Investigation of different iron sites in $\varepsilon$-Fe$_{y}$N ($2<y<3$) nanoparticles using Mössbauer Spectroscopy

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Abstract. Epsilon Iron Nitride has a wide range of nitrogen solubility in its lattice. While the stoichiometric $\varepsilon$-Fe$_3$N has an ordered arrangement of nitrogen atoms in the octahedral voids of the hexagonal iron lattice, in non-stoichiometric $\varepsilon$-Fe$_{y}$N ($2<y<3$) the nitrogen atoms occupy the voids in a disordered manner and the coordination of Fe with nitrogen varies with the number ‘$y$’ in the lattice. Mössbauer spectroscopy, which is a nuclear spectroscopic tool, can differentiate the different co-ordination of Fe through its characteristic isomer shift values and is used for identifying the different types of iron sites. $\varepsilon$-Fe$_{y}$N ($2<y<3$) nanoparticles were prepared by the nitridation of hematite nanoparticles using ammonia at 550°C. Mössbauer spectroscopy at ambient temperature shows a superparamagnetic doublet and a sextet. Spectra at 80 K and 5 K resolve the sextets nicely and thereby the different iron sites present in the $\varepsilon$-Fe$_{y}$N ($2<y<3$) nanoparticles.

1. Introduction
Among the various iron nitride phases existing at room temperature, $\gamma'$-Fe$_4$N and $\varepsilon$-Fe$_3$N are ferromagnetic and can be used for magnetic applications due to their high saturation magnetization and Curie temperature. The phase diagram of Fe-N [1] shows a wide range of nitrogen solubility in the iron lattice while holding the hcp crystal structure. As a result it is easy to synthesize $\varepsilon$-Fe$_3$N particles. Unlike the ordered stoichiometric $\varepsilon$-Fe$_3$N, which may form through controlled nitridation and slow cooling of the material, the quenched material and the more nitrogen rich Fe$_3$N, namely $\varepsilon$-Fe$_{3}$N$_{1+x}$, has a disordered arrangement of nitrogen atoms. This creates unequal environments for different iron atoms in the lattice.

2. Experimental
The $\varepsilon$-Fe$_{3}$N$_{1+x}$ nanoparticles were synthesized by treating hematite particles with ammonia gas at a temperature of 550°C for 3 hours and quenching after the reaction. Nitrogen content was estimated by the Kjeldahl’s method [2] and has been further confirmed by the C-H-N analyzer. The result shows a composition of $y=2.6$. The characterization of this material has been carried out by XRD, SEM, and VSM. The presence of different iron sites has been probed by Mössbauer spectroscopy. Room temperature Mössbauer measurements were performed using a $^{57}$Co source incorporated in Rh matrix.
using a commercial spectrometer supplied by Wissel. Low temperature measurements were performed in a He bath cryostat. The spectra were analyzed by the Win-normos software.

3. Results and discussions

The X-ray diffraction data showed the presence of a single phase hexagonal structure. Commonly, the X-ray diffraction technique is well suited to get the positions of the interstitials of well-defined stoichiometric interstitial solid solutions. When the interstitial atom has a wide range of solubility in the lattice by maintaining the parent ordered type structure, however, the X-ray data are not sufficient to get the distribution of interstitials among the available sites. On the other hand, the simple structure of the Fe-N phases leads to an unambiguous interpretation of the Mössbauer spectra.

It is important to understand the structure of $\varepsilon$-Fe$_3$N before considering the analysis of the Mössbauer spectra. In an hcp arrangement of M (Fe), each M atom is coordinated by six octahedral sites forming a trigonal prism. In an ordered stoichiometric $\varepsilon$-Fe$_3$N structure two of these sites, only the Wyckoff position 2c, are occupied by N. This coordination is called M$_2$, a metal atom coordinated with two nitrogen atoms. The Mössbauer spectrum of this compound shows a single six finger pattern corresponding to the perfect ferromagnetic $\varepsilon$-Fe$_3$N. This occurs exclusively in slowly cooled materials. This ordered structure can be destroyed either by quenching the material from higher temperature or by the extra nitrogen atoms entering the vacant interstitial sites. This disorder leads to the filling up of 2b Wyckoff sites besides the more favorable 2c sites which causes a partial formation of the environments M$_1$ and M$_3$ as reported in literature [3-5]. Mössbauer spectroscopy is able to detect the separate signals for the different environments. Literature shows that M$_1$ and M$_3$ are additionally observed besides M$_2$ for samples quenched from higher temperatures and M$_3$ is achieved for N contents higher than that in Fe$_3$N, that is Fe$_3$N$_{1+x}$. This ability of Mössbauer spectroscopy has been used to identify the various electronically different iron sites in this system. The different local environment of an iron atom occurs due to the different numbers of nitrogen atoms in its near neighbourhood. It increases with the decrease in ‘s’ electron density. In iron nitride system the nitrogen atom is considered as a ‘p’ electron donor. Due to this contribution from nitrogen ‘p’ electrons the ‘s’ electron density surrounding the iron atom decreases with increase in coordination with more nitrogen atoms. As a result, the evaluation of the isomer shift using the Mössbauer technique will help to classify different iron sites and thus the number of nitrogen atom surrounding the iron atom. The reported values show that the Fe$_y$N with $y = 3$, 2.67, 2.4 ($\varepsilon$-Fe$_{2.4}$N) exhibits a six finger pattern for different iron sites at room temperature. A doublet, reflecting paramagnetic behaviour, was observed when $y = 2$ (the $\zeta$-Fe$_2$N phase) at room temperature.

Our results obtained at room temperature show superimposed spectra comprising sextet and doublet (Figure 1(a)). As the amount of nitrogen determined was not in the range of $\zeta$-Fe$_2$N and the
material shows ferromagnetic behaviour at room temperature we can eliminate the possibility of doublets corresponding to the material $\zeta$-Fe$_2$N, a paramagnetic material at room temperature. The isomer shift data supports this argument. Accordingly, the superimposed sextet and doublet is supposed to correspond to the $\varepsilon$-Fe$_3$N phase. The existence of sextet and doublet can be understood on the basis of different contributions from the different sized particles. It is well established that the electron spin relaxation effects are very influential and critical in the analysis of complex broad non-Lorentzian Mössbauer spectrum. In the case of uniaxial superparamagnetic (ultrafine) particles, the spin relaxation process is strongly dependent on the volume (V) and anisotropy constant (K). When the spin relaxation time is comparable with the Larmor precession time, a well-defined magnetically split sextet is observed. On the other hand, if it is extremely short of the order of $10^{-11}$ or $10^{-12}$ seconds, the sextet collapses into a broad non-Lorentzian singlet or doublet depending on the contributions from quadrupole interactions.

Table 1. Hyperfine parameters of $\varepsilon$-Fe$_3$N$_{1+x}$ at different temperatures

| T (K) | Fe Site   | Isomer Shift $\delta$ (mm/s) | Quadrupole Splitting $\Delta$ (mm/s) | Hyperfine Field (T) | Width $\Gamma$ (mm/s) | Area % |
|-------|-----------|------------------------------|--------------------------------------|---------------------|-----------------------|--------|
| 298   | Sextet    | 0.36                         | -0.05                                | 15.6 ± 0.2          | 0.87                  | 47.8   |
|       | Doublet   | 0.38                         | 0.84                                 | --                  | 1.06                  | 52.2   |
| 80    | Sextet 1  | 0.46                         | -0.04                                | 24.5                | 0.29                  | 38.7   |
|       | Sextet 2  | 0.53                         | -0.03                                | 12.5                | 0.83                  | 57.3   |
|       | Doublet   | 0.51                         | 0.65                                 | --                  | 0.31                  | 4.0    |
| 5     | Sextet 1  | 0.46                         | -0.04                                | 26.1                | 0.27                  | 40.7   |
|       | Sextet 2  | 0.50                         | -0.03                                | 13.7                | 0.37                  | 59.3   |

The higher line width of the spectra points to the existence of a distribution which may be attributed to two reasons. One is a slight distribution in particle size and the other is the statistical distribution of nitrogen atoms in the vacant sites of trigonal prisms. The low temperature spectrum can be used to clear these issues. So we recorded the spectra at 80, Figure 1(b) and 5 K, Figure 2. The hyperfine parameters are given in the Table 1. The 80 K spectrum is fitted according to a model constructed with two sextets and a doublet. This model gives a better fit rather than the model which consists of only sextets. The hyperfine parameters match well with the reported values for M$_2$ and M$_3$ [3, 6]. The area fractions show that there exist more M$_3$ sites than M$_2$. The evolution of two well defined sextets which constitutes 96% of the total area indicates that most of the particles are now having KV$>>$E$_a$(thermal energy). As the temperature is lowered, the effective slow relaxation allows to observe the evolution of the magnetic sextet. The increase in magnetic hyperfine field with decrease in temperature is due to the increase in the effective spin $<s>$ through the increase in population in the lowest lying states. Even from the visual inspection of the experimental spectrum it is obvious that the predicted or the reported M$_1$ site is absent in this material. The doublet at this temperature corresponds to iron atom coordinated with more number of nitrogen atoms, which may arise due to the higher nitrogen diffusion in to the particles of very low dimensions. The higher area fraction of the M$_3$ site clearly tells the existence of larger number of iron atoms coordinated with three nitrogen atoms. It is clear from the data that the line widths are much larger than the instrumental line width and is still increasing as one move out of the center of the spectrum. This is a well-known characteristic of a distribution of hyperfine fields which also points to the existence of different types of Fe-N coordination and thus the magnetic ordering. In view of this we tried a distribution fit of the experimental data. The hyperfine field and quadrupole distribution are shown in Figures 1, 2 as well. The hyperfine field distribution centered at 25, 14 and 3 Tesla indicates that the nitrogen atoms are statistically distributed in the
available six corners of the trigonal prism centered by Fe atom. The observation of a low magnetic moment compared to the bulk value at room temperature and even at low temperature is due to the existence of fine particles and the higher nitrogen distribution.

In order to have a detailed understanding of the nature of the observed doublet and a field distribution centered at 3 Tesla at 80 K we recorded the spectra at 5 K. It (Figure 2) shows two well separated sextets. The model with three sextets which corresponds to $M_2$, $M_3 (~2/3)$ and $M_3 (~1/3)$ [6] did not give a good fitting compared to the model containing two sextets. The hyperfine parameters (Table 1) show the presence of $M_2$ and $M_3$ only. The large width of the lines, especially for the $M_3$ site, is due to the presence of a hyperfine field distribution. Figure 2 shows the distribution in the hyperfine field with a maximum probability at 26 and 13.7 T. The distribution centered at 8 T is due to the unresolved component of the hyperfine interaction associated with very small particles having higher nitrogen content which behaves as paramagnetic at room temperature and at 80 K. It is obvious from Table 1 that the area of sextets increases with decrease in temperature and the doublets have vanished at 5 K.

![Figure 2. Mössbauer spectrum recorded at 5K and its distribution](image)

4. Conclusion
Room temperature Mössbauer spectrum suggests the distribution in particle size. At lower temperatures the spectra show the presence of two iron sites. The isomer shift values corresponding to these sites indicate that the iron atoms are coordinated with two and three nitrogen atoms creating different electronic environments. The larger line width of the spectra points to the existence of a distribution of hyperfine field and quadrupole splitting. The hyperfine field distribution centered at 8T at 5K indicates the presence of very fine particles having higher nitrogen content which are statistically distributed over the available sites.

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