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Modelling the structure of homogeneous $Co_{80}Cu_{20}$ nanowires from nuclear magnetic resonance data

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A three-dimensional model of copper clusters in homogeneous $Co_{80}Cu_{20}$ nanowires was proposed, which allowed us to interpret the experimental ^{59}Co nuclear magnetic resonance (NMR) spectra. The nuclear magnetic resonance data show that in $Co_{80}Cu_{20}$ nanowires, copper atoms tend to cluster in the cobalt volume, the cluster size is estimated to be 30 atoms. Modeling of experimental NMR spectra showed that in homogeneous nanowires with the composition of $Co_{80}Cu_{20}$ copper clusters with extended shape are formed.

Keywords: nanowires, interfaces, ^{59}Co NMR, modeling, roughness.

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1. Introduction

Nanowires (NW) i.e. one-dimensional nanostructures with special magnetic properties have attracted considerable interest in recent years. Their uniqueness is attributable to their small size (nanoscale magnetism) and strong shape anisotropy. A popular method for obtaining such structures is matrix synthesis — electrochemical filling of pores with various metals in a template i.e. a special matrix. There are two main types of matrices: track membranes [1] and porous aluminum oxide [2]. The parameters of the nanowires are determined by the matrix, the growth conditions and the composition of the growth electrolyte. Matrix synthesis allows a wide range of variations in both composition and geometric properties (density of placement, direction of growth, diameter). The development of nanowires was consistent: nanowires made of one metal, homogeneous nanowires from an alloy of two or more metals, heterogeneous nanowires, consisting of alternating layers of different metals.

There are a number of works devoted to the synthesis and study of layered nanowires with alternating layers of 3d metals (cobalt, nickel, iron) and non-magnetic copper. For instance, [3] describes the preparation of nanowires from alternating layers of cobalt and copper with an observed effect of giant magnetoresistance was observed, the value of which was approximately 15%. Heterogeneous Co/Cu nanowires with a diameter of 50−200 nm, with different thicknesses of cobalt layers were studied in Ref. [4]. It was found that the magnetic properties (magnetoresistance, the process of magnetization reversal) of nanowires change when the ratio of their thickness and diameter changes. The authors of [5] studied nanowires with alternating layers of cobalt or iron with copper. It was shown that, just as in two-dimensional layered systems, the magnetic properties depend on the thickness of the non-magnetic layer. The use of layered nanowires made of two different metals for generating electromagnetic radiation of terahertz frequency was proposed in [6]. Due to the demand for the practical application of low-dimensional systems, as well as technical and fundamental interest, local study methods are required due to the physically small geometric dimensions of these objects.

One of the effective methods for studying nanowires is Mossbauer spectroscopy, which allows estimating the magnitude of the magnetic field on the core and its change with varying local core environment and magnetization. Homogeneous wires from FeNi and FeCo alloys were studied in [7] using this method. The impact of the growth voltage (i.e., the growth rate) and nanowire diameters on the spectrum parameters was determined and the correlation of the latter with X-ray diffraction data was shown. Another popular method of studying the local structure of an object is the nuclear magnetic resonance (NMR) method. The NMR method has already been previously used [8–10] to study the structure of nanowires. Homogeneous nanowires made of pure cobalt, alloy of $Co_{85}Cu_{15}$, heterogeneous Co/Cu nanowires, with nominal layer thicknesses of 10 nm, length 6 μm, pore diameter of 50 nm, polycarbonate membrane were studied in [8]. The authors showed a redistribution of the intensities of resonance lines corresponding to the FCC and HCP phases of cobalt in homogeneous nanowires made of pure cobalt. The ratio of the intensities of resonance lines from ^{59}Co nuclei was estimated and it was shown that the FCC phase prevails in homogeneous nanowires made of $Co_{85}Cu_{15}$ alloy, and it was concluded that copper clusters in the volume of cobalt are formed in these wires.

Polycarbonate membranes with a thickness of 6 μm (pore diameter 50 nm) and anodized aluminum oxide with a

thickness of 60 μm (pore diameter 200 nm) were used in the article [9]. The effect of the pore diameter and the presence of organic additives on the crystal structure of nanowires is shown: the ratio of cobalt in the phases of HCP and FCC.

A method for three-dimensional modeling of copper clusters on an atomic scale is proposed in this paper for the interpretation of experimental NMR spectra for determining the structure of homogeneous cobalt-containing nanowires.

2. Specimens and experimental methods

Nanowires for the preparation of which template matrices made of polyethylene terephthalate film were used are studied in this work. Film thickness 10 μm, pore diameter 100 nm, surface pore density — $1.2 \cdot 10^{-9}$ pores at cm^2. The films were prepared by electroplating.

Recording of NMR spectra on ^{59}Co nuclei in the absence of an external magnetic field was performed using an upgraded pulsed phase-coherent NMR spectrometer SXP 4100 manufactured by „Bruker". NMR spectra were recorded by frequency sweeping in the frequency ranges 130–260 MHz. The spectra were recorded at a temperature of liquid helium (4.2 K) in a local magnetic field — there was no external magnetic field. The spin echo signal was formed by a sequence of two coherent radio frequency pulses $\tau_{\text{pulse},x} - \tau_{\text{del}} - 2\ \tau_{\text{pulse},y} t_{\text{del}} - echo$ (modified Khan pulse sequence), creating an alternating magnetic field in a resonant coil with a sample with an amplitude of a circular component $H_1 \approx 10$ Oe. The pulse duration τ_{pulse} was 0.7 μs, the time interval τ_{del} between pulses was 13 μs. The frequency change was approximately 1 MHz. To eliminate distortion of the spectra due to interference effects and transients in the resonant circuit, a sequence with phase alternation of RF pulses was used. To increase the signal-to-noise ratio, multiple signal accumulation was carried out. The amplitude of the RF excitation pulse was controlled by maintaining a constant 50 Ohm signal amplitude induced on the antenna over the entire frequency range.

3. Modeling and discussion

Figure 1 shows the NMR spectrum of nanowires made of pure cobalt. The line I_{FCC} at a frequency of 218 MHz occurs from cobalt atoms in the FCC phase. The line I_{HCP} at a frequency of 226 MHz corresponds to cobalt atoms in the phase with a hexagonal close-packed crystal structure (HCP). The predominance of the FCC phase is probably attributable to the fact that significant tensile stresses arise with the rapid growth of nanowires [11]. An alternative reason may be a change of the acidity of the solution, which may also affect the formation of a certain type of crystal lattice: FCC or HCP [12]. A low intensity line at a frequency of about 200 MHz probably occurs due to impurities in the synthesis process.

Figure 2 shows the NMR spectrum of $Co_{80}Cu_{20}$ nanowires. The resonance line I_{FCC} dominates in nanowires with a composition of $Co_{80}Cu_{20}$, which can be attributed to the fact that the joint deposition of cobalt and copper, which has a HCC structure, results in the deposition of cobalt with a predominantly cubic structure. The copper-induced FCC structure of cobalt was also observed in Co/Cu superlattices [13]. It can be seen on the nuclear magnetic resonance spectra of $Co_{80}Cu_{20}$ nanowires that a low-frequency region of the spectrum is formed up to the frequency of 155MHz: resonance lines I_1, I_2, I_3 at frequencies of 200, 182, 164 MHz, respectively. These lines correspond to cobalt atoms in the FCC lattice, which have 1–3 copper atoms in coordination [14].

Let's evaluate the distribution of copper atoms in cobalt. Let's construct a binomial distribution of the types of the closest environment of the probe nucleus in $Co_{1-x}Cu_x$ nanowires ($x = 5,\ 10,\ 20,\ 40,\ 60$) for this purpose and compare with the experimentally determined distribution of the types of the immediate environment in $Co_{80}Cu_{20}$ nanowires (Figure 3).

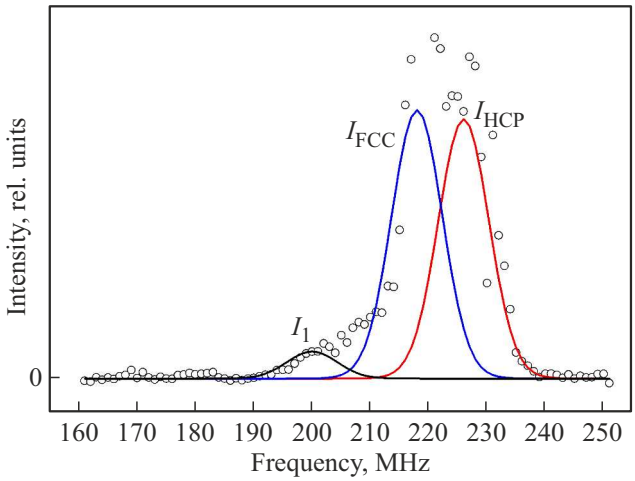

Figure 1. The NMR spectrum of nanowires made of pure cobalt.

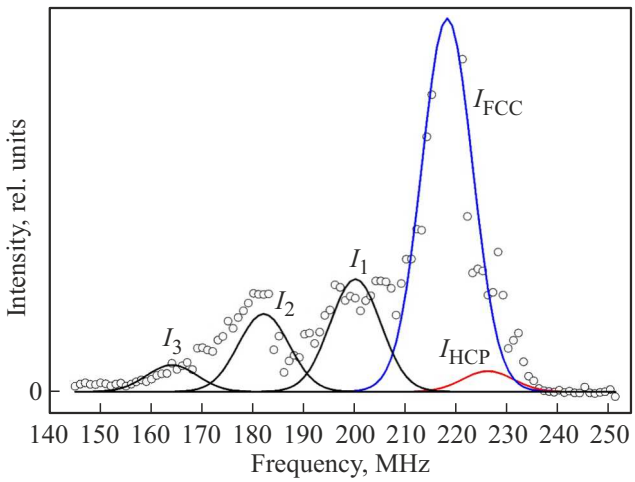

Figure 2. NMR spectrum of nanowires $Co_{80}Cu_{20}$.

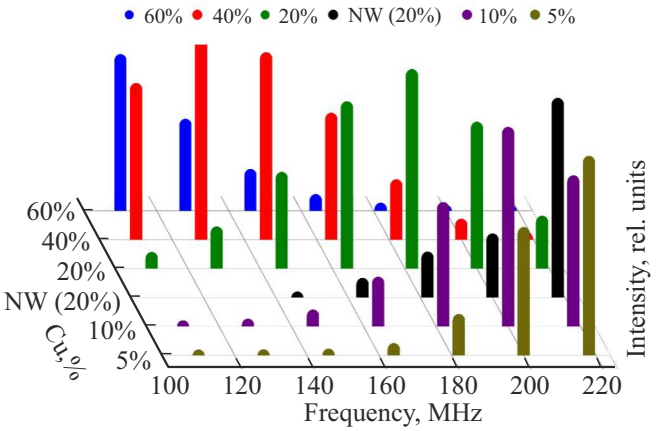

Figure 3. Binomial distribution of probe nucleus coordination types of ^{59}Co in nanowires $Co_{1-x}Cu_x$ ($x = 5$, 10, 20, 40, 60) and experimental NMR data of nanowires of $Co_{80}Cu_{20}$.

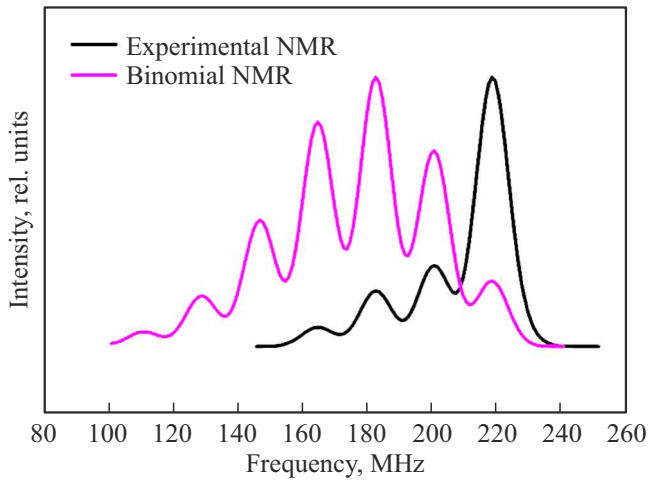

Figure 4. The model NMR spectrum for the binomial distribution of the types of coordination of ^{59}Co atoms in nanowires of $Co_{80}Cu_{20}$ and the experimental NMR spectrum of nanowires of $Co_{80}Cu_{20}$.

Figure 3 shows that the resonance line of the highest intensity is shifted to the low frequency region with an increase of x.

Let's simulate the NMR spectrum of $Co_{80}Cu_{20}$ nanowires where the configurations of the ^{59}Co nearest environment are described by a binomial distribution and compare it with the experimental NMR spectrum of $Co_{80}Cu_{20}$ (Figure 4).

Figure 4 shows a radical difference of the simulated and experimental spectra. The placement of copper atoms in the cobalt volume, in the case of nanowires Co–Cu, is not described by a statistical distribution as shown in [15]. The intensity of the resonance lines is proportional to the number of cobalt atoms with different coordination: without copper atoms, 1–3 copper atoms. Then the ratio $I_{FCC}/(I_1 + I_2 + I_3) \approx 1.84$ characterizes the actual fraction of cobalt atoms without copper in the first coordination sphere.

Let's assume for a theoretical assessment of the nature of the mutual arrangement of copper atoms that copper atoms are evenly distributed among cobalt atoms in the volume of the matrix (nanowires). Based on this, we assume that the number $N(k)$ of Co atoms with neighboring k Cu atoms can be estimated from the binomial distribution law [15]. Since the number of atoms in the first coordination sphere in the case of the FCC crystal structure is 12, then

$$N(k) = \left(\frac{12}{k}\right) x^k (1-x)^{12-k}, \qquad (1)$$

where x — the volume concentration of copper in the nanowire.

Taking into account that $x = 0.2$ in the studied nanowires, we obtain a ratio

$$N(I_{FCC})/((N(1) + N(2)) \approx 0.14,$$

that is significantly less than the ratio obtained from the experiment

$$I_{FCC}/(I_1 + I_2 + I_3) = 1.84.$$

Such a significant discrepancy may indicate an uneven distribution of copper atoms. Apparently, copper is deposited in the form of clusters in the studied nanowires. The model

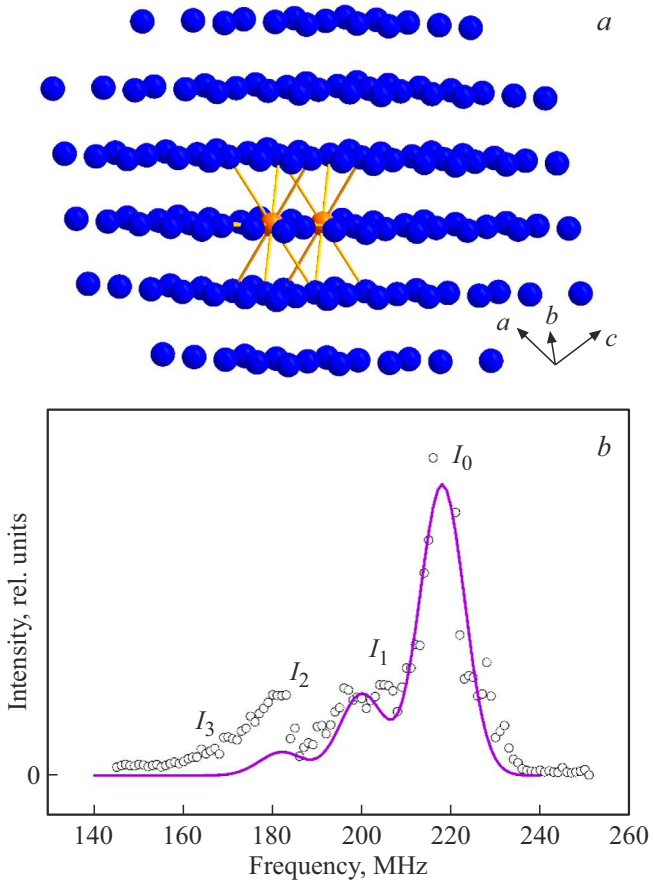

Figure 5. Placement of two copper atoms in the volume of cobalt (a). The result of modeling of the NMR spectrum, in case of placement of two copper atoms in the volume of cobalt (b).

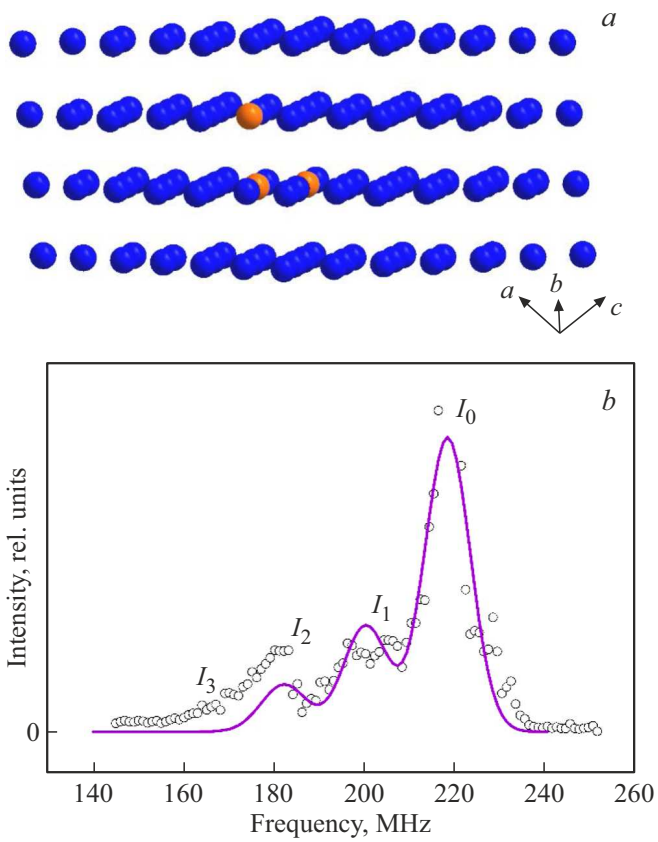

Figure 6. Placement of three copper atoms in the volume of cobalt (a). The result of modeling of the NMR spectrum in case of placement of three copper atoms in one atomic layer in the volume of cobalt (b).

proposed by the authors of [8] was used to estimate the average size of such a cluster with a side of L and a volume of L^3. It is assumed that copper clusters are cubic and consist of L^3 atoms, there are $N(k)$ Co atoms for each cluster, which have k neighbors of copper atoms, then

$$N(k) = \frac{x}{1-x}\frac{n(k)}{L^3}, \quad k = 1,\ 2,\ 4, \tag{2}$$

$$N(0) = 1 - [N(1) + N(2) + N(4)], \tag{3}$$

where x — the concentration of copper in nanowires. Using $x = 20\%$ and the ratio $I_{\mathrm{FCC}}/(I_1 + I_2) = 1.84$, we obtain that the average size of a Cu cluster with a volume of L_3 is approximately 30 atoms.

It should be noted that the formation of Cu clusters in two-component nanowires has been observed before: for example, Cu–Ni nanowires were studied in Ref. [16] and the formation of individual phases (clusters) of copper or copper oxide with a size of 5–20 nm was detected by transmission electron microscopy.

Let's perform a three-dimensional simulation of a copper cluster in the volume of cobalt. Let's take a certain volume of cobalt atoms and sequentially simulate the different placement of copper atoms in this volume. We will not consider in detail the first step that is the introduction of one copper atom, since such an introduction forms only 12 cobalt atoms with one copper atom in the coordination, which will result in a trivial form of the NMR spectrum. The visualization of the structure of nanowires with two copper atoms in the volume of cobalt and the simulated NMR spectrum, respectively, is shown in Figure 5, a and b.

It can be seen from the above figures that the presented introduction of two cobalt atoms into the copper layer provides a satisfactory coincidence of the model and experimental NMR spectra. Let's continue the development of the model by adding a third copper atom to the atomic layer, where two copper atoms are already placed (Figure 6, a) and compare the model NMR spectrum with the experimental NMR spectrum (Figure 6, b).

The obtained NMR spectrum as a result of the simulation has a better match with the experimental NMR spectrum. According to the cluster size estimate, we will construct a copper cluster consisting of 30 atoms (Figure 7, a) and a model NMR spectrum corresponding to this cluster (Figure 7, b).

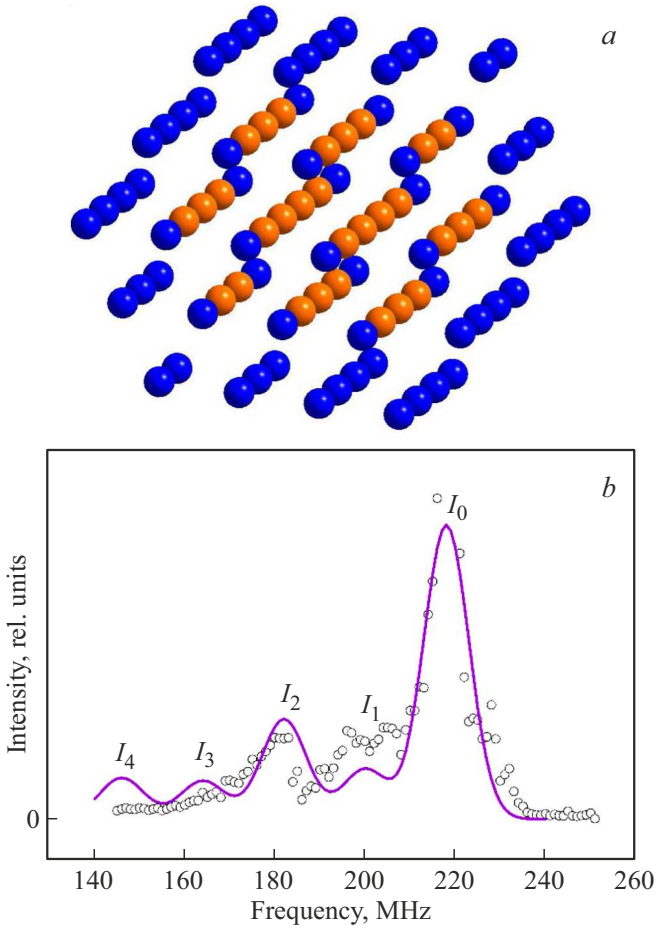

Figure 7. A copper cluster in the volume of cobalt, 30 atoms (a). The result of modeling of the NMR spectrum of a copper cluster in a cobalt volume (b).

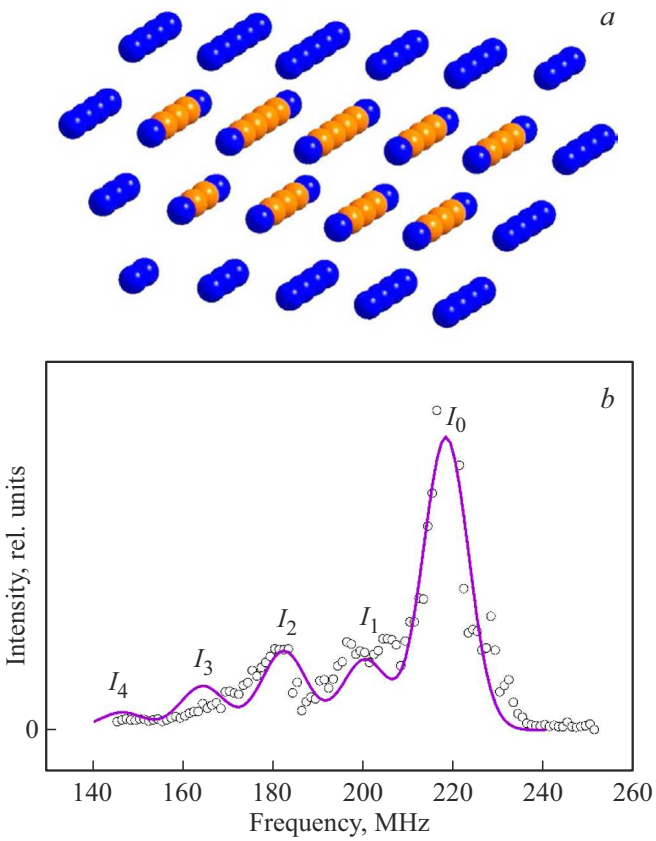

Figure 8. A copper cluster in the volume of cobalt, 28 atoms (*a*). The result of modeling of the NMR spectrum of a copper cluster in a cobalt volume (*b*).

We will make the cluster thinner, which will reduce the number of cobalt atoms with four copper atoms in the coordination. An increase of the area and a decrease of the volume of the cluster (Figure 8, *a*) with the same agglomeration allows increasing the proportion of cobalt atoms with one copper atom in the coordination (Figure 8, *b*).

The correspondence of the model and experimental NMR spectra can be considered excellent. Therefore, the model NMR spectra were constructed using three-dimensional modeling of the structure of homogeneous $Co_{80}Cu_{20}$ nanowires which allowed for interpreting the experimental NMR spectra: the placement of copper atoms in the volume of cobalt is not described by a statistical distribution in homogeneous $Co_{80}Cu_{20}$ nanowires as clusters of copper with an extended shape are formed in the volume of cobalt.

4. Conclusion

1. It was shown that the HCC phase dominates in case of the transition from homogeneous nanowires made of pure cobalt to homogeneous nanowires with $Co_{80}Cu_{20}$ composition prepared by electrodeposition, and a low-frequency spectral region is formed up to the frequency of 155 MHz, meaning the existence of copper atoms with 1–3 copper atoms in the immediate environment.

2. It was shown that the placement of copper atoms in the cobalt volume is not described by a statistical distribution in the case of the studied nanowires, and copper atoms are prone to clustering. The assessment of the agglomeration of copper clusters based on nuclear magnetic resonance data showed that the clusters consist of about 30 atoms.

3. A three-dimensional model of a copper cluster in the volume of cobalt homogeneous nanowires is proposed, which allows constructing model nuclear magnetic resonance spectra for the interpretation of experimental NMR spectra.

4. It was shown by using three-dimensional modeling that it is necessary to maximize the area and minimize the volume of copper clusters for describing experimental nuclear magnetic resonance spectra— they should have an extended shape.

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Conflict of interest

The authors declare that they have no conflict of interest.

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