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INVESTIGATIONS OF A $CoFe_2O_4$-FERROFLUID STRUCTURE BY MEANS OF MAGNETIC MEASUREMENTS

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Стан К. и др. E14-2012-103
Исследования структуры магнитной жидкости
с $CoFe_2O_4$-частицами при помощи магнитных измерений

Представлен анализ экспериментальных результатов исследования образца магнитной жидкости на водной основе с $CoFe_2O_4$-частицами при помощи магнитных измерений в диапазоне температур от 80 до 350 K. Для анализа и теоретической подгонки экспериментальной кривой намагничивания использованы методы магнитной гранулометрии. Также рассмотрена модель Ланжевена для логнормального распределения магнитного диаметра частиц при двух значениях температуры: 80 и 300 K.

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Stan C. et al. E14-2012-103
Investigations of a $CoFe_2O_4$-Ferrofluid Structure
by Means of Magnetic Measurements

Analysis of experimental results of a water based $CoFe_2O_4$ ferrofluid sample by means of magnetic measurements in the temperature range from 80 to 350 K is presented. For the experimental magnetization curves, the fitting magnetogranulometric methods based on the Langevin model for a log-normal distribution of the magnetic particle diameters were considered for two temperature values of 80 and 300 K.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna, 2012

INTRODUCTION

In recent years, transition-metal oxides having a spinel structure have been a subject of research for their remarkable magnetic, optical and electrical properties. In particular, ferrite nanoparticles have been extensively studied in the last decades due to their large spectrum of applications in advanced materials and biomedical applications and also, from a theoretical point of view, of the influence of the finite size of the system on the material properties [1–4]. Cobalt ferrite nanoparticles ($CoFe_2O_4$) have received increasing attention for the combination of their bulk magnetic properties (high coercivity at room temperature, moderate saturation magnetization) with the magnetic properties of typical nanoparticles (superparamagnetism) that make them ideal material for high-density information storage devices, photomagnetism, ferrofluids, hyperthermia, cancer therapy, molecular imaging agents in magnetic resonance imaging (MRI) [5–8]. Furthermore, their stability in reducing or oxidizing conditions makes them good catalytic material.

Results of the experimental investigations of water based $CoFe_2O_4$ ferrofluid sample by means of magnetic measurements are analyzed in the present paper.

EXPERIMENTAL

Details on the technique used for the synthesis of the $CoFe_2O_4$ ferrofluid nanoparticles are presented in [5, 6]. Microstructure of similar samples was investigated earlier by means of small-angle scattering of unpolarized neutrons [7]. In the present study, the magnetization curves were recorded at the Department of Magnetism, Lomonosov Moscow State University [9] in the temperature range from 80 to 350 K in magnetic fields till 16 kOe. The analysis of the magnetic properties of this ferrofluid is focused on experimental results obtained at two temperature values of 80 and 300 K.

The experimental recording of the magnetization versus magnetic field intensity are presented in Fig. 1 as two loops corresponding to: $T = 80$ K (squares) and $T = 300$ K (circles). It is observed that the saturation magnetization is lower for the higher temperature. The remanence magnitudes, extracted from the hysteresis curves as the intersection of the loop with vertical axes, show important differences in the two temperature cases (see the inset of Fig. 1).

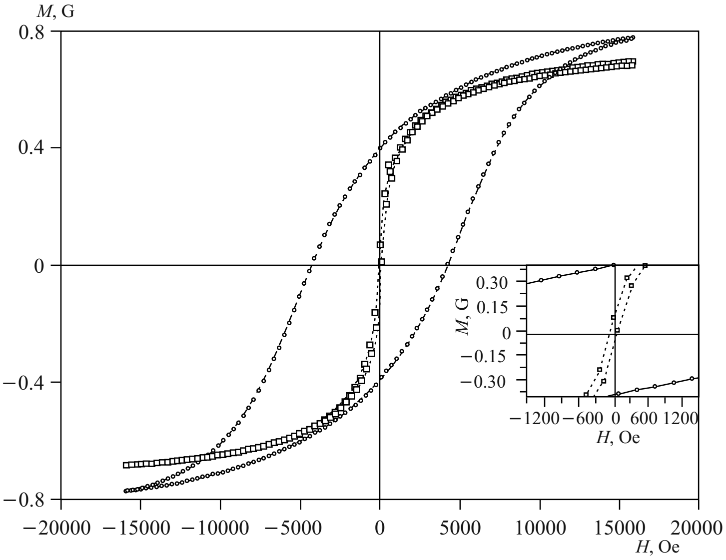

Fig. 1. Hysteresis loops: $T = 80$ K (circles), $T = 300$ K (squares)

The coercive field, defined as the intensity of the magnetic field, required to reduce the magnetization of the sample to zero, shows a significantly higher value for lower temperature. The coercive field at room temperature is 112 Oe, while at 80 K it reaches a value of 4.11 kOe.

The experimental observations show no important changes of the magnetic moment of the sample in the temperature range between 270 and 80 K as shown in Fig. 2.

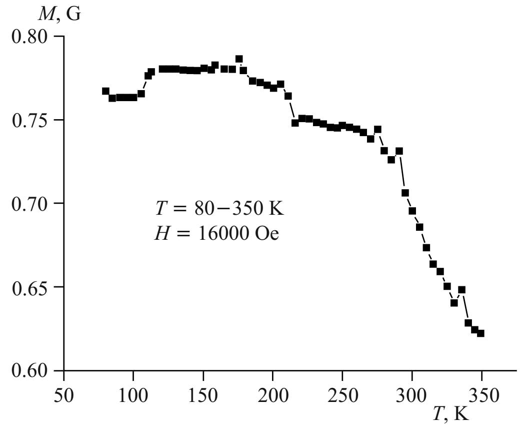

Fig. 2. Saturation magnetization versus temperature T

RESULTS AND DISCUSSION

For the experimental magnetization curves fitting magnetogranulometric methods based on the Langevin model for a log-normal distribution of the magnetic particle diameters are considered.

According to the Langevin model of paramagnetism, the ferrofluid is considered as composed by noninteracting spheres with a permanent dipolar magnetic moment rotating together with the particle when applying an external magnetic field. The macroscopic magnetization is obtained as a result of the combined action of magnetic moments orientation induced by the external field and a destabilization produced by the Brownian motion. In a dilute sample of monodisperse ferromagnetic colloids in which dipolar interactions between particles can be neglected, the magnetization can be described with the ideal Langevin model: $M(H) = M_{\text{sat}} L(\xi)$, where $L(\xi) = \coth(\xi) - 1/\xi$ is the Langevin function of variable $\xi = \mu_0 m H / k_B T$ with μ_0 — vacuum permeability, m — particle magnetic moment, H — magnetic field intensity, k_B — Boltzmann constant, T — temperature and M_{sat} — the saturation magnetization of the ferrofluid.

The correction of this model by taking into account the polydispersity and the particle interactions leads to noticeable deviations from the ideal Langevin behavior [10]. The polydispersity can be introduced by assuming a log-normal distribution function of the particle size (i.e., diameter D):

$$f(D) = \frac{1}{\sqrt{2\pi} S D} \exp\left(-\frac{\ln^2(D/D_0)}{2S^2}\right), \tag{1}$$

with parameters D_0 defined by ln D_0 as the mean value of $f(D)$ and S — the mean deviation of $f(D)$ from its mean value, known to properly describe the particle-size distribution in ferrofluids [11].

The magnetogranulometric analysis of the ferrofluid sample performed at temperature $T = 300$ K, where the Langevin model is applicable, is based on the hypothesis of noninteracting particles, according to which the values of D_0, S, and n can be computed using the value of initial susceptibility from the slope of the curve M versus H in the neighborhood of the origin, and the values of H_0 and M_{sat} from the extrapolation of the linear part of the curve $M = f(1/H)$ [9]. The mean particle diameter D_m was computed using the relation:

$$D_m = D_0 \exp\left(\frac{S^2}{2}\right). \tag{2}$$

The experimental results obtained for $T = 80$ K cannot be treated using the Langevin model. On the assumption that the saturation magnetization is a consequence of the effect of a total orientation of all individual magnetic moments in the direction of the external field, we can compute the mean magnetic diameter at this temperature assuming the hypothesis that the density of particles does not change with temperature [12]. With this assumption one can use the formula:

$$D_{m,80} = D_{m,300} \left(\frac{M_{s,300}}{M_{s,80}} \cdot \frac{M_{\mathrm{sat},80}}{M_{\mathrm{sat},300}} \right)^{1/3}, \tag{3}$$

in which the ratio $M_{s,300}/M_{s,80}$ was computed using the data given in [13]. The results of magnetogranulometric analysis of the ferrofluid at $T = 300$ K and $T = 80$ K are presented in the Table.

Magnetogranulometric analysis results of the ferrofluid sample

T, K	M_{sat}, G	$1/H_0$, Oe^{-1}	χ_i	S	D_0, nm	D_m, nm
80	0.91	5.30E-4	1.19E-3	0.41	6.55	7.13
300	0.68	1.71E-3	6.31E-4	0.23	6.30	6.47

The reconstructed probability distributions based on the computed parameters from the Table are shown in Fig. 3.

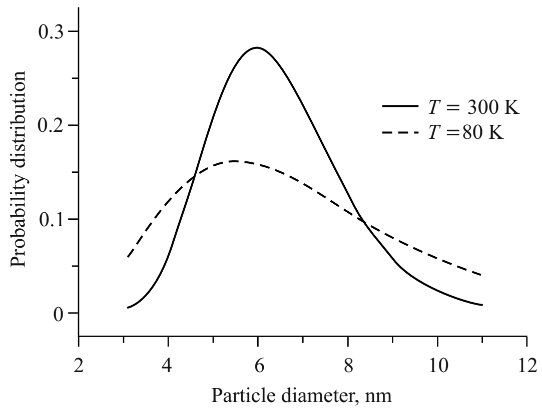

Fig. 3. Probability distribution functions for particle diameters for the two temperatures

SUMMARY

Experimental investigations of a $CoFe_2O_4$ ferrofluid sample show that the saturation magnetization value is higher at lower temperature. The values of the magnetic remanence and of the zero field magnetization (coercive field) demonstrate a significant increasing for lower temperature.

From the experimental magnetization curve at 300 K, using the Langevin model for a log-normal distribution of the magnetic particle diameters [9], the parameters of distribution are computed and the probability distribution function is reconstructed. The analysis is extended to the case of 80 K temperature value, where the Langevin model is no more valid and the corresponding log-normal distribution is obtained.

The comparison of the two distributions shows an increasing in the value of the mean magnetic diameter and a significant spreading of the diameters range at the lower temperature.

This behavior might be a consequence of the increase of the mean volume of the ferromagnetic core of nanoparticles with the decreasing of temperature. Our experimental result, similar to those presented in [12], is consistent with the «core-shell» model in which the paramagnetic layer existing at room temperature on the surface of nanoparticles is gradually becoming ferrimagnetically ordered as temperature decreases. The consequence of this change might be the increase of the mean volume of the magnetic core of nanoparticles with the decrease of temperature.

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