Quenching of superparamagnetic relaxation in $NiFe_2O_4$ nanoparticles at room temperature

Quenching of superparamagnetic relaxation in NiFe$_2$O$_4$ nanoparticles at room temperature

M K Roy and H C Verma[1]

Department of Physics, IIT Kanpur, Kanpur-208016, India

E-mail: hcverma@iitk.ac.in

Abstract
Nanoparticles of NiFe$_2$O$_4$ are synthesized using a chemical route involving reactions of nitrates of Ni and Fe, and citric acid. The particles with size as small as 8 nm do not show any superparamagnetic relaxation in room temperature Mössbauer spectroscopy. This suggests that the particular preparation process yields a magnetic structure where the magnetic moments are strong enough to quench superparamagnetism. Over-occupancy in tetrahedral sites is suggested to be a possible explanation.

1. Introduction

Study of magnetic nanoparticles has attracted considerable attention in recent years because of their interesting physical properties (size and surface effects [1–5], quantum tunnelling of magnetization [6], etc) and wide range of applications (high density magnetic recording media [7], giant magnetoresistive sensors [8], ferrofluids [9, 10], gas sensors [11, 12] etc). Most of the magnetic nanoparticle technological applications depend on the magnetic order of the nanoparticles being stable with time. However, with decreasing particle size the magnetic anisotropy energy per particle responsible for holding the magnetic moment along certain directions becomes comparable to the thermal energy. When this happens, the thermal fluctuations induce random flipping of the magnetic moment with time, and the nanoparticles lose their stable magnetic order and become superparamagnetic. Thus, the demand for further miniaturization comes into conflict with the superparamagnetism, and this defines the so-called 'superparamagnetic limit' in recording media. Since superparamagnetic behaviour is a primary enemy to faithful operation of nanodevices and nanoparticle memories, it is vital to provide an extra source of anisotropy to the small size of particles, leading to magnetization stability.

Mössbauer spectroscopy has been very effective in probing the magnetic structure, especially in the case of nanosize ferrite particles. The nanosize shows up in a Mössbauer spectrum in different ways that can distinguish between superparamagnetism where a six-line

---

[1] Author to whom any correspondence should be addressed.

pattern collapses to a doublet, collective magnetic excitation where the magnetic moments fluctuate about an easy axis resulting in a reduced hyperfine magnetic field B_{hf}, and a non-equilibrium cation distribution resulting in absorption area ratio being different from what can be expected from cationic affinities.

Nickel ferrite is an inverse spinel ferrite in which iron occupies both tetrahedral and octahedral interstitial sites in the fcc oxygen lattice. These two inequivalent sites give rise to two six-line patterns in the Mössbauer spectrum with characteristic parameters. However, if the thermal energy is sufficient to allow for rapid fluctuation of the magnetic moment about an easy axis leading to zero effective hyperfine field, the sextets collapse to superparamagnetic doublet. Even if the thermal energy is not sufficient to allow for superparamagnetic relaxation, it can still lead to oscillation of the particle magnetic moment about an easy axis, leading to six-line patterns with lower B_{hf}. Obviously the smaller is the particle the greater is the chance for superparamagnetic relaxation.

It has been recently pointed out that the magnetic parameters of nanosize ferrites depend not only on the size but also on the preparation process [13–17]. Thus $NiFe_2O_4$ of size 12 nm prepared by co-precipitation of Ni and Fe hydroxides followed by hydrothermal heating at high pressure resulted in a well split six-line pattern [17], whereas most of the earlier studies on Ni ferrite of comparable size showed superparamagnetic collapse. All these samples show the same feature in x-ray diffraction such as a pure crystalline phase with broadened peaks. This means particles of the same material having the same size and the same crystalline properties can still differ in magnetic structure, and this difference can be brought about by altering the preparation process.

In this paper we report the observation of a complete quenching of superparamagnetic relaxation for $NiFe_2O_4$ particles of average size as small as 8 nm. The particular chemical pathway used in this preparation is employed for the first time for Ni ferrite preparation to the best of our knowledge.

2. Experimental details

Nanosize nickel ferrites of different particle sizes were prepared by using the combination of ferric nitrate, nickel nitrate and citric acid. Aqueous solutions of iron and nickel salts were prepared separately in stoichiometric proportions by dissolving the salts in deionized water under constant magnetic stirring condition and then the solutions were mixed together. Citric acid solution was prepared separately and added to the aqueous salt solution with cation to citric acid ratio 1:3. The solution was heated at 80 °C with continuous magnetic stirring for one hour. The heated solution was allowed to cool at room temperature and finally it was dried at 100 °C in an oven to form a fluffy mass, which was crumbled to form the precursor powder. This precursor powder was heated at different temperatures from 400 to 800 °C for one hour with a temperature stability of ±2 °C to get nickel ferrite particles of different sizes.

The crystallographic structure and phases of the samples were characterized by x-ray diffraction (XRD) using Cu Kα radiation. The XRD spectra of the samples were recorded with a Seifert ISO Debyeflex 2002 under identical conditions to minimize the experimental errors in the quantitative analysis of crystallite size. Transmission electron micrographs (TEMs) were collected to see the particle morphology. A small amount of the sample powder was put in acetone and it was ultrasonicated for a few minutes. A drop of this was put on a carbon coated grid and was allowed to dry up. This was used as the TEM sample.

Mössbauer spectroscopy is used to elucidate the local structure and magnetic properties of the samples through the hyperfine interactions. Mössbauer spectra were recorded at room temperature in a transmission geometry using a conventional ^{57}Fe constant acceleration
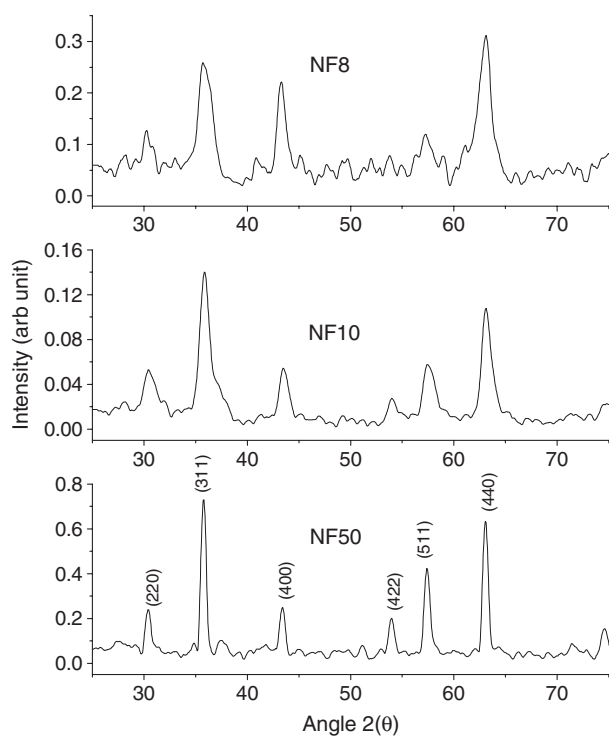
Figure 1. X-ray diffraction patterns of nickel ferrite particles prepared at temperatures of 400 °C (NF8), 450 °C (NF10) and 800 °C (NF50).

Mössbauer spectrometer employing a 25 mCi ^{57}Co/Rh source. The spectra were analysed using the least squares method assuming Lorentzian lineshapes. The isomer shift (IS) and quadrupole splitting (QS) have an uncertainty of about 0.04 mm s^{-1} and the hyperfine magnetic field B_{hf} has an uncertainty of about 0.1 T. Relative areas are accurate up to 2%.

3. Results and discussions

3.1. Particle size determination

Figure 1 shows the x-ray diffraction patterns of the NiFe$_2$O$_4$ samples obtained by heating the precursor powder at different temperatures. The data were smoothened by averaging over neighbouring points. All the peaks in the pattern can be identified to come from the spinal structure of NiFe$_2$O$_4$, showing that the samples are formed in the pure phase. As is clear from visual inspection of the XRD patterns, the peaks are quite broad for the sample made at 400 °C and gradually sharpen as the heating temperature is increased. The broadening in XRD peaks may come from different sources, the main contributors being the reduced particle size and strain in the crystal. Indeed, reduction of particle size below a threshold itself causes strain in the crystal because of broken and incomplete bonds on the surface. The broadenings of the most intense XRD peaks (311) of NiFe$_2$O$_4$ are extracted by recording the XRD pattern of a well crystallized silicon standard and correcting for the instrumental broadening. Assuming the broadening to come primarily from particle size, we used the Scherrer formula to get the average particle size. The three samples prepared at temperatures of 400, 450 and 800 °C have
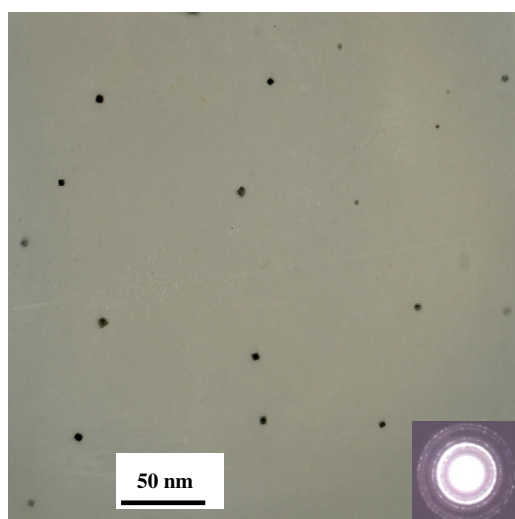
Figure 2. TEM photograph and SAD pattern of 8 nm nickel ferrite particles.
(This figure is in colour only in the electronic version)

average particle sizes of 8, 10 and 50 nm respectively. We call these samples NF8, NF10 and NF50. The number attached to 'NF' gives the average particle size in nanometres.

The precursor of $NiFe_2O_4$ has been prepared directly from the reaction of nitrate salts with citric acid at $80\,^\circ C$. In this method no precipitation is needed and the reaction hardly takes one hour. Also the reaction temperature needed is only $80\,^\circ C$. From the XRD results we find that this reaction is capable of producing nanosize $NiFe_2O_4$ particles in pure phase and with controlled particle size. The annealing temperature gives a good handle to control the particle size.

Figure 2 shows the TEM micrograph of NF8 particles. The particles appear to be roughly of the same size. The average particle size as seen in TEM micrograph is similar to that obtained from XRD peak broadening. This also shows that each particle is a single grain. The selected area diffraction pattern (SAD pattern) shows good crystallinity of the particles.

3.2. Mössbauer studies and quenching of superparamagnetism

Figure 3 shows the Mössbauer spectra of different $NiFe_2O_4$ samples recorded at room temperature and table 1 gives the Mössbauer parameters. In all the spectra only sextets are present. The absence of a doublet in the Mössbauer spectrum for NF8 at room temperature gives the signature that superparamagnetic relaxation is completely quenched, even for the particles of average size 8 nm only. Indeed, the B_{hf} values of the sextets in the spectrum (50.6 T for B sites and 49.3 T for A sites) are significantly less than the values expected for the bulk sample (54.8 and 50.6 T), showing that the magnetic moments fluctuate about an easy axis. Going from NF8 to NF10, these B_{hf} values increase, showing less pronounced collective magnetic excitations.

Nanosize $NiFe_2O_4$ has been prepared by many workers using various methods and studied using Mössbauer spectroscopy. Thus Abuquerque et al [18] prepared this sample by reaction of Ni and Fe nitrates with NaOH in solution form. The precipitate was annealed at various temperatures to get pure phase Ni ferrite of average particle size from 4 to 15 nm. All these samples gave a strong superparamagnetic doublet in their Mössbauer spectra at room
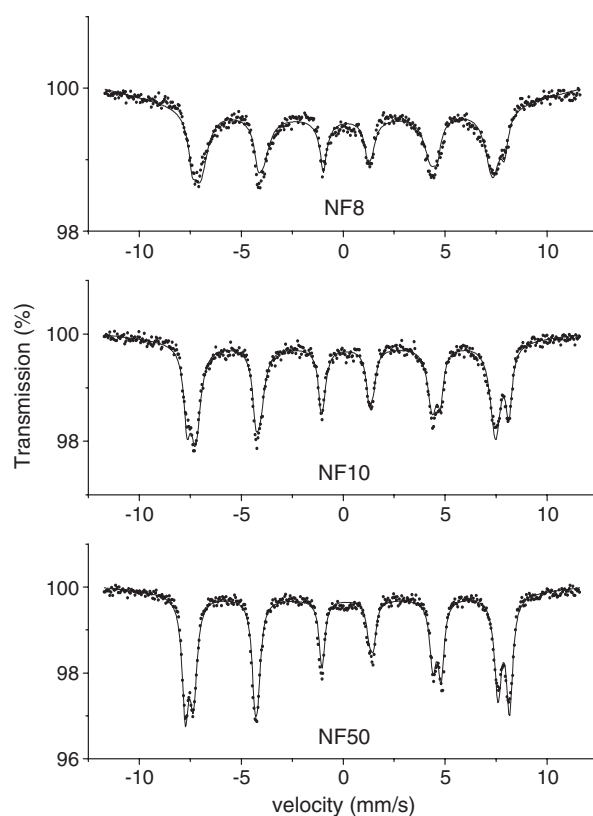
Figure 3. Mössbauer spectra for 8, 10 and 50 nm nickel ferrite samples recorded at room temperature.

Table 1. Mössbauer parameters of the spectra corresponding to NiFe$_2$O$_4$ samples.

Sample	Measurement temperature (K)	IS (mm s^{-1})	QS (mm s^{-1})	Width (mm s^{-1})	B_{hf} (T)	Area (%)
NF 8	295	0.33	0.04	0.36	50.6 (B site)	23
		0.26	−0.009	0.68	47.3 (A site)	77
NF 10	295	0.33	0.012	0.34	52.1 (B site)	33
		0.22	−0.02	0.49	48.6 (A site)	67
	16	0.42	−0.19	0.57	55.8 (B site)	32
		0.35	−0.21	0.65	51.8 (A site)	68
NF 50	295	0.32	−0.02	0.33	52.5 (B site)	51
		0.21	0.01	0.37	49.3 (A site)	49

temperature. Only the 15 nm sample showed some evidence of an unresolved sextet component superimposed on a strong superparamagnetic doublet. Ma *et al* [3] also prepared nanosize NiFe$_2$O$_4$ using chemical route. The Mössbauer spectrum of the 8 and 12 nm samples were largely made up of superparamagnetic doublets. Prasad *et al* [19] prepared nanosize NiFe$_2$O$_4$ by refluxing the solution of Ni and Fe salts with citric acid for 15 h followed by drying and heating. They report all samples with particle size less than 21 nm to show partial or complete superparamagnetic relaxation giving rise to a doublet component in the Mössbauer spectrum.

The absence of superparamagnetism for 8 and 10 nm particles of $NiFe_2O_4$ observed in the present work shows that the present samples have a magnetic structure different from most of the samples synthesized by other methods in the comparable size range.

Superparamagnetism occurs when the magnetic anisotropy energy is comparable or greater than the thermal energy kT. The magnetic energy is proportional to the volume and the magnetic moment of the particle. The quenching of superparamagnetism in our 8 and 10 nm samples show that the magnetic moments of our particles are larger than most of the $NiFe_2O_4$ particles of the same size made by other methods. The magnetic moment of the nickel ferrite nanoparticles depends on the broken bonds on the surface, spin canting on the surface, cationic distribution in the tetrahedral and octahedral sites, vacancies at cationic and oxygen sites, etc. Ma *et al* [3] have made an estimate that about 44% of atoms reside in the surface layer (0.7 nm) for a nickel ferrite particle of size 8 nm. In view of this large fraction, it is reasonable to assume that the effect of surface atoms will be most dominative in determining the magnetic moment. Kodama *et al* [20] have shown from the calculation of magnetic spin interaction energy that the spins of the surface atoms are canted and this reduces the magnetic moment. Such canting has been confirmed by doing Mössbauer spectroscopy in high longitudinal magnetic field on $NiFe_2O_4$ particles made by mechanical milling [21], chemical precipitation [22] etc. The surface effect will reduce the magnetic moment and will help in superparamagnetic fluctuation. The Mössbauer results on the NF8 and NF10 samples indicate that either the surface canting is not pronounced in the present samples or there are other effects which are strengthening the magnetic moment.

3.3. Over-occupancy in tetrahedral A sites

In purely inverse spinel ferrites, half the iron atoms occupy the A sites and the rest occupy the B sites. Nickel ferrite in the bulk state has this configuration (inverse parameter $= 1$). The A-site iron atoms give rise to a sextet of smaller IS and smaller B_{hf} and the B-site iron atoms give a sextet of larger IS with larger B_{hf} [23–25]. Assuming the same recoil-free fraction, the relative areas of the two sextets in the Mössbauer spectra should be the same.

Due to the nanosize, the cationic preferences may change. If the inversion is not complete, some of the Ni will come to the A-site, sending an equal number of Fe atoms from A to B sites. This will increase the area of the B site. But we see the opposite behaviour in our case. In NF8 the area corresponding to the A site is 77% and that corresponding to the B site is only 23%. In NF10 also the trend is the same, the areas being 67% and 33%, and finally for NF50 we have areas 51% and 49% for the B site and A site respectively. Hence NF50 has the same configuration with respect to occupancy of A and B sites as expected from a bulk size powder. So the as prepared nickel ferrite samples show a systematic deviation from the standard A- and B-site occupancy as the particle size is decreased. Such behaviour was also shown in the nanosize Ni ferrite obtained by ball milling [21]. In that case, an extra B_{hf} was fitted to the data and was assigned to the cations present at grain boundaries. However, not much supporting evidence assuming such an extra site was reported in that work. Upadhyay *et al* [17] have also obtained a similar result in 12 nm Ni ferrite prepared by the hydrothermal route, where the A-site area was larger than that of B sites.

We have tried to fit the data for a three-sextet configuration but such a fit gave unphysical and unacceptable parameters. This means that either there are only two sextets corresponding to the A and B sites, or if a third sextet is present it is superimposed on the main peaks in a way difficult to resolve.

To resolve any hidden sextet in the superimposed form we have applied an external magnetic field of 1 T in the plane of the sample. This external magnetic field should give further
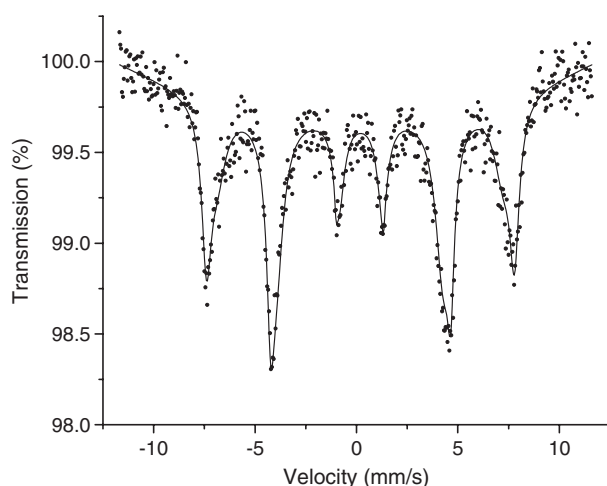
Figure 4. Mössbauer spectra for 10 nm nickel ferrite recorded at room temperature in the presence of 1 T external magnetic field applied parallel to the plane of the sample.

insight about the cationic distribution, as the spectral subcomponents belonging to different sublattices shift in different ways in the applied magnetic field. In the case of a spinel ferrite, where Fe belongs to two crystallographic sites, the applied magnetic field gets added to the B_{hf} of the tetrahedral site and subtracted from the B_{hf} of the octahedral B-site. Thus, the positions of the sextet peaks will get changed and this change will be site specific. If there is a third sextet corresponding to a third environment, it is likely to get resolved in presence of external magnetic field. However, NF10 spectrum recorded under 1 T external field (figure 4) gives no indication of any third peak. So finally we fitted two sextets and the area corresponding to tetrahedral and octahedral came out to be 68% and 32% respectively, the same as that in the zero field situation.

From figure 4 it is also visible that the intensities of second and fifth peaks have become the largest. This shows that the magnetic moments have aligned themselves with the applied magnetic field and the intensities are governed by $\theta_m = 90°$ between the magnetic moments and the γ-ray direction. We know that Ni ferrite is a high permeability material. From the enhanced intensities of the second and fifth peaks one can conclude that this property is retained even for the particles of size 10 nm.

The absorption areas may be different for the same occupancy of Fe in the two sites if the recoil-free fraction is different for the two environments. Previous data on bulk NiFe$_2$O$_4$ show that the areas corresponding to the two sites are almost equal, indicating that recoil-free fractions f for the two sites are not very different in large size particles. But in nanometric samples, including that prepared by the chemical route, where magnetic ordering is drastically different from that in the samples of comparable size prepared by other routes, we cannot be sure of equality or near equality of the f-fraction. This issue can be better addressed if one records Mössbauer spectra at a low temperature where lattice vibrations are considerably reduced and any difference in the f-fraction is accordingly quenched. If the Mössbauer spectrum at low temperatures also gives similar enhancement of tetrahedral absorption area, the recoil-free fraction cannot be held responsible for this anomalous distribution area. Figure 5 shows the Mössbauer spectrum of Ni ferrite at 16 K. The parameters associated with the spectra are given in table 1. The spectrum is best fitted with two sextets of B_{hf} 51.8 and 55.8 T which belong to the tetrahedral A sites and octahedral B sites respectively. Here also the relative
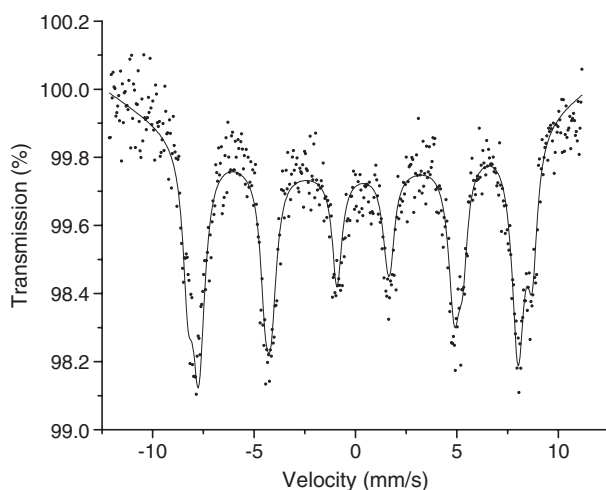
Figure 5. Mössbauer spectrum for 10 nm nickel ferrite recorded at 16 K.

areas of A and B sites are 68% and 32%, respectively, that is, the same as observed at room temperature within the experimental errors. This shows that the enhanced tetrahedral area is not coming from different lattice dynamics at A and B sites.

In a cubic unit cell of spinel ferrite there are 64 tetrahedral and 32 octahedral sites present. Of these only eight and 16 respectively are occupied by the cations. Ruling out the significant effects of grain boundaries and difference in recoil-free fraction of ^{57}Fe at tetrahedral and octahedral sites, we propose that the enhanced Mössbauer absorption area on tetrahedral sites may be due to over-occupancy in these sites. More than eight tetrahedral sites per unit cell are occupied by the Fe atoms, resulting in large relative absorption at these sites.

The proposal of over-occupancy in the tetrahedral sublattice can also explain the quenching of superparamagnetism. The magnetic moment in spinel ferrites is due to the difference in sublattice magnetization of tetrahedral and octahedral sublattices (ferrimagnetic ordering). If significantly more Fe atoms are sitting into one sublattice, the difference of the two sublattice magnetizations will increase. This will increase the particle magnetic moment and hence the chance of superparamagnetic relaxation may become weak.

4. Conclusion

Nickel ferrite nanoparticles are synthesized by a chemical route involving Ni and Fe nitrates and citric acid. The whole reaction occurs in solution form at a temperature of 80 °C in just one hour. By annealing the dried precursor at different temperatures pure phase NiFe$_2$O$_4$ nanoparticles of different sizes are obtained. Superparamagnetism is completely quenched in the 8 and 10 nm samples, where the Mössbauer spectrum is composed of only six-line patterns. The relative area of the sextet corresponding to the A sites is much larger than that corresponding to the B sites, which is opposite to what is expected from an inverse or partially inverse nickel ferrite. Results suggest that more than eight tetrahedral A sites per unit cell are populated in the present samples and these are occupied by Fe atoms. This can also explain the increase in magnetic moment and hence quenching of superparamagnetism.

References

[1] Kodama R H 1999 *J. Magn. Magn. Mater.* **200** 359
[2] Hendricksen P V, Linderoth S and Lindgård P-A 1993 *Phys. Rev.* B **48** 7259
[3] Ma Y G, Jin M Z, Liu M L, Chen G, Sui Y, Tian Y, Zhang G J and Jia Y Q 2000 *Mater. Chem. Phys.* **65** 79
[4] Berkowitz A E *et al* 1999 *J. Magn. Magn. Mater.* **196** 591
[5] Nathani H and Mishra R D K 2004 *Mater. Sci. Eng.* B **113** 228
[6] Chudnovsky E M and Gunther L 1988 *Phys. Rev. Lett.* **60** 661
[7] Parker F T, Spada F E, Cox T J and Berkowitz A E 1996 *J. Magn. Magn. Mater.* **162** 122
[8] Parkin S S P, More N and Roche K P 1990 *Phys. Rev. Lett.* **64** 2304
[9] Virden A E and O'Grady K 2005 *J. Magn. Magn. Mater.* **290/291** 868
[10] Makovec D *et al* 2005 *J. Magn. Magn. Mater.* **289** 32
[11] Gopal Reddy C V, Manorama S V and Rao V 1999 *Sensors Actuators* B **55** 90
[12] Yang L, Xie Y, Zhao H, Wu X and Wang Y 2005 *Solid-State Electron.* **49** 1029
[13] Kinemuchi Y *et al* 2002 *Thin Solid Films* **407** 109
[14] Šepelák V *et al* 2004 *J. Magn. Magn. Mater.* **272–276** 1616
[15] Son S, Taheri M, Carpenter E, Harris V G and McHenry M E 2002 *J. Appl. Phys.* **91** 7589
[16] Huang X and Chen Z 2004 *J. Magn. Magn. Mater.* **280** 37
[17] Upadhyay C, Verma H C and Anand S 2004 *J. Appl. Phys.* **95** 5746
[18] Albuquerque A S *et al* 2001 *J. Magn. Magn. Mater.* **226–230** 1379
[19] Prasad S and Gajbhiye N S 1998 *J. Alloys Compounds* **265** 87
[20] Kodama R H *et al* 1996 *Phys. Rev. Lett.* **77** 394
[21] Chinnasamy C N *et al* 2001 *Phys. Rev.* B **63** 184108
[22] Morrish A H and Haneda K 1981 *J. Appl. Phys.* **52** 2496
[23] Gismelseed A M and Yousif A A 2005 *Physica* B **370** 215
[24] Sileo Elsa E and Jacobo S E 2004 *Physica* B **354** 241
[25] Menzel M, Šepelák V and Becker K D 2001 *Solid State Ion.* **141/142** 663