

# Ferromagnetic Resonance and Magnetic Anisotropy of 3d-Metal Wires with Composition Gradients

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**Abstract**—Results are presented from investigating the ferromagnetic resonance spectra of arrays of Co–Ni and Co–Fe–Ni wires with different composition gradients, deposited into polycarbonate track-etched membranes. The effect interfaces and concentration gradients have on the effective fields of the investigated wires is examined. An anomalous angular dependence of the fields of ferromagnetic resonance is observed for the wire arrays at a pore density of ~18% in the membrane.

**Keywords:** wires with gradients of composition, electroless deposition, ferromagnetic resonance, magnetic anisotropy

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## INTRODUCTION

Magnetic composite nanowires deposited into pores of various matrices are good candidates for creating new highly sensitive sensors, magnetic memory cells, micromagnets, and microwave (e.g., tunable microwave filters) and spintronic devices [1–5]. The magnetic behavior of nanomaterials is determined by their size and features of the crystal structure and arrangement of constituents. From this viewpoint, it is best to create nanowires with different geometries and compositions in order to obtain a unique combination of properties. The deposition of metals from solutions opens up the prospect of the low-temperature synthesis of various composition-modulated systems. By creating the magnetic potential of a specific, predetermined wire shape through the synthesis of materials with a concentration gradient, we can control fundamental characteristics of technical importance [6–9].

It should be noted that the magnetic properties of nanowire arrays can differ from those of individual wires. The effective anisotropy of a nanowire array is affected by both the shape and magnetocrystalline anisotropies of individual nanowires and the anisotropy of a nanowire ensemble induced by the dipole–dipole interaction in it, which ultimately determines the magnetic properties of the magnetic nanowires–matrix composites [8, 10].

This work presents results from investigating the ferromagnetic resonance (FMR) spectra of wire arrays based on 3d metals with different architectures (linear Ni concentration gradient, core–shell, or multi-segment) deposited into a polycarbonate track-etched membrane matrix.

## EXPERIMENTAL

Arrays of Co–Ni wires were formed in 0.4- $\mu\text{m}$  pores of polycarbonate track-etched (PCTE) membranes via chemical deposition based on the reduction of metal salts from aqueous solutions. The solutions for depositing wires into membrane pores included metal salts (nickel sulfate  $\text{NiSO}_4$ , cobalt sulfate  $\text{CoSO}_4$ , or Mohr’s salt  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ ), a complexing sodium citrate  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  additive, and an ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$  pH stabilizer (buffer solution). Sodium hypophosphite  $\text{NaPO}_2\text{H}_2$  was used as the reducing agent. Deposition was done at a temperature of 80°C, and the pH value was maintained by adding an NaOH solution.

We synthesized Co–Ni wires with different composition gradients along the wire axis inside a PCTE membrane pore with a linear Ni concentration changed from 30 to 70 at % (smooth series A) and a stepwise change. The wires with the stepwise compo-

**Table 1.** Characteristics of the FMR spectra of the gradient wires

Series	Co BMS	Ni BMS	Co CMS	Fe CMS	Ni CMS	Co DCS	Ni DCS	CoNi AGr	CoNi E
$H_r$ , kOe	1.15	2.3	1.14	0.51	1.68	0.95	2.1	2.4	1.2
$\Delta H$ , kOe	0.9	1.3	0.5	0.3	0.8	0.8	1.15	0.9	0.4
$H_{\text{eff}}^{\text{cal}}$ , kOe	4.4	1.5	4.4	5.45	1.5	5.1	1.76	2.48	2.48
$H_{\text{eff}}^{\text{exp}}$ , kOe	2.3	1.16	2.32	2.95	2.29	2.51	1.36	1.06	2.26

sition gradient were obtained in several modifications: Co/Ni wires (series B), Co/Fe/Ni wires consisting of alternating layers (MS) of different compositions (series C), and wires with the coaxial Co@Ni phase segmentation (CS) consisting of a cylindrical cobalt core in a nickel shell (series D). The wall thickness of the nickel tubes was  $\sim 100$  nm and the cobalt core was  $\sim 200$  nm in diameter. Wires from a Co–Ni alloy with a uniform distribution of elements along the wire axis (series E) were also synthesized. We described the procedure for depositing the wires with the chemical composition gradient into PCTE membrane pores in detail in [11]. The Co and Ni content gradients along the wire axis were controlled via energy-dispersive X-ray (EDX) analysis. The synthesized samples were studied on S5500 and TM3000 Hitachi scanning electron microscopes with an EDX attachment and on a DRON-3 X-ray diffractometer. The field dependences of magnetization were measured with a vibrating sample magnetometer. FMR spectra were recorded at a frequency of 9.4 GHz.

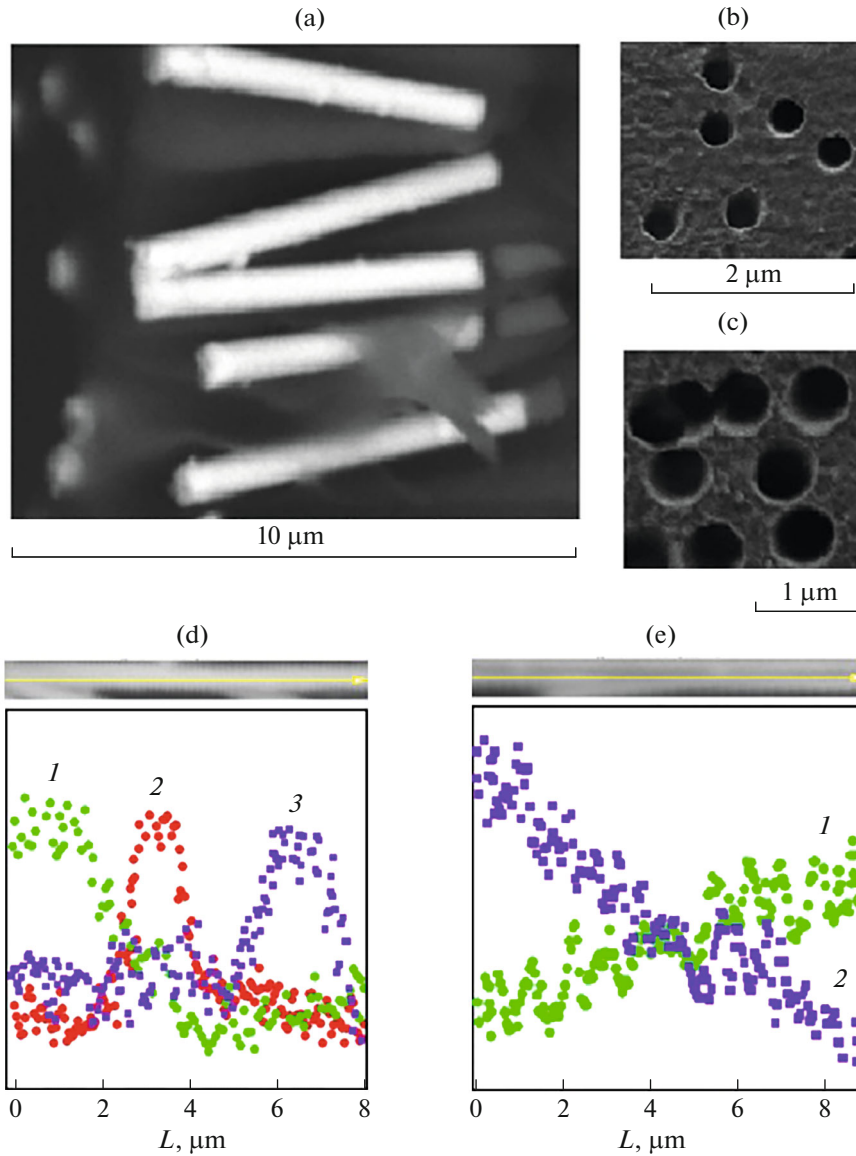
## RESULTS AND DISCUSSION

Our scanning electron microscopy investigations of wire samples of different compositions showed that the wires in the PCTE membrane pores were indeed composite materials with the chemical composition of the core and shell for the CS wires and individual segments for the MS wires corresponding to the process requirements. Figure 1 presents SEM images of the Co–Ni wires and the PCTE membrane surfaces with different pore densities, along with the distribution of elements along the wire axis with the linear (Fig. 1c) and stepwise (Fig. 1d) concentration gradients. It should be noted that in chemical deposition, phosphorus is reduced along with metal ions. Some phosphorus is therefore always contained in wires obtained using sodium hypophosphite as a reducing agent, depending on the amount of a reducing agent in the deposition solution and the pH of the latter. The content of phosphorus in the deposited alloy in turn determines the grain size and the type of the crystal lattice

[12]. In this work, the content of phosphorus in the Co(P), Ni(P), and Fe(P) alloys was no higher than 5 at %. According to X-ray diffraction data, the Ni and Co alloys in all the wires were crystalline with an fcc structure.

It was established that the FMR spectra of the homogeneous wires (with no concentration gradient) deposited into membrane pores with a nominal diameter of  $d \sim 400$  nm consisted of one absorption line with resonance fields  $H_r$  of 1.3 kOe for the cobalt wire (1.1 kOe at  $d \sim 200$  nm), 1.64 kOe for the nickel tube, 1 kOe for the nickel wires, and 1.2 kOe for the Co–Ni alloy wires. The FMR spectra of the investigated Co/Ni, Co/Fe/Ni, and Co@Ni wires with different composition profiles consist of several peaks. Decomposing the spectra into individual resonance peaks corresponding to different elements of the composite wires showed that the positions of the peaks did not coincide with those of the peaks in the reference samples, in contrast to the data reported in [3]. Characteristics of the FMR spectra (resonance fields and resonance absorption linewidths  $\Delta H$ ) for the wires with different composition gradients are given in Table 1. Creating a stepwise concentration gradient of both modifications raised the  $H_r$  and  $\Delta H$  values for the Ni segments considerably, while the  $H_r$  value for the Co and Fe segments changed by no more than 12%. The  $H_r$  value for the gradient CoNi wires doubled upon smooth modulation of the composition, relative to the  $H_r$  value for the homogeneous CoNi alloy wires.

The magnetic anisotropy of a nanowire array is determined by two main contributions, the first of which is made by the shape of the magnetic anisotropy of an individual wire. The corresponding contribution to the total anisotropy field is  $H_{\text{sh}}$ . The second contribution is made by the magnetic dipole coupling between the wires and produces easy-plane magnetic anisotropy (the plane of easy magnetization coincides with that of the membrane), which is characterized by field  $H_{\text{dip}}$ . The contribution to magnetic anisotropy made by the texture of a crystal with an fcc lattice of the Co and Ni segments can be considered minor,



**Fig. 1.** (a) SEM images of Co–Ni wires. Top view of PCTE membranes with porosities of (b) 7 and (c) 18%. Data from EDX analysis showing the stepwise gradient of the contents of (1) Co, (2) Fe, and (3) Ni (d). The smooth gradient of (1) Co and (2) Ni (e) along the rod axis.

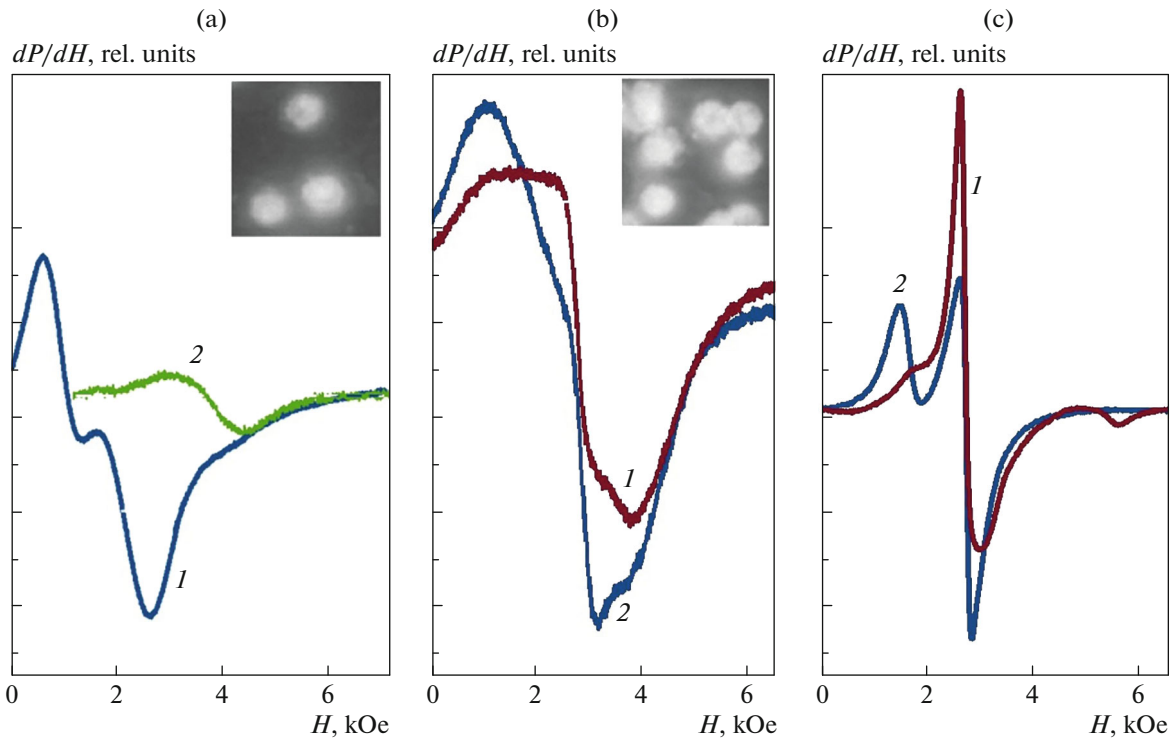
compared to the shape of the anisotropy. The contribution from dipole–dipole interaction between the wires can be estimated as  $H_{\text{dip}} = 6Pf\pi M_s$ , where  $P$  is the porosity of the material;  $f$  is the filling factor, estimated from the electron microscopy data;  $M_s$  is the saturation magnetization [3]; and the contribution from shape anisotropy is  $H_{\text{sh}} = 2\pi M_s$ . We finally have  $H_{\text{eff}} = 2\pi(3P - 1)M_s$ .

When a field is applied along the wire axis, the Kittel equation [13] has the form

$$\frac{\omega}{\gamma} = H_r + 2\pi M_s (1 - 3Pf), \quad (1)$$

where  $\gamma = g\mu_B/h$  is the gyromagnetic ratio,  $g = 2$ ; and  $P$  is the porosity of the material. The second term of this equation turns to zero at a membrane porosity of  $\sim 35\%$ , and the resonance field for a composite consisting of an array of metal nanowires in PCTE membrane pores is isotropic. The  $H_r$  value thus depends on neither the wire's magnetization (the composition of the alloy) nor the orientation of the sample relative to the external field.

Figure 2 shows FMR spectra for coaxial wires measured at different orientations of the wire axis, relative to the external field for membranes with different pore densities. Decomposing the composite spectrum into individual resonance peaks showed that along with

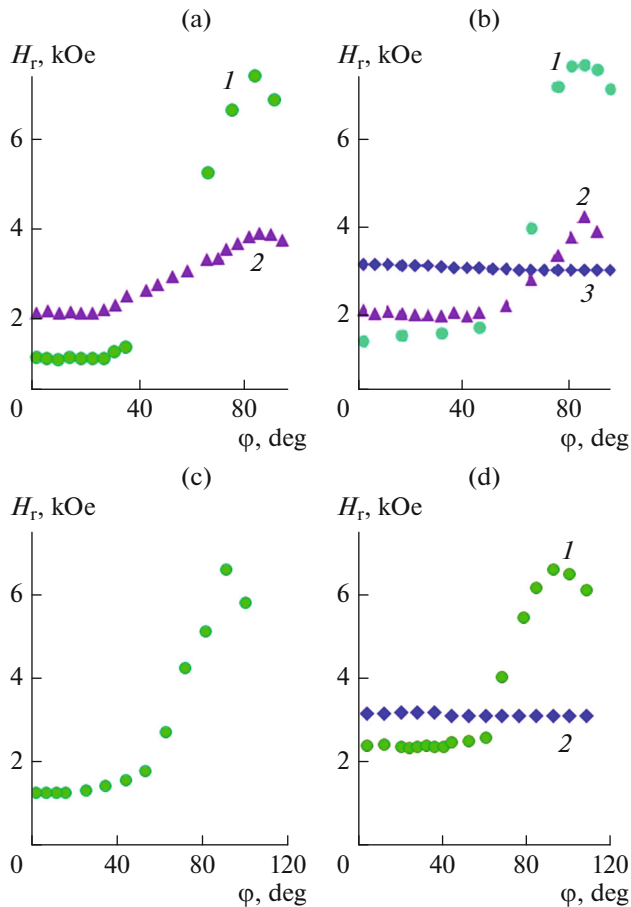


**Fig. 2.** FMR spectra of the coaxial Co@Ni wires for the membranes with pore densities of (a) 7 and (b) 18%. (c) Co–Ni wires with a linear Ni concentration gradient for the membrane with a pore density of 18%, measured at different orientations of the wire axis relative to an external field applied (1) along the wire axis and (2) perpendicular to it. Insets show SEM images of the surface of the corresponding PCTE membranes with the deposited Co@Ni wires.

peaks corresponding to a Co core and a Ni shell, the spectrum includes an additional peak that apparently corresponds to an ensemble of composite wires. We can see that as the pore density grew to 18%, the value and field coordinates of this additional peak in the FMR spectrum remained virtually independent of the direction of the external field. This sample, which was a plate made of an anisotropic composite material, made a strong isotropic contribution to the resonance microwave absorption. We attribute this behavior to the contribution from dipole–dipole interaction being comparable to that of shape anisotropy at a wire distribution density of  $\sim 18\%$ . Figure 3 shows angular dependences of FMR fields  $H_r(\varphi)$  (where  $\varphi = 0$  corresponds to an external field directed along the wire’s axis) for wires with different concentration profiles. With a membrane pore density of 5–7%, the  $H_r(\varphi)$  dependence has a form close to the behavior of a ferromagnetic sample in the form of an elongated cylinder with a large aspect ratio (Figs. 3a, 3c). The angular dependence of the anomalous resonance fields for one of the peaks in the composite microwave absorption spectrum at  $P > 18\%$  (resonance field  $\sim 3200$  Oe remains virtually the same at any orientation of the external field relative to the wire’s axis) is characteristic of the FMR spectra of composition-modulated wires with both stepwise (Fig. 3b) and linear (Fig. 3d) gradients

of the concentrations of elements along the wire’s axis. The anomalous  $H_r(\varphi)$  angular dependence for the wires is observed at a pore density lower than the one predicted by Eq. (1) for an infinite cylinder, due possibly to an additional contribution to the anisotropy field from modulation of the wire’s composition, interfaces, or a change in the shape anisotropy of the wires caused by their finite length ( $\sim 8 \mu\text{m}$ ). The additional  $H_{\text{eff}}$  anisotropy was estimated by using Eq. (1) to compare the experimental and calculated  $H_r$  values (Table 1). The observed additional contribution to  $H_{\text{eff}}$  for a Co@Ni core–shell rod (2.6 kOe) is greater than for a two-segment Co/Ni rod (2.1 kOe). We assume this contribution came from interfaces of the composite rods. The greater contribution to  $H_{\text{eff}}$  in the core–shell rods is then explained by an interfacial surface area larger than the analogous area of multi-segment rods.

The inhomogeneity of the Co or Ni concentrations at the layer boundaries can induce gradient anisotropy effects (i.e., local changes in the effective magnetic anisotropy along a rod’s axis). Such deviations of magnetic anisotropy can vary the resonance fields in different segments of the wires and increase the FMR linewidth. The FMR linewidth for the Ni/Co, Co@Ni, and gradient CoNi wires do indeed exceed



**Fig. 3.** Angular dependences of the FMR resonance field for coaxial Co@Ni wires in the PCTE membranes with porosities of (a) 5 and (b) 18% for (1) a Co core, (2) a Ni shell, and (3) an additional peak.  $H_r(\varphi)$  dependences for (c) homogeneous Co–Ni wires in a PCTE membrane with a porosity of 5% and (d) gradient Co–Ni wires in a PCTE membrane with a porosity of 18% (for (1) Co–Ni alloy and (2) an additional peak);  $\varphi = 0$  corresponds to an external field directed along the wire axis.

the values for the homogeneous samples by 40, 60, and 55%, respectively.

## CONCLUSIONS

Chemical deposition into PCTE membrane pores was used to obtain wire arrays with different composition profiles: coaxial (Co@Ni) and longitudinal (Co/Ni and Co/Fe/Ni) step segmentation, and a linear change in the element concentration along the Co@Ni alloy wire axis. It was found that a gradient wire array exhibits isotropic microwave absorption at an ~18% density of pores in a membrane. It was shown that the characteristics of the FMR spectra of the composites can be controlled by varying the wire architecture (gradient, core–shell, or multi-segment) and the morphological features (porosity) of the matrix.

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

## REFERENCES

- Pereira, A., Palma, J.L., Vázquez, M., et al., *Phys. Chem. Chem. Phys.*, 2015, vol. 17, p. 5033.
- Rial, J. and Proenca, M.P., *Nanomaterials*, 2020, vol. 10, p. 2403.
- Darques, M., Spiegel, J., de la Torre Medina, J., et al., *J. Magn. Magn. Mater.*, 2009, vol. 321, p. 2055.
- Parkin, S.S. Hayashi, M., Thomas, L., et al., *Science*, 2008, vol. 320, no. 11, p. 190.
- Wang, D.-S., Mukhtar, A., Wu, K.-M., Gu, L., and Cao, X., *Materials*, 2019, vol. 12, p. 3908.
- Zeng, M., Yang, H., Liu, J., and Yu, R., *J. Appl. Phys.*, 2014, vol. 115, p. 17B514.
- Zagorskiy, D.L., Doludenko, I.M., Kanevsky, V.M., et al., *Bull. Russ. Acad. Sci.: Phys.*, 2021, vol. 85, no. 8, p. 848.
- Yang, H., Li, Y., Zeng, M., et al., *Sci. Rep.*, 2016, vol. 6, p. 20427.
- Méndez, M., Gonzalez, S. Vega, V., et al., *Crystals*, 2017, vol. 7, no. 3, p. 66.
- Bran, C., Ivanov, Y.P., Kosel, J., et al., *Nanotechnology*, 2017, vol. 28, no. 9, p. 095709.
- Denisova, E.A., Chekanova, L.A., Komogortsev, S.V., et al., *IEEE Trans. Magn.*, 2022, vol. 58, no. 2, p. 2300805.
- Iskhakov, R.S., Chekanova, L.A., and Denisova, E.A., *IEEE Trans. Magn.*, 1997, vol. 33, no. 5, p. 3730.
- Kittel, C., *Phys. Rev.*, 1948, vol. 73, no. 2, p. 155.

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