CHAPTER 4

RESULTS AND DISCUSSION

Considerable work has been reported on the optical absorption and luminescence properties of alkali halide crystals containing thallous ion impurity.[1,2,19,92,110-115] Comparison of the absorption phenomena in "pure" and thallium-doped alkali halides clearly indicates that the introduction of thallium markedly changes the absorption properties 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 the thallium incorporation are present in the lattice. The nature of the absorption processes that give rise to the bands introduced by thallium has been studied in considerable detail. One approaches this problem from the tight binding approximation, that is, it is assumed that the transitions of the ion in the solid are essentially the same as in the gas. Only the energy levels are believed to be shifted as a result of interactions of the valence electrons with the crystal[1]. The experimental situation in KCl:Tl phosphor is particularly simple for thallium concentrations $\sim 10^{-4}$ mole percent or less. In many of their properties such lightly doped crystals are like "pure" crystals whereas more heavily doped crystals ($\sim 10^{-2}$ mole percent or more) are remarkably different. In the latter type, one observes both absorption and emission bands that are not present in lightly doped crystals. The present discussion is limited only to the phosphors of heavily doped type in which the thallium concentration is of the order 10^{-1} mole percent. In what follows, the results obtained for annealed and quenched specimens (I and II) will be presented and discussed first. Subsequently, the results for annealed and slowly cooled specimen (III) will be considered.

Figures 1(a) through 1 (h) represent the absorption data taken on specimen I. (annealed for 50 hrs. and quenched) in the wavelength region 200-650 $m\mu$. Figures 1(a) and 1(b) exhibit the absorption spectra of the specimen before and after ultraviolet irradiation respectively, both measured at the same temperature ($\sim$ 110° K). The behaviour of the absorption bands, produced by irradiation near liquid nitrogen temperature, was followed up with the rise in temperature of the specimen. Figures 1(c) to 1(h) illustrate the absorption spectra when the specimen was warmed to an annealing temperature, held there momentarily and then cooled to liquid nitrogen temperature for the measurement of the absorption spectrum. It is clearly seen that large scale spectral changes occur due to warm-up of the specimen. In general, because of relatively strong absorption in the ultra violet region and weak absorption in the visible region, in all the absorption runs, the spectra in the ultra violet region were recorded on scale 2 and those in the visible on scale 1 of the Carry spectrophotometer. The actual recordings of the spectra show slight variations in the peak positions of the absorption bands, mainly in the ultraviolet region. The wavelengths used to identify these bands are :205, 214, 225, 242, 260, 290 and 300 mμ.

Specimen I :

The absorption bands observed at 110° K before irradiation (fig. 1 a) are 214, 225, 242 and 260 mμ. At the same temperature, after irradiation (fig. 1b), the spectrum is obviously modified and becomes complicated. Besides the appearance of new bands at ∼ 205, 248, 254 and 290 mμ, a significant decrease in the intensities of 214, 225, 242 and 260 mμ bands is apparent. In addition, weak absorption bands are observable at ∼ 365, 550 and 610 mμ.

Warming the specimen to 160° K (fig. 1c) gives rise to an additional absorption band at ∼ 300 mμ. and the bands at ∼ 205, 214, 225, 242, 248, 254 and 260 mμ undergo further decrease in their intensities.

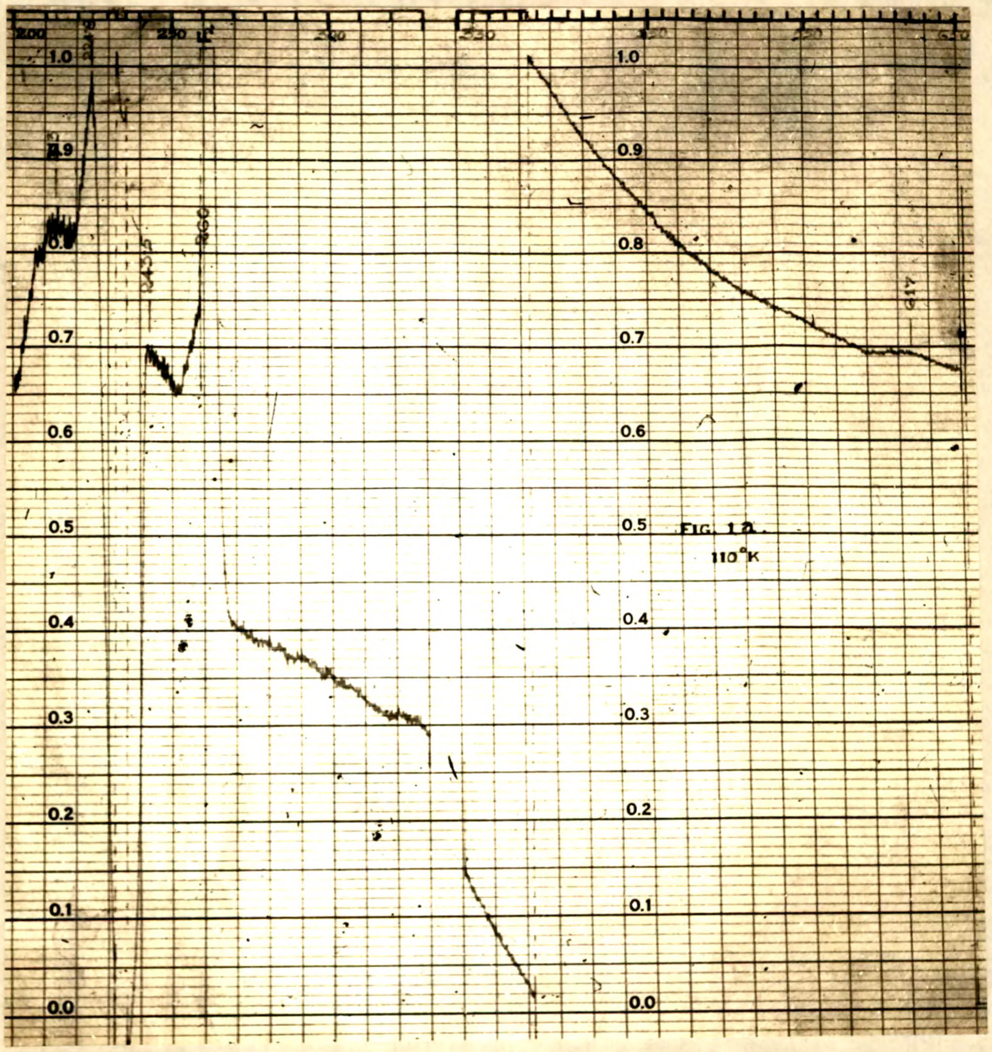

200
250 μ
300
350
400
500
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
224.5
243.5
260
617

FIG. 1a.
110°K

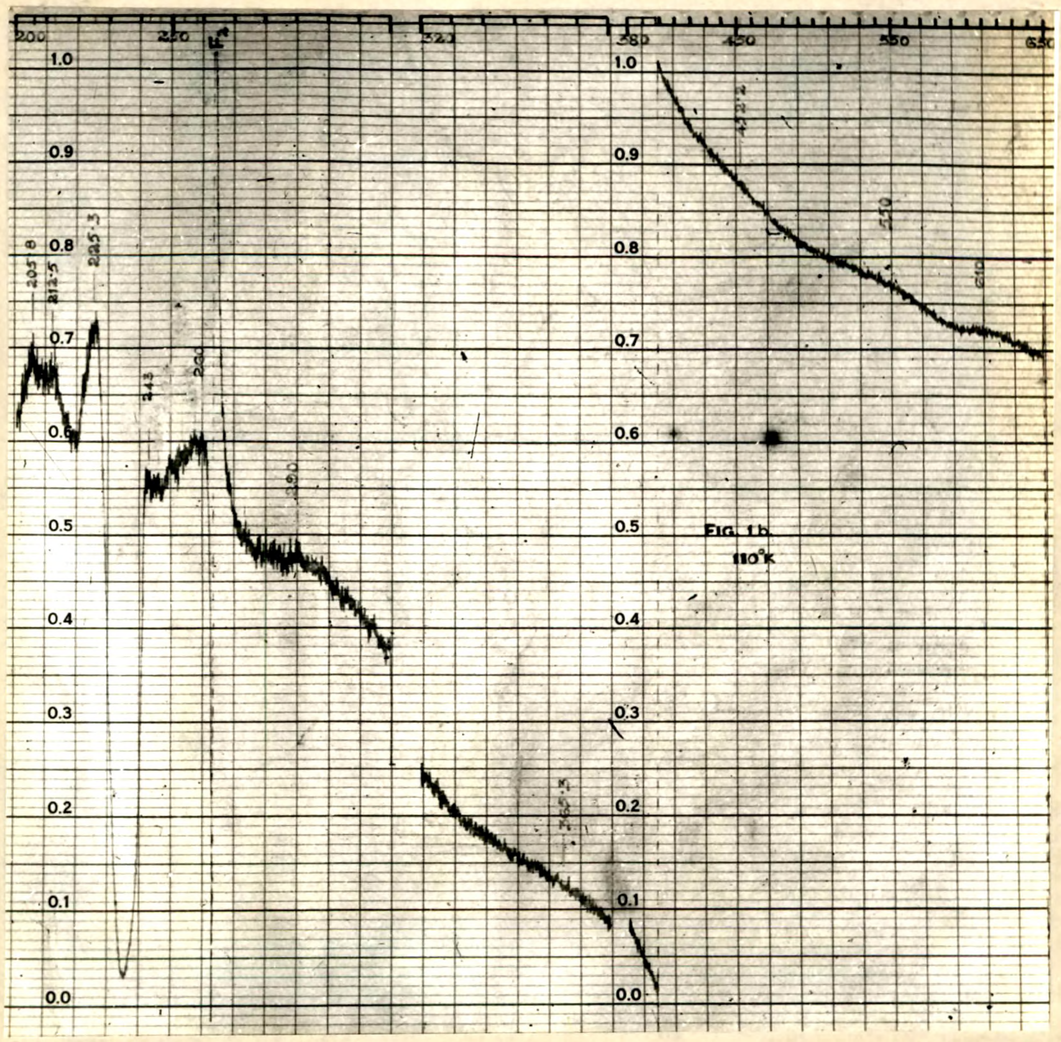

200
250
F_2
320
380
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
205.8
212.5
225.3
243
260
290
365.3
432.2
550
610

FIG. 1b.
110°K

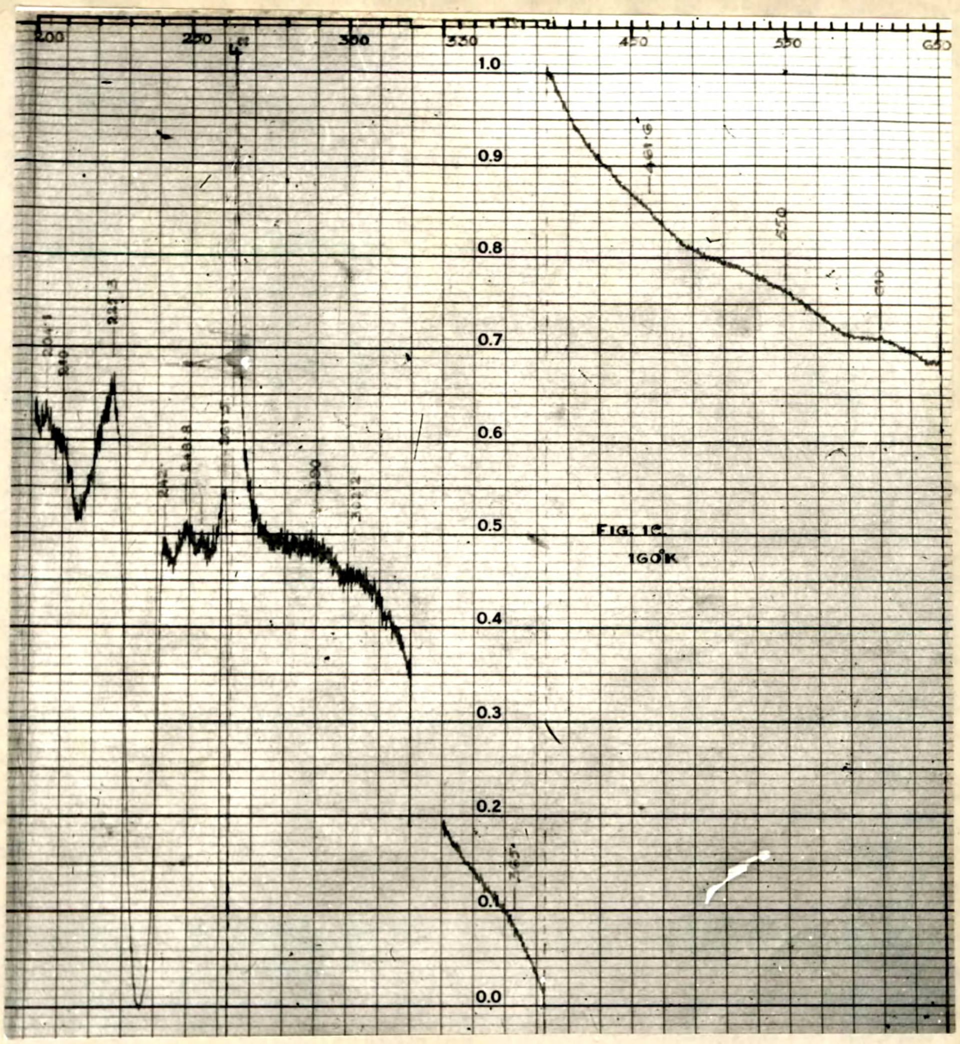

200
250
300
350
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
204.1
210
222.3
242
248.8
261.5
280
302.2
365
461.9
550
610

FIG. 1C
160°K

When the specimen is heated to 190° K (fig. 1d) the absorption bands at 205 and 248 mμ vanish and the band at 214 becomes sharp. A new weak absorption around 325 mμ is discernible. The remaining bands emerge with little changes in their intensities.

Heating the specimen to 240° K (fig. 1 e) brings about some interesting development in the spectrum. There is a small but sharp rise in the F-band region around 535 mμ and in the ultraviolet region the band at 290 mμ undergoes a pronounced enhancement in its intensity. There is a general increase in the absorption below 290 mμ and the absorption band at 205 mμ re-appears.

When the specimen is warmed to 270°K (fig. 1f), the sharp absorption band at 535 mμ vanishes and the one at 290 mμ is considerably suppressed although there is overall increase in the absorption in the range examined. Two new absorption bands at ~ 435 and 490 mμ are clearly seen. The absorption at 205 has become quite sharp.

On warming the specimen to 325° K (fig. 1g) the twin peaks at 435 and 490 mμ disappear and there is a general decrease in the intensities of all the remaining absorption bands. A shift in the absorption band at 225 mμ to 230 mμ is apparent.

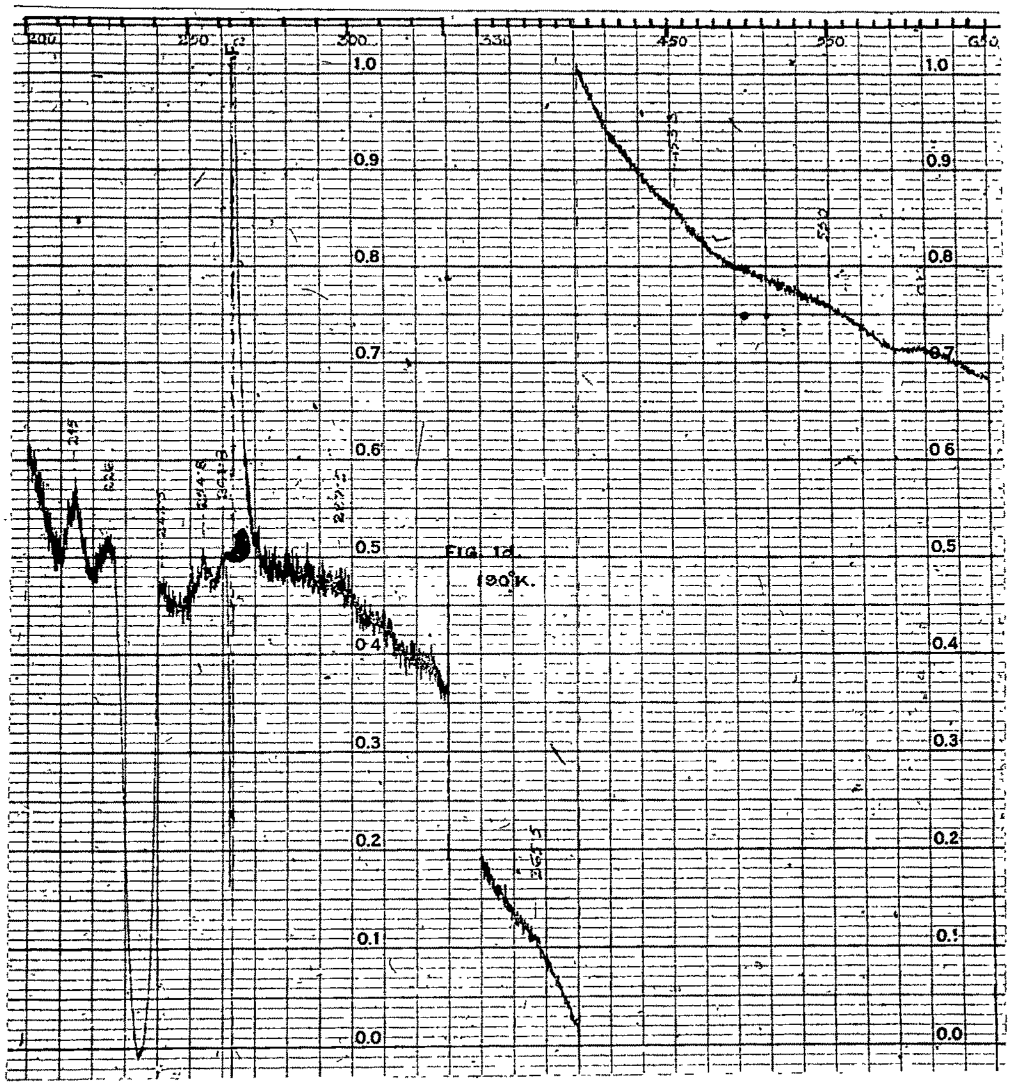

200
250
300
330
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
254.8
261.3

FIG. 14.

190°K.

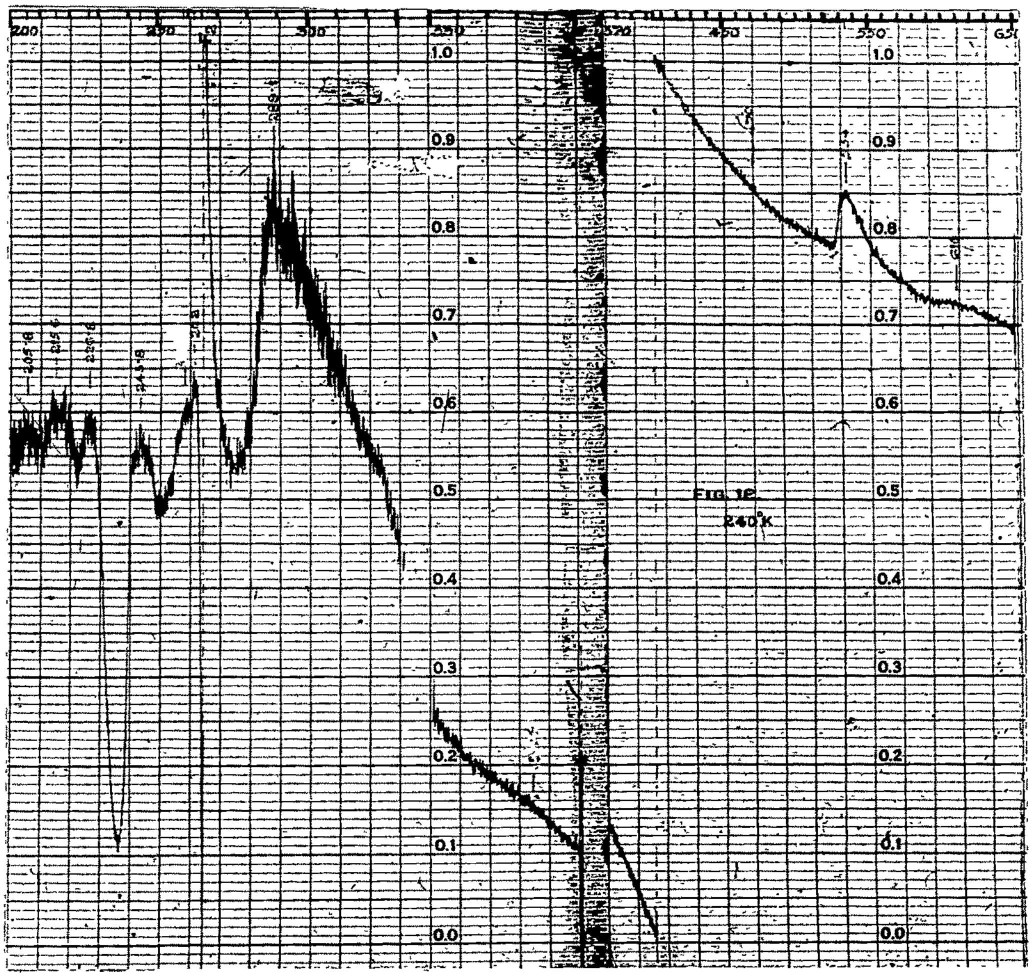

200
250
300
350
370
450
550
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
205.8
215.6
226.8
245.8
271.8
289.4
610

FIG. 12
240°K

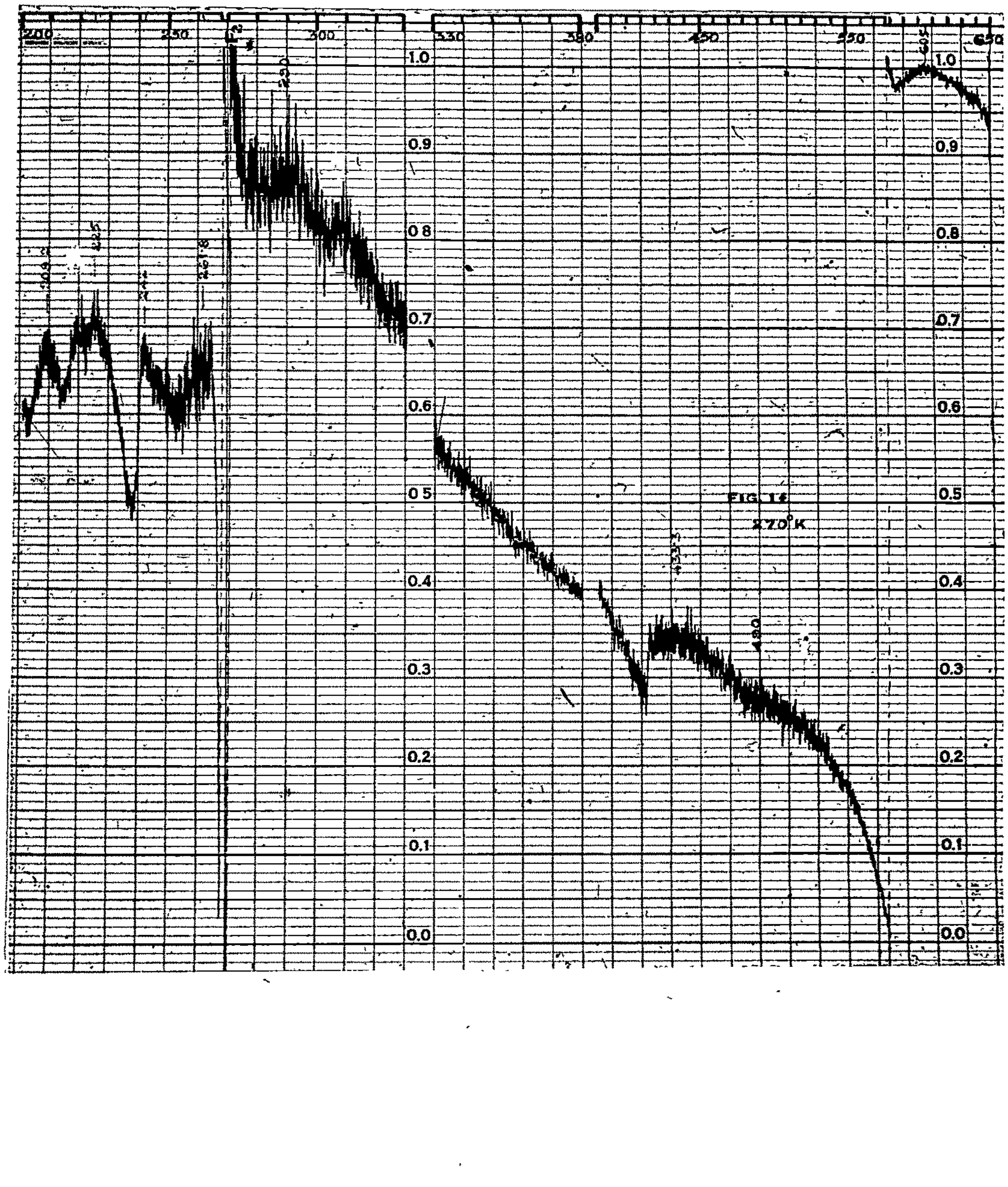


FIG. 14

270°K

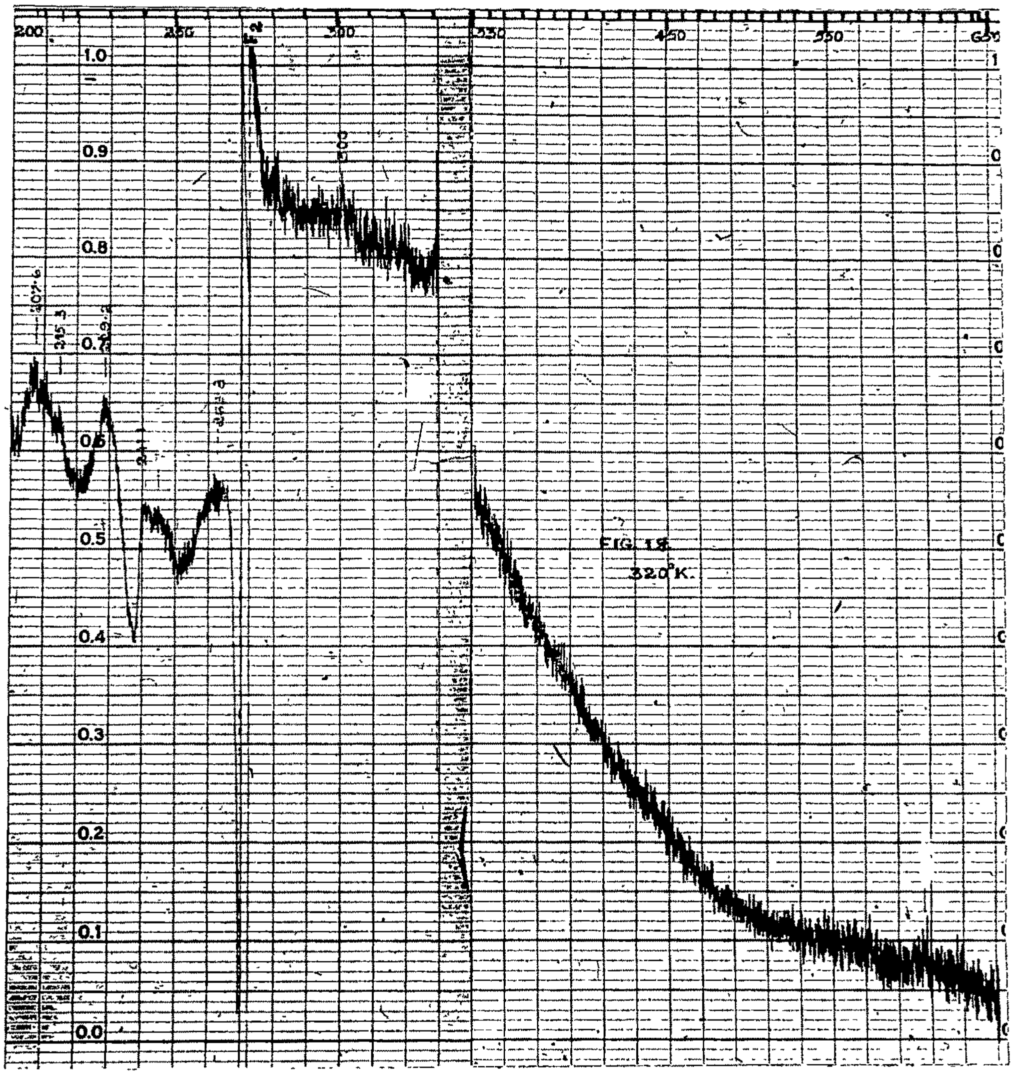

200
250
300
350
450
550
600
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
207.6
215.3
229.2
241
262.3
300

FIG. 18

320°K.

When specimen is heated to 360° K, there is marked decrease in the sharpness of 242 and 260 mμ bands and significant changes in the V_2-V_3 region are observed.

Specimen II :

The absorption spectra for specimen II are less complicated compared to those for specimen I. However, the changes in the intensities of the observed absorption bands, with respect to various annealing temperatures, follow more or less the same pattern.

Before irradiation, at 140° K, one observes absorption bands at 214, 242 and 260 mμ (fig. 2a). It is worth noting that the sharp and prominent absorption band at 225 mμ observed in specimen I is conspicuously absent in specimen II.

After irradiation, at 140° K, the observed bands undergo marked decrease in their intensities and weak absorptions at ∽ 205, 300, 365 and 550 mμ appear (fig. 2b).

Warming the specimen to 230° K (fig. 2c) leads to slight increase in the intensities of 214, 242 and 260 mμ bands, disappearance of 205 mμ band and emergence of a band at 290 mμ.

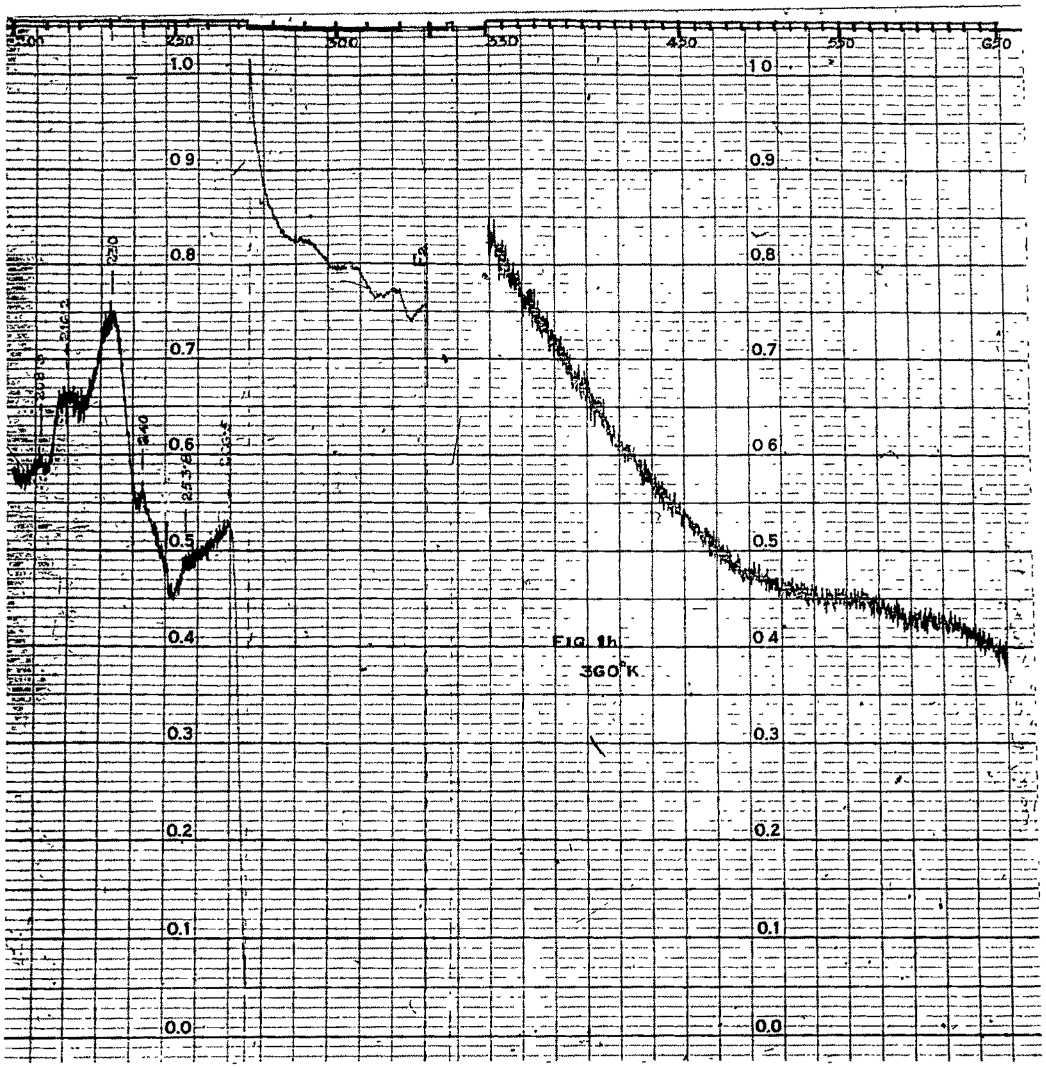

200
250
300
350
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
208.9
216.2
230
240
253.8
263.4
52

FIG. 1h

360°K.

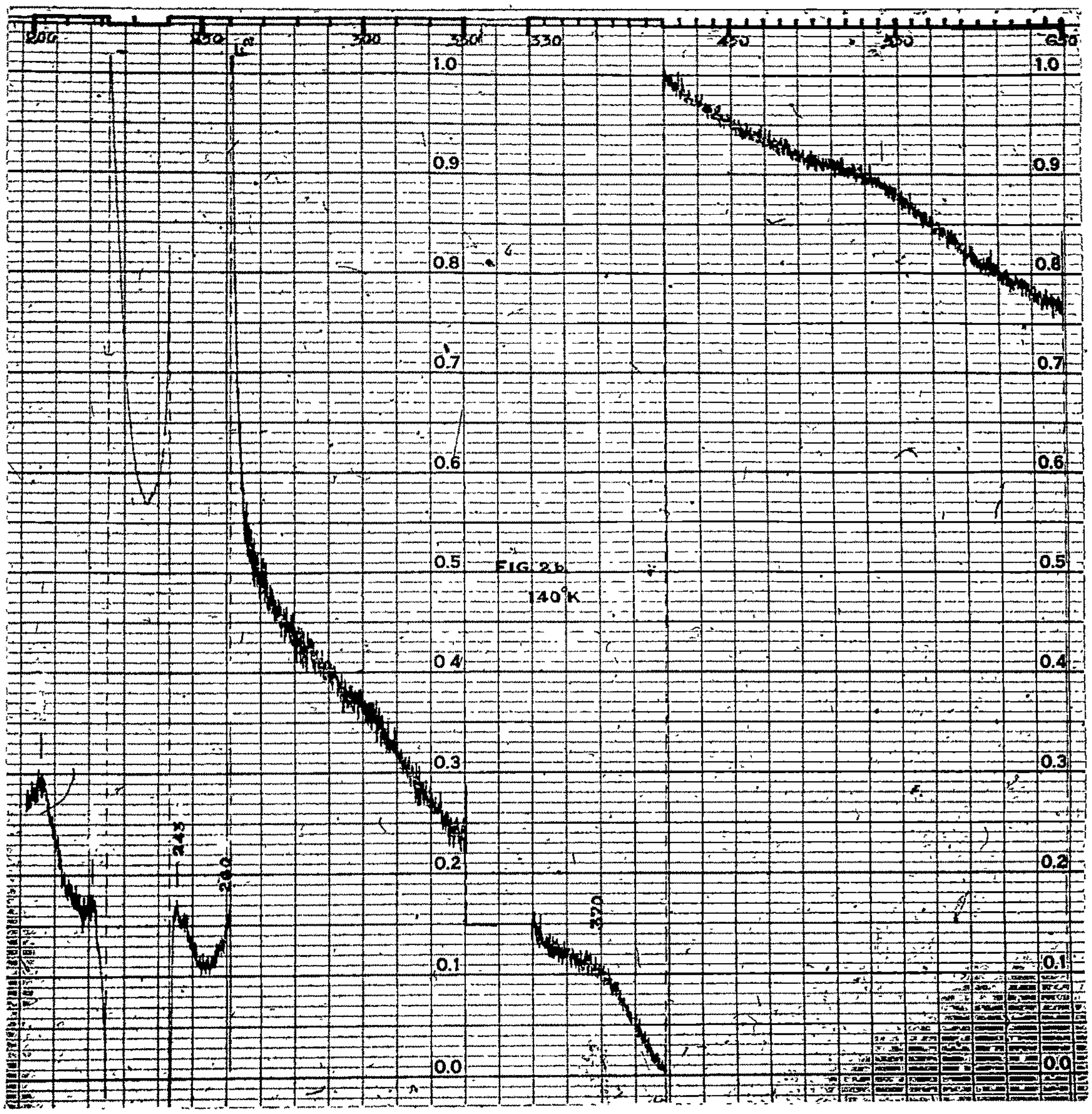

200
250
300
350
330
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
243
260
320

FIG 2b

140°K

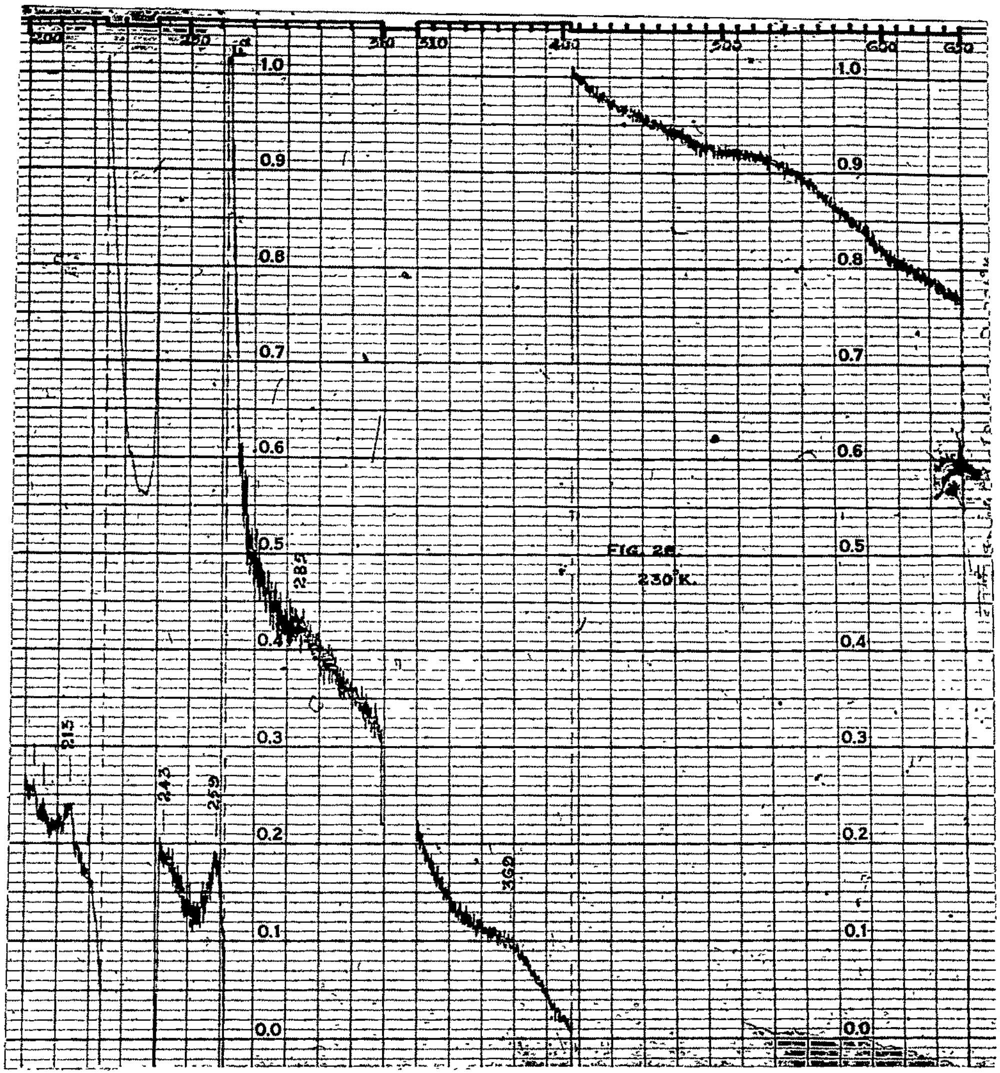

200
250
310
510
400
500
600
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
215
243
259
285
369

FIG. 28.
230°K.

When the specimen is heated to 260° K (fig. 2d) a sharp absorption at 575 mμ in the F-band region is observed as in specimen I. A further increase in the intensities of 242 and 260 mμ bands and in poorly resolved bands at 205 and 214 mμ is observable.

Heating the specimen to 325° K (fig. 2e) decreases the intensity and sharpness of 242 and 260 mμ bands . The band at 205 reappears and instead of 214 mμ there is a band at 220 mμ.

On warming the specimen to 360° K (fig. 2f) the sharpness of 242 and 260 mμ bands decreases further and additional changes in the V_2-V_3 region take place.

In the analysis of the above results, attempts are made to suggest models for the centres associated with some of the absorption bands. The proposed structures for the absorption centres are either in the form of modifications of the previously suggested models or constitute new suggestions. Barring the absorption bands at 225 and 260 mμ, the absorption bands in KCl:Tl reported by Delbecq et al[19] and observed in the present work are assumed to originate in the centres proposed by them. The bands observed will be discussed in the following sections either singly or

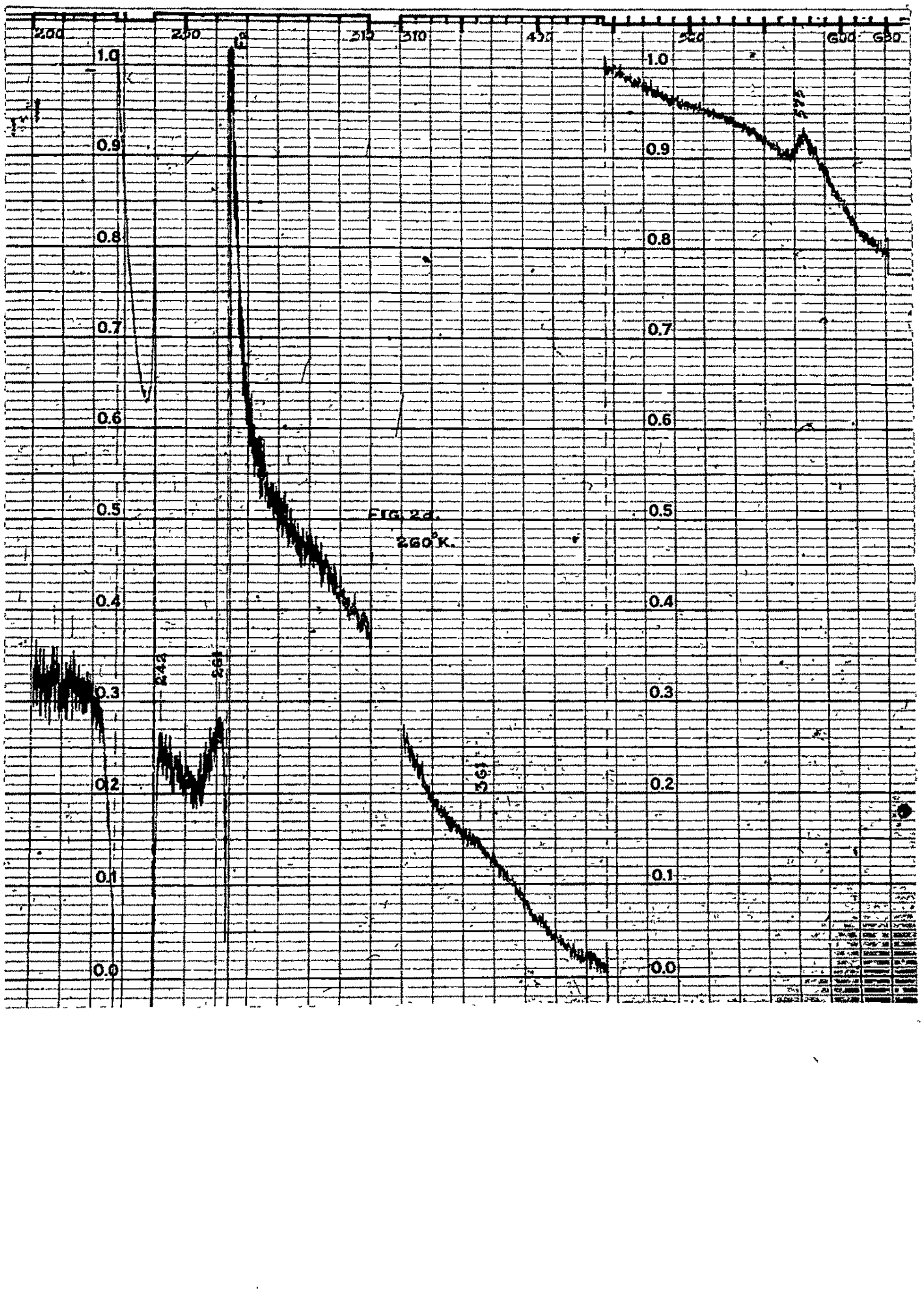

200
250
310
310
400
500
600
620
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
242
263
361
575

FIG 2a.
260°K.

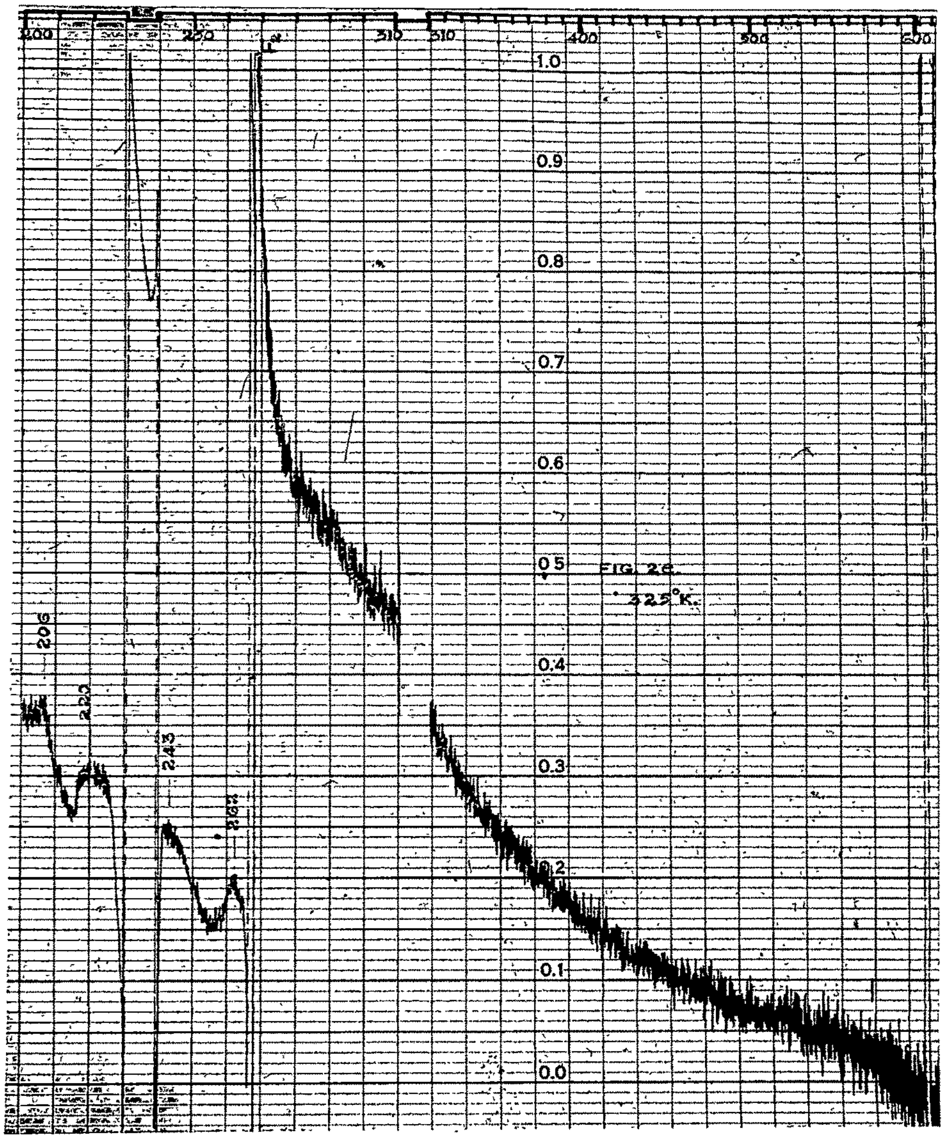

200
250
310
310
400
500
600
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
206
220
243
262

FIG. 2e.
325°K.

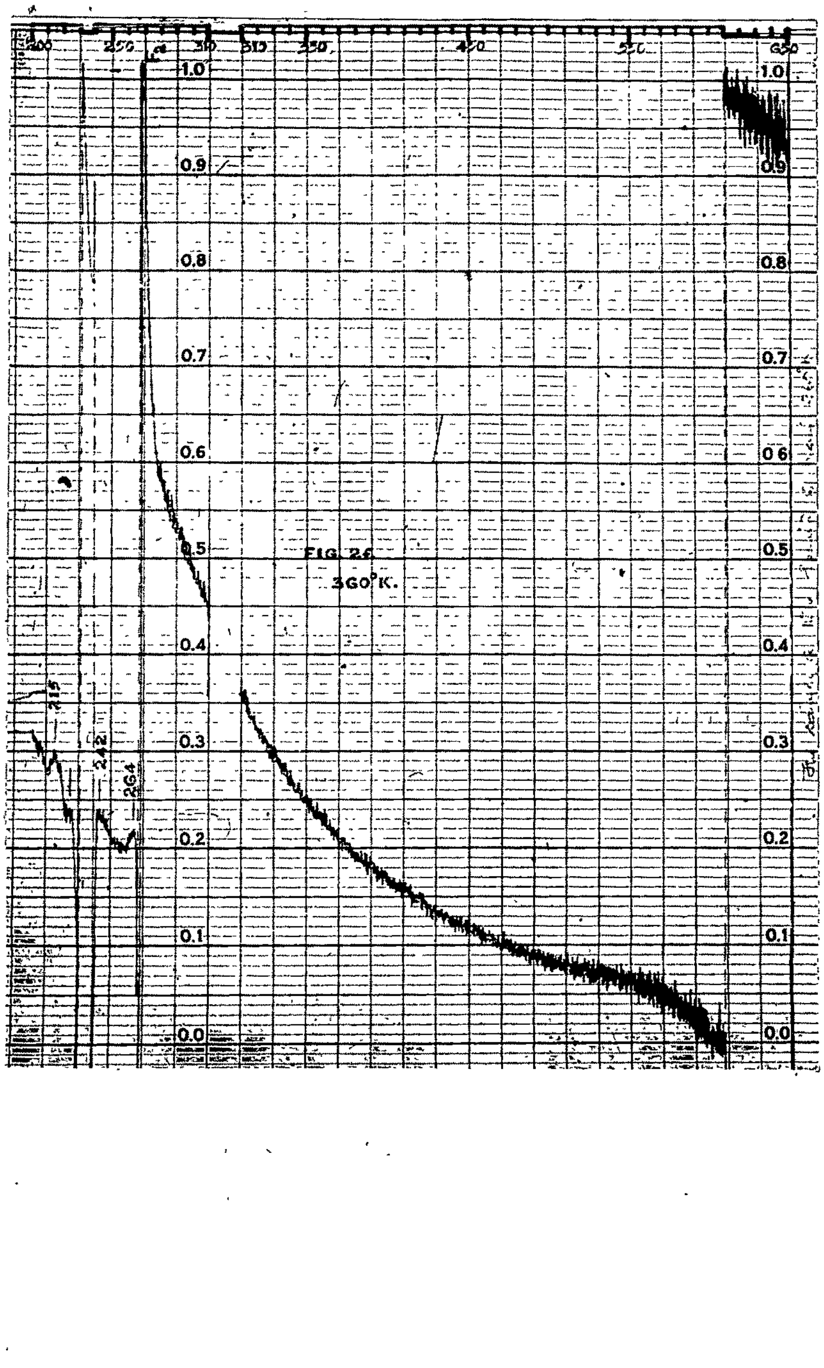

200
250
300
300
350
400
500
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
215
242
264

FIG. 26

360°K.

in group, depending on the convenience.

205 mμ band :

Because of its temperature dependence reported earlier by Forro[116], Seitz [1] suggested that the 205 mμ absorption band in KCl:Tl could be due to forbidden transitions ${}^1S_0 \rightarrow {}^3P_2$ in substitutional Tl^+ ion. Pringsheim[117] considered it to be due to electron transfer from a Cl^- ion to a neighbouring Tl^+ ion, on the basis of the similarity between the absorption of KCl:Tl crystal and aqueous solution of KCl:Tl. Utilizing Seitz' approach, Johnson and Williams[6] suggested that this absorption band could be due to a forbidden transition in Tl^+ ion. However, in their later publication[13] they identified the internal metastable states ${}^3P_0$ and ${}^3P_2$ within Tl^+ ion as principal trapping levels and therefore, according to them, the possibility of the forbidden transition being responsible for the 205 mμ absorption was ruled out. Modifying the calculations of Von Hippel[118] on electron transfer absorption in KCl at 162 mμ by difference in ionization energy of Tl° atom and K° atom, Johnson and Williams[13] found for KCl:Tl an absorption at 210 mμ which was suggested to be in close agreement with 205 mμ absorption.

Later work however, revealed that this band can be found in all synthetic KCl crystals grown without the intentional addition of impurities. Akpinar[119] studied the effect of various additions and atmospheres on this band in KCl and concluded that it was due to compounds containing oxygen. Experiments by Rolfe[120] and by Etzel and Patterson[82] have shown that most synthetic crystals (melt-grown) of alkali halides contain a substantial concentration of OH^-ions built into the lattice. They found that the absorption band is proportional to the concentration of hydroxyl ions in the crystals. This band has been called by them as the "OH" band. With more recent work by Patterson and Kabler[121], OH^- emerges as rather well understood system in so far as its ultraviolet optical properties are concerned.

It is therefore believed that the 205 mμ band, observed in KCl:Tl, is not the characteristic of thallium but owes its existence to the presence of OH^-ions in KCl crystal.

214 mμ band :

This band has been reported in the excitation spectra of heavily-doped KCl:Tl by Ewles and Joshi[11] and Patterson[9]. They found that the band grows as the thallium concentration increases. Ewles and Joshi argued that since 214 mμ band also appears in absorption of KCl:Tl crystal and aqueous solutions containing thallium, whatever the anion, Fromherz and Lih's[122] conclusion that it is due to a transition in Tl^+ ion must be accepted. As mentioned above, it is now a well established fact that laboratory grown alkali halide crystals have OH^- ions unavoidably present in them. Further, it is known that in pure water a certain number of OH^- ions are present as a result of the reaction $H_2O \rightleftarrows H^+ + OH^-$. In view of the possible secondary reaction of Tl^+ ions with water in aqueous solution of KCl:Tl (with lower halide concentration) it is suggested that instead of isolated Tl^+ ion one should consider Tl^+-OH^- complex to be responsible for 214 mμ absorption in KCl:Tl crystal. The 214 mμ in KCl:Tl crystal can then be either due to transition between the electronic states of the Tl^+ ion adjacent to an OH^- ion or due to electronic transfer from OH^- ion to neighbouring Tl^+ ion. The latter possibility is ruled out since such an electron transfer would create Tl° atom which is suggested to act as an efficient trap for the electron near liquid nitrogen temperature[19, 123, 124, 72] In partial modification of the concept advanced earlier,[11] it is therefore suggested that 214 mμ absorption in KCl:Tl crystal, observed before excitation, may be due to electronic transitions in the internal "perturbed" states of the Tl^+ ions replacing K^+ ions in the lattice. The perturbation is caused by the OH^- ion on adjacent site. Just as hydroxide, when present as $Ca(OH)_2$, does not contribute to 205 mμ band in KCl[82] so also OH^- ion partner of the Tl^+ ion may be ineffective in giving rise to this band.

Before excitation, both the specimens I and II show a well defined absorption band at ∽ 214 (figs. 1a and 2a). The absorption in this band is considerably suppressed after excitation (figs. 1b and 2b).

Kerkhoff et al [125, 126] and Fischer and Grundig [127] made an extensive study of the photochemical decomposition of OH^- in KCl, KBr and NaCl doped with hydroxyl ions. Illumination into the OH^- band at 80° K generates the U_2 band (interstitial hydrogen) and a band lying on the short-wavelength side of the OH^- band. This band is believed to arise from substitutional O^-. Both of these bands bleach when the sample is warmed to room temperature. It has been suggested that in KCl the U band is generated by the warm-up instead of the original OH^- band according to the following reaction.

Illumination: $OH^- + h\nu\,(OH^-) \longrightarrow O^- + H^\circ_i$

Warm-up : $2\,H^\circ_i \longrightarrow H_2$

$2\,O^- \longrightarrow O_2 + 2\,e^- + 2$ anion vacancies

e^-+anion vacancy + $H^\circ_i \longrightarrow$ U Centre

On the lines suggested by Kerkhoff, it is believed that the irradiation of the specimen with ultraviolet light results in the decomposition of OH^- ions and consequently suppresses the 214 mμ absorption. The decomposition of OH^- ions will ultimately lead to the formation of U centres in a way indicated above. It is known that as the temperature is increased, the U band broadens and shifts to lower energy. Variation in the absorption between 200-220 mμ observed in the present work, when the specimen is heated to different temperatures, may be, to a certain extent, due to the changes following above reactions and due to changes in the U band absorption with temperature.

The observed growth of 214 mμ band in KCl:Tl with the increase in thallium concentration[11] can be understood on the basis of the statistical interpretation of the formation of the centre in which Tl^+ ion and OH^- ion occupy adjacent sites. In annealed and quenched specimens the Tl^+ and OH^- ions in solid solution will be randomly dispersed in the volume of the specimen. The concentration dependence of the generation of 214 mμ band arises from increased probability of getting a Tl^+ ion as nearest neighbour to an OH^- ion as the concentration of thallium in the crystal increases.

225, 242 and 260 mμ bands:

It is seen from figs. 1 and 2 that these absorption bands show a striking similarity with respect to their narrow linelike absorption. An important clue to the structure of the centres responsible for 242 mμ absorption in KCl: Tl was given by Fromherz et al[122,128÷130]. They found that an aqueous solution of TlCl saturated with KCl had a distinct absorption band with a maximum at 242 mμ. On the other hand, a KCl crystal doped lightly with TlCl exhibited an absorption band at 247 mμ. From their experiments, Fromherz et al concluded that the 242 mμ band observed in aqueous solution of KCl:Tl and the 247 mμ in solid phosphor are identical and hence they originate in the same centre. The absorption in aqueous solution has been ascribed to complex ions of the type $(TlCl_n)^-$. Such ions are characterized by the appearance of narrow selective absorption bands. Because of similarities between the behaviour of the solid KCl:Tl phosphors and their aqueous solutions, the complex ion model was also supported by Hilsch[131] and Pringsheim[117,132]. These authors considered electron transfer processes, in charged complexes of the type $(TlCl_n)^-$, more likely as causes of the absorption bands in KCl:Tl crystal and water solution of KCl:Tl. However, this model relegated into background soon after Seitz[1] published his substitutional thallous ion model for the luminescance centres in thallium-doped alkali halides. Certain optical properties of the phosphor have been described with some success using this model and a configuration coordinate diagram proposed by Seitz and developed quantitatively for KCl:Tl by Williams[2]. Later it was found that the substitutional ion model was inadequate to explain all the experimental data in KCl:Tl phosphor[8,9,11]. The excitation and absorption data on KCl:Tl have clearly demonstrated that besides isolated Tl^+ ions other more complex centres are active in the A and B band regions of Seitz' terminology. In KCl:Tl the spectral positions of A and B bands are

247 and 207 mμ respectively. Patterson[4] observed that single symmetric absorption band, in the A region in KCl:Tl, found at low temperatures became quite asymmetric upon warming to room temperature. This appeared to be due to the growth of a second band at 253 mμ. From the abrupt shift of the A band which accompanies the change in structure from NaCl-type to CaCl - type at high pressures, it was suggested that 247 mμ band might arise from single Tl^+ ions surrounded by Cl^- ions in CsCl arrangement while the 253 mμ band might be due to an isolated Tl^+ in an NaCl arrangement. In addition to these bands which appear in absorption, an additional band at 262 mμ appears in the excitation spectrum of KCl:Tl for the visible emission[6,7,8]. Since the emission due to 262 mμ excitation varied as the square of thallium concentration, it has been suggested that 262 mμ band arises from pairs of nearby thallous ions called dimer centres $(Tl^+)_2$.

From their excitation spectra measurement of KCl:Tl crystals, Ewles and Joshi[11] suggested that the absorption bands observed in aqueous solution of KCl:Tl are additionally observed in the spectra of solid KCl:Tl phosphor if the phosphor has very high thallium content. Results obtained in the present work substantiate this hypothesis as seen from fig. 1c wherein the 248 mμ absorption, attributed to isolated substitutional Tl^+ ion, appears as a well defined band by the side of 242 mμ absorption. To account for the observed effects, Ewles and Joshi concluded that there should be more than one species of Tl centres in the solid phosphor if the concentration of thallium is very high. Some of these centres may be substitutional Tl^+ ions either isolated or having other substitutional Tl^+ ions in the neighbourhood and some may be in the aggregated states of the type $(TlCl_n)^-$ at special sites such as dislocations or grain boundaries.

It is suggested that the 225, 242 and 260 mμ bands presently discussed are closely related to complex ions of $(TlCl_n)^-$ type. In order to test the feasibility of the models suggested it would be worthwhile to consider the possible manner in which incorporation of thallium and chlorine take place in specimens I and II. The method utilized in the preparation of these specimens consisted of enclosing KCl crystals and TlCl powder in a hard glass tube which was then sealed and heated to around 550°C. Since the annealing temperature was sufficiently high, the KCl crystal was actually heated in the atmosphere of TlCl vapour. Thallium halide molecules are very loosely bound in the excited state and hence the TlCl molecule may get thermally split up into two neutral atoms[133]. Heating of KCl crystal in the atmosphere of Tl^o and Cl^o atoms would lead to the adsorption of these atoms on the surface of the crystal. The adsorbed Tl^o and Cl^o atoms may diffuse to the interior of the crystal and subsequently transformed into Tl^+ and Cl^- ions. As a result of high temperature annealing and subsequent rapid cooling most of the thallium and excess chlorine will be retained by the specimen in widely dispersed state. It is suggested that the mechanism of introduction of excess halogen in alkali halides may not be similar to that accepted in the case of excess alkali introduction. This point will be dealt with on the basis ofthe available information.

Except for the initial work extensively carried out by Mollwo[134,135] a survey of the literature shows that comparatively little work has been done on the V bands formed by additive coloration. Following the discovery that X-irradiation of the alkali halides can produce absorption bands in the ultraviolet region of the spectrum[56], emphasis was placed on the study of radiation-induced V bands. It is easier in many respects to generate these bands by irradiation than by additive coloration. Major advances have been made in understanding the radiation damage processes in alkali halide crystals over the past few years. Radiation damage in alkali halides produces, in addition to the F band in the visible, various optical absorption bands in the ultraviolet region called the V bands. Seitz[37] proposed that the V bands were due to holes trapped at cation vacancies or vacancy aggregates. However, Seitz' models of the V centres are now considered extremely doubtful. The development and verification of V centre models have been the outgrowth of spin resonance studies coupled with polarized light measurements. These measurements have conclusively established that some of the ultraviolet bands formed by irradiation at low temperature are electron-deficit halogen-molecule centres, which complement the F centre in one way or another[124,136-138]. This suggests that, unlike the alkali metal, there is a strong tendency for the halogens to form a molecular bond. The concept is therefore gaining ground that it is more appropriate to regard the V centres as halogen molecules or molecular ions which are incorporated in the lattice in various ways[139,66,67,140,141,70]. Only recently has the role of interstitials in the radiation-damage processes of the alkali halides has been appreciated. It has been suggested, with the help of a large body of experimental evidence, that Frenkel pairs are created in the negative ion sub-lattice by the displacement of ions from their normal sites[59,60,70,142-150]. The simple negative ion interstitial becomes unstable at temperatures near 25°K and the neutral interstitial associated with the H-centre at temperatures near 40°K. The stability of interstitials at higher temperatures, as indicated by volume expansion and lattice parameter measurements, is associated with the formation of various halogen "molecular" species in the crystal matrix. These "molecules" may be assoicated with point defects and impurities in the positive ion sub-lattice. More recent experiments[142,151,152] have tended to confirm the hypothesis that interstitial centres were produced even in the case of room temperature irradiation. Thus it is now believed that Frenkel-pair production occur under ionizing radiation at all temperatures and that many of the observations indicating more than one type of F centres could more probably be attributed to the presence of different interstitial species. The Frenkel-pair production does not involve the sub-lattice of alkali ions, that is, no alkali ion vacancies or interstitials need be formed and no trapping of charge by defects that may exist in this sub-lattice is required.

Since the radiation damage process is now believed to produce primarily negative ion vacancy-halogen interstitial pair and further since the V centres are regarded mostly as species of halogen molecules or molecular ions, one would be justified in assuming that the basic reaction in the production of V bands, either by X-irradiation or by additive coloration of alkali halides with excess halogen, is the creation of interstitial-vacancy pairs. It is therefore presumed that in the specimens I and II of the present work interstitial Cl^- ions may have been produced.

Because of the striking resemblence in the absorption at 242 mμ between water solution of KCl:Tl and solid KCl:Tl phosphor, it is suggested that the absorption at 242 mμ and two others of apparently same nature, at 225 and 260 mμ, originate in the complex ions of the type $(TlCl_n)^-$. It is proposed that such complex ions may be formed in the crystal if its configuration, involves either an interstitial Cl^- ion or ions. The substitutional Tl^+ ion with its surrounding six nearest-neighbour chlorine ions forms a configuration which is electrically neutral relative to the KCl matrix. Hence the occupation by a Cl^- ion of the interstitial site, most probably coplanar with the Tl^+ ion and the surrounding four Cl^- ions, will transform the above neutral complex into charged complex of the type $(TlCl_n)^-$. Possibility of the complex ion having a planar configuration has been suggested earlier by Delbecq et al, from a different standpoint, in the case of KCl:Ag[153] and later extended to KCl:Tl[19] to explain the occurrence of 220 and 260 mμ absorption bands.

The following plausible models are suggested for the centres responsible for 225,242 and 260 mμ absorption bands. It is proposed that the 242 mμ absorption band arises in a species of centres each of which contains one substitutional Tl^+ ion, six Cl^- ions surrounding the Tl^+ ion and one Cl^- ion at interstitial position coplanar with the Tl^+ ion and the surrounding four Cl^- ions. The 260 mμ absorption band is suggested to originate in a species of centres each of which has a configuration similar to the one associated with 242 mμ band except that instead of a single Tl^+ ion a pair of nearby substitutional Tl^+ ions is involved. The 225 absorption band is also suggested to be due to a centre similar to the one proposed for 242 mμ band however, the difference is in the number of interstitial Cl^- ions. In this case, instead of one, two interstitial Cl^- ions are suggested. Thus each one of proposed models can be looked upon as species of centres equivalent to a complex ion $(TlCl_n)^-$ in the crystal matrix. The choice of two interstitial Cl^- ions for the centres associated with 225 mμ absorption band is made on the basis of results obtained in the present work. This band is observed in the absorption of specimen I which has been subjected to prolonged annealing at elevated temperature during its preparation. The band is absent in the absorption spectrum of specimen II which was annealed at the same temperature but for a period nearly half of that for specimen I. Annealing over a longer duration will increase the probability for the creation of two interstitial Cl^- ions near a given Tl^+ ion.

From figs. 1(b) and 2(b) it is observed that the absorption bands at 225,242 and 260 mµ undergo decrease in their intensities after irradiation with ultraviolet light near liquid nitrogen temperature. This effect is attributed to the creation of Tl^o atoms in each of the complex ion species due to the transfer of electron from interstitial Cl^- ion to the neighbouring Tl^+ ion, during irradiation. The absorption of a photon results, then, in an excited centre consisting of an interstitial chlorine atom and an electron localized on the Tl^+ ion. The loss of electron by the interstitial Cl^- ion will give rise to a polyhalide ion or halogen molecular ion $(Cl_n)^-$. In a chemical sense, an interstitial halogen atom is equivalent to an H centre. (An H centre comprises a Cl_2^- molecule-ion situated at a single halide ion site alongwith two halide ions adjacent to this site, all lined up in the <110> directions). The neutral interstitial (halogen atom) is known to become unstable at temperatures near 40°K. Hence it is suggested that the molecular ions presently proposed may be gaining in stability due to their association with impurity ions, other point defects or dislocations. Since 225, 242 and 260 mµ bands are generated with high concentration of TlCl and rapid cooling of specimens, the centres responsible for these bands may be situated at special sites such as internal surfaces or dislocations which would be expected to be developed under such conditions. By virtue of their associated elastic strain field, dislocations may act as very effective interstitial traps.

It is not possible to speculate on the structure of the different molecular ion species, formed after irradiation, until more information is available. The changes in the absorption spectra when the specimen is warmed to different annealing temperatures will now be discussed with reference to specimen I. After irradiation around 110°K (fig. 1 b), besides decrease in the intensities of 225, 242 and 260 mµ bands, one also observes poorly resolved bands in the region between 240 to 260 mµ. There are bands in this region which are indicative of the presence of isolated Tl^{+} ions. Appearance of a weak band at 290 mμ suggests the formation of a low concentration of Tl^{++} ions. When the specimen is warmed to 160°K (fig. 1 C), besides other bands, the spectrum consists of the Tl^{+} ion bands at 248 and 254 mμ, the Tl^{++} ion band at 290 mμ and Tl^{0} atom band at 300 mμ. The formation of isolated Tl^{0} atoms may be due to thermally induced migration of a fraction of molecular ions from their sites during warm-up. In a perfect crystal, the mobility of the molecular ion can be induced by thermal reorientation which merely involves the reformation of the covalent bonds with other halogen neighbours already in space. In such a case, no ionic jump would be necessary. In the present case, the suggested molecular ions become mobile probably due to diffusion of Cl^{0} atom from its site. As the temperature is raised further to 190°K (fig. 1 d), the conspicuous change in the spectrum is the disappearance of Tl^{+} ion band at 248 mμ. It has been experimentally detected that the V_k centre (Cl_2^-) begins to undergo translation motion in the crystal starting at 170°K. A weak absorption at 365 mμ indicates the formation of a low concentration of Cl_2^- centres. They may also be playing their role, though not important, in bringing about the configurational changes in the absorption centres. When the specimen is heated to 240°K (fig.1 e), one observes a pronounced band at 290 mμ and a small but sharp rise at 535 mμ in the F-band region. With the increase in temperature, the diffusion rate of the molecular ions would increase and it is apparent that a large fraction of these molecular ions is trapped at Tl^{+} ions to form Tl^{++} ions. A fraction of the molecular ions which have migrated to the Tl^{o} atoms may get annihilated by recombination with electrons from Tl^{o} atoms and thereby increase the intensities of the absorption bands at 225, 242 and 260 mμ bands as observed in fig. (1 e). The origin of the sharp band in the F band region will be discussed independently. On warming the specimen to 270°K (fig.1 f), the absorption at 290 mμ is considerably suppressed and two new absorptions at 435 and 490 mμ are observed. It may be noted that the absorption at 290 mμ, indicative of the presence of Tl^{++} ions, mainly subsides after heating the specimen to 270°K. Since above about 200°K the migration of vacancies become operative, the absorption bands at 435 and 490 mμ may be due to association of single +ve ion vacancies or aggregates of vacancies with Tl^{++}ions. As will be discussed in the following section, the absorption in the F band region is believed to arise from M centres. These centres decompose on warming the specimen to 270°K as is evident from the disappearance of the peak at 535 mμ. An electron in an aggregate centre will be irreversibly removed if it be induced to recombine with the hole. A Tl^{++} ion is a likely centre for this and hence it is suggested that a fraction of the Tl^{++} ions are annihilated by electron capture. The capture process would involve creation of excited thallous ions in the $^3P_1$ state. The excited thallous ions then emit the characteristic 298 mμ emission. The electron capture at Tl^{++} ions and consequential recombination luminescence is probably the cause for the fluctuations in the movement of the recorder pen in the wavelength region around 290 mμ as observed in fig.(1 f). Increase in the intensities of 225,242 and 260 mμ bands suggests further destruction of molecular ions by recombination with electrons from Tl^{o} atoms. When the specimen is warmed to 325°K (fig. 1 g) the twin absorption bands at 435 and 490 mμ vanish probably because of thermally induced dissociation of vanancies from Tl^{++} ions. The bands at 290 and 300 mμ, belonging to Tl^{++} ions and Tl^{o} atoms respectively, also undergo reduction in their intensities to the extent of losing their identities. Further heating the specimen to 360°K (fig.1.h) markedly changes the absorption in the V_2-V_3 region and weak absorption bands around 320 mμ are observed.

In his study of the absorption of TlCl vapour Butkow[154] reported absorption bands around 320 mμ. Hence the absorption bands around 320 mμ observed in KCl:Tl crystal may be due to undissociated TlCl in the lattice.

It is of interest to note that the major changes in the V_2-V_3 region begin to occur at temperature above 250°K when vacancy diffusion becomes significant. Since higher temperature favours marked configuration changes in this region, the diffusion of vacancies may be the main process involved. Further, since $(TlCl_n)^-$ centres appear to become unstable above 325°K, the interstitial Cl^- ion migration, due to release from trap,may also be one of the processes bringing about configurational changes.

Except for the absence of sharp absorption at 225 mμ, the absorption spectrum for specimen II exhibits all the absorption bands observed in specimen I, before irradiation. The variation in the intensities of 242 and 260 mμ bands with temperature is similar to the one observed in specimen I. The prominent growth of 290 mμ band, after heating to around 240°K, observed in specimen I, does not take place in specimen II. Instead however, a small rise at this wavelength is observable. As in specimen I, small but conspicuous rise in the

F band region, when the specimen is heated to around 250° K, is clearly seen. Changes in the V_2-V_3 region become more apparent when the specimen is heated above 250° K. All these results can be interpreted on the lines of those obtained for specimen I.

Absorption in F band region :

Considerable work has been done to determine the nature of the centres which give rise to the R, M and N optical absorption bands in alkali halide crystals. The principal result of this effort has been increasing support for models which describe these centres as aggregation of F centres. Van Doorn and Haven[39] first suggested that the M centre is composed of the simplest F centre aggregation namely, two nearest-neighbour F centres lying along [110] lattice direction. Studies of F and M centre equilibria in both additively[41] and X-ray[155] coloured crystals as well as the results of magnetic resonance[156] investigations have supported the F_2 model of the M centre. For irradiation at room temperature, the concentration of F centre is connected to that of the M centre by a relationship of the form

$$n_M = S\, n_F^2$$

where n_M and n_F are the numbers of M and F centres respectively and S is a temperature dependent proportionality factor. It has been found that for irradiation at liquid helium or liquid nitrogen temperatures the proportionality factor is independent of temperature. This suggests that thermal motion does not play a role in the formation of M centres from F centres, but that an M centre is formed whenever two F centres are created in adjacent sites.

Room temperature irradiation of crystals containing M centres with M light polarized along a [011] direction produces a dichroic F[52] as well as M band indicating that M centre optical transitions underlie the F band[51]. In KCl, the primary transition of the M centre, now called the M_1 band, peaks at 800 mμ. Other transitions of the M centre include the M_2 and M_2' band, which underlie the F band. In KCl, their peak positions are at 556 and 539 mμ respectively.[51] The assumption of "hidden" bands of R and other higher aggregate centres under the F band has been made to explain the various dichroic effects observed.[45]

The broad absorption in the F band region observed after irradiation of the specimen (figs. 1 b and 2 b) may be due to aggregate centre absorption under the F band. It is suggested that the sharp absorption observed in the F band region in figs. 1 e and 2 d is due to thermal aggregation of the centres around 250° K which results in the formation of either M_2 or M'_2 centre. It is probably simpler to remove an electron from an existing F aggregate centre than to synthesize the desired centre from its electronic and vacancy components. Lüty[157] proposed a mechanism for the optical conversion of F→M centres based on the coulomb interaction between an F' centre and an F centre that has lost its electron. The process involves repeated creation of F' centre from F centres via an electron transfer initiated by the F light illumination. At the temperatures for which F-light produces F centre aggregation the F' centre is thermally unstable and will give up its extra electron after some time, returning to its F centre configuration. If only the vacancy is considered, the bleached F centre is essentially an α centre and the process of F → M conversion may be represented as shown below.

$$(F+F) \xrightarrow{h\nu} (\alpha + F') \xrightarrow{\text{Thermally}} (F+F) \xrightarrow{h\nu} \ldots \rightarrow M$$

Rabin[54] observed the thermal growth of the M band near 250° K in KCl irradiated at liquid nitrogen temperature. The F' centre is known to be unstable in the temperature region around 250° K at which this aggregation takes place and hence Rabin suggested thermoluminescent production of F' centre to explain the observed behaviour.

Recent measurement by Farge et al[158] on the creation of M and R centres in LiF also indicate that M centres result from F aggregation due to the migration of centres. However, these workers observe intermediate M^+ (or F_2^+) state and suggest a mechanism that can be represented as below.

$$(F+F) \longrightarrow \alpha + F \xrightarrow{\text{diffusion}} M^+ + e \longrightarrow M$$

The equation, giving Kinetics of this conversion, implies that each reaction obeys first order Kinetics. This means that in these experiments only close α -F pairs form M^+ centres and that the concentration of available electrons is large compared to the concentration of M^+ centres. The authors propose that the attraction between the F centre and an α centre arises from an electron exchange interaction between two vacancies rather than from a polarization of the F centre by the α centre. This mechanism has the advantage of also being able to explain the formation of M centres by thermal aggregation reported earlier by Rabin and also observed in the present work.

The problem of the kinetics of transformation of the M^+ centres into M centres is more difficult. It is clear that this reaction is produced by electrons released in the lattice. Quite likely electrons are released during changes of configurations[159] of interstitials such as the V_4 centre [160,69] or the Hayes and Nichols centre[80]. In the present experiments the thermal release of electrons from Tl° atoms is suggested to be instrumental in effecting $M^+ \dashrightarrow M$ transformation. Evidence in support of this assumption will be presented in the next section.

Absorption of slowly, cooled specimen :

The absorption spectrum of annealed and slowly cooled specimen (specimen III), when measured at temperature near liquid nitrogen, exhibits two prominent bands at 238 and 275 mμ and three weak bands at 210, 248 and 305 mμ (fig. 3 a) When the specimen is subjected to ultraviolet irradiation, at the same temperature, the absorption bands at 238 and 275 mμ disappear and a number of very weak absorption bands appear in the wavelength region 200 to 300 mμ (fig. 3 b). Simultaneously, the absorption at 305 mμ indicative of the presence of Tl° atoms, becomes little more conspicuous. Since the radiation induced absorption bands are very weak and further, since the spectra resulting from pulse annealing give rise to additional poorly resolved peaks, it is not possible to gain information regarding the behaviour of absorption peaks individually. Hence the absorption spectra obtained at intermediate annealing temperatures are not presented for discussion. Fig. (3c) exhibits the absorption spectrum obtained after warming the specimen to 230° K wherein the absorption at 640 mμ is quite apparent. This absorption has been

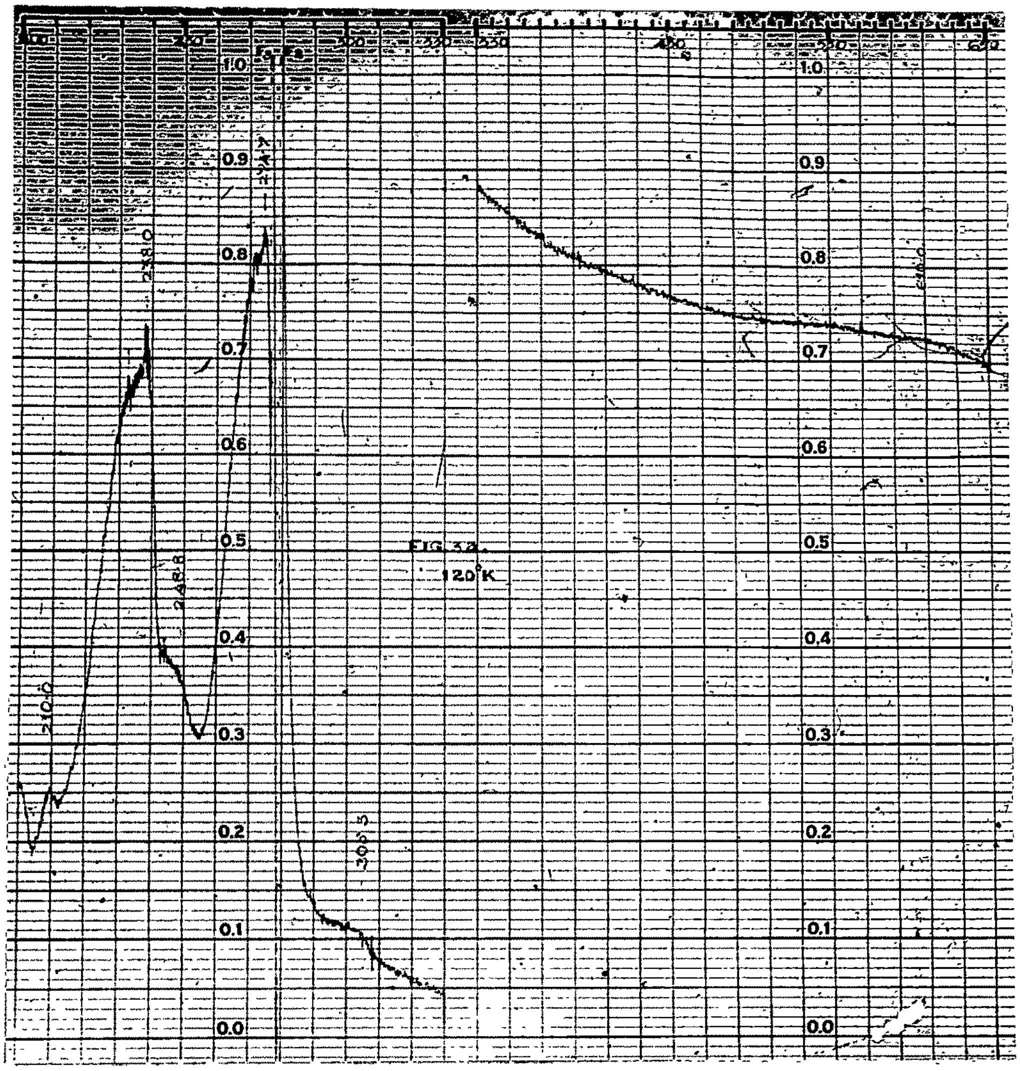

200
250
300
320
350
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
248.0
248.8
210.0
305.5
640.0

FIG 3a.
120°K

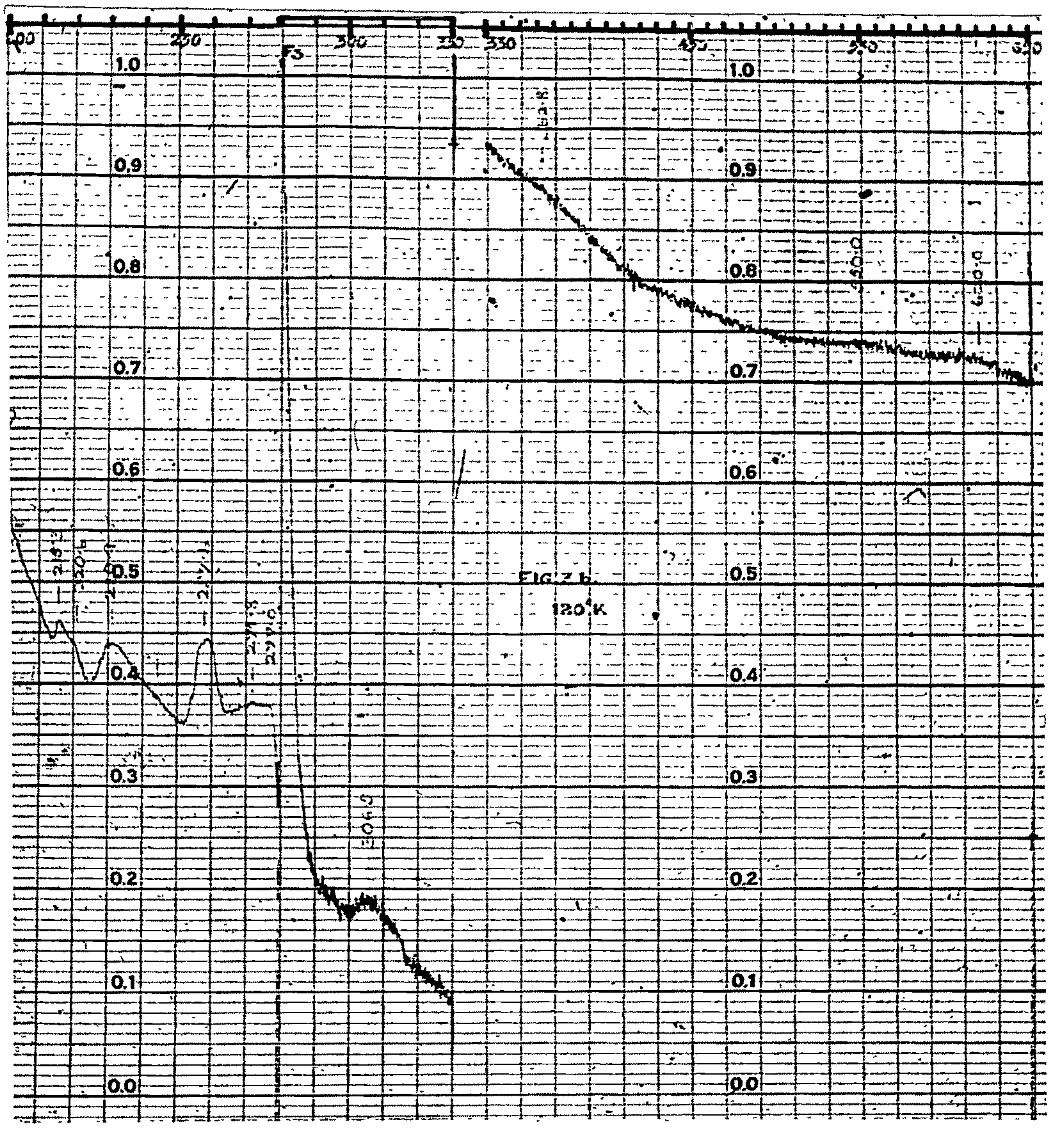

200
250
300
350
350
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
304.0

FIG.2 b.

120°K

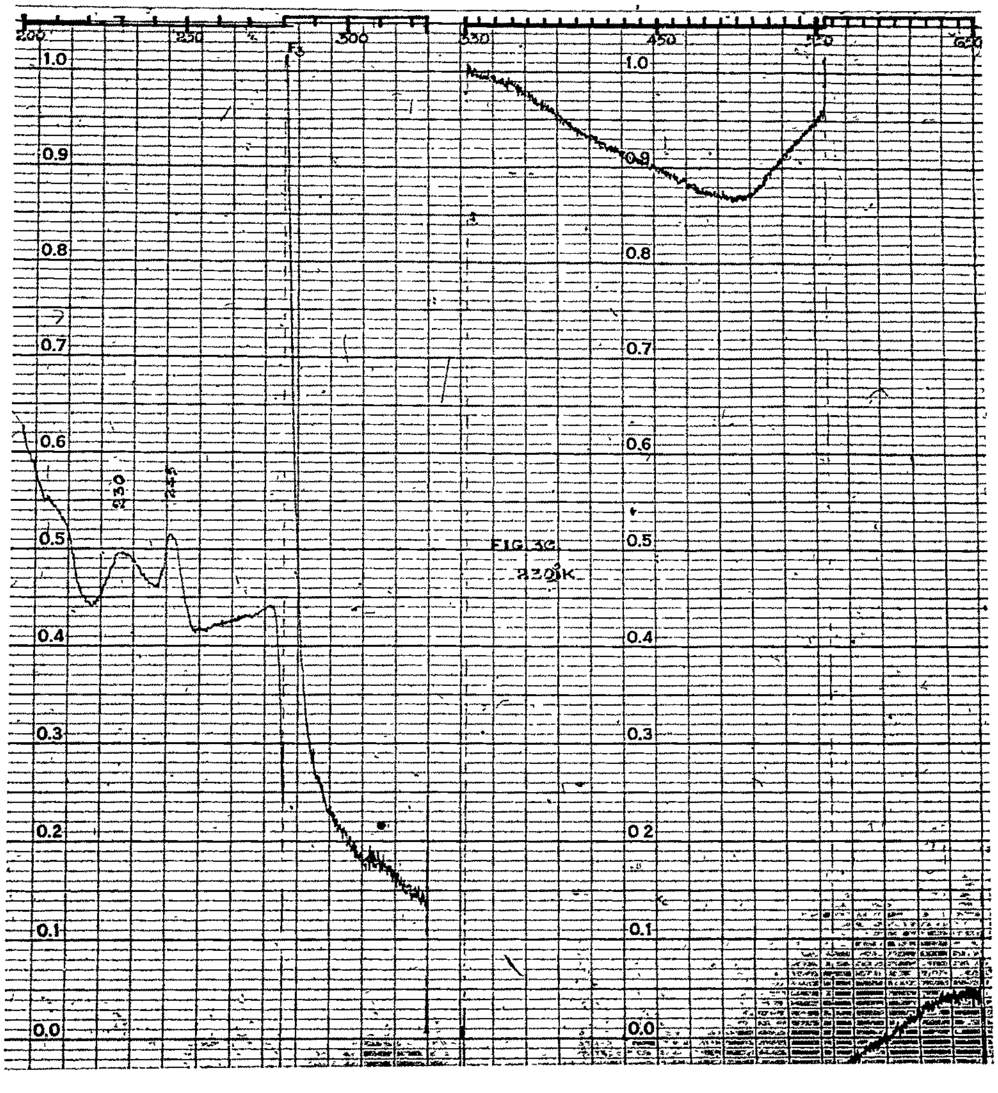


FIG. 3C

230K

200
250
300
350
450
550
650
F3
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
230
245

ascribed by Delbecq et al[19] to Tl° atoms. When the specimen is heated to 270°K (fig. 3d) the absorption at 640 mμ vanishes and a sharp band develops with peak around 550 mμ.

Because of suspected importance of oxygen and hydrogen-containing impurities, Christy et al[161] have studied the effect of annealing KCl crystals in various atmospheres. They observed that samples annealed in ordinary air develop a large absorption band at 197 mμ and smaller bands at 234 and 270 mμ. Annealing Harshaw KCl crystals in moist and dry oxygen, nitrogen, helium and argon atmospheres, Christy et al established that the only one to produce the absorption bands was moist oxygen. The structure of the resulting centres are not known. It can only be said that the centres responsible for these bands are intimately related to the presence of oxygen. In his study of the absorption bands due to colloids, Etzel[162] observed, in additively coloured NaCl crystals, absorption bands due to U centres as well as O_I and O_{II} centres connected with oxygen. The latter two absorption bands were observed to have their peak positions around 230 and 280 mμ. After exposure to ultra-violet irradiation, the U, O_I and O_{II} bands were observed to be considerably suppressed.

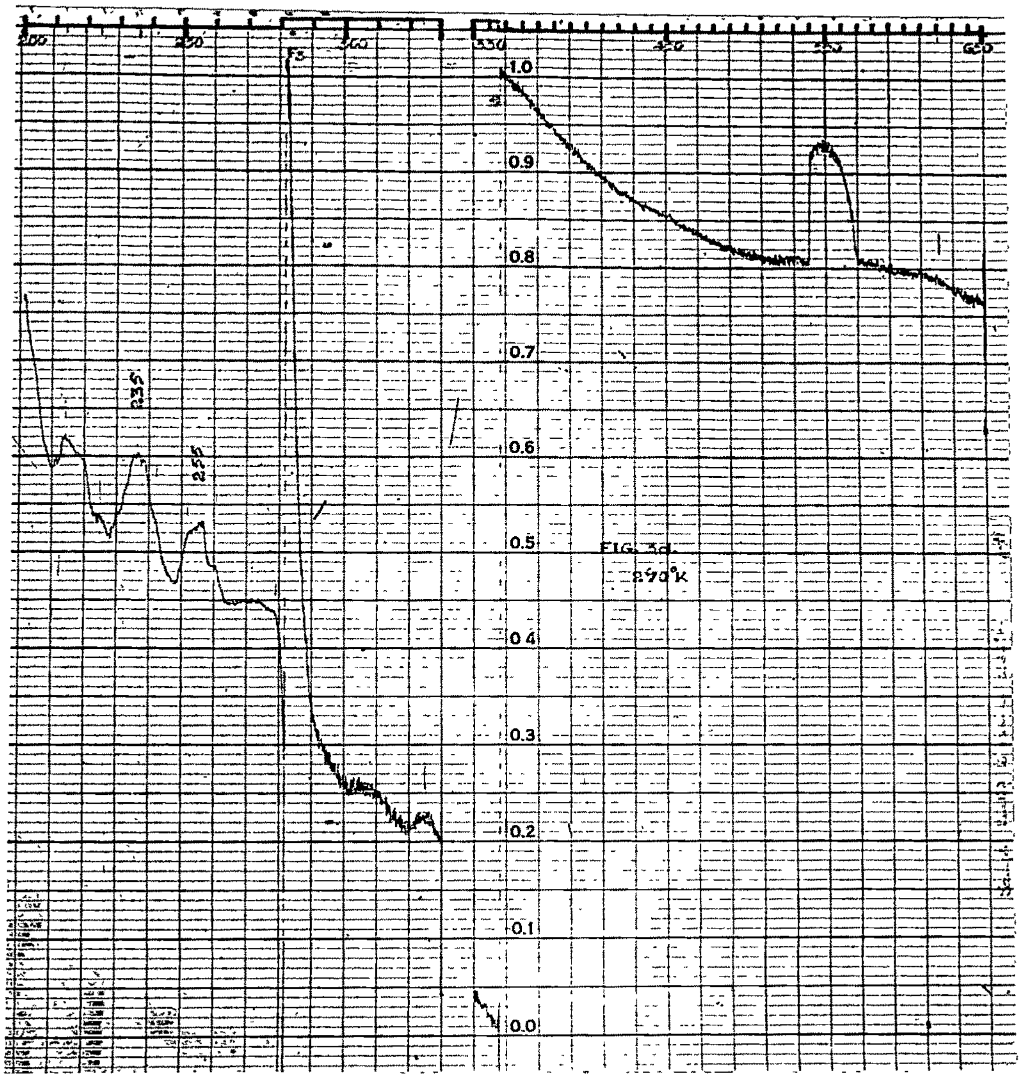

200
250
F3
300
330
450
550
650
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
235
255

FIG. 3a.
290°K

One feature of the centres responsible for 238 and 275 mμ bands observed in the present work, strikingly similar to the hydrogen (U) centres and hydroxyl ion (OH^-) centres, is that after absorption there is a strong tendency for the centres to dissociate. These bands have their peak positions nearly coinciding with those observed previously by Christy et al. It is, therefore tentatively suggested that these bands may be due to centres connected with oxygen. Irradiation with ultraviolet light, near liquid nitrogen temperature, results in the erasure of these bands obviously due to photochemical decomposition of the related centres. On warming the specimen to 230° K (fig. 3d), one observes a conspicuous absorption at 640 mμ attributed by Delbecq et al[19] to the presence of Tl° atoms. In the following absorption run, recorded after heating the specimen to 270° K, the 640 mμ absorption vanishes and a sharp absorption band at 550 mμ appears. The reciprocal relationship between the two absorption bands provides evidence for the suggested ~~Kineetics~~ Kinetics of conversion of M^+ into M. Obviously this reaction is produced by electrons released in the lattice by Tl° atoms.

Slow cooling will induce vacancy agglomeration and hence chances of two negative ion vacancies occupying sites in the matrix at short distance from each other will increase. Besides, in a slowly cooled specimen most of the thallium in solid solution will precipitate out as a separate phase and hence a KCl:Tl crystal of this type will behave like a lightly doped crystal. In such crystals, electrons freed from Tl° atoms will encounter more negative ion vacancies than Tl^+ ions and thus more F centres will be formed. It may be noted that by virtue of their higher electron affinity than potassium, thallous ions have greater capture cross-section for electron than either K^+ or negative ion vacancies next to K^+. Thus, both agglomeration of vacancies and precipitation of thallium out from matrix make the process of M centre formation, by thermal aggregation, more efficient. On this basis, rather prominent development of the M band absorption in slowly cooled crystal is understandable.

KCl:Tl Thermoluminescance in the room temperature region :

Recently Delbecq et al[19] have reported that the thermal glow peak in KCl:Tl at 300° K results when electrons are thermally released from thallium atoms into the conduction band and recombination of these electrons and Tl^{++}ions takes place. Since this concept is different from the one advanced earlier by Joshi et al[16] to explain the occurrence of this glow peak in KCl:Tl, additional experiments were performed to obtain more information regarding the properties of the glow peaks around room temperature.

Glow curves have been recorded for a number of KCL:Tl specimens after irradiation at room temperature. The characteristic glow curves obtained in the case of various samples are presented for discussion. In accordance with the general practice each peak in the glow curve is designated by the temperature at which it appears. The glow peaks discussed are those at 300,325 and 350° K. Slight variations from these positions on the temperature scale are observable in the figs. In all the glow curves the intensities are given in arbitrary units. KCl:Tl phosphors are known to exhibit two main emission bands, one in the vissible and the other in the ultraviolet. Preliminary investigations with filters separating the two regions indicated that the gross features of the individual glow peaks, with respect to various pretreatments of the specimen, remained the same and hence a discrimination between the two regions was considered unnecessary.

The typical glow curves obtained after ultraviolet irradiation at room temperature of KCl:Tl specimens prepared by different methods and of varying thallium concentrations are presented in fig. 4. Curves 1 and 2 are obtained with powder samples prepared by crystallisation from aqueous solutions with Tl concentrations 0.15

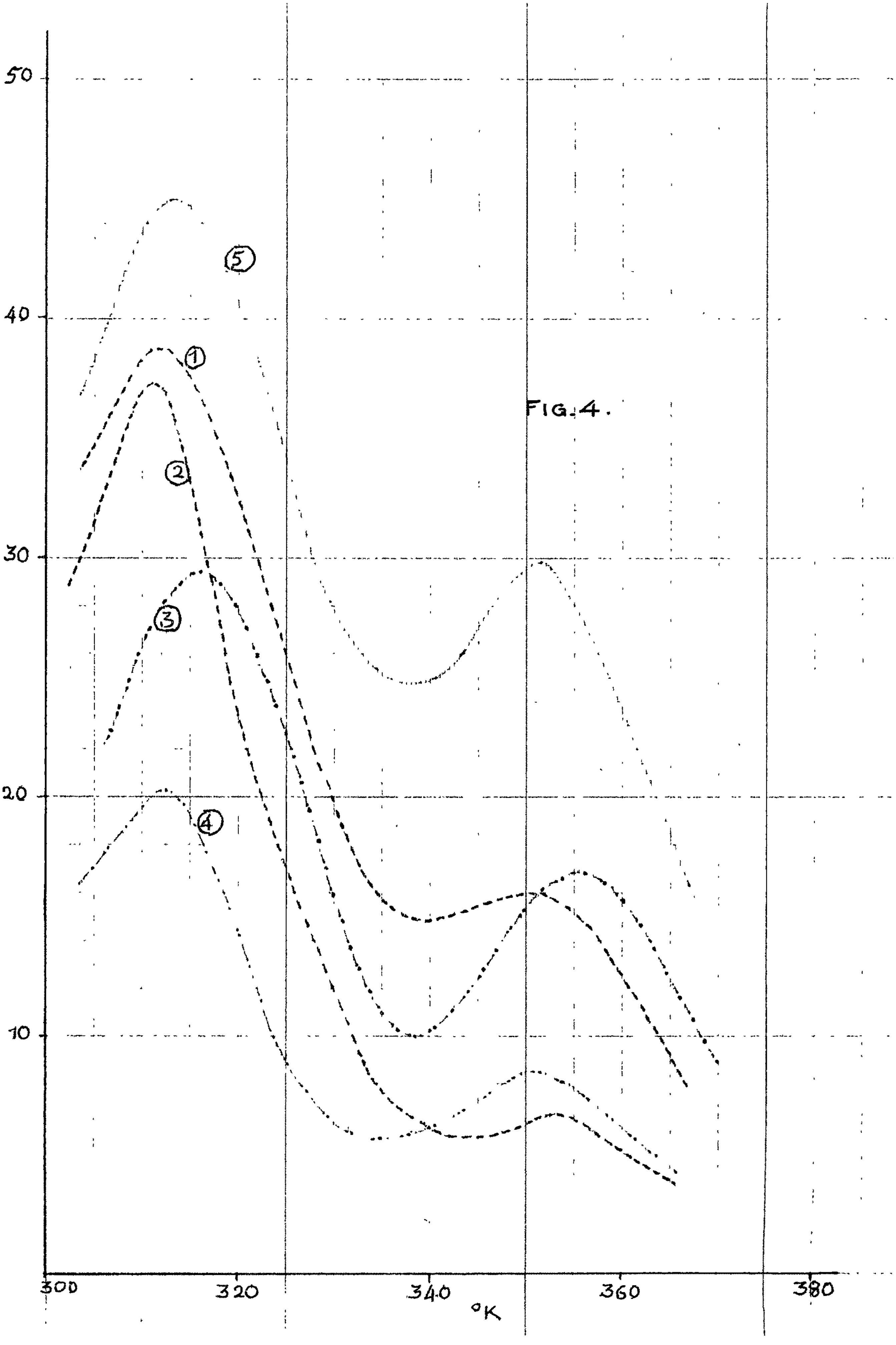
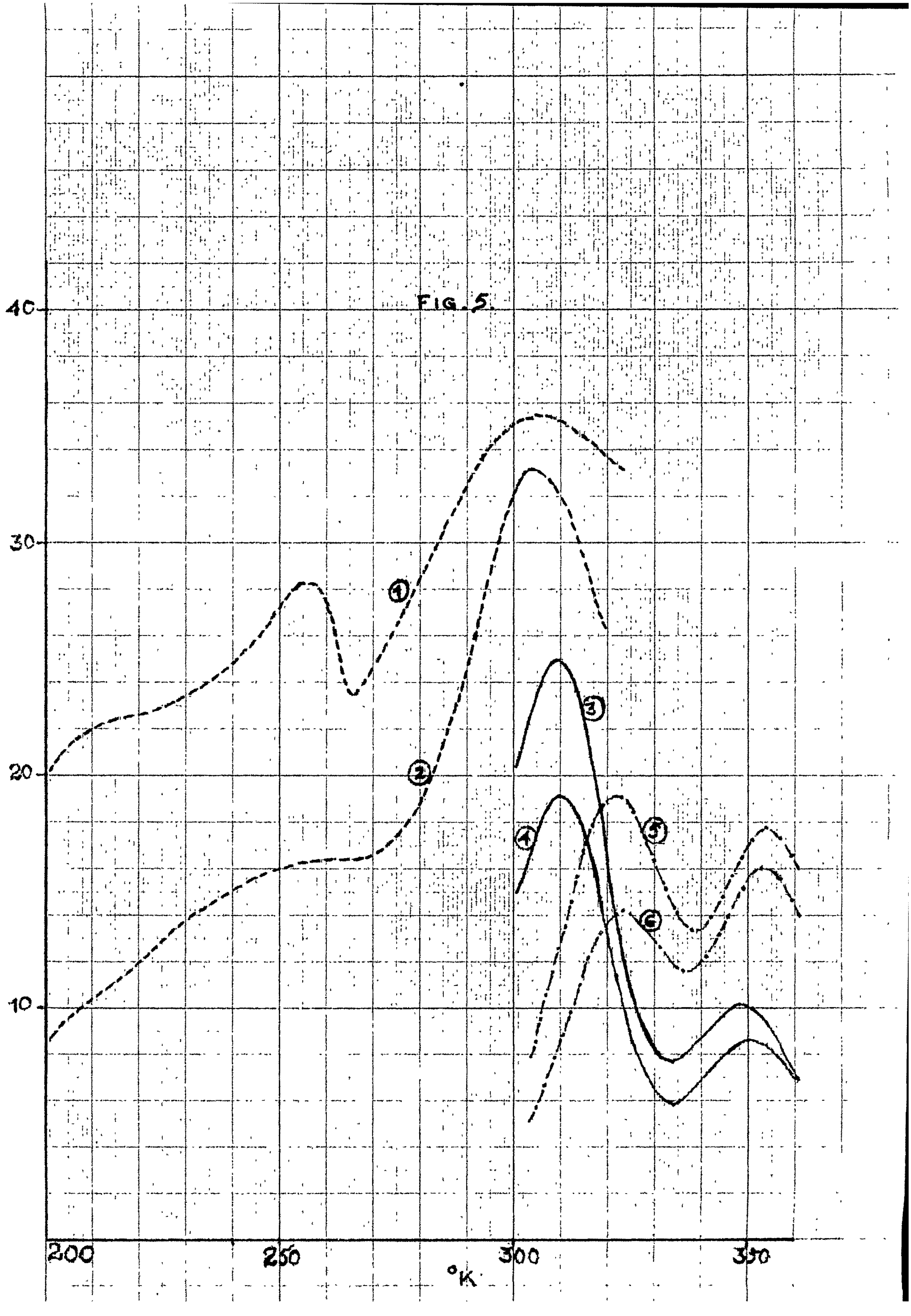


FIG. 4.

and 0.3 mole percent respectively. Curves 3 and 4 are for the powder samples pressed into the form of tablets and curve 5 is for a sample prepared by quenching the melt. In general two main glow peaks are observed around 310 and 350° K. The 310° K peak is identified as the 300°K glow peak, the shift in the peak position being attributed to the difference in the irradiation temperature. For example, the curves for KCl:Tl samples irradiated with ultraviolet light near liquid nitrogen temperature and room temperature are presented in fig. 5. In this fig. curves 1 and 2 are obtained with samples after ultraviolet irradiation at liquid nitrogen temperature and curves 3 and 4 are for specimens irradiated at room temperature. Curves 5 and 6 are obtained with ultraviolet irradiation at room temperature and recorded 4 and 6 minutes after the stoppage of excitation. It is evident from the fig. that the position of the first glow peak is dependent on the temperature of irradiation. Moreover, it is of interest to note that for a decay time of few minutes after the stoppage of irradiation, the peak position shifts to higher temperature and is observed around 325°K (curves 5 and 6). One of the methods of resolving the peaks when they merge is to subject the specimen to cycles of heating and cooling without re-excitation. Such a technique used in the case of a sample prepared from melt is presented

FIG. 5.



in fig. 6. A weak glow peak is observed at 325° K in the second heating run without re-excitation. Curves 3 and 4 are for KCl:Tl specimens prepared from solution and melt respectively, and recorded immediately after u.v. irradiation at room temperature. The presence of a weak shoulder at 325° K is discernible in these curves. The results imply that the traps corresponding to 300 and 325°K glow peaks are different in nature.

If the powder samples are subjected to prolonged X-irradiation in visible light and the glow curves recorded subsequently, two glow peaks at 325 and 350° K, are observed (fig. 7, curve 1). On the other hand, if the samples are X-irradiated in dark, the thermoluminescence recorded shows a very prominent glow peak around 350°K (fig. 7,curve 2) Fig. 8 exhibits the glow curves for a KCl:Tl specimen after room temperature X.-irradiation in the dark for short durations. Curves 1,2 and 3 are for 5, 10 and 15 minutes X-irradiation in the dark. It is seen that the 350°K glow peak develops strongly and overshadows the 325° K glow peak as the irradiation time is increased.

Thermoluminescence study of "pure" and Tl-doped KCl single crystals after x-irradiation was also carried

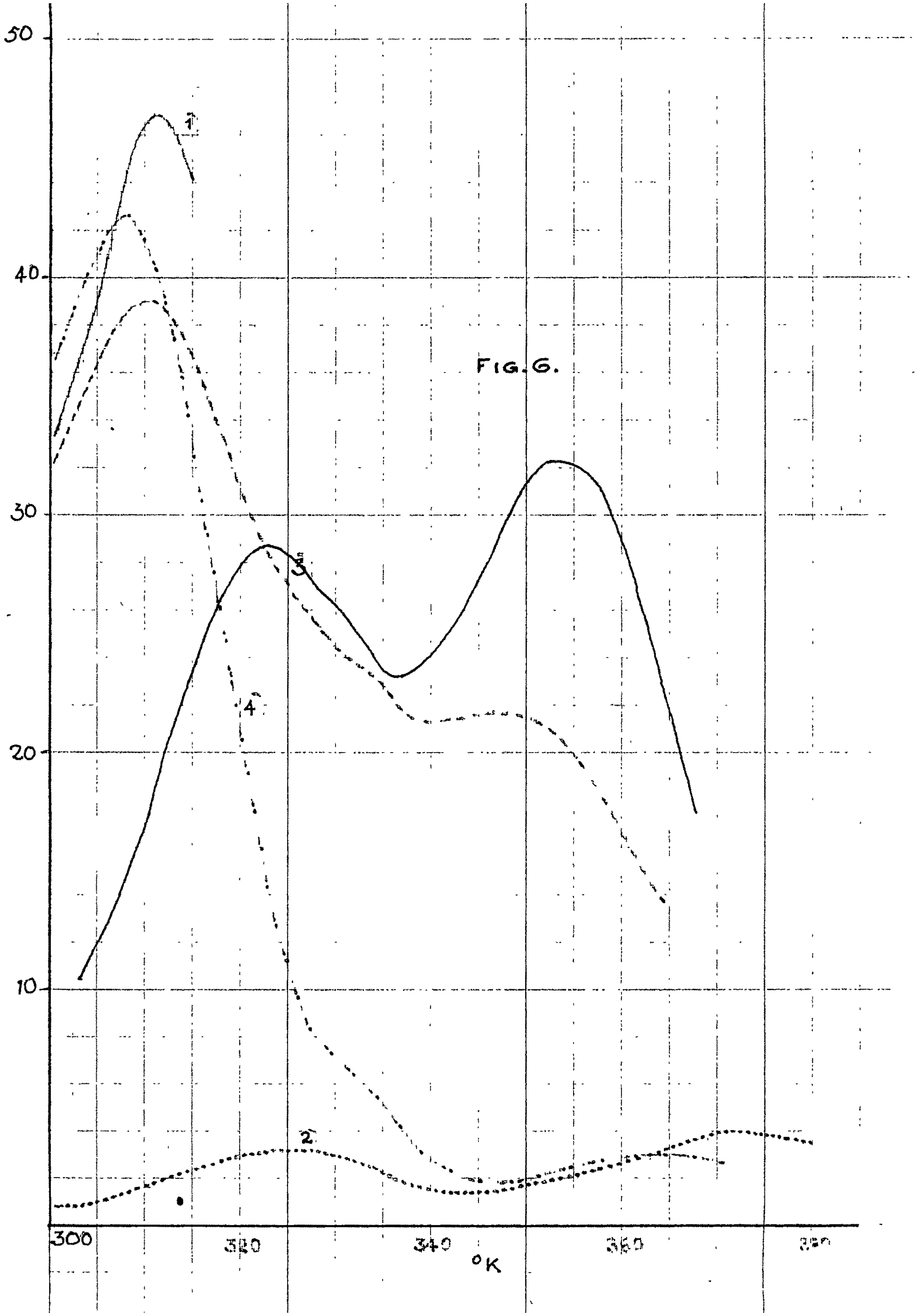


FIG. 6.

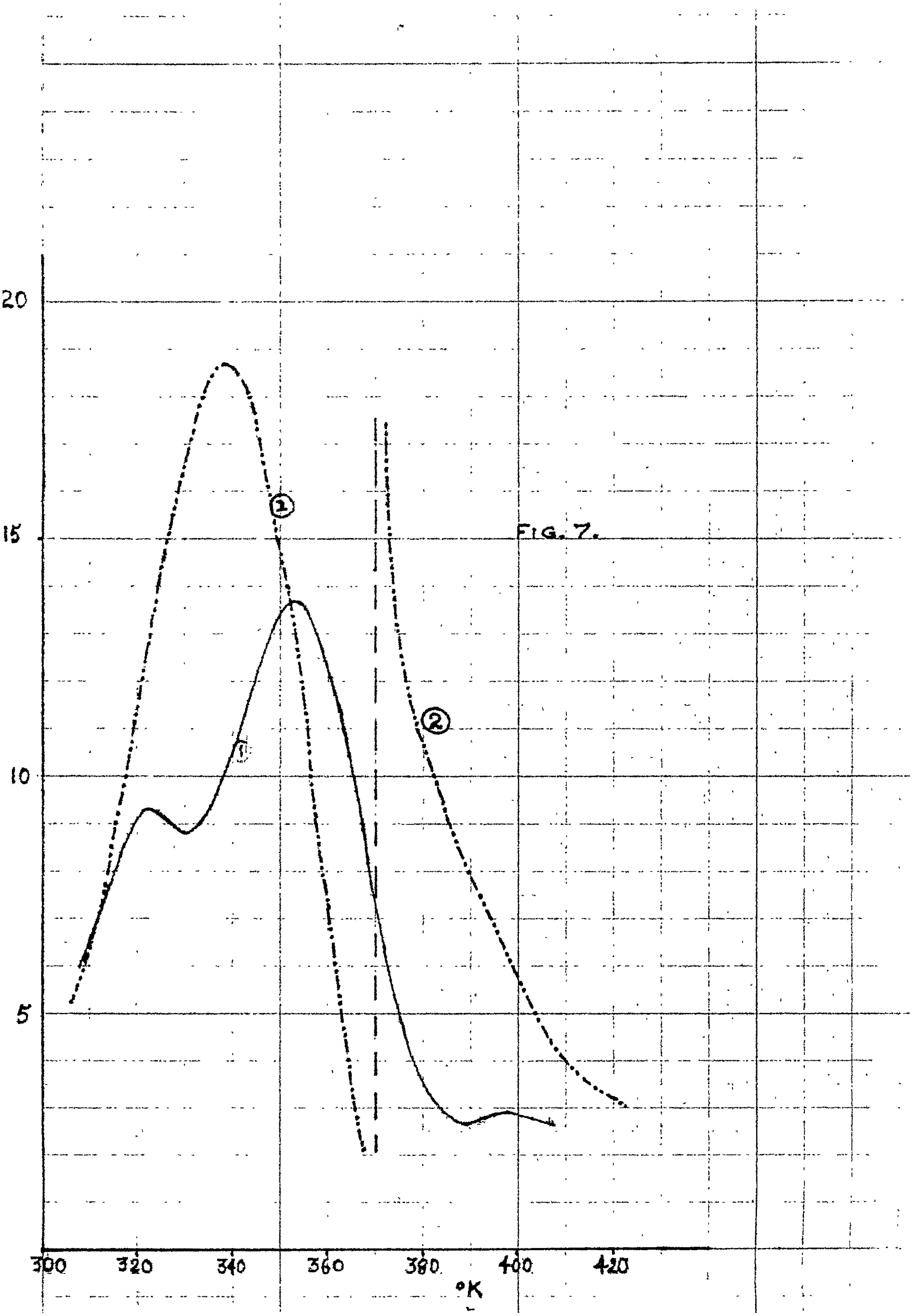


FIG. 7.

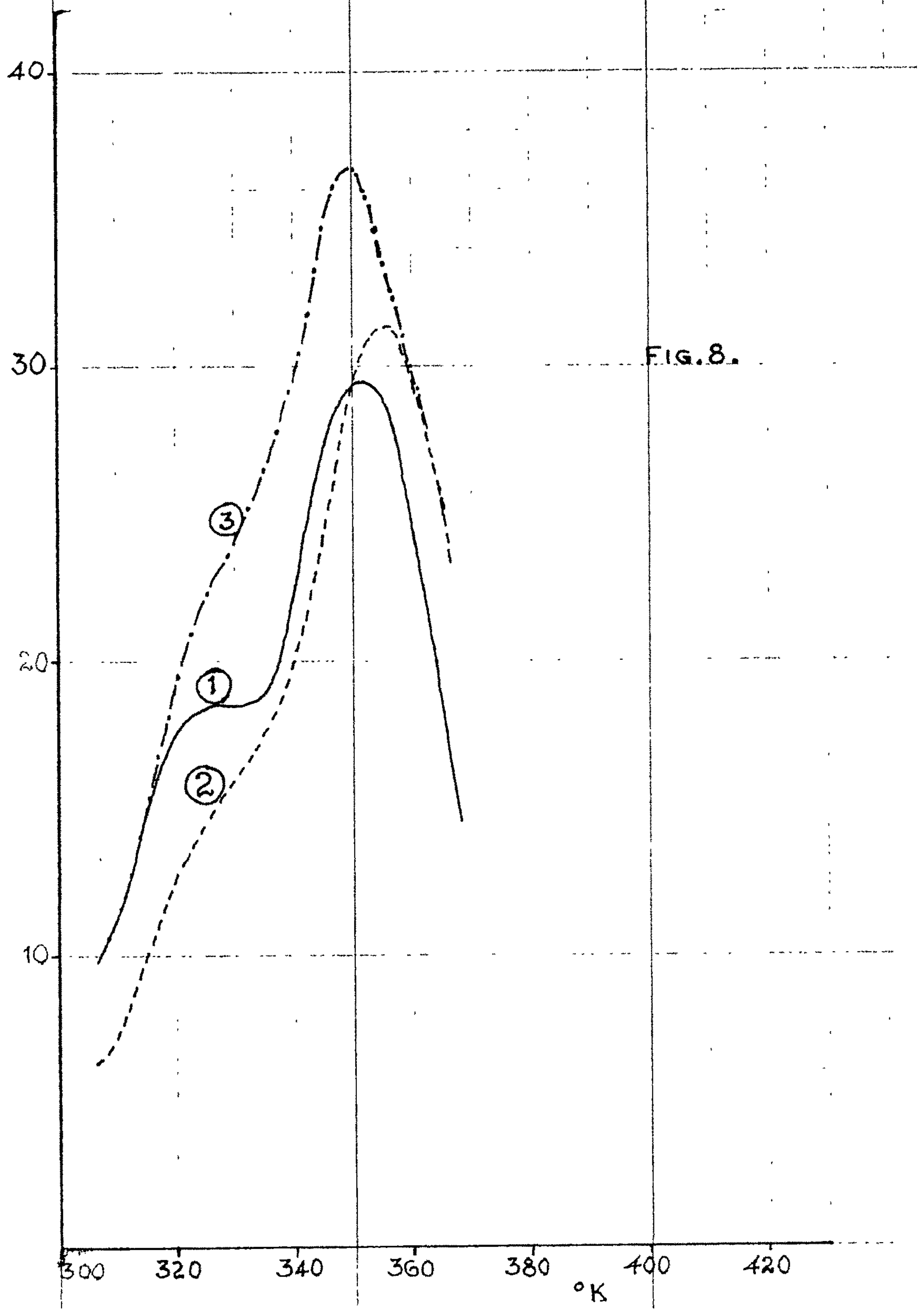


FIG. 8.

out. "Pure" crystal does not show any measurable peak in the room temperature region, after prolonged x-irradiation in the dark, even at the maximum sensitivity of the detector. (fig. 9; curve 1) A KCl:Tl crystal, obtained by thermal diffusion of TlCl, exhibits in its glow curve a pronounced glow peak at 325° K when irradiated, in the dark at room temperature, either with ultraviolet light or x-rays. In the fig. curve 2 is for ultraviolet irradiation and curve 3 for x-irradiation of the specimen. Besides 325°K glow peak, a sharp shoulder around 350°K is also observable in curve 3.

It has been suggested before by Joshi et al[16] that the glow peak at 300°K is due to a species of phosphorescence centres formed by a Tl^+ - negative ion vacancy complex in the region of the lattice away from dislocation and that the glow peak at 350°K is due to a similar complex but in the vicinity of a charged dislocation. It has been proposed that during ultraviolet irradiation, an electron from Tl^+ ion is transferred to the adjacent negative ion vacancy which results in the formation of Tl^{++} ion and F centre on neighbouring sites. Such direct ionization of Tl^+ ion by ultraviolet irradiation cannot be ruled out since the electrons are excited from impurity levels rather than from valence band. In fact, coloration

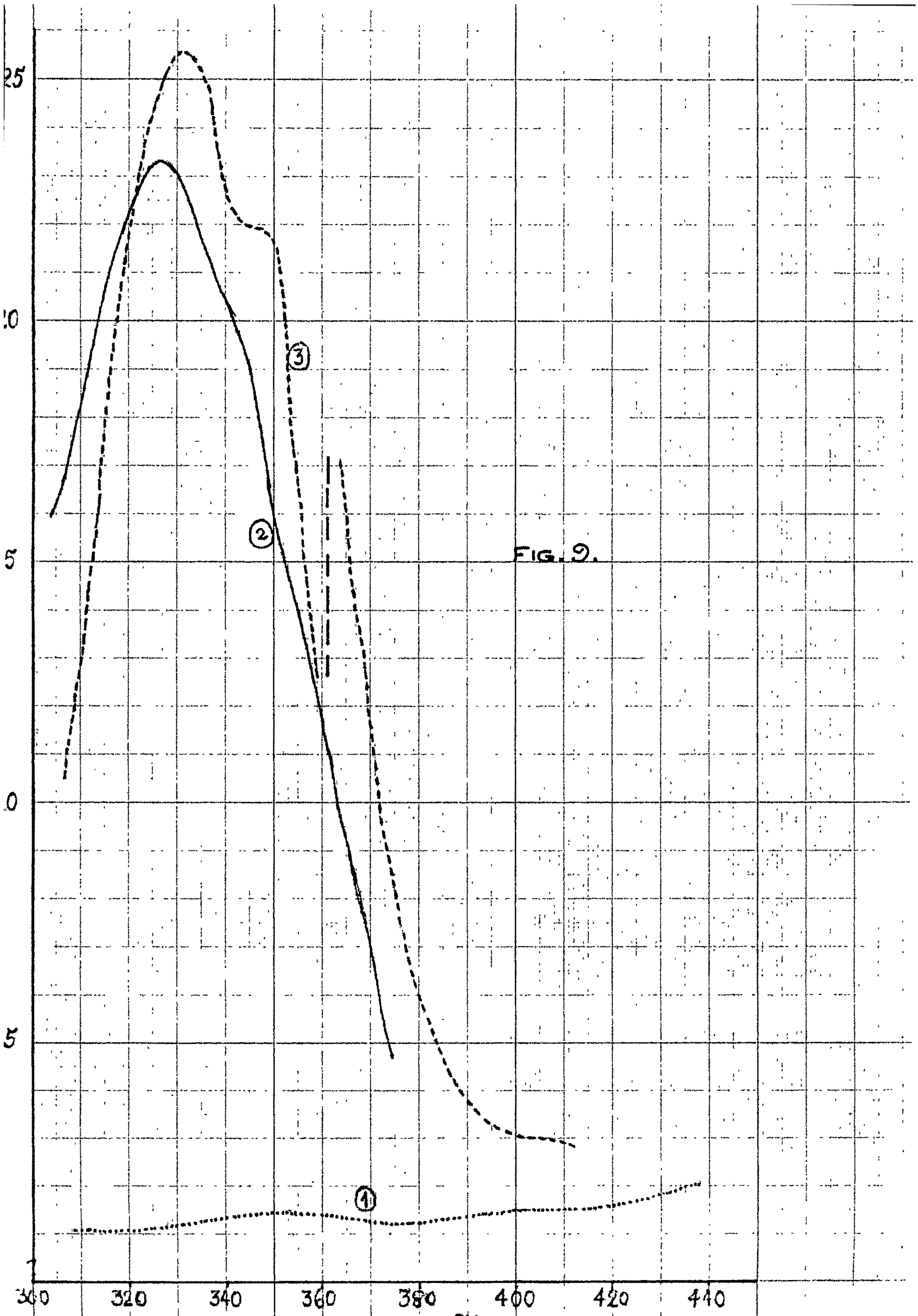


FIG. 9.

of alkali halides by ultraviolet irradiation has been known for a long time[163-165]. However, it was generally considered to be a property of the impure crystals i.e. filling of existing vacancies rather than the creation of new ones. It is only recently that experiments have demonstrated the creation of F centres in nominally pure crystals[166,167]. Pooley[168] has suggested a theoretical explanation of ultraviolet coloration via exciton decay.

The thermoluminescence emission of KCl:Tl has been suggested by Joshi et al[16] to result from tunnelling between the F centre and the adjacent Tl^{++}ion in which the electron from F centre and trapped hole, Tl^{++}, recombine radiatively. There is now a general agreement that below about 500°C dislocations (edge components) in alkali halides are negatively charged with a surrounding cloud of positive charges namely, negative ion vacancies. Since an electron trapped at a negative ion vacancy, in the neighbourhood of a negatively charged dislocation, will be more resistant to thermal bleaching than the one trapped at a vacancy away from dislocation, the Tl^{+}-negative ion vacancy complex in the vicinity of a dislocation has been assigned to 350° K glow peak. When a KCl:Tl specimen is subjected to cyclical succession of excitation at room temperature, heating to around 450°K and cooling, significant changes in the intensities of the 300 and 350°K glow peaks have been observed[16]. These changes occur in a manner depending on the time that elapses between two consecutive thermal cycles. If the glow curve is recorded immediately after the previous heating run, one observes progressive decrease in the heights of the two glow peaks. On the other hand, if the time interval between two consecutive cycle is sufficiently large (~ 15 hrs.) the two glow peaks regain their strength. Such changes in the trap distribution brought about by thermal cycling indicate that the primary process, in the formation or destruction of the phosphorescence centres associated with the two glow peaks, is the vacancy diffusion. Vacancies are known to be sufficiently mobile in the room temperature region.

In KCl:Tl, a new glow peak at 325° K has been observed in the present work. This peak appears with 350° K glow peak if the specimen is simultaneously irradiated with x-rays and illuminated with visible light. It is completely overshadowed due to strong development of 350° K glow peak after prolonged x-ray irradiation of the specimen in the dark (fig. 7). The latter result suggests that there is no one-to-one correspondence between the phosphorescence centres responsible for 325 and 350° K glow peaks. This is borne out by the results obtained by subjecting the specimen to x-ray exposures of short durations (fig. 8). The 350°K glow peak is observed to grow more rapidly compared to 325° K peak.

The behaviours of 325 and 350° K glow peaks are qualitatively similar to those noticed in colour centre work. It has been reported by Christy et al[66] that the rates of production by x-rays for F and V_3 centres are closely linked, so that both kinds are probably formed in the same elementary process. On the other hand, the numbers of the two kinds of centres are not necessarily equal so that F centres are formed without the corresponding formation of V_3 centres. This means that some of the holes are trapped elsewhere than at a V_3 centre. This type of problem in coloration phenomena, in which large concentration of electron centres and only a few hole centres are observed, arises in general in both pure and impure alkali halide crystals. It is now believed that trapped-electron colour centres are formed by a mechanism which involves the production of interstitial halogen atoms. These interstitial atoms may diffuse together at room temperature to form halogen molecules or molecular-ions which are stable chemically and may or may not give rise to observable optical absorption bands. As a result, the number of F centres formed may not be proportional to the number of traps giving rise to V band absorptions.

F centres will naturally be prevented from growing in number if the visible light is allowed to fall on the specimen during x-ray irradiation. On the other hand, the concentration of F centres will continue to increase with the increase in the irradiation dose, if the excitation is carried out in the dark. A parallel behaviour of 350° K glow peak observed in the present work (figs. 7 and 8) suggests that this glow peak is related to trapped-electron type centres since only such centres have been reported to have absorption in the visible region. As mentioned above, the model for 350° K glow peak has been suggested to be related to F centres near dislocations[16], which is consistent with the present analysis. The changes in the relative heights of 325 and 350° K glow peaks with the duration of x-ray irradiation in the dark (fig. 8) clearly indicate that for 325° K glow peak there is a tendency to saturate whereas the 350° K glow peak grows with the increase in the irradiation dose. It is believed that 325° K glow peak may be related to certain species of halogen molecular-ion (i.e. halogen molecule or higher aggregate that has captured a hole) complementary to the F centre. This would of course mean that some of the holes are trapped at some other molecular-ions which are produced together with F centre by the same primary act of generation and therefore complementary to F centres. The association of molecular-ion species with 325° K glow peak is also in agreement with the results presented in fig. 9. It is clearly seen from the fig. that a KCl:Tl specimen, in which TlCl was introduced by thermal diffusion, exhibits a pronounced glow peak at 325° K. As discussed earlier in the thesis, it is believed that in such specimens interstitial Cl^- ions are present which after irradiation of the specimen, lead to the creation of halogen molecular-ions. Thus, it is suggested that the 325° K glow peak is related to species of centres of trapped-hole type and 350° K glow peak to those of trapped-electron type.

Effect of optical bleaching on 300° K glow peak :

On the basis of their experimental results, Delbecq et al[19] suggested that in KCl:Tl the thermal glow peak at 300° K arises because Tl° atoms become thermally unstable around 280° K and release electrons into the conduction band. These electrons are trapped at

Tl^{++} ions and produce Tl^{+} ion in the $^{3}P_1$ state. These excited thallous ions then emit the characteristic 298 mμ emission. The steps involved can then be represented by

$$Tl^{\circ} \longrightarrow Tl^{+} + e^{-}$$

$$e^{-} + Tl^{++} \dashrightarrow Tl^{+}\ (^{3}P_1) \dashrightarrow Tl^{+}\ (^{1}S_0) + h\nu_{298}$$

In view of the proposed thermal stability of Tl°atoms, this is a very attractive proposal but the results reported previously by Joshi et al[16] and those obtained in the present work on optical bleaching argue against it.

The effect of F-light illumination on 300°K glow peak was investigated and the results obtained are presented in fig. 10. It has been observed that the efficiency of bleaching is poor if the specimen is illuminated with F-light at room temperature than at liquid nitrogen temperature. Hence, the bleaching with F-light was performed at liquid nitrogen temperature. In fig. 10, curves 1, 2, 3 and 4 represent glow curves obtained in consecutive thermal cycles in each of which the specimen was subjected to irradiation with ultraviolet light at liquid nitrogen temperature, heated to 330°K and then cooled . During thermal cycling two effects must be distinguished in the decrease of the glow peak height : decrease due to

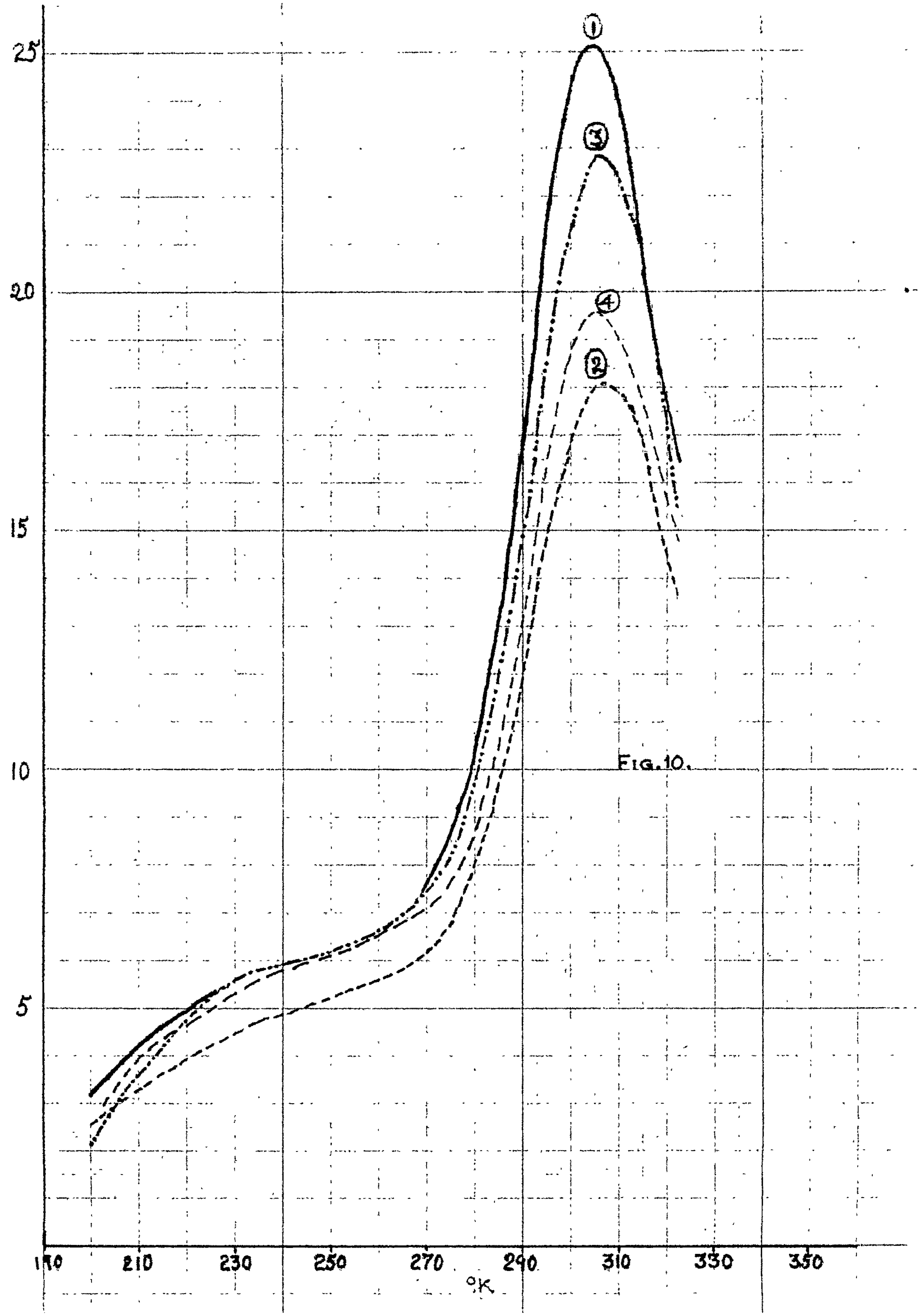


FIG. 10.

bleaching by F-light and purely thermal bleaching in the dark. In the case of curve 2, the irradiated sample was bleached with F-light for 6 minutes before measurement. On the other hand, curves 1, 3, and 4 were recorded after ultraviolet excitation and 6 minutes decay. Although part of the decrease in the height of the glow peak occurs as a result of thermal cycling, the much larger decrease in its height, after optical bleaching, in the second cycle (curve 2) and increase in the height, without optical bleaching, in the third cycle (curve 3) reflect real decomposition of F centres due to optical bleaching. This suggests that a negative ion vacancy is an obvious possibility as a trapping site. There does not appear to be any reason for avoiding the conclusion that in KCl:Tl phosphor Tl^{+} ions act as emitting centres since emission bands characteristic of Tl^{+} ion have been observed in the phosphorescence and thermoluminescence emission of the phosphor.

On the basis of the above inferences, it seems reasonably clear that the thermal glow peak at 300°K results from the recombination of the electron, released from F centre, with the hole at Tl^{++}. KCl:Tl phosphor exhibits phosphorescence of long duration and yet no photoconductivity has been observed. It was therefore suggested by Joshi et al[16] that the Tl^{+} ion and negative ion vacancy have close spatial association with each other. The thermoluminescence mechanism has been suggested to involve the transfer of the electron from Tl^+ to the neighbouring negative ion vacancy, during irradiation at low temperature, and subsequent release of the electron from the trap and its tunnelling to the excited state of the Tl^+ion. If tunnelling is important, it seems likely that this takes place over a relatively short distance and that Tl^+ ion and negative ion vacancy may not necessarily be the nearest-neighbours. The steps suggested are -

$$F \dashrightarrow \text{negative ion vacancy} + e^-$$

$$e^- + Tl^{++} \dashrightarrow Tl^+\,(^3P_1) \dashrightarrow Tl^+\,(^1S_0) + h\nu_{298}$$

One may argue that the presence of nearby thallous ion should influence the width of the F band at half - height. Markham and Hersh[169] made measurement of half-height width and the point of maximum absorption on F band in single crystals of KCl, KBr, and KI both pure and thallium doped wherein the concentration of Tl^+ ions was approximately ten times the concentration of F centres. They concluded that doping does not influence the F centres directly. Similar conclusion was also reached earlier by

Smakula[163] from his study on NaCl:Tl. The problem is similar to the one encountered in V_K centre studies. Castner and Kanzig[123] and Delbecq et al[72] found that the reasonance spectrum of the V_K centre is identical in pure KCl and in KCl doped with Tl^+, Ag^+ or Pb^{++}. Statistically, the probability of having an impurity ion next to Cl_2^- is small if both are randomly distributed. However, the possibility of nonrandom distribution cannot be ruled out.

Some observations on the behaviour of the absorption spectrum of specimen II after ultraviolet irradiation at room temperature may be reported. It is seen from fig. 11 that irradiation induces a strong F-band absorption and also a noticeable absorption at 290 mμ. The latter is indicative of the generation of Tl^{++} ions in the specimen. One may therefore conclude that a fraction of the F centres and Tl^{++} ions are produced in the same primary process, during irradiation. This premise is further substantiated by the results presented in fig. 12. This figure exhibits the changes in the absorption in the second run recorded fifteen minutes after the completion of the first absorption run. Decrease in the F band height and the suppression of 290 mμ absorption, during intermediary decay period of fifteen minutes, are obvious in the figure. One may therefore reasonably assume that the electron-hole

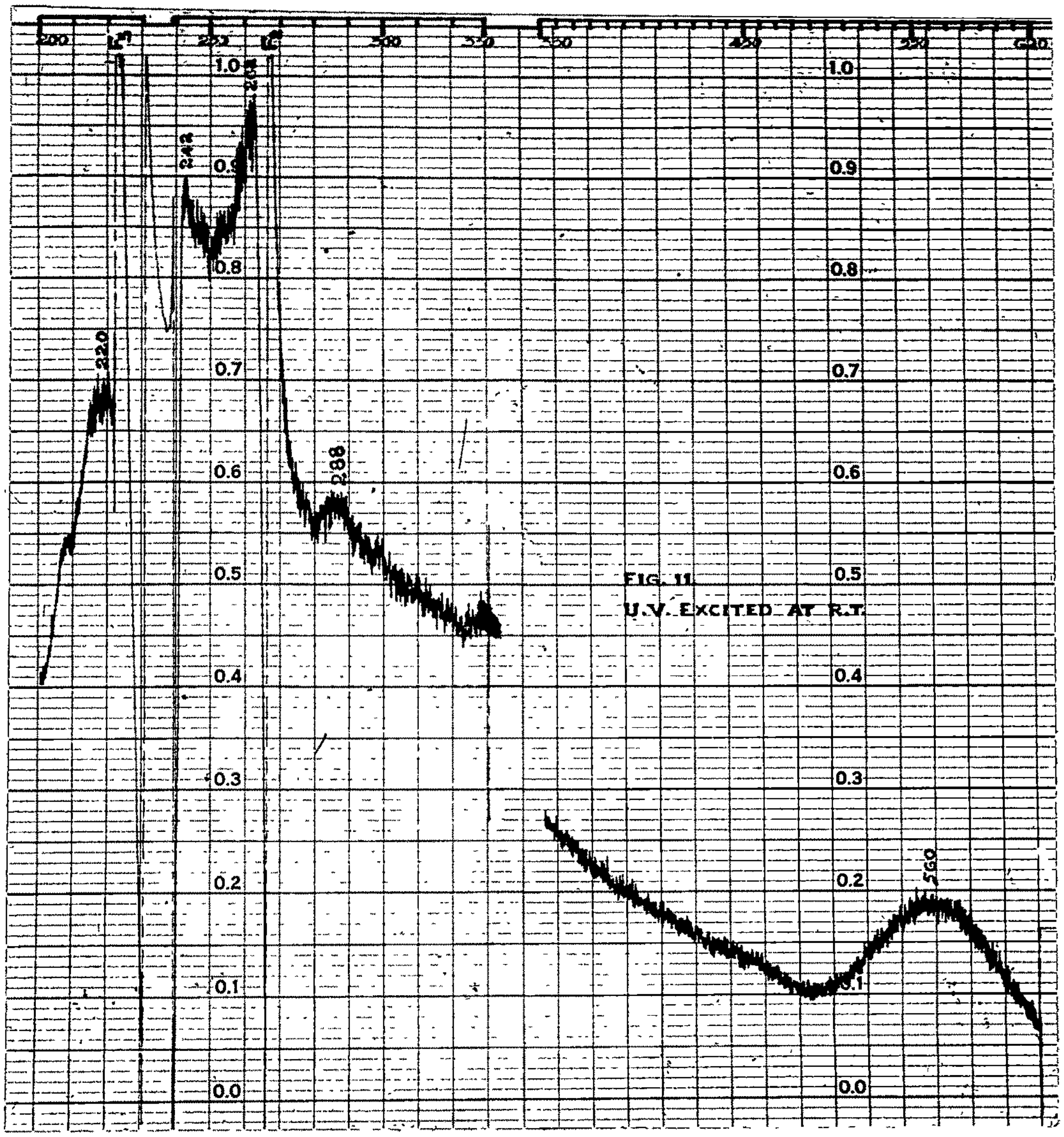


FIG. 11
U.V. EXCITED AT R.T.

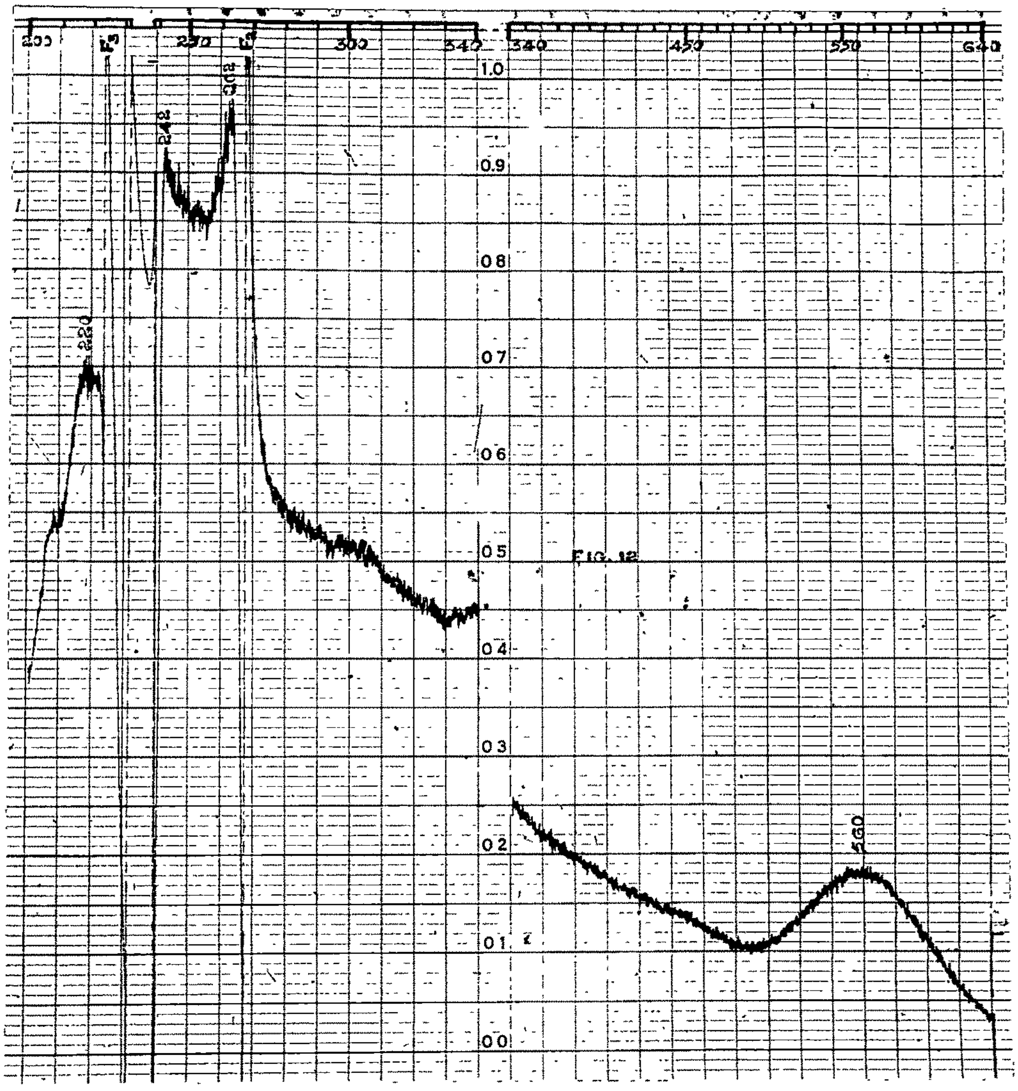

200
250
300
340
340
450
550
640
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
220
248
282
560

FIG. 12

recombination in the phosphorescence decay involves F-centre electrons and holes at Tl^{++} ions.

In summary, the configurational changes in the phosphorescence centres, associated with 300°K glow peak in KCl:Tl, due to thermal cycling and the decrease in the strength of this glow peak, due to F-light illumination of the specimen, are consistent with a model of the phosphorescence centre consisting of a Tl^{+} ion and a negative ion vacancy as suggested by Joshi et al[16]. These results are difficult to understand on the basis of the concepts advanced by Delbecq et al[19] according to which thermal release of electrons from Tl° atoms are considered important in the thermoluminescance process at 300° K.