CHAPTER 3

LUMINESCENCE OF POTASSIUM CHLORIDE PHOSPHORS

Alkali halide phosphors have evoked considerable interest of a fundamental nature for the past 30 years. The absorption spectra of all alkali halides exhibit striking similarity when they are activated with thallium. The three principal absorption bands were labelled by Seitz[2] as 'A', 'B', and 'C' bands. The spectral positions of these bands in KCl:Tl are 247, 206, and 195 mμ respectively, with the relative strength as $C > A > B$.

The principal emission band at 305 mμ and a weaker emission band at 475 mμ were then attributed to the 247 mμ and the 195 mμ absorption bands respectively.

The electronic configuration of the ground state of the Tl^+ ion in gas is $6S^2$ and the electronic state is $^1S_0$. The first excited state of the free ion has the configuration 6S6P and contains the electronic states $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$.

Seitz's model considers the luminescent centre to be a thallium ion replacing an alkali ion in its regular lattice position. The interaction between the emission centre and the crystal lattice was treated by means of the configuration co-ordinate model which utilized a single configuration co-ordinate to give the distance between the luminescent ion and its nearest neighbours in the surrounding lattice. Taking the cue from this model, Williams[3] made detailed calculations of the energies of the ^1S_o and $^3P_1$ states of the Tl^+ ion in KCl starting from the values available for free ion. A similar scheme was adopted later, by Johnson and Williams[5] for the $^1P_1$ state. Seitz - Williams theory associates the observed absorption bands for KCl:Tl with the following transitions:

195 mμ $^1S_o \longrightarrow {}^1P_1$

247 mμ $^1S_o \longrightarrow {}^3P_1$

206 mμ $^1S_o \longrightarrow {}^3P_2$ (very weak)

For the $^1S_o \longrightarrow {}^3P_1$ transition, because of the spin - orbit coupling, the selection rule $\Delta S = 0$ is not strong. The transition will be forbidden if the coupling is purely of Russel - Saunders type. The spin - orbit interaction is considered as a very weak perturbation[40]. In order to account for the observed long lasting phosphorescence of KCl:Tl, Johnson and Williams[5] attributed the electron trapping characteristics to ^3P_o and $^3P_2$ states, since the transitions

$$^1S_o \longrightarrow {}^3P_o$$

and $^1S_o \longrightarrow {}^3P_2$

are forbidden.

In the initial Williams' theory, the blue emission in the region 475 - 490 mμ was ascribed to $^1P_1 \longrightarrow {}^1S_0$ transition. Thus the long-wave emission band was associated with short-wave absorption band, with a large Stoke's shift. Later observations by Eby and Teegarden[41] and by Johnson and Williams[42] of a high energy emission at liquid nitrogen temperature in the region of 'A' band has simplified the position. Since the emission at 247 mμ overlaps the absorption band, the emission is strongly re-absorbed at room temperature. The present scheme is as follows:

247 mμ	absorption	$^1S_0 \longrightarrow {}^3P_1$
305 mμ	emission	$^3P_1 \longrightarrow {}^1S_0$
195 mμ	absorption	$^1S_0 \longrightarrow {}^1P_1$
247 mμ	emission	$^1P_1 \longrightarrow {}^1S_0$

The visible blue emission at 475 mμ is still not explained satisfactorily. Williams[43] believes that both this emission and the short wave length emission at 305 mμ , originate from isolated substitutional Tl^+ ion with different excited or vibrational state.

In spite of its many striking features, the Seitz - Williams theory has been robbed of its impeccability by the accumulation of data obtained from many workers. We shall review them in brief.

According to the assumption of Williams, the same excitation spectrum should be observed for the 305 and 475 $m\mu$ emissions. Investigation of room temperature excitation on KCl:Tl phosphors by Butler[44] has cast doubts over this point. Patterson and Klick[45] have proposed different thallium centres rather than one centre. Eppler and Drickamer[46] observed a shift in the 'A' absorption band towards shorter wavelength during the pressure - induced phase change. The results of the studies on pressure effects on the configuration co-ordinates of KCl:Tl[47] have also gone against the assumptions of Williams and Johnson. Objections to the calculations of Williams and his co-workers have been raised by Knox and Dexter[8]. From the excitation spectra of KCl:Tl, Ewles and Joshi[10] have shown that the transitions are the combined effects of the activator ion and of other crystalline defects in the host lattice.

On the basis of the band theory of solids, a phosphor exhibiting long-term phosphorescence should also show photoconductivity; but KCl:Tl system turns out to be an exception to this rule. Seitz[2] suggested the metastable energy levels within Tl^+ ions as trapping sites, to explain this anomaly. As stated earlier in this chapter, ^3P_o and $^3P_2$ states were identified as "electron traps" by Johnson and Williams. According to them, these two traps contribute to the two glow peaks appearing at 200°K and 300°K, in the thermoluminescence curve of KCl:Tl. Ewles and Joshi[10] reported the appearance of the same two glow peaks in potassium chloride activated with barium and strontium. The results were more poignant in that, even specpure potassium chloride, evaporated and compressed, exhibited the same two peaks.

The long-term phosphorescence decay of KCl:Tl revealed a wide distribution of trapping levels, instead of the two principal traps. From these observations, as well those given above, it was not difficult to infer that the traps responsible for the luminescence in KCl:Tl were independent of the impurity ion, and that they were characteristic of other crystalline defects in the host lattice[10].

Electron traps are responsible for the persistence of phosphorescence, and they decide the kinetics of recombination of electrons with holes, which yield the luminescent photons. The highly localised atomic centre where the recombination takes place is termed, in a broad sense, the "luminescent centre". Thermoluminescence and phosphorescence form the versatile combination of investigative techniques for the detailed study of trapping sites in luminescent materials.

Randall and Wilkins[48], who carried out the pioneer work on thermoluminescence, suggested that the glow peaks exhibited by phosphorescent materials were due to electrons released from a number of electron - excess centres. Many attempts have been made in the past few years to correlate the glow peaks in the alkali halides, with the colour centres[49 to 54]. However, the exact nature of the correlation between a glow peak and a species of colour centres suggested to be responsible for its occurrence, has not been clearly understood. According to Hill and Schwed[52] and Bonfiglioli et al[53], different peaks arise due to electron - deficient centres having different capture cross-sections for electrons, which are released to the conduction band thermally from a single electron - excess centre. Halperin and his school believe that the glow peaks are due to recombination of electrons and holes after the thermal release from their appropriate trapping levels, which are characterized by specific activation energies. The localized energy levels just below the conduction band serve as electron traps, and those just above the valence band serve as hole traps.

On the basis of the model of Hill and Schwed, and Bonfiglioli et al, every peak should give emission that is different from those of other peaks — and the authors claim to have observed this plurality of emission in the thermal glow curves of NaCl. According to them, the activation energies for all the peaks are the same.

Both these features have been contradicted by Halperin et al, who obtained different thermal activation energies for the glow peaks of NaCl and KCl, as well as a common emission band in the peaks[50,55].

Dutton and Maurer believe that thermoluminescence results from the recombination of holes released from V_1 centres with electrons from F centres[56]. Halperin et al[55] assume that at specific temperatures corresponding to the glow peaks, charge carriers of either sign depending upon the peak, are released thermally and the recombination yields emission of light. Based on an experiment performed by Stoddard[57] on sodium chloride, Braner and Israeli[58] recently studied the effects of illumination on the thermoluminescence of alkali halides. Crystals were x-irradiated at room temperature and then cooled in the dark to the temperature of liquid nitrogen, followed by illumination into F or V absorption bands of the crystal. When the crystal was warmed, glow peaks appeared in the region between liquid nitrogen temperature and room temperature. The peaks obtained after F band illumination were termed "electron peaks" and the missing glow peaks, obtained after the V band illumination were termed the "hole peaks". The authors infer from these studies that in sodium chloride, most of the low temperature peaks are electron peaks. Unfortunately, this interesting technique did not yield a complete picture for KCl, in regard to its hole peaks.

The luminescence of alkali halides largely depends upon their thermal history[9,10,55,59 to 65]. Halperin and his co-workers observed that while heat - treatment affected UV - excited luminescence, x-ray induced luminescence and thermoluminescence, the effect was more pronounced in thermoluminescence. They attributed this to an increase in the efficiency of supply of charge carriers for radiative transitions[55]. Halperin and Schlesinger[62] suggest that heat - treatment promotes the diffusion of vacancies into the crystal, which in turn enhances the thermoluminescence.

Many reports on the effects of mechanical strain on the alkali halide luminescence are also available[9,10,46,47,59,61,63 to 67]. Pressure effect experiments permit differentiation of phenomena resulting from asymmetries with respect to equilibrium position. Pressure sensitivity of phosphorescence allows the location of "cross-over points" in the configuration co-ordinate diagrams[47].

In recapitulation one can say that any successful model for ultraviolet - excited alkali halide luminescence should be able to explain the processes of trapping and liberation of charge carriers, without the accompaniment of photoconductivity. Simultaneously, it should account for the characteristics of luminescence emission which depend upon the impurity ions, present either due to deliberate incorporation, or due to insufficient purification. Many of the previous models,and those suggested very recently[68,69], failed to account completely for the above observations.

An attempt has been made in this thesis to study the genesis and characteristics of the various types of trapping sites, operative under optical excitation, and observed in potassium chloride. Nature of the emitting centres has been dealt upon. Probable identities of the models for trapping sites at different depths that are tentatively drawn, with the suggested models for different colour centres, are also indicated.