CHAPTER 1

INTRODUCTION

The investigations of the properties resulting from the incorporation of foreign ions into a crystal lattice have proved to be of considerable importance in the study of solid state physics. It has been generally observed that the addition of impurities to the crystal has a marked influence on the fundamental physical properties of the crystal. Some of the striking effects brought about by the introduction of impurities are those of luminescence and related optical and electrical phenomena.

The rapid progress made in the field of luminescence of solids has helped to bring about a deeper understanding and coordination of the various branches of solid state physics and hence the methods and concepts of the luminescence processes in solid phosphors occupy a key position in the study of solid state physics. The major concepts in the field of luminescence stem from the researches on the alkali halide phosphors and these materials are still the predominant subjects for study in the present-day luminescence research. The alkali halides are in many ways ideal solids for theoretical and experimental study. Their lattices are cubic and many of their properties are profoundly affected by strong coulomb interactions which result from the highly ionic nature of these solids. Their large binding energies ($\sim$200 k cal/mole) result in high melting points ($\sim$1000°k) which offers a vast range of temperatures over which phenomena may be studied. The large electronic band gaps ($\sim$8 ev) of these solids result in a wide range of optical transparency and thus a very broad spectral region is available for the study of the effects of impurities, vacancies and other crystalline defects.

A small amount of thallium introduced into an alkali halide produces a luminescent material of considerable fundamental interest. Such a phosphor exhibits two strong absorption bands on the long wavelength side of the fundamental absorption edge. To explain this phenomenon, Seitz[1] proposed a model in which activator ions enter the lattice substitutionally at cation sites. The Seitz model is better suited to detailed theoretical study and has been the basis for the only quantitative computations yet attempted in luminescent system[2,3]. Later experimental results however revealed that the apparent simplicity of the thallium-doped alkali halide system was an illusion and that a more complex problem must be dealt with before a complete solution is obtained. Typical are the facts that both the A and C bands (of Seitz' terminology) are quite asymmetric at room temperature but sharpen into essentially symmetric bands at low temperatures[4]; that an additional emission band has been found in the A absorption band region[5] and that excitation of the two emission bands occurs in two separate portions of the A band rather than in a single one[6-8]. Excitation and high temperature absorption study of KCl:Tl led Patterson[9] to conclude that in KCl:Tl there are at least three bands in A region and two each in the B and C regions. To account for these and some other results, some authors[4,10,11] suggested that more than one type of centre is involved while others adopted the configuration coordinate curves for the single centre model to include some of the new information.

Most of the earlier investigators studied the optical properties of alkali halide crystals containing thallium mainly in low concentrations (10^{-3} mole per cent or less). Yuster and Delbecq[12] studied the absorption spectra of KI crystals containing thallium in rather high concentrations. At high concentrations, they found new absorption bands whose maximum absorption coefficients varied as the square of the thallium concentration. Similar results were also reported in the case of other alkali halides. It was therefore concluded that the new bands arise when two thallous ions occupy the neighbouring sites. Study of the excitation spectra by Ewles and Joshi[11] of KCl:Tl specimen differing in thallium concentration (0.07 to 5 mole per cent Tl) revealed some of the excitation bands in heavily-doped KCl:Tl crystals which were previously observed in the absorption spectra of water solutions of KCl:Tl. It has been suggested that these absorptions in solutions are due to charged complex ions of the type $(TlCl_n)^-$. It was therefore suggested that some of the new absorption bands observed in heavily-doped KCl:Tl crystals might be due to charged complex ions.

The present work was undertaken for the purpose of obtaining more information about the absorption of heavily-doped KCl:Tl crystals. Comparatively little is known about the absorption of KCl crystals containing very high thallium concentration ($\backsim 10^{-1}$ mole per cent and above). In fact, a study of this sort seemed necessary in order to be able to evaluate the extent to which earlier proposed models describe this system. The investigation includes measurement of absorption spectra before and after ultraviolet irradiation of the specimen near liquid nitrogen temperature and their subsequent changes due to pulse annealing. The kinds of centres suggested to explain the absorption spectra are: (i) isolated substitutional Tl^+ions (ii) substitutional Tl^+ ions with OH^- ions on neighbouring anion sites (iii) two Tl^+ ions at neighbouring K^+ sites and (iv) charged complex ion centres of $(TlCl_n)^-$ type.

The facts regarding thermoluminescent behaviour of thallium-doped alkali halides, in which KCl:Tl has been studied in more detail, are also of interest. Thermoluminescence is a relatively complex process since it involves a trap, a luminescent centre, and the transfer (during heating) of an electron or hole from the trap to the luminescent centre. The basic facts which one wishes to know about a particular thermoluminescent process are the atomic nature of the trap and luminescent centre, and whether an electron or hole is transferred between them. In the case of KCl:Tl, Johnson and Williams[13] observed that on warming a KCl:Tl crystal, after ultraviolet irradiation at liquid nitrogen temperature, glow peaks appeared at 205° and 300°K. It was proposed that as a result of ultraviolet irradiation, thallous ions are excited to $^1P_1$ and $^3P_1$ bound states from which they then decay into the metastable $^3P_0$ and $^3P_2$ states. They further proposed that on warming the crystal, thallous ions in these metastable states are thermally raised to states from which radiative transitions to the ground state are possible.

From their thermoluminescence measurements Ewles and Joshi[11] reported the occurrence of the same two glow peaks in KCl activated with impurities other than thallium. These results led them to conclude that the trapping sites are not due to internal metastable states of the impurity ions but are due to crystalline imperfections other than the impurity ions. In the light of later work by Joshi et al[14,15] these imperfections were identified as ion vacancies. Since the coloration phenomenon in solids is intimately bound up with the presence of ion vacancies it was further suggested that the phosphorescence centres are closely related to various types of colour centres. Recently Joshi et al[16-18] interpreted the thermoluminescence emission in KCl:Tl as resulting from the thermal destruction of a certain species of colour centres and subsequent release of the electrons or holes which recombine radiatively with their counterpart at the emission centre. Based on these concepts, it has been suggested that a glow peak in KCl:Tl at 300°K results from the tunnelling between an F-centre electron and nearby Tl^{++} ion in which the electron and the hole recombine radiatively.

From their thermal glow curve study of γ-irradiated KCl:Tl crystals, Delbecq et al[19] put forward a different hypothesis for the occurrence of glow peaks in KCl:Tl at 205° and 300°K. The 205°K glow peak is suggested to be caused by diffusion of Cl_2^- and the subsequent electron-hole recombination involving nearby pairs of Cl_2^- and Tl^o atom. The high temperature glow peak at 300°K is proposed to result when electrons are thermally released from thallium atoms into the conduction band and recombination of these electrons and Tl^{++} ions take place.

The hypothesis presented by Delbecq et al for the occurrence of 300°K glow peak is different from the one proposed by Joshi et al. It was therefore felt that a detailed study of the thermoluminescence of KCl:Tl in the room temperature region would be worthwhile in gaining clearer understanding of the properties of 300°K glow peak. The results obtained from these studies and their significance are discussed.