INTRODUCTION

Alloys have intrigued scientists since a long time because of their basic and technological interest [1.1-1.4]. They make an interesting study not only to physicists but also chemists and metallurgists [1.5,1.6]. Recently with the advent of several alloy systems showing interesting properties viz metallic glasses, high $T_c$ superconductors etc, the study of alloys have gained a new momentum. To understand the structure of complicated systems it is first necessary to study the simpler alloys.

Transition metals and their alloys are of particular interest because of their unfilled $d$-bands, high degree of $sp$-hybridization and complicated Fermi surfaces [1.7,1.8]. Because of these, they are more difficult to understand. The $d$ states of the transition metals have energies comparable to the valence $s$ states but because of their greater angular momentum they are more localised. So when two or more of them form an alloy they show some interesting properties.

It is, in principle, possible to predict the behaviour of metals and alloys from their ground state electronic structure, and electron momentum density is one of the useful observables for getting this information. There are several probes which are readily available to study the electron momentum densities of materials [1.9]. They are a) photons, b) electrons and c) positrons.

The electrons interact very strongly but they can be used only for gases or ultra thin samples.

Positrons [1.10,1.11] are gaining ground as an useful tool because of their good momentum resolution. But their main disadvantage is their charge and so they cannot probe too near the ion cores as they are repelled by them. Especially for the $3d$ transition elements and their alloys which have localised $d$ orbitals, the
positron overlooks them and hence much information is lost. Moreover the resultant spectrum will be as the positron sees it and has to be interpreted correctly. However, lot of work, especially the study of Fermi surfaces etc have been done by using positrons as probes.

On the other hand, photons are uncharged and are thus very penetrating. They can thus probe all the electrons equally well. The probes are generally x-rays or gamma-rays.

Compton profile [1 12] is a one dimensional projection of the electron momentum density. It can give reliable information about the electronic structure of solids because the shape of the Compton profile is sensitive to the state of the valence electrons of the atoms which combine to form the condensed phase of the material. This follows from the observation that the momentum space wave function is the Fourier transform of the position space wave function. Consequently, the outermost electrons which form bands are spread out in position space and are highly localised in momentum space giving sharply peaked contributions to the Compton profile. Conversely, the contribution from inner electrons close to the nucleus spreads out to high momenta. From an experimental point of view, the lack of coherence in Compton scattering experiments also makes the results rather insensitive to the degree of perfection of the sample. This is a boon in disguise when this technique is compared with various other methods such as positron annihilation which gives complementary information about the bonding in solids but are critically dependent on the perfection of crystal samples.

Till recently, only limited attention had been given to Compton scattering of disordered alloys because there had been no good theoretical calculation to support it. But recently, with the development of the KKR-CPA [1.13 - 1 16] method which
enables the electronic structure of alloys to be calculated with nearly same accuracy as that of metals, much advancement is made in the study of alloys. It is possible that the experimental results can now be compared with theoretical calculations.

It has been realised that the comparison between experiment and theory can be fruitfully carried out by comparing not only the profiles but also via the Fourier transformed profiles called the reciprocal form factors \([1 17 - 1 21]\). These give information of the crystal wavefunction in the position space. Since the core electrons are localised in position space, their contribution is confined to only a few Angstrom units and thus gets clearly separated out from valence electrons. Hence the effect of the valence electrons can be studied in a more unambiguous manner by looking at the autocorrelation function data.

In this thesis, we will be discussing the Compton profile results of some of the 3d transition metals and their alloys. Some of the alloy results are found to be quite interesting. In Chapter II we give a brief introduction to electron momentum density distribution underlying the importance of this study. Electron momentum distribution of some simple systems is given for having a clear physical insight to the problem. We also discuss the idea underlying the Compton scattering experiments. Starting with the energy momentum conservation rules, we proceed step by step to finally analyse a real solid. We also explain the impulse approximation under which the theory of Compton scattering provides a simple relation between the scattered intensity and the electron momentum distribution integrated over planes perpendicular to scattering vector. The autocorrelation function and its properties are also discussed as it forms an alternate way of interpreting the data.

Chapter III is devoted to the description of the experimental set-up and the discussion of the various corrections applied to the raw data to finally arrive at the
true profile

$T_{1x}N_{1-1-x}$ is an interesting alloy system, and it shows some strange mechanical properties at $x = 0.5$. It becomes a "shape memory" alloy at this concentration. Chapter IV is devoted to the discussion of this [122] and several other alloys. It is found that in the low momentum region there is a peaking of the $J(q,x)$ vs $x$ curve for the $T_{1x}N_{1-1-x}$ alloys at the composition $x = 0.5$. The observed peaking can be qualitatively explained as due to the result of charge rearrangement between 3d and 4s states of the individual metals of the alloy. This is consistent with the x-ray emission spectroscopy data. As a part of systematic study of nickel based alloys we also studied the $Cr_xNi_{1-x}$ alloys [123]. In this case also the profile is seen to have similar variation with composition showing the same peaking effect around $x = 0.5$

The other nickel based alloy which has been studied by us is $Fe_{0.51}Ni_{0.49}$ [124]. Unlike the $T_{1x}N_{1-1-x}$ and $Cr_xNi_{1-x}$ alloys which show peaking of the profile at equiatomic concentration, the Compton profile of this alloy shows very little solid state effects. The binding in this alloy seems to be similar to metallic binding in individual metals. Any charge transfer effect in this will be only between the 3d states of the individual metals in which case there will be no change in the profile because the 3d profiles of nickel and iron are very nearly the same. Charge transfer between 3d states was earlier predicted by soft x-ray appearance potential spectroscopy (SXAPS) studies.

In the present study we also measured Compton profiles of some chromium based alloys such as $Cr_{0.12}Co_{0.82}$ and $Cr_{0.19}Ti_{0.81}$ [125]. In these alloys also we find no alloying effects. This is consistent with the results of nickel based alloys mentioned above which also show very small or no alloying effect at low alloy concentration. Study of these alloys at other composition would have been very
useful to see the dependence of alloying effect on composition and we plan to take them up in our future studies

Out of the two copper based alloys studied, the $Cu_{0.975}Be_{0.025}$ alloy [1,26] is a dilute alloy of copper with beryllium and the $Cu_{0.63}Zn_{0.37}$ ($\alpha$-brass) [1,27] alloy is a more concentrated alloy of copper with Zinc. Fermi surface studies of these alloys have been made using positron annihilation technique but no Compton profile studies have been made so far. Positron annihilation studies on these alloys have been made to look into the Fermi surface changes of copper upon alloying. In $Cu_{70}Zn_{30}$ $\alpha$ - brass the positron data did not show the presence of any Fermi surface neck. This behaviour is not consistent with the rigid band predictions. However the x-ray K-absorption measurements by You and Azaroff agree with the rigid band model. The theoretical calculations based on SCF-KKR of Copper-Zine sp-metallic compound has shown that there are about 0.14 electrons transferred from Zinc, out of which 0.08 electrons go to copper and the remaining 0.06 electrons go to the interstitial positions. Band structure calculations for the $Cu_{0.7}Zn_{0.3}$ $\alpha$-brass have also predicted charge transfer from Zinc to copper. Our present study on $Cu_{0.63}Zn_{0.37}$ was aimed to look at the charge transfer effects and our result shows that any charge transfer from one metal to the other has to be small. Solid state effects are also found to be small for this alloy. In the case of $Cu_{0.975}Be_{0.025}$ we also find not much alloying effect except that there is some difference in the autocorrelation function at distances beyond 5 a.u. suggesting that dilute alloying, to some extent, affects only the periodic part of the electronic wavefunction. Our result also suggests that the theoretical Compton profile calculations on copper are not correct and this maybe because of the fact that the calculations have neglected the electron correlation effects.
Finally chapter V gives conclusion and final remarks on the future prospectus of electron momentum density studies in alloys.
References


