Remanence magnetization of iron oxide particles with different size distribution

Yu I Dikansky, A G Ispiryan and S A Kunikin
North Caucasus Federal University, chair of general and theoretical physics, Stavropol, Russia

E-mail: SKunikin@yandex.ru

Abstract. Remanent magnetization curves for two samples of iron oxide particles with different size distributions were investigated. It was observed that the isothermal remanent magnetization curve and the DC demagnetization remanence curves are strongly depended on fine particle size. Moreover, it was figured out that remanent curves are quite complicated for the assembly of larger particles. In terms of remanence dependence analysis, it was shown that favourable interaction mechanism for the assembly of iron oxide particles strongly depends on particle size. The isothermal remanent magnetization curves were analysed in terms of the Stoner-Wohlfarth model. It leads to determine particle anisotropy field. It was found that the anisotropy field depends on particle size. It was assumed that observed differences related to different magnetic structure of particles.

1. Introduction

Fe₃O₄ magnetic nanoparticles have attracted the attention of the researchers in various fields such as physics, medicine, and biology. Of the many proposed uses of iron oxide nanoparticles, the most promising examples are cancer treatment by magnetic hyperthermia [1, 2], magnetic resonance and particle imaging [3, 4], magnetic biosensing [5] as well as magnetic drug targeting [6]. The required magnetic response of the nanoparticles is typically determined by the application and is in turn intrinsically dependent on the structural properties of the particle system. For individual particles, the theoretical framework regarding the correlations between the structural properties, such as size and shape, and magnetic properties, such as magnetic moment [7] and relaxation times [8–10], are well established.

One of the major drawbacks of these Fe₃O₄ nanoparticles is their interaction caused by strong magnetic dipole-dipole attractions between particles. This led to a general tendency to aggregate particles.

During recent years, remanent magnetization measurements have been extensively used for the estimation of interaction effects in fine-particle systems [11, 12]. The technique is based on a comparison of the principal remanence curves, the isothermal remanent magnetization curve (IRM), and the DC demagnetization remanence curve (DCD). The IRM curve is obtained on an initially demagnetized sample by applying a positive magnetic field $H$ which is then turned off, and the remanence is measured. A larger field is then applied, and the routine is repeated until magnetization saturation is reached. The DCD curve is measured by first saturating the sample and then measuring the remanence magnetization after application of progressively larger fields opposite directed to
saturation field. All remanence curves are normalized to the saturation remanence. For a system of noninteracting single-domain particles with uniaxial anisotropy, the IRM and DCD are related to each other via the Wohlfarth equation

\[ DCD(H) = 1 - 2IRM(H) \]

Henkel [13] noted that the variation of DCD with IRM measured for heterogeneous alloys gave plots showing positive or negative curvature. The IRM curve depends on the method by which the demagnetized state is produced, [14] as from DC, AC, or thermal demagnetization. The noninteracting case for AC or thermal demagnetized state corresponds to a Henkel plot with a slope greater than 2. In paper [15] authors have used the remanence curves to estimate interactions in granular thin films, due to the so-called $\delta M$ Henkel plot, which is a direct measure of the deviation from the linearity;

\[ \delta M(H) = m_d(H) - (1 - 2m_s(H)) \]

Where $m_d(H)$ and $m_s(H)$ are normalized to saturation DCD and IRM curves respectively.

Negative $\delta M$ is usually taken to indicate “demagnetizing” interactions in the sense that the interactions have the effect to stabilize the demagnetized state, for example, by the formation of flux closure structures related to dipolar interaction. Positive values $\delta M$ are usually attributed to interactions promoting the magnetized state.

In this paper, we will discuss the IRM curves for different samples of iron oxide assembles. Our aim is to figure out differences caused by the size distribution of fine particles.

2. Experiment and discussion

In this paper, we provide measurements of IRM and DCD curves for 2 samples of iron oxide particles. Investigated samples are ferrofluids with different particle size distribution. Iron oxide particles were synthesized with the co-precipitation method. Fine particles stabilized by oleic acid and dispersed in kerosene. Particles volume concentration was the same for both samples and equal 12.7%. Particle size distribution was investigated by means of magnetic granulometry. Initially, we measured the magnetization curve of samples at room temperature via Lake Shore 7410 VSM. The curve was fitted by model function, shown in [16]. Coefficients of fitting lead us to fine particle size distribution.

![Figure 1](image.png)

**Figure 1.** The size distribution function for samples 1 and 2.

Measurements of IRM and DCD were done with Cryotronics S700X SQUID. First, a sample should be demagnetized. We used 2 stages to reach the best results. Stage 1, sample holder filled by the liquid sample at room temperature and placed in zero field. In this state, particles can move freely, and this leads to demagnetization. Stage 2, sample demagnetized in AC regime. After the demagnetizing routine sample was cooled to a certain temperature (5 K). Measurements were done in a standard way: a positive magnetic field is applied on sample, then field turn off, and we acquire the isothermal remanent magnetic moment. Step-by-step we increase magnetics filed and acquire
magnetization data in the same manner as explained previously. When measurements were finished, we apply a positive magnetic field of 1.5 T and magnetize sample. After 20 min waiting, we turn off the magnetic field. To acquire the DCD curve, we do a similar operation as for IRM but in this case, we use a negative magnetic field.

In our case ensemble of magnetic particles is in Results in the form of Henkel plots of IRM and DCD, and $\delta M$ for both samples are shown in figure 2 and figure 3. Acquired data processed to find normalized to saturation value in a next manner: $m_s(H) = M_{DCD}(H)/M_{IRM}(H_{sat})$ and $m_s(H) = M_{IRM}(H)/M_{IRM}(H_{sat})$. Deviation of these quantities from dependence predicted by Stoner-Wohlfarth theory firstly interpreted in terms of interparticle interactions by Henkel [13]. To obtain information about interactions we must express this data with quantity

$$\delta m(H) = m_s - (1-2m_s(H)).$$

For positive values of $\delta m(H)$, the exchange coupling is the dominant process. The negative values mean that the dipolar interaction is the favourable mechanism [17, 18]. Firstly, the method of $\delta m(H)$ dependence and Henkel plots were used for the analysis of thin films and multidomain objects. In [19] it was proved that this method can be used to analysis of magnetic properties of fine particle ensembles. It is possible to do this in cases of low temperature below the blocking temperature. In our case data were acquired at the temperature of 5 K. It is lower than the blocking temperature of 53 K. Blocking temperature was determined in terms of ZFC-FC routine. These results are not presented due to its trivialism.

![Figure 2](image1.png)

*Figure 2.* Remanence curves for sample 1. 1 – IRM, 2 – DCD, 3 – $\delta m$.

Remanence curves for sample 2 are shown in figure 3. In weak field $\delta m$ negative, while in the strong field it changes the sign to positive. Curves show a trivial tendency for magnetic nanoparticles [20].

Meanwhile, for sample 2 one can find nonmonotonic dependence of curves figure 3. Initially, both IRM and DCD curves are typical. At field greater than 56 kA/m the first pivot point observed. The second one was observed in the field about 247 kA/m. Moreover, $\delta m$ curve is more complex than the same for sample 1. In a weak field, it is negative, and in the moderate field, it is positive. While in the strong magnetic field it becomes negative. Observed dependence is not trivial and quits surprisingly. The nature of non-monotonic dependence is not clear.

One of the simple IRM modelling strategies is based on the Stoner-Wohlfarth model for assembly of uniaxial magnetic particles. Switching time in this case determined as

$$\tau = \tau_0 \exp(\Delta E/kT)$$

where
$\Delta E$ is the switching energy barrier. To take into account the temperature, which enables the particle’s magnetization switching over $\Delta E$, we will assume that the reversal occurs when $\tau \leq \tau_m$, where $\tau_m = 27$ s is the acquiring time. The dependence of the energy barrier on the magnetic field is well described by

$$\Delta E(H) = K_{\text{eff}}V\left[1 - H/H_{\text{SW}}^0\right]^{3/2}$$  \hspace{1cm} (1)

Where $K_{\text{eff}}$ is magnetic anisotropy constant, $V$ is particle volume and $H_{\text{SW}}^0$ is switching field at zero temperature. The magnitude of the switching field depends on the angle between the easy axis of the particle and direction of the applied field. For the case of non-zero temperatures $H_{\text{SW}} = H(\theta,T)$. For a given temperature, it is possible to separate dependence on temperature and easy axis orientation and express the previous equation in the form $H(\theta,T) = tH(\theta)$. Where

$$t = 1 - \left[\frac{25kT}{K_{\text{eff}}V}\right]^{2/3}$$

depends on temperature and does not depend on the easy axis direction. The magnitude of the switching field is in the range $H_A/2 \leq H_{\text{SW}}^0 \leq H_A$, where $H_A = 2K_{\text{eff}}/\mu_0M_s$ anisotropy field and $M_s$ is saturation magnetization of the material. Introducing the reduced field

$$h = H/(\tau H_A)$$  \hspace{1cm} (2)

it becomes possible to state equation for IRM for assembly of magnetic particles with size distribution $\rho(V)$ as

$$IRM(H,T) = \frac{M_s}{2} \int_{V_{\text{min}}}^{V} \frac{1-x^3}{1+x^3}V\rho(V)dV$$  \hspace{1cm} (3)

Where $V$ is the volume of the particle and we have

$$x = \frac{1+2h^2 - \sqrt{12h^2 - 3}}{2(1-h^2)}$$  \hspace{1cm} (4)

Expression (3) gives us a possibility for the fitting of acquired data and find some properties of particles like $H_A$, but the problem is in size distribution function. Actually $\rho(V)$ is not the same thing that shown at figure 1. Distribution function determined by the method of magnetic granulometry includes the contribution of both superparamagnetic and non-superparamagnetic particles. But for the case of $\rho(V)$ we exclude superparamagnetic particles because it does not take effect on remanence.

But we can solve the problem by using of remanence susceptibility. At a certain temperature, it introduces as

$$\chi_{\text{IRM}} = \frac{dIRM(H)}{dH}.$$  \hspace{1cm} (5)

Assume that at a certain temperature $\rho(V)$ do not depends on the magnetic field magnitude. Than twice derive equation (3) by the magnetic field $H$ one can find that (5) has maxima at $2x^3 = 1$. The solution for this is value $a = 3\sqrt{2}$. Substituting $a$ into equation (3) we have
\[ h = \frac{2a^2 + a + 2 + \sqrt{8a^4 + 8a^3 + 3a^2 - 4a + 2}}{2(a+1)^2} \quad (6) \]

And finally
\[ tH_A = \frac{H_{\text{max}}}{h} \quad (7) \]

here \( H_{\text{max}} \) is the magnetic field corresponding to maxima of (5).

![Image](image_url)

**Figure 4.** Normalized IRM susceptibility of sample 1 and sample 2.

To find experimental dependence of \( \chi_{\text{IRM}}(H) \) we fit acquired data by splines and then derive fitted curve. Computed \( \chi_{\text{IRM}}(H) \) curves are shown in figure 4. One can find that maxima of \( \chi_{\text{IRM}}(H) \) for sample #1 correspond to the magnetic field of 12.7 kA/m while for sample #2 to 39.8 kA/m.

When the temperature is low it is possible to state that
\[ \left( \frac{25kT}{K_{\text{eff}}V} \right)^{2/3} \ll 1. \quad (8) \]

This means that value
\[ t = 1 - \left( \frac{25kT}{K_{\text{eff}}V} \right)^{2/3} \approx 1. \quad (9) \]

Rearranging equation 7 we have
\[ H_A = \frac{H_{\text{max}}}{t \cdot h} \]

Taking the magnitude of magnetic anisotropy constant \( K_{\text{eff}} = 1.1 \times 10^4 \text{J/m}^3 \) from [22], one finally is able to find the particle anisotropy field. Its corresponding computed value for sample #1 is about 11.9 kA/m whereas for sample #2 it is 37.3 kA/m. The result for sample #1 is in a good agreement with well-known data [23]. Meanwhile, the computed anisotropy field for sample #2 is substantially greater. We note that in [24] the authors presented the results on anisotropy fields for the particles with uniaxial and cubic anisotropies. For the uniaxial case, their value is quite close to that observed for sample #1. For the cubic particles the reported anisotropy field is about 80 kA/m, i.e., about 3 times greater than the one that we observe for sample #2. Comparing our results to those of [24], we conclude that the iron oxide particles in the two investigated samples do differ not only in size but most probably possess different magnetic structure.
3. Conclusion
We have presented results of investigations of remanence magnetization on the size distribution of fine particles. In terms of Henkel plots, it was shown that particles in assembly change dominant interaction mechanism with the change of the external magnetic field. It was figured out that susceptibility also differs for investigated samples. We show the way of determination of particles properties by means of susceptibility analysis. It was figured out that particles with different size have different anisotropy field. Analysis of the anisotropy field leads us to the conclusion that particles have different magnetic structure. Smaller particles are uniaxial, while larger particles have cubic anisotropy.

Acknowledgements
Support by the Ministry of Science and Higher education of Russian Federation and RFBR (project 18-03-00279) is acknowledged.

References
[1] Khandhar A P, Ferguson R M and Krishnan K M 2011 Monodispersed magnetite nanoparticles optimized for magnetic fluid hyperthermia: Implications in biological systems J. Appl. Phys. 109 173–5
[2] Kudr J, Haddad Y, Richtera L, Heger Z, Cernak M, Adam V and Zitka O 2017 Magnetic Nanoparticles: From Design and Synthesis to Real World Applications Nanomaterials 7 243
[3] Wawrzik T, Schilling M and Ludwig F 2012 Perspectives of Magnetic Particle Spectroscopy for Magnetic Nanoparticle Characterization Magn. Part. Imaging pp 41-5
[4] Draack S, Viereck T, Kuhlmann C, Schilling M and Ludwig F 2017 Temperature-dependent MPS measurements Int. J. Magn. Part. Imaging 3 3–6
[5] Bender P et al 2017 Structural and magnetic properties of multi-core nanoparticles analysed using a generalised numerical inversion method Sci. Rep. 7 45990
[6] Mascolo M C, Pei Y and Ring T A 2013 Room Temperature Co-Precipitation Synthesis of Magnetite Nanoparticles in a Large ph Window with Different Bases Materials (Basel) 6 5549–67
[7] Scherer C and Neto A M F 2005 Ferrofluids - Properties and applications Brazilian J. Phys. 35 718–27
[8] Dikansky Y I, Ispiryan A G, Kunikin S A and Rodionov A V 2018 Temperature dependence of ferrofluid susceptibility. Influence of particle size distribution Magnetohydrodynamics 54 65-72
[9] Fannin P C 2002 Magnetic spectroscopy as an aide in understanding magnetic fluids J. Magn. Magn. Mater. 252 59–64
[10] Fannin P C and Charles S W 1994 On the calculation of the Neel relaxation time in uniaxial single-domain ferromagnetic particles J. Phys. D. Appl. Phys. 27 185–8
[11] Hillion A, Tamion A, Tournus F, Gaier O, Bonet E, Albin C and Dupuis V 2013 Advanced magnetic anisotropy determination through isothermal remanent magnetization of nanoparticles Phys. Rev. B - Condens. Matter Mater. Phys. 88 1–6
[12] Tournus F 2015 Modelling of isothermal remanence magnetisation curves for an assembly of macrospins J. Magn. Magn. Mater. 375 194–209
[13] Henkel O 1964 Remanenzverhalten und Wechselwirkungen in hartmagnetischen Teilchenkollektiven Phys. Status Solidi 7 919–29
[14] Vieira C A M, Gomes R C, Silva F G, Dias A L, Aquino R, Campos A F C and Depeyrot J 2019 Blocking and remanence properties of weakly and highly interactive cobalt ferrite based nanoparticles J. Magn. Condens. Matter 31 175801
[15] Kelly P E, O’Grady K, Mayo P L and Chantrell R W 1989 Switching mechanisms in cobalt-phosphorus thin films IEEE Trans. Magn. 25 3881–3
[16] Ivanov A O and Kuznetsova O B 2006 Magnetogranulometric analysis of ferrocolloids:
Second-order modified mean field theory *Colloid J.* **68** 430–40

[17] Mamusa M, Sirieux-Plénet J, Perzynski R, Cousin F, Dubois E and Peyre V 2015 Concentrated assemblies of magnetic nanoparticles in ionic liquids *Faraday Discuss.* **181** 193-209

[18] Stingaciu M, Andersen H L, Granados-Miralles C, Mamakhel A and Christensen M 2017 Magnetism in CoFe$_2$O$_4$ nanoparticles produced at sub- and near-supercritical conditions of water *Cryst. Eng. Comm.* **19** 3986–96

[19] García-Otero J, Porto M and Rivas J 2000 Henkel plots of single-domain ferromagnetic particles *J. Appl. Phys.* **87** 7376–81

[20] Varvaro G, Agostinelli E, Laureti S, Testa A M, García-Martin J M, Briones F and Fiorani D 2008 Magnetic anisotropy and intergrain interactions in L1$_0$ CoPt(111)/Pt(111)/MgO(100) PLD granular films with tilted easy axes *J. Phys. D. Appl. Phys.* **41** 134017

[21] Pramanik A K and Banerjee A 2010 Interparticle interaction and crossover in critical lines on field-temperature plane in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ nanoparticles *Phys. Rev. B - Condens. Matter Mater. Phys.* **82** 1–9

[22] Ferguson R M, Khandhar A P, Jonasson C, Blomgren J, Johansson C and Krishnan K M 2013 Size-Dependent Relaxation Properties of Monodisperse Magnetite Nanoparticles Measured Over Seven Decades of Frequency by AC Susceptometry *IEEE Trans. Magn.* **49** 3441–4

[23] Shliomis M I 1974 Magnetic fluids *Sov. Phys. Uspekhi* **17** 153

[24] Chariaou M, Rahn-Lee L, Kind J, Garcia-Rubio I, Komeili A and Gehring A U 2015 Anisotropy of Bullet-Shaped Magnetite Nanoparticles in the Magnetotactic Bacteria Desulfovibrio magneticus sp. Strain RS-1 *Biophys. J.* **108** 1268–74