

Superparamagnetism of $\text{Fe}_3\text{O}_4\text{--Fe}_{3-x}\text{Ti}_x\text{O}_4$ Composites: Micromagnetic Modeling

P. V. Kharitonskii^a, K. G. Gareev^a, A. Yu. Ralin^{b,*}, and E. S. Sergienko^c

^a Saint Petersburg Electrotechnical University “LETI”, St. Petersburg, 197022 Russia

^b Far Eastern Federal University, Vladivostok, 690922 Russia

^c Saint Petersburg State University, St. Petersburg, 199034 Russia

*e-mail: ralin.ayu@dvfu.ru

Received October 14, 2022; revised November 21, 2022; accepted November 24, 2022

The magnetic properties of $\text{Fe}_3\text{O}_4\text{--Fe}_{3-x}\text{Ti}_x\text{O}_4$ composites synthesized by various methods were simulated based on the model of an ensemble of magnetostatically interacting particles. The results are in good agreement with the hysteresis characteristics of the samples calculated earlier in the framework of the model of chemically heterogeneous two-phase particles. It is shown that the used approach is also applicable to the samples consisting mainly of superparamagnetic particles in which the saturation remanent magnetization is provided by the particles blocked due to the magnetostatic interaction.

Keywords: composites, non-stoichiometric magnetite, micromagnetic modeling, two-phase particles, magnetostatic interaction, superparamagnetism, effective spontaneous magnetization

DOI: 10.1134/S0031918X22601779

INTRODUCTION

Solid solutions of $\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti})_{-2}\text{O}_4$ iron oxides (magnetite, maghemite, hematite, etc.) with the presence of titanium are often called “titanomagnetites” and denoted as $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$. They can have significant spontaneous magnetization and high catalytic activity, so they are used as a renewable catalyst in organic synthesis [1–5]. The number of titanium atoms in the crystal lattice of titanomagnetites sets the ratio of the content of divalent and trivalent iron cations. Therefore, the particles may be a regulated reduction–oxidation system, which is used in the biotransformation of iron nanomaterials and production of metalloenzymes [6, 7]. A considerable part of magnetic rocks contains exactly titanomagnetites, therefore, by studying them, it is possible to obtain data on the evolution of the lithosphere and the Earth’s magnetic field, see, e.g., [8].

In a series of experiments presented in [9–11], $\text{Fe}_3\text{O}_4\text{--Fe}_{3-x}\text{Ti}_x\text{O}_4$ composites containing titanomagnetite were synthesized by different methods under thermodynamically different conditions. To study their physicochemical properties, a comprehensive approach was applied, including analysis of the structure, phase, and elemental composition, study of the magnetic characteristics, and theoretical modeling.

It was shown in [9–12] that three groups of ferromagnetic particles can be distinguished in all the studied samples: the strongly magnetic fraction of

chemically heterogeneous particles (magnetite/maghemite–titanomagnetite), the weakly magnetic fraction (hematite, goethite, and other iron hydroxides), and superparamagnetic particles belonging to the first two fractions. The main contribution to the remanent magnetization is made by few-domain (pseudo-single-domain) chemically heterogeneous particles.

The study of superparamagnetic magnetite nanoparticles [13] showed that the critical size of the transition to the single-domain state at room temperature is about 11 nm. However, for spherical particles, this value is known to be about 30 nm [14]. The underestimation of the size may be due to the fact that the authors of [13] assumed the particles to be non-interacting, although their earlier works [15, 16] show that the concentration of magnetite grains is large enough and the magnetostatic interaction must be significant. The situation is similar for hematite nanoparticles [17].

In [11, 12], the model of two-phase particles (TP) [18] was used to describe the magnetic states of chemically heterogeneous particles, taking into consideration their magnetostatic interaction. An ensemble of cubic two-phase particles with characteristic size a and phase volumes: $(1-\varepsilon)a^3$ —magnetite phase and εa^3 —titanomagnetite phase was considered. It was assumed that the easy magnetization axes of the phases are parallel to the interphase boundary. Then, in the absence of an external field, the magnetic

moments in the phases are either opposite in direction or their directions coincide. Applying an external field along the easy axes does not increase the number of possible states of a particle, but it changes the values of their relative fraction. The number of particles in different states was calculated on the basis of the statistical Boltzmann distribution.

This allowed calculating the remagnetization fields of the particles and estimating the hysteresis characteristics of the first fraction, which agree well with the experimental data (taking into consideration the contributions of the other fractions). The possibility of applying the same model to “superparamagnetic” samples was demonstrated [12].

Since the magnetostatic interaction even at small volume concentrations of the ferrimagnetic ($\sim 1\%$) can significantly affect the magnetization processes [19], it is necessary to consider the interaction parameters more accurately. One can use the mean-field approximation for which the random field distribution functions are calculated [20].

In works [9, 10], the theoretical model of single-domain magnetostatically interacting ferrimagnetic particles with effective spontaneous magnetization (SDEM) was verified. This parameter allowed us to phenomenologically take into consideration the magnetic and chemical heterogeneity of the particles. The model is described in more detail further in the section “Theoretical Modeling”.

The purpose of this work is to bring the two considered models of TP and SDEM into agreement for all synthesized samples and to substantiate more strictly the applicability of the two-phase particle model for superparamagnetic samples.

SYNTHESIS PARAMETERS AND HYSTERESIS CHARACTERISTICS OF THE SAMPLES

The samples of three series synthesized by different methods are simulated. The synthesis of composites based on the $\text{Fe}_m\text{O}_n\text{-TiO}_2$ system (series T) was performed by magnetite precipitation in a suspension of submicron TiO_2 [9, 10]. 4 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 2 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (molar ratio 2 : 1) were dissolved in 100 mL of distilled water and dispersed in a solution of 0.5, 1.0, or 2.0 g of TiO_2 powder (samples T05L/T05H, T10L, and T20L/T20R respectively). 10 mL of 25% aqueous ammonia solution was added to the suspension. The resulting magnetic precipitate was washed using a Nd–Fe–B permanent magnet until pH 7 and no chloride and sulfate ions were present. The powders were dried at room temperature and subjected to hydrothermal treatment (Table 1).

The samples of the Cp series were obtained by joint precipitation of salts ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ in the molar ratio of 2:1) and an aqueous solution of TiCl_4 [11]. The samples of the P series were obtained

Table 1. Sample treatment conditions: temperature, pressure, medium, time

Series	Sample	Conditions
T	T05L	240°C, 50 MPa, H_2O , 4 h
	T10L	240°C, 50 MPa, H_2O , 4 h
	T20L	240°C, 50 MPa, H_2O , 4 h
	T05H	470°C, 42 MPa, H_2O , 4 h
	T20R	Untreated
	Cp	CpIn
CpH4		240°C, 50 MPa, H_2O , 4 h
CpH4Ar		240°C, 30 MPa, H_2O (Ar), 4 h
CpS24		250°C, 70 MPa, $\text{C}_3\text{H}_8\text{O}$, 24 h
CpS72		250°C, 70 MPa, $\text{C}_3\text{H}_8\text{O}$, 72 h
P	PIn	Untreated
	PH4	240°C, 50 MPa, H_2O , 4 h
	PS4	250°C, 70 MPa, $\text{C}_3\text{H}_8\text{O}$, 4 h

by precipitation of the titanium-containing component on previously obtained magnetite/maghemite particles (we also used $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ in the molar ratio of 2:1 and an aqueous solution of TiCl_4) [11]. Aqueous ammonia solution was used as a precipitant. To remove residual chloride and sulfate ions, the obtained precipitates were washed with distilled water using a permanent Nd–Fe–B magnet until reaching pH 7. The powder was dried at 40°C and subjected to hydrothermal (distilled water—samples CpH4, CpH4Ar, and PH4) or solvothermal (dehydrated isopropanol – samples CpS24, CpS72, and PS4) treatment (Table 1). When synthesizing the CpH4Ar sample, in order to remove dissolved gases, the water was treated with ultrasound and boiled, and the autoclave volume not filled with water was purged and then filled with inert gas (Ar 99.998%).

Table 2 shows the experimental hysteresis characteristics of the studied samples [9–11]: saturation magnetization M_s , saturation remanence M_{rs} , coercive force H_c , remanence coercivity H_{cr} .

According to magnetic granulometry [21], two groups of samples can be distinguished. For the first nine samples in the upper part of the table, the M_{rs}/M_s ratios are in the range of 0.11–0.23 and H_{cr}/H_c in the range of 2–3. Consequently, the first group of samples is dominated by single- and few-domain particles. Sample T20R from the second group can be attributed to the superparamagnetic type since the same ratios for it are 0.012 and 3.7, respectively. For the last three samples in the lower part of the table (P series), the M_{rs}/M_s values are two orders of magnitude lower (0.002–0.003) than in the first group and the hysteresis loop is very narrow, i.e. they also belong to the superparamagnetic type. For these samples, it was not

Table 2. Hysteresis characteristics of the samples

Sample	M_s , A m ² /kg	M_{rs} , A m ² /kg	$\mu_0 H_c$, mT	$\mu_0 H_{cr}$, mT
T05L	26.4	2.9	5.6	14.9
T10L	19.5	2.1	4.8	12.6
T20L	14.1	1.9	6.0	13.8
T05H	23.8	4.2	8.8	18.3
CpIn	26.1	3.3	5.4	15.6
CpH4	17.3	4.0	9.0	17.6
CpH4Ar	32.9	5.5	8.9	20.5
CpS24	33.7	5.4	8.0	18.8
CpS72	33.2	5.0	8.3	20.2
T20R	28.9	0.35	0.51	1.9
PIn	40.1	0.11	0.12	–
PH4	31.2	0.07	0.08	–
PS4	41.1	0.13	0.12	–

Table 3. Magnetizations M_s and M_{rs} of the corresponding three fractions for the first group of samples

Sample	M_{s1} , A m ² /kg	M_{rs1} , A m ² /kg	M_{s2} , A m ² /kg	M_{rs2} , A m ² /kg	$M_{s\ sp}$, A m ² /kg
T05L	10.1	2.9	0.3	0.07	16.0
T10L	7.3	2.0	0.2	0.05	12.0
T20L	6.2	1.8	0.3	0.08	7.6
T05H	22.1	3.8	0.6	0.36	1.1
CpIn	13.9	3.2	0.3	0.08	11.8
CpH4	15.7	3.5	0.8	0.50	0.8
CpH4Ar	27.1	5.1	0.6	0.35	5.3
CpS24	25.0	5.1	0.4	0.24	8.3
CpS72	22.6	4.8	0.4	0.18	10.2

Table 4. Concentrations C of the corresponding three fractions for the first group of samples

Sample	C_1	C_2	C_{sp}
T05L	0.05	0.17	0.34
T10L	0.04	0.16	0.32
T20L	0.03	0.20	0.27
T05H	0.11	0.40	0.02
CpIn	0.07	0.20	0.22
CpH4	0.08	0.40	0.02
CpH4Ar	0.14	0.28	0.08
CpS24	0.11	0.27	0.12
CpS72	0.10	0.25	0.16

possible to determine the value of H_{cr} experimentally. However, knowing the value of H_c , the minimum value of H_{cr} for these samples was accepted in the calculations, taking into consideration the condition $H_{cr}/H_c \geq 10$ [21].

THEORETICAL MODELING

To bring the two models (TP and SDEM) into agreement, let us give more detailed results of calculations using the TP model, since the works [11, 12] only specified the ranges of values for some characteristics.

Tables 3 and 4 contain data for the samples of the first group for which the best agreement with the experiment was obtained with the following parameters: the average size of the two-phase particles is 60 nm, the relative thickness of the titanomagnetite phase is in the range of 0.05–0.20 depending on titanium content, and the total volume concentration of the ferrimagnetic is 0.5–0.6.

Table 3 shows that the main contribution to the remanent magnetization is made by the first fraction, which consists mainly of few-domain chemically heterogeneous particles. Therefore, we will further analyze and coordinate the magnetic properties of this fraction.

The data in Table 4 generally correlates well with the synthesis conditions. For example, the minimum number of superparamagnetic particles in samples T05H and CpH4 is associated with strong oxidation of the magnetic material under the action of temperature in the first case or exposure to a hydrothermal environment in the second case.

Table 5 shows the calculated values of the spontaneous magnetizations of the magnetite I_{s11} and titanomagnetite I_{s12} phases. The I_{s11} values are lower than for the single-domain magnetite grain because of magnetic heterogeneity (grain size is 60 nm) and non-stoichiometry of the first phase. The remanence coercivity values H_{cr1} were calculated within the TP model. The coercive force values of the first fraction H_{c1} were calculated from the H_{cr1} values taking into consideration the interaction between the particles and the chaotization of their easy axes [11].

Tables 6 and 7 present the data for the samples of the second group containing mainly superparamagnetic particles for which the best agreement with the experiment was obtained for the following parameters: the average size of the two-phase particles for sample T20R is 30 nm, for the P series samples is 13 nm, the relative thickness of titanomagnetite phase is 0.05 and 0.10, respectively (the absolute thickness values are approximately equal: 1.5 nm and 1.3 nm). In this group, the first fraction with volume concentration C_{1b} , which determines the saturation remanence of the sample, is represented by the particles blocked due to magnetostatic interaction. The third fraction with

concentration C_{nb} contains unblocked particles of the first two fractions. As for the samples of the first group, the total volume concentration of the ferrimagnetic is in the range of 0.5–0.6.

We can see that the parameters of sample T20R noticeably differ from the others. This is explained by the fact that it is borderline between the single-domain and superparamagnetic states in terms of the average particle size (30 nm).

Table 8 shows the spontaneous magnetizations of the magnetite I_{s11} and titanomagnetite I_{s12} phases accepted in the calculation. Additionally, the concept of spontaneous magnetization calculated from saturation remanence (I_{rs11} and I_{rs12}) was introduced, since in a zero external field there is a significant decrease in the magnetic moments of the phases due to the influence of thermal fluctuations [22]. Coercive forces H_{cr1} and H_{c1} were calculated similarly to the samples of the first group.

In the TP model, magnetization of the sample was calculated in the approximation of a uniform distribution of random fields of interaction H_i in the interval from $-H_{max}$ to $+H_{max}$:

$$M(H_e) = \frac{1}{2H_{max}} \int_{-H_{max}}^{H_{max}} M(H_e, H_i) dH_i, \quad (1)$$

Here, $M(H_e, H_i)$ is determined by the number of particles in different magnetic states [11]. Then, in the first approximation, the magnetization calculation is reduced to the case of non-interacting particles, taking into consideration the reduction of the critical fields by the H_{max} value. For conditionally weak and conditionally strong magnetostatic interaction [19]:

$$\begin{aligned} H_{max} &\approx 5C_1 I_{s1} \text{ at } C_1 < 0.07; \\ H_{max} &\approx 1.3\sqrt{C_1} I_{s1} \text{ at } C_1 > 0.07, \end{aligned} \quad (2)$$

where I_{s1} is the average spontaneous magnetization of the two-phase grain. The characteristic interaction field H_{max} is mainly determined by the parameters of the two-phase particle fraction, since the spontaneous magnetization of the weakly magnetic fraction I_{s2} is two orders of magnitude lower than I_{s1} .

It is known that, at sufficiently high concentrations of the ferrimagnetic, magnetization of the sample is significantly affected by the magnetostatic interaction. Besides, as indicated above, the interaction leads to blocking the magnetic moments of a part of the superparamagnetic particles which contribute to the remanent magnetization. Using the mean-field approximation, we can calculate the random field distribution functions for any volume concentrations of the ferrimagnetic [20] and take these factors into consideration more strictly.

Using the model of interacting single-domain particles [23] and the known values of magnetizations M_s

Table 5. Spontaneous magnetizations of I_{s11} and I_{s12} phases, coercive force H_{c1} , and remanence coercivity H_{cr1} of the two-phase particle fraction for the first group of samples

Sample	I_{s11} , kA/m	I_{s12} , kA/m	$\mu_0 H_{c1}$, mT	$\mu_0 H_{cr1}$, mT
T05L	400	380	14.6	52.0
T10L	400	380	9.8	35.1
T20L	400	380	13.6	45.8
T05H	400	380	4.8	28.2
CpIn	400	380	8.0	35.1
CpH4	400	380	7.8	35.1
CpH4Ar	400	380	6.6	35.1
CpS24	460	440	8.3	40.5
CpS72	450	430	8.7	40.7

Table 6. Magnetizations M_s and M_{rs} of the corresponding three fractions for the second group of samples

Sample	M_{s1b} , A m ² /kg	M_{rs1b} , A m ² /kg	M_{s2b} , A m ² /kg	M_{rs2b} , A m ² /kg	$M_{s nb}$, A m ² /kg
T20R	23.7	0.23	0.5	0.116	4.7
PIn	22.9	0.11	0.3	0.004	17.0
PH4	12.8	0.06	0.2	0.007	18.1
PS4	25.9	0.13	0.3	0.001	15.0

Table 7. Concentrations C of the corresponding three fractions for the second group of samples

Sample	C_{1b}	C_{2b}	C_{nb}
T20R	0.12	0.34	0.09
PIn	0.12	0.17	0.21
PH4	0.07	0.16	0.31
PS4	0.13	0.19	0.19

Table 8. Spontaneous magnetizations of I_{s11} and I_{s12} phases, coercive force H_{c1} , and remanence coercivity H_{cr1} of the two-phase particle fraction for the second group of samples

Sample	I_{s11} , kA/m	I_{rs11} , kA/m	I_{s12} , kA/m	I_{rs12} , kA/m	$\mu_0 H_{c1}$, mT	$\mu_0 H_{cr1}$, mT
T20R	400	15	380	13	0.64	2.46
PIn	400	8	380	7	0.24	0.99
PH4	400	10	10	5	0.11	0.58
PS4	400	11	380	10	0.16	0.88

Table 9. Effective spontaneous magnetizations $I_{rs\text{ eff}}$ of samples of the second group

Sample	$I_{rs\text{ eff}}$, kA/m
T20R	15.1
PIn	7.9
PH4	9.5
PS4	10.9

and M_{rs} , effective spontaneous magnetization I_{eff} of the particles can be calculated (SDEM model). Introduction of the concept of I_{eff} is related to the heterogeneous distribution of magnetic moment over the grain volume, which is determined by the formation of domain and vortex-like structures, as well as by the chemical heterogeneity of the grain [24–26].

To find the I_{eff} value of the first fraction, we solved the inverse problem of matching the theoretical values of magnetization M_{TPh} and M_{SD} calculated by the TP and SDEM models, respectively. Dimensionless magnetization:

$$\zeta_{\text{TPh}} = \frac{M_{\text{TPh}}}{C_1 I_{\text{eff}}}, \quad C_1 = N \frac{V}{V}. \quad (3)$$

Here, N is the number of ferrimagnetic particles with an average volume v and concentration C_1 in a sample of volume V . Magnetization of a system of uniaxial ferrimagnetic particles randomly distributed in a cylindrical volume is determined using a modified method of moments and Gram–Charlier series [9, 20]:

$$\zeta_{\text{SD}} = \frac{M_{\text{SD}}}{C_1 I_{\text{eff}}} = \text{erf}\left(\frac{x_0}{\sqrt{2}}\right) - \varphi_u(x_0) \times \left[\frac{\gamma_1}{3} H_2(x_0) - \frac{\gamma_2}{12} H_3(x_0) - \frac{\gamma_1^2}{36} H_5(x_0) \right]. \quad (4)$$

In our calculations, $x_0 = (H_0 + H_e + H_m)/\sigma$, where H_0 is the particle remagnetization field, H_e is the external field, and H_m and σ are the mean and RMS values of the interaction field, respectively. Note that the concentration values calculated within the TP model were used in the SDEM model (Tables 4 and 7). The average remagnetization field of an individual particle H_0 is determined from experiment as remanence coercivity H_{cr} . Function $\varphi_u(x_0)$ is the probability density of the normal distribution, where γ_1 is asymmetry, γ_2 is kurtosis, and H_2 , H_3 , H_5 are Hermite polynomials of 2nd, 3rd and 5th order, respectively. Magnetization ζ_{SD} depends on I_{eff} through the moments of the distribution function.

The values of effective spontaneous magnetizations $I_{s\text{ eff}}$ and $I_{rs\text{ eff}}$ are found from the condition of equality of functions $\zeta_{\text{TPh}}(I_{\text{eff}})$ and $\zeta_{\text{SD}}(I_{\text{eff}})$ by substituting values M_s and M_{rs} for the first fraction from Tables 3 or 6.

For the saturation magnetization, the results for all samples when both models (TP and SDEM) were applied coincide completely, since the external field is large ($H_e = 5570$ kA/m). For the saturation remanent magnetization, the $I_{rs\text{ eff}}$ value obtained by the SDEM model should be multiplied by the $H_{\text{cr1}}/H_{\text{c1}}$ ratio, which takes into consideration the scattering of the easy axes of the particles and the appearance of vortex and domain structures in a zero external field [11].

For the samples of the first group, the value of $I_{rs\text{ eff}}$ is obtained equal to average spontaneous magnetization I_{s1} , which is close to I_{s11} (see Table 5), since the thickness of the titanomagnetite phase is small.

For the blocked particles that contribute to the remanent magnetization in the samples of the second group, the time-averaged non-zero magnetic moment is equal to (see, e.g., [11]):

$$m(v, H_i) = v I_s \tanh\left(\frac{v_b(H_i) I_s |H_i|}{kT}\right) = v I_{rs\text{ eff}}, \quad (5)$$

where I_s is the spontaneous magnetization of the ferrimagnetic at temperature T , $v_b(H_i)$ is the critical volume of the particle whose magnetic moment remains stable when the H_i interaction field acts on the particle. In this case, the blocking volume

$$v_b(H_i) = \begin{cases} v_b / \left(1 + \frac{|H_i|}{H_0}\right)^2, & |H_i| \leq H_0; \\ v_b / \left(\frac{4|H_i|}{H_0}\right), & |H_i| > H_0. \end{cases} \quad (6)$$

Remagnetization field $H_0 \approx H_{\text{cr1}}$, $v_b \approx 50kT/(I_s H_0)$ is the blocking volume at $H_i = 0$ [27].

Then, for the superparamagnetic samples (Table 9) $I_{rs\text{ eff}}$ is significantly smaller than for the samples of the first group, because the magnetic moments of fewer particles are blocked in the zero external field.

Comparison of the data in Tables 8 (TP model) and 9 (SDEM model) shows good agreement between the values of I_{rs11} (the relative thickness of the titanomagnetite phase is small, so its contribution to the magnetic moment of the particle is insignificant) and $I_{rs\text{ eff}}$, which confirms the validity of using the TP model for superparamagnetic samples.

CONCLUSIONS

Thus, this paper demonstrates the consistent applicability of the two theoretical models that take into consideration the magnetostatic interaction between ferrimagnetic particles to describe the magnetic properties of the synthesized $\text{Fe}_3\text{O}_4\text{--Fe}_{3-x}\text{Ti}_x\text{O}_4$ composites.

The advantage of the two-phase model is the explicit consideration of chemical heterogeneity and magnetostatic interaction between phases using the method of magnetic rectangles [28], which allows cal-

culating the number of particles in different magnetic states and remagnetization fields.

The advantage of the model of single-domain particles with effective spontaneous magnetization is a more strict consideration of magnetostatic interaction at any concentration of ferrimagnetic particles, as well as less complicated calculations if the expansion of the random interaction field distribution function is limited to the first few terms (Gram-Charlier or Edgeworth series) [20].

It has been demonstrated that both models can be applied not only to samples containing mainly single-domain and few-domain chemically heterogeneous ferrimagnetic particles, but also to samples consisting mainly of superparamagnetic, including chemically heterogeneous, particles in which the saturation remanent magnetization is provided by blocked particles due to magnetostatic interaction.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Y. Zhong, X. Liang, Y. Zhong, J. Zhu, S. Zhu, P. Yuan, H. He, and J. Zhang, "Heterogeneous UV/Fenton degradation of TBBPA catalyzed by titanomagnetite: Catalyst characterization, performance and degradation products," *Water Res.* **46**, 4633–4644 (2012).
2. J. Zhang, C. Zhang, G. Wei, C. Zhang, J. Zhu, H. He, and X. Liang, "Catalytic activity of titanomagnetite in heterogeneous fenton reaction: Contribution from structural Fe^{2+} and Fe^{3+} ," *J. Nanosci. Nanotechnol.* **17**, 7015–7020 (2017).
3. D. Azarifar, Y. Abbasi, and O. Badalkhani, "Sulfonic acid-functionalized titanomagnetite nanoparticles as recyclable heterogeneous acid catalyst for one-pot solvent-free synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones," *J. Iran. Chem. Soc.* **13**, 2029–2038 (2016).
4. D. Azarifar, R. Asadpoor, O. Badalkhani, M. Jaymand, E. Tavakoli, and M. Bazouleh, "Sulfamic-acid-functionalized $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles as novel magnetic catalyst for the synthesis of hexahydroquinolines under solvent-free condition," *Chem. Select* **3**, 13722–13728 (2018).
5. D. Azarifar, O. Badalkhani, and Y. Abbasi, "Silica-modified magnetite Fe_3O_4 nanoparticles grafted with sulfamic acid functional groups: an efficient heterogeneous catalyst for the synthesis of 3,4-dihydropyrimidin-2(1H)-one and tetrahydrobenzo[b]pyran derivatives," *J. Sulfur Chem.* **37**, 656–673 (2016).
6. J. Liu, C. I. Pearce, C. Liu, Z. Wang, L. Shi, E. Arenholz, and K. M. Rosso, " $\text{Fe}_{(3-x)}\text{Ti}_x\text{O}_4$ nanoparticles as tunable probes of microbial metal oxidation," *J. Am. Chem. Soc.* **135**, 8896–8907 (2013).
7. C. I. Pearce, O. Qafoku, J. Liu, E. Arenholz, S. M. Heald, R. K. Kukkadapu, C. A. Gorski, C. M. B. Henderson, and K. M. Rosso, "Synthesis and properties of titanomagnetite ($\text{Fe}_{(3-x)}\text{Ti}_x\text{O}_4$) nanoparticles: A tunable solid-state Fe(II/III) redox system," *J. Colloid Interface Sci.* **387**, 24–38 (2012).
8. M. W. McElhinny and P. L. McFadden, *Paleomagnetism: Continents and Oceans* (Academic Press, San Diego, 2000), p. 386.
9. P. Kharitonkii, S. Kirillova, K. Gareev, A. Kamzin, A. Gurylev, A. Kosterov, E. Sergienko, A. Valiullin, and E. Shevchenko, "Magnetic granulometry and Mössbauer spectroscopy of synthetic $\text{Fe}_m\text{O}_n\text{-TiO}_2$ composites," *IEEE Trans. Magn.* **56**, 7200209 (2020).
10. P. V. Kharitonkii, A. A. Kosterov, A. K. Gurylev, K. G. Gareev, S. A. Kirillova, N. A. Zolotov, and Yu. A. Anikieva, "Magnetic states of two-phase synthesized $\text{Fe}_m\text{O}_n\text{-Fe}_{3-x}\text{Ti}_x\text{O}_4$ nanoparticles: experimental and theoretical analysis," *Fiz. Tv. Tela* **62** (9), 1527–1530 (2020).
11. P. Kharitonkii, N. Zolotov, S. Kirillova, K. Gareev, A. Kosterov, E. Sergienko, S. Yanson, A. Ustinov, and A. Ralin, "Magnetic granulometry, Mössbauer spectroscopy, and theoretical modeling of magnetic states of $\text{Fe}_m\text{O}_n\text{-Fe}_{3-x}\text{Ti}_x\text{O}_4$ composites," *Chinese J. Phys.* **78**, 271–296 (2022).
12. P. V. Kharitonkii, Yu. A. Anikieva, N. A. Zolotov, K. G. Gareev, and A. Yu. Ralin, "Micromagnetic simulation of $\text{Fe}_3\text{O}_4\text{-Fe}_{3-x}\text{Ti}_x\text{O}_4$ composites," *Fiz. Tv. Tela* **64** (9), 1323–1327 (2022).
13. H. Y. Hah, S. Gray, C. E. Johnson, J. A. Johnson, V. Kolesnichenko, P. Kucheryavy, and G. Goloverda, "Mössbauer spectroscopy of superparamagnetic Fe_3O_4 nanoparticles," *J. Magn. Magn. Mater.* **539**, 168382 (2021).
14. D. J. Dunlop, "Superparamagnetic and single-domain threshold sizes in magnetite," *J. Geophys. Res.* **78**, 1780–1793 (1973).
15. P. Kucheryavy, J. He, V. T. John, P. Maharjan, L. Spinu, G. Z. Goloverda, and V. L. Kolesnichenko, "Superparamagnetic iron oxide nanoparticles with variable size and an iron oxidation state as prospective imaging agents," *Langmuir* **29**, 710–716 (2013).
16. C. E. Johnson, J. A. Johnson, H. Y. Hah, M. Cole, S. Gray, V. Kolesnichenko, P. Kucheryavy, and G. Goloverda, "Mössbauer studies of stoichiometry of Fe_3O_4 : characterization of nanoparticles for biomedical applications," *Hyperfine Interact.* **237**, 27 (2016).
17. I. A. Al-Omari, V. Narayanaswamy, S. Halder, H. H. Hamdeh, S. Alaabed, A. S. Kamzin, Gopi C. V. Muralee, A. Khaleel, B. Issa, and I. M. Obaidat, "Mössbauer investigations in hematite nanoparticles," *Bioint. Res. Appl. Chem.* **12**, 4626–4636 (2016).
18. A. Yu. Ralin and P. V. Kharitonkii, "Magnetic metastability of small inhomogeneous ferrimagnetic particles," *Fiz. Met. Metalloved.* **78** (3), 38–43 (1994).
19. V. P. Shcherbakov, "On the distribution function of molecular fields in systems with randomly distributed centers of interaction," *Fiz. Met. Metalloved.* **48** (6), 1134–1137 (1979).
20. A. S. Al'miev, A. Yu. Ralin, and P. V. Kharitonkii, "Distribution functions of dipole-dipole interaction fields of dilute magnets," *Fiz. Met. Metalloved.* **78** (1), 28–34 (1994).
21. J. L. Kirschvink, D. S. Jones, and B. J. MacFadden, *Magnetite Biomineralization and Magnetoreception in*

- Organisms. A New Biomagnetism* (Plenum, New York, 1985), p. 682.
22. A. Yu. Ralin and P. V. Kharitonskii, "Effect of thermal fluctuations on the stability of the magnetic state of small two-phase ferrimagnetic particles," *Phys. Met. Metallogr.* **93** (2), 109–114 (2002).
 23. P. V. Kharitonskii, "Magnetostatic interaction of superparamagnetic particles scattered in a thin layer," *Fiz. Tv. Tela* **39** (1), 185–186 (1997).
 24. A. P. Roberts, T. P. Almeida, N. S. Church, R. J. Harrison, D. Heslop, Y. Li, J. Li, A. R. Muxworthy, W. Williams, and X. Zhao, "Resolving the origin of pseudo-single domain magnetic behavior," *J. Geophys. Res. Solid Earth* **122**, 9534–9558 (2017).
 25. M. Starowicz, P. Starowicz, J. Żukrowski, J. Przewoźnik, A. Lemański, C. Kapusta, and J. Banaś, "Electrochemical synthesis of magnetic iron oxide nanoparticles with controlled size," *J. Nanoparticle Res.* **13**, 7167–7176 (2011).
 26. A. P. Roberts, L. Tauxe, D. Heslop, X. Zhao, and Z. Jiang, "A critical appraisal of the "Day" diagram," *J. Geophys. Res. Solid Earth* **123**, 2618–2644 (2018).
 27. L. Néel, "Théorie du traînage magnétique des ferromagnétiques en grains fins avec application aux terres cuites," *Ann. Géophys.* **5**, 99–136 (1949).
 28. P. V. Kharitonskii and A. M. Frolov, "Simulation of magnetostatic interaction in multilayer structures," *Izv. VUZov. Fiz.* **53** (3-2), 197–200 (2010).

SPELL: 1. ok