CHAPTER-I

GENERAL INTRODUCTION, SCOPE OF THE PRESENT WORK AND CONCLUSION

1.1. General :

Many physical properties of an ionic solid can be satisfactorily explained. On the assumption of periodic potential produced by ions inside the crystal. In an actual crystal various kinds of defects , accidental or intentional, are likely to be present, and these defects cause perturbation in the periodic potential giving rise to localised energy states which sometimes may drastically modify physical properties of crystals. For example, incorporation of Pb or Sn⁺⁺ in KCl produces new absorption bands in u.v., and enhances electrical conductivity in the extrinsic range. Similarly, Calcium fluoride crystals doped with Dy +++ or Pr +++ give rise to very strong luminescence bands both in the u.v. and visible region. Therefore, it is a common practice to produce defect impurity centres in an otherwise perfect crystal and to study some important physical properties which in turn yield more information which would not have been forthcoming from a defect-free crystal.

1.2. The Rare-Earths :

The **rare-earth** atoms generally fall into two series,

the lanthanides and the actinides, both are characterized by the presence of an unfilled inner shell of electrons, the 4f and 5f shells respectively. The electrons contained in these shells are shielded by outer electrons from any strong interaction with their surroundings, and it is the optical and magnetic properties of these f electrons that are of interest. In the lanthanide series, the rareearths are chiefly trivalent (Cerium, and to a lesser extent, praseodymium and terbium may also be tetravalent ; samarium, europium, and ytterbiun are often divalent) and it is principally the properties of the trivalent ions which are important rather than those of the neutral atoms. All trivalent ions have the Xenon like rare gas shell of 54 electrons in common and contain, in addition, N number of 4f electrons, with N ranging from zero (La^{3+}) to $14(Lu^{3+})$ with the two extremes considered by many not strictly belonging to the rare-earth group.

1.3. Calcuium Fluoride :

Calcium Fluoride is an ionic crystalline material and is a convenient host for studying rare-earth ions in solids. Its lattice can be visualized as a simple cubic array of F ions with every other body center occupied by a Ca²⁺ ion. It has high transmission from 1250 A.U. to 9 microns,

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adequate hardness for cutting and polishing, and is insoluble in water. The lattice constant is 5.45 A.U. (1,2).

1.4. Colour Centres in Calcium Fluoride :

The majority of the defects in CaF_2 Crystals are found to be of the anti-Frenkel type involving equal concentrations of negative ion interstitials and vacancies. Yttrium is a very common impurity which is generally present in CaF_2 crystals. If proper precautions are not taken during growth of the crystal, it may also contain anionic impurity like Oxygen. These samples usually have the "four band" colour centre spectrum first seen by Smakula³. It was later shown that the addition of yttrium impurities could enhance the spectrum^{4,5} and that the colour centre has the symmetry of an F center next to a yttrium substitutional impurity⁶. A positive identification of F centre was made by Arends⁷ and M centre by Cavenett et al⁸.

1.5. <u>Charge Compensation and Reduction of Trivalent Rare-</u> Earth Ions by Ionizing Radiation in CaF₂

Trivalent rare-earth ions can be introduced into calcium fluoride lattice by adding appropriate rare-earth trifluoride to the CaF_2 charge before placing it in the crystal growing furnance. Most of the rare-earth ions

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substitutionally occupy Ca lattice sites, but they are more stable in the trivalent state. This additional positive charge requires compensation. Several different methods of compensation have been identified by optical and magnetic resonance experiments. The type and symmetry of compensation is strongly dependent on the starting materials used to grow the crystal, the method of growing, and thermal treatments given to the crystal. In Oxygen-free crystal, the extra positive charge of a RE^{3+} ion replacing a Ca^{2+} ion is usually compensated by an interstitial fluoride ion. Depending on the positions of these interstitial fluoride ions various symmetries around the impurity ion may result. If the compensating interstitial fluoride ion is located far away from the RE^{3+} ion, the symmetry of the local environment is cubic⁹ On the other hand, if the F interstitial ion occupies the centre of an adjacent cube next to the cube in which the RE^{3+} has replaced the Ca^{2+} ion, the symmetry becomes tetragonal. The F interstitial ion can also occupy the centre of the unfilled cube next to the cube containing the RE³⁺ ion along one of its diagonals ; this must ensure trigonal symmetry of the environment for the impurity ion. Other ways of charge compensation are also possible; for example, the replacement of one of the Ca^{2+} ions by a single charged cation (such as Na⁺), when two triply charged ions replace three Ca^{2+} ions. In these cases the symmetry is even lower.

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