

## Time dependent magnetization of a $\text{Zn}_{0.1}\text{Fe}_{0.9}\text{Fe}_2\text{O}_4$ fine magnetic particle system

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**Abstract.** The time dependent magnetization measurements of the fine particles (100 Å) of  $\text{Zn}_{0.1}\text{Fe}_{0.9}\text{Fe}_2\text{O}_4$  ferrite system at 68 K are reported. The time decay of magnetization is found to be logarithmic. The time dependent co-efficient varies with the applied field and is maximum at coercive field. The value of anisotropy obtained from the variation of time dependent co-efficient with field agrees well with earlier results.

**Keywords.** Fine particles; anisotropy.

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### 1. Introduction

A magnetic fluid is a sterically stabilized colloidal dispersion of ultrafine single domain ferro or ferrimagnetic particles in a suitable carrier liquid. This colloidal system exhibits a superparamagnetic (SP) behaviour at room temperature [1] and under the action of magnetic field it develops structural ordering similar to those of crystalline solids [2] or dipolar glasses [3]. Therefore, this system can serve as a model system to study the characterization of soft condensed materials.

The time dependent behaviour of magnetization, also known as magnetic viscosity is a well-known phenomenon observed in many magnetic systems and it arises from the thermal activation of magnetization changes over energy barriers. In a magnetic fluid this barrier is usually due to anisotropy [1]. The presence of anisotropy energy hinders the relaxation of magnetic system and gives rise to magnetic viscosity. In a magnetic fluid thermal equilibrium may be reached by two different relaxation mechanisms (1) Brownian rotational diffusion, (2) Neel relaxation mechanism [1]. The dominant mode of magnetization process of particle will be that which has the shortest relaxation time. In fact, large particles relax via Brownian rotation while small particles through Neel rotation. As magnetic fluid contains a distribution of particle size both mechanism will, in general contribute to the magnetization for temperature greater than the freezing point of the carrier liquid. But in an applied magnetic field the final state would be the same irrespective of the relaxation process. Recently we have studied electron spin resonance (ESR) of  $\text{Zn}_{0.1}\text{Fe}_{0.9}\text{Fe}_2\text{O}_4$  magnetic fluid between temperature 77 K to 300 K and have shown the effect of these two relaxation mechanisms on ESR linewidth and resonance field [4]. In the present paper

the results of time dependent magnetic property of this sample at 68 K are presented. The results show that the magnetization is time dependent and found to be logarithmic. The anisotropy value obtained from time dependent co-efficient agrees well with that obtained from ESR results.

## 2. Theory

In the present system the data were obtained at 68 K, which is well below the freezing point of the carrier liquid (in the present case it is kerosene, which has the temperature of freezing at around 200 K). Therefore in the system, Neel relaxation mechanism will only contribute and this is governed by a relation [5]

$$\tau^{-1} = f_0 \exp(-\Delta E/kT), \quad (1)$$

where,  $\Delta E$  is the height of the energy barrier,  $k$  and  $T$  are the Boltzmann constant and temperature, respectively. The pre-exponential factor  $f_0$  has typical values between  $10^8$  to  $10^{13} \text{ s}^{-1}$ . For a system of uniaxial particles having their easy axes aligned along the field direction, the height of the energy barrier is

$$\Delta E = KV(1-h)^2. \quad (2)$$

$K$  is the anisotropy constant and  $V$  is the volume of the particle.  $h = H/H_K$  and  $H_K$  is the anisotropy field. Therefore eq. (1) can be written as

$$\tau^{-1} = f_0 \exp[-(KV/kT).(1-h)^2]. \quad (3)$$

According to Bean [6], a critical volume,  $V_{sp}$ , below which the particles are superparamagnetic depends on the experimental measurement time,  $t$ . Therefore by setting  $t = \tau$ , a critical volume in zero magnetic field can be written as

$$V_{sp}(0, t) = kT/K[\ln(tf_0)]. \quad (4)$$

However, in a negative field,  $H$  (i.e. initially sample is saturated for  $H > 0$  and then reduced to  $H < 0$ ), the relaxation time and critical volume are dependent on the magnitude of this field by [6]

$$V_{sp}(h, t) = [kT.\ln(tf_0)]/[K(1-h)^2]. \quad (5)$$

In a magnetic fluid there exists distribution of particle sizes, resulting in three different contributions to the magnetization in the system which can be written as [7]

$$\bar{M}(h, t) = - \int_0^y L(y, h) f(y) dy + \int_y^\infty f(y) dy - \int_y^y f(y) dy, \quad (6)$$

where  $y$  is the reduced diameter  $D/D_m$ .  $D$  and  $D_m$  are the diameter of the particle and median diameter of the system, respectively,  $f(y)$  is the particle size distribution function and  $L(y, h)$  is the Langevin function.  $M$  is the reduced magnetization,  $M/M_s$ , and  $M_s$  is the saturation magnetization of the fluid. The first integral in (6) represents the contribution to the magnetization from the superparamagnetic fraction of the system. The second term represents the contribution from those blocked particles which remain at positive saturation and the last term represents the contribution from

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those initially blocked particles which have made the transition into the field direction. Now if  $t_0$  is an arbitrary time at which the measurement has started, the change in magnetization over the period of time  $t_0$  to  $t$  is

$$\Delta \bar{M}(h, t) = -2 \int_y^y f(y) dy = \bar{M}(h, t) - \bar{M}(h, t_0). \quad (7)$$

During the time of experiment  $y$  does not vary appreciably, so one can expand the integral in (7) in power series and truncate after the first term. Thus

$$\Delta \bar{M}(h, t) = -2 \left[ \frac{kT}{KV_m} (1-h)^{-2} \cdot f(y(h, t_0)) \cdot \ln(t/t_0) \right]. \quad (8)$$

In a magnetic fluid, normally the size distribution obeys log-normal distribution function given by [1]

$$f(y) = (1/\sqrt{2\pi y\sigma}) \exp[-(\ln y)^2/2\sigma^2]. \quad (9)$$

Substituting (9) in (8) and considering  $t_0 = 100$  s, (8) becomes

$$\Delta \bar{M}(h, t) = -[2/(75\sqrt{2\pi\sigma})] \cdot \ln(t/100) \cdot \exp[-(\ln y(h, t_0 = 100))^2/2\sigma^2]. \quad (10)$$

Hence, the magnetization varies linearly with  $\ln t$ . The co-efficient  $S$  (known as magnetic viscosity coefficient) is

$$S = [2/(75\sqrt{2\pi \cdot \sigma})] \cdot \exp[-(\ln y(h, t_0 = 100))^2/2\sigma^2]. \quad (11)$$

The above equation can also be written in terms of coercive force,  $H_c$  for a system with randomly oriented easy axes as [7]

$$S = S_{\max} \exp[-(\ln[(H_K - H_c)/(H_K - H)])^2 \cdot 2/9\sigma^2]. \quad (12)$$

Equation (12) predicts that  $S = S_{\max}$  for  $H = H_c$ .

### 3. Sample preparation and measurements

#### 3.1 Formation conditions and preparation details

Ultrafine particles of 10% Zn substituted magnetite were prepared by chemical co-precipitation technique. Detailed experimental procedure is discussed elsewhere [4]. Particles were coated with oleic acid and dispersed in ISOPAR-M carrier. The fluid was centrifuged at 3000 rpm for 30 min. The substitution of ions was confirmed by atomic mass absorption ( $\text{Fe}/\text{Zn} = 28.9$ ).

#### 3.2 Structural characterization

X-ray powder diffraction pattern was recorded on Philips diffractometer, PW 1130/90 using  $\text{CuK}\alpha$  radiation with a graphite monochromator mounted in the diffracted beam. The particle size and its distribution were measured using GEC-AEI Cornith 275 electron microscope having a linear resolution of 10 Å.

### 3.3 Magnetization measurements

Room temperature and low temperature magnetization measurements were carried out using vibrating sample magnetometer (VSM) PAR155 fitted with Oxford Instruments CF1200 flowing gas cryostat. The measurements of time dependence were taken by saturating the sample in 10 kOe and then reducing the field to the required value. The time taken for the field to stabilize after setting the current in the magnet was measured and found to be  $\sim 10$  s. As soon as the required field was set, the clock was started and magnetization was measured at regular intervals of time for each field.

## 4. Results and discussion

### 4.1 Structural properties

Figure 1 shows the X-ray diffraction pattern for the powder. Structure was found to be single phase fcc spinel with a lattice constant of  $8.392 \pm 0.001$  Å. Measurements of the line width were made to give estimates of the particle size using the Debye-Scherrer expression. The value thus obtained was 92 Å. In order to find out the cation distribution, Rietveld analysis was done. The cation distribution thus obtained is

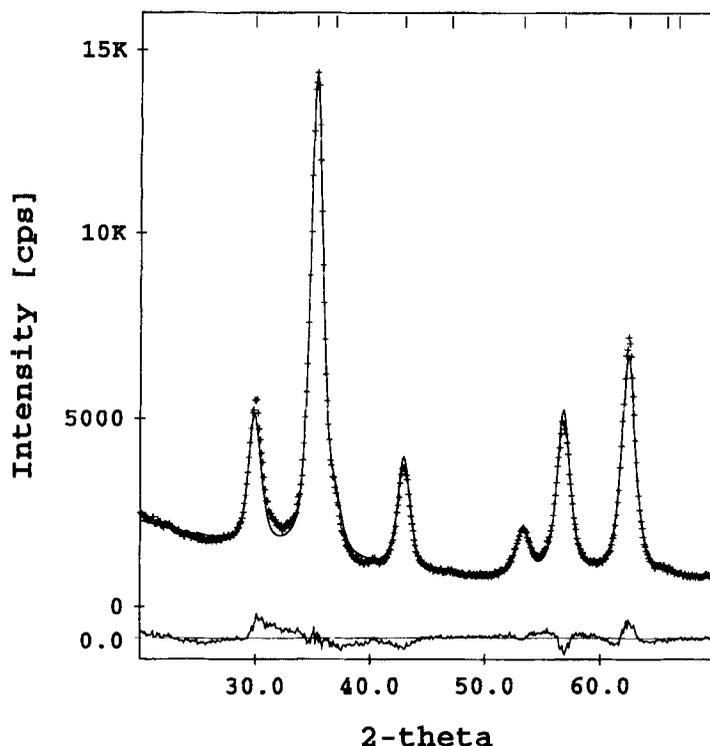


Figure 1. X-ray diffraction pattern of Fe-Zn sample.

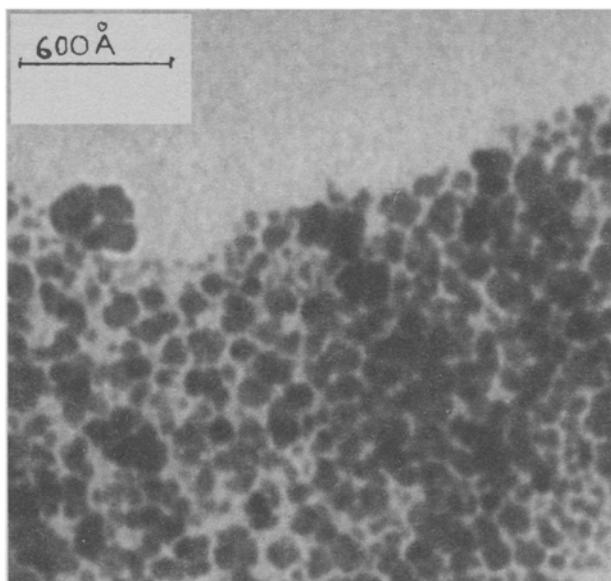


Figure 2. Electron microscope photograph for Fe-Zn sample.

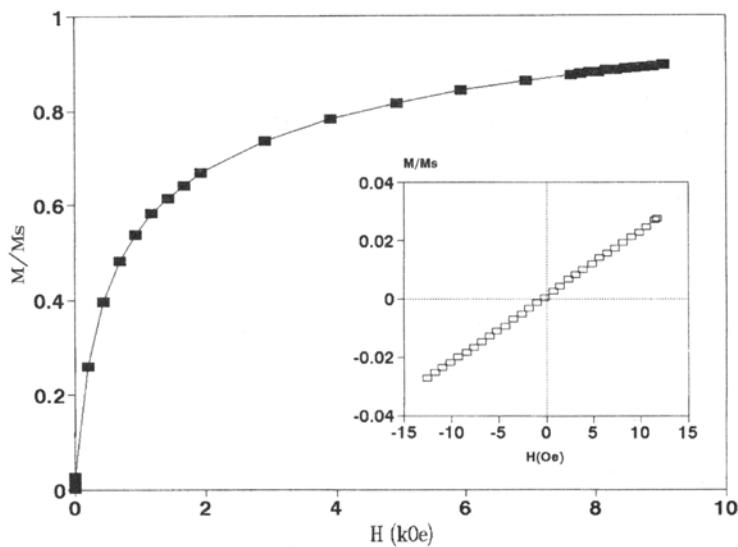


Figure 3. Room temperature reduced magnetization curve for the Fe-Zn sample. Inset: Low magnetic field data.

This result is in contradiction with the earlier results obtained for the bulk sample, where Zn occupies only tetrahedral A-site. But it has been reported that in the case of the sample synthesized by co-precipitation technique, Zn can occupy both the tetrahedral A-site and octahedral B-site of the spinel structure [8].

Figure 2 shows the electron microscope for the system. The particle diameter distribution obeys log-normal size distribution with a median diameter  $D_m = 90 \text{ \AA}$  and the standard deviation of reduced diameter  $\sigma = 0.36$ [9]. This value of particle size is in good agreement with the X-ray data.

#### 4.2 Magnetic properties

The magnetization measurement shows that the system is superparamagnetic at room temperature (figure 3). Using the method of Chantrell *et al* [10], the median diameter and the standard deviation of the log-normal volume distribution were obtained from the room temperature magnetization data assuming particles to be spherical. The value thus obtained were  $D_m = 87 \text{ \AA}$  and  $\sigma = 0.38$ . This observed size represents the magnetic core size rather than the physical size. The saturation magnetization of the particles at room temperature was 62 emu/gm and increased to 64 emu/gram at 68 K. Figure 4 shows the 68 K magnetization curve. The sample exhibits ferromagnetic behaviour at 68 K i.e. having both coercivity and remanence.

Figures 5a–5c show the magnetization of the system as a function of time,  $t$ , for different values of the field,  $H$ . The solid line through the data point is the fit to eq. (10). The co-efficient,  $S$ , obtained from the fit are plotted in figure 6. The solid line shown is a curve calculated from eq. (12) using the value of  $H_c = 135 \text{ Oe}$ ,  $H_K = 550 \text{ Oe}$  and  $\sigma = 0.22$ . Figure 6 shows the good fit between theory and experiment. A maximum is observed at  $H = 135 \text{ Oe}$  which agrees well with the observed coercivity at 68 K (130 Oe).

It is known that the anisotropy field ( $H_K$ ) for uniaxial particles is  $2K/I_{sb}$ , where  $I_{sb}$  is the bulk saturation magnetization and  $K$  is the anisotropy constant. Therefore in order to derive the value of  $K$  one needs the bulk saturation magnetization value for the system at that temperature. One way to obtain is to calculate the  $I_{sb}$  from the cation distribution assuming that this value does not change significantly ( $< 5\%$ ) with temperature for the given temperature range, i.e. 0 K to 68 K. This is reasonable because the Curie temperature ( $T_c$ ) of this sample is much higher than room temperature.

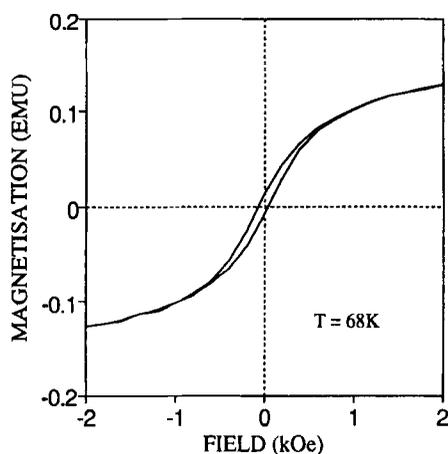


Figure 4. Magnetization versus applied field at 68 K.

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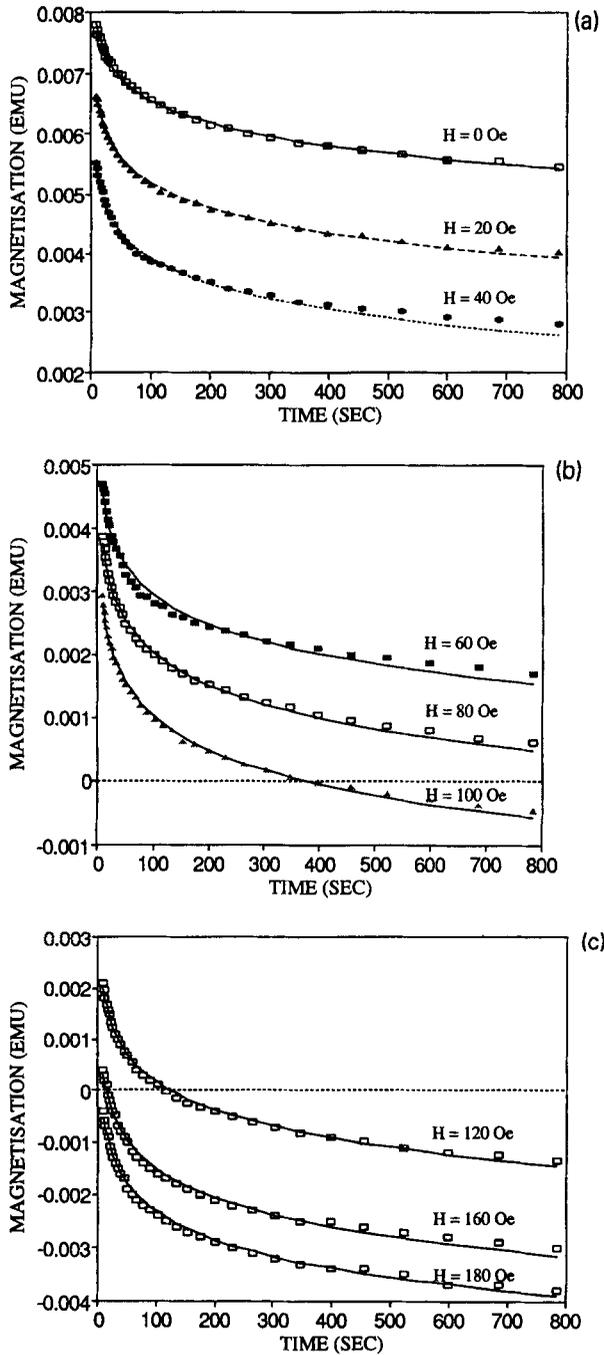


Figure 5a-5c. Time dependent magnetization curves for different field values. Line is the fit to eq. (10).

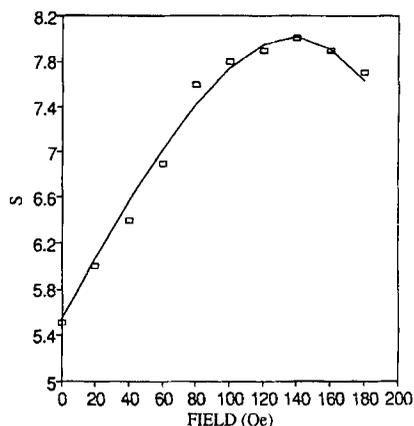


Figure 6. Magnetic viscosity co-efficient,  $S$ , versus field.

Therefore the value of  $T/T_c$  is  $< 0.1$  at 68 K and for this  $I/I_{sb}$  is 0.98. Considering this fact and taking spin only magnetic moment of the ions, the  $I_{sb}$  for this particle was found to be 87 emu/gm. Using this value of bulk saturation magnetization, the value of  $K$  was found to be  $1.2 \times 10^5$  erg/cc. This value is in agreement with the value obtained from ESR study ( $1.0 \times 10^5$ ) [9]. The observed difference in the value of magnetization of the bulk and the present sample may be due to the surface pinning effect as observed in the case of Mn substituted magnetite [11].

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