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Structure of interfaces in heterogeneous cobalt-containing nanowires from NMR data

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Three-dimensional modeling of the interface structure of heterogeneous cobalt-containing nanowires has been performed. The detailed structure of copper−cobalt embedding at the cobalt-copper interface in Co/Cu layer nanowires was constructed using nuclear magnetic resonance data. The evaluation of the state of the interfaces showed that the thickness of the interfaces in the studied heterogeneous nanowires is not less than 0.8 nm (four atomic layers).

Keywords: nanostructures, interlayer boundaries, spectroscopy, modeling.

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1. Introduction

In recent years, one-dimensional structures — ferromagnetic nanowires having unique physical properties are subject of active studies [1–5]. The magnetic nanowires are applied in devices of magnetic recording and spin electronics and sensors [6]. Currently one of the effective methods of such nanostructures manufacturing is method of matrix synthesis [7–9]. There are two main types of matrices: porous aluminum oxide [10,11] and polymer track membranes [12,13]. The nanowire parameters are determined by the type of used matrix, manufacturing mode, electrolyte composition [14,15]. Nanowires passed several stages of development: nanowires comprising one metal; nanowires comprising alloy of several metals (homogeneous); and layered nanowires, being alternating layers of different metals (heterogeneous).

Currently in reading heads of hard drives the spin valves with effect of giant magnetoresistance (GMR), discovered by Firth and Grunberg in 1988 are used [16]. GMR effect means change in electric resistance under applied external magnetic field. For the first time GMR effect was observed in multilayer structures comprising alternating layers of magnetic and nonmagnetic metals. Electrical resistance change of these structures is due to spin-depending scattering of electrons on interfaces (interlayer boundaries) [4]. As the interfaces of layered nanowires have nanosize scales, use of local study methods is necessary.

One of the effective local methods is method of nuclear magnetic-resonance (NMR). Earlier NMR method was applied to study structure of homogeneous (single- and two-component) and heterogeneous cobalt-containing nanowires [13,17,18]. Mainly, analysis of experimental spectra of NMR of cobalt-containing nanowires provides information on presence and ratio α- and β-modifications of cobalt — HCP and FCC crystal lattices, respectively.

In present paper a 3D model of interfaces of heterogeneous nanowires Co/Cu is proposed in atomic scale, ensuring interpretation of NMR experimental spectra on ^{59}Co based on distribution of ultrathin fields in interface region of nanowires.

2. Specimens and experimental methods

The nanowires under study are product of electrical deposition in template matrices of polyethylene terephthalate film 10 μm thick and with diameter of pores 100 nm, surface density of pores — $1.2 \cdot 10^{-9}$ pores per cm^2.

NMR spectra on nuclei ^{59}Co are recorded in zero external magnetic field using modernized pulse phase coherent spectrometer „Bruker“ SXP 4100. Spectra were registered by method of sweeping over frequency in range 250−140 MHz. The spectra were registered at temperature 4.2 K in local magnetic field. Signal of spin echo is formed by sequence of two coherent radio frequency (RF) pulses (modified Khan pulse sequence):

$$\tau_{\text{pulse,x}} \rightarrow \tau_{\text{delay}} \rightarrow 2\tau_{\text{pulse,y}} \rightarrow \tau_{\text{delay}} \rightarrow \text{echo}.$$

To register NMR signal from nuclei ^{59}Co in nanowires the metering coil of flat solenoid type, Figure 1, was manufactured. The above described sequence of RF pulses created in coil with sample an alternating magnetic field with amplitude of the circular component H_1 about 12 Oe. Pulse width was 0.7 μs, delay between pulses — 13 μs, spectrum was registered with frequency interval 1 MHz. To eliminate distortion of the spectra due to interference effects and transients in the resonance circuit, a sequence with phase alternation of RF pulses was used. The amplitude

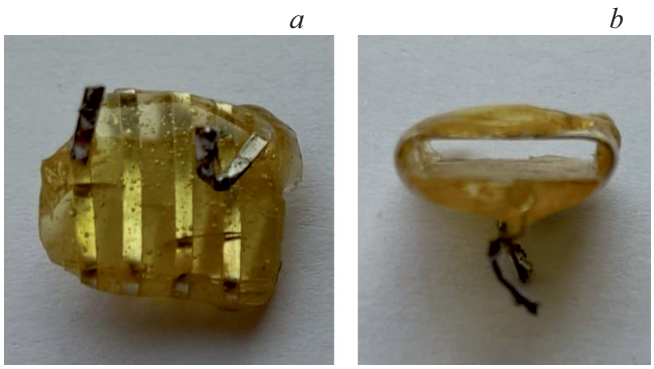

Figure 1. Metering coil to register NMR signal from nuclei ^{59}Co for nanowires: *a*) plan view; *b*) side view.

of the RF excitation pulse was controlled by maintaining a constant signal amplitude induced on the antenna 50 Ω over the entire frequency range.

3. Results and discussion

As it was stated in the Introduction, one of the important objective when studying layered nanowires is determination of the interfaces structure. In 2D structures of superlattice type different approaches were suggested to model interlayer boundaries: 2D presentation of monolayer interstitials with length l and distance d between them [19], development of previous model considering concentration profiles of several atomic layers [20]. The latest paper mentions the difficulty of modeling the detailed structure of interfaces. Due to this in [20] it is supposed that accidental distribution of atoms of cobalt and copper in mixed layers.

In present article we suggested to make detail structure of interfaces using 3D modeling based on information about the local magnetic fields distribution, this information is obtained from the NMR experimental spectra. Essence of NMR method use means: as result of ultrathin interaction on nuclei ^{59}Co the local magnetic fields are induced, their value and direction are determined by the magnetic structural features of nearest environment of nucleus-probe. Using NMR method it is possible to determine the nature of distribution of these local magnetic fields in systems under study. The design induction of ultrathin field is 22.8 T [21], experimental value is 21.6 T for β-modification of cobalt. It is known, that one cobalt atom replacement by copper atom in the nearest environment of the nucleus-probe results in decrease in resonance frequency by 16–18 MHz. This dependence of resonance frequency on composition of the nearest environment can be described by the following expression:

$$H_{hf} \approx H_{hf}^{b} - \Delta H_{hf}^{1}(n^{b} - n^{1}), \qquad (1)$$

where H_{hf}^{b} — ultrathin field in bulk material, n^{b} — coordination number in bulk material, shift ΔH_{hf}^{1} (-1.8 T — -1.6 T [19]), n_1 — number of cobalt atoms in nearest environment. Note that in multilayer nanostructures with copper layers asymmetric interfaces are expected [22].

Figure 2 shows experimental NMR spectrum of heterogeneous nanowires with layers thickness 30 nm. We can see the resonance line of maximum intensity I_0, corresponding to β-modification of cobalt — FCC-lattice. Absence of resonance line at frequency about 226 MHz means absence of α-modification of cobalt in nanowires under study. Besides, this Figure shows position of resonance lines I_j, where j — number of cobalt atoms replaced by copper atoms in coordination of selected cobalt atom. I. e. line I_1 corresponds to cobalt atoms in the coordination of which one cobalt atom is replaced by a copper atom, I_2 — cobalt atoms, where in nearest environment two cobalt atoms are replaced by copper atoms, etc. resonance frequencies for different types of environment are determined by the expression (1), and are about 200, 182, 164 MHz for lines I_1, I_2, I_3 respectively. Earlier [23] using electronic microscopy it was shown that these nanowires have layered structure. The performed X-ray diffraction studies showed that nanowires under study had no texture. Also consider that in multilayer nanostructures with copper layers asymmetric interfaces are expected [22]. Based on this data we make 3D modeling of interfaces structure in heterogeneous nanowires Co/Cu. Let's consider interlayer boundary supposing texture (111), where interstitial if copper atoms in cobalt layers have shape of pyramid (Figure 3, *a*), and corresponding to such interstitial design NMR spectrum (Figure 3, *b*).

Upon copper interstitial into cobalt in form of pyramid on the design NMR spectrum the excessive intensity of line I_4 is observed. This is due to the close atoms arrangement in the first atomic layer of cobalt. interstitial with depth of two atomic layers (chain) decreases area of contact between interstitial and interface — Figure 4, *a*, corresponding design spectrum — Figure 4, *b*.

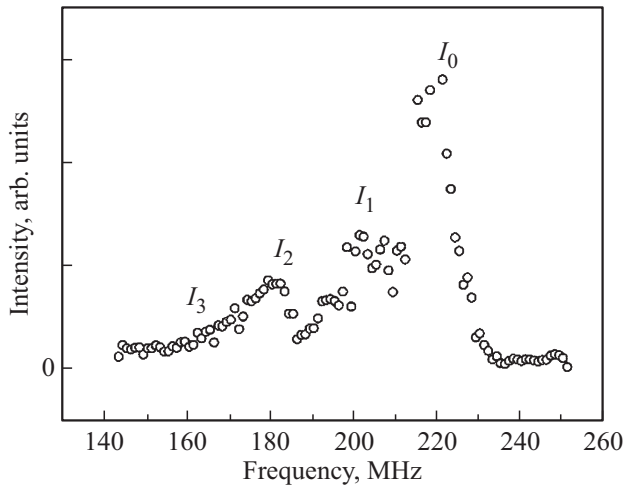

Figure 2. Experimental NMR spectrum of heterogeneous nanowires with layers thickness 30 nm.

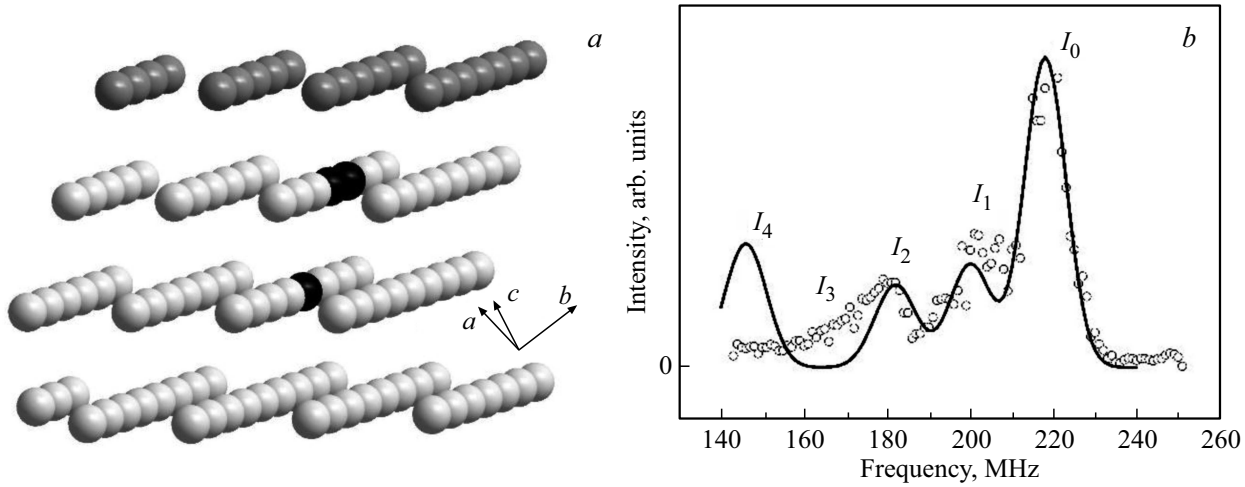

Figure 3. *a*) Interface of nanowires Co/Cu, interstitial in form of pyramid; *b*) design NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

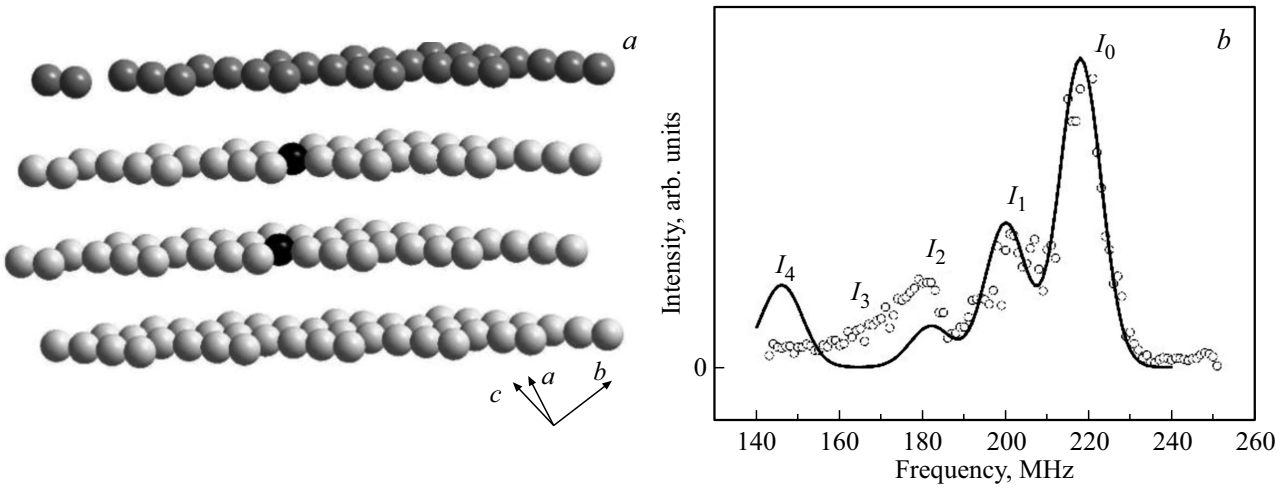

Figure 4. *a*) Interface of nanowires Co/Cu, interstitial with depth of two atomic layers; *b*) design NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

Such form results in intensity decreasing of resonance lines I_4 and I_2. Upon increase in interstitial depth by one atomic layer (total 3 atomic layers) intensity of the resonance line I_1 significantly increases, as large number of cobalt atoms occurs with one copper atom in coordination. It is possible to reduce the intensity of this resonance line by adding one copper atom to the existing interstitial copper atoms along the entire interstitial region, Figure 5. Figure 5, *b* shows satisfactory degree of coincidence between the design and experimental NMR spectra.

Decrease in intensity of resonance line I_4 relative to intensity of lines $I_1 - I_3$ is possible by depth increase of interstitial copper in cobalt (Figure 6). Figure 6, *b* shows high degree of coincidence between the design and experimental NMR spectra. But such interface structure is implemented at formed in nanowires texture (111), so we shall consider such configuration of interstitial for cases with texture (100) and (110).

Figure 7 shows interface structure for texture (100) and design NMR spectrum corresponding to such interface configuration, in this case spectrum has lower degree of coincidence with the experimental spectrum for resonance lines I_1 and I_4. Let's now make the suggested interface structure for the texture (110), Figure 8.

Figure 8, *b* shows that line I_4 has intensity lower then on experimental spectrum, line I_2 has excessive intensity.

Figure 9 summarizes the obtained design spectra and shows high degree of coincidence of design and experimental NMR spectra. Modeling of interfaces structure based on data of nuclear magnetic resonance showed that depth of copper entering into cobalt in the interface region of heterogeneous nanowires Co/Cu if at least four atomic layers or over 0.8 nm.

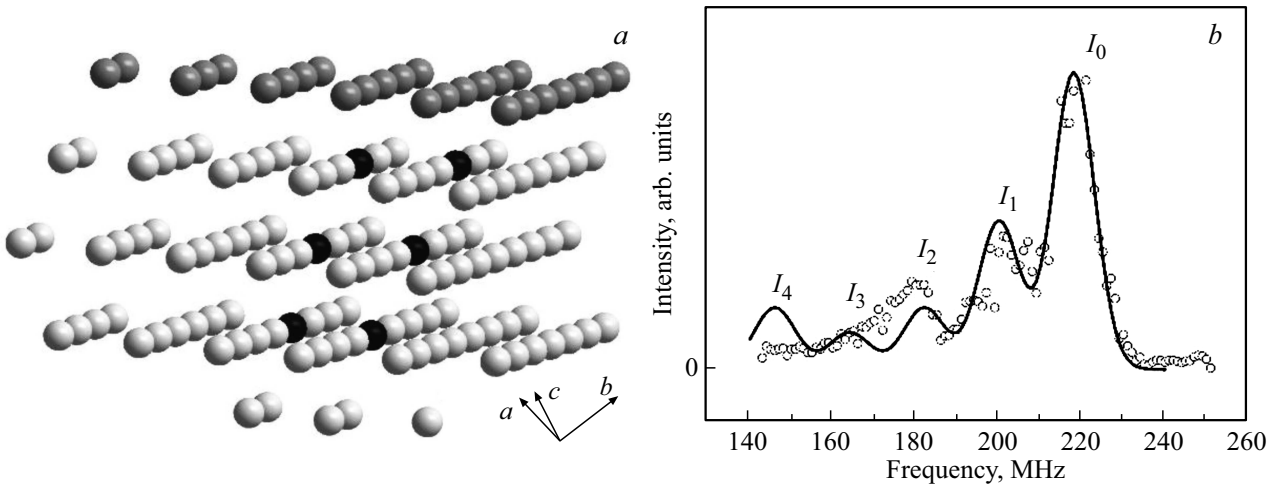

Figure 5. *a*) Interface of nanowires Co/Cu, interstitial with depth of three atomic layers and width of two atoms; *b*) design NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

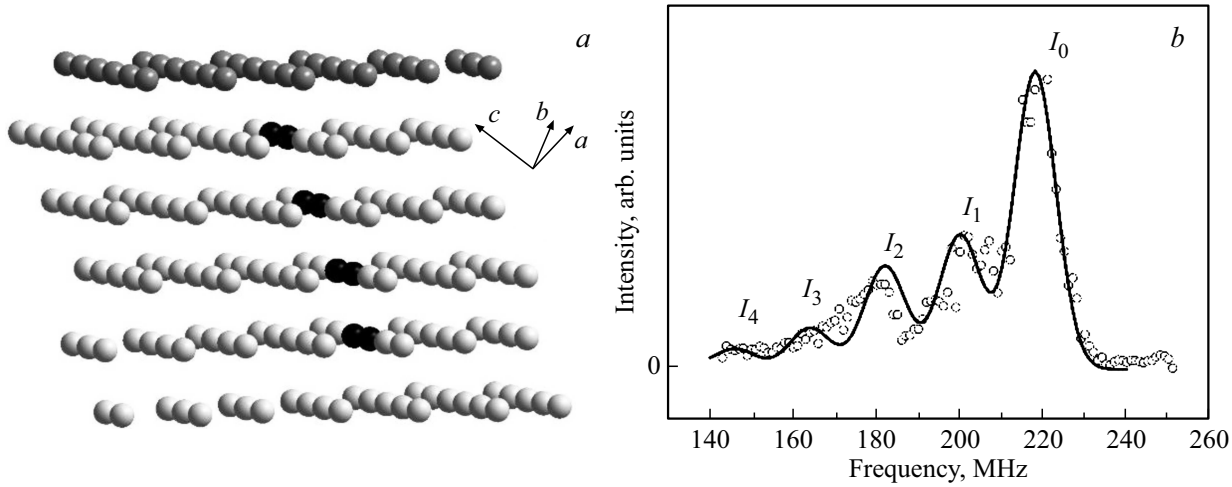

Figure 6. *a*) Interface of nanowires Co/Cu, interstitial with depth four atomic layers and width two atoms; *b*) result of modeling on NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

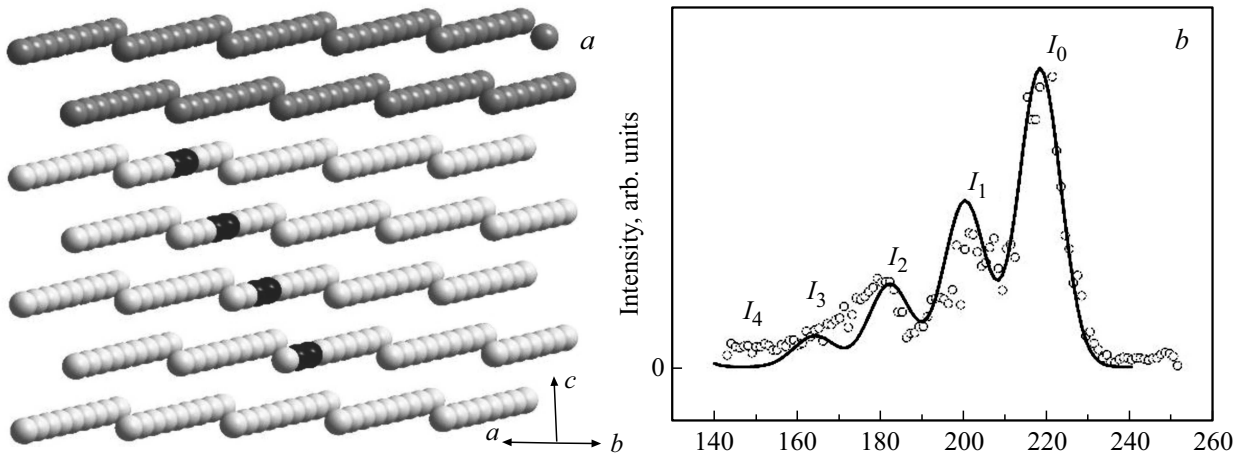

Figure 7. *a*) Interface of nanowires Co/Cu, interstitial with depth of four atomic layers and width of two atoms, texture (100); *b*) result of modeling of NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

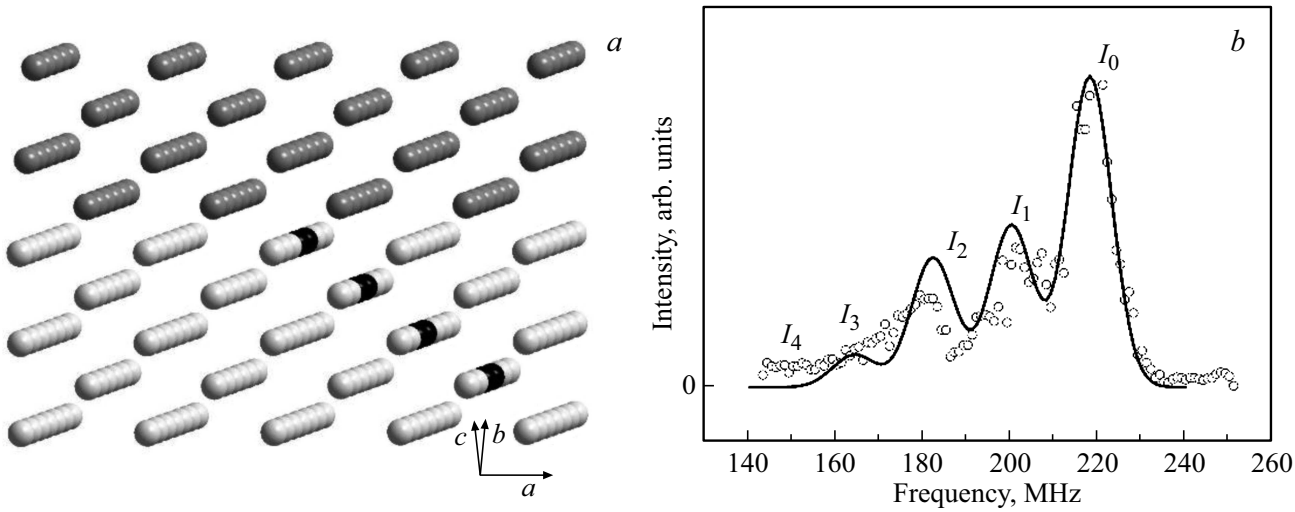

Figure 8. *a*) Interface of nanowires Co/Cu, interstitial with depth of four atomic layers and width of two atoms, texture (110); *b*) result of modeling of NMR spectrum on nucleus ^{59}Co. Color designation: copper — dark-gray, cobalt — light-gray, copper interstitials in cobalt — black.

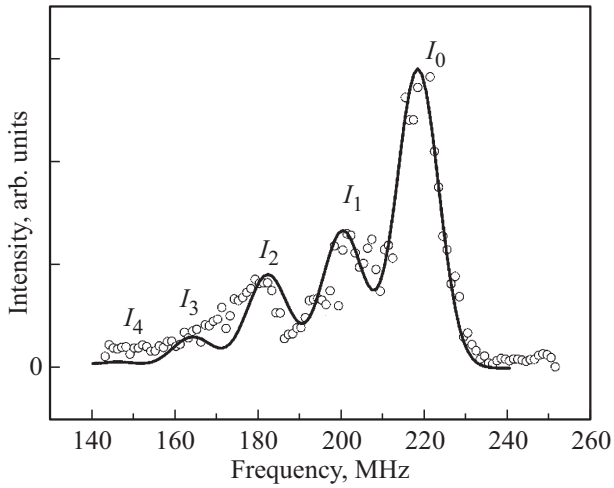

Figure 9. Design and experimental NMR spectra for nanowires with layers thickness 30 nm.

4. Conclusion

The experimental NMR spectra provide distribution of local ultrathin fields in heterogeneous nanowires Co/Cu. Using 3D modeling the Co/Cu interfaces structure is made in studied cobalt-containing nanowires. It is shown that interface thickness in these nanowires is at least four atomic layers, i. e. over 0.8 nm, interstitial copper in cobalt has needle shape.

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Conflict of interest

The authors declare that they have no conflict of interest.

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