Chapter 1

Introduction

Introduction:

The basic properties of a solid are strongly related to the spatial charge distribution, which includes the static as well as dynamic aspects. Hence the knowledge of charge distribution is essential for understanding the minute details of the material. Thus it is interesting to study these aspects in detail. The study of the interaction of the atomic nucleus and the extranuclear fields give rise to many interesting phenomena. Hyperfine interactions takes place between the nucleus and extranuclear fields like that from the electronic shell, crystal lattices or from external applied magnetic fields. The non spherical charge distribution at a site creates Electric Field Gradient (EFG) in non cubic solids. This interacts with the electric Quadrupole moment of the probe nuclei in the material, which results in the splitting or a shift in the electronic and nuclear levels. In the Hyperfine interaction studies what is measured is a product of the nuclear and atomic quantities, which give information about nuclear moments, the spin structure, charge state of the probe nuclei and also the local environment around the probe. If nuclear quadrupole moment is known EFG can be evaluated. The determination of the nuclear magnetic dipole moments and quadrupole moments have contributed in the development of nuclear models, characterization of the materials, lattice dynamics etc.

Hyperfine Interaction techniques are used to study the ground state as well as the excited states. Conventional spectroscopic techniques like the NMR and NQR are used to find out the distribution of the electric charge surrounding a nuclear site. Non conventional techniques like the Mössbauer effect and Perturbed angular correlation technique are capable of probing the hyperfine interactions. Mössbauer technique is now widely used in elucidating the nature of chemical bonding in molecules and compounds (Material Science), in Nuclear Physics, Geology, Biology and fields like archeology, medicine etc. The details of the above techniques can be found in different books and review articles. [1-7]

The microscopic study of materials gives insight into many complex phenomena like electrical, magnetic, semiconducting and superconducting properties. In these methods the incident particle or the emergent radiation that comes out of the materials is studied which consists of the information regarding the materials.

The basic properties of the solids can be drastically altered by the addition of impurities to it. It is well known that controlled doping even at PPM levels can drastically modify electrical properties of semiconductors. This is also with the case with the magnetic materials.

The first experimental studies of the Electric Field Gradient in metals were reported in 1953 by knight [8]. After the pioneering work of Raghvan [9] large amount of experiments were performed to find out systematics [10, 11] of the EFG in metals. The experimental investigations of EFG revealed some systematic trends.

- A proportionality between electronic and ionic contribution of EFG, Viz. the so called the universal correlation.

$$V_{el} = -KV_{ZZ}{}^{latt} (1-\gamma_{\infty}) \quad [12]$$

- A correlation of the EFG in impurity host systems with the impurity valence. [13]
- A $T^{3/2}$ behaviour for the temperature variation of the EFG in metals [14].

$$V_Q(T) = V_Q(0) (1-BT^{-3/2})$$

The basic features of the original universal correlation proposed by Raghavan et. al. was reproduced theoretically in some pure systems [14-16]. But theoretical interpretation of the impurity system remains unsolved. Partially successful approaches of [17-18] Nishiyama et. al. for temperature dependence of several pure metals was achieved by using parameter free simple pseudopotential model and by taking lattice vibrations.

Magnetic materials are characterized chiefly by two quantities: [19-23]

- Macroscopic observables like the susceptibility, magnetic anisotropy, Curie temperature, critical behaviour near magnetic phase transition.
- Microscopic properties like magnetic long range and short range ordering, spin fluctuations, the role of conduction and localized electrons in the magnetic coupling producing the ordered arrangements etc.

Mössbauer study allows determination of the local fields in intermetallics, alloys, and compounds for the study of the static and the dynamic properties separately.

The hyperfine interaction is very sensitive to the local charge and spin arrangements. It is also sensitive to the electronic structure surrounding the atom under study [20]. From these one can measure

- ♦ The Electric hyperfine fields which arise due to the lattice, if a deviation in cubic symmetry exists in the alloy, compound, intermetallics etc.
- ♦ Magnetic hyperfine fields due to the unpaired spin of the s orbital and dipole contributions from the unfilled electronic shells in the transition elements.

A combined effect can also exist due to the combined effect of the above two. This will give rise to both the Electric and the magnetic hyperfine interactions. The combined effect of the magnetic and electric hyperfine interaction gives rise to complicated interactions in case of non cubic materials.

The 3d elements and the rare earths show a variety of magnetic phenomena when incorporated as dilute systems. When the concentration is not low they can be studied by Mossbauer technique. The other technique that can be used for dilute systems are the Time Differential Perturbed Angular correlation (TDPAC) etc. The magnetic properties in these systems can be due to individual transition metals or ions. Hence the study of stable and local moments is an area of importance in magnetism. When the impurity atoms are present in the system the electrons in the outer most shells form a part of conduction band and the impurity is left with partially filled d or f levels. The impurity can make hybridisation with its d or f electrons, with the host atoms or the conduction electrons and may result in magnetic moment to survive, which may not be stable. Fe shows a stable moment of ~1 μ_B with spin fluctuation temperature of θ~30 K in Ti but is non magnetic in Al. Also a very high value of spin fluctuation temperature ~0 K is observed in case of Fe in Au [43, 44]

Chapter one of the thesis provides a general introduction and brief review of earlier work done by other workers. The theoretical background of Mössbauer technique and general theory of Hyperfine interaction (HFI), superconductivity and local moment are discussed in Chapter two. The chapter Three consists of experimental methodology, instrumentation, Data reduction and analysis.

The EFG studies in semimetals are of special importance due to their interesting semi-metallic characteristics. Their properties are in between that of the metals and the insulators. The systematic trends of the EFG found in some metals are also found in some semimetals. The EFG data for the impurities in the metallic hosts are extensively known. EFG studies in semimetals and semiconductors are of interest as conduction electron contribution can be changed over a large range by a small variation in temperature. The sp metal probes in sp metal hosts show an approximate probe valence dependence of EFG. But 3d metal probes behave differently. In the FeSb dilute alloy system the reported value of Quadrupole splitting (QS) 1.29 ± 0.01 mm/sec at room temperature (24) is nearly the same as the QS of $FeSb_2$ compound which is 1.28 ± 0.01 mm/sec (25). To check this aspect of compound formation, samples with the general formula Fe_XSb_{1-X} were prepared. The Fe concentration was varied from X =0.0015 to 0.20 in Sb. It was seen from the present study that at concentrations more than a critical concentration there is an inherent urge of Fe-Sb to form $FeSb_2$ compound. The method of sample preparation also seems to play an important role in these types of study. We observed that some kind of magnetic ordering at low concentrations, which was hitherto not seen at these concentrations before.

The results of these studies and the EFG dependence on Fe concentration in Sb are discussed in chapter four.

Semiconducting alloys whose lattice is made in part of substitutional magnetic atoms are known as semimagnetic semiconductors. $Cd_{1-x}Mn_xTe$, $Hg_{1-x}Fe_xSe$, $Pb_{1-x}Gd_xTe$, $Ga_{1-x}Mn_xAs$ are some of the examples of such systems (26, 27, 28, 29). These materials possess some unique features like

- The existence of magnetic phenomena in a host with a simple crystallographic structure.
- The possibility of controlled doping of magnetic ion concentration, impurities etc.
- Typical transport and optical properties.

But these systems of type $(A_{1-x})^{II} M_x B^{IV}$ like $Cd_{1-x}Mn_xTe$, $Hg_{1-x}Fe_xSe$ etc. have both Cd and Te or Hg and Se as a part of the lattice and in which magnetic atoms like Mn or Fe are incorporated. In all the earlier studied diluted magnetic semiconductors, the concentration of B site chalcogenides was in equal proportion to the cation A. But we have not come across a study in which the concentration of these chalogenides Te or Se is altered. The present system differs in this respect. Here we have taken semimetal Sb as the host and incorporated Fe as an impurity and Se concentration was varied and attempted to study the effect of Se concentration on the FeSb dilute system.

The general formula of the system is $Fe_XSb_{1-X-Y}Se_Y$. For Fe concentration of 0.002 in Sb we have varied Se concentration (Y) and its effect was studied. The concentration dependence study of Fe in Sb has revealed that for Fe concentration greater than 0.002 compound formation of $FeSb_2$ takes place. To investigate the role of Se at higher concentration of Fe, the Fe concentration was also changed keeping the Se concentration constant. The details of the study are discussed in chapter five of the thesis.

Since the discovery of High T_C superconductivity (HTSC) it has become one of the most interesting and highly challenging field. It has also opened up an entirely new direction for the understanding of the superconductivity and other related phenomenon. Even after several years of the discovery of the superconducting materials and many attempts to explain the superconducting phenomenon, a satisfactory explanation of the effect is still eluding. These oxide superconductors also show all the basic properties of type I and type II conventional superconductors, like the Meissener effect, zero resistance, Josephson effect etc. In type I superconductors the coherent length is much large compared to the penetration depth while in type II superconductors the magnetic field penetrates farther than the coherent length (30, 31).

High T_C cuprate superconductors are extreme type II superconductors e.g. $YBa_2Cu_3O_{7-\delta}$ (123 or YBCO). It is also one of the most studied one. This is a complex oxide with two dimensional CuO_2 plane. Their two dimensionality makes its behaviour highly anisotropic. Substitutions of the metallic dopants in these HTSC have played an important role in understanding these systems. They have also thrown light on many interesting and intricate facts. The Partial substitutions of impurities like Fe, Co, Ni, Zn, V, Cr etc. at the Cu site have given us insight to many interesting and important phenomena of both normal and superconducting phases (30 - 35). These substitutions at Cu(I) and Cu(II) site have their own importance due to their close ionic size and similar orbitals to that of Cu. Divalent Ni and Zn go to Cu(II) site where as trivalent Fe and Co go to Cu(I) site. Also for the other 3-d ions like Mn and Cr techniques like neutron diffraction and EXAFS measurements could not throw light on their site occupancy due to overlapping of different lines or poor data.

But present Mossbauer results showed that Cr and Mn goes predominantly to Cu(I) site. Also the effect of Ca^{2+} substitution at the rare earth Y^{3+} site have been extensively investigated to understand the relation between oxygen disorder, optimum charge carrier density and superconducting properties. The substitutional effects on the structural changes and electronic properties have been extensively studied (36 - 41). These studies have enhanced our understanding and role played by the charge, spin, site occupancy of the dopant elements. Also the depression of T_C in these HTSC with different dopants like Fe, Co, Zn, etc. don't seem to have a direct correlation with their magnetic character which causes the cooper pair breaking.

Unlike the orthorhombic YBCO system, $LaBaCaCuO_{7-\delta}$ (LBCCO) has tetragonal structure. This system is found to remain tetragonal for all values of oxygen (42) unlike the orthorhombic 123 whose structure changes with the oxygen content from orthorhombic for $\delta = 0$ to tetragonal for $\delta = 1$. Inspite of so many studies in this field the picture remains gloomy about the mechanism of the superconductivity in these compounds.

In the orthorhombic system $YBa_2Cu_3O_{7-\delta}$ in which substitutions have extensively been studied by various methods including Mössbauer spectroscopy, but very little is known about tetragonal LBCCO system. Also not many studies have been done regarding the structural changes and role of oxygen in both the systems. This compound has similar structure as tetragonal Re-123 system, with both O(1) and O(5) sites completely occupied and hence no structural changes are observed even after doping. The chapter six deals with details of this study. We have varied the Fe concentration from 1% to 8% and comparative study is made between YBCO and LBCCO systems.

Finally the results and discussion of the thesis work are presented in the summary chapter.

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