Anomalous Ground State in Fe$_{1-x}$Ni$_x$ Invar alloys

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Abstract

This paper reports high resolution X-ray photoelectron spectroscopy (XPS) studies on Fe$_{1-x}$Ni$_x$ (x=0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9) alloys down to 10 K temperature. Core levels and Auger transitions of the alloys except the invar alloy (x=0.4) exhibit no observable temperature induced changes. The invar alloy exhibits changes in the core levels below 20 K temperature that strongly depend on the core level. Such core level dependent changes with temperature were attributed to the precipitation of spin glass like phase below 20 K only in the invar alloy. Ni L$_3$M$_{45}$M$_{45}$ Auger transition also supported such precipitation below 20 K.

PACS: 71.20.-b, 71.10.Hf, 79.60.-i

1 Introduction

Magnetic properties of Fe$_{1-x}$Ni$_x$ alloys exhibit various anomalies depending on composition and temperature. The magnetic phase diagram of the alloy system is enormously rich. The alloys exhibit ferromagnetic behaviour for all compositions. The fcc Fe$_{1-x}$Ni$_x$ alloys show complex magnetic behaviour and exist in different magnetic states[1]. The low Ni concentration fcc alloys (35-40% Ni) exhibit almost no thermal expansion over a wide range of temperatures[1][2][3] around the room temperature and are called invar alloys. The first model explaining the Invar anomaly was developed by Weiss and is known as 2γ-state model[4]. According to this model Fe exists in two magnetic states, a high spin-large volume state and a low spin-small volume state. When the temperature is increased low spin states get more populated at the cost of high spin states and thus there is a decrease in volume which compensates the increase of volume due to increase in temperature. First principle calculations carried out on ferromagnetic γ-Fe, ordered Fe$_3$Ni and random fcc Fe$_{1-x}$Ni$_x$ alloys suggest the existence of two magnetic states[5][6][7][8][9][10][11][12][13][14][15][16].

A recent neutron scattering experiments indicated that Ni moment gradually increases from 0.62µ$_B$ on the Ni side to 0.95µ$_B$ on the Fe side, on the other hand Fe moment rises from 2.2µ$_B$ for pure Fe to a maximum of 3.1µ$_B$ at x=0.75 and then drops to 2.6µ$_B$[17]. In the bcc phase the Ni moment levels off at 1.25µ$_B$ which is twice that of in pure Ni. This suggests that Ni moment is enhanced in the proximity of Fe. As per the theoretical predictions Ni has local moment of about 0.7-0.8µ$_B$ almost independent of the surrounding[18][19].

Core level of magnetic alloys exhibit splitting related to the local magnetic moment of the atom or ion. Such splitting is called exchange splitting and is used as a finger print of the existence of local magnetic moments. The splitting is caused by exchange interaction between the unpaired electron left in the
core level after photo emission with the unpaired electrons in the valence shell, i.e. 3d shell. Exchange splitting of 3s core level in 3d transition metals was first reported by Fadley et al [20]. Since then numerous studies have focussed on exchange splitting in s levels and used it as a probe to identify the local magnetic moments. The exchange splitting depends on the core level as the strength of exchange integral with the valence shell varies from core level to core level. In the Invar region of Fe-Ni alloys Fe exists both in high spin and low spin states which produce different exchange split peaks [21, 22, 23, 24]. The core levels in metallic alloys also suffer from intra and inter atomic screening effects. The inter atomic screening depends on temperature where as intra atomic screening is not expected tp depend on temperature.

In this study, we have investigated Fe and Ni core levels and their temperature dependence in Fe\textsubscript{1-x}Ni\textsubscript{x} alloys for \(x=0\) to 1. These studies indicated that Fe possesses two magnetic states called high spin and low spin states and the population of these states depends on temperature. The core level spectra of Fe and Ni are anomalous at low temperatures. The outer core levels suffer from inter-atomic screening effects. On the other hand in the deep core levels, the effect of inter-atomic screening is nominal.

### 2 Experiment

Fe\textsubscript{1-x}Ni\textsubscript{x} (\(x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9\)) have been prepared by arc melting method as described elsewhere[25]. X-ray photoelectron spectroscopy(XPS) measurements have been carried out using PHOIBOS 150 MCD Energy Analyzer from Specs GmbH at a base pressure of \(4\times10^{-10}\) Torr using monochromatic AlK\(_\alpha\) radiation of energy 1487 eV as excitation source. The total resolution of the spectrometer was measured as the width of the Fermi step taken on clean silver sample at 10 K and was found to be 0.7 eV. The spectrometer has been calibrated using Ag Fermi level as the zero of the binding energy. The alloy surfaces were cleaned by scrapping in-situ in ultra high vacuum using a diamond file mounted on a wobble stick. The scrapping was repeated until the core level line shapes do not exhibit further changes. The surface cleanliness was ascertained by negligibly small O 1s and C 1s core level intensities.

XPS measurements have been carried out at various temperatures from 300 K to 10 K. The experimental temperatures were reached using an open cycle helium cryostat, LT-3M from Advance Research Systems, USA. Survey scans were recorded from 200 to 1490 eV kinetic energy for the alloys. The binding energy of the electrons is calculated by subtracting the kinetic energy from the Fermi energy obtained from the valence band of clean silver sample. The survey scans were used to check the impurities on the surface. The high resolution scans were recorded for 2p, 3s, 3p core levels and also for valence band.

### 3 Results and Discussion

The survey scans recorded for the alloys of Fe\textsubscript{1-x}Ni\textsubscript{x} (\(x=0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9, 1.0\)) at 300 K and 10 K temperatures are shown in figures 1 and 2 respectively. All the features observed in the spectra have been identified and indexed in the figures. The survey scans at both the temperatures exhibit extremely low or zero intensity for C 1s (285 eV) and O 1s (530 eV) core levels. These spectra suggest good quality of the prepared alloys with no impurity atoms. All the core levels of Fe and Ni, valence band and some of the intense Auger features like L\textsubscript{3}M\textsubscript{23}M\textsubscript{23} and
Figure 1: The survey scans of Fe$_{1-x}$Ni$_x$ alloys recorded at 300 K temperature using monochromatic AlK$_\alpha$ radiation. The composition of the alloys is given in the figure legend.

Figure 2: The survey scans of Fe$_{1-x}$Ni$_x$ alloys recorded at 10 K temperature using monochromatic AlK$_\alpha$ radiation. The composition of the alloys is given in the figure legend.

Figure 3: Monochromatic AlK$_\alpha$ excited Ni 2p and Fe 2s spectra of pure Fe, Fe$_{0.8}$Ni$_{0.2}$, Fe$_{0.6}$Ni$_{0.4}$ alloys recorded at 300 K and 10 K temperatures. The spectra at 10 K are overlaid on the spectra at 300 K. Fe 2s data of pure Fe is shown for reference. Inset (a) shows the Ni 2p$_{3/2}$ spectra recorded at 10 K, 20 K, 40 K and 300 K temperatures. Inset (b) shows the Fe 2s spectra of Fe$_{0.6}$Ni$_{0.4}$ alloy recorded at 300 K and 10 K. The composition of the alloy is indicated below the graph on the left side.

L$_3$M$_{45}$M$_{45}$ of both Fe and Ni are indicated in the figures. The valence band (VB) signal comprising of 3d and 4s states of Fe and Ni are seen near zero binding energy.

Figure 3 shows Ni 2p spectra of Fe$_{0.8}$Ni$_{0.2}$ and Fe$_{0.6}$Ni$_{0.4}$ alloys recorded at 300 K and 10 K temperatures. On the low binding energy side of Ni2p$_{3/2}$ peak, a broad Fe 2s feature is observed. The Fe 2s peak of pure Fe is also shown for reference. The main peak in the 2p spectra correspond to the final state 2p$_{3/2}^3$3d$^5$4s$^1$ and the satellite at 6 eV on high binding energy side is due to the final state 2p$_{3/2}^3$3d$^7$4s$^2$ in which there are two holes localized on the site. The first hole in 2p$_{3/2}$ core level is created by the incident X-ray and the second hole in 3d states formed due to the interaction of the 2p$_{3/2}$ core hole.
with 3d electrons\[^{26, 27}\]. A similar satellite, \(2p_{1/2}^{1} 3d^{9}4s^{2}\) is observed for \(2p_{1/2}^{1} 3d^{10}4s^{1}\) main feature as indicated in the figure 3. The main \(2p_{1/2}\) peak to its satellite separation is only 5.0 eV as shown in the figure. The spectra recorded at 300 K and 10 K overlap exactly for Fe\(_{0.8}\)Ni\(_{0.2}\) alloy, but the 10 K spectrum of Fe\(_{0.6}\)Ni\(_{0.4}\) alloy looks slightly broader in the 2p region and seems to be narrower in Fe 2s region.

The temperature induced difference in the \(2p_{3/2}\) core level is shown in inset (a) in figure 3. The \(2p_{3/2}\) peak at 10 K developed more intensity on the high binding energy side of the peak compared to that of the \(2p_{3/2}\) peak at 300 K. The inset also includes the spectra recorded at 20 K and 40 K temperatures which match exactly with the spectrum at 300 K. The Fe 2s states of pure Fe and Fe\(_{0.8}\)Ni\(_{0.2}\) samples split into three features which occur at 844.9 eV, 838.6 eV and 833.9 eV respectively. The Fe 2s states of pure Fe and Fe\(_{0.8}\)Ni\(_{0.2}\) alloy taken at 300 k and 10 K temperatures overlap exactly on each other. The Fe\(_{0.6}\)Ni\(_{0.4}\) alloy exhibits almost flat Fe 2s states with no structures due to splitting. Interestingly, the temperature seems to have a profound effect on the low binding energy side of the 2s states. The Fe 2s states at 10 K temperature exhibit a decrease in intensity at around 833.9 eV compared to the Fe 2s at 300 K temperature. The temperature induced change in Fe 2s is shown in inset(b) of the figure. The intensity on the high binding energy side increased at 10 K at the cost of the intensity at low binding energy.

The broadening observed on the high binding energy side of Ni 2p main peak at 10 K temperature is interesting and needs further attention.

The \(2p_{3/2}\) peak along with 6 eV satellite of Fe\(_{0.6}\)Ni\(_{0.4}\) alloy at 300 K and 10 K tempera-

![Figure 4: Monochromatic AlK\(\alpha\) excited Ni 2p\(_{3/2}\) spectra of Fe\(_{0.6}\)Ni\(_{0.4}\) alloy recorded at (a) 300 K and (b) 10 K temperatures. Dots indicate the experimental spectra and lines indicate the numerical fitting using Gaussian-Lorentzian sum function.](image-url)
peak (P1) occurs at 852.9 eV and two satellites at 856.7 eV and 859.3 eV respectively shown in figure 4(a). The full width at half maximum (FWHM) of the main peak is 1.2 eV and that of satellites, S1 and S2 is 2.5 eV and 3.2 eV respectively. The separation between the main peak and the satellite S2 is 6.4 eV. The satellite S2 is called 6.0 eV satellite. The spectrum at 10 K of Fe$_{0.6}$Ni$_{0.4}$ alloy is deconvoluted into five different features as shown in the figure 4(b). The main feature, 2p$_{3/2}$ consists of two peaks at 852.6 eV and 853.1 eV binding energies. The extra feature came up at 853.1 eV at 10 K has more intensity compared to the feature at 852.6 eV. The satellites S1 and S2 are observed at 856.9 eV and at 859.1 eV respectively. Interestingly, a new satellite S3 with low intensity developed at 860.5 eV in 10 K spectrum.

The satellite separation for Ni 2p$_{1/2}$ core level is about 5.0 eV which is smaller than the satellite separation of 2p$_{3/2}$ which is about 6.4 eV. Using hard X-ray photoemission studies, the satellite energies for 1s, 2p$_{1/2}$, 2p$_{3/2}$ core levels were found to be 4.0, 4.6 and 6.0 eV respectively[28]. The satellite separation depends on the core level of interest.

Ni 2p spectra along with Fe 2s states recorded at 300 K and 10 K for the alloys with x=0.3, 0.5, 0.6, 0.7, 0.9 and 1.0 excited by monochromatic AlK$\alpha$ radiation are shown in figure 5. The spectra taken at 300 K and 10 K temperatures match well for each of the alloy shown. The composition is indicated on the right side just below Fe 2s states for each alloy. The spectra exhibited core level shifts (CLS’s) in the main peaks 2p$_{3/2}$ or 2p$_{1/2}$. The calculation of the CLS from 2p$_{3/2}$ is ambiguous as Fe 2s states are very close in energy to 2p$_{3/2}$. Therefore, we have used 2p$_{1/2}$ peak to obtain the CLS’s which are shown in the inset of the figure with Ni concentration. The CLS’s are positive for all alloys and exhibit a linear dependence with negative slope on increasing Ni concentration. The maximum shift of 0.27 eV was observed for x=0.2 alloy, for which the spectrum is shown in the figure 3. Observed CLS’s for each alloy were found to be same at 300 K and 10 K temperatures. Interestingly, the 6 eV satellite separation from the main peak gradually increases with increasing Fe content. For pure Ni, the satellite separation is 6 eV.

Figure 5: Monochromatic AlK$\alpha$ radiation excited Ni 2p spectra along with Fe 2s recorded at 300 K and 10 K temperatures for Fe$_{1-x}$Ni$_x$ alloys. The composition of the alloy is indicated below the spectra on the right side in the figure. The spectra at 10 K are overlayed on the spectra taken at 300 K.

Fe 2p spectra of pure Fe, Fe$_{0.8}$Ni$_{0.2}$, Fe$_{0.6}$Ni$_{0.4}$ along with L$_3$M$_{23}$M$_{23}$ Auger feature of pure Ni metal are shown in figure 6. The Fe 2p spectra in the alloys are complicated due to the superposition of Ni L$_3$M$_{23}$M$_{23}$ Auger structure which overlaps with Fe 2p$_{3/2}$ peak.
Figure 6: Monochromatic AlK$_\alpha$ radiation excited Fe 2p spectra of Fe$_{1-x}$Ni$_x$ ($x=0, 0.2, 0.4, 1$) alloys recorded at 10 K and 300 K temperatures. The spectra at 10 K are overlayed on the spectra at 300 K. Ni L$_3$M$_2$M$_3$ Auger feature of pure Ni is shown for reference. Inset shows Fe 2p$_{3/2}$ recorded at 10 K, 20 K, 40 K and 300 K temperatures. Sample composition is indicated below the spectra on the left side in the graph.

The spectra recorded at 10 K temperature are overlayed on the spectra at 300 K. The spectra of pure Fe and Fe$_{0.8}$Ni$_{0.2}$ samples match exactly for both the temperatures, whereas the spectra of Fe$_{0.6}$Ni$_{0.4}$ alloy recorded at 10 K is broader compared to that of at 300 K. The temperature induced broadening in 2p$_{3/2}$ peak is shown in the inset of the graph. The 2p$_{3/2}$ peak at 10 K clearly indicates a broadening on the high binding energy side of the peak. The inset also includes the spectra taken at 20 K and 40 K temperatures, which match well with the spectra at 300 K. The 2p$_{3/2}$ peak along with 3.6 eV satellite of Fe$_{0.6}$Ni$_{0.4}$ alloy at 300 K and 10 K temperatures is shown in figure 7. The spectra recorded at 300 K and 10 K were numerically fitted using asymmetric Gaussian-Lorentzian sum function discussed earlier. The spectrum recorded at 300 K is deconvoluted into four peaks. The main 2p$_{3/2}$ peak (P1) occurs at 707 eV and a satellite at 709.8 eV as shown in figure 7 (a). The FWHM of the main peak is 1.5 eV and that of the satellite S is also 1.5 eV. The separation between the main peak and the satellite S is 2.8 eV. Two Ni LMM Auger peaks A1 and A2 occur at 712.4 eV and 702.4 eV respectively. The FWHM of A1 and A2 features are 2.4 eV and 2.5 eV respectively. The spectrum at 10 K of Fe$_{0.6}$Ni$_{0.4}$ alloy is deconvoluted into five different features as shown in the figure 7 (b). The main feature, 2p$_{3/2}$ consists two peaks at 706.5 eV (P1) and 707.2 eV (P2) binding.
energies. The features at 712.7 eV (A1) and 702.7 eV (A2) at 10 K have more intensity compared to the spectrum at 300 K temperature. The satellite (S) observed at 710.5 eV has a FWHM of 2.5 eV. The Fe 2p spectra of Fe\(_{1-x}\)Ni\(_x\) (x=0.3, 0.5, 0.6, 0.7, 0.9) alloys excited by monochromatic AlK\(\alpha\) radiation are shown in figure 8. The spectra recorded at 10 K are overlayed on the spectra at 300 K to observe the temperature induced changes if any. For these alloys, spectra at both the temperatures match exactly.

Figure 8: Monochromatic AlK\(\alpha\) radiation excited Fe 2p spectra of Fe\(_{1-x}\)Ni\(_x\) (x=0.3, 0.5, 0.6, 0.7, 0.9) alloys recorded at 10 K and 300 K temperatures. The spectra at 10 K are overlayed on the spectra at 300 K. Sample composition is indicated above the spectra on the left side in the graph.

Ni 3s and Fe 3s spectra excited by monochromatic AlK\(\alpha\) radiation are shown in figure 8. The spectra recorded at 10 K are overlayed on the spectra at 300 K to observe the temperature induced changes if any. For these alloys, spectra at both the temperatures match exactly.

Figure 9: Monochromatic AlK\(\alpha\) radiation excited (a) Ni 3s and (b) Fe 3s spectra of Fe\(_{1-x}\)Ni\(_x\) alloys recorded at 10 K and 300 K temperatures. The spectra at 10 K are overlayed on the spectra at 300 K. Sample composition is indicated above the spectra on the left side in the graph.

Figure 10 shows the spectra of Ni 3p and Fe 3p core levels of Fe\(_{1-x}\)Ni\(_x\) alloys recorded at 10 K and 300 K temperatures using monochromatic AlK\(\alpha\) radiation as excitation source. The spectra taken at 10 K are overlayed on the spectra taken at 300 K to observe temperature induced changes. Both Ni 3p and Fe 3p spectra recorded at 300 K and 10 K temperatures match exactly for all the alloys.
except for Fe$_{0.6}$Ni$_{0.4}$ alloy. The spectra at 10 K exhibit an extra broad feature at high binding energy of about 3.0 eV and 3.2 eV for Ni 3p and Fe 3p spectra respectively.

The temperature evolution of new features observed at 10 K for Ni 3p and Fe 3p was studied by recording spectra at 40 K and 20 K temperatures also for Fe$_{0.6}$Ni$_{0.4}$ alloy. The monochromatic AlK$_\alpha$ excited 3p and 3s spectra of Ni and Fe in Fe$_{0.6}$Ni$_{0.4}$ invar alloy recorded at 300 K, 40 K, 20 K and 10 K are shown in figure 11. The spectra recorded at 20 K, 40 K and 300 K match exactly with each other for both 3p and 3s spectra of Fe and Ni. On the other hand the spectra taken at 10 K temperature exhibits a high binding energy feature in 3p and 3s core levels of Fe and Ni. The separation of the new feature from original 300 K feature depends on the core level.

Figure 12 shows the numerically fitted Ni Fe$_{0.6}$Ni$_{0.4}$ 3s and Fe 3s spectra at 300 K and 10 K. Black line indicates the experimental spectra and red line indicates the numerical fitting using AGL sum function.
The Ni 3s spectrum at 300 K temperature of the invar alloy has been de-convoluted into two features at 110.8 and 117.6 eV binding energies with 3.7 and 2.5 eV FWHM respectively as shown in figure 4.12(a). On the other hand the Ni 3s spectrum of the alloy at 10 K is de-convoluted into three features at binding energies 110.8, 113.5 and 117.5 eV with FWHM 2.6, 2.5, 3.6 eV respectively as shown in the figure 12(b). Fe 3s spectrum at 300 K is deconvoluted into three peaks at 90.9, 95.0 and 97.6 eV binding energies with FWHM 3.5, 3.7 and 2.5 eV respectively as shown in figure 12(c). Fe 3s at 10 K is de-convoluted into three peaks with binding energy positions 91.1, 93.8 and 95.5 eV with FWHM 3.1, 1.5 and 1.9 eV respectively.

Figure 13 shows the numerically fitted Ni 3p (a) 300 K, (b) 10 K and Fe 3p (c) 300 K, (d) 10 K spectra of Fe_{0.6}Ni_{0.4} alloy. Black line indicates the experimental spectra and red line indicates the numerical fitting using AGL sum function.

3p and Fe 3p spectra at 300 K and 10 K of Fe_{0.6}Ni_{0.4} alloy using AGL Sum function (equation 1). The Ni 3p spectrum at 300 K temperature of the invar alloy has been de-convoluted into two features at 66.3 and 68.4 eV binding energies with 2.0 and 2.0 eV FWHM respectively as shown in figure 13(a). The Ni 3p spectrum of the alloy at 10 K is also de-convoluted into two features at binding energies 66.2 and 69.1 eV with FWHM 1.5 and 1.5 eV respectively as shown in the figure 13(b). Fe 3p spectrum at 300 K is deconvoluted into two peaks at 52.8 and 55.1 eV binding energies with FWHM 1.8 and 1.6 eV respectively as shown in figure 13(c). The Fe 3p at 10 K is de-convoluted into two peaks with binding energy positions 52.9 and 55.7 eV with FWHM 2.0 and 2.0 eV respectively.

Figure 14 shows valence band spectra of Fe_{1-x}Ni_{x} (x=0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9, 1.0) alloys recorded at 10 K and 300 K. Spectra at 10 K are overlayed on the spectra at 300 K.

Figure 14 shows valence band spectra of Fe_{1-x}Ni_{x} alloys at 300 k and 10 K excited by monochromatic AlKα radiation. Spectra at 10 K are overlayed on the spectra at 300 K to emphasise the changes occurring due to temperature. Except for the Fe_{0.6}Ni_{0.4}...
alloy, the valence bands at 300 K and 10 K of all the alloys match exactly. The 10 K spectrum of the Fe$_{0.6}$Ni$_{0.4}$ invar alloy exhibits a shift of 0.15 eV towards high binding energy compared to that of 300 K spectrum.

The wide scans of the Fe$_{1-x}$Ni$_x$ alloys indicated negligible or no surface contaminants like carbon or oxygen. The observed changes in the spectra with composition or temperature are solely due to the changes in the properties of alloys. Ni 2p and Fe 2p spectra exhibit an asymmetric broadening on the high binding energy side for Fe$_{0.6}$Ni$_{0.4}$ alloy at 10 K. Such spectral changes are usually observed if there is a new phase precipitation that has different chemical shift compared to the phase at room temperature. But in 3s and 3p spectra of Fe and Ni, a new broad feature well separated from the feature at room temperature came up at 10 K. If the new feature is due to chemically different phase, the chemical shift is expected to be same for all core levels or the deep core level (2p) should have more chemical shift as the chemical shift is due to the influence of increase in effective nuclear charge. This rules out that the observed spectral changes in 2p, 3s and 3p of Fe and Ni have any chemical origin. Interestingly, both Fe and Ni core levels exhibit similar changes at 10 K, which suggests that the new feature has no relation with the change of spin state as the spin state of Ni is not expected to change with temperature. The observed changes in the spectra take place between 20 K and 10 K temperatures. Below 20 K, Fe$_{0.6}$Ni$_{0.4}$ alloy is either in mixed magnetic state containing both ferromagnetic (FM) and antiferromagnetic (AFM) regions or in spin glass state. In Fe-Ni alloys, the interaction between Fe atoms separated by shortest distance is antiferromagnetic whereas nearest neighbour Fe-Ni and Ni-Ni interactions are ferromagnetic (FM). In these alloys competing interactions are expected. Dubinin and Dubinin suggested long range antiferromagnetic ordering in invar FeNi alloys, but neutron diffraction studies did not show long range order. A reentrant temperature induced ferromagnetic spin glass transition was observed in Fe-Ni invar alloys. The three peak structure observed in Fe 3s agrees well with the reported data for Fe$_{65}$Ni$_{35}$ alloy suggesting the existence of two magnetic states of Fe at room temperature. Most of the photoemission studies concentrated on Fe 2s at room temperature or at higher temperatures. But there are no XPS studies reported in Fe-Ni invar alloys at low temperatures particularly below 20 K to the best of our knowledge.

Fe 2s states split into three peaks. The two low binding energy features appearing at 834.5 and 838.9 eV binding energy are due to the exchange coupling of the 2s core hole with the unpaired electrons in 3d level of the same atomic site. The observed exchange splitting is about 4.5 eV. The exchange splitting is of atomic origin and suggests local magnetic moment on Fe site. For pure Fe and other high Fe concentration Fe$_{1-x}$Ni$_x$ alloys up to x=0.3, a clear three peak structure is observed in Fe 2s. Whereas high Ni concentration alloys exhibit a flat Fe 2s state. But the width of the 2s state extends from 846.0 eV to 831.0 eV binding energy for all the alloys studied. The redistribution of spectral weight is observed in the exchange split components of Fe states at 10 K. The high binding energy feature in Fe 2s observed at 844.3 eV is due to the core hole screening by extended electron states from 4s band. Such a three peak structure was observed previously for Fe 2s states in FeF$_2$. Fe 3s spectra of x=0.4 alloy was deconvoluted into three features as shown in the figure.
13(c). Such a three peak structure suggests two possible Fe magnetic states\[21, 22, 23, 24\]. In invar alloys Fe can exist in high spin and low spin states depending on the environment. The Fe-Ni invar alloys are inhomogeneous at microscopic level and possess three magnetically and crystallographically different phases\[30\].

In Fe-Ni invar alloys, there are two high spin ferromagnetic phases with fcc (γ) and bcc (α) structures having Fe magnetic moments 2.8 \(\mu_B\) and 2.2 \(\mu_B\) respectively. The third fcc phase (γ') has low spin of 0.5\(\mu_B\) on Fe becomes antiferromagnetic below 20 K. The α and γ' phases get precipitated at low temperatures. The γ' phase precipitates cause domain wall pinning that leads to spin glass state formation\[21, 22\].

The observations suggest that at low temperature 3s and 3p spectra are more influenced compared to 2p spectra. The new feature can not be related to exchange splitting as the exchange splitting in Fe 2s state is 4.4 eV and 3s, 3p states should have exchange splitting much larger than 4.4 eV. But the new features are observed with a separation less than 3.5 eV with reference to the feature observed at 300 K. The outer core levels are more affected than inner core levels. This may happen when there is a difference in screening mechanism of the core hole at 10 K to that of at 300 K.

In invar alloys, if an Fe atom is surrounded by zero to nine Fe atoms is in low spin state and the Fe atom in the surrounding of ten to twelve Fe atoms takes high spin state. In the low spin state, Fe moment is compensated by surrounding Ni atoms. In invar alloys strong moment-volume instabilities were reported which give rise to invariance of thermal expansion around room temperature. The reported core level data show no changes for the temperature range from 300 K to 20 K. But at 10 K, a drastic change occurs, which can be attributed to a large precipitation of antiferromagnetic, γ' phase. The γ' phase is a low spin phase and Fe surrounded by more Ni atoms compared to the Fe high spin state. The core hole screening occurs due to intra atomic and interatomic charge relaxation.

The intra atomic charge is not affected by the temperature and remains same at 300 K and 10 K temperature. The extra atomic charge relaxation depends on the surrounding and has strong temperature effect. When the γ' phase precipitates at low temperatures, there are Fe atoms in the surrounding of more Ni atom. At room temperature though there are two surroundings for Fe, both have similar inter atomic screening due to delocalized electrons. When the temperature is lowered to 10 K, electrons are localized and the two Fe sites in the surrounding of more Ni atoms and less Ni atoms are distinctly seen in XPS. The same scenario is valid for Ni atoms also. Therefore, the anomalies in 3s and 3p levels of Fe and Ni at 10 K are due to the changes in the screening effect of inter-atomic charge.

4 Conclusion

The random Fe\(_{1-x}\)Ni\(_x\) (x=0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.9) alloys were prepared by arc melting method and were investigated using high resolution X-ray photoelectron spectroscopy (XPS) technique. The 2s, 2p, 3s, 3p core levels of Ni and Fe and the valence band spectra were recorded down to 10 K temperature. The invar alloy (Fe\(_{0.6}\)Ni\(_{0.4}\)) exhibits anomalous temperature dependence in the core levels of Fe and Ni. The Ni 2p and Fe 2p spectra exhibit a broadening on the high binding energy side of the spectra at 10 K. On the other hand 3s and 3p spectra of Fe and Ni in the in-
var alloy exhibit a broad high binding energy feature at 10 K. The spectra at 20 K, 40 K and 300 K match exactly for the core levels. The marked difference in 3s and 3p core levels at 10 K compared to that of 2p core level is attributed to the changes occurring in screening charges. The well screened feature occurs at high binding energy as observed for both 3s and 3p spectra of Fe and Ni. At room temperature the well screened feature is not observed. The core hole screening effect is also seen in 2p core levels of Fe and Ni for invar alloy, as with well screened state occurring 0.44 eV high binding energy, the effect of screening on the deep core hole is less compared to the outer core holes.

Acknowledgement

Author would like to thank greatly Prof. V. R. R. Medicherla, SOA University, Bhubaneswar, Dr. R. Rawat, UGC-DAE Consortium for Scientific Research, Indore and Prof. K. Maiti, TIFR Mumbai for providing experimental facility carried out in this paper.

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