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Magnetic behaviour of nano-particles of $Fe_{2.8}Zn_{0.2}O_4$

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Abstract. Magnetization measurements are reported on a nano-particle sample of Zn-substituted spinel ferrite $Fe_{2.8}Zn_{0.2}O_4$ in the temperature range 20–300 K. Analysis of small-angle neutron scattering data shows the sample to have a log-normal particle size distribution of median diameter 64.4 Å and standard deviation 0.38. Magnetization evolves over a long period of time t going nearly linearly with $\log t$. Magnetic anisotropy, estimated by fitting M–$\log t$ curve, shows many fold increase over that of bulk particle sample. Major enhancement owes to disordered moments in surface layer. In the nano-particle state as well increasing amount of Zn causes anisotropy to decrease.

Keywords. Nano-particles; magnetic relaxation; anisotropy.

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1. Introduction

Magnetic behaviour of nano-particles has been the subject of much interest [1–4]. Literature reports show that reduction of particle sizes down to nano-size region causes drastic changes in saturation magnetization and magnetic anisotropy. We have undertaken work on the series $Fe_{3-x}Zn_xO_4$ for examining the influence of the substitution of Zn in the spinel Fe_3O_4. Here we present results on a nano-particle sample of $Fe_{2.8}Zn_{0.2}O_4$ and compare them with those on nano-particles of a less Zn-substituted ferrite, viz., $Fe_{2.9}Zn_{0.1}O_4$, obtained in our earlier study [4].

2. Experimental details and sample characterization

Nano-particle sample has been prepared following wet chemical process. Details are given in ref. [4]. X-ray diffraction (XRD) pattern confirmed cubic phase with a cell constant of 8.29 Å. Width of the (3 1 1) reflection (see figure 1), using Scherrer equation [5], gives an average particle size of ∼70 Å. Size distribution of the particles has been estimated using small-angle neutron scattering (SANS) measurements on

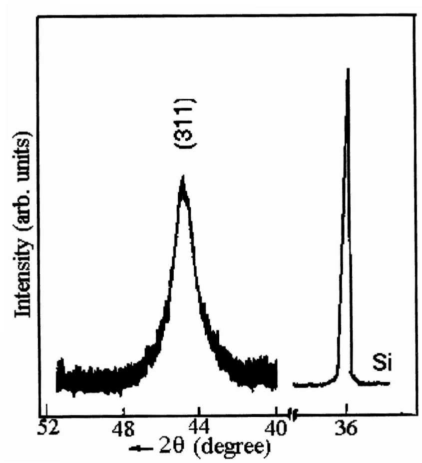

Figure 1. (3 1 1) reflection line from the X-ray diffraction pattern of the nano-particle sample recorded with FeK_α radiation (a reflection line of diffraction pattern of a bulk particle sample of Si is shown for comparison).

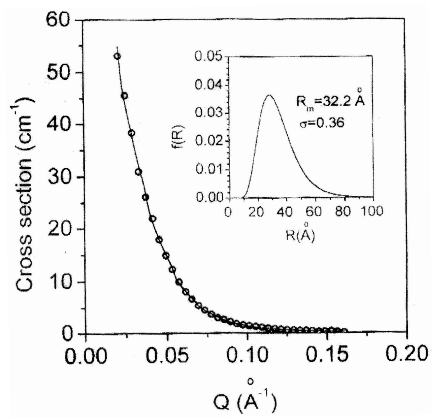

Figure 2. Small-angle neutron scattering distribution from ferro-fluid sample comprised of the nano-particles. Fitted pattern (see text) is shown by a continuous line. The particle size distribution is shown in the inset.

ferro-fluid sample (from which the dried particle sample was obtained) at Dhruva reactor, BARC, Mumbai [6]. Figure 2 shows results on SANS measurements. The measurements have been made using neutrons of mean wavelength 5.2 Å. Assuming spherical shape and a log-normal particle size distribution, this curve yields a distribution of median diameter $D_{\rm m} = 64.4$ Å and standard deviation $\sigma = 0.38$ (inset to figure 2).

Magnetization measurements have been made on a vibrating sample magnetometer (PARC-make) and using a liquid nitrogen cryostat for temperatures down to 85 K and closed cycle refrigerator for temperatures down to 20 K.

3. Results and discussion

Figures 3a and 3b show variation of magnetization M with magnetic field H recorded at 300 K and 20 K respectively. The observations are suggestive of superparamagnetic behaviour at 300 K. Non-zero finite values of $H_{\rm c}$ and $M_{\rm r}$ at 20 K (see inset to the figure) show that blocking temperature is above 20 K. Extrapolation of M vs. $1/H$ curve at 20 K to $1/H \to 0$ gives a value of ~33 emu/g for $M_{\rm s}$ which is much less than 98 emu/g the value for Fe_3O_4. Substitution of a small amount of Zn cannot account for the drastic reduction in moment. Thus the much reduced $M_{\rm s}$ in the nano-particle sample implies that moments in the surface layer, outside a core of ordered moments, are in a state of frozen disorder.

Figure 4 shows Langevin function fitting on the M–H data at 300 K. It gives a log-normal particle size distribution corresponding to median diameter $D_{\rm m} = 70$ Å

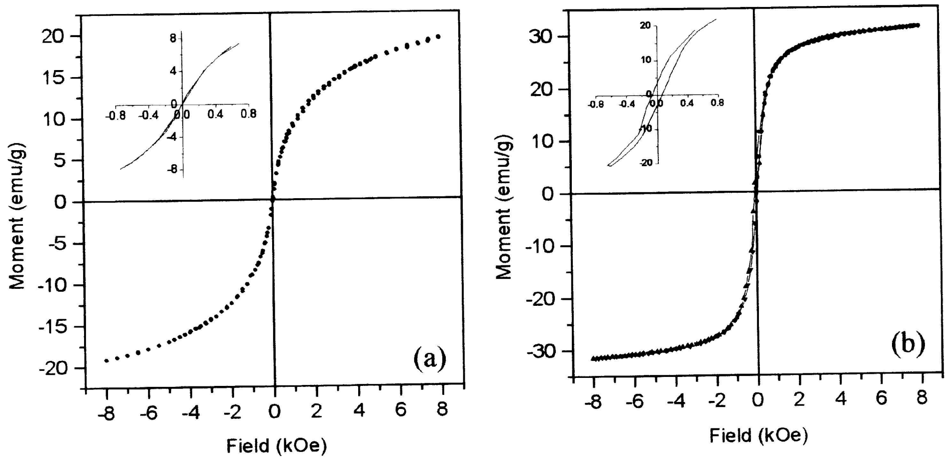

Figure 3. Magnetization–field curves recorded at sample temperatures (**a**) 300 K and (**b**) 20 K. Inset to figures show expanded low field region.

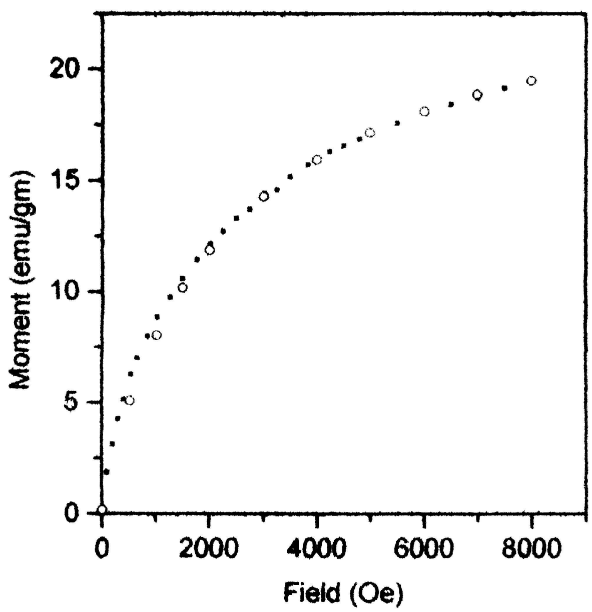

Figure 4. Magnetization–field curve recorded at 300 K shown by solid squares along with Langevin function fitting shown by open circles (for details, see text).

and standard deviation $\sigma = 0.40$. This distribution is about the same as provided by SANS measurement on the same sample of nano-particles dispersed in kerosene.

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

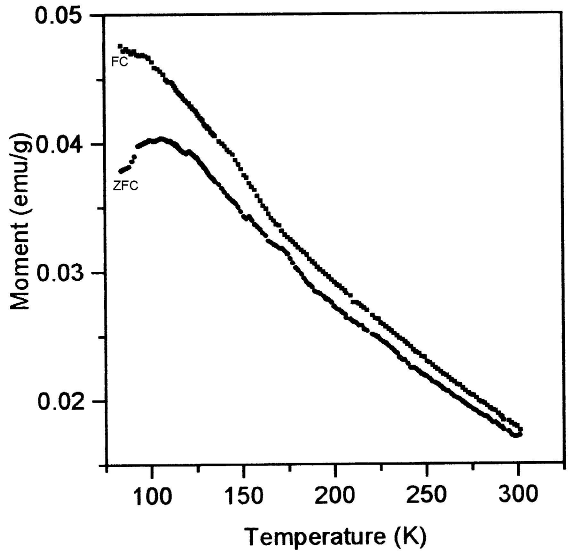

Figure 5. Magnetization–temperature curve recorded in ZFC and FC modes (see text) in an external magnetic field of 5 G.

field of 5 G. The ZFC pattern has been recorded by first cooling the sample from 300 K to 85 K in zero magnetic field, then applying the magnetic field and warming the sample up to 300 K in the presence of the field and recording the moment in this warming cycle. FC pattern has been obtained by first cooling the sample from 300 K down to 85 K in the external field and then warming it up to 300 K and recording the moment. Appearance of a peak in the ZFC curve due to 'blocking' mechanism owes to the competition between the thermal energy and the magnetic anisotropy energy of fine particles. Departure of FC curve from the ZFC one is suggestive of relaxation. Figure 6 depicts evolution of magnetization M with observation time t in a field of 5 G after zero-field cooling of the sample. Observed near linear variation of M with log t is suggestive of the existence of a distribution of energy barriers.

The shape of the M–log t curve has been fitted by taking into account the particle size distribution provided by Langevin function fitting and assuming the constant τ_0 in the relation, for relaxation time, $\tau = \tau_0 \exp(KV/kT)$. Here, τ_0 is 10^{-9} s; K is the anisotropy constant, V the volume of the particle, k the Boltzmann constant and T is the temperature. Details of the fitting procedure are given in ref. [4]. Figure 6 shows the fitting obtained assuming two sets of values of K: 200 kJ/m^3 for particles with $D < 50$ Å and 60 kJ/m^3 for particles with $D > 50$ Å. Attempts to fit in a single value of K for the entire distribution did not succeed. In fact K might be a varying function of D. Nevertheless, these characteristic weighted values of K bear two important points. Firstly, as inferred in ref. [4] on our work on $Fe_{2.9}Zn_{0.1}O_4$, nano-sizing of the particles results in increase in magnetic anisotropy by several folds. This is borne out by 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 [7]). The fact that the reported values are at a higher temperature

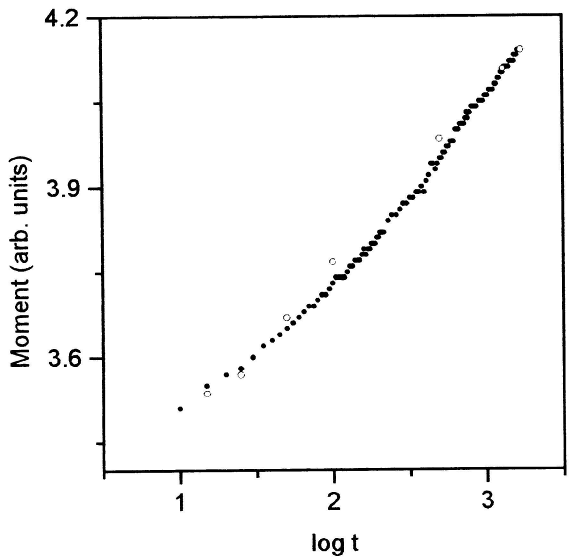

Figure 6. Magnetization M as a function of logarithm of observation time t recorded in ZFC mode at a sample temperature of 85 K; filled circles are the data points. Calculated points taking into consideration the particle size distribution and two values for magnetic anisotropy constant (see text) are also shown, for some observation time, by open circles.

would account for only a minor drop. (This is suggested by reported values of -9 kJ/m^3 and -15.9 kJ/m^3 for bulk particles' sample of $Fe_{2.84}Zn_{0.16}O_4$ at 290 K and 90 K respectively [7]). Further, as inferred in our study of $Fe_{2.9}Zn_{0.1}O_4$, the fact is that for smaller particles, within the assembly of nano-particle sample, K is much larger and would owe to frozen disordered spins in the surface layer. Now, for nano-particles of $Fe_{2.9}Zn_{0.1}O_4$, the estimated values of K are: 400 kJ/m^3 for $D < 50$ Å and 115 kJ/m^3, for $D > 50$ Å. Comparison of these values with those of $Fe_{2.8}Zn_{0.2}O_4$ under study here shows that in the nano-particle state as well increasing amount of Zn results in lowering of K.

In conclusion, our present study shows that, outside a core of ordered spins, moments in the surface layer are disordered. Nano-sizing of the particles results in manifold enhancement in magnetic anisotropy and increasing amount of Zn results in lowering of the anisotropy in the nano-particles state as well.

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