MÖSSBAUER STUDIES OF

SOME DILUTE ALLOYS AND SUPERCONDUCTING COMPOUNDS

Summary of the Thesis submitted to

The Maharaja Sayajirao University of Baroda

for the degree of

Doctor of Philosophy

in

Physics

By

Mitesh Sarkar

Department of physics
Faculty of science
The M. S. University of Baroda
Vadodara – 390 002

September, 2001

Summary

The aim of the present work was to study the Fe concentration dependence of Fe$\underline{Sb}$ dilute system, probe impurity interaction in Fe-Sb-Se systems and effect of multiple substitutions in YBCO systems. Electric quadrupole interaction and magnetic dipole interaction in these systems were studied. The Mossbauer spectroscopic technique was used for the purpose. Microscopic studies of materials have always been of immense interest, which provides us extremely important information about various phenomena, observed in materials. These studies give insight into many complex phenomena like electrical, magnetic, semiconducting as well as superconducting properties.

Hyperfine interaction techniques are widely used to gather information about material. The properties of solids particular of semiconductors and semimetals can be drastically changed by adding impurities in it. This is also true in case of magnetic materials.

The Electric Quadrupole interaction studies in semimetals are of special importance due to their semi metallic characteristics. Their properties are intermediate to insulators and true metals. The systematic trends found in metals are also found to be valid in some semimetals. Some semimetals like Sb showed

very different behaviour. Part of the present study is based on concentration dependence of Fe in Sb and impurity impurity interaction of Fe-Se in Sb matrix (host). Electric Quadrupole interaction is affected due to the conduction electrons.

Electric Quadrupole interaction studies in dilute alloys, particularly in semimetals and semiconductors are of interest as conduction electron contribution can be changed over a large range by the addition of small amount of impurities. It is interesting to study the 3d metal probes in the semimetal Sb. In the Fe<u>Sb</u> dilute alloy system the reported value of Quadrupole splitting (QS) is 1.29±0.01 mm/sec at room temperature which is nearly the same as QS of $FeSb_2$ compound 1.28±0.002 mm/sec.

As these two values of QS are overlapping within errors we tried to study the Electric Quadrupole interaction with the variation of Fe concentration in Fe<u>Sb</u> systems. To check whether there is any compound formation in Fe<u>Sb</u> system samples with general formula Fe_XSb_{1-X} were prepared where the Fe concentration was varied from X=0.0015 to 0.20. It was found that in the concentration range of $0.005 \leq X < 0.10$ there is an inherent urge for Fe and Sb to make $FeSb_2$ compound. For $X \geq 0.10$, FeSb compound phase starts to form along with $FeSb_2$ compound phase. At X=0.50 the formation of FeSb compound phase is complete. For X=0.0025 a magnetic interaction is observed along with formation of $FeSb_2$

compound. For X≤0.002 only a magnetic interaction is found. It is observed that the sample preparation technique also plays an important role. In order to find the origin of the observed magnetic interactions we did a neutron depolarisation study. Neutron depolarisation technique can rule out Fe clusters of dimension >100 Å. The neutron depolarization study showed that there are no clusters of Fe or other magnetic configuration >100 Å size. The Mossbauer spectra for the X ≤ 0.0025 showed Fe to be in a high charge state (~ +4 or more). Hence Sb behaves as an acceptor of electron and has a charge state of –3 or more. This result in a sharp mismatch of volume which can make Fe to behave like an isolated ion surrounded by large Sb ions. Details of this work is described in Chapter 4.

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. But these systems like $Cd_{1-x}Mn_xTe$, $Hg_{1-x}Fe_xSe$ etc. have both Cd and Se or Hg and Se as a part of the lattice and in which magnetic atoms like Mn or Fe are incorporated at the Cd or Hg sites. So far no study was found where the concentration (proportion) of the chalcogens. The present study deals with this aspect in detail. Here we have taken semimetal Sb as the host and incorporated Fe at a very low concentration and the proportion of Se is varied. This study also gives us at low concentration the impurity impurity interaction in the host Sb. This type of system has not been reported so far.

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 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 check the role of Se at higher concentration of Fe, the Fe concentration was also changed keeping the Se concentration constant.

It can be seen that for $0.005 \leq X < 0.10$ in Fe_XSb_{1-X} samples a quadrupole doublet is seen corresponding to $FeSb_2$ formation. But the introduction of Se (Y=0.004) in X=0.008 samples resulted in magnetic interaction along with a Quadrupole splitting. This indicates that Se inhibit the formation of $FeSb_2$ at higher Fe concentration. But further increase in Se was found to decrease the field. Also Se is found to bring an additional magnetic site which was not seen in the Fe_XSb_{1-X} samples. This field was attributed to the RKKY interaction of Fe-Fe via. Sb and Se. This work is presented in Chapter 5.

Chapter 6 deals with the study of Multiple substitutions in the 123 high T_c (HTSC) superconducting compound with the formula $(Y_{1-Z}Ca_Z)Ba_2(Cu_{1-X-Y}Fe_YM_X)_3O_{7-\delta}$ where M = Mn, Cr, Co, Ni and Zn. Substitutions of impurities in high Tc superconductors have played a major role in understanding these systems. Partial substitutions of impurities like Fe, Co, Ni and Zn at Cu-site in Y-123

(YBCO) has given many interesting features of these materials. All these impurities substituted at Cu-site have detrimental effect on T_c. From the present results it can be concluded that the percentage site occupancy of Fe at the Cu(I) and Cu(II) sites depends only on the availability of lattice oxygen and the site occupied by the 3-d ion. The hole doping due to presence of Ca^{2+} at Y^{3+} site seems to have no direct relation on the percentage site occupancy of Fe at any particular Cu site. The present study also indicates that Mn, Cr and Co preferentially occupy Cu(I) site where as Ni and Zn prefer Cu(II) site.

Unlike the orthorhombic system $YBa_2Cu_3O_{7-\delta}$ in which substitutions have extensively been studied by various methods including Mössbauer spectroscopy, very little is known about tetragonal LBCCO ($LaBaCaCu_3O_7$) system. Also less comparative study has been done regarding the structural changes and role of oxygen in both the systems. The general formula for the system is $LaBaCaCu_{3-X}Fe_XO_7$. The Fe concentration was varied from 1% to 8% and comparative study is made between YBCO and LBCCO systems. It is seen that in the case of LBCCO even when only 1% Fe was substituted at the Cu sites, about 35% of Fe goes to the Cu(II) site unlike in the case of multiple substituted YBCO inspite of the oxygen content in these systems being quite high. Also when the concentration of Fe is increased, more and more Fe goes to Cu (II) site, which seems to be the reason for sharp reduction of T_c in these systems.

To conclude 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) is discussed in Chapter Two. The chapter Three consists of experimental methodology, instrumentation, data reduction and analysis. The chapter four of the thesis consists of Fe concentration dependence study of FeSb system. The chapter five contains details of the probe (Fe) impurity (Se) interaction in Sb matrix. The concluding chapter six deals with the multiple substitutions in YBCO. Also a part of the chapter consists of concentration dependence study of Fe in LBCCO system and its comparison with YBCO.