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Effect of thermal annealing on phase transformations and ordering of the magnetic texture of Fe_3O_4/Nd_2O_3 nanocomposites

Abstract. The paper presents the results of a study of the effect of thermal annealing on the phase transformations and subsequent ordering of the magnetic texture and superfine magnetic parameters in Fe_3O_4/Nd_2O_3 nanocomposites obtained by chemical deposition and subsequent mechanochemical synthesis. X-ray phase analysis and Mössbauer spectroscopy were used to characterize the properties of the obtained Fe_3O_4/Nd_2O_3 nanocomposites. Thermal annealing was carried out in an oxygen-containing medium in the temperature range of 400°C – 1000°C for 5 hours followed by cooling for 24 hours until reaching room temperature. The phase transformation dynamics of $Fe_2O_3/NdFeO_3 \rightarrow NdFeO_3 >> Fe_2O_3 \rightarrow NdFeO_3$ type was established using X-ray phase analysis. According to the data of Mössbauer spectroscopy it was established that the domination of the $NdFeO_3$ phase in the nanocomposite structure at annealing temperatures above 800°C leads to an ordering of the magnetic texture and an increase in the value of the superfine magnetic field to 502.8 kE, approaching the values characteristic of the Fe_2O_3 structure (513 kE).
Key words: magnetic nanocomposites, thermal annealing, structural ordering, Mössbauer spectroscopy, phase transformaitons.

Introduction

One of the important conditions for the practical application of magnetic nanocomposites or nanoparticles as the basis for magnetic sensors, catalysts for the decomposition of organic dyes, or purification of aqueous media from heavy metals is knowledge of the ultrafine magnetic parameters and their correlation between the degree of structural ordering, phase composition, and magnetic characteristics [1-5]. In most cases, the magnetic properties of nanocomposites are strongly dependent on the phase composition, as well as on the presence of disordered regions in the structure related to the processes of particle formation during synthesis. As a rule, the formation of nanostructures proceeds due to non-equilibrium processes and is accompanied by the formation of metastable states, leading to distortion and deformation of the crystal lattice [4-7]. As a result, these deformations lead to the formation of vacancy defects, or voids, in the structure, which negatively affect the domain structure and superfine parameters. Dopants, which are used to modify and enhance the performance of the investigated composites, also play an important role in the magnetic properties of nanocomposites, especially of complex compositions. The introduction of dopant into the structure may be accompanied by partial substitution of atoms in the lattice nodes, thereby deforming not only the crystal structure, but also changing the magnetic properties and the nearest environment of the atoms [8,9]. As a rule, doping or substitution of atoms occurs during the formation of nanocomposites, including the initiation of phase transformations processes as a result of external influence, one of which is thermal annealing at increased temperatures [10-12].

During thermal annealing, the main effect of changing the properties of materials is associated with a change in the value of thermal vibrations of atoms, which leads to an increase in their mobility and the possibility of filling the voids formed during synthesis with free atoms, which in turn leads to both ordering and the formation of new phases. Moreover, thermal annealing has a great influence on the change in the stoichiometric ratio of the elements at high temperatures, which is associated with a partial displacement of oxygen from the structure, which leads to an increase in the contributions of metals to the stoichiometry of nanocomposites. Therefore, in spite of the large number of scientific works and previous studies in this direction, there are still many unresolved questions in this direction related to the study of the effect of structural features and phase composition [13-20] changing as a result of thermal annealing in the Fe_3O_4/Nd_2O_3-based nanocomposites, the interest in which is due to their great potential for application as photocatalysts, absorbents for water purification and biomedical applications, including hyperthermia [15-20].

The aim of this work is to establish the correlation between the degree of structural ordering and phase transformations in Fe_3O_4/Nd_2O_3 nanocomposites with the parameters of the superfine magnetic structure as well as the value of the superfine magnetic field.

Experimental part

The synthesis of Fe_3O_4/Nd_2O_3 nanocomposites was conducted in two stages. The first stage included chemical precipitation of Fe_3O_4 nanoparticles from iron chloride solutions followed by reduction in the form of chemical precipitate, purification from impurities by washing and drying. The second stage consists of mechanochemical mixing of Fe_3O_4 nanoparticles obtained by chemical precipitation with Nd_2O_3 nanoparticles. The mechanochemical synthesis was carried out using a PULVERISETTE 6 planetary mill (Fritsch, Germany), with a grinding speed of 400 rpm and grinding time of 1 hour. For mixing, Fe_3O_4 and Nd_2O_3 were used in a 1:1 ratio. The resulting mixture was removed from the stirring cup made of tungsten carbide and placed in sealed flasks to avoid oxidation processes.

Thermal annealing was chosen to initiate the processes of phase transformations in the synthesized structures, since according to the X-ray phase analysis in the initial state the obtained mixture is an amorphous-like structures without a pronounced crystalline phase. Thermal isochronous annealing was carried out in a SNOL muffle furnace (SNOL, Russia) in the temperature range of 400-1000°C for 5 hours followed by cooling the samples together with the furnace for 24 hours until reaching room temperature. The choice of the temperature range is due to the processes of phase transformations initiated in this range, which makes it possible to study them in more detail.

The phase composition of the investigated Fe_3O_4/Nd_2O_3 nanocomposites was studied by X-ray phase analysis realized on an X-ray diffractometer D8 Advance Eco (Bruker, Germany). Diffractograms were taken in Bragg-Brentano geometry, in the angular range of 2θ=25-75°. The diffractograms were interpreted using the Diffrac EVA v.4.2 software code.

The superfine magnetic field parameters of synthesized Fe_3O_4/Nd_2O_3 nanocomposites were studied by Mössbauer spectroscopy. The measurements were carried out on a MS1104Em spectrometer (Rostov-on-Don, Russia). A ^{57}Co source in the Rh matrix was used as a gamma ray source. Mössbauer spectra were taken at room temperature. Decoding was performed using the SpectrRelax software code.

Results and discussion

For the dynamics of phase transformations in Fe_3O_4/Nd_2O_3 nanocomposites as a function of thermal annealing temperature, the X-ray phase analysis method was applied to determine the phase composition of the investigated structures. The change in phase composition reflects the processes of phase transformations as well as the mechanisms accompanying the change in the properties of the materials depending on the conditions of external influences. The results are presented as a series of diffractograms of the studied Fe_3O_4/Nd_2O_3 nanocomposites in Figure 1. The general view of the obtained diffractograms reflects not only the change in the phase composition of the studied structures, but also the processes associated with the deformation and ordering of the crystal structure depending on the annealing temperature. At an annealing temperature of 400°C two phases were observed in the structure of nanocomposites: Fe_2O_3 with a rhombohedral lattice type and $NdFeO_3$ with an orthorhombic lattice type. The ratio of these phases in the structure is close to the ratio of 1:1. However, the analysis of the shape of the lines indicates a strong disorder of the crystal structure, as well as its unformed and the presence of a large number of amorphous inclusions in the structure. The presence of the Fe_2O_3 phase in the nanocomposite structure is characteristic for phase transformations of the $Fe_3O_4 \rightarrow Fe_2O_3$ type occurring at sintering temperatures above 300°C. At the same time in the temperature range of 300-500°C this phase is strongly disordered due to the incompleteness of the phase formation processes. The presence of the $NdFeO_3$ phase in the structure of nanocomposites is due to the processes of mechanochemical synthesis and subsequent thermal annealing, leading to a partial replacement of iron ions by neodymium ions in the nodes of the crystal lattice, due to the presence of Nd_2O_3 in the structure.

Increasing the annealing temperature to 600°C leads to an increase in the contribution of the $NdFeO_3$ phase in the structure, which indicates the processes of substitution and partial displacement of the Fe_2O_3 phase. In this case, the $Fe_2O_3/NdFeO_3$ phase ratio according to the X-ray phase analysis is 35/65 with $NdFeO_3$ dominance. It can also be noted that thermal annealing leads to an increase in the contribution of structural ordering expressed in a change in the shape of diffraction lines and a decrease in their asymmetry, which indicates ordering and a decrease in strain stresses. This ordering is due to the processes of thermal annealing of point defects and filling of vacancies, as well as a change in the ratio of phases in the composite under study, which indicates an ordering of the structure.

At a temperature of 800°C the process of phase transformations of the type $NdFeO_3 \gg Fe_2O_3 \rightarrow NdFeO_3$ ends with the complete dominance of the $NdFeO_3$ phase and the displacement of the Fe_2O_3 phase. Meanwhile, changes in the shape of the diffraction lines, indicating ordering of the structure, are also observed. This process is due to the fact that for magnetic nanoparticles based on iron oxide, at temperatures above 600°C the processes of phase transformations stop, and further change in annealing temperature leads only to structural ordering accompanied by enlargement of particle size and change in their geometry. In this connection, the presented results of X-ray diffraction of the studied samples at 1000°C indicate ordering processes, and are expressed in clear symmetric diffraction reflexes, characteristic of highly ordered crystal structures.

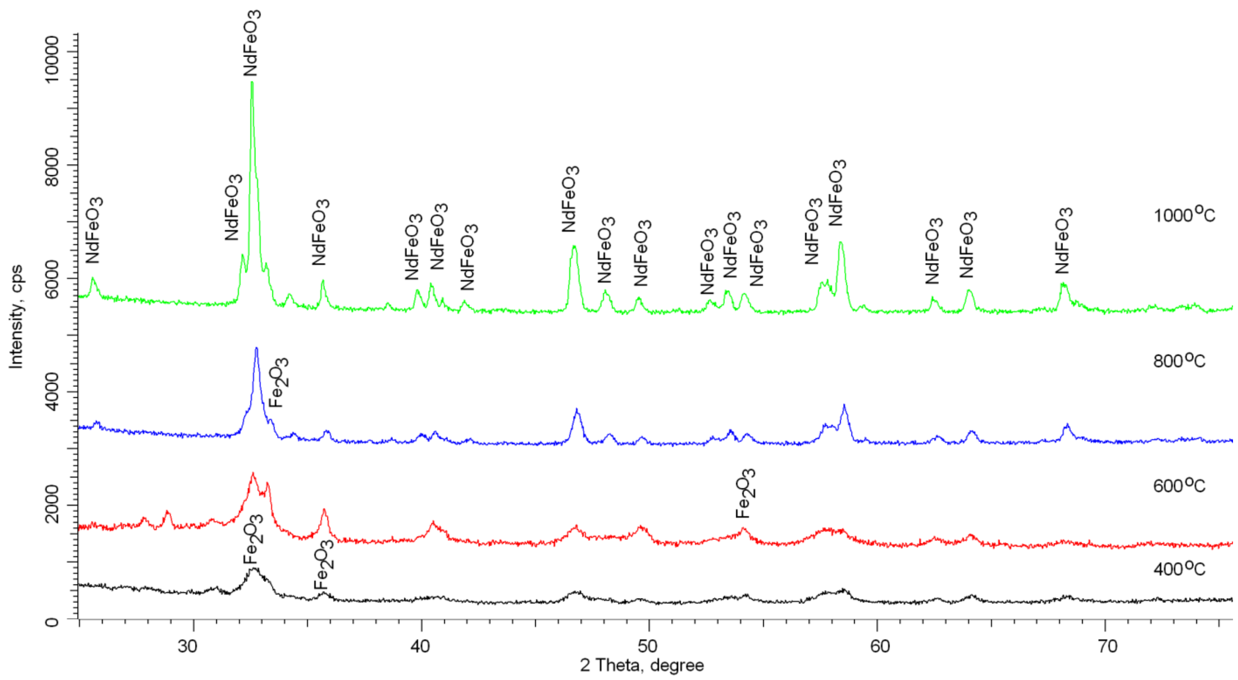

Figure 1 – Dynamics of X-ray diffractograms of the studied Fe_3O_4/Nd_2O_3 nanocomposites.

Figure 2 shows the results of measuring Mössbauer spectra of the studied Fe_3O_4/Nd_2O_3 nanocomposites obtained by mechanochemical synthesis by grinding the initial components in the ratio 1:1 and subsequent thermal isochronous annealing in the temperature range of 400-1000°C for 5 hours. According to the general concepts, the obtained spectra can be characterized by the presence of a quadrupole doublet, characteristic of the disordered structure, and a Zeeman sextet, characterizing the magnetically ordered component of nanocomposites.

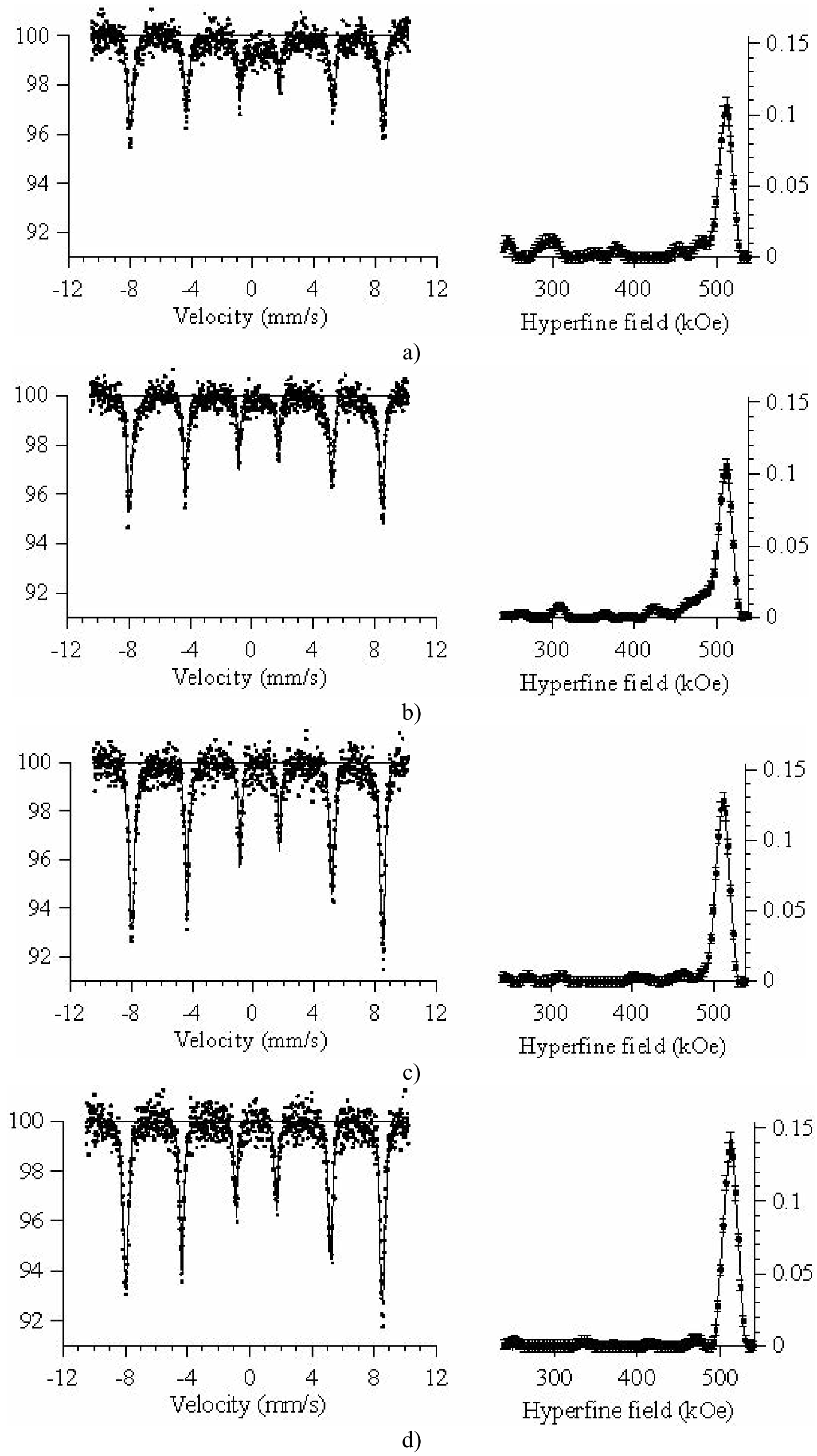

Figure 2 – Mössbauer spectroscopy results of the samples annealed at different temperatures: (a) 400°C; (b) 600°C; (c) 800°C; (d) 1000°C.

The general appearance of the obtained spectra depending on the annealing temperature is characterized by two types of changes. The first type is characterized by changes in the intensities of the partial spectra lines characteristic of the doublet and sextet, which indicates changes in the intensities of the contributions characteristic of the ordered and disordered magnetic structure in nanocomposites. This behavior is caused by a change in the concentration of point defects in the structure due to their partial annealing and subsequent annihilation, which leads to an ordering of the structure. Figure 3 shows the results of changes in the contribution intensities for the doublet and sextet as a function of the annealing temperature of the nanocomposites.

As can be seen from the presented data, an increase in the annealing temperature of nanocomposites leads to an increase in the contribution of the zeeman sextet characteristic of an ordered magnetic structure, while at temperatures above 800°C a complete displacement of the quadrupole doublet is observed, which indicates structure ordering, and the absence of disordered areas related to amorphization or destruction of samples. The second type of changes is associated with changes in the shape and width of spectral lines, indicating ordering of the superfine magnetic parameters with increasing structural ordering of the synthesized composites. The decrease in the contribution from the quadrupole doublet characteristic of the disordered regions confirms the results of the X-ray phase analysis of the investigated samples.

Figure 4 shows the results of the relationship between the magnitude of structural ordering according to X-ray diffraction data and the ratio of intensities *($1-I_{doublet}/I_{sextet}$)*, which characterizes the degree of magnetic ordering in the structure.

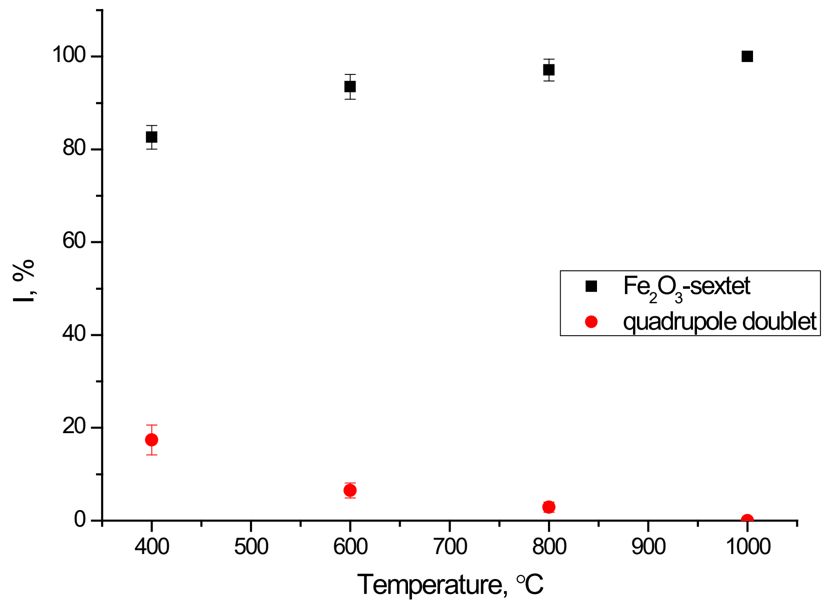

Figure 3 – Change of the ratio of Zeeman sextet and quadrupole doublet intensities.

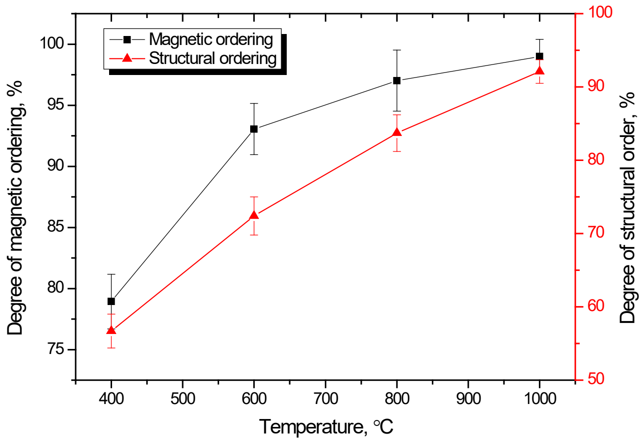

Figure 4 – Results of changes in the values of structural and magnetic ordering.

As can be seen from the presented data, an increase in the annealing temperature leads to structural and magnetic ordering by a similar mechanism, consisting in the fact that a decrease in the defect fraction in the structure due to substitution processes and subsequent formation of the $NdFeO_3$ phase leads to an increase in the degree of crystallinity and a decrease in amorphous inclusions in the structure. In turn, the reduction of the contribution in the Mössbauer spectra of the quadrupole doublet, which is characteristic of the paramagnetic state of the substance, indicates an ordering of the magnetic texture, as well as a change in the value characteristic of the superfine magnetic field. Figure 5 shows the results of the relationship between the change in the value of the structural ordering of the crystal lattice of the phases under study and the value of the superfine magnetic field characteristic of the Zeeman sextet.

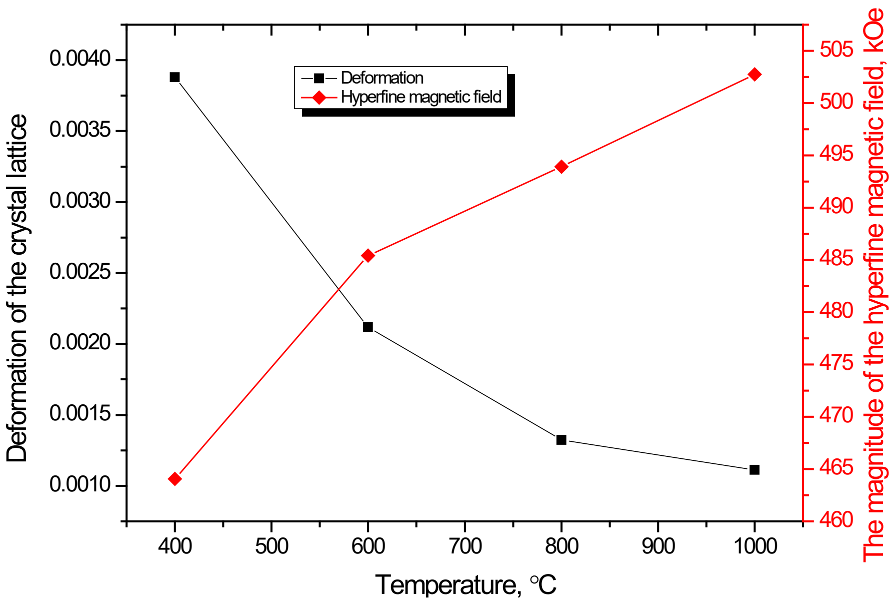

Figure 5 – Results of crystal lattice deformation and superfine magnetic field values.

From the data presented in Figure 5 it can be seen that the decrease in the lattice deformation is more pronounced in the temperature range 400-800°C, which is characteristic of the phase ordering and displacement of the Fe_2O_3 phase and the subsequent dominance of the $NdFeO_3$ phase. Meanwhile, in the temperature range of 800-1000°C the deformation contribution reduction is insignificant, which indicates the reduction of the deformation contribution in the structure, as well as the completion of the phase transformations and subsequent transformations. At the same time, the change in the phase composition of nanocomposites leads to an increase in the value of the superfine magnetic field, which also indicates the ordering of the magnetic textures of samples.

Conclusion

This article is devoted to the study of the correlation between structural and magnetic ordering as a result of phase transformations in Fe_3O_4/Nd_2O_3 nanocomposites initiated by thermal annealing in the temperature range 400-1000°C. With the method of X-ray phase analysis the dynamics of phase transformations of the type $Fe_2O_3/NdFeO_3$ → $NdFeO_3$ >>Fe_2O_3→ $NdFeO_3$ was established. The kinetics of the contributions change for the Zeeman sextet, which is typical of the structurally ordered magnetic phase, and the quadrupole doublet corresponding to the disordered regions and amorphous inclusions in the structure of Fe_3O_4/Nd_2O_3 nanocomposites have been established as a result of the investigations. It was determined that the quadrupole doublet contribution is completely displaced at annealing temperatures above 800°C, which corresponds to the ordering of the crystal structure and superfine magnetic parameters.

Further research will be aimed at studying the corrosion resistance of the synthesized nanostructures in order to determine their resistance to external influences.

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