Exchange Interaction in Fe$_{1-x}$Ni$_x$ Alloys: XPS Study

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Abstract

In this paper, high Fe-concentration Fe$_{1-x}$Ni$_x$ alloys were investigated using high resolution X-ray photoelectron spectroscopy (XPS) down to 10K temperature. The Fe 2s core level exhibits three features, two low binding features corresponding to exchange interaction between ionized 2s core level and the unpaired 3d electrons. The high binding energy feature corresponds to the screening of 2s core hole by 4s conduction electrons. Our studies suggest high local magnetic moments on Fe sites.

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1 Introduction

Fe-Ni alloys have been extensively studied due to the invar property exhibited by the alloys with nickel concentration around 35%. Charles Edward Guillaume was awarded 1920 physics nobel prize for the discovery of invar effect in these alloys. The magnetic phase diagram of Fe-Ni alloys is very complicated. Fe-Ni alloys possess bcc structure for low Ni concentration of about 25% and the alloys transform to fcc structure above 25% Ni concentration. Recently many researches focused their attention on Fe-Ni invar alloys as it was suggested that the invar property is related to non-collinear magnetic structures in the alloys. Abrikosov et.al predicted that the invar alloys, Fe$_{65}$Ni$_{35}$ first transforms into a ferromagnetic system with local magnetic moments on Fe sites, pointing antiparallel to the net magnetization which promote non-collinear magnetic structure inside ferromagnetic matrix. The local Fe and Ni magnetic moments exhibit a weak dependence on concentration of the alloys. Ni magnetic moment is about 0.6-0.7$\mu_B$ and that of Fe is about 2.5-2.7$\mu_B$ in these alloys. Fe-Ni alloys are extensively used in recording industry, in making watches and cryogenic dewars.

This paper presents the study of exchange splitting in 2s core level of Fe in Fe$_{1-x}$Ni$_x$ alloys using high resolution X-ray Photoelectron Spectroscopy (XPS). Our results suggest that Fe has local magnetic moment that does not exhibit a dependance on composition for high Fe concentration alloys.

FeNi alloys exhibit anomalous magnetic, elastic and structural properties. The phase diagram of Fe$_{1-x}$Ni$_x$ alloy system is very complicated and is still being investigated. Pure Fe metal possesses bcc structure ($\alpha$-phase) and exhibits a structural transition to fcc structure ($\gamma$-phase) upon alloying with Ni at around a Ni concentration of 30% and maintains the same structure up to 100% of Ni concentration. Both $\alpha$ and $\gamma$ phases form disordered alloys by metastable quenching. Ordered alloys form for 50% (FeNi) and...
75%(FeNi$_3$) of Ni concentrations. But FeNi ordered phase can not be formed by simple annealing. The fcc phase exhibits complex magnetic behavior and is known to exist in different magnetic states \[7\] similar to pure fcc Fe \[8\]. Charles Edouard Guillaume was awarded the 1920 Physics Nobel Prize for the discovery of Invar effect (invariance of thermal expansion over a wide range of temperature) in iron-nickel ferromagnetic alloys with a nickel concentration of 35\% \[9\].

FeNi alloys are extensively used in recording industries. Fe possesses complicated structural and magnetic phase diagrams. Complication increases manifold upon alloying. When alloyed with Ni, Fe magnetic moment increases with Ni concentration both in bcc and fcc phases. Abrikosov et.al \[10\] predicted that Fe$_{65}$Ni$_{35}$ FM alloy first transforms into a ferrimagnetic system with local moments on Fe atom, surrounded mostly by Fe atoms, pointing antiparallel to the net magnetization. Such spin flip sites promote non-collinear magnetic structures inside FM matrix. Local Fe and Ni magnetic moments exhibit a weak dependence on concentration of FeNi alloy. This results in a linear increase of average magnetic moment with Fe concentration. In these alloys Ni moment is about 0.6-0.7$\mu_B$ and that of Fe is 2.5-2.7$\mu_B$ \[?\]. Curie temperature becomes maximum at a particular concentration and then decreases. Such a behaviour is explained due to increase of effective exchange integrals with Fe concentration and increasing frustration and increase of the range of exchange integrals at Fe-rich end. Several theoretical studies indicated $J_{FeFe}$ near neighbour exchange integral is negative in FeNi alloys indicating antiferromagnetic coupling between Fe atoms. In random alloys, due to inhomogeneities, some antiferromagnetic clusters may exist on the ferromagnetic matrix.

Neutron scattering studies suggested local magnetic moments for both iron and nickel atoms in FeNi alloys. The values of magnetic moments are marginally different from the pure metal values \[11\]. Magnetic moment drops below 40\% Ni concentration due to the increase of antiferromagnetic behaviour as Fe-Fe nearest neighbour interactions start to dominate \[12\]. When Ni added to the system, the stability of the FM solution increases. Pure Ni metal exhibits short range ferromagnetic ordering whereas fcc Fe exhibits long range oscillating behaviour \[?\]. Various exchange integral values reported are $J_{FeFe}=-6$meV, $J_{NiNi}=57$meV and $J_{FeNi}=45$meV \[13\].

The origin of observed anomalous properties of FeNi alloys is not yet well understood till date. The origin of invariance of bulk modulus and magnetic moment with pressure can be understood by measuring the structure of these alloys at various pressures. A systematic and detailed temperature dependent structural study is highly desirable to understand the Martensitic transition in these alloys. Study of magnetic and transport properties of FeNi alloys is essential from both fundamental and applied points of view.

## 2 Experiment

The physical properties of Fe$_{1-x}$Ni$_x$ alloys are highly sensitive to method of preparation and temperature of annealing. Therefore it is essential to properly characterize the alloys before any conclusions be made on the properties of these alloys. The high purity (99.99\%) Fe and Ni metals were used for preparing the alloys which ensures that the contribution from the impurities to the properties of the alloys is negligible. The arc melting was done
in water cooled copper hearth and thus the impurities entering to the alloys from copper hearth is diminished. In some preparation methods like solid state reaction methods, the crucible are heated to heat the mixture and there is a possibility of getting impurities to the samples from heated crucibles. The annealing was carried out by wrapping the alloys in molybdenum and putting them in an evacuated quartz tube. The temperature of annealing was kept purposefully low to avoid the formation of compounds. The annealing done under high vacuum in a closed quartz tube further ensures that the alloys get no impurities during the annealing also.

The high Fe concentration alloys, Fe$_{0.8}$Ni$_{0.2}$ and Fe$_{0.7}$Ni$_{0.3}$ were prepared by arc melting technique[14] and were characterized by X-ray diffraction(XRD)method. The magnetic properties were measured down to 5 K using SQUID magnetometer. The resistivity and magneto-resistance were measured down to 5 K using four probe method. Fe$_{0.8}$Ni$_{0.2}$ alloy possesses bcc structure and Fe$_{0.7}$Ni$_{0.3}$ alloy has a mixed phase both fcc and bcc.

The XPS measurement were carried out using a PHOIBOS 150 MCD Energy Analyzer from Specs GmbH at a base pressure of 4X$10^{-10}$ 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

Figure 1 shows the XRD patterns of Fe$_{1-x}$Ni$_x$ alloy obtained using CuK$_\alpha$ radiation. Fe$_{0.8}$Ni$_{0.2}$ is in bcc phase. The indexing of the peaks were done using PowderX software[15] [16].

Temperature dependent resistivity for Fe$_{0.8}$Ni$_{0.2}$ alloy recorded in both cooling and heating cycles are shown in figure 2.
The data presented in figure 2 indicates a phase transition occurring during cooling. The FeNi alloy exhibits a martensitic transition. Figure 3 shows the M-H loops for Fe$_{0.8}$Ni$_{0.2}$ and Ni are recorded at 10 K (LT) and 300 K (RT) temperature using monochromatic AlK$_\alpha$ radiation. The composition of the alloys is given in the figure legend.

The survey scans recorded for the alloys of Fe$_{1-x}$Ni$_x$ (x=0.0, 0.2, 1.0) at 10 K (LT) and 300 K (RT) temperatures are shown in figures 4 (a) and 4 (b) 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$_3$M$_{23}$M$_{23}$ and 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 is also seen near zero binding energy.

Figure 5: Ni 2p and Fe 2s spectra of Fe, Fe$_{0.8}$Ni$_{0.2}$ and Ni are excited by monochromatic AlK$_\alpha$ radiation at 10K temperature.

Figures 5 (a) and 5 (b) show the XPS spectra of Ni 2p and Fe 2s regions recorded at 10K and 300K temperatures for Fe$_{1-x}$Ni$_x$ alloys. The XPS data for pure Ni and Fe metals is also shown for comparison. The Ni 2p$_{3/2}$ peak occurs at a binding energy of 852.7 eV and Ni 2p$_{1/2}$ at 870.0 eV with a spin orbit splitting of about 17.3 eV which remains nearly same for pure Ni and alloys. On the low binding energy side of Ni 2p$_{3/2}$, a broad Fe 2s structure with three fine features is observed for the alloys. Interestingly pure Fe also exhibits similar 2s structure as the alloys. The fine features are designated as A,B,C in the figures. The satellites observed at the higher binding energy side of the 2p peaks corresponds to well known 6 eV satellites observed for Ni. Interestingly the satellite in alloys exhibit a shift of about 1 eV towards high binding energy compared to pure Ni. The behaviour of satellites is similar at 10 K and the 300 K temperatures as shown in figures 5 (a) and 5 (b).

Figure 6: Integral background subtracted Fe 2s spectra of figure 5.

Fe 2s structure has been deconvoluted by numerically fitting the features A,B and C using Gaussian-Lorentzian sum function after subtracting an integral background[18]. The features A,B and C occur at around 843.8 eV, 838.4 eV and 833.8 eV binding energy respectively. The features B and C corresponds to exchange splitting of Fe 2s level due to the unpaired electrons present in 3d level. The exchange splitting observed is around 5.0 eV which agrees with the exchange splitting observed previously in FeF$_2$[19]. The high binding energy features C at 838.4 eV is due to the screening of the core hole by 4s conduction electrons.

When a core electron is photoemitted from Fe 2s shell, a photo hole with spin and
angular momentum is created. The spin of the photo hole interacts with the total spin of the valence shell of the ion (Fe 3d) via exchange interaction and gives rise to two final states depending on whether the spin of the core hole is parallel or antiparallel to the spin of the valence shell. The energy difference between the parallel and antiparallel configurations is called exchange splitting and is given by

\[ \Delta E_{\text{ex}} = \frac{2S+1}{2l+1}G(l) \]

where \( S \) is the total spin of the valence shell and \( l \), the orbital quantum number of the outer shell (3d) and \( G(s,l) \) the exchange integral\[19, 20\]. The exchange splitting is proportional to the number of unpaired electrons in the outer 3d shell. The Fe metal is ferromagnetic and has magnetic moment of about 2.7\( \mu_B \) gives an exchange splitting of about 5.7 eV. The magnetic moment of Fe exhibits a weak dependence on the alloy composition so is the exchange splitting. As Fe 2s spectra are scarcely studied in the literature \[19\], we use Fe 3s data reported for comparison\[21\]. The Fe 3s data reported on several oxide systems agree with the our data as in oxides 4s electrons participate in the bond formation and in alloys 4s electrons become delocalised. In both the cases F 3d shell is localized on the site and give rise to exchange splitting. These results suggest the core hole is screened by either 4s electrons or 3d electrons. When screening occurs via 3d electrons exchange splitting takes place.

4 Conclusion

High purity Fe\(_{0.8}\)Ni\(_{0.2}\), Fe\(_{0.7}\)Ni\(_{0.3}\), Fe\(_{0.6}\)Ni\(_{0.4}\) by metallic alloys have been prepared by arc melting method and were investigated using high resolution resolution X-ray Photoelectron Spectroscopy. The position of 6 eV satellite shifts to higher binding energy by about 1 eV compared to pure Ni metal suggesting the variation in the number of outer electrons in the atomic site. Our Fe 2s core level spectra suggest strong local magnetic moments for Fe.

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