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Effect of pH on the interparticle magnetic interaction in ensembles of barium hexaferrite particles

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The pH effect on the parameter of interparticle magnetic interaction of a compacted system of oxide ferromagnet is studied. An unpredictable change in the sign of the interparticle interaction parameter Δm at 300 K was found after the surface of microcrystals was treated with of acid and alkali solutions. The observed effect confirms the decisive role of surface spins in the interparticle interaction.
Keywords: interparticle magnetic interaction, barium hexaferrite, pH effect.

Вплив pH на міжчастинкову магнітну взаємодію в ансамблях частинок гексафериту барію. *І.О.Ведерникова, А.О.Коваль, М.М.Івашура, А.А.Івашура, О.М.Борисенко*

Досліджено вплив pH на параметр міжчастинкової магнітної взаємодії ущільненої системи оксидного феромагнетику. Виявлено зміни знака параметра міжчастинкової взаємодії Δm при 300 К у результаті обробки поверхні мікрокристалів розчинами кислоти та лугу. Ефект, який спостерігається, підтверджує вирішальну роль поверхневих спінів у взаємодії між частинками.

Исследовано влияние pH на параметр межчастичного магнитного взаимодействия уплотненной системы оксидного ферромагнетика. Обнаружено изменение знака параметра межчастичного взаимодействия Δm при 300 К в результате обработки поверхности микрокристаллов растворами кислоты и щелочи. Наблюдаемый эффект подтверждает решающую роль поверхностных спинов во взаимодействии между частицами.

1. Introduction

Nanotechnology is a field of growing interest for many physicists and chemists and for pharmacists as well. Currently, the development of nanotechnology in pharmacy and medicine is focusing on the design of new magnetically controlled drug delivery systems with ferrite nanoparticles [1–10]. The use of finely dispersed ferrite particles in drug delivery systems involves the study of specific properties of individual particles and their ensembles. An important factor for a magnetically concentrated medium (tightly packed powder, emulsion, magnetic liquid) is the interparticle magnetic interaction, which is extremely sensitive to internal and external factors. Internal factors are particle size and degree of their orientation, magnetic moment, magnetic state, and effective magnetic anisotropy. External factors include the concentration of magnetic particles, temperature and the magnitude of the magnetic field (MF).

The interparticle magnetic interactions in ferrite powders were considered in a number of works [11–15]. The sign of the interparticle magnetic interaction parameter can be either positive or negative. A negative value of the interaction parameter corresponds to the stabilization of the magnetized state of the sample and prevents an increase in magnetization under the action of an applied magnetic field. A positive value of the interaction parameter contributes to the magnetization of the sample. The prevalence of interactions of one sign or another in a particle system depends on many factors, such as packing density, degree of texture, magnetic parameters of the material, and external influence (magnetic field, temperature).

When creating new magnetically controlled drug delivery systems for internal use, it is important to predict the functional magnetic parameters of nanoparticles and their possible changes in aggressive media of the gastrointestinal tract and other physiological fluids. This approach allows us to predict the magnetic behavior of the dosage form and to assess its ability to be magnetically controlled.

The idea was to study the parameter of interparticle magnetic interaction of a compacted system of oxide ferromagnet particles and to analyze how the interaction is influenced by the changes in the physical and chemical state of the particle surface as a result of the treatment of particles with aggressive acid and alkali solutions.

2. Experimental

The system of nanoparticles of highly anisotropic barium hexaferrite was chosen as the object of study of collective effects. $BaFe_{12}O_{19}$ particles were obtained using a coprecipitation technique:

$$BaCl_2 \times 2H_2O + 12FeCl_3 \times 6H_2O + \\ + 19Na_2CO_3 \times 10H_2O \; x \to t^\circ \\ x \to t^\circ \; BaCO_3 \times 12FeO(OH)\downarrow + 18CO_2 + \\ + 38NaCl + 234H_2O,$$

$$BaCO_3 \times 12FeO(OH)\downarrow x \to \\ \to 800\,C^\circ \; BaO \cdot 6Fe_2O_3 + CO_2\uparrow + 6H_2O.$$

The morphology of samples was analyzed using an electron microscope JEOL JSM-820 [16]. In certain parts of the gastrointestinal tract, the concentration of hydrogen cations varies from pH = 1.6 (aggressive acidic medium of stomach) to pH = 9.0 (upper part of the large intestine). Samples 2 and 3 (S2, S3) were obtained by treatment (T = 37°C, t = 60 min) of initial sample 1 (S1) with HCl solution (pH = 1.6) and NaOH solution (pH = 9.0), respectively.

The magnetic study of the parameter of interparticle interactions was performed using a vibrating magnetometer VSM EV9 Microsense at room temperature. In order to investigate the magnetic interactions, the Henkel plot method was used [17]: comparison between the isothermal remanent magnetization (m_r) and the demagnetization remanence (m_d).

The remanent magnetization curve $m_r(H)$ was measured starting from the demagnetized state of the sample with applying a MF with a positive sign, after removing the sample. The remanent demagnetization curve $m_d(H)$ was measured after applying reverse MF up to the maximal value for previously saturated sample. The dependences $m_r(H)$ and $m_d(H)$ for a system of non-interacting single-domain magnetically uniaxial particles with a uniformly random distribution of their orientations are related, according to Wohlfarth [18], by the relationship:

$$m_d(H) = 1 - 2m_r(H).$$

For the theoretical model, the dependence m_d vs m_r (the Henkel plot) is linear with m_d varying from 1 (for $m_r = 0$) to −1 (for $m_r = 1$). Any deviation from the linearity in the $m_d = f(m_r)$ plot for a system of real particles indicates the presence of interaction. In the modified Kelly method [19], the parameter Δm is introduced as a quantitative measure of the interparticle magnetic interaction:

$$\Delta m = m_r(H) - (l - 2m_d(H)).$$

The plot of Δm versus the applied MF is known as a Δm plot. It is a characteristic of the deviation of the experimental value of m_d from that calculated by the Wohlfarth equation. This parameter determines the sign and strength of the interaction depending on the applied field.

3. Results and discussion

The particles of the experimental sample had a lamellar hexagonal shape, mostly isometric — the diameter was twice the thickness (d/h ~ 2) (Fig. 1). The particle sizes of the synthesized barium hexaferrite were $\langle d \rangle$ = 450 nm, $\langle h \rangle$ = 270 nm. The particle diameter does not exceed the upper limit of

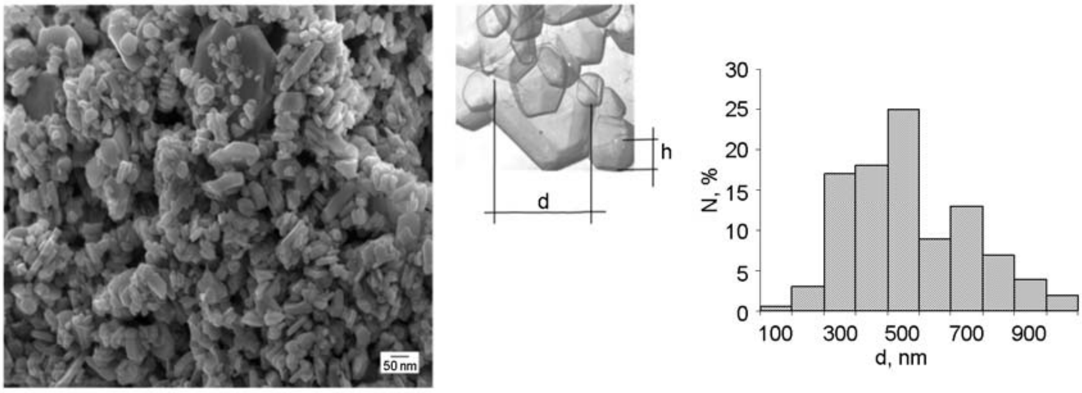

Fig. 1. Electronic photograph and the normalized size distribution function for particles (sample 1) of barium hexaferrite.

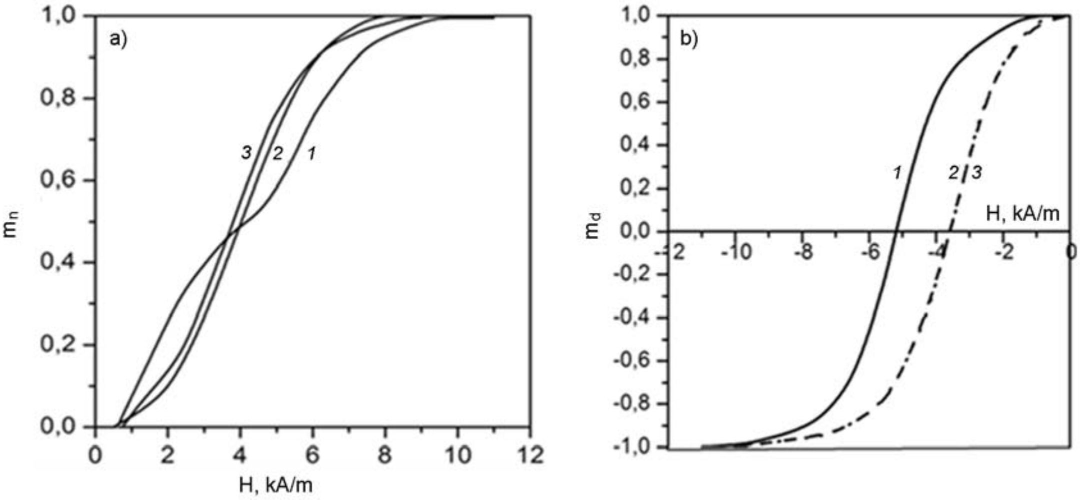

Fig. 2. MF strength dependences of isothermal residual magnetization (a) and residual magnetization (b) for samples S1 (*1*), S2 (*2*), S3 (*3*).

single-domain morphology; therefore, they can be used as an object for studying magnetic properties, interparticle magnetic interaction, deviation from stoichiometry and physicochemical state of the surface in a wide range of temperatures and MF parameters.

The dependence of the isothermal remanent magnetization (Fig. 2a) for samples with modified surfaces S2 and S3 differs from the dependence obtained for sample 1. The dependence $m_r(H)$ for S1 has a pronounced saddle-shaped area, which is absent on similar curves for S2 and S3. The shape of the $m_d(H)$ dependences is the same for all samples.

These basic dependences (Fig. 2) were used to draw the Henkel plot $m_d = f(m_r)$ (Fig. 3a). For an ensemble of single-domain, chaotically oriented non-interacting particles with uniaxial magnetic anisotropy, the Henkel plot is linear. Any deviation from the linearity indicates the presence of interaction and its sign. As can be seen, for all samples the experimental curves deviate from the Wohlfarth's theoretical linear dependence. This indicates the presence of interparticle interaction in the experimental systems.

The observed dependences were rather different. For the sample 1, the curve is noticeably convex, which indicates a positive sign of the interaction. For particles modified with an acid solution (sample 2), the curve is slightly concave; therefore, the interparticle interaction has a negative sign. For particles modified with an alkali solution (sample 3), the Henkel graph is alternating; this fact indicates that in the system of particles, the resulting interparticle magnetic interaction changes the sign from positive to negative depending on the field strength.

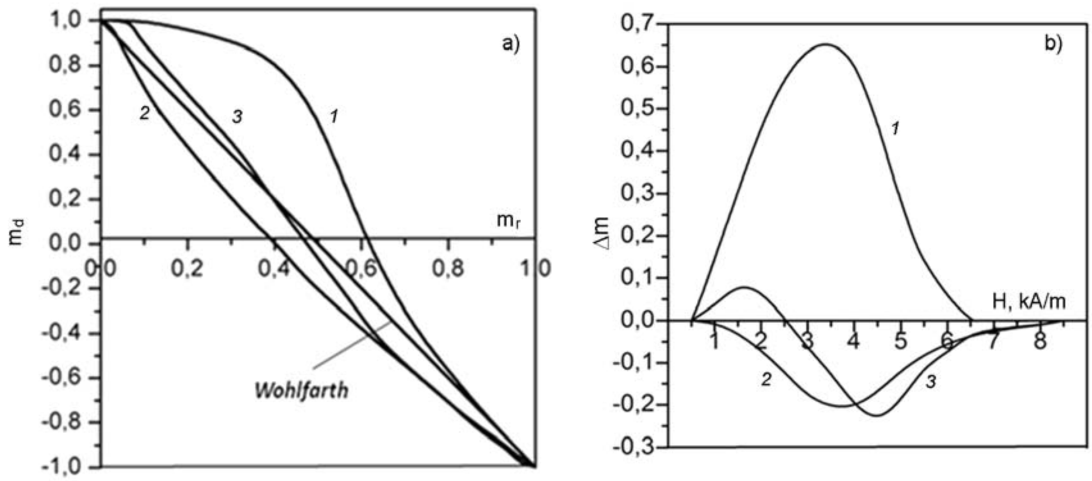

Fig. 3. Henkel plots (a) and Δm plots (b) for samples S1 (*1*), S2 (*2*), S3 (*3*).

The degree of the interparticle magnetic interaction Δm, which quantitatively illustrates the influence of the magnetic field on the particle interaction, was determined by the method of constructing the modified Kelly graph. The delta — graph (Fig. 3b) determines the deviation from the Wohlfarth's ratio for a system of non-interacting particles. This deviation determines the degree of the interparticle magnetic interaction, which is calculated from the equation:

$$\Delta m(H) = m_d(H) - [1 - 2m_r(H)].$$

From the analysis of the obtained results (Fig. 3b) it was found that $\Delta m \neq 0$ for all samples in the range of irreversible magnetization $(H_0^{(1)} - H_0^{(2)}) \simeq 0.5 \div 8.5$ kA/m.

For reversible magnetization ($H<0.5$ kA/m and $H>8.5$ kA/m), $\Delta m = 0$, as it should be. For sample 1, the degree of interparticle magnetic interaction is $\Delta m > 0$ (in the entire MF range). For particles with a modified surface (samples S2 and S3), the curves noticeably differ not only from sample 1, but also from each other. The previous analysis of Fig. 2a shows that for S2, the parameter $\Delta m < 0$ in the entire MF interval, while for S3, the parameter Δm has a variable sign. The negative Δm values are usually taken as indicative of the prevalence of demagnetizing (e.g., dipole-dipole) interactions; the positive Δm values are attributed to the interactions promoting the magnetized state (e.g., direct exchange interactions).

The maximum value of the parameter Δm is indicative. For the initial sample 1, the maximum value is $\Delta m^{\max} \approx 0.65$ and corresponds to the MF strength of 3.5 kA/m. For samples 2 and 3, the maximum degree of interaction decreased significantly (almost 3 times). For sample 2, the absolute value of the parameter is $|\Delta m^{\max}| \approx 0.2$ and is achieved, as for sample 1, with MF strength of 3.5 kA/m. For sample 3, two maxima with different signs of interaction are observed. The positive interaction has a maximum of $\Delta m^{\max} \approx 0.1$ in the field of 1.75 kA/m, the interaction of the negative sign acquires the maximum value at the MF strength of 4.5 kA/m, the absolute value is $|\Delta m^{\max}| \approx 0.25$.

Based on the fact that barium hexaferite particles have been proposed for use as part of a magnetically controlled X-ray contrast agent for diagnostics of the hollow organs of the gastrointestinal tract, studies of the magnetic properties of S2 in comparison with the original sample 1 were performed. The study of the main magnetization curve at room temperature showed that both samples reach the magnetic saturation at MF strength $H \approx 1353$ kA/m. This value is close to the field strength of magnetocrystalline anisotropy (H_a) of barium hexaferrite. The magnetization in the specified MF is 300 kA/m. The study of the temperature dependence of the initial magnetic susceptibility (Fig. 4) showed that for S2 this parameter is almost 1.5 times higher than the susceptibility of S1.

Since the initial magnetic susceptibility characterizes the property of the material to magnetization in MF ($H << H_a$), the re-

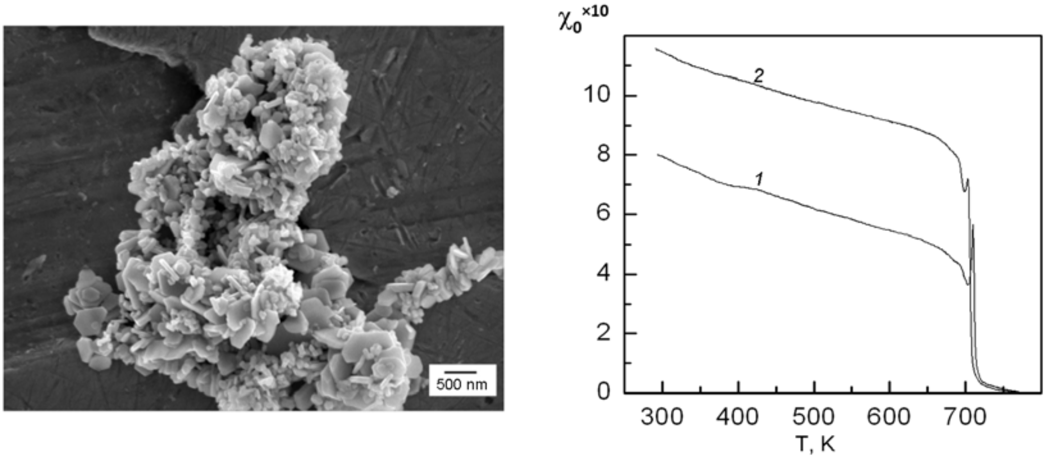

Fig. 4. Electronic photograph of S2; temperature dependences of the initial magnetic susceptibility for samples S1 (*1*); S2 (*2*).

corded growth of this parameter allows predicting the improved functional ability of the dosage form with magnetic nanoparticles. This effect can be manifested in the developed of novel drug delivery systems, e.g. a tool for magnetically controlled X-ray diagnosis of diseases of the hollow organs of the gastrointestinal tract.

4. Conclusions

Treatment of barium hexaferite particles with aggressive (strong acidic and basic) solutions significantly reduces the parameter of the resulting interparticle magnetic interaction Δm by almost three times. An increase in the initial magnetic susceptibility of 1.5 times was observed under the influence of an aggressive acid solution, which corresponds to the pH of digestive juices.

References

1. V.Koppisetti, B.Sahiti, *Int.J.Drug Develop. Res.,* **3**, 260 (2011).
2. P.Lokwani, *Int.J.Res. Pharm.Biomed.Sci.*, **2**, 465 (2001).
3. J.Agnihotri, S.Saraf, A.Khale, *Int.J.Pharm. Sci.Rev. Res.*, **8**, 117 (2011).
4. T.K.Indira, P.K.Lakshmi, *Int.J.Pharm.Sci. Nanotechn.*, **3**, 1035 (2010).
5. D.Emerich, C.Thanos, *J.Drug Target*, **15**, 163 (2007).
6. G.Goya, V.Grazu, M.Ibarra, *Current Nanosci.*, **4**, 801 (2008).
7. I.A.Vedernikova, *Rev. J. Chem.,* **5**, 289 (2015).
8. I.Vedernikova, *Int.J.Pharmtech. Res.*, **8**, 394 (2015).
9. I.Vedernikova, *Int.J.Pharm. Pharm.Sci.*, **7**, 177 (2015).
10. I.Vedernykova, Ye.Levitin, L.Klimenko, *Pharmakeftiki*, **3**, 133 (2020).
11. G.Muscas, G.Concas, S.Laureti et al., *Chem. Chem.Phys.*, **20**, 28634 (2018).
12. M.S.Seehra, H.Shim, P.Dutta et al., *J.Appl. Phys.*, **97**, 1063 (2005). https://doi.org/10.1063/1.1854911
13. A.Abu-Bakr, A.Zubarev, Philosophical Transactions of the Royal Society A. Mathematical, Physical and Engineering Sciences, **377**, (2019), https://royalsocietypublishing.org/doi/10.1098/rsta.2018.0216.
14. M.Knobel, W.C.Nunes, H.Winnischofer, *J. Non-Crystall. Solids*, **353**, 743 (2007).
15. S.Morup, M.Hansen, C.Frandsen, *Beilstein J. Nanotechnol.*, **1**, 182 (2010).
16. I.A.Vedernykova, A.A.Koval, O.V.Antonenko et al., *J.Pharm.Sci.Res.*, **10**, 2122 (2018).
17. O.Henkel, *Phys.Status Solidi*, **7**, 919 (1964).
18. E.P.Wohlfarth, *J.Appl.Phys.*, **29**, 595 (1958).
19. P.E.Kelly, K.O'Grady, P.L.Mayo et al., *IEEE Trans.Magn.*, **25**, 3881 (1989).