

# Magnetic resonance in superparamagnetic zinc ferrite

JITENDRA PAL SINGH\*, GAGAN DIXIT<sup>†</sup>, R C SRIVASTAVA<sup>††</sup>, HEMANT KUMAR<sup>††</sup>,  
H M AGRAWAL<sup>††</sup> and PREM CHAND<sup>‡</sup>

Department of Applied Science, Krishna College of Engineering, Ghaziabad 201 007, India

<sup>†</sup>Materials Science Division, Inter University Accelerator Centre, New Delhi 110 067, India

<sup>††</sup>Department of Physics, Govind Ballabh Pant University of Agriculture and Technology, Pantnagar 263 145, India

<sup>‡</sup>Indian Institute of Technology, Kanpur 208 016, India

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**Abstract.** In the present work, we have synthesized zinc ferrite nanoparticles by nitrate method. Presence of almost zero value of coercivity and remanence in the hysteresis of these samples shows the superparamagnetic nature at room temperature. Electron paramagnetic resonance spectroscopy performed on these samples in the temperature range 120–300 K indicates the systematic variation of the line-shapes of the spectra with temperature. Both  $g$ -value and peak-to-peak linewidth decrease with increase in temperature. The variation of  $g$ -values and peak-to-peak linewidth with temperature has been fitted with existing models and we observed different values of activation energies of the spins for both the samples.

**Keywords.** Nanoparticles; magnetic materials; electron paramagnetic resonance spectroscopy.

## 1. Introduction

It is well established that bulk zinc ferrite is an antiferromagnetic material having a Néel temperature of 10 K. It exhibits normal spinel structure i.e. all the  $Zn^{2+}$  remain at  $A$ -site (tetrahedral) and all the  $Fe^{3+}$  remain at  $B$ -site (octahedral) (Cullity 1971). This material has become a material of great attention for scientific community from last two decades due to its extremely different magnetic behaviour in nanoregime compared to its bulk counterpart (Roy *et al* 2006; Xue *et al* 2007; Singh *et al* 2008a, b; Sultan and Singh 2010). Nanosized zinc ferrite shows superparamagnetism at room temperature followed by its mixed spinel structure. The magnitude of magnetization and degree of cation inversion are affected by the particle size in nanoregime. In this context, various authors have investigated the size dependent properties of nanosized zinc ferrite and observed increment in cation inversion with decrease in particle size resulting in enhancement in magnetization for smaller sized systems (Roy *et al* 2006; Xue *et al* 2007; Singh *et al* 2008a, b; Sultan and Singh 2010). Apart from particle size, other properties are very much sensitive to the method of syntheses (Sato *et al* 1990; Jaydevan *et al* 1994; Ahn *et al* 2002; Yu *et al* 2003; Hofmann *et al* 2004; Shenoy *et al* 2004; Nakashima *et al* 2007; Azam *et al* 2009). Mechanism of magnetization in the system was studied by various authors who observed that magnetization in this system cannot only be explained by superparamagnetism but it may have ferrimagnetism, simultaneous existence of ferri and antiferromagnetism, ferromagnetism and spin-glass state (Chinnasamy *et al* 2000; Lee *et al* 2002; Shim *et al*

2006; Yao *et al* 2007). It has also been observed that not only the magnitude of magnetization but also the nature of magnetic ordering depends on the method of preparation (Singh *et al* 2012).

To establish the mechanism of magnetization in nanosized zinc ferrite synthesized by chemical route, we have done Mössbauer, electron paramagnetic resonance spectroscopy (EPR) followed by vibrating sample magnetometer measurement. The synthesized system exhibits superparamagnetism as investigated at room temperature by Mössbauer and EPR spectroscopy (Singh *et al* 2008a, b, 2010). In-field Mössbauer spectroscopy at low temperature performed on these samples indicate that nanosized zinc ferrite exhibits antiferromagnetic ordering below blocking temperature (Singh *et al* 2012). To get information about the spin-dynamics of nanosized system, EPR spectra was recorded at high temperature ranging from 300–850 K. It was investigated that responsible phenomena for relaxation mechanism is not only governed by direct and Orbach process but some other exchange processes are also affecting this mechanism and are discussed in detail elsewhere (Singh *et al* 2009). Also these samples indicate different variations of  $g$ -value and peak-to-peak linewidth with temperature, which depends upon the particle size. In the present work, we have further extended EPR study at low temperature (120–300 K) for similar particle size in order to investigate spin dynamics in superparamagnetic zinc ferrite at low temperature.

## 2. Experimental

Zinc ferrite nanoparticles were synthesized by nitrate route annealing, the precursor at 300 and 500 °C (Singh *et al*

\*Author for correspondence (jitendra\_singh2029@rediffmail.com)

2008a, b). The crystalline phase and structure were studied with the help of X-ray diffractometer using  $\text{CuK}\alpha$  radiation. The morphology and size of these nanoparticles were estimated from high resolution transmission electron microscopy (HRTEM). Room temperature hysteresis for all the samples was recorded by using a Princeton-109 vibrating sample magnetometer. Further, EPR spectra for both the samples were recorded in the temperature range 120–300 K by Bruker-EMX EPR spectrometer.

### 3. Results and discussion

Synthesized samples exhibit pure spinel phase and the crystallite size of these samples are 13 and 19 nm corresponding to sintering temperatures 300 and 500 °C, respectively. These samples are coded as ZF13 and ZF19 and detailed analysis of their structural and morphological properties have been published (Singh *et al* 2013). Figure 1 shows room temperature hysteresis for the samples ZF13 and ZF19. Almost zero value of coercivity and remanance in these nanoparticles show the presence of superparamagnetism. The higher value of magnetization is observed for sample ZF13 compared to ZF19 and is relevant with other studies of nanosized zinc ferrite (Chinnasamy *et al* 2000; Lee *et al* 2002; Roy *et al* 2006; Shim *et al* 2006; Yao *et al* 2007; Singh *et al* 2012).

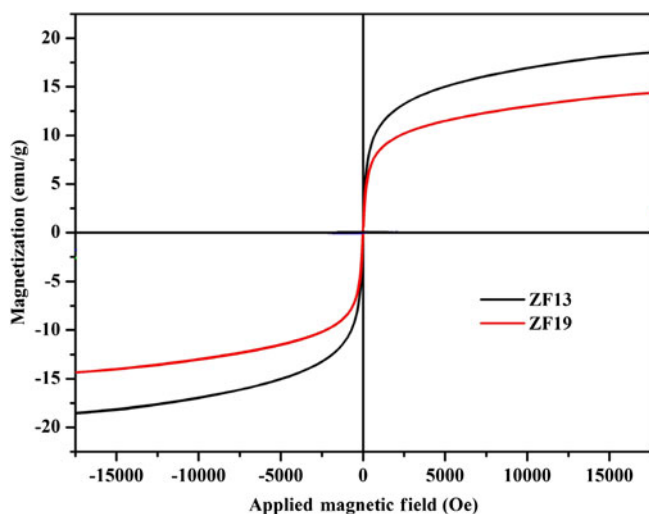
Figure 2 shows X-band EPR spectra of the samples at different temperatures in the range 120–300 K. A visual inspection of EPR spectra shows that samples ZF13 and ZF19 have one moderate resonance signal at all temperatures. We have estimated  $g$ -value from EPR spectra by using the formula (Poole and Farach 1971):

$$g = \frac{h\nu}{\beta H_r},$$

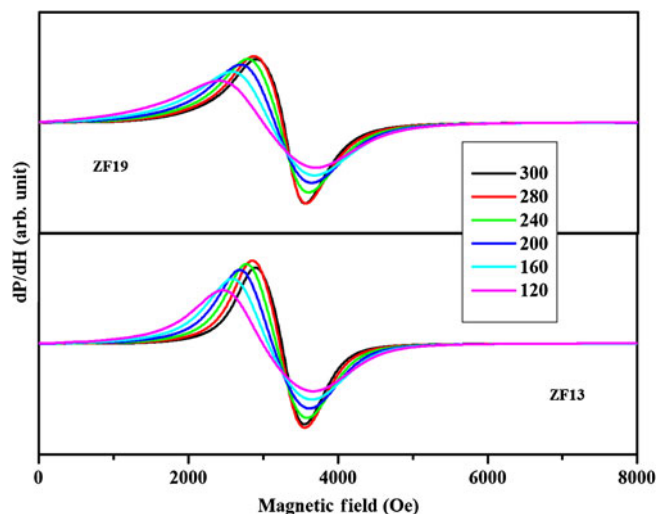
where  $H_r$  is the resonance field,  $\nu$  the frequency and  $\beta$  the Bohr magneton. For both the samples,  $g$ -value ( $\sim 2.253 \pm$

0.006) at 120 K is almost same within the experimental error but at room temperature ZF19 has smaller  $g$ -value compared to ZF13 (table 1). It is clear from this table that  $g$ -values decrease with increase in temperature for both the samples. Similar behaviour of  $g$ -values with temperature has also been reported for other ferrite systems (Singh *et al* 1993; Wu *et al* 2004; Dixit *et al* 2012) and may be attributed to the effect of reduction in magnetic ordering with temperature. In the present work,  $g$ -values are slightly higher compared to that obtained from our previously synthesized zinc ferrite system (Singh *et al* 2008a, b).

The values of peak-to-peak linewidth ( $\Delta H_{PP}$ ) of samples ZF13 and ZF19 are  $1219 \pm 16$  and  $1294 \pm 16$  Oe, respectively at 120 K. Both samples exhibit decrease in the value of  $\Delta H_{PP}$  with increase in temperature and attain almost same value of  $\sim 649 \pm 16$  and  $645 \pm 16$  Oe at room temperature (table 1). The linewidth of EPR signal for any ferrite material generally originated from two sources: (i) magnetic dipole interactions among particles and (ii) superexchange interactions between magnetic ions through oxygen ions. Linewidth may get broadened or narrowed depending upon the interaction inside the material. Dominant dipole interactions give rise to large linewidth and  $g$ -factor, however, small linewidth and lower  $g$ -values are observed, where superexchange interactions are dominant (Li *et al* 2000). Higher value of  $\Delta H_{PP}$  at low temperature shows dominancy of dipolar interaction among the particles. This result is in agreement with EPR study performed on nickel ferrite nanoparticles (Dixit *et al* 2012), however, occurrence of narrow peak-to-peak linewidth at room temperature in these samples may be due to dominant superexchange interaction. The increased temperature will provide extra thermal energy to the atoms, thereby increasing motion of the ions. This causes stronger superexchange interaction among the cations through oxygen ions, consequently,  $\Delta H_{PP}$  and  $g$ -factor decrease with increase in temperature (Singh *et al* 1993). Temperature variation of linewidth and  $g$ -values of Ni–Zn ferrite has been



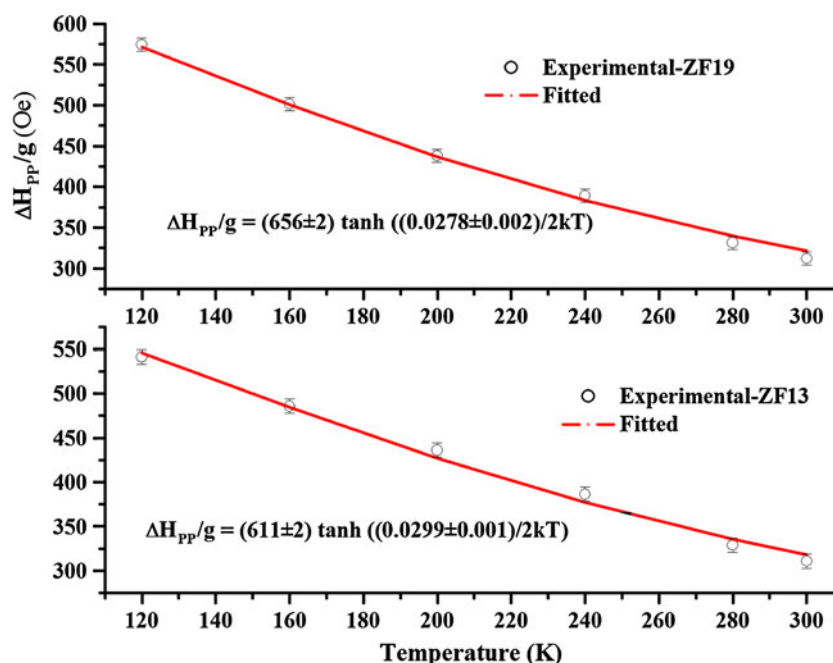
**Figure 1.** Hysteresis curves of samples ZF13 and ZF19 at room temperature.



**Figure 2.** X-band EPR spectra of samples ZF13 and ZF19 at different temperatures.

**Table 1.** Peak-to-peak linewidth ( $\Delta H_{PP}$ ) and  $g$ -value of samples ZF13 and ZF19.

Temperature (K)	ZF13		ZF19	
	$\Delta H_{PP}$ (Oe) $\pm$ 16	$g$ -value $\pm$ 0.006	$\Delta H_{PP}$ (Oe) $\pm$ 16	$g$ -value $\pm$ 0.006
120	1219	2.253	1294	2.254
160	1068	2.198	1096	2.186
200	938	2.151	938	2.141
240	820	2.123	820	2.107
280	688	2.093	688	2.077
300	649	2.089	645	2.066

**Figure 3.** Variation of  $\Delta H_{PP}/g$  with temperature (blank circles show data points and red line is fitting to these points).

given by the following relation and may be applied to zinc ferrite (Wu *et al* 2004; Singh *et al* 2011)

$$\frac{\Delta H_{PP}}{g} = \frac{5\beta S n}{R^3} \tanh\left(\frac{\Delta E}{2kT}\right),$$

where  $\Delta E$  is the activation energy,  $n$  the total number of magnetic centres,  $R$  the average particle distance and  $S$  the effective spins of magnetic centres. According to this equation,  $\Delta H_{PP}/g$  as a function of temperature has been plotted. Assuming  $S$ ,  $n$  and  $R$  almost constant within the measured temperature range, data points were fitted by the above equation (figure 3). Fitting shows change in slope of the data points for both the samples. The values of  $\Delta E$  obtained after fitting are  $0.0299 \pm 0.001$  and  $0.0278 \pm 0.001$  eV for samples ZF13 and ZF19, respectively. The values corresponding to factor  $5\beta S n/R^3$  are  $611 \pm 2$  and  $656 \pm 2$  for the samples ZF13 and ZF19. The differences in these values and slope may be related with the various factors that generally occur in nanoferrites with changes in crystallite size. These

factors are different values of cation inversion and spin canting in both the samples. A detailed study carried out by using in-field Mössbauer spectroscopy on zinc ferrite nanoparticles of similar crystallite size indicates different values of cation inversion and spin canting at different sites (Singh *et al* 2012).

#### 4. Conclusions

Superparamagnetic zinc ferrite was synthesized by nitrate method. Synthesized samples exhibit superparamagnetism at room temperature. The value of magnetization is lower for the large crystallite-sized sample. EPR study performed for these samples indicate the dominance of superexchange interaction at higher temperature, while dipolar interaction at low temperature. The difference in values of activation energy of spins for both the samples has been attributed to the different values of cation inversion and spin canting.

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## References

- Ahn Y, Choi E J, Kim S, An D H, Kang K U, Lee B G, Baek K S and Oak H N 2002 *J. Korean Phys. Soc.* **41** 123
- Azam A, Chaman M and Naqvi A H 2009 *Int. J. Nanopart.* **2** 383
- Chinnasamy C N, Narayanasamy A, Ponpandian N, Chattopadhyaya K, Guerault H and Greneche J H 2000 *J. Phys.: Condens. Matter* **12** 7795
- Cullity B D 1971 *Introduction to magnetic materials* (New York: Addison Wesley)
- Dixit G, Singh J P, Srivastava R C and Agrawal H M 2012 *J. Magn. Mater.* **324** 479
- Hofmann M, Campbell S J, Ehrhardt H and Feyerherm R 2004 *J. Mater. Sci.* **39** 5057
- Jaydevan B, Tohji K and Nakatsuka K J 1994 *Appl. Phys.* **A76** 3625
- Lee S H, Broholm C, Ratcliffe W, Gasparovic G, Huang Q, Kim T H and Cheong S-W 2002 *Nature Mater.* **418** 856
- Li L, Li G, Smith R L and Inomata H 2000 *Chem. Mater.* **12** 3705
- Nakashima S, Fujita K, Tanaka K, Hirao K, Yamamoto T and Tanaka I 2007 *Phys. Rev.* **B75** 17443
- Poole C P and Farach H A 1971 *Relaxation in magnetic resonance* (London: Academic Press)
- Roy M K, Halder B and Verma H C 2006 *Nanotechnology* **17** 232
- Sato T, Haneda K, Seki M and Iijima T 1990 *Appl. Phys.* **A50** 13
- Shenoy S D, Joy P A and Anarantharaman M R 2004 *J. Magn. Mater.* **269** 217
- Shim J H, Lee S, Park J H, Han S J, Jeong Y H and Cho Y W 2006 *Phys. Rev.* **B73** 064404
- Singh J P, Srivastava R C, Agrawal H M, Kushwaha R P S, Chand P and Kumar R 2008a *Int. J. Nanosci.* **7** 21
- Singh J P, Srivastava R C, Agrawal H M and Kushwaha R P S 2008b *Hyperfine Int.* **183** 221
- Singh J P, Srivastava R C, Agrawal H M and Chand P 2009 *Int. J. Nanosci.* **8** 523
- Singh J P, Srivastava R C, Agrawal H M, Kumar R, Reddy V R and Gupta A 2010 *J. Magn. Mater.* **322** 1422
- Singh J P, Srivastava R C, Agrawal H M, Chand P and Kumar R 2011 *Curr. Appl. Phys.* **11** 532
- Singh J P, Dixit G, Srivastava R C, Agrawal H M, Reddy V R and Gupta A 2012 *J. Magn. Mater.* **324** 2553
- Singh J P, Dixit G, Srivastava R C, Agrawal H M and Kumar R 2013 *J. Alloys Compd.* **551** 370
- Singh S, Srivastava R C, Chand P, Khan D C and Wigner P E 1993 *Solid State Commun.* **85** 45
- Sultan M and Singh R 2010 *J. Phys.: Conf. Ser.* **200** 722090
- Wu K H, Chang Y C, Chen H B, Yang C C and Horng D N 2004 *J. Magn. Mater.* **278** 156
- Xue H, Li Z, Wang X and Fu X 2007 *Mater. Lett.* **61** 347
- Yao C et al 2007 *J. Phys. Chem.* **C111** 12274
- Yu S H, Fujino T and Yoshimura M 2003 *J. Magn. Mater.* **256** 420