Mössbauer and magnetic studies for the coexistence of $\varepsilon$-Fe$_{3-x}$Ni$_x$N and $\gamma'$-Fe$_{4-y}$Ni$_y$N phases in Fe-Ni-N nanoparticles

N S Gajbhiye$^{1,2}$ & Sayan Bhaattacharyya$^1$

$^1$Department of Chemistry, Indian Institute of Technology, Kanpur 208 016
$^2$Institute of Nanotechnology, Forschungszentrum Karlsruhe, P.O. Box 3640, 76021 Karlsruhe, Germany

E-mail: nsg@iitk.ac.in

Received 15 February 2007; revised 26 July 2007; accepted 2 August 2007

Nanocrystalline $\varepsilon$-Fe$_{3-x}$Ni$_x$N ($x = 0.5$-0.8) particles are synthesized by precursor technique and nitridation of decomposed products in NH$_3$ (g) at 673 K. A small fraction of fcc $\gamma'$-Fe$_{4-y}$Ni$_y$N phase (space group: F43m) is precipitated along with the formation of $\varepsilon$-Fe$_{3-x}$Ni$_x$N hexagonal structure (space group: P6$_3$/mmc). The Mössbauer spectrum at room temperature for all the compositions shows the presence of superparamagnetic doublet, which is attributed to $\varepsilon$-Fe$_{3-x}$Ni$_x$N phase and two sextets corresponding to the corner Fe (Fe$^2+$) and fcc Fe (Fe$^3+$), in $\gamma'$-Fe$_{4-y}$Ni$_y$N. The added Ni atoms preferentially substitute the Fe$^3+$ positions. The isomer shift, quadrupole splitting and hyperfine field values vary with the Ni content. The zero-field cooled (ZFC) and field-cooled (FC) curves indicate strong interparticle interactions and surface spin-glass-like state is realized from the low temperature features. The magnetization curves are saturated at 5 K, due to the dominating ferromagnetic nature of the $\gamma'$-Fe$_{4-y}$Ni$_y$N phase.

Keywords: Nanoparticle, Iron-nickel nitride, Mössbauer, Spin canting, Superparamagnetism

IPC Code: B82B, G01J3/28

1 Introduction

In the recent times, researchers have extensively explored the possibility of various magnetic nanoparticles, which have potential applications in recording media, data storage industry, bio-medical applications and catalysis$^1$. Among them, the iron nitride (Fe-N) nanoparticles are important, since they have giant magnetic moments and also they are not susceptible to oxidation like the normal metal nanoparticles. Among the Fe-N phases, $\varepsilon$-Fe$_3$N and $\gamma'$-Fe$_4$N compounds are noteworthy. However, the intermixing of N-2p states with Fe-3d states reduces the number of unpaired d-electrons and hence the magnetic moments$^2$ are lower than $\alpha$-Fe. Reports of substitution of various elements in fcc $\gamma'$-Fe$_4$N and hexagonal $\varepsilon$-Fe$_3$N lattice are available in the literature$^{3,4}$. Nickel has the tendency to stabilize the austenite $\gamma'$-Fe$_3$N phase, and only high pressures$^5$ can stabilize the hcp phase ($\varepsilon$-phase). When fcc $\gamma'$-FeNi alloys are nitried, they form (Fe$_{1+y}$Ni$_{1-y}$)N and $\gamma$-Fe-Ni-N compounds having the $\gamma'$-Fe$_3$N structure$^{6,8}$. Hence, the stabilization of a hexagonal Fe-Ni-N phase at normal pressures and ambient conditions is quite challenging. We have reported earlier the stabilization of the pure $\varepsilon$-Fe$_{3-x}$Ni$_x$N phase with low concentrations$^9$ of Ni. Hence, above a critical Ni concentration and with certain reaction conditions, the coexistence of $\varepsilon$-Fe$_{3-x}$Ni$_x$N and $\gamma'$-Fe$_{4-y}$Ni$_y$N phases is likely to occur. The purpose of this work is to investigate the Fe-Ni-N nanoparticles, with the coexistence of $\varepsilon$-Fe$_{3-x}$Ni$_x$N and $\gamma'$-Fe$_{4-y}$Ni$_y$N phases. We have investigated the atomic ordering with room temperature$^{57}$Fe Mössbauer spectroscopy and the magnetization experiments are performed to probe the low temperature magnetic ordering in these nanoparticles.

2 Experimental Details

$\varepsilon$-Fe$_{3-x}$Ni$_x$N ($x = 0.5$-0.8) nanoparticles were synthesized by the precursor technique. Aqueous solutions of 0.22 (N) Fe(NO$_3$)$_3$.9H$_2$O and 0.35 (N) Ni(NO$_3$)$_2$.6H$_2$O were mixed corresponding to the stoichiometric ratios of Fe and Ni in $\varepsilon$-Fe$_{3-x}$Ni$_x$N. The citric acid solution was added and the solution was refluxed at 343 K for 12 h. The decomposition of the citrate precursors in air at 773 K for 4 h, resulted in
ultra-fine Fe-Ni-oxide particles.

The nitridation is carried out under flowing NH$_3$ (g) at 673 K for 12 h to get the desired Fe-Ni-N nanostructured phases. The stoichiometry of the final products was confirmed by chemical analysis. X-ray diffractograms (Rich Seifert model Isodebyeflex 2002) were recorded using CuK$\alpha$ radiation. The average particle size was calculated from the X-ray line broadening of (101) plane reflection using Scherrer’s formula and TEM micrographs. Mössbauer spectra were recorded using a $^{57}$Co source embedded in Rh matrix. The spectrum was then analyzed by using software PC-MOS (CMTE Electronik, Germany). The values are presented relative to metallic iron. The magnetization measurements were performed in a SQUID magnetometer in the temperature range 5-300 K.

3 Results and Discussion

Analysis of the XRD patterns, with the help of Rietveld analysis program, confirms the $\varepsilon$-Fe$_3$N hexagonal structure, with space group $P6_3/mmc$ as the major phase and precipitation of an additional fcc $\gamma'$-Fe$_{4-y}$Ni$_y$N phase with space group $P43m$ (Fig. 1).

The goodness of fit (ratio of weighted pattern R-factor and pattern $R$-factor) is $\sim$1.5 for all the compositions, which represents a sufficiently good fit. The lines in the difference plot (Fig. 1) indicate the difference in intensity between the observed and calculated peaks, which is due to the variation in the local electron density and temperature factors. In $\varepsilon$ phase, the lattice parameter $a$ varies from 0.2669(1) nm to 0.2771(1) nm and $c$ from 0.4259(1) nm to 0.4419(1) nm, as calculated from the XRD-Rietveld refinement. The XRD crystallite size is calculated to be 25 nm for all the compositions. TEM confirms the particles to be spherical with average diameter ($D$) of 30 nm and size distribution $\sigma(D) = \pm 0.5$. For $x = 0.1$-0.4, only $\varepsilon$-Fe$_{3-x}$Ni$_x$N phase is stabilized without the appearance of $\gamma'$-Fe$_{4-y}$Ni$_y$N phase.

The Mössbauer spectra recorded at 300 K for $x = 0.5$-0.8 systems are shown in Fig. 2. The doublet indicates superparamagnetic nature of the $\varepsilon$-Fe$_{3-x}$Ni$_x$N phase and the two sextets correspond to the ferromagnetic $\gamma'$-Fe$_{4-y}$Ni$_y$N phase. The ferromagnetic particles become superparamagnetic, when the thermal energy overcomes the anisotropy energy and disturbs the magnetic order. $\gamma'$-Fe$_{4-y}$Ni$_y$N phase contains the $\gamma'$-Fe$_{3}$N crystal structure while $\varepsilon$-Fe$_{3-x}$Ni$_x$N phase has the $\varepsilon$-Fe$_3$N structure. $\gamma'$-Fe$_{3}$N...
has a higher bulk saturation magnetization ($\sigma$) value [208 emu/g (0 K)] than $\varepsilon$-Fe$_3$N [bulk $\sigma$ value is 133 emu/g (0 K)]. Also the anisotropy energy of $\gamma$-Fe$_4$N is quite large$^{10}$. Thus, the thermal disordering cannot destroy the six-line spectra of $\gamma$-Fe$_4$$\gamma$-Ni$_y$N phase at room temperature, even though the same time-scale for $^{57}$Fe Mössbauer experiment is involved. In the $\gamma$-Fe$_{4-y}$Ni$_y$N phase, $\gamma$ is calculated to be 0.7, 0.8, 0.9 and 1.1 for $x = 0.5, 0.6, 0.7$ and 0.8, respectively, using the best fit with calculated parameters to the experimental XRD spectra in Rietveld analysis. The calculated XRD patterns with different reasonable $y$ values (considering the atomic percentage of nickel) are fitted with the experimental data and the best fit is obtained with the above $y$ values. However, the percentage of the $\gamma$-Fe$_{4-y}$Ni$_y$N phase is below 20% (as determined by XRD-Rietveld analysis) and hence, the relative intensities of the sextets are comparatively smaller than the intensity of the doublet corresponding to the major $\varepsilon$-Fe$_{3-y}$Ni$_y$N phase. From the Mössbauer data, the relative % of the $\gamma$-Fe$_{4-y}$Ni$_y$N phase is 11.3, 14.1, 19.1 and 20.6 for $y = 0.7, 0.8, 0.9$ and 1.1, respectively, which agrees very well with the results of the XRD-Rietveld analysis. The doublet is not due to the paramagnetic $\varepsilon$-phase (such as $\varepsilon$-Fe$_2$N$_x$), which may arise from the increase in nitrogen concentration in the lattice. Rather, the nitrogen stoichiometry is confirmed by Kjeldahl’s analysis$^{11}$ and also the ferromagnetic $\varepsilon$-Fe$_2$N phase is justified by Rietveld refinement of the XRD patterns.

In the $\varepsilon$-Fe$_{3-y}$Ni$_y$N phase, the added Ni atoms replace the Fe atoms randomly and N retains the regular positions. The relatively high quadrupole splitting values for the doublet component indicates partial covalent bonding between Fe and N atoms and deviation from the octahedral coordination around the Fe nucleus in $\varepsilon$-Fe$_2$N lattice. The high line width values indicate the broad distribution of particle size in these nanoparticles. The isomer shift values for the doublet component do not change with the increase in Ni concentration and hence justifies the random distribution of Ni in $\varepsilon$-Fe$_{3-y}$Ni$_y$N lattice. Also, the isomer shifts suggest smaller $s$-electron density and greater electron densities at $p$- and $d$-orbital of Fe in $\varepsilon$-Fe$_{3-y}$Ni$_y$N phase (Fig. 3). The $\gamma$-Fe$_{3-y}$Ni$_y$N phase consists of the $\gamma$-Fe$_2$N lattice, which crystallizes in perovskite (cubic) type structure with N atoms occupying the octahedral interstices in an ordered way. There are two non-equivalent Fe-sites, one occupying the corners (Fe$^c$) and the other at $fcc$ positions (Fe$^f$) of the cube. When Ni substitutes Fe in $\gamma$-Fe$_{4-y}$Ni$_y$N, Ni can occupy either or both the Fe$^c$ and Fe$^f$ sites. Due to the two different Fe sites in $\gamma$-Fe$_4$$\gamma$-Ni$_y$N, the Mössbauer spectra will show two sextets. Also, the spectral fit using one sextet does not produce a good result. The two sextet components, sextet 1 and sextet 2, are attributed to the face-center position (Fe$^f$) and corner position (Fe$^c$) of the $\gamma$-Fe$_4$$\gamma$-Ni$_y$N lattice, respectively (Table 1). In this case it is considered that the electric field gradient (EFG) is directed along the body diagonal of the $fcc$ lattice and hence the EFG axis of all the Fe$^c$ sites make the same angle with the magnetic field and the hyperfine structure of all the Fe$^c$ sites is identical$^{12}$. If the axis of symmetry of the EFG is normal to the face in which the site lies, two sets of Fe$^c$ spectrum lines will appear in the ratio 2:1, since 2/3 of the Fe$^c$ sites have their EFG axis perpendicular to the magnetic field and 1/3 have them parallel. The sextet 2 has larger hyperfine field but lower intensity as compared to sextet 1, since the added Ni atoms preferentially substitute for the Fe$^c$ sites (Table 1). The calculations for determining the relative Ni occupation at Fe$^c$ and Fe$^f$ sites in $\gamma$-Fe$_{4-y}$Ni$_y$N has been discussed in detail in the literature$^{13}$. The percentage of Ni atoms occupying the Fe$^c$ sites ($P_{Ni}^c$) in $\gamma$-Fe$_{4-y}$Ni$_y$N phase is 90.2, 88.2, 69.1 and 37.9 for $y = 0.7, 0.8, 0.9$ and 1.1, respectively. The quadrupole splitting values have opposite signs for the Fe$^c$ and Fe$^f$ sites, due to different geometrical orientations. The large variation of line widths is attributed to the inhomogeneity of the interaction field due to Ni substitution.

![Fig. 3.—Plots of specific magnetization as a function of field for $\varepsilon$-Fe$_{4-y}$Ni$_y$N ($x = 0.5-0.8$) nanoparticles at 300 K.](image)
The magnetization \( \sigma(H) \) curves are nearly saturated at 300 K (Fig. 3) and 5 K (Fig. 4). The \( \sigma \) values at 300 K are 14.3, 15.3, 29.7 and 36.0 emu/g and at 5 K, 47.9, 57.5, 58.8 and 66.0 emu/g for \( x = 0.5, 0.6, 0.7 \) and 0.8, respectively. The superparamagnetic fraction of the particles also exists at 5 K and hence, the \( \sigma \) values are even lower than that of bulk \( \varepsilon \)-Fe\(_3\)N. The reduction in \( \sigma \) values at 300 K is attributed to the presence of superparamagnetic fractions, spin pairing effects, surface spin canting and spin non-collinearity at the surface of the particles. The ZFC and FC curves at 250 Oe external field (Fig. 4 inset) clearly indicate the mixture of the superparamagnetic \( \varepsilon \)-Fe\(_3\)xNi\(_x\)N and ferromagnetic \( \gamma' \)-Fe\(_4\)yNi\(_y\)N phases. The blocking temperature is at or above 300 K and the domination of the ferromagnetic nature of the \( \gamma' \)-Fe\(_4\)yNi\(_y\)N phase prevents the observation of the weak features such as the dipolar interaction (densely packed particles). The ZFC/FC curves show strong irreversibility, due to the strong interparticle interactions and an applied field of 250 Oe cannot dominate this interaction field. Although, with increase in external field, the irreversibility decreases, but still persists even at an applied field of 1 T. A small hump is observed at 50-65 K in the ZFC curve for all the samples (shown by arrow in Fig. 4 inset), which can be attributed to the spin-glass freezing temperature. X-ray photoelectron spectroscopy studies indicate a thin surface oxynitride/oxide layer. The oxide layer has the varied compositions of Fe-Ni-O and is antiferromagnetic in nature\(^{14,15} \). This oxynitride/oxide surface layer is very thin (<1 nm), amorphous and hence, not observed in the XRD patterns. It occurs due to surface oxidation of the nitride materials\(^6 \). Such a thin antiferromagnetic surface layer shows its effect on magnetization at low temperatures, when it is coupled with the spins of the ferromagnetic core. Hence, spin canting arises from the disordered spins at the interface between the ferromagnetic nitride and the antiferromagnetic surface oxynitride/oxide layer. At low enough temperatures, the canted spins freeze and this gives rise to a spin-glass-like state, which has very short range order. Hence, the weak ZFC humps below 65 K may be attributed to the spin-glass-like ordering at the surface of the nitride nanoparticles.
4 Conclusion

The Mössbauer spectra at 300 K for ε-Fe$_{3-x}$Ni$_x$N ($x = 0.5-0.8$) nanoparticles, show one superparamagnetic doublet for ε-Fe$_{3-x}$Ni$_x$N phase and two sextets corresponding to two different Fe sites in ferromagnetic γ'-Fe$_{4-y}$Ni$_y$N phase. The Ni atoms preferentially occupy Fe$^2$ sites for $y = 0.7$, 0.8 and 0.9 and Fe$^3$ sites for $y = 1.1$. The magnetization curves at 300 K and 5 K are nearly saturated due to the dominant ferromagnetic character of the γ'-Fe$_{4-y}$Ni$_y$N phase. The surface oxynitride/oxide layer over the nitride core gives rise to spin canting and the disordered surface spins freeze below 65 K which is indicative of a spin-glass-like ordering.

Acknowledgement

The authors acknowledge MHRD, New Delhi, for the financial support during this research work.

References