High field magnetization of the colloidal Mn–Zn ferrite

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Abstract

The magnetic properties of a hydrocarbon based colloid (stabilized by oleic acid) of polydisperse chemically co-precipitated $Mn_{0.5}Zn_{0.5}Fe_2O_4$ particles are discussed in the paper. Two fractions are separated from an initial ferrofluid sample by centrifugation. X-ray diffraction measurements show the crystal structure of the particles and a broadened shape of the diffraction lines. Mean particle diameters 6.2 nm (the light fraction) and 9.7 nm (the heavy one) were determined by TEM measurements. The magnetization of the colloids is measured by VSM up to 12 T. A significant slope in the magnetization curves in the high field region is displayed for both samples in the temperature interval from 100 to 295 K. Two methods are used to estimate the spontaneous magnetization of the material: a high field approximation of the magnetization curve by $M(H) = M_s(1 - kT/mH) + xH$ and a decomposition of the magnetization curve in a spectrum of Langevin functions of varying magnetic moments. Both methods give practically identical results. Evaluation of the spontaneous intrinsic magnetization shows a slight dependence of the relative pyromagnetic coefficient $M_s^{-1}\partial M_s/\partial T$ on particle size. © 1999 Elsevier Science B.V. All rights reserved.

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The magnetic properties of small particles of Mn–Zn ferrites are of great importance in the design of thermosensitive magnetic fluids. The samples for investigation are prepared in the Institute of Physics, University of Latvia. The $Mn_{0.5}Zn_{0.5}Fe_2O_4$ particles are prepared using a chemical co-precipitation method from water solutions of Mn, Zn and Fe salts [1]. The particles are covered with oleic acid and dispersed in a hydrocarbon carrier. Two fractions are separated from the initial colloid by centrifugation to obtain samples of different particle sizes. X-ray diffraction spectra of the precipitated particles are measured by a diffractometer DRON-4 at $\lambda = 0.229$ nm. It is shown that the samples contain crystals of a structure similar to that of a bulk Mn–Zn ferrite, but with broadened diffraction lines. The size of the particles is determined from TEM measurements using a microscope EMB-100. The mean size for two of the samples is given in Table 1.

The magnetization measurements are performed in the Department of solid state physics, Chalmers University of technology, employing a vibrating sample magnetometer from Oxford instruments,

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Table 1
Comparison between magnetic moment and size of ferrite particles at 295 K

Sample	$\langle D \rangle$ (nm)	$\langle V \rangle$ (cm^3)	m_E (emu)
DF37E	6.2	1.69E-19	1.91E-17
DF37F	9.7	7.1E-19	6.22E-17

Fig. 1. The field dependence of the magnetization for three samples at 100 K: DF37I – initial colloid, DF37E – light fraction, DF37F –heavy fraction.

Fig. 2. The spectra of magnetic moment for two samples at 295 K: DF37E – light fraction, DF37F – heavy fraction.

Ltd. Isothermal magnetization in magnetic fields up to 12 T is measured in the temperature range 100–295 K. There is no sign of magnetic saturation for any of the samples in the temperature interval from 100 to 295 K. This can be seen from Fig. 1 which represents the magnetization curves for the initial colloid and its light and heavy fractions at 100 K. A difference in the level of magnetization of those samples is a consequence of the change of particle concentration under the centrifugation.

Two methods of analysis of the magnetization curves are used to estimate the spontaneous magnetization of the material. The first one assumes that the intrinsic magnetization in high fields exceeds the spontaneous magnetization of the particles and that it depends linearly on the external field. Then the asymptotic form of Langevin function is applied to take the superparamagnetism into account: $M(H) = M_s(1 - kT/mH) + xH$. Three parameters – M_s (spontaneous magnetization), m (mean magnetic moment) and x (high field susceptibility) – serve to fit with the experimental magnetization curve in the high field region. An alternative to this method is to approximate the whole magnetization curve by a sum of Langevin functions to obtain the spectrum of magnetic moments which characterize the orientation process of the magnetization of monodomain particles.

$$M(H) = \sum_i^N n_i m_i L(m_i H/kT) \tag{1}$$

Here m_i is the present parameters and n_i the calculated parameters. The parameters n_i are calculated by the regularization method referred in [2]. Here we assume that also the 'nonrotational' part may be formally approximated by the superposition of Langevin functions independent of the physical reason. The results of such calculations for
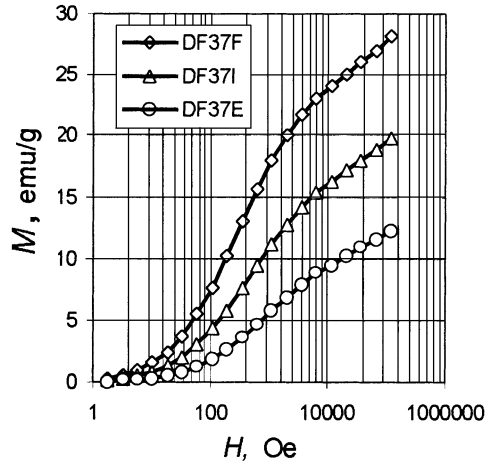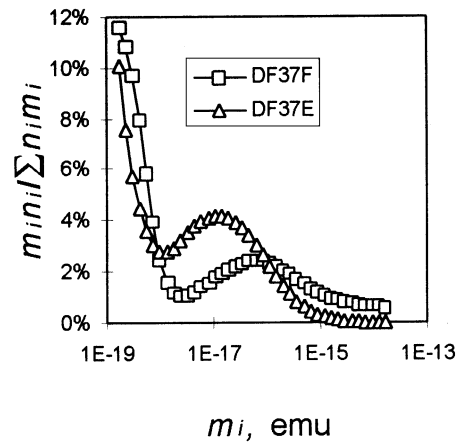
samples DF37E and DF37F at $T = 295$ K are shown in Fig. 2. We clearly see two parts in the spectra of magnetic moments. The part of low magnetic moments, obviously, reflects the paramagnetic magnetization of the particle material, therefore, the sum (1) in this region should be considered to be a formal approximation only. The region of high moments reflects the orientation processes of the magnetic moments, the location
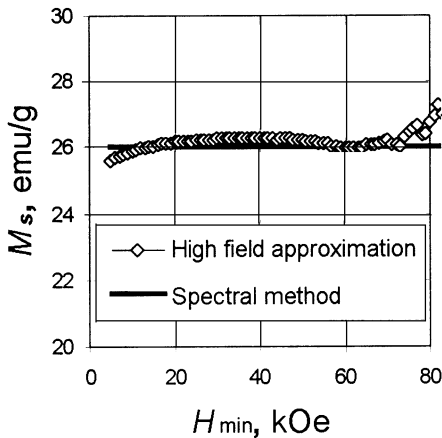
Fig. 3. The comparison of the high field approximation with the spectral method for sample DF37F – light fraction, at the temperature 100 K.

Fig. 4. The dependence of the spontaneous magnetization on temperature for two of the samples.

and the width of the spectral peak characterize the size and polydispersity or, possibly, a physico-chemical nonhomogeneity of monodomain particles. The sum of this part of the spectrum allows us to evaluate the spontaneous magnetization. Both methods of analysis give similar results (see Fig. 3). Nevertheless, the spectral method seems to be more preferable than the method of high field approximation, because we do not need to choose the minimal field or to use an assumption of the linearity of the magnetization in the high field region.

A detailed consideration of the superparamagnetic parts of the spectra shows that the position of the superparamagnetic maximum in the distribution curves corresponds to results of the centrifugal separation. Sample DF37F (the heavy fraction) has a maximum in the region of high magnetic moments and sample DF37E (the light fraction of
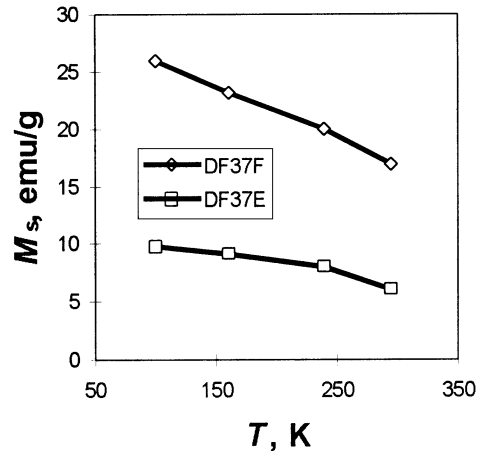
DF37I) in the region of low magnetic moments. The location of these maxima m_E for both samples are shown in Table 1.

The spontaneous intrinsic magnetization detected by using spectral methods is shown in Fig. 4. For both the samples the M_s falls approximately twice when the temperature is increasing from 100 to 295 K. The relative pyromagnetic coefficient $M_s^{-1} \partial M_s / \partial T$ does not depend on the particle size. The interval of examined temperatures is too short to estimate of Curie temperature.

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