PRAMANA
— journal of
physics

Vol. 61, No. 3
September 2003
pp. 617–624

Magnetic behaviour of nano-particles of $Fe_{2.9}Zn_{0.1}O_4$

SUBHASH CHANDER, SUDHISH KUMAR*, ANJALI KRISHNAMURTHY‡, BIPIN K SRIVASTAVA and V K ASWAL†

Department of Physics, University of Rajasthan, Jaipur 302 004, India

*Department of Physics, M.L. Sukhadia University, Udaipur 313 002, India

†Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

‡Author for correspondence

Email: bksri_jp1@sancharnet.in

MS received 24 April 2002; revised 3 February 2003; accepted 1 April 2003

Abstract. DC magnetization measurements are reported in the temperature range 20–300 K on a poly-disperse nano-particle sample of the spinel ferrite $Fe_{2.9}Zn_{0.1}O_4$ with a log-normal size distribution of median diameter 43.6 Å and standard deviation 0.58. Outside a core of ordered spins, moments in surface layer are disordered. Results also show some similarities with conventional spin glasses. Blocking temperature exhibits a near linear variation with two-third power of the applied magnetic field and magnetization M evolves nearly linearly with logarithm of time t. Magnetic anisotropy has been estimated by analysing the M–log$t$ curve. Anisotropy values show a large increase over that of bulk particle samples. Major contribution to this enhancement comes from the disordered surface spins.

Keywords. Magnetism; magnetic relaxation; nano-particles; spinel ferrites.

PACS Nos 75.60.-d; 76.60.Es; 75.50.Tt; 75.30.Gw

1. Introduction

In the area of magnetism of fine particles, modifications in saturation magnetization and anisotropy as effected by reduction of particle sizes, magnetism of surface layers and the dynamic behaviour of magnetization have been the subjects of recent interest (e.g. [1–8] and references therein). Studies, for example on $ZnFe_2O_4$, have shown that reduction of particle sizes may lead to reduction of saturation magnetization and changes in site occupation [7,8]. In the present work, we have undertaken to examine the question of modification in magnetic anisotropy when particles are sized down to nano-scale and that of analogy of magnetic relaxation of nano-particles with that known for conventional spin glasses. For this purpose, we have chosen a Zn-substituted spinel ferrite, viz., $Fe_{2.9}Zn_{0.1}O_4$. Literature reports show that in bulk particle state of the samples, substitution of Zn causes the magnetic anisotropy to decrease. Also, for a composition close to the one undertaken for the present study, values of magnetic anisotropy are available in the literature in its bulk particle state and this would facilitate comparison.

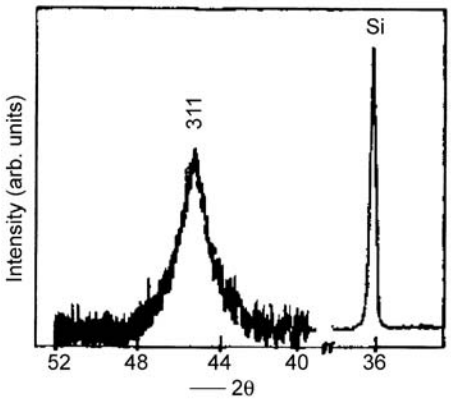

Figure 1. The 311 reflection line from the X-ray diffraction pattern of the nano-particle sample recorded with FeK_α radiation (a reflection line of diffraction pattern of a bulk particle sample of Si is shown for comparison).

On the sample of nano-particles of $Fe_{2.9}Zn_{0.1}O_4$ we have examined its DC magnetic behaviour including the dynamic behaviour. Results on particle size distribution, dependence of magnetization and blocking temperature on the magnetic field, and temporal relaxation of magnetization, are presented. The value of magnetic anisotropy is estimated by analysing magnetic relaxation and it is found to have increased, vis-à-vis in bulk particle state, by more than an order of magnitude.

2. Experimental details and sample characterization

For obtaining dried particles of $Fe_{2.9}Zn_{0.1}O_4$ in the nano-size range, first we prepared a ferrofluid (FF) comprised of this ferrite. The FF has been prepared using wet chemical process [9] using oleic acid as surfactant; kerosene has been used as the dispersing medium and the fluid has been centrifuged at 12000 rpm. Subsequently carrier liquid has been removed, by repetitive washing with acetone, providing dried particles of the ferrite coated with a mono-layer of oleic acid molecules. Characterization of the single phase nature has been done using powder X-ray diffraction (XRD) which confirmed cubic phase with a cell constant of 8.29 Å. XRD pattern has been recorded at 300 K, using FeK_α radiation, on a Philips make powder diffractometer PW1840. Considerably broadened lines in the XRD pattern are indicative of the presence of nano-sized particles. The width of the 311 reflection (cf. figure 1), using Scherrer equation [10], gives an average particle size of 49.4 Å. The particle size distribution has been obtained by analysing small angle neutron scattering (SANS) data. SANS measurements have been made on the ferrofluid sample at Dhruva reactor, Bhabha Atomic Research Centre, Mumbai. Details of the SANS spectrometer can be seen in [11]. Figure 2 shows results on SANS measurements. Assuming spherical shape and a log-normal distribution for the particle sizes, this curve yields a size distribution with median diameter $D_m = 43.6$ Å and standard deviation $\sigma = 0.58$ (inset to figure 2).

The DC magnetization measurements have been made on a vibrating sample magnetometer (VSM; PARC make, model 155) and for variation of temperature down to 18 K,

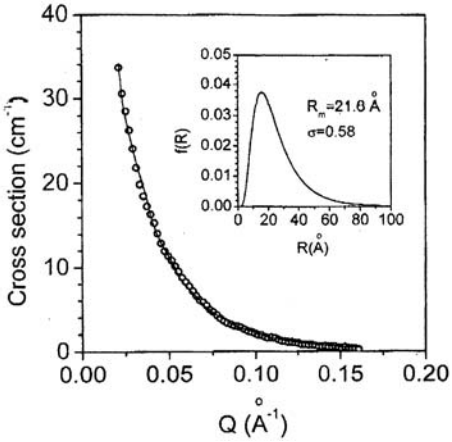

Figure 2. Small angle neutron scattering distribution from ferrofluid sample comprised of the nano-particles. Fitted pattern (continuous line) assuming spherical shape and log-normal particle size distribution with mean diameter $D_m = 43.6$ Å and standard deviation $\sigma = 0.58$ is also shown. In the inset is shown the particle size distribution.

a closed cycle refrigerator cryostat has been used. For calibration of the VSM a small cylindrical piece (2.4 mm in diameter and 2.4 mm long) of pure nickel has been used. For sample measurements, the powder has been compacted to about the same height in a sample cup of identical inner diameter.

3. Results and discussion

Figures 3a and 3b show variation of magnetization M with magnetic field H recorded at 295 K and 21 K respectively; insets to the figures show expanded plots. The 21 K curve shows a small but non-zero coercivity of 35 Oe. At 295 K it is almost zero. The observations are suggestive of a superparamagnetic behaviour at 295 K and also that the blocking temperature is greater than 21 K. Further, the M–H measurements at 21 K suggest that saturation magnetization M_s in the present sample should be much less than 98 emu/g which is the value for Fe_3O_4 [12]. Extrapolation of M vs. $1/H$ curve to $1/H \to 0$ gives a value of $\sim$26 emu/g for M_s. Now, Fe_3O_4 is an inverse spinel. If Zn^{2+} goes to the tetrahedral site, it should result in an enhancement in magnetization as against an observed reduction and if it goes to an octahedral site there must be only $\sim$10% reduction in magnetization. The much reduced M_s in the nano-particle sample implies that outside a core of ordered moments, those in the surface layer are in a state of frozen disorder. Kodama and Berkowitz, in their study of nano-particles of $NiFe_2O_4$ and γ-Fe_2O_3, have found evidence for disordered surface spins [5].

In figure 4 we show Langevin function fitting on the M–H data at 295 K. This fitting has been obtained with an M_s value of 98 emu/g (of Fe_3O_4) and provides a particle size distribution given by median diameter $D_m = 50$ Å and standard deviation $\sigma = 0.70$. A broader distribution provided by M–H curve of the dried particles, than that given by SANS measurement on the same sample of nano-particles dispersed in carried liquid, shows that

the particles are not entirely without any interaction among themselves, particularly so in the dried state.

Figure 5 shows a plot of magnetization vs. temperature (M–T) recorded in the zero field cooling (zfc) and field cooling (fc) modes in an external magnetic field of 50.8 gauss. The zfc pattern has been recorded by first cooling the sample from 295 K to 21 K in the zero magnetic field, then applying the magnetic field and warming the sample up to 295 K in the presence of the field and recording the moment in this warming cycle. Field-cooled pattern has been obtained by first cooling the sample from 295 K down to 21 K in the external field and then warming it up to 295 K and recording the moment. Two features are noticeable: (i) the zfc curve exhibits a peak at ∼80 K and (ii) the fc and zfc curves considerably depart from each other below this peak temperature. Appearance of a peak in the zfc curve owes

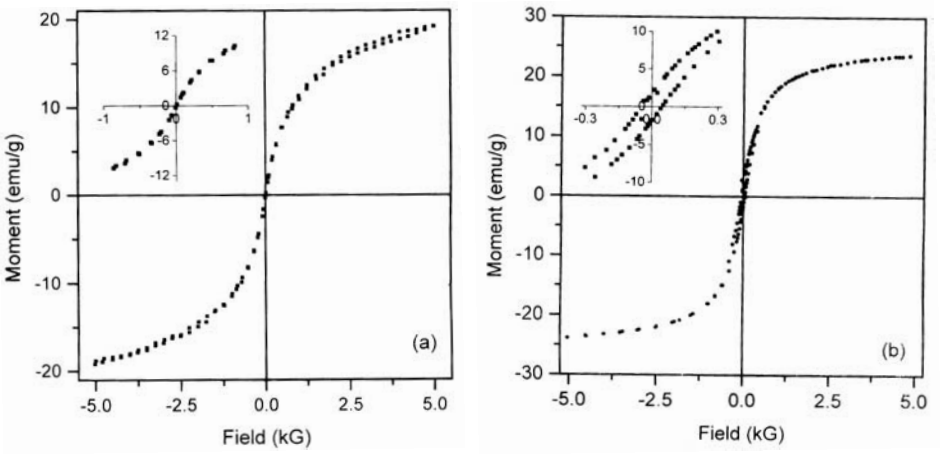

Figure 3. Magnetization–field curves recorded at sample temperatures (**a**) 295 K and (**b**) 21 K. Insets to figures show expanded low field region.

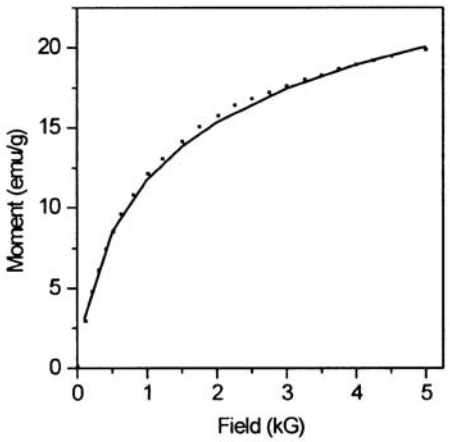

Figure 4. Magnetization–field curve recorded at 295 K along with Langevin function fitting.

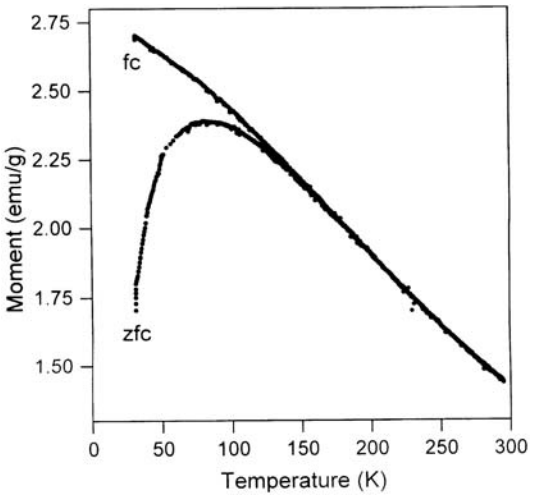

Figure 5. Magnetization–temperature curve recorded in zfc and fc modes (cf. text) in an external magnetic field of 50.8 gauss.

to 'blocking' mechanism arising from a competition between the thermal energy and the magnetic anisotropy energy of the fine particles. Departure of fc curve from the zfc one is suggestive of temporal relaxation, viz., evolution of magnetization with time.

In figure 6a, M–T curves recorded in zfc mode in the presence of different magnetic fields are shown. The blocking temperature T_B shifts downwards with increasing H. Figure 6b shows that T_B approximately varies as $H^{2/3}$. This is interesting in the context of an observed linear variation of the freezing temperature (of spins) with two-third power of the applied external magnetic field in conventional spin glasses [13]. Almeida and Thouless predicted such a variation in the temperature–field phase diagram for spin glasses [14].

Further, for studying temporal relaxation of magnetization, we have recorded M as a function of observation time t after zero field cooling of the sample, in a field of 15 gauss and at a sample temperature of 21 K. Figure 7 plots the same as a function of logarithm of time. A near linear M–log$t$ curve is suggestive of the existence of a distribution of energy barriers. These two observations, viz., linear variation of T_B with $H^{2/3}$ and the temporal relaxation are suggestive of a spin glass-like behaviour [13,15]. It is to be noted that Jonsson *et al* [3,6] observed aging of magnetization in the nano-particle sample of γ-Fe_2O_3 dispersed in carrier liquid which is taken as a greater characteristic of the spin glass-like feature.

For obtaining an estimate of magnetic anisotropy we fitted the observed M–log$t$ curve. Figure 7 depicts the fitting as well. For arriving at the fitting, magnetization m' has been calculated for particles of different sizes and for an observation time t using the relation $m' \sim 1 - \exp(-t/\tau)$ and then total m for a sample of distributed sizes has been obtained by summing m' for particles of different sizes weighted with the log-normal distribution. For obtaining relaxation time τ, we have used the relation [16] $\tau = \tau_0 \exp(KV/kT)$, where τ_0 is of the order of 10^{-9}–10^{-13} s (the fitting shown in figure 7 is obtained for $\tau_0 = 10^{-9}$ s), K is the magnetic anisotropy constant (for which we tried different values to arrive at a fitting) and V is the particle volume. Proceeding in this way m has been computed for different

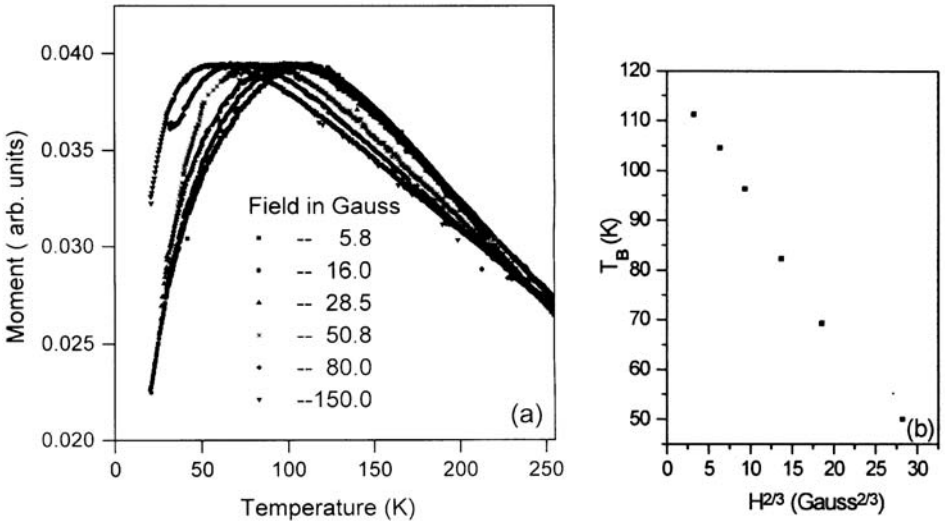

Figure 6. (**a**) Magnetization-temperature curves recorded in zfc mode in the presence of different external magnetic fields H and (**b**) a plot of blocking temperature T_B vs. $H^{2/3}$.

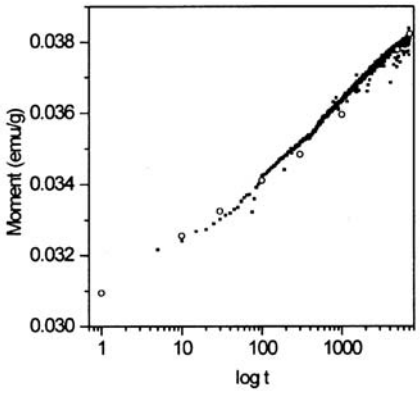

Figure 7. Magnetization M as a function of logarithm of observation time t recorded in zfc mode at a sample temperature of 21 K. Calculated points taking into consideration the particle size distribution and two values for magnetic anisotropy constant (see text) are also shown for some observation times by open circles.

observation times t and then these values have been normalized to the experimental value at some particular t.

Now, an attempt to fit in M–log$t$ curve with only one value of K for the entire particle size distribution ($D_m = 50$ Å, $\sigma = 0.70$), whenever a reasonable fitting is obtained at longer observation times, the calculated points at initial times come much higher than the experimental values. This would suggest that K could be a varying function of particle diameter D. Figure 7 shows a fitting obtained assuming two sets of values of K : 400 kJ/m^3

for particles with $D < 50$ Å and 115 kJ/m^3 for particles with $D > 50$ Å. There is no obvious reason why below and above a certain particle diameter K should differ so much; as we remarked K should be a varying function of D. Nevertheless, these characteristic weighted values of K bear two important points. Firstly, a comparison with the values reported for bulk particle-sized Fe_3O_4 and $Fe_{2.84}Zn_{0.16}O_4$, viz., -11 kJ/m^3 and -9 kJ/m^3 respectively, both at about 300 K [12], shows a huge increase in anisotropy for the nano-particle sample over the bulk particle samples. Even after accounting for the lower temperature of observation in the present case, major increase would owe to nano-particle nature of the sample. It may be mentioned that in the case of bulk particles' sample of $Fe_{2.84}Zn_{0.16}O_4$, in going from 290 K to 90 K, anisotropy increases from -9 kJ/m^3 to only -15.9 kJ/m^3 [12]. Secondly, for the smaller particles K is much larger. It may be noted at this stage that in pure magnetite the reported critical size for switch-over from multi-domain to single-domain nature is $\sim$500 Å [17]. Accordingly, all the particles in the present ferrite sample of low Zn substitution should be of single domain type. Higher K values for smaller particles would thus owe to frozen disordered spins at the surface.

4. Conclusions

DC magnetization measurements have been made on a poly-disperse nano-particle sample of Zn-substituted spinel ferrite $Fe_{2.9}Zn_{0.1}O_4$ having a log-normal particle size distribution with parameters of median diameter 43.6 Å and standard deviation of 0.58. The study shows interesting analogies with conventional spin glasses in the form of an observed linear variation of the blocking temperature with two-third power of the applied magnetic field and a near-linear variation of magnetization with observation time over a long period. Outside a core of ordered moments, those in the surface layer are disordered. Analysis of temporal relaxation gives an estimated magnetic anisotropy of 400 kJ/m^3 for particles with diameter $D < 50$ Å and 115 kJ/m^3 for particles with diameter $D > 50$ Å. These values are higher, by about an order of magnitude, than those reported for a spinel ferrite of a close by composition in its bulk particle state. In addition to the single domain nature of the core, it is the disordered spin surface which would contribute to this enhancement in a large proportion.

Acknowledgements

Financial support from Inter University Consortium for DAE Facilities (IUC-DAEF), Mumbai Centre, India, is gratefully acknowledged. SC is grateful to IUC-DAEF for the award of a research fellowship.

References

[1] A H Morrish and K H Haneda, *J. Appl. Phys.* **52**, 2496 (1981)
[2] D Lin, A C Numes, C F Majkrzak and A E Berkowitz, *J. Magn. Magn. Mater.* **145**, 343 (1995)
[3] T Jonsson, P Svedlindh and P Nordblad, *J. Magn. Magn. Mater.* **140–144**, 401 (1995)
[4] R W Chantrell, G N Coverdale, M El-Hilo and K O'Grady, *J. Magn. Magn. Mater.* **157**, 250 (1996)

[5] R H Kodama and A E Berkowitz, *Phys. Rev.* **B59**, 6321 (1999)
[6] T Jonsson, P Nordblad and P Svedlindh, *Phys. Rev.* **B57**, 497 (1998)
[7] V Šepelák, U Steinike, D Chr. Uecker, S Wißmann and K D Becker, *J. Solid State Chem.* **135**, 52 (1998)
[8] G F Goya and H R Rechenberg, *J. Appl. Phys.* **84**, 1101 (1998)
[9] R V Upadhyay and R V Mehta, *Pramana – J. Phys.* **41**, 429 (1993)
[10] B D Cullity, *Elements of X-ray diffraction* (Addison Wesley, Reading, Mass., 1959) p. 132
[11] V K Aswal and P S Goyal, *Curr. Sci.* **79**, 947 (2000)
[12] S Chikazumi, *Physics of magnetism* (Robert E. Kreiger Publ. Co., Florida, 1978)
[13] C Paulsen, J Hamida, S J Williamson and H Maletta, *J. Appl. Phys.* **55**, 1652 (1984)
[14] J R L de Almeida and D J Thouless, *J. Phys.* **A11**, 983 (1978)
[15] K Binder and A P Young, *Rev. Mod. Phys.* **58**, 801 (1986)
[16] C P Bean and J D Livingston, *J. Appl. Phys.* **30**, 120S (1959)
[17] F D Stacey and S K Banerjee, *Physical principles of rock magnetism* (Elsevier Scientific Publishing Co., Amsterdam, 1974) p. 59