Characterization of magnetic nano materials by Mössbauer spectroscopy

Sangeeta Thakur1, S C Katyal1, A Gupta2, V R Reddy2 and M Singh3

1 Jaypee University of information technology, Waknaghat, Solan 173215, INDIA
2 UGC-DAE Consortium for scientific research, Khandwa Road, Indore 452017, INDIA
3 Department of physics, Himachal Pradesh University, Shimla 171005, INDIA

Email: megha2k6@gmail.com

Abstract. The use of a non-destructive nuclear-physical method, namely 57Fe Mössbauer spectroscopy, is discussed for the investigation of magnetic and structural arrangement of Fe-based nano-crystalline nickel-zinc-indium ferrites (NZIFO). Nano NZIFO particles (Ni0.58Zn0.42InxFe2-xO4) with varied quantities of indium (x = 0, 0.1, 0.2) have been chemically synthesized through a reverse micelle reaction and investigated by X-ray diffraction, transmission electron microscopy and by magnetic and Mössbauer spectral studies. Here a comparison between low-temperature and room temperature Mössbauer spectra is presented. Well defined sextets at 5 K provide information about the structure and magnetic states of atoms located in different structural positions. The dependence of Mössbauer parameters, viz, isomer shift, quadrupole splitting, linewidth and hyperfine magnetic field on In3+ concentration have been discussed. Detailed Mössbauer results, as well as the interest of these materials both for applied science perspectives are presented. Mössbauer results are also supported by magnetization data. With these interesting ferromagnetic properties Indium substituted nano nickel-zinc ferrites have potential applications in magnetic storage data.

1. Introduction
Nanoparticles spinel oxides are attracting increasing interest in research because of their potential applications in nanoscience and technology [1-3] and also for fundamental understanding of the strikingly different properties of the same material when the particle size approaches the atomic scale level [4-8]. Some of the novel properties in magnetic nanoparticles, such as superparamagnetism, quantum magnetic tunneling, and surface spin effects [1,9-10] have generated further interest in the study of nanoparticles spinels. Although spinel ferrite nanoparticles have been synthesized by a variety of methods such as high-energy ball milling, [11] co-precipitation, [12] and sol-gel method, [13] microemulsion synthesis allows for the formation of high quality nanoparticles with controllable size and composition through minor adjustments to the synthesis conditions [14-15]. We have recently reported the synthesis of NZIFO nanoparticles using reverse micelle microemulsion procedure [16]. The reverse micelle procedure has resulted in a more repeatable synthesis of similar sized nanoparticles. We have already reported the Mössbauer characterization and magnetic properties of NZIFO particles at room temperature [16], in this paper, we are reporting on the properties of nanoparticles at low temperature 5 K.

2. Experimental
Nanoparticles of NZIFO were synthesized by reverse micelle technique [16]. The phase structure of nano ferrites was analyzed by XRD (Rigaku Geiger Flex 3KW diffractometer) using Cu Kα source. The morphology of powders was studied using a transmission electron microscope (TEM). Low temperature (5 K) Mössbauer measurements are carried out using Janis made cryostat. NORMOS software was used for the quantitative evaluation of the Mössbauer spectra. Magnetization measurements were carried out on a SQUID magnetometer.

3. Results and discussion
XRD patterns of the reverse micelle synthesized ferrites show a typical spinel structure for nano nickel-zinc ferrite (NZFO) and NZIFO particles [16]. The sample x = 0.2 contains a slight trace of hematite (Fe2O3) in

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addition to the spinel phase [16]. TEM of NZFO and NZIFO particles shows the spherical nature of the particles with the size distribution range of 8-12 nm and 15-25 nm respectively [16, 17]. Low temperature Mössbauer spectra for all samples are taken at 5 K. As clearly shown in Fig. 1, the superparamagnetic relaxation is suppressed at 5 K, and the Mössbauer spectrum consists of broadened sextets only. The broad shape of Mössbauer spectral lines for NZIFO samples provide clear evidence of a wide distribution of magnetic fields acting at the Fe$^{3+}$ nuclei in the nanoparticles.

As the indium ion content is increased a broadening and splitting of the outer lines of the spectrum is observed with a change in their intensity. The broadening of the spectral components is obviously caused by the superimposition of several Zeeman sextets corresponding to the Fe$^{3+}$ ions located at various different magnetically nonequivalent positions formed as a result of the addition of diamagnetic ions. For samples $x = 0, 0.1$ we obtained the best fit by employing five sextets in the Mössbauer spectra, one accounting for Fe$^{3+}$ in the tetrahedral sites (A) and four for the octahedral sites [B] of the spinel structure. In addition to those a sixth spectrum (M2) is used for sample 0.2 for the traces of hematite. The hyperfine fields at both crystallographic sites for NZIFO particles are reported in Table 1. The spectrum of the nano NZFO sample (Figure 1, taken from ref. [18]) has the average magnetic hyperfine fields $B$(A) = 50.94 T and $B$ [B] = 52.88 T, values that are well comparable with those of the bulk material [19]. At 5 K, the hyperfine fields increases as the concentration of In$^{3+}$ ions increases from 0 to 0.1 (Table 1). At $x = 0.2$, hyperfine field at (A) site decreases more rapidly than the [B] site field. Increase in hyperfine field with indium concentration upto 0.1 could be explained on the particle size distribution [20]. The variation of the effective hyperfine field for the sample $x = 0.2$ could be understood on the basis of supertransferred hyperfine fields (H$_{STHF}$). The magnetic hyperfine fields at the [B] site are due to the net magnetization of the nearest neighbor (A) site through A-B superexchange and the B-B interaction. Since Indium is diamagnetic and decrease in hyperfine magnetic field of (A) site indicates that for higher concentration of In$^{3+}$ ions ($x > 0.1$) some of them migrate to the [B] sites also, which reduces the magnetization of the particles at [B] site. Consequently the hyperfine field at the (A) site decreases. Our results indicate that the s-electron density at the Fe$^{3+}$ nucleus is not affected by In$^{3+}$ substitution, since the isomer shift, for a particular nuclear transition of the Mössbauer source is dependent only on the s-electrons charge density of the absorber. The values of the isomer shift at (A) and [B] sites show that iron is in the Fe$^{3+}$ state [20]. The observed difference between the isomer shift at 5 K and 300 K are fully explained by the temperature dependent second order Doppler shift of the lines. Figure 2a shows the variation of magnetization with the applied field for all the three samples at 5 K. The magnetization of NZFO sample does not saturate even at the maximum field attainable (H = 50 kOe), while NZIFO particles attain saturation magnetization in the applied field.

![Mössbauer spectra of NZIFO particles at 5 K.](image)
Table 1. Mössbauer parameters for NZIFO particles at low temperature 5 K.  < B> represents the average hyperfine field acting at the B site

| Sample | Subspectrum | WID (mm) | IS (mm/s) | Q.S. (mm/s) | B (T) | AREA (%) |
|--------|-------------|----------|-----------|-------------|-------|----------|
|        | (A)         |          |           |             |       |          |
| x = 0  |             | 0.58 ±0.02 | 0.38 ±0.01 | 0.23 ±0.03  | 50.94 ±0.00 | 21.70%   |
|        | [B]         |          |          |             |       |          |
|        | B1          | 0.50 ±0.00 | 0.58 ±0.01 | -0.12 ±0.03 | 54.64 ±0.10 | 19.23%   |
|        | B2          | 0.68 ±0.00 | 0.66 ±0.03 | -0.33 ±0.07 | 53.31 ±0.10 | 24.73%   |
|        | B3          | 0.50 ±0.00 | 0.45 ±0.02 | 0.06 ±0.04  | 52.07 ±0.00 | 16.48%   |
|        | B4          | 0.65 ±0.01 | 0.60 ±0.02 | -0.04 ±0.001| 51.5 ±0.00  | 17.86%   |
|        |             |          |          |             |       |          |
| x = 0.1|             | 0.65 ±0.00 | 0.28 ±0.04 | 0.27 ±0.07  | 52.72 ±0.2 | 22.73%   |
|        |             |          |          |             |       |          |
| x = 0.2|             | 0.50 ±0.00 | 0.54 ±0.01 | -0.05 ±0.02 | 51.04 ±0.10| 15.39%   |
|        |             |          |          |             |       |          |
|        | (A)         | 0.53 ±0.00 | 0.60 ±0.01 | -0.06 ±0.10 | 54.89 ±0.76 | 19.63%   |
|        | [B]         |          |          |             |       |          |
|        | B1          | 0.52 ±0.00 | 0.58 ±0.13 | -0.05 ±0.00 | 55.18 ±0.90 | 15.39%   |
|        | B2          | 0.54 ±0.00 | 0.58 ±0.01 | -0.03 ±0.00 | 53.39 ±0.08 | 20.96%   |
|        | B3          | 0.50 ±0.00 | 0.50 ±0.01 | 0.06 ±0.01  | 52.32 ±0.00 | 19.63%   |
|        | B4          | 0.50 ±0.00 | 0.45 ±0.00 | 0.12 ±0.00  | 51.16 ±0.17 | 9.02%    |

For x = 0 sample the saturation magnetization, M_{sat} (30.15 emu/g) is determined by extrapolating the M versus 1/H curve to 1/H = 0. The M_{sat} value for x = 0.1, 0.2 samples are 45.68, 28.68 emu/g respectively. The particular lack of saturation in NZFO sample is attributed to surface spin-canting [21]. Variation of the saturation magnetization with indium content upto 0.1 shows that indium ions initially occupy tetrahedral site and thus the overall magnetic moment increases. This consequently raises the saturation magnetization of the system. Decrease in saturation magnetization for x>0.1 sample indicates that some of the Indium ions migrate to the [B] sites also, which reduces the overall saturation magnetization. The results observed are in accordance with previous study on indium doped ferrites [22-25]. The rapid decrease of the saturation magnetization for sample x = 0.2 may also be the formation of antiferromagnetic phase with spinel phase [16]. The coercive field of samples x = 0, 0.1, 0.2 are 322.0, 242.0 and 305.0 Oe respectively (Figure 2b).

Figure 2. (a) Variation of magnetization with applied field (b) Part of the curves near the origin showing the remanence and coercivity for all samples
The low inferred values of coercivity and squareness ratio as 0.222, 0.332, 0.342 for samples x = 0, 0.1 and 0.2 respectively are in agreement with the well established soft magnetic character of NZIFO particles [16]. It is clear that low temperature magnetic behaviors are consistent with Mössbauer measurements. The results discussed above on NZIFO nanoparticles along with previously published at room temperature indicate a rather surprising behavior of spinel nanoparticles prepared in reverse micelle technique.

4. Conclusion

In conclusion, low-temperature Mössbauer studies on nanosamples of NZIFO particles corroborate the result of room temperature Mössbauer measurements done on these samples and show that Indium enters preferentially into the (A) site. NZIFO nanoparticles show promising properties: high saturation magnetization and hyperfine field close to that of the bulk materials. Such interesting behavior appears to be clearly related to two main factors: good crystallinity of the nanoparticles and the departure from the classical cation distribution in the spinel structure. Sample x = 0.1 exhibits high saturation magnetization and hyperfine field close to that of the bulk material which show the applicability of this sample for magnetic storage data.

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