CHAPTER III

LUMINESCENCE OF THALLIUM DOPED ALKALI HALIDES

(A) Luminescence of Undoped Alkali Halides:

As stated earlier, at low temperature i.e. below the boiling point of liquid nitrogen (77°K); KCl, NaCl and KBr in the pure state luminesce with very high efficiency. Timusk[1] observed a weak luminescence in these systems at 300°K. At 12°K these compounds were also studied for their emission spectra after exposure to ultraviolet radiation.

Investigations of the nature of the centre responsible for the intrinsic luminescence of the alkali halides was carried out by performing two experiments at low temperature. First of all, Weeks and Teegarden[3] showed that exposure to ultraviolet light at 93°K produced F or F' bands in the alkali halides and their irradiation in these bands gave rise to emission identical with the intrinsic luminescence. Presumably an electron released from an F or F' centre reaches a trapped hole via conduction band and gets captured into an excited state about the hole from which radiative recombination occurs. Edgerton[30] suggested that the hole involved in this process might be self-trapped, rather than trapped at a defect.

Kabler[4] and Murray and Keller[5] studied the luminescence of the alkali halides stimulated by X-irradiation at low temperature. These workers demonstrated that the intrinsic luminescence can also be stimulated by irradiation in the F or F' bands formed by previous exposure to X-rays at low temperature, in analogy with the experiment of Weeks and Teegarden[3]. Further, in a series of experiments involving the use of polarised light, Kabler[4] and Murray and Keller[5] showed that the hole trap involved in the luminescent centre is the well-known self-trapped hole, or V_k centre. The symmetry of this centre has been described by Castner and Kanzig[31]. The optical properties of the V_k centre have been studied by Delbecq and Co-workers[32] and by Hersh[33]. The centre is caused by covalent bonding between two neighbouring negative ions, one of which has lost an electron.

Absorption spectra of the alkali halides except LiF and LiI have been measured at 10°K by Teegarden and Baldini[34]. An earlier set of measurements covering the same series of salts and including LiI

at 80°K was made by Eby et al.[35]. Fragmentary measurements at different temperatures have been carried out by Teegarden[36] and Fischer and Hilsch[37], who obtained data on LiI, and by Onaka[38] and Milgram and Givens[39], who measured the absorption of LiF in the soft X-ray region at room temperatures.

Excitation spectra for each of the emission bands observed in RbI at 80°K have been obtained by Edgerton[30]. The short wavelength emission band is most efficiently excited by energies higher than the peak of the first exciton band, while the low energy band is preferentially excited in the long-wavelength tail of the first exciton band. An excitation spectrum has been measured by Weeks and Teegarden[3] for the total luminescence of a KI crystal. This spectrum differs from that of RbI, in that all the radiation from the KI crystal was incident on the detector, whereas the radiation from the RbI was dispersed by a monochromator, to select one or the other of the emission bands. All the excitation spectra exhibit strong minima at the peak of the first exciton bands in these compounds. It is interesting to note that while minima occur also at

the positions of the higher energy absorption bands, they are not nearly as pronounced.

Measurements of the emission spectra of RbI and KI single crystals have been carried out at 12°K by Ramamurthi and Teegarden[2]. A typical spectrum of excitation at 205 nm in RbI was studied. Although bands analogous to those occuring at 80°K are observed at the lower temperature, others also appear, which are not resolved or are quenched.

(B) Luminescence of Thallium-Doped Alkali Halides

The ions Tl^+, In^+, Sn^{++} and Pb^{++} all have outer electronic configurations s^2. When one of these is substituted for an alkali ion, several new absorption bands arise. Of these impurities, Tl^+ ion has been by far the most widely studied. Thallium doped alkali halide phosphors have evoked considerable interest of a fundamental nature for the past 30 years. Extensive bibliography related to the work on thallium activated alkali halides is given by Curie[28]. The absorption spectra of all alkali halides, in general,

exhibit similarity when they are activated with thallium. The three principal absorption bands are labelled by Seitz[7] as A, B and C bands. The spectral positions of these bands in KCl:Tl are 247, 206 and 195 nm respectively, with the relative strength as C > A > B. The principal emission band at 305 nm and a weaker emission band at 475 nm were attributed to the 247 nm and the 195 nm absorption bands respectively.

Early experimental work on the thallium doped alkali halides, principally the work of Hilsch and Pohl[40-42] and co-workers at the university of Gottingen, was given a theoretical interpretation by Seitz[7]. His treatment established a model which has been used in the interpretation of experimental work on many different impurities in the alkali halides. This model emphasised the importance of free thallous ion states, modified only by a cubic crystalline field, in the electronic structure of the thallous ion centre, although the role of electron transfer states was considered qualitatively. The details of the Seitz' model and its modification by Williams are given below:

The information available about KCl:Tl phosphor when Seitz gave his model was that it has one absorption band peaking at 247 nm and two overlapping bands with peaks at 195 nm and 206 nm. There are two possible mechanisms which could be responsible for these absorption bands. (i) In pure alkali halide crystals it was shown by Hilsch and Pohl[40-42], Schneider and O'Bryan[43] that this absorption could be due to the transition of an electron from a halide ion to an adjacent alkali ion. The work required to shift an electron to a thallous ion from a neighbouring halide ion will be less because of the higher ionization potential of thallium than that of any alkali metal. Such transitions will therefore give absorption lines on the long wavelength side of the fundamental absorption of KCl. (ii) The second alternative is that the whole of the absorption is due to the thallous ion itself. Seitz favoured the second alternative. The reasons for such an assumption are as follows:

(1) There is a characteristic pattern of the three absorption peaks in the case of all the alkali halides activated with thallium. The positions of these peaks shift only slightly as the alkali or halogen ions are changed.

(2) No photoconductivity is excited in the KCl:Tl phosphor simultaneously with the phosphorescence. This indicates that the excited electron is not raised into a free conduction band but is retained within the sphere of attraction of the Tl^+ ion.

(3) The peaks show none of the doublet structure which Hilsch and Pohl[40-42] have associated with the doublet state of the halogen atom.

(4) There is very small temperature dependence of the peak positions of the absorption and emission bands.

From this data Seitz concluded that the luminescent centres were thallous ions replacing the alakli metal ions of the crystal lattice. When a thallous ion replaces an alkali metal ion in the crystal its energy level will be modified. Seitz attempted an evaluation of this modified energy level scheme on the following lines.

In the unexcited state the interaction of the thallous ion with the lattice consists of electrostatic attraction and homopolar repulsion (negative Van der Waals forces). In the first excited state the excited electron is shared

by the adjacent ions and the charge distribution is not the same as for the excited thallous ion in the free state. In this excited state the electrostatic attraction remains the same as in the normal state but the interaction between closed shell configuration of electrons is different. This causes the energy levels of the excited states to be depressed relative to those of free ion.

By such considerations Seitz arrived at a disposition of levels in KCl:Tl crystals. The configuration of the ground state of the Tl^+ ion is $6s^2$ and the state is $^1S_0$. That is, the spins of the two S electrons are anti-parallel. From the spectroscopic studies of free Tl^+ ion it is known that the lower excited states arise from the configuration 6s 6p and consist in order of increasing energy of $^3P_0^0$, $^3P_1^0$, $^3P_2^0$ and $^1P_1^0$ states. The two strong absorption bands 247 and 195 nm are identified by Seitz with the two most probable transitions $^1S_0 \longrightarrow {}^3P_1$ and $^1S_0 \longrightarrow {}^1P_1$ respectively. If the cubic symmetry of the crystal around thallous ion is perfect, then other transitions are forbidden, but a local lack of symmetry may cause one or more of them to be present in absorption.

Seitz assumes the absorption band 206 nm to be due to such transitions. The absorption spectra of KCl:Tl phosphor have thus been ascribed by Seitz to the transitions between the ground state and the four P states of Tl^+ ion which are supposed to be displaced by Madelung potential in such a way that the wavelength characteristic of the isolated Tl^+ ion appear in the spectrum of the crystal as bands with peaks at 195 and 247 nm. Electronic transitions $^1S_0 \longrightarrow {}^3P_1$, $^1S_0 \longrightarrow {}^3P_2$ and $^1S_0 \longrightarrow {}^1P_1$ are assumed to be giving rise to 247, 206 and 195 nm absorptions respectively.

Subsequently Williams[8] attempted to show that the significant luminescent properties of KCl:Tl phosphor can be derived quantitatively from theory. He calculated the energy of $^1S_0$ and $^3P_1$ states of the Tl^+ ion in KCl from first principles and the properties of the constituent ions. The terms considered were those arising from the Madelung, repulsive, Van der Waals, ion dipole and coulomb overlap forces. The energies of these two states were computed as functions of the distance between the thallium ion and its nearest neighbour chlorine ions so that quantitative configuration co-ordinate curves were obtained. From these curves it is possible to

compute the peak positions and the temperature dependence of the band widths of the 247 nm absorption and 305 nm emission bands corresponding to $^1S_0 \rightleftarrows {}^3P_1$ transitions. Further, it is indirectly concluded that from selection rules the second allowed transition $^1S_0 \rightleftarrows {}^1P_1$ accounts for the 195 nm absorption and the 475 nm emission.

It is also possible to compute the configurational co-ordinate curves for simple systems from absorption and emission data[44]. A similar scheme was followed by Johnson and Williams[16] who proposed a configuration co-ordinate curve for $^1P_1$ state using experimental data as a base. In addition, tentative co-ordinate curves for the $^3P_0$ and $^3P_2$ states have been proposed by them[45] to account for the observed trapping effect.

Knox[10] re-examined the role of electron transfer states in the electronic structure of Tl^+ ion centre in KCl:Tl system on the basis of previous experimental work. He concluded that the importance of such states may be greater than previously thought, especially in a quantitative explanation of oscillator strengths and the spin-orbit interaction responsible for the separation between the A and C bands. The appearance of additional

absorption bands at higher energy than the C band can also be attributed to electron transfer states, according to Knox. Furthermore, recent experimental work has revealed structure in the absorption bands of the thallous centre and analogous bands of isoelectronic impurities, such as Sn^{++} ion, which indicate that the centre due to these impurities may not be as symmetric as previously thought. This idea is borne out by the discovery that the luminescence of many of these centres can be polarized. In what follows, the experimental work on the absorption, emission, phosphorescence and thermoluminescence of thallium-doped alkali halides is discussed.

(C) Thallium Absorption

As mentioned above according to Seitz[7], the absorption band in KCl:Tl at 247 nm corresponds to the transition $^1S_0 \longrightarrow {}^3P_1$, and the strong band at highest energy (195 nm) corresponds to the transition $^1S_0 \longrightarrow {}^1P_1$. The small band lying between them at 206 nm was attributed to the transition $^1S_0 \longrightarrow {}^3P_2$, partially allowed because of vibrational perturbations.

Yuster and Delbecq[46] carried out the measurements on KI:Tl at 77°K. They have shown that the C band ($^1P_1$) actually consists of three components at lower temperature. They also observed four typical absorption bands in KI:Tl labelled A (283 nm), B (245 nm), C (234 nm) and D (226 nm). The D band in KI:Tl lies between the C band and onset of the fundamental absorption of the crystal. This band, which has since been discovered in KCl:Tl by Kuwabara and Aoyogi[47], is at too low energy to be due to higher lying states of the thallous ion. Yuster and Delbecq[46] suggested that this band is analogous to the α and β bands which appear in the alkali halides, i.e. due to transitions on anions which surround the Tl^+ ion. It is also possible that the D band is due to a charge transfer state involving a transition from an anion to the Tl^+ ion as suggested by Knox[10]. Wagner has studied the absorption spectrum of KCl:Tl at many different Tl concentrations, and at both room temperature and 77°K. His work bears out the discovery of Patterson[19] that both the A and C bands are not single. The C band shows a triplet structure analogous to that observed in KI:Tl. These structures exist in other thallium phosphors and even more pronounced in Pb^{++} and Sn^{++} phosphors (Fukuda[48] and Zazubovich et al.[49], Wagner[50]).

The cause of this splitting is not completely clear, although a number of proposals have been made to explain it. These proposals fall into three categories: (1) Local asymmetry due to the presence of other charged ions or vacancies nearby; this was suggested by Zazubovich et al.[49] to explain results on Sn^{++} and could be important for Pb^{++} as well; (2) Asymmetry due to a static distortion in the otherwise perfect lattice that removes the cubic symmetry; and (3) Dynamical Jahn-Teller effect.

The one another alkali halide system that has received substantial attention is NaI (Tl). Although NaI is deliquescent and therefore requires special experimental precautions, the usefulness of NaI (Tl) as a high-energy particle detector (Hofstadter[51]) had led to further study of its properties (Van Sciver and Hofstadter[52]; Van Sciver[53,54,55]; Eby and Jentschke[56]; Herb and Van Sciver[57]; Vaidanich[58]; Herb[59]). Much of the interest has centred on the 'dimer' or pair centre which is discussed later.

In the case of isolated Tl^{+} ion in NaI one observes the usual A, B and C absorption bands

located at 292 nm, 248 nm and 234 nm respectively at 17°K (Vaidanich[58]). There appears to exist a D band $\sim$ 230 nm which is very close to the fundamental absorption. Apparently the excitation spectrum in NaI(Tl) is rather similar (qualitatively) to that of KI:Tl, and the same sort of arguments regarding its origin might apply.

Recently Delbecq et al.[60] studied the trapping and annihilation of electrons and holes in KCl:Tl system. In an associated absorption study they obtained a number of absorption bands which they attributed to the presence of Tl^{+}, Tl^{++} and Tl^{0} centres. The absorptions at 247, 209 and 195 nm have been identified as the wellknown A, B and C bands (Seitz's terminology) respectively. The bands at 380, 250, 300, 640, 1260 and 1500 nm have been attributed by these authors to Tl^{0} atoms and the bands at 220, 262, 294 and 364 nm have been ascribed to Tl^{++} ions.

(D) Thallium Emission

The situation regarding thallium emission is rather complex. Until recently the absorption spectra

of the thallium-doped alkali halides received more attention than the details of the emission spectra. For example, prior to 1959 it was believed that the emission spectra were independent of excitation energy and that in many of the alkali halides only one emission band appeared. In fact there are typically several emission bands whose intensities, polarizations and lifetimes are dependent upon temperature and the wavelength and polarization of the exciting light. Although several schemes have been advanced to explain these phenomena, a complete understanding has not yet been reached.

Some of the details of the phenomena associated with KI:Tl, measured by Edgerton and Teegarden[11,61] are as follows. At room temperature, excitation in A, B or C bands produces a broad emission peaking at 413 nm. At 80°K, excitation in the A band yields an emission at 430 nm whereas excitation in the B and C bands produces this emission along with one at 305 nm. And at 12°K these two bands are joined by three new ones. Excitation in the A band yields intense emission at 336 nm and weak emission at $\approx$ 430 nm. B band absorption is followed by emission at 287 and 336 nm. C band absorption yields 279 nm, 336 nm, 305 nm

and 430 nm emissions and absorptions in the D band yield intense emission at 430 nm and 336 nm.

Although these data, and similar data taken for KCl and KBr, appear rather complicated, Edgerton and Teegarden were able to devise a scheme with which to interpret them and correlated this scheme with a hypothetical configuration co-ordinate plot. In this scheme, the 413 emission comes from the $^3P_0$ state, the 336 nm emission from $^3P_1$, the 305 nm from one of the $^3P_2$ states (split in the cubic field), the 287 nm from the other of the $^3P_2$ states and the 279 nm from $^1P_1$. The appearance and disappearance of these bands as a function of temperature could be interpreted in terms of radiationless transitions; for example, at 300°K excitation into any band would be followed by a radiationless transition to $^3P_0$, from which 413 nm emission arises. Also, certain of the emissions seem to involve the reabsorption of emitted radiation, followed by lower energy emission. For example, radiation emitted at 279 nm could be reabsorbed in the A band; this leads to a "hole" in the 279 nm emission spectrum.

Analogous measurements of KCl:Tl and KBr:Tl have been made by Edgerton and Teegarden[11], Williams and Johnson[62] and Lushchik and Co-workers[63]. The emission spectra of these compounds are not as complex as that found for KI:Tl. However, high energy emission bands, not previously observed, have been found in these two additional cases. In KCl:Tl, besides the well-known band at 305 nm, a band centred near the position of the A absorption band has been discovered at 80°K and 12°K. This emission band is strongly reabsorbed in the A band, so that its position is hard to determine accurately. Only these two bands are well defined. However, it should be noted that several workers, including Edgerton[30], Edgerton and Teegarden[61], Patterson and Klick[18] and Patterson[19] have presented the evidence that the band which appears at 305 nm is actually composed of two strongly overlapping bands.

Experiments on the polarization of emission agree in certain respects with the foregoing model. It was first shown by Klick and Compton[64] that, when KCl:Tl is irradiated at 4°K with linearly polarized light in the A band region, the emitted light is also linearly polarized, preferentially along (1 0 0)

axis. The polarization is not present at 77°K. Since then, these experiments have been extended by others. Edgerton[65] investigated polarization properties of the absorption and emission bands of KI:Tl at low temperature. He found that A band excitation led to polarized emission at 336 nm; B and C band excitation yielded polarization in the 289 nm and 279 nm bands respectively, and no polarization in the 305 nm, 336 nm or 413 nm bands.

An emission band at 475 nm in KCl:Tl, which has been reported in earlier work and has played a considerable role in theoretical discussions (Knox[10], Williams and Johnson[62]), appears not to be due to a simple substitutional thallous ion. Its intensity relative to the bands just described depends upon the concentration of the impurity and the state of perfection of the crystal (Ivanova et al.[66]). In single crystals with low concentrations of thallium it does not appear. At 80°K it is known that excitation in the A band produces only the 305 nm band, while excitation in the C band produces both emission bands. Detailed investigations of the excitation spectrum of KCl:Tl have not been made at the lower temperatures.

In the emission spectrum of KBr:Tl, two poorly resolved bands appear at 300°K. These are more completely resolved at 80°K, and a new band appears at 260 nm centred on the A absorption band, so that it is reabsorbed at the centre. At 12°K the 362 nm band is quenched relative to the shorter wavelength emission. It is known that at 300°K excitation in the A, B or C bands produces the same emission. At 80°K excitation in the A band produces the two bands at 362 nm and 310 nm, while excitation in the B and C bands produces all three emission bands. No detailed measurements of the excitation spectrum appear to have been made at temperatures below about 80°K.

It is interesting to note that the emission spectra of all three systems at 12°K (or extrapolated to 0°K), and at 100°K look very much the same. There is one emission band at longer wavelengths than any of the absorption bands and emission which strongly overlaps and is absorbed by the A band. It has been suggested by Edgerton and Teegarden[11] that the emission spectra of KBr:Tl and KCl:Tl at different temperatures can be

explained in the same terms used in the foregoing for KI:Tl if it is assumed that as the host anion gets lighter the $^3P_0$ and $^3P_1$ levels approach each other, while at the same time the $^1P_1$ and $^3P_2$ levels approach each other. In this interpretation the 362 nm band of KBr:Tl is attributed to the $^3P_0$ level and the 310 nm band is attributed to the $^3P_1$ level. The band (or bands) which superimposed on the A absorption band is attributed to $^1P_1$ or $^3P_2$ or both. In KCl:Tl the same interpretation is given to the high-energy emission band. It is suggested by these workers that the lower-lying component of the 305 nm band of KCl:Tl is due to $^3P_0$ and that the higher-energy component originates from $^3P_1$.

Measurement of the emission spectrum of NaI:Tl at 12°K was recently made by Vydanitch and Teegarden[67]. Their observations are interesting in that they also indicate that the A band is not single at these temperatures. Excitation on the long wavelength side of the A band in the heavily doped NaI crystals results in emission at 435 nm. This emission band is analogous to the 430 nm band of KI:Tl and hence it has been ascribed to the $^3P_0$ state by Edgerton and Teegarden[61]. At high temperature this band appears during irradiation

in the A band but at 12°K it is quenched in lightly doped crystals. Irradiation in the peak of the A band in both NaI and KI at 12°K produces a shorter wavelength emission that is ascribed to the $^3P_1$ state in the discussion above.

(E) Thallium - Dimer Centre

In alkali halides that are very heavily doped with thallium, one may observe both absorption and emission bands that are not present in more lightly doped crystals. These absorption bands were first studied by Yuster and Delbecq[46] in KI:Tl, where two groups of double bands occur to the low energy side of the A band and the B band. Since the absorption of these bands varied as the square of the thallium concentration, Yuster and Delbecq suggested that these bands were associated with pairs of nearby thallium ions. Similar bands are found in NaI:Tl and in KCl:Tl.

It is interesting to note that, although the dimer absorption bands fall rather close to the single ion, or monomer bands, the emission bands are quite distinct from one another. In KCl:Tl, as mentioned

earlier, an emission band associated with dimer lies at 479 nm much lower in energy than any of the monomer bands. In NaI:Tl, the main dimer band lies at 324 nm (Van Sciver[53]), which is much higher in energy than the main monomer emission band. It is not at all clear why the order of the two bands is so different in the different systems.

(F) Other s^2 ions

Work on these ions has been pursued much less vigorously than work on Tl^+ ion and the literature on them is correspondingly less plentiful. From a theoretical point of view, nearly all that was said about Tl^+ ion can also be applied here.

There are two main sources of experimental data on these systems. The first of these is a paper by Zazubovich et al.[49] which summarizes the extensive experimental work of Lushchik and collaborators (see, for example, Lushchik and Lushchik[63]). Investigations of absorption, excitation and emission spectra have been made by these workers on monovalent Ga, In, Tl; divalent Ge, Sn, Pb and trivalent Sb, Bi, all of which have the s^2 configuration in their ground states.

Another source of data is the paper by Fukuda[48]. Fukuda has concentrated on the optical absorption spectra and has made a careful study of In, Sn and Pb in NaCl, KCl and KBr. He has investigated particularly the bands in the near ultraviolet region, the splittings of absorption bands and the oscillator strength ratio of the C band to that of the A band.

Emission data on these systems are rather meager. Much of the data were obtained at room temperature; from experience with Tl^+ ion, low temperature data are expected to be considerably more complex, interesting and useful. Of interest are the polarization characteristics observed (Zazubovich et al.[49]), even at room temperature. Although at this temperature there is no polarization in the monovalent centres, some (10-20 %) polarization in a (100) direction is observed with the divalent centres and even more ($\gtrsim$ 75%) with the trivalent centres.

(G) Phosphorescence and Thermoluminescence

The thermoluminescent behaviour of pure and doped alkali halides has been studied extensively with the

hope that luminescent properties of the crystals can be understood in terms of the observed properties of individual glow peaks. Thermoluminescence is a relatively complex process since it involves a trap, a luminescent centre and the transfer (during warm-up) 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. Introduction of thallium into alkali halide markedly changes the property of the host material. It is usually accepted that most, if not all, of the thallium is incorporated substitutionally, and that no additional vacancies due to thallium addition are present in the lattice. In the case of thallium doped potassium chloride, Johnson and Williams[21] observed that on warming a KCl:Tl crystal, after ultraviolet irradiation at liquid nitrogen temperature, glow peaks appeared at 205 and 300°K. They proposed that as a result of the ultraviolet irradiation, thallous ions are excited to $^1P_1$ and $^3P_1$ bound states from which Tl^+ ions decay into the metastable $^3P_0$ and $^3P_2$ states. According to them, on warming the crystal, thallous ions in the metastable

states are thermally raised to states from which radiative transitions to the ground states are possible.

From their thermoluminescent measurements Ewles and Joshi[68] reported the occurrence of the same two glow peaks in KCl activated with impurities other than thallium. It was therefore suggested that the trapping sites are not due to internal metastable states of the impurity but are due to crystalline imperfections other than the impurity ions. Subsequently, similar suggestion was also made by Halperin and Schlesinger[69] and Hersh and Hadley[70]. In the light of their later work, Joshi et al.[71,72] identified these imperfections as ion vacancies. Since the colouration phenomenon in solids is intimately bound up with the presence of ion vacancies, it was further proposed that a phosphorescence centre (complex formed by the association of the emission centre and the trapping site) responsible for a given glow peak may be closely related to a certain species of colour centres. Based on these concepts, Joshi et al.[73-75] interpreted the thermoluminescence in KCl:Tl as resulting from the

thermal destruction of a particular type of colour centres and subsequent release of the electron or the holes which recombine radiatively with their counterpart at the emission centre. In thallium doped alkali halide phosphors, the Tl^{+} ions have been suggested to act as emission centres. This feature of the phosphor is easier to understand because of the existence of impurity absorption bands at energies short of that required for electron-hole production. As a result of this, it is possible to excite completely localized thallium states without the complications of storage. Comparison of this localized emission with that resulting from recombination has helped to identify recombination sites and processes. Since in thallium doped alkali halide phosphors the emission is like that from thallium fluorescence, it has been suggested that the electrons and holes are generated by the ionizing radiation and that recombination occurs at thallium Sites[60,71,72].

According to the band theory of solids, it is known that the incorporation of impurity ions or the presence of ion vacancies in the crystal leads to

the localized energy levels in the forbidden band. The energy levels near the conduction band serve as electron traps and are, if occupied, detected optically as F-type colour centres. On the other hand, energy levels near the valence band may trap positive holes and become V-type centres. Thallium activated alkali halides exhibit phosphorescence of long duration and yet no appreciable photoconductivity has been observed. It was therefore suggested that in these phosphors the emission centre and the trapping site may have close spatial association with each other[76,77]. The thermoluminescence mechanism has been suggested to involve, during irradiation, the transfer of an electron either from a Tl^+ ion to an electron trap near the conduction band or from the valence band to a Tl^+ ion thereby trapping a hole near the valence band. In the first case, during warm-up of the phosphor, the electron will be raised thermally from the ground state of the trap to the excited state below the conduction band from where it is suggested to return to the Tl^+ ion by a tunneling process[73]. In the second case, on heating the phosphor, the hole will be raised thermally from

the ground state of the trap to the excited state above the valence band and the resulting electron-hole recombination takes place at the hole centre adjacent to the hole trap[75].