Chapter 1

Introduction

1.1 Alloys

Alloy is a solid solution or physical mixture of two or more elements one of which is a metal. Alloys usually contain a single phase solid solution of elements or a mixture of metallic phases. Single phase solid solutions are called homogeneous alloys and the mixture of phases are called inhomogeneous alloys. Physical properties of alloys are usually very different from those of individual constituents. Solubility of constituent elements in solid state is an important parameter for preparation of solid solutions. An alloy with two constituents is called a binary alloy and an alloy of three constituents is called a ternary alloy. Alloys, unlike metals, usually do not possess a single melting point as the individual constituents melt at their own melting points. Thus an alloy has a melting range which starts from the melting point of the constituent with lower melting point and ends with that of of the constituent with higher melting point. The temperature at which melting just begins is called solidus and the temperature when melting just ends is called liquidus.

Binary alloys can be classified into two categories called substitutional or interstitial depending on the relative atomic sizes of the atoms involved. When the atoms are of similar size, the atom exchange method is usually favored, where some of the atoms of one metal are replaced with atoms of another metal. These alloys are called substitutional alloys which exhibit only slight structural distortions depending on the little size mismatch of atoms. Usually, substitutional alloys exhibit distortions of few percentage on the lattice parameter. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms. In interstitial alloys, one
type of atom is much smaller than the other, so that they cannot replace each other. The smaller atom becomes trapped in the void spaces between the bigger metal atoms. The carbon steel is an example of an interstitial alloy, where the small carbon atoms fit into interstices of the iron base. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are replaced with nickel and chromium atoms.

**Substitutional Alloys**

![Substitutional Alloys](image)

**Interstitial Alloys**

![Interstitial Alloys](image)

Figure 1.1: Pictorial representation of substitutional and interstitial alloys

When we take a metal with A type atoms and substitute randomly another metal with B type atoms which are of similar atomic size as A, we get disordered or random AB alloy as shown in figure 1.1. If metal B is periodically substituted into metal A, we get an ordered AB alloy. We can also get random or disordered interstitial alloys when we distribute a very small metal atom, C randomly at interstitial sites of metal A whose atomic size is much bigger than the size of C. In a similar way we can also generate an ordered interstitial alloy by placing atoms C into interstitial sites of A in a periodic manner. In this thesis, our focus is on random substitutional alloys.
1.1.1 Transition Metal Alloys

The transition metal alloys have garnered both scientific and technological interest for many decades. These systems often exhibit unusual magnetic, transport and optical properties that are quite different from those of constituents. The interesting properties of these systems typically are governed by the relative binding energies, relative population and hybridization effects of $d$ electrons of valence bands in the two parent metals. Electronic structure of binary alloys is a subject of study for several years due to the complexities involved in understanding the charge transfer between their constituent atoms upon alloying [1–13]. The direction and character of charge transfer upon alloy formation between the constituents decides the electronic and magnetic properties of alloys. Estimation of charge transfer and its direction becomes crucial to the understanding of alloy properties. Alloy formation also leads to intra-atomic charge redistribution which also affects bonding and electronic properties of the alloy. Many alloys exhibit properties which are useful for practical applications and the understanding of their electronic structure is the primary step. Random binary alloy surfaces are of importance in surface chemistry where compositional variables are exploited to tailor properties of expensive catalytic components [14–16]. Alloys of noble metals with a transition metal exhibit radical changes of behaviour which is associated with the presence of impurity $d$ states; Kondo phenomenon and virtual bound state formation are striking examples [17–21]. When the transition metal forms a virtual bound state, electronic properties of the alloy is primarily decided by the noble metal. But, the transition metal introduces disorder into the alloy which also modifies the electronic structure. Disorder induced localization of electrons is a well known phenomena in condensed matter physics. [22]. In this thesis transition metal alloys were investigate primarily using Photoelectron Spectroscopy (PES). Main features of which are given below

1.2 Photoelectron Spectroscopy

In 1887, Hertz observed the phenomenon of photoelectric effect. The phenomenon was explained by Einstein in the year 1905 introducing the concept of photon [23]. Photoelectron Spectroscopy is based on Photoelectric effect [24–27]. Photoelectrons are emitted from the surface of a metal if the incident photon energy is more than work function of the given metal. But in photoelectric effect only photo current is measured using low photon energies in the visible or ultra violet region. On the other hand photoelectron spectroscopy measures the kinetic energies of photoelectrons emitted by
high energy photons like X-rays or low energy UV photons. Absorbed photons of sufficient energy by atoms in a solid liberate electrons. These electrons travel through the solid and comes out of the surface if their kinetic energy is higher than the work function of the solid. Photons penetrate into few micrometers into the solid and liberate electrons. But, the electrons being charged particles, interact with other electrons and also with the ions of the solid and loose their energies while moving to the surface. Kinetic energy of the electron just after the emission from an atom is given by

\[ E_K = h\nu - E_B \] (1.1)

Where, \( E_B \) is the binding energy of the electron at the atomic energy level from where the electron is liberated. \( E_K \) will gradually decreases as the electron moves up to the surface. If it looses considerable energy then the measured \( E_K \) is less than the original \( E_K \) of the electron which leads to the higher value of \( E_B \) for atoms below certain depth from surface. The loss in energy of electrons in the solid is predominantly due to electron-electron interactions over a wide range of energies. But at very low kinetic energies, the losses are primarily due to electron-phonon interactions. There is some characteristics depth called average inelastic electron mean free path (IMFP) which depends on the electron kinetic energy and also on the material in question. After the electron comes out from the surface within a depth smaller than IMFP, the approximate electron kinetic energy is given by,

\[ E_K = h\nu - E_B - \phi \] (1.2)

Where, \( \phi \) is the work function of the surface of the solid. IMFPs have been measured for several materials as a function of electron kinetic energy and surprisingly the data of all the materials fall on a universal curve as shown in the figure 1.2 [24, 28]. This curve exhibits a broad minimum in IMFP, at about 50 eV kinetic energy. These IMFPs are of few monolayers for energies up to few keV, which suggests that the photoelectron spectroscopy is extremely surface sensitive. Photoelectron detection depth in solids is only few monolayers from the surface. Electrons emitted below this depth get scattered inelastically and transfer a part of their energy to the remaining electrons and phonons in the solid and thus loose the memory of quantum state of emission. These inelastically scattered electrons contribute to the step like background of the photoelectron spectrum. The blue region indicates that the IMFP becomes minimum in the region 20-50 eV electron kinetic energy. This energy region is mostly accessible when He II is used for valence band excitation. Pink region indicates the 6 eV kinetic energy region mostly occurs when He I radiation is used for exciting valence bands. These regions are shown to indicate that the high energy He II radiation is more surface sensitive compared to low energy He I radiation.
Figure 1.2: Energy dependence of inelastic mean free path of electron in solids

Photoelectron spectrometer consists of a photon source (X-ray, UV) of excitation, a solid sample and an electron detector are shown in figure 1.3. Photoelectrons after being emitted from the sample should reach the detector without losing their energy. During the travel from the sample surface to the detector, electron collides with gas particles and loose energy. To prevent such losses this experiment should be conducted in vacuum which is a gas free environment. But the creation of the vacuum requires vacuum pumps, gauges and vacuum chambers. At least a vacuum of about $10^{-6}$ Torr is re-
quired for the electrons to travel about a meter without loosing their energy. Though the photoelectric effect was known from 1887, due to unavailability of vacuum technology, photoelectron spectroscopy could not be developed. It took few decades for the development of the vacuum technology which led to the development of photoelectron spectroscopy. A layout of a typical photoelectron spectrometer is shown in figure 1.4, where the source, sample and detector are housed in a vacuum chamber. There is another stringent condition on vacuum regarding the cleanliness of the sample surface. Any solid exposed to atmosphere gets contaminated on the surface due to the adsorption of impurities like oxygen, carbon and nitrogen. As the PES is highly surface sensitive, the photoelectron signal obtained from such contaminated surfaces contains predominantly oxygen and carbon obscuring the actual signal from the sample of interest. For removing such contamination, sample surface needs to be cleaned inside the vacuum chamber. In the vacuum level of $10^{-6}$ Torr range, a monolayer of contamination gets accumulated on the surface in 1.5 s, making the experiment impossible on a fresh surface. For typical photoemission experiments, clean surface should be maintained at least for a period of 1 hr which can be achieved by a vacuum of $10^{-10}$ Torr or better which comes under ultra high vacuum (UHV) range.

Figure 1.4: Layout of a Photoelectron Spectrometer
1.2.1 Surface Cleaning Methods

In-situ surface cleaning is the most essential part of any photoemission experiment. The most used in-situ surface cleaning techniques are (i) cleaving (ii) scrapping with diamond file and (iii) argon ion bombardment or sputtering. Cleaving of a layer of crystal plane can be done for single crystals along a cleavable plane in UHV. This produces the cleanest surface, but limited only for single crystalline samples. All the single crystals do not possess cleavage plane. Therefore this cleaning technique is limited to single crystals which possess cleavage plane. Scrapping with a diamond file is used mostly for bulk samples like hard pellets made of powders. In this technique a diamond file is fixed to a wobble sticks which can be moved in the vacuum chamber without disturbing the vacuum. The sample surface is rubbed with the diamond file to remove top surface of the sample and expose fresh surface. This technique can be used only for bulk samples with hard surface and not useful for thin films. This technique has the advantage that it will not alter the surface composition though it makes the surface rough. The third technique is mostly used for thin films in combination of argon ion bombardment and heating of the sample. As there is no physical contact with sample surface, technique is well suited for thin film samples. Ion bombardment usually changes the surface composition of multi component systems. When the sample is heated the sputtered surface regains its original composition. Sputtering is usually done with argon ions of energy 500-5000 eV. Photoelectron Spectroscopy can be divided into two categories depending on the excitation source used namely (i) X-ray Photoelectron Spectroscopy (XPS) and (ii) Ultra-Violet Photoelectron Spectroscopy (UPS). In XPS, an X-ray of energy about 1500 eV is used. Most widely used source are AlK$_\alpha$ ($h\nu = 1486.6$ eV) and MgK$_\alpha$ (1253.6 eV) radiations. In UPS He I ($h\nu = 21.22$ eV) and He II (40.81 eV) radiations are widely used. In case of XPS, X-rays can induce photoelectrons emitted from core atomic energy levels as well as valence electrons. X-ray have high photoionization cross section for core electrons where as cross section is low for valence electrons. For this reason, XPS is widely used for studying core electrons. The source line width of AlK$_\alpha$ and MgK$_\alpha$ are 0.85 eV and 0.7 eV respectively. These lines become very sharp when a monochromator is used. He I and He II lines are extremely sharp and have very high cross sections for valence bands and thus provide good valence band signal with very high energy resolution.
1.2.2 Characteristics of X-ray Photoelectron Spectrum

X-ray photoelectron spectra of materials exhibit several general features like steplike background, core levels and chemical shifts, multiplet splitting of core levels, shake up and shake off satellites, disorder broadening etc. which are described briefly below.

1.2.3 Steplike Background

Core levels in XPS spectrum lie on a step like background which occurs due to the inelastically scattered electrons. Electrons emitted below a depth greater than the IMFP, would loose energy due to inelastic scattering while traveling to the surface and contribute to the background at higher binding energies. This implies that high binding energy side of the peak has more background compared to the low binding energy side and thus photoelectron peaks sit on an asymmetric background. The step height of the background is proportional to the intensity of the peak as shown in the figure 1.5, which also shows how photoelectron peak becomes asymmetric due to inelastic electrons. XPS spectrum in general exhibits sharp core levels on step like inelastic background. Photoelectron emission follows the equation given by (1.2). All the core levels for which \( l \neq 0 \) (orbital angular momentum) are doublets with the intensity ratio given by \( 2j+1 \) (where \( j = l + s \), \( j \) = total angular momentum and \( s \) = spin angular momentum) of the corresponding peaks. Each core level XPS peak possesses certain energy width which depends on the source, analyzer and also on the level from which it is emitted. The total observed energy width of the peak is given by,

\[
\Delta E = \sqrt{\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2 + \Delta E_d^2}
\]  

(1.3)

where \( \Delta E_n = \) natural broadening or lifetime broadening, \( \Delta E_p = \) natural energy width of the characteristic X-ray line used, \( \Delta E_a = \) analyzer resolution and \( \Delta E_d = \) disorder induced broadening due to disorder in the materials which also includes temperature dependent phonon broadening along with the disorder in the lattice. Usually thermal disorder broadening is very small and negligible compared to the broadening caused by lattice disorder. The thermal broadening is of the order of \( k_B T \) which is about 0.026 eV at room temperature. \( \Delta E_n \) can be estimated from the uncertainty principle,

\[
\Delta E_n \cdot \Delta t \simeq h \Rightarrow \Delta E_n = \frac{h}{\Delta t}
\]  

(1.4)

where \( \Delta t \) is the life time of core hole. Valence levels are also observed in XPS close to the Fermi energy. Due to the creation of the core hole in photoemission, there is a possibility for Auger electron
emission described below. In XPS, one can detect all elements except H and He due to very low photo-ionization cross section for H and He. It becomes a very powerful tool for elemental identification. The binding energy observed in XPS is very sensitive to the chemical environment around the atom of interest. The environment dependent shift in binding energy is usually referred to as chemical shift or core level shift. For example, the binding energy of Cu2p level in CuO is different from the binding energy of Cu2p level of pure Copper. In case of CuO, copper is surrounded by oxygen atoms and thus the B.E. of Cu2p is different to that of pure copper where Copper is surrounded by only copper atoms.

Adjacent to the core level XPS peaks, some satellites are usually observed. With non monochromatic X-ray sources, some X-ray satellites are also observed. But these satellites are not observed with monochromatic sources like monochromatic AlK\(_\alpha\) radiation. But non-monochromatic AlK\(_\alpha\) source produces an X-ray satellite due to K\(_{\alpha3,4}\) at 9.6 eV lower in binding energy with an intensity of 10% compared to that of induced by the K\(_{\alpha1,2}\) component of the AlK\(_\alpha\) X-ray line.
1.2.4 Auger Electrons

A core hole created by a primary source of excitation like X-rays or electrons, is occupied by an electron transition from upper levels. The energy available in this transition may come out as photon radiation or another electron from one of the upper levels. The secondary electron emitted in a radiationless process is called Auger electron. When the radiation is emitted, the process is called X-ray fluorescence. Auger electron emission and X-ray fluorescence occur as a consequence of creation of core hole. These processes are pictorially shown in figure 1.6. Auger electrons are emitted along with photoelectrons in XPS. These Auger electrons are called X-ray excited Auger electrons and the corresponding spectroscopy is called X-ray excited Auger electron Spectroscopy (XAES). The K-Auger electron emission and K-X-ray fluorescence are competing events. One of them occurs at the cost of other. The Auger electron and the K-X-ray yields are shown in the figure 1.7. [29]. Auger yield is predominant for low Z-elements and K-X-ray fluorescence dominates for high Z-elements. Auger electron kinetic energies are characteristics of the atom of origin. There are three levels involved in Auger process. If the binding energies of the levels involved are \( E_i \), \( E_j \), \( E_k \) and the original hole is

![Figure 1.6: X-ray Photoemission and Auger Processes](image)

![Figure 1.7: Relative yields of K-Auger and K-X-ray fluorescence](image)
created in the level \(i\) and the hole at \(i\) is filled by the electron in \(j\) and eventually electron from level \(k\) emitted. The kinetic energy of the Auger electron is given by equation

\[
E_{ijk} = E_i - E_j - E_k^* \quad (1.5)
\]

\(E_k^*\) represents the Binding energy of the level \(k\) with a hole in the level \(j\). The Auger transition corresponding to the above atomic energy levels is represented as \(ijk\). For example, we observe Auger transitions KLL, LMM etc.

### 1.2.5 Multiplet Splitting

Core level photoelectron lines of some compounds which contain unpaired electrons in their valence shells split into two or more peaks. Such splitting in core levels is called multiplet splitting. For example, Mn\(^{2+}\) ions has 5 unpaired electrons in its 3d shell. When an electron is photo-emitted from 3s level, another unpaired electron is produced. If the spin of the electron left in 3s level is parallel to that of 3d electrons, then exchange interaction takes place resulting in a lower energy compare to the case of antiparallel spin. Thus the core level 3s which is otherwise expected to be a single line will split into two. Multiplet splitting of non-s levels is more complicated and exhibits lot of features.

### 1.2.6 Shake-up and Shake-off Satellites

When the photoelectron is excited from an atom, the valence electrons feel as if the nuclear charge is more compared to neutral atom. This core hole potential acts as a major perturbation to valence electrons and leads substantial reorganization of the valence electrons. In this process one of the valence electron may be excited to unfilled levels above. The energy required for this transition is not available for the photoelectron and thus the kinetic energy of the photoelectron is lower than the value otherwise expected. The lower kinetic energy gives rise to higher apparent binding energy and produces a distinct feature at high binding energy side of the main photoelectron line. The shake-up process can be described by the equation [25]

\[
(nl)^q(n'l')^p \xrightarrow{h\nu} (nl)^{q-1}(n''l'')^{p-1}(n''''l''')^1 + \text{photoelectron.} \quad (1.6)
\]

where \(nl\) is the filled subshell containing \(q\) electrons from where the photoelectron is ejected, \(n'l'\) is the outer subshell containing \(p\) electrons from which the second electron is excited. The outer subshell
may be filled or partially filled. \( n''l'' \) is the empty higher bound state to which the second electron is excited.

Strong satellites are observed for transition metal compounds which have unpaired electrons in the valence shell, 3\( d \). The satellite intensity is much higher than that expected from atomic like shake-up (about 10\%) which lead a great deal of discussion [24, 30]. In transition metal compounds, due to core hole potential on the metal ion, electron transfer from ligand (oxygen) to metal takes place. This explains why closed shell systems (Cu\(^+\), 3\( d^{10} \)) do not exhibit shake-up satellites, whereas open shell systems (Cu\(^{2+}\), 3\( d^{9} \)) exhibit strong shake-up satellites [31]. However, for transition metal compounds, shake-up is a poor description of the process, a preferable description is that strong configuration interaction occurs in final state due to relaxation [30]. Shake-up satellites can be used to distinguish Cu\(^{2+}\) ion from Cu\(^{1+}\) ion. Tetrahedral Ni\(^{2+}\) produces strong satellites compared to square planar Ni\(^{1+}\) [32].

In the process similar to shake-up, valence electrons can be excited to unbound continuum state or valence electron is completely removed which is referred to as shake off process. In this process, the resulting final state of the atom contains two holes, one in the core level and the other in the valence level. This process produces a broad structure far away from the main peak compared to the shake-up process. Shake-off features fall in the region of broad inelastic tail making it difficult to observe experimentally. However, a weak shake-off is usually observed on the inelastic tail of C 1s peak of polymers [33]. Shake-off Process can be represented by the equation [25]

\[
(nl)^{q}(n'l')^{p} \xrightarrow{h\nu} (nl)^{q-1}(n'l')^{p-1}(E_{kin}''l'')^{1} + \text{photoelectron}. \tag{1.7}
\]

Where \( E_{kin}'' \) is the empty higher unbound continuum state to which the second electron is excited.

### 1.2.7 Asymmetric Core Level Photoelectron Peaks of Metals

Core level photoelectron peaks of insulators and semiconductors are symmetric whose line shape can be described as a combination of Gaussian and Lorentzian functions, where the Gaussian takes care of the instrumental broadening and the Lorentzian represents the life time or natural broadening. Symmetric core levels observed for non metals can be described using Gaussian-Lorentzian sum function [34] given by

\[
GL(x, p, w, h, m) = h[(1 - m)e^{-Qln^{2}} + \frac{m}{1 + Q}] \tag{1.8}
\]
where \( Q = \left( \frac{2(x-p)}{w} \right)^2 \) and \( p, w, h \) and \( m \) are peak position, Full Width at Half Maximum (FWHM), area under the peak and Gaussian Lorentzian mixing ratio \( (m = 0 \text{ for } 100\% \text{ Gaussian and } m = 1 \text{ for } 100\% \text{ Lorentzian}) \) respectively. On the other hand metal core level photoelectron peaks exhibit asymmetry on the high binding energy side whose shape can not be simulated using symmetric Gaussian-Lorentzian sum function given by equation (1.8). Metals contain a continuous distribution of unfilled one electron levels above the Fermi energy. These unfilled levels are available for shake-up like processes following core electron emission. In this case electrons are excited just above the Fermi energy leading to very low energy excitation. Therefore, a continuous tailing observed for the core level on the high binding energy side instead of a discrete peak in ordinary shake-up process.

Doniach and Šunjić developed a line shape to describe the metal core level photoelectron peaks using the phase shifts of scattered conduction electrons by the core hole potential [35]. The line shape obtained by them is given by

\[
DS(E, \alpha, F, E_0) = \frac{\cos \left[ \frac{\pi \alpha}{2} + (1 - \alpha) \tan^{-1} \left( \frac{E - E_0}{F} \right) \right]}{\left[ F^2 + (E - E_0)^2 \right]^{\frac{1-\alpha}{2}}}
\]

(1.9)

where \( \alpha \) represents the asymmetric parameter that provides the degree of asymmetry in the core level, \( F \) represents the FWHM of the peak, \( E_0 \) represents the peak position and \( E \) is the energy variable scan through the peak either side. Putting \( \alpha = 0 \), the DS function becomes to pure Lorentzian function.

### 1.2.8 Core Level Shift (CLS)

Electrons that occupy energy levels of high binding energy which are closer to the nucleus are called core electrons. These electrons possess binding energies which can be well resolved by different experimental techniques. The binding energy, \( E_B \) of a core-electron in an atom is highly sensitive to the chemical environment surrounding the atom. Measurement of such environment dependent binding energies can be used to gain a deeper insight into the electronic structure and bonding properties of the system under study. As \( E_B \) is sensitive to the local environment in which the atom of interest is immersed, it can be used as a tool to determine local structure and bonding.

The binding energy of a core electron of an atom, \( A \) of a binary alloy \( A_{1-x}B_x \) is usually different from the binding energy of the corresponding core electron in the pure metal, \( A \) due to the difference in chemical environment around atom, \( A \). The difference in binding energies of a particular core level of an atom in the alloy and the pure metal is called as core level shift (CLS). The measured CLS can be expressed as

\[
E_{CLS}^{exp} = E_B^{A_{1-x}B_x} - E_B^A,
\]

where \( E_B \) indicates the binding energy of the core level of
interest. In this case metal core level binding energy works as a reference. Core level shifts are also
called as chemical shifts. The word chemical shift is used for compounds where chemical bonding
or inter atomic charge transfer is involved. Chemical shifts were unambiguously observed for the
first time in 1964 by Hagstrom and co-workers [36]. Since then the chemical shifts have been used
as a routine technique to identify and distinguish between different chemical species in a system.
Observed Chemical shifts were described by ESCA potential model, which is the oldest model deved-
oped. In ESCA potential model which relates the observed CLS in XPS to on site potential, \( \Delta V \) is
given by [37],

\[
E_{CLS} = \Delta V - \Delta E_R
\]  

(1.10)

\( \Delta E_R \) is the core hole relaxation energy, a contribution to the shift from the remaining electrons, as they
screen the charge imbalance caused by the core hole and is called the final state shift. \( \Delta V \) is directly
related to the charge present on the site and is referred as initial state shift. But in theoretical models
the initial and final state effects are calculated separately. Therefore, the simplest way to estimate \( \Delta V \)
associated with charge on an atom in different environments within Potential model [38, 39] is,

\[
\Delta V = q(k - 14.4\alpha^M/R)
\]  

(1.11)

where \( q \) denotes the net charge on an atom, \( k \) is a constant equal to Coulomb repulsion integral
between the core and the valence electrons and \( \alpha^M \) denotes the Madelung constant and \( R \) denotes
the nearest-neighbor distance. The estimated charge, \( q \) on an ion from observed CLS agrees well
for the molecular or ionic solids where the shifts are usually greater than few eV. Gelliis [39] used
ESCA potential model for molecules and his results agree well with the equation (1.10). But, this
model seems to have failed to explain observed CLS in metallic alloy systems. The application of this
model to face centred cubic CuPd alloy by Cole et. al [40] to determine the charge transfer has been
questioned by Faulkner et. al [12], who investigated CuPd, AgPd and CuZn alloys using first principle
calculations based on density functional theory [41], which did not provide any correlation between
ESCA potential and CLS. Similar results have been obtained by Methfessel et.al from the theoretical
calculations of CLS on MgAu alloys [42], which also did not find correlation between CLS and the
charge transfer in the system. Many such studies on metallic alloys lead to the conclusion that there
may be CLS without actually having interatomic charge transfer in metallic systems. The CLSs are
related to various properties like cohesive energy [43], heat of mixing [44], segregation energy [45]
and charge transfer [38]. Weinert & Watson [46] pointed out five important factors (i) interatomic
charge transfer (ii) changes in the screening of the final state of the core-hole (iii) changes in the
energy position of the Fermi-level relative to the center of gravity of bands (iv) intra-atomic charge transfer between the orbitals (sp ↔ d) (v) redistribution of charge due to bonding and hybridization which contribute to CLS.

Several Models have been proposed to explain CLS in metallic alloys. These models include (i) Initial State Model (ii) Complete Screening which includes both initial and final state effects and charge excess functional model [47]. Complete screening picture could provide satisfactory explanation for CLS observed for AgPd, CuNi, CuAu, NiPd, CuZn and PdZn alloys by Steiner and Hüffer [48] in their classic paper in 1981, whereas the initial state model could explain the shifts only in one of the components of the alloys like for Cu, Ag, Zn and found to fail for Ni and Pd [49]

1.2.9 Surface Core Level Shift (SCLS)

Surfaces of many clean metals exhibit slightly different core level shifts for the bulk and surface atoms [50–55]. This difference in binding energy is due to the lack of symmetry for surface atoms in the direction normal to the surface. Atoms on the top surface are exposed to vacuum, whereas atoms below the surface are under the shadow of surface atoms. Due to the lack of symmetry, core level binding energy of surface atoms differ from that of bulk atoms.

1.2.10 Core Disorder Broadening (CDB)

In the previous section, CLS, a rigid shift of the core level binding energy of an alloy with respect to its pure metal counter part has been described, which depends on the macroscopic or average composition of the alloy. In a random binary alloy, the local or microscopic change in composition from site to site which gives rise to CLSs which are very close by on either side of the binding energy of the core level in the alloy. This leads to the broadening of the core level spectrum to that of pure metal, which is called as core disorder broadening. A perfectly ordered alloy, where metal atom, A is distributed maintaining translational periodicity will not exhibit CDB, but exhibits CLS. The energy width of the core level photoelectron peak in ordered alloys is same as that of the pure metal. But the disordered or random alloys exhibit CDB. The broadening in the core levels is very small and could not be observed experimentally by XPS in earlier days, due to the low resolution. Experimental observation of the CDB was possible only after the development of high resolution XPS machines. First observation of CDB was by Cole et al. for Cu 2p\(_{3/2}\) of CuPd alloys [38]. There after many alloy
system have been investigated and found to exhibit CDB [40, 56–59]. The disorder broadening of the Cu 2p core line in CuPd was attributed to formation of local potential due to charge transfer and evaluated in terms of a potential model [38, 40, 60–62]. Apart from local composition changes, local lattice relaxation can contribute to CLS. Core disorder broadening is known to manifest as a Gaussian broadening and adds up in quadrature [38, 57, 58, 63, 64]. The core disorder broadening (CDB) can be deduced experimentally from the total Gaussian width (GW) and the instrumental broadening (IB) which is same as GW in pure metal using the relation [64],

\[ CDB = \sqrt{GW^2 - IB^2} \]  

(1.12)

1.3 Formulation of the Problem

Disorder plays an important role in deciding the physical properties of crystalline systems. Practically, it is not possible to produce hundred percent ordered materials. There will be some amount of disorder in any system. There are several ways of introducing disorder. It is possible to change the physical properties of a system in a controllable manner by introducing disorder gradually by varying a known parameter which changes the disorder. For example, alloying a metal with another of similar atomic size is an easy way of introducing chemical disorder into a metal. In these alloys due to size matching some of the atoms of parent metal are randomly replaced or substituted by a new one and forms random or substitutional alloy. The alloys exhibit spectacular properties if one of the metals is a noble metal and the other is a transition metal. Interestingly, physical properties of such alloys are very different from that of the constituent metals and exhibit exotic phenomena such as Kondo phenomenon, Virtual bound states and magnetic phenomena [18, 65–68]. Alloy composition becomes a vital parameter in deciding the properties of alloys. For example virtual bound states and Kondo phenomenon are expected only at low concentrations of the transition metal and magnetic phenomena occur at high concentrations of transition metal. These phenomena are usually driven by partially filled d band of the transition metal. But, the behavior of electrons depends on the amount of disorder in the alloy. It becomes very crucial to derive the electronic structure of alloys to understand the origin of all the exotic phenomena they exhibit. Calculating the electronic structure of disordered metal is not straight forward due to the lack of translational periodicity. For disordered binary alloys, electronic structure calculations become very tedious and in most cases not tractable.
In an ideal periodic solid, all atoms occupying the equivalent positions in the crystal unit cell have exactly the same properties. In a disordered system even chemically equivalent atoms can be different depending on their surroundings. In disordered alloys, local environment around the atomic sites changes randomly giving rise to a continuous distribution of environments. This is a fundamental property of non-periodic solids. Photoelectron spectroscopy (PES) can directly look into the local surrounding of atomic sites. Photoelectron spectra like core levels, Auger transitions and valence bands are extremely sensitive to the local surrounding in which the atomic site of interest, is immersed in.

Table 1.1: Standard data of Copper (Cu), Nickel (Ni), Silver (Ag) and Palladium (Pd) collected from WebElements

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Ni</th>
<th>Ag</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>29</td>
<td>28</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>63.546</td>
<td>58.5934</td>
<td>107.8682</td>
<td>106.42</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>8.96</td>
<td>8.902</td>
<td>10.5</td>
<td>12.02</td>
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<tr>
<td>Melting Point (K)</td>
<td>1356.6</td>
<td>1726</td>
<td>1235.1</td>
<td>1825</td>
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<td>Boiling Point (K)</td>
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<td>3005</td>
<td>2485</td>
<td>3413</td>
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<tr>
<td>Atomic Radius (pm)</td>
<td>128</td>
<td>124</td>
<td>144</td>
<td>137</td>
</tr>
<tr>
<td>Atomic Volume (cc/mol)</td>
<td>7.1</td>
<td>6.6</td>
<td>10.3</td>
<td>8.9</td>
</tr>
<tr>
<td>covalent Radius (pm)</td>
<td>177</td>
<td>115</td>
<td>134</td>
<td>128</td>
</tr>
<tr>
<td>Magnetic Ordering</td>
<td>Diamagnetic</td>
<td>Ferromagnetic</td>
<td>Diamagnetic</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Fm-3m</td>
<td>Fm3m</td>
<td>Fm3m</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Unit cell Volume</td>
<td>4.72x10^{-29}m^3</td>
<td>4.37x10^{-29}m^3</td>
<td>6.28x10^{-29}m^3</td>
<td>5.8x10^{-29}m^3</td>
</tr>
<tr>
<td>Lattice Structure</td>
<td>FCC</td>
<td>FCC</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td>Lattice Constant (Å0)</td>
<td>3.610</td>
<td>3.520</td>
<td>4.090</td>
<td>3.890</td>
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</table>

Substitutional CuNi and AgPd disordered alloys form in FCC structure with negligible volume effects due to the similar atomic radii of Cu, Ni and Ag, Pd as shown table 1.1 [69]. Pure metals of these elements possess FCC structure. Cu and Ag are noble metals with flat $s$ and $sp$ states respectively near the Fermi level. Whereas, Ni and Pd are transition metals with partially filled $d$ bands occurring at the Fermi level. In both the alloys, transition metals form virtual bound states at low concentrations of transition metal.
CLSs of Cu 2p and Ni 2p in CuNi alloys have been measured by Steiner and Höffner [48] way back in 1981 and by Barbieri et al. [70] in 2004. Both these studies indicated negative CLSs for Cu 2p and Ni 2p and are non-linear with composition. Recent theoretical calculations done under complete screening picture by Olovsson et al. [71] agree well for both Cu and Ni CLSs. Whereas the initial state calculation agrees only for Cu CLS and fails for Ni CLS. CDB in CuNi alloys has not been reported so far in the literature. CLS in AgPd alloys have been measured and the compositional dependance of CLSs have been explained theoretically [13, 48, 49, 72]. CDB has been observed in Ag 3d$_{5/2}$ of Ag$_{1-x}$Pd$_x$ alloys [13, 58]. Interestingly, in Pd 3d$_{5/2}$ of Ag$_{1-x}$Pd$_x$ alloys, the CDB is highly suppressed and practically no broadening was observed. Single crystalline PdAg(100) surface alloys studied by Medicherla & Drube [64] exhibited unexpectedly large CDB for Ag 3d$_{5/2}$ and no CDB observed for Pd 3d$_{5/2}$. As single crystalline alloys possess long range order, one would expect no disorder broadening. AgPd alloys with very low Pd concentration are not investigated for CLS and CDB. These alloys exhibit spectacular physical properties due to the formation of Pd virtual bound state.

Auger transitions are finger prints of elements and are extremely sensitive to the local surrounding. These transitions can also conceive disorder of the material in the spectra. The simulations on core-core-core Auger transitions of various alloys suggested the clear observation of Auger disorder broadening despite the fact that the larger life time broadening in Auger transitions [73]. Disorder broadening has been experimentally observed in Ag M$_{4.5}$N$_{4.5}$N$_{4.5}$ Auger transition of Ag$_{0.5}$Pd$_{0.5}$ alloy compared to that of pure Ag [74]. The Auger energy shifts and Auger disorder broadening are observed experimentally in alloys with Auger transition involving only core levels. But, such investigations on Auger transitions involving two final holes in the valence band are scarce [74].

The magnetic and mechanical properties of thin layers of Cu/Ni are different from those of homogeneous CuNi alloys or their metallic counter parts [75]. Theoretical investigations of Ni monolayer on Cu suggested a significant influence of the position of Ni layer on the magnetic properties of the system [76]. The magnetic anisotropy in Cu/Ni/Cu(100) thin film system depends on the thickness of Ni layer and for thickness ranging from 15 to 135 Å perpendicular magnetic anisotropy develops [77]. The magnetic moment in Ni/Cu/Si(100) system was found to decrease with the decreasing thickness [78].
In this thesis, CLSs, CDB, Auger shifts and broadening have been investigated for Cu\(_{1-x}\)Ni\(_x\) and low Pd concentration Ag\(_{1-x}\)Pd\(_x\) random alloys along with surface and interface studies of Cu/Ni bilayer on Si(100).

### 1.3.1 Motivation and Purpose of the Present Study

Alloys of noble metal with a transition metal exhibit unusual physical properties. Noble metals possess flat s band near the Fermi level whereas the transition metals have intense d band close to the Fermi level. Unusual properties of these alloys are derived from the mixing of the itinerant s band of noble metal and localised d band of transition metal. Most striking phenomenon of such alloys is the formation of virtual bound states of transition metals d states. Unexpected Core Disorder Broadening (CDB) was observed by Medicherla and Drude [64] in PdAg (100) ordered surface alloys. Ordered surface alloys are expected to exhibit sharper core level photoelectron lines compared to that of disordered bulk alloys. We believe that, this anomalous result has some fundamental origin related to strain induced in the alloy during formation.

In this thesis, CLS and CDB of two disordered alloys namely Cu\(_{1-x}\)Ni\(_x\) \((x = 0.1, 0.3, 0.5, 0.7, 0.9)\) and Ag\(_{1-x}\)Pd\(_x\) \((x = 0.02, 0.05, 0.1, 0.15, 0.25)\) which are mixtures of a noble metal and a transition metal. Both these alloys are expected to exhibit virtual bound states. Main objective of the thesis is to study the effect of disorder core levels, Auger transitions and valence bands of the alloys. High resolution XPS and UPS have been employed for the purpose. We have also investigated the interfacial alloying of Cu/Ni bilayer on Si(100) surface using XPS, AFM and SQUID techniques. The composition dependence of observed CDBs have been compared with NRA-CEFM model calculations.

### 1.4 Overview of the thesis

In this thesis, we have investigated Cu\(_{1-x}\)Ni\(_x\) \((x = 0.1, 0.3, 0.5, 0.7, 0.9)\) and Ag\(_{1-x}\)Pd\(_x\) \((x = 0.02, 0.05, 0.1, 0.15, 0.25)\) disordered alloys and also a Cu/Ni bilayer on Si(100) surface using Photoelectron Spectroscopy, AFM and SQUID measurements. Core levels, valence bands and Auger transitions have been observed and analysed their composition dependance for bulk alloys. For bilayer, modification of surface and interface morphology by argon ion beam sputtering has been studied. Surface and
interface core levels of Cu and Ni also we investigated. Thesis has been divided into seven chapters as described briefly below;

**Chapter 1** describes alloys, photoelectron spectroscopy and its characteristic and the formulation of the thesis problem.

**Chapter 2** describes the technical aspects of various methods used for sample preparation and characterisation. A brief account of experimental methods like X-ray Diffraction Technique (XRD), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and Superconducting Quantum Interference Devices (SQUID-VSM) measurements has been provided along with arc melting and vacuum deposition methods of preparation.

**Chapter 3** deals with XPS and XAES measurements and data analysis of Cu$_{1-x}$Ni$_x$ alloys. It focuses on CLS and CDB in Cu 2p and Ni 2p core levels and also energy shift and energy broadening of LMM Auger spectra of Cu and Ni. Charge excess theoretical model has been used to explain CDB in Cu 2p.

**Chapter 4** This chapter gives an account of the composition dependence of CLS and CDB in Ag 3d and Pd 3d photoelectron spectra. It also discusses the virtual bound states of Pd.

**Chapter 5** presents the studies of Auger Electron Spectroscopy (AES) of bulk CuNi and AgPd disordered alloys. In both the alloys, energy shift and energy broadening of Auger spectra are observed which depend on composition. The M$_{4,5}$ VV Auger transition of Ag and Pd have been discussed.

**Chapter 6** presents the surface and interface morphology of Cu/Ni bilayer using AFM and the corresponding core levels using XPS. Argon ion beam is used for the modification of surface morphology.

**Chapter 7** gives the summary and main conclusion of the results obtained for different alloy systems studies in this thesis.