

CHAPTER 1

INTRODUCTION

The last two decades have witnessed a remarkable growth in the study of luminescence which has elucidated much broader areas of the Solid State Physics. Hence the methods and concepts of the luminescence processes in solid phosphors occupy a key position in the study of Solid State Physics. The techniques of the investigation used in the various branches of Solid State Physics have facilitated precise analysis and rational interpretations of the luminescent phenomena. The striking progress made in the field of semiconductors has aided the preparation of pure materials, as well as those containing controlled amount of specific impurities. All these, and many other factors have been responsible in the consolidation of luminescence as a special aspect of Solid State Physics.

Crystalline luminescent solids are usually called phosphors. Nevertheless, since for most of the practical applications finely divided powdered materials are either desirable or acceptable, much work has been done on powdered inorganic phosphors¹. The defect pattern, which governs the luminescent mechanism, can be pictured with comparative ease, in a single crystal on the basis of the well-established theories and concepts of Solid State Physics. The analysis adopted for single crystal phosphors

can, with slight modifications, be applied to the powdery samples, as the powdered specimens are the integrated bulks of microcrystals. Much of the work reported in this thesis is done with powdery phosphors and wherever necessary, comparisons have been obtained using single crystals grown from the melt.

The present work is mainly concerned with the thallium - activated potassium chloride system in which both the absorption and the emission of energy are suggested to occur in the same localized centre. The other two categories of luminescent systems are as follows:¹

- (i) The system in which absorption occurs in one centre and luminescence is emitted by another centre, the energy transfer taking place without accompanying movement of charge carriers. The sensitized luminescence of alkaline earth sulphides, and manganese - activated phosphors fall in this group.
- (ii) The system in which the transport of energy by charge carriers is the dominant feature. Such is the case of sulphide (ZnS) phosphors. Charge transfer mechanism also explains photoconductivity and electroluminescence.

In spite of the fact that the alkali halides activated with thallium ions form comparatively simpler system, the optical processes in them have been eluding a satisfactory solution. The specific model for KCl:Tl luminescence, proposed by Seitz², and reinforced by the quasi - theoretical treatment of Williams et al^{3 to 7} and of Knox and Dexter⁸, has failed to vindicate itself in the light of the accumulated experimental data. While the isolated substitutional Tl^+ ion model proposed by Seitz and Williams could successfully predict the positions of the absorption and emission bands in KCl:Tl system, the assumptions about the trapping sites for electrons did not tally with the results obtained from phosphorescence and thermoluminescence measurements. Further work by Joshi⁹ and Ewles and Joshi¹⁰ led them to suggest that the trapping sites responsible for the luminescence in KCl:Tl, were the characteristics of the crystalline defects other than the impurity ions.

Imperfections in ionic crystals are largely influenced by the conditions that prevailed during their growth, the impurities present in them, and the physical treatments to which the crystals are subjected.

Consequently, defects are present in the crystal in various configurations, leading to trapping sites of different nature and characteristics. The rapid progress in the understanding of the colour centres during the recent years has enabled us to offer qualitative analysis and hence to speculate on the nature of the electron and hole trapping sites in potassium chloride in particular, and generally in alkali halides.