# STUDY OF MAGNETIC INTERACTIONS IN A COMPOSITE WITH A MIXTURE OF γ-$Fe_2O_3$ AND $CoFe_2O_3$ NANOPARTICLES

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Received November 15, 2024

Revised December 14, 2024

Accepted December 30, 2024

**Abstract.** We studied magnetic interactions in promising biomedical composites based on a piezoactive PVDF matrix with a mixture of soft magnetic γ-$Fe_2O_3$ (FO) and hard magnetic $CoFe_2O_4$ (CFO) nanoparticles by conducting IRM-DCD and FORC analyses. It was determined that the addition of a mixture of soft and hard magnetic nanoparticles to the polymer base of the composite leads to an increase in the magnetic interaction fields $\Delta H_u$ from ~ 1300 to ~ 1500 Oe and to the formation of two main magnetic phases in the composite.

**Keywords:** *magnetic interactions, magnetoelectric composites, FORC-analysis*

**DOI:** 10.31857/S03676765250415e7

## INTRODUCTION

The growing number of musculoskeletal diseases requires the search for new effective methods of bone tissue repair[1] . Tissue engineering and regenerative medicine offer strategies for bone repair using scaffolds that stimulate stem cell differentiation in the osteogenic direction[2] . In order to reproduce *in vitro/in vivo* conditions of stem cell differentiation on scaffolds, it is necessary to take into account mesostructural features of bone (rigidity, porosity, internal microstructure) and to ensure that cells are exposed to a combination of different physical stimuli, such as

magnetic, electrical and mechanical stimuli, as they play an important role in the regulation of stem cell activity[3] . Among the variety of materials potential for use as scaffolds for bone tissue engineering, polymer composites possessing magnetoelectric (ME) effect can provide such a set of properties. The direct ME effect is the energy transfer from the ferromagnetic phase to the segmentoelectric phase: the application of an external magnetic field leads to a change in the size of the magnetostrictive component, which due to the mechanical coupling of phases leads to deformation of the piezoelectric component, which, in turn, changes the electric polarization (change in the sign or magnitude of polarization) [4]. The development of such multiferroic materials, with controlled magnetoelectric response, has received much attention in recent years ,[56] . It is possible to modify the properties of magnetoelectric composites at the micro- and nanoscale by changing the mechanical coupling of the magnetic and piezoelectric phases[7] . Therefore, an important role in creating a composite with the given properties is played by the choice of matrix type, which is conditioned by a number of additional requirements to it: lightness, miniaturization, ease of processing, flexibility and wear resistance, bionutrality[8] . Classical ceramic materials used in the creation of ME composites do not possess these properties, so for biomedical applications piezoelectric ceramics are replaced by piezoelectric flexible polymers such as polyvinylidene fluoride (PVDF) or poly(PVDF). "PVDF") or poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), as well as other PVDF-based copolymers and polymer blends[9] , which not only have the properties listed above, but are also commercially available and environmentally friendly materials .[10]

To obtain optimal magnetoelectric properties, different filler options can be chosen as magnetic and electrical phases, e.g. particles, wires, anisotropic lamellar structures[7] . The choice of the type of magnetic filler is determined by the magnitude of its magnetostriction and magnetic properties (magnetization, susceptibility, coercivity)[11] . For composites with nano- and microparticles, in addition to the main mechanism of the magnetoelectric effect due to the magnetostrictive properties of ferromagnetics, there is a contribution associated with the tendency of particles, their aggregates and ensembles to displacement and rotation in the piezoactive matrix under the action of an external magnetic field[12] . The combination of the two mechanisms makes it possible to achieve the strongest mechanical effect on the matrix, which leads to an increase in the piezo effect and, consequently, to an increase in the magnetoelectric effect[13] . The tendency of particles to rotate and displace can be enhanced by magnetic (e.g., dipole-dipole) interactions determined, among other things, by the distance between particles, their aggregates and ensembles[14] . It is possible to change the configuration of particles and their aggregates in the polymer at the stage of composite fabrication. As a consequence, the magnetoelectric effect of the obtained composite will directly depend on the magnetic interactions incorporated during its fabrication .[15]

Thus, the study of interactions of ferromagnetic nanoparticles and their aggregates in a piezoelectric matrix is important for the optimization of the magnetoelectric coupling coefficient, a key parameter of magnetoelectric cell scaffolds for tissue engineering. The aim of this work is to analyze magnetic interactions in composites based on piezoactive matrix PVDF and magnetically hard $CoFe_{(2)}$

$_{O4}$nanoparticles using IRM-DCD (Isothermal Remanent Magnetization, Direct Current Demagnetization) dependences and FORC (First Order Reversal Curve) diagrams and to determine the influence of additional fillers - magnetically soft γ-$Fe_{(2)}$ $_{O(3)}$nanoparticles and $BaTiO_{(3)}$microparticles - on them.

## MAIN PART

Polyvinylidene fluoride (PVDF) polymer was used as a polymer matrix for the fabrication of composites. To prepare the solution, PVDF granules were dissolved in dimethylformamide (DMF) in a weight ratio of 1:4 at a temperature of 40° C with subsequent stirring until the polymer granules were completely dissolved. The dissolution time was 45 minutes. $CoFe_{(2)\,O4}$and γ-$Fe_{(2)\,O3}$nanoparticles, which were used as ferromagnetic filler for the composite, were synthesized by sol-gel self-combustion and co-precipitation methods. The nanoparticles were mixed with the second part of the solvent and dispersed in the precursor polymer solutions prepared beforehand in an ultrasonic bath for 2 h. Piezoelectric $BaTiO_{(3)}$ (BTO) particles were added to the solution in the same step as the ferromagnetic particles. The solution of particles and polymer precursor was applied to a clean glass substrate using a coating blade with the distance from the substrate to the blade fixed (the method of fabrication was the doctor blade or doctor Blade method [4, 5]). The solvent was vaporized by heating the composites in an oven at 75° C for 15 min.

The magnetically soft phase of the ferromagnetic filler was maghemite nanoparticles (γ-$Fe_{(2)\,O3}$) with bulk and linear crystallite sizes of 7 nm and 9.6 nm, respectively, determined by X-ray diffractometer and transmission electron

microscope[16] . Cobalt ferrite nanoparticles ($CoFe_2O_4$) with a size of 23 nm served as the magnetosolid phase[17] . Piezoelectric barium titanate ($BaTiO_3$) particles with a size of 2 μm were obtained by solid-state grinding, and they are used in the composite to increase the number of piezoelectric polymer phase formation centers; at the same time, BTO particles can have a negligible effect on the interparticle interaction .[18]

To investigate the magnetic interactions in the composite, a comparative analysis of the magnetic characteristics of samples with three types of filler: CFO, CFO-BTO blend and CFO-FO blend was carried out (the hysteresis loops of the samples are shown in Figure 1). The field dependences of the residual magnetization were obtained following two measurement protocols:

– Isothermal Remanent Magnetization (IRM) - measurement of the residual magnetization of the sample after application and removal of the magnetic field, the strength of which increases with each measurement step in the range $H_R$= 0-1.1 Tesla ($H_R$- return field).

– Direct Current Demagnetization (DCD) - measurement of the residual magnetization of the sample after the procedure of changing and removing the magnetic field in which it is placed: (1) application of a saturation magnetic field ($H_S$= -1.1 Tesla); (2) application of a reverse magnetic field whose strength increases in the range $H_R$= 0 - 1.1 Tesla with each measurement step; (3) removal of the field.

The switching field distribution (SFD - switching field distribution) - the first derivative of the $M_{(DCD)}(H_R)$ dependence - is plotted in Fig. 2 for all the composites studied. For nanocomposites with CFO particles, the SFD dependence has a maximum in the field of 2.2 kE, while for nanocomposites with a mixture of CFO-FO particles,

the SFD maximum corresponding to the switching field of magnetization of cobalt ferrite nanoparticles shifts to the region of lower fields and is located in the field of 2.0 kE. This effect can be caused by the interparticle dipole interaction between magnetically soft and magnetically hard particles. At the same time, the SFD-distribution shows a sharp increase in susceptibility when approaching the zero field, which may be caused by the submagnetizing effect of the magnetically soft iron oxide phase, which does not change the residual magnetization as a consequence of superparamagnetic relaxations and, consequently, does not change the SFD-distribution. In low fields, the superparamagnetic iron oxide nanoparticles are magnetized and, by creating an additional field, cause the magnetization switching of some cobalt ferrite nanoparticles. The addition of diamagnetic BTO microparticles has no significant effect on the switching field distribution compared to the composite sample containing only CFO particles (Fig. 2b).

The type of nanoparticle interactions can also be analyzed by the Kelly plot: $\delta m(H) = M_{(DCD)} - (1 - 2 \cdot M_{(IRM)})$, where $\delta m(H)$ is the parameter responsible for the integral magnetic characteristics of the system, including data on interparticle interactions. According to the Stoner-Wohlfahrt model, the shift of δm dependences to the region of negative values indicates the predominance of dipole-dipole interparticle interactions in each of the composites considered, which is in agreement with the observations made previously. Fig. 2d shows that the addition of superparamagnetic FO nanoparticles to the composite with CFO cobalt ferrite leads to an increase in the modulus value of $\delta m$ in the local minimum region (the region that corresponds to the remagnetization of the CFO nanoparticles) by about a factor of two. When diamagnetic

BTO microparticles are added, there is an increase in the modulus $\delta m$ value in the region of local minimum, which may indicate the enhancement of magnetic interactions between CFO particles in the composite. However, the change in modulus $\delta m$ is sensitive not only to interparticle interactions but also to the configuration of the particle agglomerates, the influence of which cannot be accounted for correctly in the analysis within this work. The Kelly plot analysis protocol is characterized by fast measurement and construction speed, easy interpretation of data for simple nanoparticle systems, however, for the considered multiphase system it turned out to be inapplicable due to the impossibility to resolve the contributions to the total energy of the system from various factors.

For a more detailed study of magnetic interactions, the FORC analysis method (FORC: First Order Reversal Curve) was used, based on the study of a large number of partial magnetization curves (FORC curves) of samples. By comparing the course of private magnetization curves among themselves, it is possible to judge about the type of interaction; SFD- and FORC-diagrams are used to qualitatively and quantitatively study the interactions of magnetic phases in the system. The FORC-curve measurement protocol: (1) the sample is magnetized by applying a saturation magnetic field; (2) the external magnetic field is reduced to the value $H_{(r)}$ (return field); (3) the field dependence of the magnetic moment value of the sample is measured when the external magnetic field, $H_{(a)}$ (applied field), is increased to saturation. The obtained field dependence of the magnetic moment of the sample from the return field ($H_r$) to the saturation field is called FORC - curve. To perform a correct analysis of interaction processes in magnetic systems, it is necessary to measure at least one hundred FORC-

curves. Further, to perform FORC-analysis, it is necessary to carry out mathematical processing of the obtained data. For this purpose, a set of SFD-curves (SFD - distribution of switching fields) for all measured FORC-curves is first plotted on one graph (SFD-graph). SFD-curve is the first field derivative defined as

$$SFD = \left(\frac{\partial m}{\partial H_a}\right)_{H_r}. \quad (1)$$

As the return field increases, a shift of the SFD curves relative to the SFD curve obtained in the saturation fields (i.e., relative to the initial curve, for the measurement of which the applied return field is equal in modulus and opposite in direction to the saturation field) may appear on the graph. By its magnitude and direction, the change in switching fields for each magnetic phase in the system is analyzed. The magnetic interactions of the phases of the system are evaluated by the FORC-diagram, which is constructed from the FORC-distribution:

$$\rho = -\frac{1}{2}\left(\frac{\partial^2 M}{\partial H_a \partial H_r}\right). \quad (2)$$

$H_c$and $H_u$, - key parameters for analyzing magnetic interactions of multiphase systems - the coercivity field and the magnetic phase interaction field, are defined as follows:

$$H_c = \frac{H_a - H_r}{2}; \; H_u = \frac{H_a + H_r}{2}. \quad (3)$$

$H_C$and $H_u$are diagonal axes in the FORC-diagram. The range of values of the interaction fields in the composite ($\Delta hu$) is determined by the FORC-diagram as the width of the peak of the distribution function$\rho$ $(H_a, H_r)$ along the interaction axis, $H_{(u)}$ (Fig. 3a).

Fig. 3a shows the obtained FORC-curves, SFD-graph and FORC-diagram for the composite containing only magnetic CFO nanoparticles. The presence of two magnetic phases is clearly observed both in the SFD-graph (two peaks) and in the FORC-diagram (regions 1 and 2 in Fig. 3a). Their occurrence in a composite with magnetically hard particles is related to aggregation of particles and their distribution in the matrix: region 2 in Fig. 3a characterizes the magnetic phase. 3a characterizes the magnetic phase associated with the interaction of particles inside the agglomerates, and region 1 in Fig. 3a characterizes the magnetic phase associated with the interaction between agglomerates[18] . For the composite with CFO particles, in the SFD plots, the first peak (region 1) stands out rather weakly relative to the second peak, and in the FORC distribution, region 1 has less intense brightness than region 2. This indicates a weak dipole-dipole interaction between agglomerates in the polymer, which may be due to the large distance between them. At the same time, the interaction of particles within agglomerates (region 2 in Fig. 3a) is characterized by a wider region of switching fields (elongation along the $H_c$axis in the diagram), which indicates the presence of a strong dipole-dipole interaction within the aggregates, according to the work[19] . The magnitudes of the interaction fields of the CFO magnetosolid particles in the composite are determined from the diagram as the width of region 2 along the interaction axis, $\Delta hu$~ 1300 Å. Fig. 3b presents the data of the analysis of the composite with an additional filler - segmentoelectric BTO particles. FORC distribution for such a composite shows that the addition of BTO particles to nanocomposites does not lead to significant changes in their macroscopic magnetic properties: two regions are also observed in the FORC diagram, SFD plots are characterized by two similar peaks to

Fig. 3a peaks. The magnitudes of the interaction fields of magnetosolid CFO particles in the presence of BTO increase, $\Delta hu \sim$ E. For composites fabricated from a mixture of magnetically soft and magnetically hard nanoparticles (Fig. 3c), the FORC diagram has a different shape from the diagrams in Figs. 3a and 3b look. The presence of a magnetically soft phase with a remagnetization maximum in a near-zero external magnetic field (region 1 in the SFD diagram and FORC diagram) is clearly expressed. The enhancement of the brightness of the near-zero peak and its broadening both along the interaction axis and the coercivity axis (Fig. 3c relative to 3a and 3b) indicate a strong dipole-dipole interaction of the magnetically soft particles inside the clusters. In addition, the relative enhancement of the brightness of region 1 compared to region 2 in the FORC diagram, as well as the sharpening of peak 1 in near-zero fields in the SFD plot, indicate that some of the clusters of magnetically hard particles in the presence of clusters of magnetically soft particles are remagnetized in lower fields (enclosed in region 1): during remagnetization, FO particles create a positive sub-magnetization field for CFO particles[20] ; the remaining part of the magnetosolid phase is remagnetized in the same field region in which the remagnetization of CFO filler in composites with CFO and CFO-BTO particle mixture occurred (region 2). The magnitudes of the magnetic particle interaction fields in the magnetosolid phase are increased, $\Delta h_u \sim$ 1500 Å (the FORC-diagram inset in Fig. 3c shows an enlarged region 2 with enhanced color contrast for better visualization of the response of the magnetosolid phase).

## CONCLUSION

Thus, we have studied magnetic interactions in PVDF composites with different fillers: magnetically hard $CoFe_2O_4$ particles; a mixture of magnetically hard $CoFe_2O_4$ particles and diamagnetic piezoelectric $BaTiO_3$particles; a mixture of magnetically soft $\gamma$-$Fe_{(2)}O_3$and magnetically hard $CoFe_2O_4$ particles. According to the results of magnetic properties investigation using IRM-DCD dependences and FORC analysis method, it was determined that the addition of a mixture of magnetically soft nanoparticles to the polymer composite with $CoFe_2O_4$ particles leads to an increase in the magnetic interaction fields of the magnetically hard nanoparticles from $\Delta h_u$~ 1300 to ~ 1500 Å. It is found that two magnetic phases are formed in each composite, associated with two types of interactions - between magnetic nanoparticles and between nanoparticle agglomerates.

The results obtained are important for understanding the influence of magnetic filler properties and magnetic interactions on the functional properties of the magnetoelectric composite, which finds its use in biomedical applications as a cellular scaffold that promotes accelerated cell growth and change.

FUNDING

This work was supported by the Russian Science Foundation (project No. 21-72-30032).

ACKNOWLEDGEMENT

The authors are grateful to Vorontsov S.A. for the fabrication of the composites investigated in this work.

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## FIGURE CAPTIONS

Figure 1. Field dependence of magnetization measured at room temperature of PVDF-based composites with CFO nanoparticles (blue, solid line), CFO-BTO (blue, dashed line) and CFO-FO (green).

Figure 2. Field dependence of residual magnetization $M_{DCD}$and switching field distribution (SFD) of nanocomposites filled with CFO particles (a), CFO-BTO (b), CFO-FO (c). Field dependence of the particle interaction intensity ($\delta m$) for all samples (d).

Figure 3. FORC curves and SFD plot (left); FORC diagrams (right) for composites with CFO (a), CFO-BTO (b), CFO-FO (c) particles. The FORC-diagram inset for the

CFO-FO composite shows an enlarged region 2 with enhanced color contrast for better visualization of the response of the magnetosolid phase.

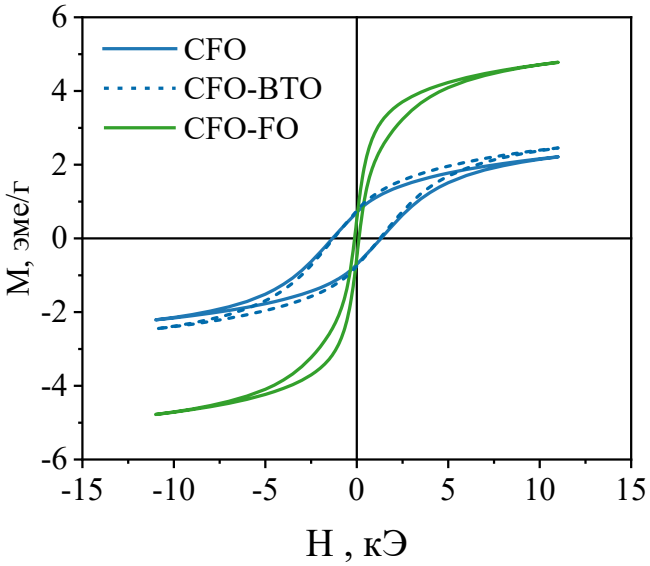



Fig. 1.

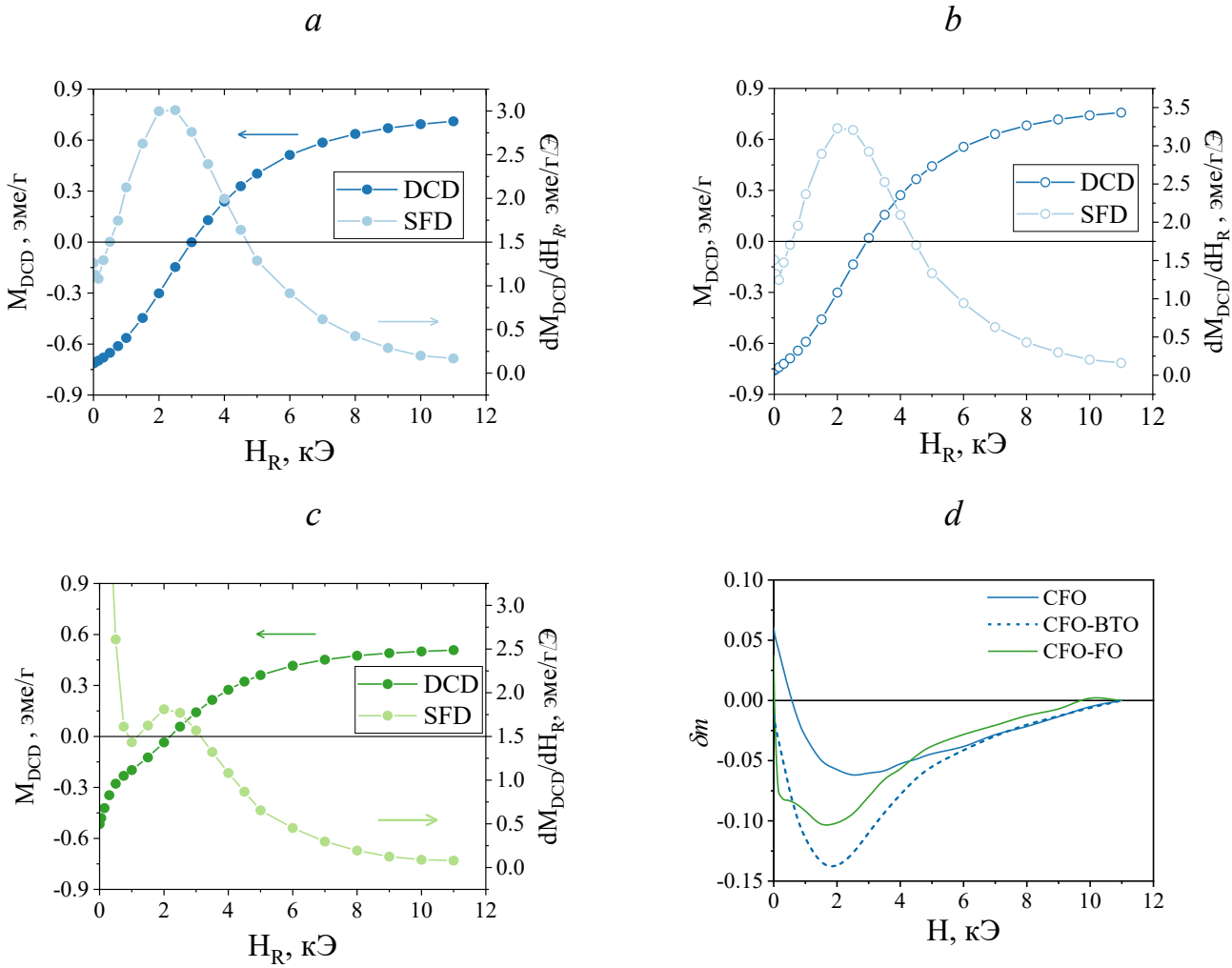
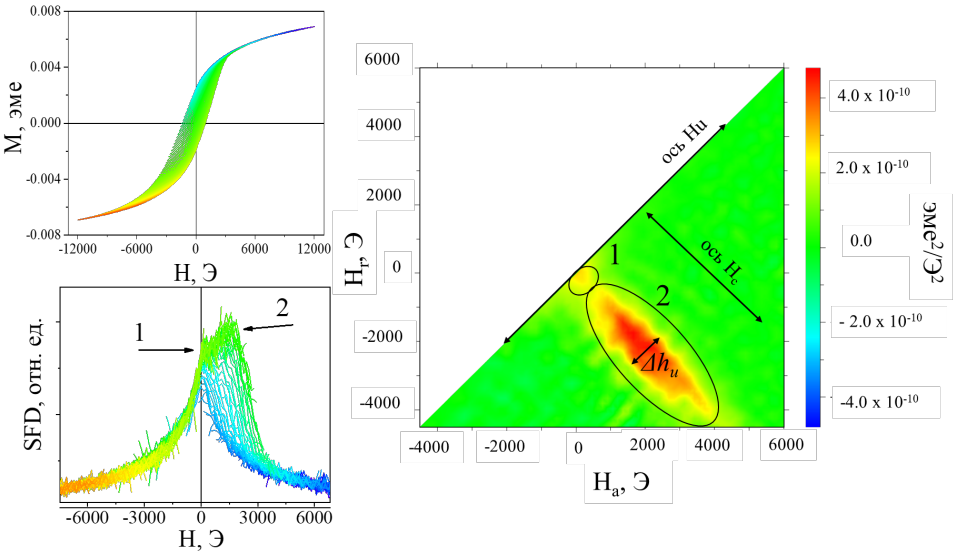

a
b
c
d
DCD
SFD
$M_{DCD}$, эме/г
$dM_{DCD}/dH_R$, эме/г/Э
$H_R$, кЭ
CFO
CFO-BTO
CFO-FO
δm
H, кЭ

Fig. 2

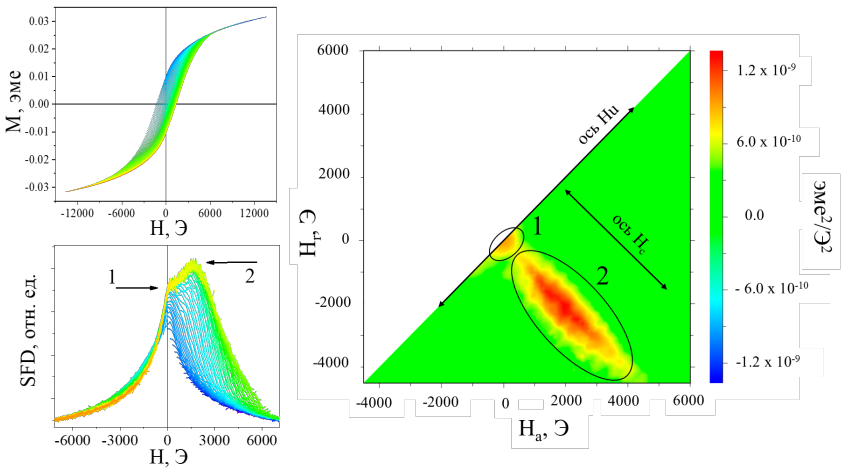
*a*

CFO




*b*

CFO-BTO




*c*

CFO-FO

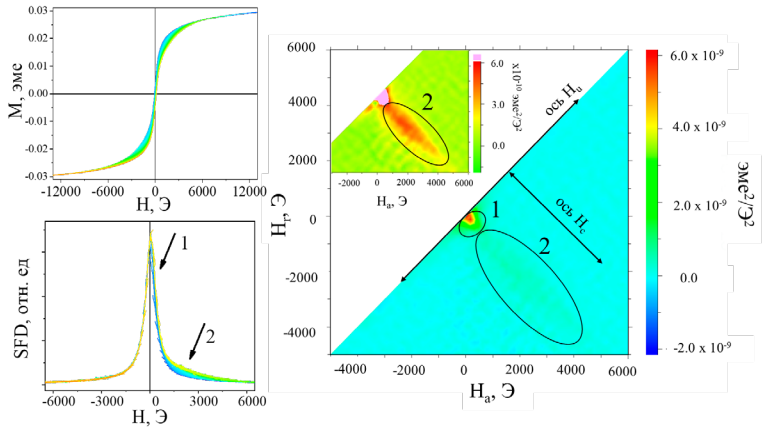



Fig. 3.