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I

CHAPTER

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MÖSSBAUER STUDIES IN FERRIC ASBENIUM SULPHATE DOPED WITH Cu²⁺/Ni²⁺

III.1 Introduction

III.2 Results of Mössbauer Spectra of Cu²⁺/Ni²⁺

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ollowing Mössbauer's discovery\textsuperscript{1,2} of recoilless gamma-ray emission and absorption, it became clear that this effect—commonly referred to as the "Mössbauer effect"—would be genuinely applicable to a very broad spectrum of physical and chemical investigations. Many of the chemical and solid state applications of the Mössbauer effect\textsuperscript{3-6} depend on the fact that the available gamma-ray line widths are small compared to the characteristic energy of interaction of nuclei with their surrounding electrons. Before Mössbauer's discovery, the possibility of being able to resolve the nuclear hyperfine structure by observing the gamma-ray between nuclear levels had been universally discounted, although some indirect measurement like $\gamma-\gamma$ correlation experiments and nuclear alignment experiments did give some marginal insight into the nuclear hyperfine structure. It is the influence of the chemical environment on the emission and absorption of $\gamma$-radiation that constitutes the basis of applications of the Mössbauer effect to chemical investigations.

Following this discovery, the possibilities for studying the influence of the crystal structure and of the electronic shells of atoms on nuclear transformations (in particular, on the energy of $\gamma$-quanta) has come into perspective. The phenomenon is characterized by an unusually high resolving ability. The Mössbauer effect manifests itself quite distinctly against a background of other nonresonance processes of absorption and
scattering of \( \gamma \) -quanta in solid bodies. The room tempera\-tural\-nuclide studies of Fe\(^{2+}\) ions in solids are not possible due to the shortening of electronic relaxation times by lattice defects. To get a direct information about the covalency and bonding of Fe\(^{2+}\) ions in solids at RT the Møssbauer Effect is the only tool available. A detail account of the relative merits and demerits of the Møssbauer Effect (ME) over the optical absorption, \( R \) and other conventional methods is given in chapter I (I.1).

Although a lot of theoretical and experimental work has been done on the study of quadrupole-interactions in solids by Møssbauer spectroscopy, there are areas which need further consideration. Present thesis is an attempt to exploit them such areas (i) to investigate the imperfections and quadrupole interactions in Co\(^{57}\) doped single crystals of KBr (cub\( \sigma \) symmetry) and, (ii) to study the crystal field and covalency effects on nuclear quadrupole interaction in a transition metal ion complex Fe (Br\(_5\)Cl\(_4\))\( \cdot \)H\(_2\)O (known as Tutton salt) diluted with Cu\(^{2+}\) ions and Ni\(^{2+}\) ions separately. The study of iron group elements doped in alkali halides have been the subject of considerable interest mostly after the work of Watkins\(^{12}\). In recent years, the impurities in alkali halide crystals have been found to have a profound influence on the relaxation process as in alkali halides in general and the interest has rapidly grown in such studies partly because of their importance in and related to the optical and electronic processes in solids and partly because of many practical applications of impurity doped alkali halides, e., in radiation detectors, dark trace screens etc, wi
doubly or triply charged ionized impurity is doped in an alkali halide crystal, the number of cation vacancies is enhanced in the crystal due to the mechanism of charge compensation. Several interesting observations of quadrupole interactions have been observed. From the observed Mossbauer spectrum of Ce$^{57}$ doped single crystals, the charge conversion of the impurity ions and the observed lattice symmetry around the impurity ion are discussed on the basis of proposed models.

Ferrous ammonium sulphate hexahydrate (FAS) is a very stable ionic compound and the high spin Fe$^{2+}$ ion exhibit very interesting results due to covalency and crystal field effects. Although, susceptibility$^{14,15}$ PMR$^{16}$ and optical studies$^{17}$ have been made on FAS, a basic understanding of $3d$ electron distribution at the Fe$^{2+}$ ion is missing. The present study of F$^{-7}$ diluted with Ce$^{2+}$ ion is undertaken with the hope that the information obtained from the results of quadrupole interaction would be of great help to develop a more realistic model to explain better all the experimental results. A very interesting variation of the quadrupole splitting with concentration of paramagnetic impurities like Ce$^{2+}$ and Ni$^{2+}$ is observed and an attempt to explain the results both qualitatively and quantitatively is made.

For Mossbauer effect measurements a simple cam drive in a mechanical drive operable in a constant velocity mode is used. The Mossbauer source is mounted on this drive and the sodium iodide crystal is used to detect the γ-rays transmitted through...
the absorber. The observed spectra are repeated on another spectrometer which consists of an electromagnetic type drive 

Theoretical models are proposed to explain the variation 
of quadrupole splitting. As a consequence, an analysis is 
reported to estimate the covalent bond energies between a few 3d metal ions. The covalency effects on ferrous tauton salts 
and the correlation with optical measurements is clearly 
brought out.

Though the summary, evaluation and recommendations based 
on this work are given at the end of this thesis, the important 
conclusions of this work are as follows. When iron is doped in 
KBr single crystal, ferric iron goes to an interstitial site, a 
conclusion which does not immediately follow from other studies. 
When an divalent impurity like Ca$^{2+}$ ion is doped in FAS, the 
Fe$^{2+}$ ion takes up two nonequivalent sites as far as KFG is 
concerned. The quadrupole splitting shows an interesting 
variation with the concentration of the doped Ca$^{2+}$ ions. This 
variation is used to calculate the heteronuclear bond energy 
between transition metal ions, a parameter of immense importance 
in the understanding of chemical structure.