MOSSBAUER STUDIES AND MAGNETIC INTERACTIONS IN NON-METALLIC CRYSTALS

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PREFACE

The study of imperfections and magnetic interactions in solids have been the subject of extensive studies during the past few decades[1,2] and these studies constitute a major part of the total research efforts in the field of solid state physics. The discovery of nuclear resonance absorption of recoilless gamma-rays, in 1958 by R.L. Mossbauer[3,4], has provided a new ingenious nuclear tool to investigate the above properties in the solids. In the past decade Mossbauer's discovery has been exploited to study imperfections and magnetic interactions in non-metallic crystals. Present thesis is a further attempt to (i) exploit this phenomenon to investigate the effect of coloration on impurity centers in non-metallic crystals and (ii) investigate magnetically induced quadrupole and quadrupole-like effects. For this purpose the results of (i) the experimental investigations on Co^{57} diffused uncolored and colored single crystals of NaCl, KCl, KBr and KI using Mossbauer technique and (ii) the theoretical analysis of magnetically induced electric-field-gradient in Fe^{2+} ion in a high-spin axially distorted crystal-field are reported in this thesis. The detailed outline of the problems dealt here is as follows.

The perfect alkali halide crystals are transparent in the visible and the near visible region of the electromagnetic spectrum[2]. This transparency persists even at elevated temperatures and also in the presence of the lattice vacancies[1,2]. However, these crystals can be colored by adding stoichiometric excess of their metal constituents or by exposure to the ionizing radiations. The transparency of such crystals no longer persists after this coloration[2]. In recent years, the impurities in the alkali halide crystals have been found to have a profound influence on the coloration processes in alkali halides[2,5-10] and the interest has rapidly grown in such studies partly because of their importance in understanding the optical and the electronic processes in solids and partly because of many practical applications of impurity doped alkali halides such as in radiation dosimeters, dark trace screens etc. Several interesting after-coloration effects in impurity doped alkali halides have been observed. The charge conversion of the impurity ions and the change in the lattice symmetry around the impurity ion are some of the effects observed in recent years. These effects have been mainly studied using ionic conductivity, optical absorption and electron paramagnetic resonance (EPR) techniques.

The ionic-conductivity measurements have a disadvantage that one relies on the slight curvature of the conductivity isotherms for quantitative information[11]. After the classic work of Watkins[12], electron paramagnetic resonance has become a powerful tool for studying the after-coloration effects on the impurity ion in non-metallic crystals. Electron nuclear double resonance (ENDOR) is an another powerful method which has emerged in the recent years and provides information with high degree of precision. However, EPR and ENDOR techniques help in the analysis of paramagnetic impurities alone. Mossbauer spectroscopy has emerged in the recent years as a new ingenious nuclear tool for studying impurities in non-metallic crystals. Further, unlike the EPR technique, the Mossbauer effect is observed even in non-paramagnetic impurity centers.

No work on coloration effects on impurity ions using Mossbauer technique has appeared so far in spite of the vast potentials of such studies (as discussed in some detail in Chapter III of this thesis). In view of this, the Mossbauer study of uncolored and colored crystals in Co^{57} doped alkali halides was undertaken. For this purpose a simple cam driven mechanical Mossbauer source drive, operatable in a constant velocity mode, was fabricated. The Mossbauer spectrometer being (consisting of source drive, absorber and gamma-ray detecting unit) a delicate, precise and sensitive system, needs a very careful fabrication and operation. Using this Mossbauer set up (which is described in detail in Chapter II) the results obtained for the proposed study are given in Chapter III. The choice of Co^{57} as Mossbauer source in the present work was based on the fact that it has a good probability of exhibiting the nuclear resonance effect even at temperatures much higher than room temperature and that it has long half-life (273 days).

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. The mean-square amplitude of the vibrations of the impurity centers, their charge state and the degree of ionicity as well as the microscopic symmetry of the impurity ions have been found to be influenced in most of the samples studied. Another interesting observation was the line broadening of the Mossbauer lines following additive coloration. The optical bleaching of the colored Co^{57} diffused crystals was found to have no effect on the Mossbauer lines.

In spite of various limitations of the Mossbauer technique particularly an appreciable line broadening in non-metallic solids, the results of the present work clearly indicate that Mossbauer spectroscopy can be employed to obtain new informations about the after coloration effects on the impurity centers in non-metallic crystals.

In Chapter IV of the present thesis is discussed a different aspect of the Mossbauer effect which was theoretically investigated. As a result of the Mossbauer studies in many cubic and noncubic compounds and the study of imperfections in Co^{57} doped ionic non-metallic crystals it had been concluded that there could not exist any quadrupole splitting of the Mossbauer lines in case of cubic symmetry around the iron ions[13,14]. This fact is of fundamental importance and it enables one to apply Mossbauer spectroscopy for the structural analysis. However, very recently several investigations have shown a nonzero quadrupole splitting (and thus a nonzero electric-field-gradient, EFG) in a cubic symmetric crystal-field[15-20]. In several cases it has been attributed to the presence of a static Jahn-Teller distortion[20] and to the strain induced effects[19]. In the magnetically ordered materials an important feature observed[15-18] was the appearance of the EFG below the magnetic transition temperature. Theoretical investigations have been reported recently using the crystal field approach for the Fe^{2+} high-spin ion in tetrahedral and octahedral crystal-fields[21,22]. For a magnetically ordered crystal having a noncubic crystal-field there can exist two different origins of EFG - the usual direct quadrupole interaction and the magnetically-induced quadrupole interaction. In view of the basic importance of the quadrupole splitting parameter in the structural analysis of the material, a detailed study of the magnetically-induced EFG at the nucleus of a high-spin Fe^{2+} ion in the distorted cubic crystal-field was undertaken and these results form the text of Chapter IV of this thesis.

Several interesting results, such as enhancement of the magnetically-induced part of the EFG with increasing crystal-field distortion and the higher temperature dependence of the magnetically-induced effects are deduced.

There may be an additional origin of an apparent EFG due to second-order effect of the nuclear magnetic hyperfine interactions. Clauser and Mossbauer[23] have considered these effects for rare-earth ions. No efforts have so far been made to consider such an effect for the Fe^{2+} ions. In Chapter IV such an effect for Fe^{2+} ion is also considered.

The work reported in the thesis has resulted in the following research publications:

1. Magnetically Induced Nuclear Quadrupole Interaction in Cubic Fe^{2+}, Pseduo Quadrupole Interaction, J. Phys. Chem. Solids 31, 872 (1970).

2. Application of Mossbauer Spectroscopy to Study the Defect Centers in Non-metallic Crystals, Proc. Nucl. Phys. and Solid State Phys. Symposium, Madurai, Dec. (1970) Abstract only.

3. Magnetically Induced Electric Field Gradient at the Nucleus of High-spin Fe^{2+} Ion in Distorted Cubic Crystal Field, Phys. Rev. B3, 1649 (1971).

4. Mossbauer Studies in Uncolored and Colored Co^{57} Diffused Single Crystals of NaCl and KCl, Communicated.

5. Mossbauer Studies in Co^{57} Diffused Single Crystals of KBr and KI by Additive Coloration, Communicated.

The earlier work reported (1) on recoilless fraction and thermal shift for I^{129} Mossbauer transition in CsI in Phys. Lett. 25A, 503 (1967) and (2) on the vibrational spectrum and the specific heat of TlCl in J. Phys. Soc. Japan 26, 621 (1969) has not been included in this thesis.

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