the framework of the electron density functional theory (DFT) [9] using the basis of plane waves and ultra-soft pseudopotentials. The calculation was carried out using the scattered wave (SW) method in accordance with the band theory of crystals – an analogue of the Corringi-Cohn-Roxter method adapted for cluster models. The SW method is based on the formalism of multiple scattering of an electron wave on a system of potentials; it allows calculations for clusters of several atoms and large systems based on the coordinates of atomic nuclei. The interaction of electrons is described by the averaged values of periodic fields described by the MT potential [10]. The software package Quantum Espresso was used for the calculation [11].

Results and Discussion

In the first stage, a model of an octahedral cluster for iron, a face-centered modification of the crystal lattice, including six atoms was constructed (Fig. 2a). Next, a graph of the probability density of electronic states for this cluster was obtained (Fig. 2b).



a *b*

Figure 2. Octahedral cluster of fcc iron of six atoms: *a* – general view; *b* – dependence of the probability density of the distribution of electronic states on the energy of electrons with spin up and down

According to the spectrum data (Fig. 2b), it can be concluded that the electronic moments with dissimilar spins are uncompensated. The calculated average effective magnetic moment per atom was 1.67 μ_B/atom.

This result contradicts the data obtained for the magnetization of austenitic steels having a HCC lattice, which does not exhibit ferromagnetic properties for massive samples [8].

An octahedral cluster of six atoms can be transformed into a cluster formation consisting of densely packed tetrahedra. According to [12], an octahedron can be turned into three connected tetrahedra by switching one chemical bond between two of the six atoms (Fig. 3).

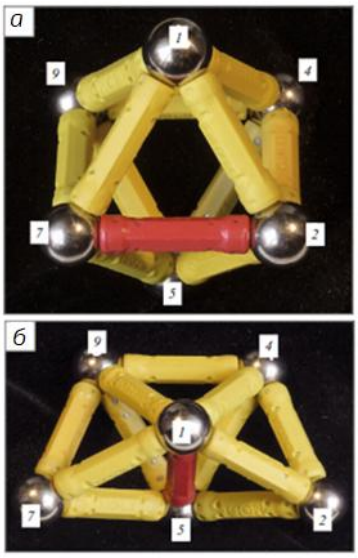
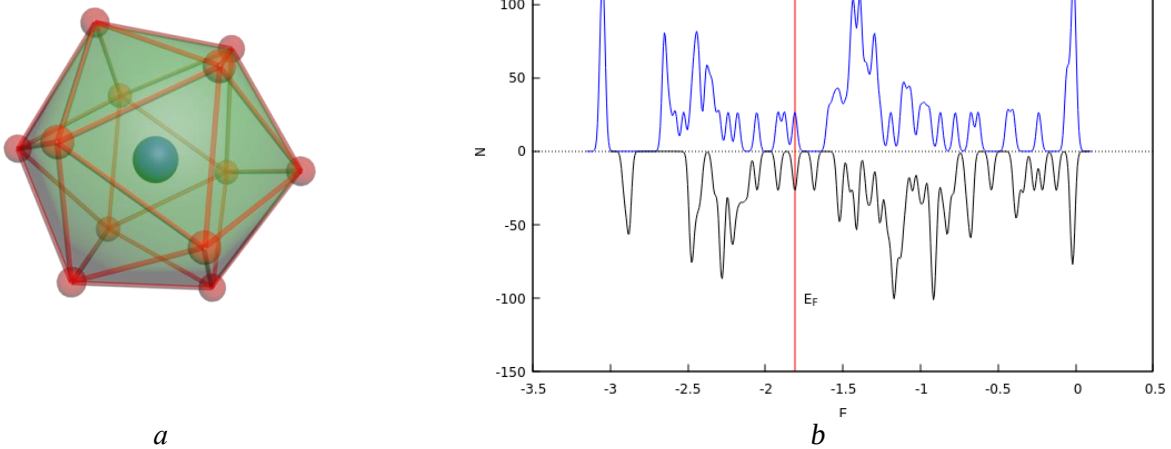


Figure 3. Transformation of nanoclusters: *a* – model of a hexagonal cluster;
b – model of a cluster of three tetrahedra [12]

Tetrahedral assemblies can be organized in different ways. The most famous example is the Frank-Kasper structure FK-12 [13], which corresponds to an icosahedron. Such an assembly can be constructed from twenty close-packed tetrahedra (Fig. 4a).



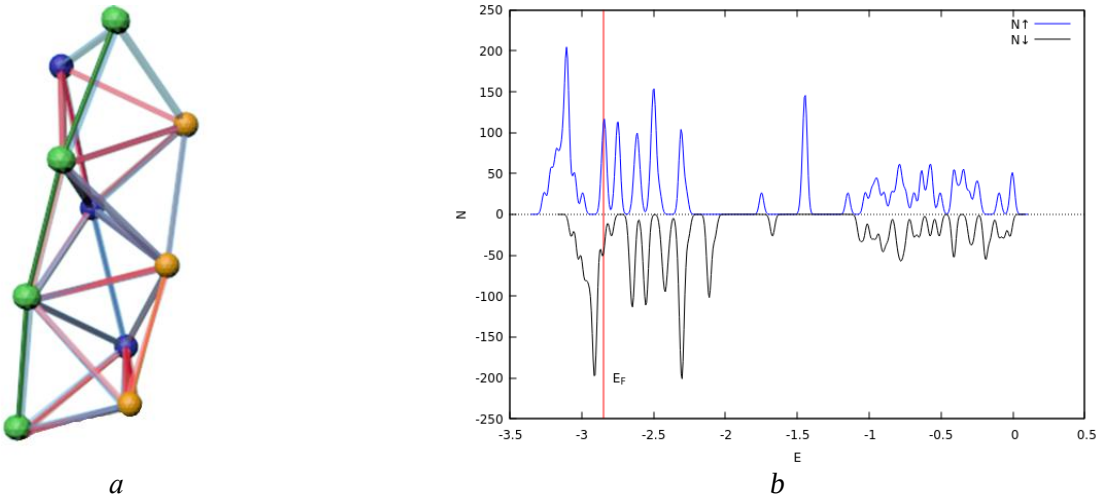
a *b*

Figure 4. Icosahedral iron cluster of 13 atoms: *a* – general view;
b – dependence of the probability density of the distribution of electronic states on
the energy of electrons with spin up and down; the red line corresponds to the Fermi energy

The calculation of the density of the electronic states of the icosahedral cluster (Fig. 4b) showed that the average magnetic moment is 0.21 μ_B/atom.

The FK-12 structure, along with FK-14, appears in Gadfield steel (110G13L) during plastic deformation on the deformation or fracture surface. Gadfield steel is also austenitic, however, exhibits nonzero magnetization under mechanical action [14].

There are various possibilities for packing tetrahedra in a nanocluster. Thus, the appearance of a cluster in the form of a tetrahedral spiral for compounds Ni_4Ti_3, Al_4C_3, and others was shown in [12, 15, 16]. The formation of such a structure is associated with the possibility of the transition of an octahedral cluster into a group of three tetrahedral (see Figure 3). Figure 5a shows a nanocrystalline iron cluster, which is a spiral of seven tetrahedra. For such a tetrahedral assembly, a spin-polarized density of electronic states is constructed (Fig. 5, b), the average magnetic moment per atom was 0.26 μ_B/atom.



a *b*

Figure 5. Spiral iron cluster, composed of seven tetrahedra: *a* – general view; *b* – dependence of the probability density of the distribution of electronic states on the energy of electrons with spin up and down

When constructing further coordination spheres (Fig. 6) using tetrahedral clusters, the number of atoms on the surface increases exponentially. The central atom in the center is common to all spirals. The first row of tetrahedra is located on the top and has 12 generalized atoms on the surface. The second row has 20 atoms on the surface, the third has 32 atoms, the fourth has 52 atoms, etc. (Fig. 6). However, according to the Delaunay rule [6], it is impossible to realize in three-dimensional space a densely packed structure of an icosahedron containing over 2 coordination spheres.

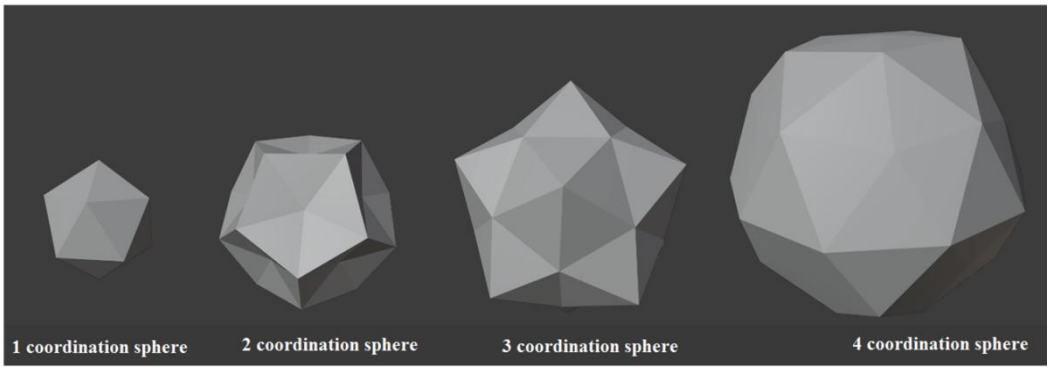
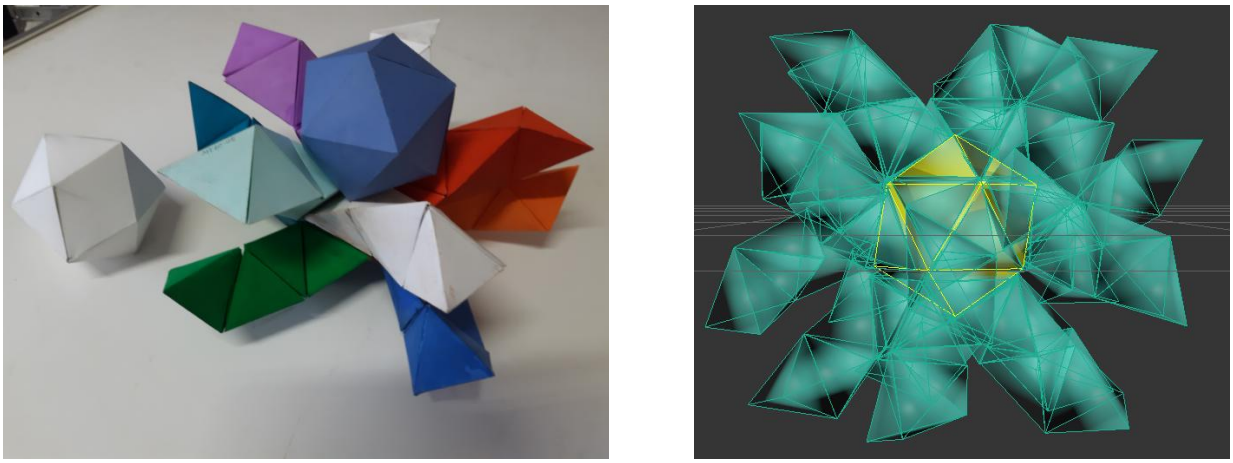


Figure 6. Evolution of coordination spheres from tetrahedral clusters: from the first to the fourth

The next stage of the simulation was a combination of a spiral and an icosahedral cluster. When twenty tetrahedral spirals are tightly packed (Fig. 7), an icosahedron containing 13 atoms is formed in the first coordination sphere. There are 20 atoms in the 2nd coordination sphere. Here, the first 3 tetrahedra from each of the 20 spirals are connected in concert. Further, each spiral grows independently in the direction from the center perpendicular to the faces of the icosahedron of the 1st coordination sphere. Each spiral has 10 atoms, six of which are packed in 3 tetrahedra located in 2 coordination spheres. The remaining 4 atoms of each spiral are packed into "tails" of 4 tetrahedra. The total number of atoms in such positions is $4 \times 20 = 80$. Thus, the total number of atoms in a cluster packed with 20 tetrahedral spirals is $33 + 80 = 113$ atoms (Fig. 6).



a *b*

Figure 7. Combination of icosahedral and spiral iron clusters:
a – incomplete paper model; *b* – three-dimensional computer model

Figure 7 presents a structure built of twenty tetrahedral ten-atom spirals with one common atom in the center. In the second coordination sphere, an icosahedron is also formed, containing twenty atoms. This gives 33 atoms in total in the first and second coordination spheres. This structure corresponds to the experimentally obtained result with the maximum magnetization shown in Figure 1.

Conclusions

The appearance of magnetization in cluster formations is associated with the excited electronic states of those atoms that are on the surface of a nanoparticle or nanofilm. Stressed nonequilibrium electronic states arise in such systems. For cluster models of small sizes, most of the atoms are on the surface and have open bonds. Excited atoms have an increased electron density, that is, electrons are able to transition to states with higher energy, approaching the Fermi energy. In this case, the Stoner condition is satisfied, which is necessary for the occurrence of magnetization [17]. The configurations of electrons with spin up and down are different, which gives rise to uncompensated magnetic moments. Thus, the proposed models of iron nanoclusters are in satisfactory agreement with the experimental data of [1].

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Темір нанокластары мөлшеріне олардың магниттелуінің әсері

Нанокристалдардың мөлшері олардың магниттелу мөлшеріне айтарлықтай әсер етеді. Алайда, әр түрлі темір атомдарынан тұратын нанокристалды түзілімдер құрылымының барабар моделі әлі жоқ. Мақалада конфигурация мен оларды құрайтын атомдардың саны бойынша ерекшеленетін нанокристалды темір кластерлерінің кеңістіктік модельдері жасалған. Нанокристалдардың ұсынылған құрылымдарының негізі темір атомдарының тетраэдрлік тығыз оралған кластерлік жинақтары болып табылады. Ұсынылған кластерлер үшін электронды күй тығыздығының спектрлері электронды тығыздық функционалды теориясын қолдана отырып жасалған. Есептеу кристалдардың аймақтық теориясына сәйкес шашыраңқы толқындар әдісімен жүргізілді. Тетраэдрлік тығыз оралған кластерлік түзілімдерде магниттелудің пайда болуы нанокластың бетінде орналасқан атомдардың қозған электронды күйлерімен байланысты екендігі көрсетілген. Қозған атомдардың электронды тығыздығы жоғарылайды, яғни электрондар Ферми энергиясына жақындаған жоғары энергияға ие күйге ауыса алады. Бұл жағдайда магниттелудің пайда болуы үшін қажет тас өлшемі орындалады. Айналдыру жоғары және төмен электрондардың конфигурациясы әр түрлі, сондықтан өтелмеген магниттік моменттер пайда болады. Ұсынылған темір нанокластарының модельдері белгілі тәжірибелік мәліметтерге қанағаттанарлық түрде сәйкес келетіні көрсетілген.

Кілт сөздер: темір нанокластері, тетраэдрлік тығыз оралған құрылымдар, магниттік қасиеттері.

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Влияние размера нанокластеров железа на их намагниченность

Размер нанокристаллов железа существенно влияет на величину их намагниченности. Однако адекватной модели структуры нанокристаллических образований, состоящих из разного числа атомов железа, до сих пор не существует. В статье построены пространственные модели нанокристаллических кластеров железа, различающихся конфигурацией и количеством составляющих их атомов. За основу предлагаемых структур нанокристаллов взяты тетраэдрически плотно упакованные кластерные сборки атомов железа. Спектры плотности электронных состояний для предлагаемых кластеров построены с использованием теории функционала электронной плотности. Расчет проводился методом рассеянных волн в соответствии с зонной теорией кристаллов. Показано, что появление намагниченности в тетраэдрических плотноупакованных кластерных образованиях связано с возбужденными электронными состояниями атомов, расположенных на поверхности нанокластера. Возбужденные атомы имеют повышенную электронную плотность, то есть электроны способны переходить в состояния с более высокой энергией, приближающейся к энергии Ферми. В этом случае выполняется критерий Стоунера, необходимый для возникновения намагниченности. Конфигурации электронов со спином вверх и вниз различаются, поэтому возникают некомпенсированные магнитные моменты. Показано, что пред-

ложенные модели нанокластеров железа удовлетворительно согласуются с известными экспериментальными данными.

Ключевые слова: нанокластер железа, тетраэдрически плотно упакованные структуры, магнитные свойства.

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