

Magnetic properties of Fe-based nanoparticle assembly

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Abstract

The magnetic properties of an assembly of very small Fe nanoparticles with an average diameter of the order of 3–5 nm are studied both experimentally and theoretically. The particles are dispersed in a polyethylene matrix with mass concentration 5%. The stray magnetic field of the samples with sizes $1 \times 1 \times 0.2$ mm is measured by means of scanning SQUID microscope at 77 K as a function of external magnetic field. The presence of a weak remanent magnetization indicates a magnetic ordering in the samples studied at rather high temperatures. A distribution of the particle volumes or partial agglomeration of the particles within the assembly is suggested to be responsible for this unexpected behavior. © 2002 Elsevier Science B.V. All rights reserved.

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Magnetic properties of nanometer scale particles are promising for various important technological applications [1]. In the present paper the magnetic behavior of an assembly of Fe nanoparticles with an average diameter of the order of 3–5 nm is studied both experimentally and theoretically. The particles are dispersed in polyethylene matrix with mass concentration 5%. To obtain very small Fe nanoparticles, a decomposition of $\text{Fe}(\text{CO})_5$ is used in the polyethylene-oil solution within the argon atmosphere at a temperature $T = 250^\circ\text{C}$. For the magnetic measurement a sample is prepared as a thin square platelet with size $L_x = 0.1$ cm and thickness $L_z = 0.02$ cm. A contour of the sample is shown by dashed line in the magnetic images presented in Figs. 1 and 2.

The scanning SQUID microscope [2], in which a high-temperature superconductor (HTS) DC SQUID and a sample are cooled in a cryostat at the liquid nitrogen temperature, $T = 77$ K, was used for stray magnetic

field measurement. The cryostat is placed inside of two μ -metal shields with remanent magnetic field less than $0.1 \mu\text{T}$. An external magnetic field is produced by the Helmholtz coils situated inside of the shields. Small-sized SQUID with an effective area of $800 \mu\text{m}^2$ and magnetic field sensitivity of about $100 \text{ pT/Hz}^{1/2}$ at frequencies higher than 100 Hz was used as a sensor. The SQUID measures a normal component of the stray magnetic field of a sample at a distance of a few tens of micrometers away from the sample surface.

Fig. 1a shows a two-dimensional distribution of the normal component of the magnetic induction measured in a weak (less than 100 nT) residual magnetic field of the shield at a distance $h = 150 \mu\text{m}$ above the sample surface. The magnetic image clearly shows the magnetic poles of different signs located at opposite edges of the sample. The value of the z -component of magnetic induction, B_z , varies within the range $\pm 3 \mu\text{T}$. Maximal value of B_z corresponds to the sample edges, as shown in Fig. 1b, where the result of measurement along the central line in Fig. 1a is presented. One can see that the magnetic image and the distribution of the magnetic

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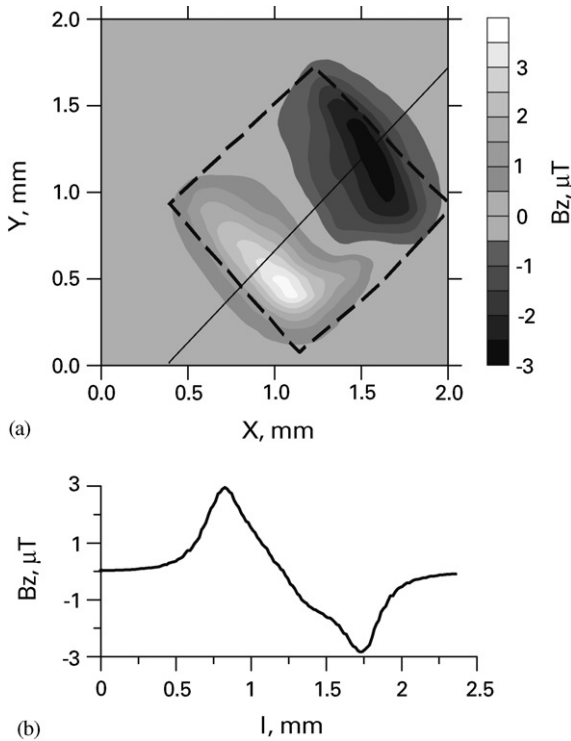


Fig. 1. (a) Grey-scale SSM image of the sample in residual magnetic field of a magnetic shield (100 nT). (b) Single trace along the central line shown in (a).

induction shown in Figs. 1a and b, respectively, correspond to a sample more or less uniformly magnetized along the square side.

Fig. 2a shows the magnetic image of the sample obtained at the same distance, $h = 150 \mu\text{m}$, from the sample surface, but for the case when the sample was previously magnetized perpendicular to its surface in a strong magnetic field of a permanent magnet. A distribution of the z -component of magnetic induction measured across the middle part of the sample is shown in Fig. 2b. One can see in Figs. 2a and b that the magnetic field distribution corresponds to the sample magnetized perpendicular to its surface. It should be noted also that the magnetic images shown in Figs. 1 and 2 were stable and reproducible after application of external magnetic field $\pm 1.2 \times 10^3 \text{ A/m}$ parallel to the sample surface.

For theoretical interpretation of the experimental data obtained, one should take into account that the distribution of the perpendicular component of the stray magnetic field shown in Fig. 1b is typical for the middle plane, $y = 0$, of a thin square platelet uniformly magnetized along the square side. The maximal value, $H_{z,\text{max}}$, of this magnetization component corresponds to the platelet edge, $x = L_x/2$. For a platelet with the thickness $L_z \ll L_x$, one can calculate

the maximal value of the stray magnetic field as $H_{z,\text{max}} \approx 2 \langle M \rangle \ln[(h + L_z)/h]$, where $\langle M \rangle$ is the average platelet magnetization and $h \ll L_x$ is the elevation of the point of the field measurement with respect to the sample surface. Taking into account the experimental value, $H_{z,\text{max}} \approx 3 \times 10^{-2} \text{ Oe}$, and using the values $L_z = 2 \times 10^{-2} \text{ cm}$ and $h = 1.5 \times 10^{-2} \text{ cm}$, one can estimate the average platelet magnetization as $\langle M \rangle = 2 \times 10^{-2} \text{ emu/cm}^3$. Bearing in mind that the mass concentration of the metal particles is only 5%, the volume fraction of the metal within the platelet is given by

$$\frac{4}{3} \pi R^3 n_{\text{Fe}} = \frac{0.05 \rho_{\text{p}}}{0.95 \rho_{\text{Fe}} + 0.05 \rho_{\text{p}}} = 9 \times 10^{-3}.$$

Here R is the average particle radius, n_{Fe} is the nanoparticle concentration, $\rho_{\text{Fe}} = 7.88 \text{ g/cm}^3$ and $\rho_{\text{p}} = 1.4 \text{ g/cm}^3$ are the densities of metal and polyethylene matrix, respectively. Therefore, the average magnetization of the metal itself can be calculated as $\langle M_{\text{Fe}} \rangle = 3 \langle M \rangle / 4 \pi R^3 n_{\text{Fe}} \approx 2 \text{ emu/cm}^3$.

At first glance, the estimated value of average magnetization is very small with respect to the saturation magnetization of pure Fe at the liquid nitrogen temperature, $M_s(77 \text{ K}) \approx M_s(0 \text{ K}) = 1740 \text{ emu/cm}^3$ [3].

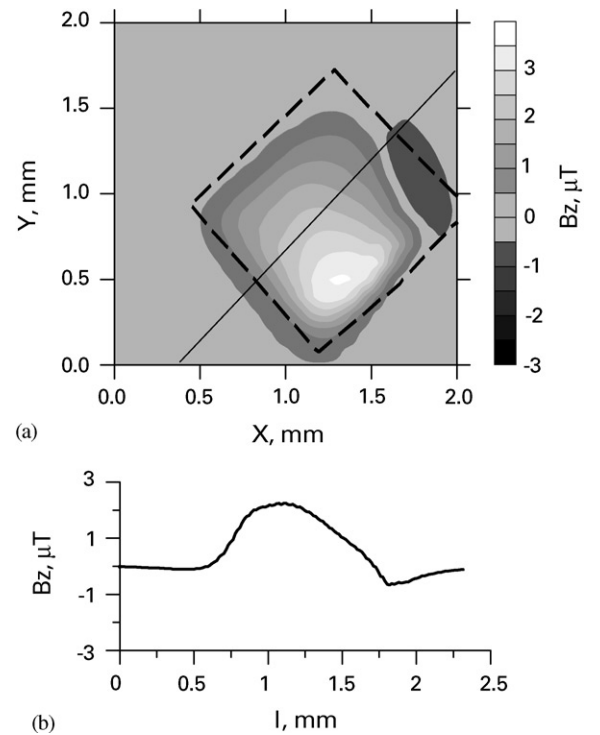


Fig. 2. (a) The same as in Fig. 1a, but for the sample magnetized perpendicular to its surface in a strong magnetic field of a permanent magnet. (b) Single trace along the central line shown in (a).

On the other hand, one should take into account that due to very small average radius of the nanoparticles, $R = 2.5$ nm, they should be in a superparamagnetic state even at liquid nitrogen temperature. Actually, the relaxation time for spherical Fe nanoparticles can be estimated by means of the relation [4]:

$$\tau = \frac{1}{f_0} \exp\left(\frac{KV/4}{k_B T}\right),$$

where K is the anisotropy constant, V is the particle volume and k_B is Boltzmann's constant. The pre-exponential factor, f_0 , is of the order of 10^9 s^{-1} , the factor $\frac{1}{4}$ in the exponent is due to cubic anisotropy of Fe particles. Using the values $K = 5.8 \times 10^5 \text{ erg/cm}^3$ at $T = 77 \text{ K}$ [3], one can obtain the numerical relation for the relaxation time $\tau = 10^{-9} \exp(0.057R^3) \text{ s}$, where R is the particle radius in nm. Then, it is easy to see that for $R = 7$ nm the relaxation time $\tau \approx 0.3 \text{ s}$, whereas it increases dramatically, $\tau \approx 10^9 \text{ s}$, for a particle with slightly higher radius, $R = 9$ nm. On the other hand, the relaxation time turns out to be negligibly small, $\tau \approx 2 \times 10^{-9} \text{ s}$, for $R = 2.5$ nm. One can see, therefore, that for the particle assembly with average diameter $R = 2.5$ nm, practically all particles should be in the superparamagnetic state even at the liquid nitrogen temperature, the remanent assembly magnetization being strictly zero. The surprising result, $\langle M_{Fe} \rangle \approx 2 \text{ emu/cm}^3$, can be explained, however, if one assumes that at least 0.1% of the particles of the given assembly have the radius $R > 8$ nm. Another possibility

to explain the experimental data is to suppose certain agglomeration of the particles within the assembly. Also, the enhanced value of the effective anisotropy constant of the particles related with our technological process can be responsible for the increase in the relaxation time of the assembly. Thus, further experiments are necessary to study the experimental situation in detail.

In conclusion, it is shown that the scanning SQUID microscope is a useful tool to study the properties of nanoparticle assembly with a very small value of the stray magnetic field. The weak remanent magnetization is measured for the Fe-based nanoparticle assembly with an average diameter of the order of 5 nm at $T = 77 \text{ K}$. Possible reasons for this unexpected behavior are discussed.

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