CHAPTER 2

SURVEY OF THE RELATED OPTICAL STUDIES IN POTASSIUM CHLORIDE

(1) COLORATION OF SOLIDS

Colour centres in solids have been studied extensively for nearly half a century, primarily because of its usefulness in the understanding of the electronic processes in solids. In the early part of this century Przibram[20] and his co-workers carried out an extensive work on the coloration and luminescence of solids which included mainly natural minerals. The major concepts in the field of colour centres originate from the researches on alkali halides crystals. Alkali halides are ideal crystals for the study of colour centres because of the extraordinarily wide range of optical transparency exhibited by them even at elevated temperatures. Historically, the first observation of the coloration of alkali halides appears to be the work of Goldstien[21], who found that when these salts are bombarded with cathode rays, they darken, each compound exhibiting its own characteristic colour. The same coloration can be produced by exposing the crystals to highly energetic radiations.

A comparison of the absorption spectrum of an alkali halide crystal before and after exposure to ionizing radiations show that strong absorption bands are generated in the crystal by the irradiation. The nature of the absorption is strongly dependent on the temperature of irradiation of the crystal. For example, absorption bands, produced during irradiation below room temperature, do not appear if the irradiation is performed at room temperature.

Of the large number of optical absorption bands which have been observed, none appears so prominently over the entire range from liquid helium temperature to room temperature as the F-band. The F-absorption band in KCl has a peak at 540 mμ at room temperature. The model of the centre responsible for this absorption band proposed by de Boer[22] which involves an electron trapped in a halogen vacancy, the electron being shared by the six nearest neighbour alkali ions seems to be established beyond any reasonable doubt. The F-absorption corresponds to an electron transition from the ^1S ground state to the ^2P excited level close to the bottom of the conduction band.

It has been reported that the peak position of the F-absorption is dependent on temperature. With decreasing temperature the band becomes narrower and its peak position shifts to shorter wavelengths. The effect of hydrostatic pressure on the F-absorption in alkali halides has been investigated by Jacobs[23] and Maisch and Drickamer[24]. It is observed that the peak of the F-band shifts to shorter wavelengths with increasing pressure. In the case of F-band in KCl, Jacobs[23] reports a shift of 169 mμ. The thermal bleaching of the F-centres has been studied by many investigators[25,26]. Braner and Halperin present evidence to show that the thermal bleaching of F-centres takes place mainly at certain characteristic temperatures. Sadlyarenko et al[27] reported the existance of F-centres with different thermal stabilities in the alkali halide phosphors. Sonder et al[28] found that the F-centre annealing occured over a broad range of temperature.

Careful measurements have revealed a small hump at the short wavelength side of the F-band and three additional, well-resolved but very weak absorption bands at wavelengths still shorter than that of the hump. The hump is called the K-band and the three weak bands are termed L_1, L_2 and L_3 bands. Lüty suggests that the F and K bands are due to transitions of the F-centre to higher bound excited states, resulting in very little photoconductivity[29]. Miyamoto et al[30] identified the K-band as due to F-centres in the field of dislocations. However, recently Spinolo et al[31] and Schnatterly [32] have given evidence in support of a model involving transitions to higher excited states of an F-centre. The L-bands, according to Lüty[29], are due to transitions of the F-centre electrons to free or unbound states which give photoconductivity even at the lowest temperatures. Klick and Kabler[33] proposed a model for L-bands as being combinations of the usual F-centre transitions, which transfer the F-centre electron to a neighbouring alkali ion and the raising of the resulting alkali atom to various excited states.

In addition to the K and L-bands, there is yet another absorption band that occurs when an alkali halide crystal is coloured with F-centres; this is termed the β-band. This band which lies on the low energy side of the fundamental exciton absorption is thought to involve the excitation of a halogen ion near the F-centre[34]. Partial bleaching of the F-band at low temperature produces a band on the low energy side of the β-band, called the α-band. The α-band has also been assumed to be due to a perturbed lattice absorption, the perturbation being due to a negative ion vacancy. The thermal destruction of the centre at low temperature - 150°K in the case of α-centres in KCl - can be caused by the diffusion of isolated vacancies so as to form vacancy pairs.

Illumination of a KCl crystal containing F-centres with light in the F-band at low temperatures causes a decrease in the F-band and a broad band on the long wavelength side appears. This has been named the F' band. Pick[35] has investigated the optical conversion of F → F' and the reverse reaction. The quantum yield for destruction of F-centres is small at low temperatures, but increases with temperature and attains a value of two at —100°C. It is believed that at temperature around -100°C, the electron trapped at the F-centre, when excited to the higher level, instead of being thrown into the conduction band, is retrapped by another F-centre to form the F' centre. In KCl, the F' centre is stable only at low temperatures, and it decomposes on warming to 200°K, regenerating the F-centres.

While F-illumination of a crystal containing F-centres at low temperatures generate F' and α-centres, the bleaching of F centres, if performed at room temperature results in the formation of a family of absorption bands appearing on the long wavelength side of the F-band. These are designated the M, R_1, R_2, N_1 and N_2 bands. These centres can also be formed by subjecting the alkali halides to prolonged X- irradiation near room temperature[36]. Based on the fact that these bands appear to be the product of F-centre coagulation, generated at the cost of F-centres, Seitz[37] proposed tentative models for these centres. According to Seitz the R_1 centre is an electron trapped at a pair of negative ion vacancies and the R_2 centre consists of a pair of F-centres. The M-centre, he suggested, involved a centre having an L-shaped configuration resulting from the association of an F-centre with a neutral pair of positive and negative ion vacancies. An intersting feature of Seitz's M, R_1 and R_2 centre models is their lack of cubic symmetry and the prediction that the luminescence of these centres should be polarized if the exciting light is polarized.

A modification of the Seitz's M-centre model has been proposed by Knox[38], which involves an alkali atom at the centre of a quartet of vacancies (two positive and two negative). From the results obtained during their study on the dichroic properties of F and M-centres[39,40] and the reaction kinetics for the formation of F and M-centres in additively coloured KCl,[41] Van Doorn and Haven suggested a model for M-centre consisting of a pair of F-centres. The Van Doorn-Haven model is in accord with the requirement of inversion symmetry[42] and the absence of dielectric loss[43]. Many investigations have been reported in the recent past which lend support to the F_2 model of M-centre[44].

Van Doorn and Haven speculated on the possibility that other F-aggregate centres might also involve more complicated coagulation of F-centres, eg., that R-centre consists of three F-centres. This possibility has been expanded by Pick[45]. The order of complexity of these models ranging from one to four F-centres corresponds to the order in which they are formed, first F followed by M, R and N-centres. Pick assumed that the R_1 and R_2 bands correspond to two transitions of the same centre comprising of three F-centres forming an equilateral triangle in the (111) plane. The N-centre has been assumed to involve four F-centres. The N-band appears to consist of two overlapping bands, N_1 and N_2. The N_1 centre is assumed to consist of a parallelogram in the (111) plane while the N_2-centre is a tetrahedron involving the four possible (111) planes. Pierce[46] studied the vibronic structure and symmetry properties of F-aggregate centres in NaCl and presents evidence in favour of the F_3-model of the R-centre. He, however, points out the possibility of an N_1-model consisting of two F-centres at diagonal positions in a unit cell and favours the Pick's N_1 model for the N_2-centre. Schnieder and Kabler[47] speculated that the N_1-centres consist of three F-centres whose arrangement is different from that of R-centre. Though the F_3 model of R-centre seems to be well-established the models for the N_1 and N_2 centres are not yet finalised.

The F-aggregate centres are in general stable in the dark in the vicinity of and below room temperature. At higher temperatures they become unstable and generally dissociate into F-centres or into other F-aggregate centres. Tomiki[48] has summarised the thermal reactions which occur above a critical temperature in additively coloured KCl as follows:

$$R_1,\ R_2 \xrightarrow{>50^\circ C} F + M + N_1 + R_3$$
$$R_3,\ N_1 \xrightarrow{\geq 100^\circ C} F + M$$
$$M \xrightarrow{>130^\circ C} F$$

The R_3 band seems to be a new band. Bron[49] has also confirmed the presence of R_3 band peaking near the R_2 band in X-rayed KCl. Hattori[50] observed that the thermal bleaching of the N_2 band is nearly identical to the thermal bleaching of the R_1 and R_2 bands. He noticed the presence of still another band which has been designated as N_{R_1}. Thus the first thermal reaction becomes

$$R_1,\ R_2,\ N_2 \xrightarrow{\geq 50^\circ C} F + M + N_1 + N_{R_1} + N_{R_2}$$

where N_{R_2} is the same as the R_3 band. The N_{R_1}, N_{R_2}, and N_1 centres bleach at temperatures around 70°C.

$$N_{R_1},\ N_{R_2},\ N_1 \xrightarrow{\geq 70^\circ C} F + M$$

In addition to these absorptions a large variety of optical absorptions ascribable to the transitions to higher excited states and to ionized aggregate centres have been reported[51-55].

For all the centres that are discussed above the absorption is due to trapped-elctrons. Irradiation with ionizing radiation can as well generate centres due to trapped-holes. This group of centres are generally known as V-centres. The nature and type of V-bands generated depend on the temperature of irradiation.

Irradiating a KCl crystal at room temperature produces two absorption bands peaking at 212 and 230 mμ named V_3 and V_2 bands respectively. The V_3 band dominates over the V_2 in strength. These centres are generated along with the usual F-centres. Alexander and Schneider[56] observed that the application of an electric field of 2000 volts/cm during F-light illumination eliminated the F-band completely leaving the V-centres unaltered.

Irradiation of alkali halides at liquid nitrogen temperature produces a prominent V_1 band and smaller V_2 and V_3 bands, together with F and F' bands. In the irradiated crystal an absorption is also produced in the short-wave ultraviolet which may be resolved into the V_2 and another band designated V_4. The V_1 band has a peak maximum at 356 mμ and V_4 peaks at 254 mμ in KCl. The V_1 band in KCl becomes thermally unstable at 128°K and is completely bleached at 173°K and above. The V_4 band is also unstable above 193°K.

Seitz[37] proposed that the V_1 band is due to a centre consisting of a hole trapped at a positive ion vacancy. According to him the V_3 and V_2 centres are the inverse of his R_1 and R_2 centre models respectively and the V_4 centre, the inverse of his M-centre model. Other models[57] for V-centres have been proposed by Varley, Nagamiya, Burstein and Oberly.

Kanzig and Woodruff[58] have suggested that the V_1 centre consists of a halogen molecule X_2 at a single anion site. A number of other models[59,60] have been proposed for the V_1 centre. There now exists strong evidence that the V_1 centre in KCl and KBr consists of an H-centre associated with an impurity Na^+ ion[61].

As an alternative to the vacancy model of V-centres proposed by Seitz, Hersh has suggested that the V_2 and V_3 bands in KI and KBr and the V_2 band in KCl arise from a centre that may be described as a linear array of halogen molecule and a halide ion. This suggestion of a molecular-type model results from studies of the absorption bands in water solutions of the alkali halides and halogens. Short-lived species of absorbing centres have been found in water solutions of halogens and alkali halides after ultraviolet irradiation. These were suggested to be X_2^- ions. The wavelength of absorption bands arising from these species are near those found for V_k and H centres in the crystalline solid. The close correspondence between the bands found in solution and V_k and H bands found in crystals lend support to Hersh's suggestion[62].

Lüty[63], Damm and Tompkins[64] have suggested that V_2 and V_3 bands are attributable to the presence of impurities in the crystal. Nadeau[65] observed that these bands do not appear in the crystals when the impurity content of the crystal is reduced considerably. A considerable amount of work has been carried out by Christy et al[66,67], on the properties of V_3-centres in alkali halides. They identified the V_3 centre as one consisting of a Cl_3^- molecular ion, oriented in the [001] direction, occupying two anion and one cation sites. Recemtly from the studies on prolarized bleaching of V_3 centre Christy has speculated[68] the model of this centre as a resonance between the three possible (100)-type orientations, i.e. as a Cl_7^{5-} molecular ion with cubic symmetry. He has further speculated that the V_3, V_2 and V_4 absorptions are all related to X_3^- structures.

The V_4-centre is produced most prominently by X-irradiation between 140°K and 200°K. Though the 254 mμ band in KCl has been designated the V_4 band earlier, Faraday and Compton[69] and Itoh[70] observed a band at 240 mμ in KCl which exhibited similar behaviour as the V_4 band in KBr and preferred to call this as the V_4 band. Kingsley[71] suggested this centre to be an antimorph of F-centre. According to Itoh[70] the V_4 centre involves a di-interstitial halogen molecule which has a <100> symmetry axis.

During irradiation of a pure KCl crystal at liquid nitrogen temperature, it is possible for some of the electrons from the 3p shell of chlorine ions to be ejected. The resulting chlorine atom associates with an adjacent negative chlorine ion. In other words, the electron deficiency is shared by the chlorine atom and the nearby chlorine ion thereby forming a Cl_2^- molecule ion. This centre has been named the V_k centre and has got an absorption at 365 mμ in KCl. It has been observed that the introduction of impurities such as Ag^+, Tl^+ or Pb^+ into the crystal increases the efficiency of formation of these centres[72]. This is understandable since the impurities act as efficient electron traps and reduce the possibility of annihilation of the hole trapped at the centre. Thermal bleaching of V_k centres occurs in pure KCl at 133°K and in KCl:Tl at 208°K.

In additively coloured crystals containing divalent metal impurities a new set of absorption bands arises which have been named the Z bands. Mainly five such bands have been observed and are designated with subscripts 1 to 5. Optical irradiation of divalent impurity-doped crystals containing F-centres with F-light generates Z_1 centres. If this crystal is then heated to around 380°K, the Z_1 centres are destroyed, some of the F-centres are reformed and Z_2 centres appear. When crystal containing mixture of F and Z_2 centres is irradiated with F-light at $\sim$180°k, the two bands decrease in concentration and Z_3 band appears along with the F' band. Additively coloured KCl:Sr specimen after prolonged F-irradiation at room temperature exhibits Z_4 band besides the Z_1 band. An interesting characteristic of Z_4 is its appearance and disappearance along with the Z_1 band. Kojima[73] observed that KCl crystals containing relatively high concentrations of Sr^{++} exhibited another band, Z_5, besides the normal Z_2 band. The models of the various Z-centres have been discussed by several authors[73-79].

X-irradiation at -80°C of crystals of KCl and KBr containing Ca^{2+}, Sr^{2+}, and Ba^{2+} has been found to produce a centre whose optical absorption is in the near ultraviolet (323 and 321 mμ for KCl:Ca and KCl:Sr respectively and 335 and 390 mμ for KCl:Ba). The centre is bleached thermally at around 232°K. Analysis of the resonance spectrum has led Hayes and Nichols[80] to suggest that it is a Cl_2^- occupying an anion-cation vacancy pair in the close neighbourhood of the impurity and is aligned innthe [100]direction. Crawford and Nelson[81] also observed this absorption but disagree with the view that it is in the vicinity of the impurity.

With the incorporation of the impurities in alkali halide lattice a number of absorption bands are observed which are characteristics of the impurity. An absorption band at 204 mμ in KCl has been found in all synthetic crystals grown without the intentional addition of impurities. The impurity responsible for this absorption is identified as the hydroxyl ions and the band is called the OH^- band[82]. It has been further established[83] that moisture and oxygen together encourage the increase in the OH-band which is proportional to the time the melt is exposed to oxygen and moisture.

The absorption band having a maximum at 216 mμ in KCl is known as the U band. The U centre has been studied extensively by Hilsch and Pohl[84] and is considered to be an H^- ion occupying a halogen ion site. U centres can be converted into F-centres by irradiation with U band light. Delbecq et al[85] has carried out paramagnetic resonance studies on KCl:KH system. They observed two more absoptions on the longer wavelength side of the U band and designated them as U_1 and U_2. The U_2 band peaks at 236 mμ in KCl. Based on their observations they have proposed models for the different centres. The U centre is a substitutional hydrogen ion on a halogen site while the U_1 and U_2 centres are suggested to be interstitial hydrogen ion and hydrogen atom respectively. The maximum rate of thermal decay of U_2 occurs at 108°K. The U_1 band has a maximum rate of decay in the vicinity of 160°K. Additive coloration of crystals containing OH band produces a U band that is proportional to the OH band height.

Kanzig and Cohen[86] observed a paramagnetic resonance signal at low temperatures in various alkali halides and they attributed it to an O_2^- impurity ion in a substitutional halide ion position. Rolfe et al[87] have studied the optical absorption spectrum of this centre. Recently Fisher et al[88] have studied the production and optical absorption of KCl containing O_2^- and O^{--} centres. They identified the absorptions at 5.09, 6.41 and 7.0 ev (243,193 and 177 mμ) as due to O_2^- and ascribed another set of absorptions at 2.82,4.34, 5.77 and 6.40 ev (439,285,215 and 194 mμ) to O^{--} centre. All bands for O^{--} have been attributed to electron transfers from O^{--} to the surrounding K^+ ions. Irradiation with ultraviolet light in the O^{--} absorption bands results in the photochemical reaction[89]

$$O^{--} + \square \longrightarrow O^{-} + F$$

The O^- centres are reported to have an absorption at 6.7 ev (185 mμ)[89].

(2) LUMINESCENCE OF POTASSIUM CHLORIDE PHOSPHORS

The crystalline luminescent solids are generally called phosphors. Because of their relatively simple structure and properties alkali halides have been subjected to extensive study. The present work is mainly concerned with the luminescence of potassium chloride activated with thallium. In this system both the absorption and the emission are suggested to occur in the same localized centre. 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[1] as A, B and

and C bands. The spectral positions of these bands in KCl:Tl are 247, 206 and 195 mμ respectively with relative strengths as C > A > B.

KCl:Tl phosphors exhibit two main emission bands; the principal emission at 305 mμ was attributed to 247 absorption and the weaker emission band at 475 mμ to the 195 mμ absorption.

The electronic configuration of the ground state of 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 substitutional thallous ion. In other words the luminescence emission is attributed to the electronic transitions in the substitutional Tl^+ ion. A configuration coordinate model which involved a single configuration coordinate for the distance between the luminescent ion and its nearest neighbours was utilized to interpret the interaction between the emission centre and the crystal lattice.

Later Williams[2] attempted a quantitative treatment of the problem. The energies of the $^1S_0$ and $^3P_1$ states of the Tl^+ ion in KCl were calculated. A similar scheme was adopted later by Johnson and Williams[13] for the $^1P_1$ state. The following transitions were associated with the observed absorption bands:

195 mμ $^1S_0 \longrightarrow {}^1P_1$
247 mμ $^1S_0 \longrightarrow {}^3P_1$
206 mμ $^1S_0 \longrightarrow {}^3P_2$ (very weak)

In order to account for the observed long- lasting phosphorescence of KCl:Tl, Johnson and Williams[13] attributed the electron trapping characteristics to the $^3P_0$ and $^3P_2$ states because the transitions

$^1S_0 \longrightarrow {}^3P_0$ and
$^1S_0 \longrightarrow {}^3P_2$ are forbidden.

The blue emission around 475 mμ was ascribed to $^1P_1 \longrightarrow {}^1S_0$ transition. Later observations by Eby and Teegarden[5] and Johnson and Williams[90] of a high energy emission at liquid nitrogen temperature in the region of the A band has simplified the position. Since the 247 mμ emission overlaps the absorption band, there is a strong reabsorption of the emission 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 transition for the 475 mμ emission is not fully understood. Williams[91] believes that both this emission and the 305 mμ emission originate from isolated substitutional Tl$^+$ ion with different excited or vibrational state.

Though the theory could successfully explain many of the then existing data, the later findings of various workers raised serious doubts regarding the validity of the Seitz-Williams theory. Williams' suggestion implies that the same excitation spectrum should be observed for the 305 and 475 mμ emissions. During his study of room temperature excitation spectrum Butler[7] obtained certain contradictory results. Patterson and Klick[8] preferred to consider different thallium centres rather than one centre. Objections to the calculations of Williams and his co-workers have been raised by Knox and Dexter[92].

On the basis of the band theory of solids a phosphor exhibiting long-term phosphorescence should also show photoconductivity; but KCl:Tl system happens to be an exception to this rule. Seitz[1] suggested the metastable energy levels of Tl$^+$ ions as trapping sites to explain this. $^3P_0$ and $^3P_2$ states were later identified as the "electron traps". Johnson and

Williams[13] ascribed the two major thermal glow peaks in KCl:Tl at 205° and 300°K to these traps. Results obtained by Ewles and Joshi[11] contradicted this assumption. They observed the same two glow peaks in KCl activated with barium or strontium. Even 'specpure' potassium chloride, evaporated and compressed, exhibited the same two glow peaks. They argued that the traps responsible for KCl:Tl thermoluminescence were independent of the impurity ion and that they were characteristic of other crystalline defects in the host lattice.

Thermoluminescence lends itself as a versatile tool for the detailed study of trapping sites in luminescent materials. Randall and Wilkins[93] suggested that the glow peaks exhibited by phosphorescent materials were due to electrons released from a number of electron-excess centres. Many of the workers[26,94-98] have speculated on the possibility of a direct correlation between the glow peaks in alkali halides and the colour centres. Hill and Schwed[96] and Bonfiglioli et al[97] suggested that different peaks arise due to electron-deficient centres having different capture cross-sections for electrons, which are released thermally from a single electron-excess centre. Halperin and his group believe that the glow peaks are due to recombination of electrons and holes after the thermal release from their appropriate trapping sites, which are characterised by specific activation energies. Localized energy levels just below the conduction band serve as electron traps and those just above the valence band serve as hole traps.

According to Hill and Schwed and Bonfiglioli et al, every peak should give emission that is different from those of other peaks. Moreover, the activation energies for all the peaks should be 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[95,99].

Dutton and Maurer[100] suggested that the thermoluminescence results from the recombination of holes released from V_1 centres with electrons from F centres. Based on an experiment performed by Stoddard[101] on sodium chloride Braner and Israeli[102] carried out measurements on the photo-stimulated thermoluminescence of alkali halides. The peaks obtained after F light illumination were termed the "electron peaks" and the ones obtained after V light illumination were termed the"hole peaks". Bossacchi et al[103] carried out a similar study and speculated on the probable models for the various glow peaks. Thermoluminescence measurements by Joshi et al$^{15-18}$ led them to suggest that the trapping sites in KCl:Tl are the ion-vacancies. They have speculated on the probable colour centres responsible for the different glow peaks in KCl:Tl.

Evidence for the relation between thermal glow peaks and colour centres has also been obtained by a number of other workers$^{104-105}$. Thermoluminescence measurements in conjunction with optical absorption studies in LiF^{106} and in KCl:Tl^{19} by Christy et al and Delbecq et al respectively lend further support to the view that thermal glow results from the thermal destruction of different types of absorbing centres and the subsequent recombination of electrons and holes at the emission centre.

The survey of the literature given above is more or less of a general nature. It is mainly intended to give a broad idea of the present line of thinking in the field of thermoluminescence.

(3) OPTICAL ABSORPTION OF KCL:TL

Optical absorption and luminescence of KCl:Tl have been the subject of detailed study in the past few years. Incorporation of thallous ions in KCl lattice introduces new absorption bands depending on the different configurations in which thallium is present. Much of the earlier work in this direction will be referred in the following sections.

Recently Delbecq et al[19] studied the trapping and annihilation of electrons and holes in KCl:Tl system. In an associated absorption study they obtained number of absorption bands which they attributed to the presence of Tl^+, Tl^{++} and Tl^o centres. The absorptions at 247, 209 and 195 mμ have been identified as the well-known A, B and C bands (Seitz's terminology)[2] respectively. The bands at 380, 250, 300, 640, 1260 and 1500 mμ have been attributed by these authors to Tl^o atoms and the bands at 220, 262, 294 and 364 mμ have been ascribed to Tl^{++} ions.

These authors have discussed the formation mechanism of the above centres in KCl:Tl on irradiation of the samples. Irradiation of these samples at 77°K with ionizing radiation results in the formation of free electrons and positive holes which may then be trapped to form Tl^o and Cl_2^-. The Cl_2^- ion can be retrapped at Tl^+ ion to form Tl^{++}, the reaction being given by

$$Tl^+ + Cl_2^- \text{ (mobile species) } \longrightarrow Tl^{++} + 2Cl^-.$$

The above authors in a later paper[107] have studied in detail the infra-red absorption of Tl^{0} atoms in γ -irradiated KCl:Tl samples. These absorptions have been attributed to the forbidden ${}^{2}P_{1/2} \longrightarrow {}^{2}P_{3/2}$ transition of the free atom.

Recently Stauber et al[108] have made a theoretical study of Tl^{+} absorptions in KCl. It is reported that thallium substitutionally introduced in alkali halide crystals gives rise to four absorption bands namely A, B, C and D bands at 5.03, 5.94, 6.36 and 7.30 ev. respectively. The transitions involved in the case of the former three have been discussed.
