

MOSSBAUER STUDIES IN CUBIC AND MONOCLINIC CRYSTALS

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PREFACE

Following Mossbauer's discovery^{1,2} of recoilless gamma-ray emission and absorption, it became clear that this effect - commonly referred to as the "Mossbauer effect" - would be germane to a very broad spectrum of physical and chemical investigations. Many of the chemical and solid state applications of the Mossbauer effect³⁻⁶ 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 Mossbauer'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 γ γ 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 γ -radiation that constitutes the basis of applications of the Mossbauer 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 γ -quanta) has come into perspective. The phenomenon is characterized by an unusually high resolving ability. The Mossbauer effect manifests itself quite distinctly against a background of other nonresonance processes of absorption and

scattering of γ -quanta in solid bodies. The room temperature EPR studies of Fe^{2+} ion 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 Mossbauer Effect is the only tool available. A detail account of the relative merits and demerits of the Mossbauer Effect (ME) over the optical absorption, EPR and other conventional methods is given in chapter I (I.3).

Although a lot of theoretical and experimental work has been done on the study of quadrupole-interactions in solids by Mossbauer spectroscopy, there are areas which need further consideration. Present thesis is an attempt to exploit two such areas (i) to investigate the imperfections and quadrupole interactions in Co^{57} diffused single crystals of KBr (cubic symmetry) and, (ii) to study the crystal field and covalency effects on nuclear quadrupole interaction in a transition metal ion complex $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (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 Watkins¹². In recent years, the impurities in alkali halide crystals have been found to have a profound influence on the coloration processes in alkali halides in general and the interest has rapidly grown in such studies partly because of their importance in understanding the optical and electronic processes in solids and partly because of many practical applications of impurity doped alkali halides, e.g., in radiation dosimeters, dark trace screens etc. when a

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 Co^{57} doped KBr single crystals, the charge conversion of the impurity ions and the change in the 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 exhibits very interesting results due to covalency and crystal field effects¹³. Although, susceptibility^{14,15} PMR¹⁶ and optical studies¹⁷ have been made on FAS, a basic understanding of 3d electron distribution at the Fe^{2+} ion is missing. The present study of FAS diluted with Cu^{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 Cu^{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 driven mechanical drive operatable 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 operatable in a constant acceleration mode and used in conjunction with a multichannel analyser.

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 tutton 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 Cu^{2+} ion is doped in FAS, the Fe^{2+} ion takes up two nonequivalent sites as far as EFG is concerned. The quadrupole splitting shows an interesting variation with the concentration of the doped Cu^{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.

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