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Influence of the $BaFe_{12}O_{19}$ Crystal Surface on the Interparticle Magnetic Interaction

L.P. Ol'khovik[1], Z.I. Sizova[1], E.V. Shurinova[1,2,*], K.A. Mozul'[1,†], A.S. Kamzin[3]

[1] *Karazin Kharkiv National University, Svoboda sq. 4, Kharkiv, 61077 Ukraine*
[2] *Ukrainian Engineering Pedagogics Academy, Universitetskaya str.16, Kharkiv, 61003 Ukraine*
[3] *Ioffe Physical_Technical Institute, Russian Academy of Sciences, Politekhnicheskaya str. 26, St. Petersburg, 194021 Russia*

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The influence of the physicochemical state of the particle surface on the interparticle magnetic interaction in a closepacked system of singledomain microcrystals of highly anisotropic hexaferrite BaFe12O19 has been studied. The efficiency of the used technique of treatment of the particle surface with acid and alkali solutions has been determined from the data on the Fe^{3+} ion concentration in the solution and on the change in the elemental composition in the nearsurface layer. It has been shown that, when the etched layer thickness is 2.5*c* (*c* is the lattice parameter of ferrite), the parameter of the resulting interparticle interaction changes qualitatively and quantitatively. The technologically accessible technique used allows the attenuation of the interparticle magnetic interaction in a system of closepacked particles by several times.

Keywords: Interparticle magnetic interaction, Singledomain particles, Oxide ferrimagnet, Surface layer.

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1. INTRODUCTION

The interparticle magnetic interaction is a factor that unpredictably influences the behavior in magnetic field of a real ensemble of particles with a size distribution and a random orientation of the easy magnetization axes. The study of this problem is substantially hampered by the dependence of the interaction parameters on the packing density, morphology, degree of particle aggregation, and the particle magnetic state. The problem of interrelation between the interparticle magnetic interaction and surface magnetic properties of particles was studied in [1].

The aim of this work is to elucidate the influence of an open crystal surface and adjacent structural defect layer with so called scanted magnetic structure [2] on the parameter of interparticle magnetic interaction in a packed system of initially disoriented singledomain microcrystals.

2. EXPERIMENTAL TECHNIQUE AND JUSTIFICATION OF THE CHOICE OF THE OBJECT UNDER INVESTIGATION

According to the known technique [3], the effect of interparticle magnetic interaction is manifested as a deviation of the experimental dependence $m_d = f(m_r)$ from the theoretical dependence

(1)

Relationship (1) is valid for an ensemble of single_domain noninteracting particles with uniaxial magnetic anisotropy and chaotic orientation of the easy magnetization axes. Along with the above noted limitations, the deviation from the linear dependence $m_d = f(m_r)$ can be due to the existence in the system of an impurity in the form of superparamagnetic and (or) multidomain particles and also the effects of incoherent rotation of magnetic moments of ions in an isolated particle. In this connection, it is appropriate to analyze the chosen object under study.

Hexagonal ferrite $BaFe_{12}O_{19}$ is a uniaxial ferriagnet with the easymagnetization axis (easiest for the nanocrystal [4]) directed along the hexagonal **c** axis [001] [5] independently of the crystal size. The magnetically stable state of the particle in the temperature range under study is provided by the high crystalline magnetic anisotropy ($K_I \cong 10^6$ erg/cm^3 [4]), i.e., small critical superparamagnetic volume as compared to the real particle volume. Therefore, as the basis object under study, we took the system of lamellar singledomain $BaFe_{12}O_{19}$ microcrystals in which the specific feature of the magnetic properties, as follows from the analysis, is exclusively provided by the surface.

As for the effects of incoherent rotation of the magnetic moments, they, as known [6], are first due to heterogeneity of the magnetic structure of a small particle. The degree of perturbation of the magnetic structure depends on the ratio of the volumes of the core and the structural_defect near_surface layer with a scanted magnetic structure. The layer thickness in the basal plane of the BaFe12O19 crystal is δ = 3–5 nm at 300 K, and the angle of scanting the magnetic moments with respect to the hexagonal axis **c** is $\langle\theta\rangle$ =20° Γ} 3° [7]. To perform the quantitative estimation of the degree of heterogeneity of the magnetic structure of the lamellar microcrystals, we used the distribution of particles over the thickness *h*. As seen from Fig. 1, $\langle h\rangle$ = 0.27 μm. In this case, the fractional contribution of the nearsurface layer $2\delta/h$ in the basal (001) planes closing the single crystal is comparatively small and is, on average, ~3% of the total particle volume.

* giperbola79@mail.ru
† monk813@mail.ru

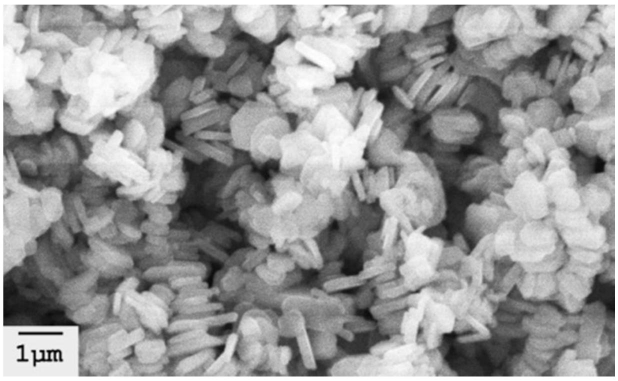

Fig. 1 – Electron microscopy image of particles of the initial BaFe12O19 powder sample and the thickness distribution of the particles.

To solve the posed problem, we used three powder ferrite samples with various prehistory of the formation of the particle surface. In the initial sample no. 1, the surface of the microcrystals was formed during their crystallization under conditions of deposition from the melt using the water_soluble flux component ($BaCl_2 \cdot 2H_2O$) [8]. It allows the separation of the ferrite particles from the flux matrix at the final stage of the technological process by washing with distillated water with no damages of it surface, i.e., with no changes of its physicochemical state in the process. Samples nos. 2 and 3 are the barium ferrite whose particles are additionally treated by various aggressive media. Table 1 gives the necessary data on the objects under study.

3. TECHNIQUE FOR ETCHING OF THE SURFACE OF MICROCRYSTALS AND ITS EFFICIENCY

Since the thickness of the nearsurface layer of the highly anisotropic hexaferrite BaFe12O19 is a relatively small, it was necessary to develop the technique of treatment of the particle surface with aggressive media. In this case, we used the HCl acid solution (pH = 1, 6) for sample no. 2 and the NaOH alkali solution (pH = 9) for sample no. 3. To state the optimal time required for etching a layer with thickness of no more than 3–5 nm and also to analyze the efficiency of this technique, we studied the solubility of the powder samples and determined the elemental composition within the near-surface layer of the particles.

To estimate the loss of the Fe^{3+} ions as a result of treatment of the particles were also used the data characterizing the elemental composition of three microcrystalline powder samples with various technological prehistory (Nos. 1–3) obtained using a scanning electron microscope with an EDX attachment at the Institute of Inorganic Chemistry of the Essen University (Germany).

Table 2 – The change of the elemental composition of the surface layer of microcrystals $BaFe_{12}O_{19}$ by treatment with aggressive media

Sample	Treatment	The change of ion content, %	
		O^{2-}	Fe^{3+}
№2	HCl solution	-18	-35
№3	NaOH solution	-35	-40

Assuming that the deviation on stoichiometry of the elemental composition of near-surface layer of the microcrystal is the same as for the macroscopic crystal before treatment, namely, an excess content of oxygen ions (~15%) and a deficit of iron ions (26%) [9], the conclusion can be made as follows. As a result of the treatment, the excess oxygen content is completely removed, and the near-surface layer initially depleted in Fe^{3+} ions additionally losses almost a half of existing Fe^{3+} ions.

The data obtained allow the prediction of the properties of individual particles of the powder samples under study and also collective effects provided by the interparticle magnetic interaction.

4. DETERMINATION OF THE PARAMETER OF THE INTERPARTICLE MAGNETIC INTERACTION

The experimental data were obtained on three powder samples with a packing factor of the particles p~ 0.4. Using the method of Henkel [10] and Kelly [11] (Fig. 2) was revealed the presence of interaction, its sign and the intensity of the interaction of the external magnetic field.

The electron microscopy image (Fig. 1) visually confirms this fact. The powder preliminarily demagnetizing sample clearly contains clusters of particles as rather extended stacks. The formation of similar

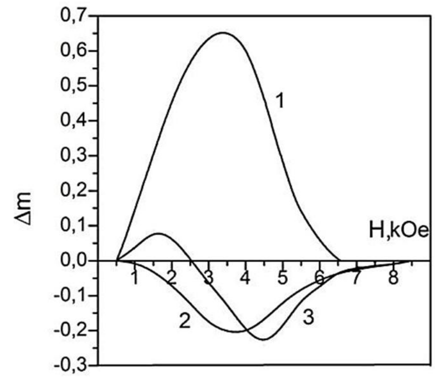

Fig. 2 – Kelly plot. The curve numbers correspond to the sample numbers

Table 1 – Information about the objects of research

Sample	Composition	Technological prehistory		<*d*>, µm	<*h*>, µm
		Method of obtaining	Method of treatment		
№1	$BaFe_{12}O_{19}$	The modified co-precipitation from the melt	-	0,86	0,27
№2	—//—	—//—	HCl solution	0,78	0,24
№3	—//—	—//—	NaOH solution		

clusters of particles is due to both the morphological peculiarities of the particles (lamellar shape) and the uniaxial crystalline magnetic anisotropy (easy magnetization axis is perpendicular to the basal plane of the particle). For the samples treated by the acid solution (no. 2) and alkali solution (no. 3) the deviation from the linearity in the plot $m_d = f(m_r)$ is substantially smaller as compared to the initial sample (no. 1). In this case, $\Delta m > 0$ for the initial sample over entire range of fields;

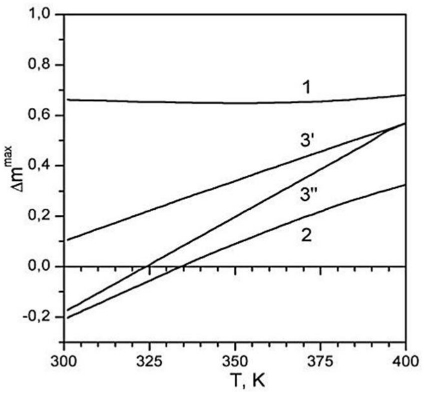

Fig. 3 – Temperature dependence of the effect of treatment of BaFe12O19 microcrystals with aggressive media: (*1*) sample No. 1, (*2*) sample No. 2; curves *3*' and *3*'' correspond to two maxima in curve *3* (Fig. 4) of sample No. 3

on the other hand, the treated samples demonstrate the changes in sign of this parameter: $\Delta m < 0$ in sample no. 2, and Δm is sign changing in field in sample no. 3 (Fig. 4). The quantity Δm^{max} is more indicative. For sample no. 2, $|\Delta m^{max}|$ ($H = 3.5$ kOe) ≅0.2; sample no. 3 demonstrates two maxima: $|\Delta m^{max}|$ ≅0.1 in the field $H = 1.75$ kOe and $|\Delta m^{max}|$ ≅ 0.2 in the field $H = 4.5$ kOe.

Thus, the effect of treatment of the particles with aggressive media is the attenuation of the interparticle magnetic interaction (at 300 K, by a factor of more than three). The attenuation of the interaction is observed in the temperature ranges that are of interest from the practical standpoint, namely, technical (300–370 K) and "therapeutic" (310–325 K) (Fig. 3).

5. CONCLUSIONS

The setting up of the experiment, namely, the choice of the object under study and technologies of treatment of the particle surface allowed us for the first time to immediately confirm the determining role of the magnetic moments of ions localized on the particle surface and adjacent structural defect layer in the formation of the interparticle magnetic interaction.

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REFERENCES

1. E. Tronc, A. Ezzir, R. Cherkaoui, C. Chaneac, M. Nogues, H. Kachkachi, D. Fiorani, A.M. Testa, J.M. Greneche, J.P. Jolivet, *J. Magn. Magn. Mater.* **221**, 63 (2000).
2. G.S. Krinchik, A.P. Khrebtov, A.A. Askochenskii, V.E. Zubov, *JETP Lett.* **17** 9, 335 (1973).
3. E.P. Wohlfarth, *J. Appl. Phys.* **29**, 595 (1958).
4. S.N. Zinenko, A.A. Murakhovskii, L.P. Ol'khovik, Z.I. Sizova, E.V. Shurinova, A.S. Kamzin, *JETP* **96** 5, 945 (2003).
5. J. Smith, H.P.J. Wijn, *Ferrites* (Philips Technical Library, Eindhoven, The Netherlands, 1959; Inostrannaya Literatura, Moscow, 1962).
6. M.E. Schabes, *J. Magn. Magn. Mater.* **95**, 249 (1991).
7. A.S. Kamzin, B. Stahl, R. Gellert, G. Klingelhofer, E. Kankeleit, L.P. Ol'khovik, and D. Vcherashnii, *Phys. Solid State* **42** 5, 897 (2000).
8. I. Borisov, N.M. Borisova, L.P. Ol'khovik, M.I. Rudenko, S.S. Tserevitinov, UA Patent no. 4 932 383 (November 15, 1994), Byul. "Promislova Vlasnist'", no. 21 (1994).
9. A.S. Kamzin, V.L. Rozenbaum, L.P. Ol'khovik, E.D. Kovtun, *J. Magn. Magn. Mater.* **161**, 139 (1996).
10. O. Henkel, *phys. status solidi* **7**, 919 (1964).
11. P.E. Kelly, K. O'Grady, P.L. Mayo, R.W. Chantrell, *IEEE Trans. Magn.* **MAG_25** 5, 3881 (1989).
12. R. Corradi, E.P. Wohlfart, *IEEE Trans. Magn.* **MAG_14** 5, 861 (1978).