# CHAPTER 5

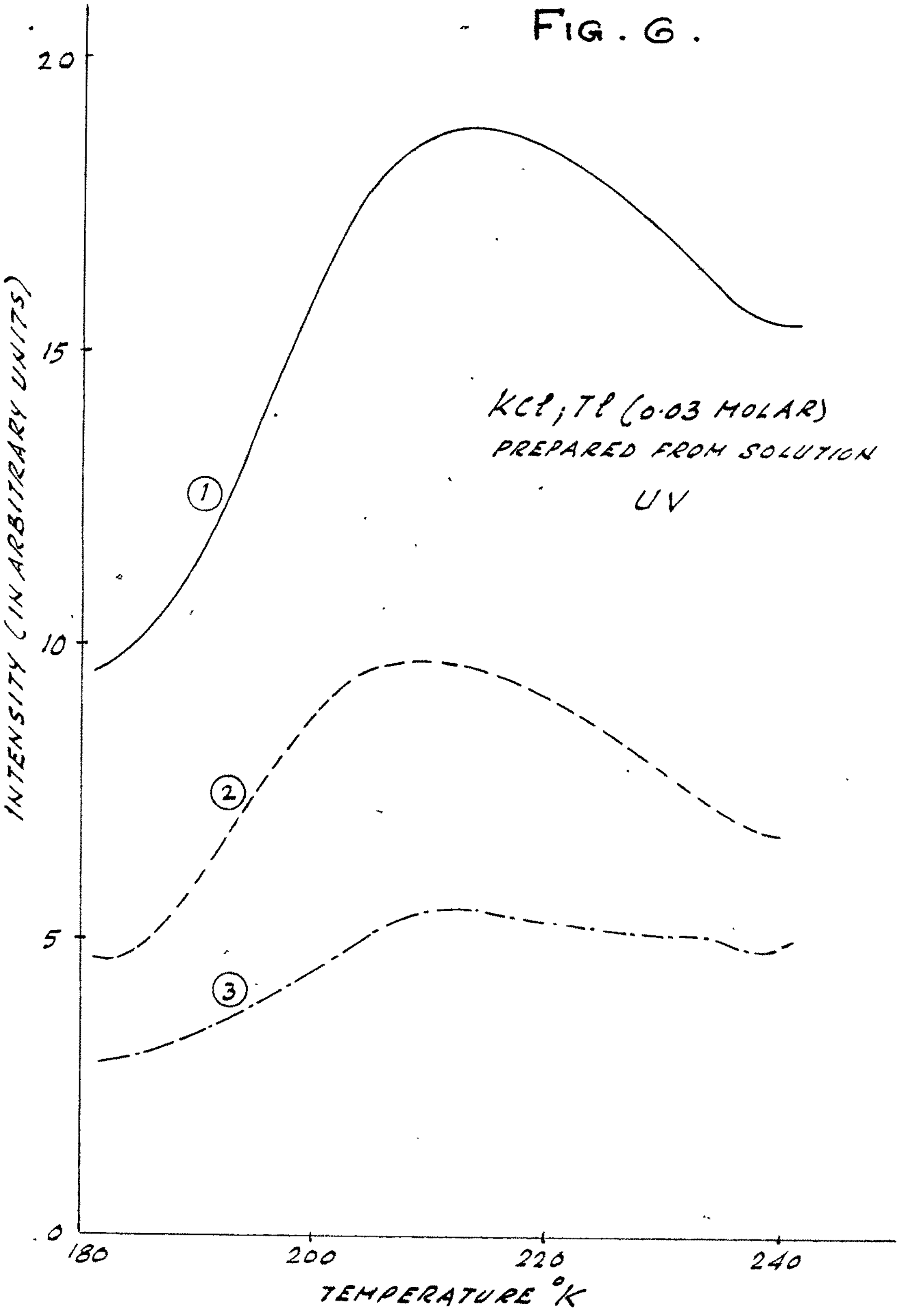
# RESULTS AND DISCUSSION

Conforming to the general practice, every peak in the thermal glow curve shall be labelled by the temperature at which it appears. The glow peaks that are observed, in the range from liquid nitrogen temperature to about 400°K, in potassium chloride, pure or activated with impurities, are the following in the order they are discussed: 200, 250, 300, 350, 175 and 140 °K. While the actual recordings of the glow curves exhibit variations in the peak temperature from those mentioned above, depending upon the nature of the impurities and the modes of preparation of the samples, the above classification can be followed in a broad sense, without losing the identities of the peaks.

## 5.1 200°K Peak

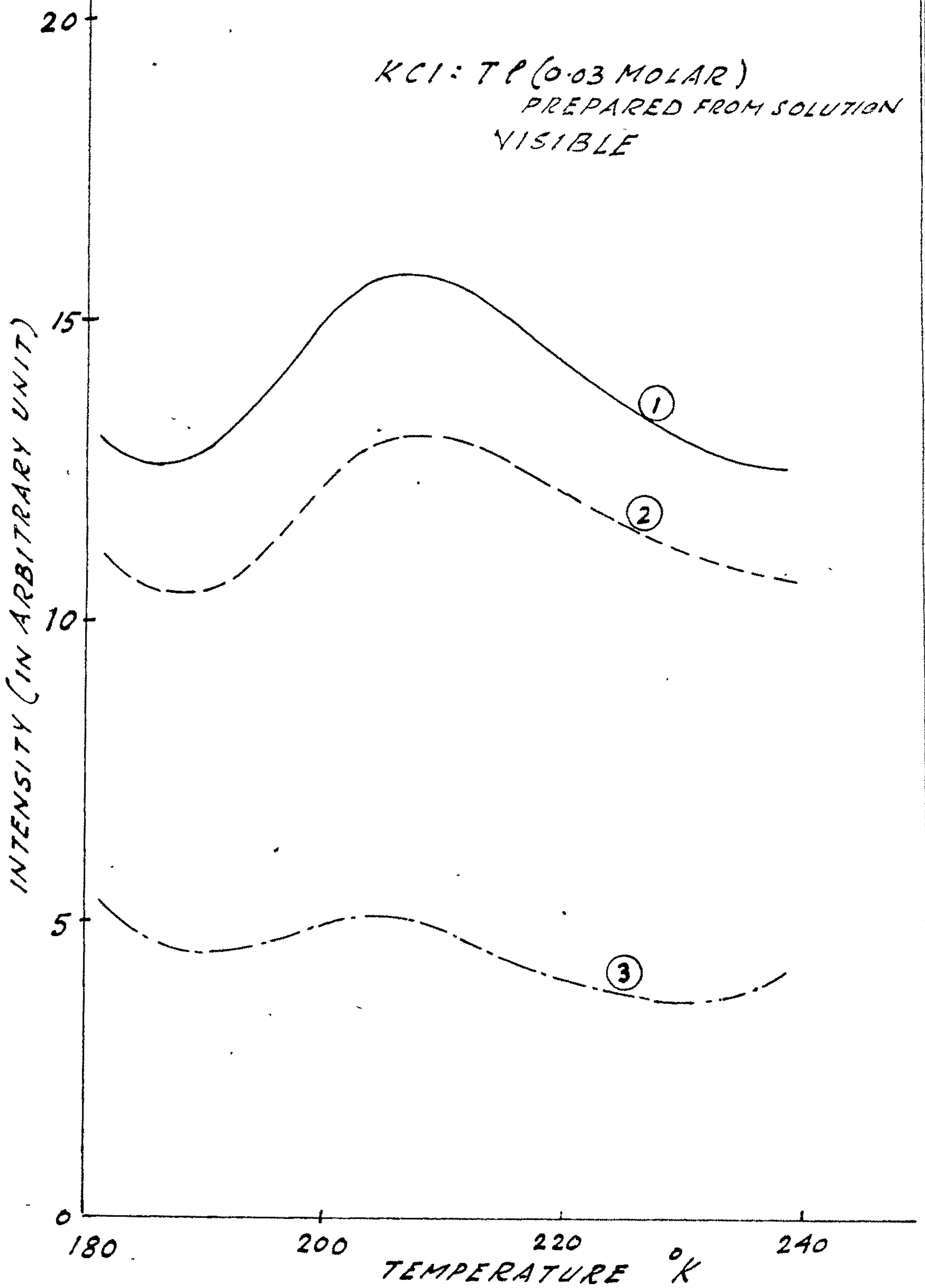
The glow curves for KCl:Tl powdery phosphor, prepared from aqueous solution and containing 0.03 molar fraction of Tl, in the region around 200°K are shown in Figures 6 and 7. Figure 6 is for the ultraviolet emission and Figure 7 is that for the visible emission of the phosphor. Curves 1, 2, and 3 in each of these figures are for the first, second and third heating runs respectively, when the phosphor

# FIG. 6.



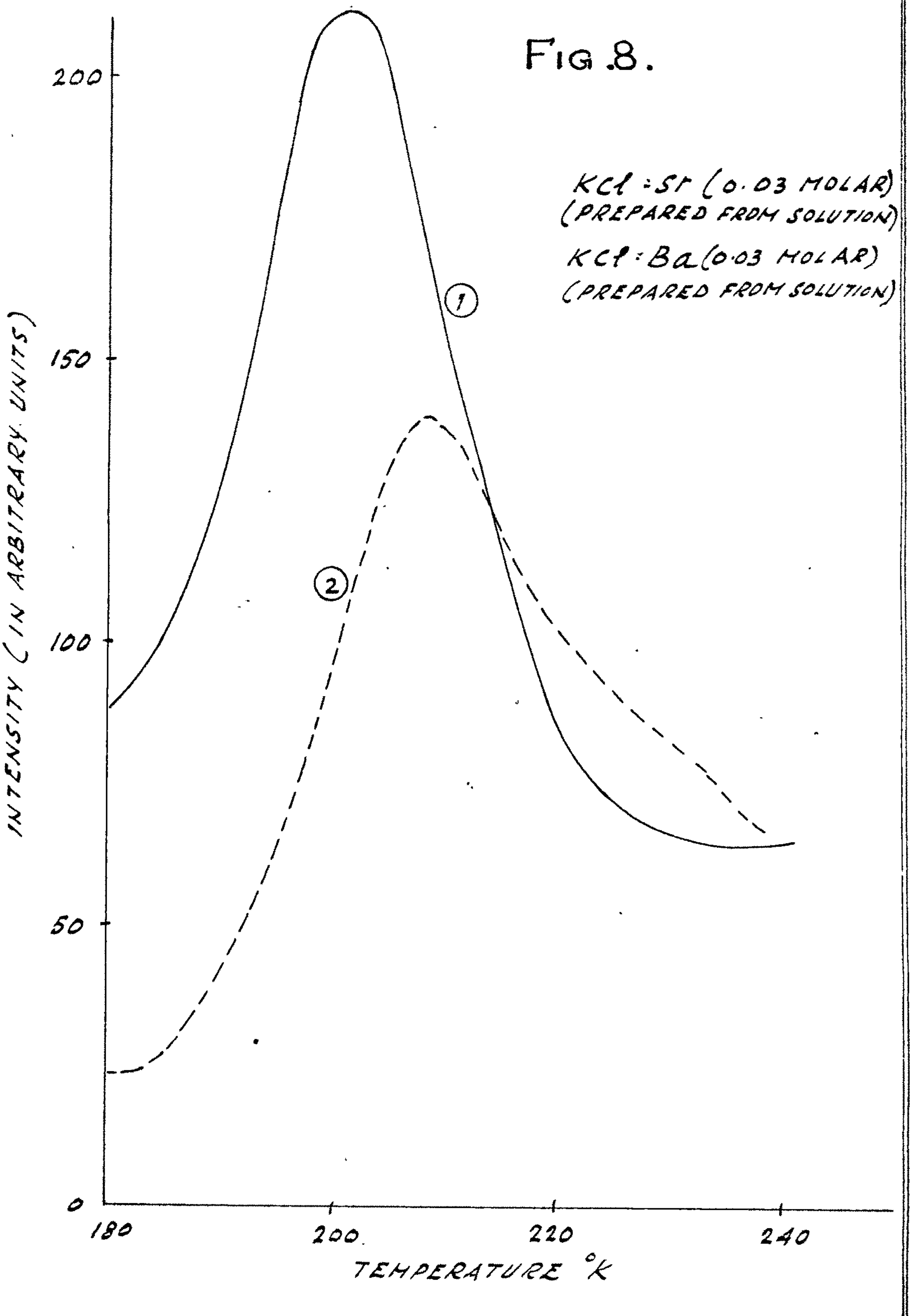
20
15
10
5
0
INTENSITY (IN ARBITRARY UNITS)
180
200
220
240
TEMPERATURE °K
①
②
③
KCl; Tl (0·03 MOLAR)
PREPARED FROM SOLUTION
UV

FIG. 7.



KCl : Tl (0·03 MOLAR)
PREPARED FROM SOLUTION
VISIBLE

FIG. 8.


KCl : Sr (0.03 MOLAR)
(PREPARED FROM SOLUTION)
KCl : Ba (0.03 MOLAR)
(PREPARED FROM SOLUTION)
①
②
INTENSITY (IN ARBITRARY UNITS)
200
150
100
50
0
180
200
220
240
TEMPERATURE °K

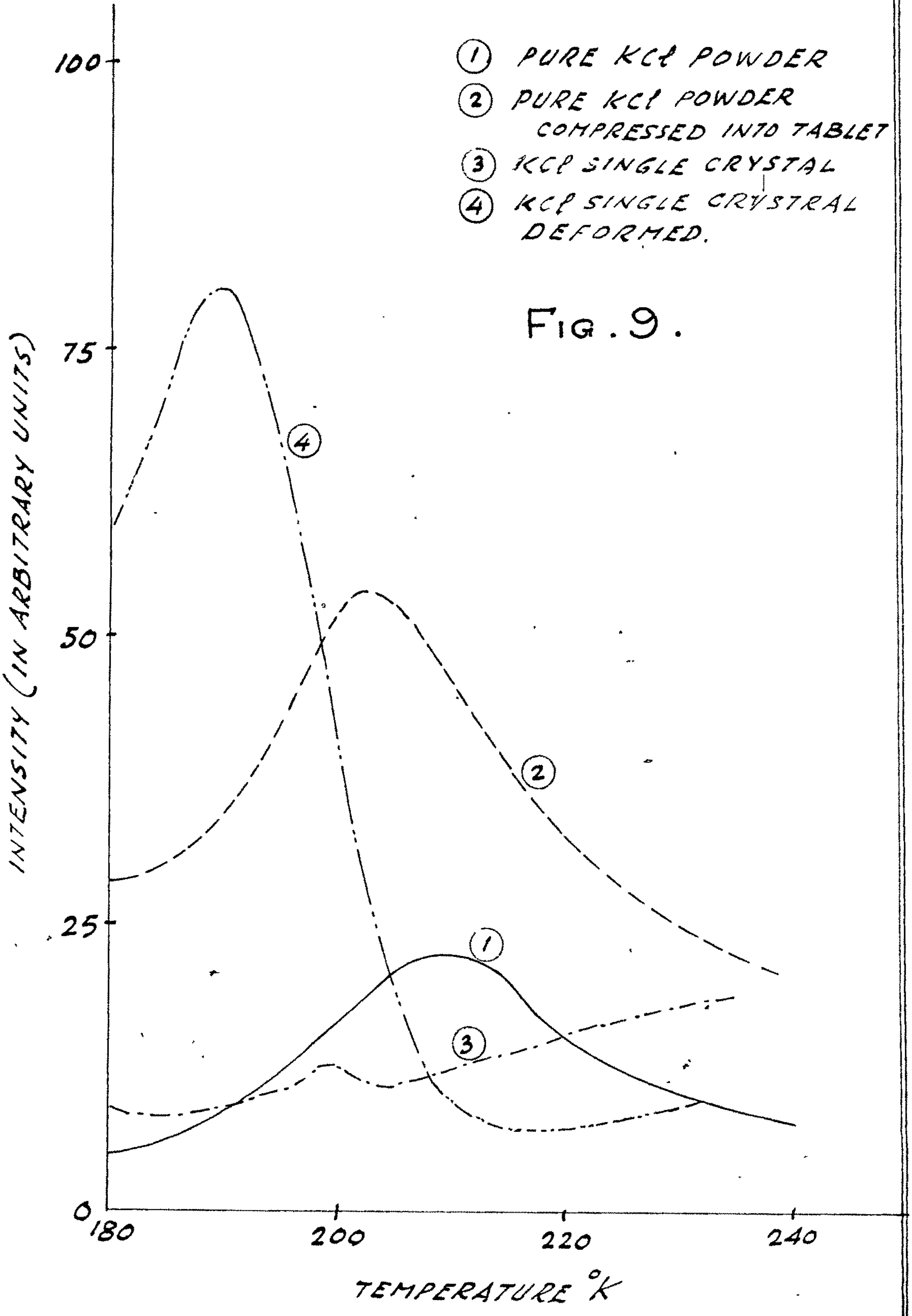

① PURE KCl POWDER
② PURE KCl POWDER COMPRESSED INTO TABLET
③ KCl SINGLE CRYSTAL
④ KCl SINGLE CRYSTAL DEFORMED.
INTENSITY (IN ARBITRARY UNITS)
100
75
50
25
0
180
200
220
240
TEMPERATURE °K
④
②
①
③

FIG. 9.

is subjected to cyclical succession of irradiation at liquid nitrogen temperature, heating to around 400°K and cooling. No correction has been made in the intensities of the ultraviolet and visible curves to allow for the variation with wavelength in the sensitivity of the photomultiplier. Hence the intensity values for the ultraviolet and visible components of the glow cannot be compared. On the other hand, the experimental factors in the glow curve measurements for a particular emission of the phosphor being identical, the intensities in the successively recorded glow curves for that emission can be compared. In order to obtain a more complete picture of the rôle of impurities, the glow curves in the case of KCl doped with impurities of higher valency have also been examined. Figure 8 indicates the glow curves for KCl activated with $Sr^{++}$ and $Ba^{++}$ by crystallisation from aqueous solution. When untreated specpure KCl specimen, either in the form of powder or single crystal, is plastically deformed there appears a pronounced glow peak at about 200°K. This is shown in Figure 9.

From the results stated above, one may say that the 200°K glow peak has the following characteristics:

(1) It appears in KCl doped with impurities such as $Tl^{+}$, $Sr^{++}$ or $Ba^{++}$.

(2) In KCl:Tl, the thermal glow at 200°K consists of emission in the ultraviolet and visible, which is the characteristic of a Tl centre.

(3) If the phosphor is subjected to the cyclical succession of irradiation, heating and cooling then the 200°K glow peak decreases in intensity for both the emissions.

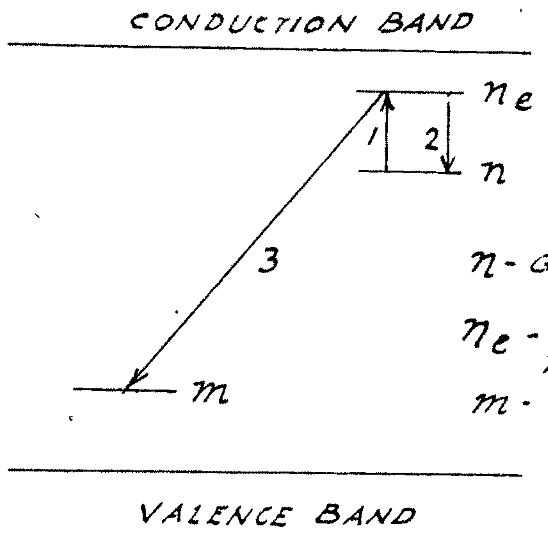
(4) This glow peak is not noticeable in 'pure' KCl. However, if 'pure' KCl specimen, either in the form of microcrystals or single crystal, is plastically deformed then the glow peak appears significant. The probable identity of the trapping sites responsible for 200°K glow peak is discussed below.

As the traps in KCl:Tl have already been identified with the defects of the host lattice other than impurity ions[63,64,68,69], and since the defects predominantly present in alkali halides are the ion vacancies, it is pertinent to imagine all the major trapping sites in KCl, doped or undoped, to be due to vacancies. The first attempt to identify trapping sites in KCl:Tl with the vacancies was made by Joshi[64]. Further, since the problem of colourability in alkali halides is bound up with the presence of ion vacancies, it may be assumed that the trapping sites are related to various species of colour centres. The claims of colour centres that do not contain vacancies shall be considered later.

It is generally known that at room temperature, free unassociated vacancies exist in alkali halides. Extra vacancies can be generated by using more energetic radiations like x-rays or $\gamma$-rays. The ultraviolet rays, which are used in the present work, cannot be thought to have sufficient energy to alter the defect pattern of the phosphor during the irradiation. Smakula[71] has reported the generation of the F centres by irradiation with wavelength corresponding to the first fundamental absorption band, which is at 167 m$\mu$ for KCl. Chiarotti and Inchauspe'[72] irradiated KBr crystal at 77°K with ultraviolet light in the exciton band and observed F and $V_1$ centres. The number of centres yielded by the irradiation were, however, limited and this might presumably be due to the inability of the radiation to generate extra vacancies in the specimen. In an earlier work, Johnson and Williams[5] used hydrogen discharge lamp for multiple excitation of KCl:Tl at 77°K and observed F and V centres. From these results, one may infer that at liquid nitrogen temperature some if not all, of the positive and negative ion vacancies, initially present in the crystal, exist as isolated or free vacancies which are effective in the formation of F and $V_1$ (Seitz's model) centres. Moreover, layers of powder phosphor, as used in the present experiments, allow the formation of these centres in larger concentrations, as revealed by the experiments of Apker and Taft[73] and of Parker[74].

As already mentioned in Chapter 3, KCl:Tl has two absorption bands, viz., 195 and 247 mμ. Absorption in 247 mμ produces only fluorescence, while that in 195 mμ produces phosphorescence along with fluorescence[75,76]. In KCl:Tl phosphor the afterglow persists for a long time after the excitation ceases. The phosphor exhibits thermoluminescence but shows no photoconductivity. To explain these characteristics of the phosphor it has been suggested that though the electron traps and Tl emission centres are two separate entities, they have a close spatial association with each other[9,10]. In other words, the phosphorescence centre is a complex formed by the close association of the emission centre and the trapping site. It has been suggested that the short wavelength (195 mμ) irradiation results in the trapping of the

FIG. 10.



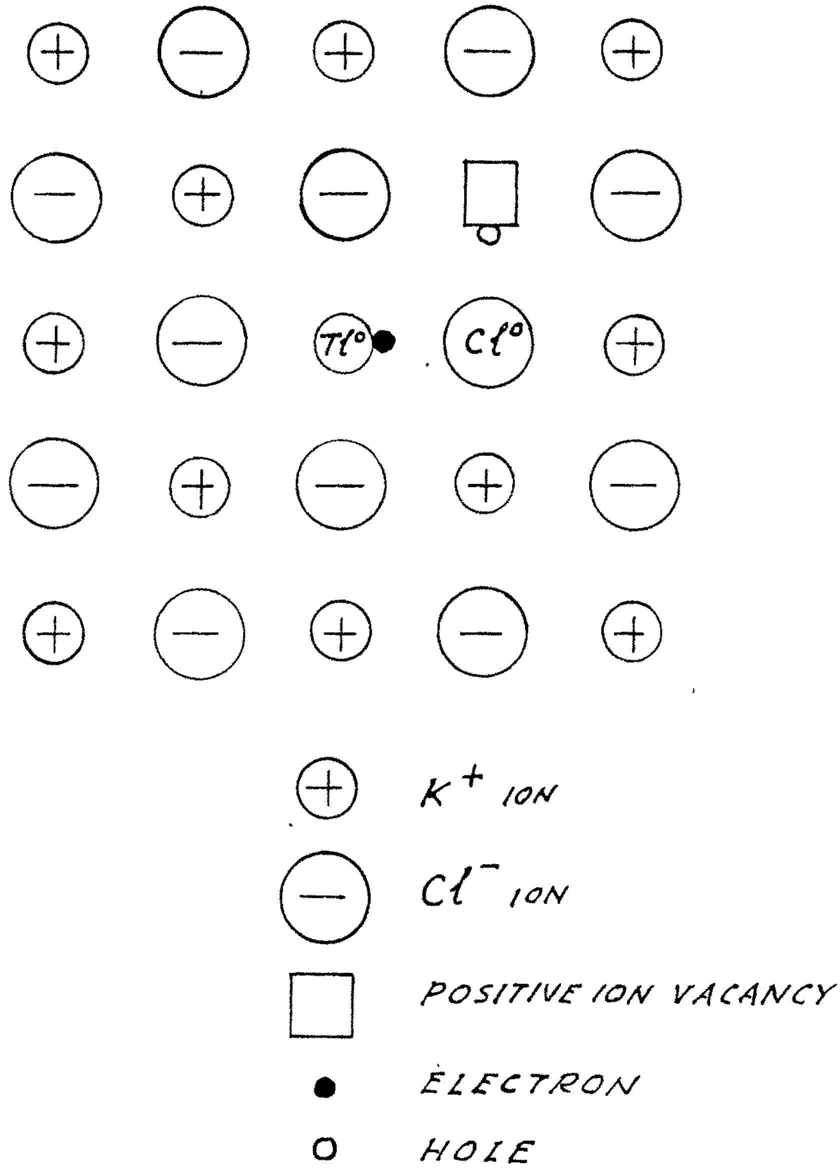
$n$ - GROUND STATE OF THE ELECTRON TRAP.
$n_e$ - EXCITED STATE OF THE ELECTRON TRAP.
$m$ - HOLE TRAP.

electrons at the adjacent trapping site. As shown in Figure 10, on warming up, the electron is raised thermally from the ground state of the trap to the excited state below the conduction band from where it recombines with the hole at the adjacent Tl centre by a tunnelling process[63,77]. After excitation, when the sample is warmed at a constant rate, the traps at different depths are emptied in succession, at temperatures decided by the thermal stability of the corresponding trap. Each glow peak will then correspond to a different trap depth.

In the case of 200°K glow peak the colour centre that readily suggests itself as trapping site is F' centre, since it is the one that has maximum rate of decomposition in the temperature region about 200°K. However, formation of these centres necessitates copious supply of free electrons. Alkali halide crystals exhibit a "step" or a peculiar shoulder in the absorption spectra, situated about 1 eV above the fundamental absorption edge, and in potassium chloride the absorption edge and the "step" appear at 167 mμ (7.3 eV) and 147 mμ (8.3 eV) respectively[78 to 80]. The strong absorption region between the edge and the step is photoelectrically inert. Based on the study of external photoemission, Taft and Philipp[81] suggested that during the illumination of alkali halide crystals with wavelengths shorter than that corresponding to the step, band - to - band transitions of electrons are stimulated. In other words, the maximum photon-energy required for obtaining free electrons in potassium chloride will be that corresponding to about 145 mμ. Hence it may be concluded that the formation of F' centres is to be ruled out, during excitation with energy less than that corresponding to 160 mμ, which is in fact greater than the short wavelength limit of the quartz envelope (viz., 180 mμ) surrounding the phosphor, used in the present experiment.

The work of Williams and his collaborators has successfully demonstrated that some of the absorption and emission characteristics of KCl:Tl phosphor can be explained on the basis of the substitutional entry of $Tl^+$ ions in KCl lattice. This is also corroborated by the study of the diffusion of $Tl^+$ ions in alkali halides[82] and the experiments performed by Klick and Compton[83] on KCl:Tl using polarised light. To explain the observed behaviour of the 200°K glow peak, the following model is suggested. Upon irradiation of KCl:Tl with ultraviolet light at liquid nitrogen temperature, a chlorine ion is

FIG. 11.



ionised and the electron is trapped at the adjacent substitutional $Tl^{+}$ ion forming $Tl^{o}$ atom. The positive hole is trapped as a $V_1$ centre (Seitz's model) i.e., as a $Cl^{o}$ atom at an adjacent positive ion vacancy as shown in Figure 11. The $Tl^{+}$ ion and the positive ion vacancy can each occupy any of the six sites which are nearest neighbours to the ionised chlorine ion.

It is suggested that on heating the phosphor to about $200^{o}K$, the $V_1$ centre becomes unstable and disappears as a result of the electron - hole recombination at the hole centre, with the emission of a photon. The impurity ion is suggested to serve as a shallower trap for the electron. The quantum efficiency of such radiative recombination is known to be very small and hence the energy difference between the excitation energy of the exciton and the energy emitted as luminescent photon is large. Immediately following recombination, the available excess energy may be localised and hence the ions that are nearest neighbours of the previously ionised chlorine ion will be in a high state of thermal agitation or vibrations. If the vibrational energy drops to a level in resonance with the excitation energy of the $Tl^{+}$ ion, the activator will get excited. The return of the excited $Tl^{+}$ ion to the ground state will be accompanied by its characteristic emission. This is a typical process of sensitized luminescence in which energy is partially transferred from one system to another, the two systems being sufficiently close. It is presumed that the energy released by recombination process at the chlorine ion may not be sufficiently energetic to excite the neighbouring $K^+$ ions.

It is proposed that the emission due to excitation of the $Tl^+$ ion will be in the ultraviolet if the $Tl^+$ ion is isolated. However, if a $Tl^+$ ion resides at any of the nearest-neighbouring sites of another $Tl^+$ ion, then there will be an inter-impurity interaction. It is believed that the visible emission in KCl:Tl phosphor results from the electronic transitions within $Tl^+$ ion perturbed by the electric field of a neighbouring $Tl^+$ ion. Thus the ultraviolet and the visible emissions of the phosphor at 200°K involve the thermal bleach of the same species of colour centres viz., $V_1$ centres. The difference in the emission is due to dissimilarity in the nature of the emitters. On this basis it is possible to understand the behaviour of the 200°K glow peak, for ultraviolet and visible emissions, with respect to Tl concentration. It has been observed that increase in Tl concentration preferentially enhances the 200°K glow peak in the visible (Figures 1 and 2 of Ref. No. 63). Increase in Tl concentration also increases the probability for two $Tl^+$ ions to occupy nearest-neighbouring sites and hence the probability for a positive ion vacancy to get trapped in the resultant electric field of two neighbouring $Tl^+$ ions also increases. As a result, the 200°K glow peak for visible emission should show relative enhancement in its intensity. The present model also explains the decrease in the intensity of 200°K peak, in the ultraviolet as well as in the visible, if KCl:Tl phosphor is subjected to cyclical succession of irradiation, heating and cooling (Figures 6 and 7). If the specimen is heated to temperature around 400°K, the thermal energy provided will stimulate migration of the positive ion vacancies from their sites. This will therefore result in the destruction of the corresponding phosphorescence centres.

Instead of thallium if any other impurity such as barium or strontium is used then by arguments similar to those presented above, one should expect in these phosphors a glow peak at about 200°K (Figure 8), since the thermal activation energy is utilised in the annihilation of the $V_1$ centre. The thermal bleach of the $V_1$ centre is accompanied by the emission characteristic of the adjacent activator. On this view it is possible to account for the occurrence of the 200°K glow peak in terms of the electron-accepting properties of the impurity ion. Slight deviations from 200°K in the bleaching temperatures of the phosphors examined may be due to differences in the recombination processes involving $V_1$ centres and different type and concentration of impurity.

It is observed in Figure 9 that the glow peak at 200°K is considerably enhanced if 'specpure' KCl powder is compressed into tablet or 'pure' KCl single crystal is deformed by stressing. To account for the observed effect, it is suggested that the methods adopted for the purifications of the salt may not be adequate to produce the high degree of purity required. For example, in 'specpure' potassium chloride, even after recrystallisation, impurities like lead, iron, and calcium may be present at concentrations well below the limits of conventional analysis[84]. Such unsuspected impurities exist in true solid solution in the salt; but are precipitated out as separate phase in the carefully annealed and extremely slowly cooled samples. When such a sample is plastically deformed, the precipitated impurities get dissolved on an atomic scale due to the dispersing action of the plastic deformation. If the impurities dissolved, be higher in valency than that of the cations of the host lattice, then the number of positive ion vacancies will simultaneously increase. In case the divalent impurities as those mentioned above are involved, then dissolution of impurities may create a divalent ion - positive ion vacancy complex in the specimen. There are experimental as well as theoretical evidences in support of the existence of such complexes[85 to 87]. Formation of such complexes lends further support to the interpretation given in the foregoing discussion that a combination of a $V_1$ centre and an impurity atom (or ion) is associated with the glow peak.

Besides the redissolution of impurities, the plastic deformation may also generate additional Schottky vacancies in the wake of moving dislocations in a signle crystal or in the microcrystals of the powdery sample. This process involves the diffusion of vacancies to or from the dislocations and there appears to be a reasonable probability that the number of randomly dispersed positive ion vacancies may increase in the volume of the specimen. The plastic deformation may thus be considered to be conducive to the creation of the emitters and additional positive ion vacancies. The occurrence of a significant glow peak at 200°K in deformed 'pure' KCl specimen is thus understandable, in a general sense, on the basis of $V_1$

centre - impurity atom (or ion) complex proposed above.

In the light of the experiments performed, Hersh and Hadley[68] attribute the glow peak at about 200°K in doped and undoped KCl, to the disappearance of $Cl_2^-$ ($V_k$ centres) and unidentified electron centres. They studied the optical absorption due to $V_k$ centres in the case of undoped KCl and KBr which had been plastically deformed, and in thallium-doped crystals not subjected to plastic deformation. They conclude that the temperature for maximum rate of disappearance of $V_k$ centres coincide with the glow peak temperature about 200°K in doped KCl or in undoped but strained KCl. In KCl:Tl or in KCl activated with any other impurity there are two principal glow peaks at about 200°K and 300°K. It has been proposed earlier by Joshi[64], also very well corroborated by the analysis in Section 5.3, that the electron traps with depth on the temperature scale around 300°K are due to single negative ion vacancies. Since the positive and negative ion vacancies must be equal in number to maintain the charge neutrality of the crystal and further, since concentration of F centres has been observed to be intimately related to the concentration of $V_1$ centres and not to that of $V_k$ centres, the second principal glow peak at about 200°K can be believed to be associated with single positive ion vacancies. This is supported by the experimental results of Johnson and Williams[5] who observed F and V centres in KCl:Tl and of Chiarotti and Inchauspe'[72] who reported F and $V_1$ centres in undoped KBr after illumination with UV light in the exciton band. Further, luminescent centres in undoped but strained KCl have been associated by Ewles and Stead[59] with positive ion vacancies.

The mechanism in relation to the model of Hersh and Hadley would involve the transfer of an electron from $Cl^-$ ion to the adjacent $Tl^+$ ion and subsequent pulling together of the resulting Cl atom with a neighbouring normal halide ion. This would give rise to a Tl atom - $V_k$ centre complex. Thermal bleaching of the $V_k$ centre at about 200°K would result in the electron - hole recombination, accompanied by the emission characteristic of the $Tl^+$ ion, and the return of the halide ions to their normal lattice sites. However, such a model cannot explain the decrease in the height of 200°K glow peak during consecutive runs of irradiation, heating (up to about 400°K) and cooling. The observed decrease in height would require one of the $Cl^-$ ions of the pair forming

$V_k$ centre to diffuse away from the $Tl^+$ ion. This seems to be very unlikely under the conditions of temperature that prevail during the experiment. Anion diffusion has been suggested to take place, below 500°C, by a vacancy pair mechanism[88]. On the basis of the model presented in this thesis, the number of $V_1$ centres (Seitz's model) in the subsequent cycles will be lessened as a result of cation vacancy diffusion at temperatures higher than the room temperature. The unidentified electron centres suggested by Hersh and Hadley in the undoped-but-strained KCl could be the impurity ions that went in solid solution as a result of plastic deformation.

The present model derives immense strength from the spin resonance studies by Delbecq et al[28]. They observed that in x-rayed KCl:Tl, the spin resonance signals due to holes disappeared simultaneously with an absorption band at 350 mμ, at 208°K. The present analysis is made using Seitz's model of the $V_1$ centre. There is also another model for $V_1$ centre viz., the $Cl_2^o$ (neutral halogen molecule) model suggested by Känzig and Woodruff[89]. They have proposed the formation of $V_1$ centres ($Cl_2^o$ model) from H centres, on the basis of the close structural and genetic relationship between them. The H centre is known to be formed by x-raying KCl at liquid helium temperature by mechanism suggested either by Varley[36] or by Klick[12]. Since the formation of H centre is a prerequisite for the production of $V_1$ centre ($Cl_2^0$ model), there is no possibility of obtaining such centres by irradiation with ultraviolet light at liquid nitrogen temperature. The present discussion is therefore made in relation to the Seitz's model of the $V_1$ centre, which is the antimorph of the F centre.

## 5.2 $250^{\circ}$K Peak

A pronounced glow peak at $250^{\circ}$K in the impurity doped KCl has been reported earlier by Johnson and Williams[5] in the case of KCl:Tl. The specimens used in their study were prepared by rapid fusion and cooling. The same glow peak is observed in 'pure' KCl if it is quenched from the melt to liquid nitrogen temperature. Work of more or less similar nature was reported in a previous paper[61]; but the significance of the results obtained was not clear. The present work aims at finding out the nature of the phosphorescence centres responsible for the glow peak at $250^{\circ}$K. The work thus involves the identification of the trapping site and the emission centre which together constitute the phosphorescence centre.

It is seen from Figure 12 that quenched 'specpure' KCl, obtained as a compact polycrystalline mass, exhibits a pronounced glow peak at $250^{\circ}$K and two subsidiary peaks around $300^{\circ}$ and $400^{\circ}$ K. The figure also indicates that if the specimen is subjected to the cyclical successions of irradiation at liquid nitrogen temperature, heating to around $450^{\circ}$K and cooling, then the glow peaks in general decrease in strength at the end of each heating run except for a small rise in the strength of $400^{\circ}$K peak at the end

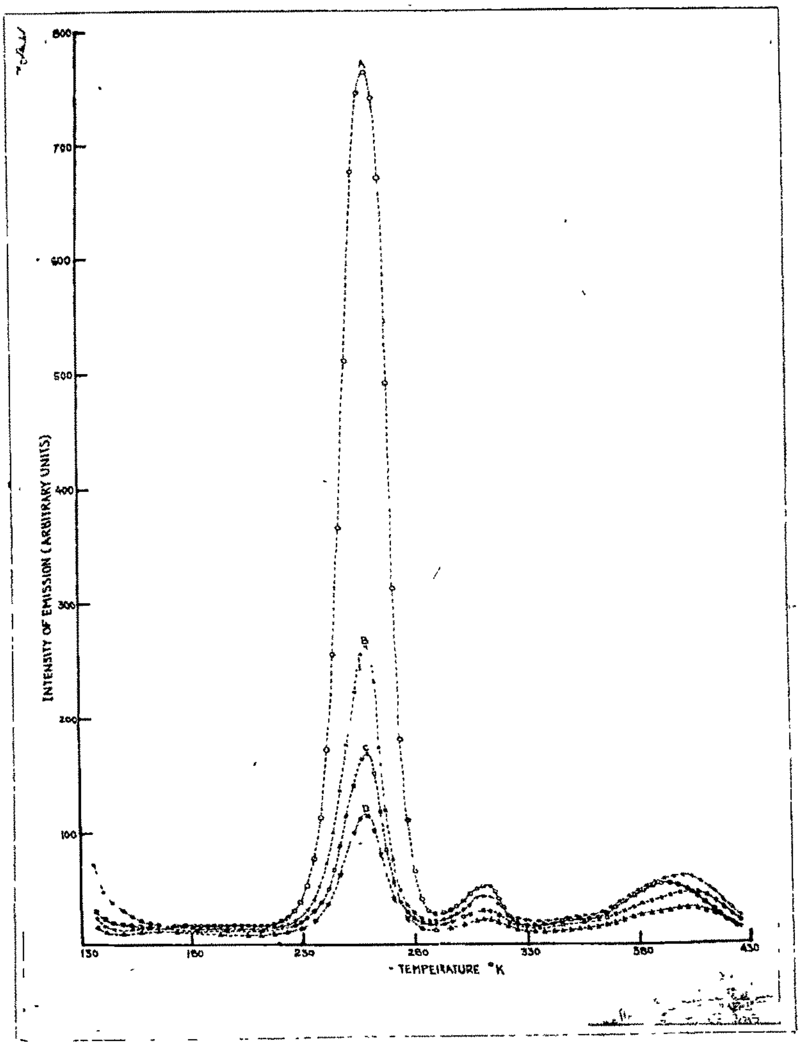


Fig. 12. Thermal glow curve of 'specpure' KCl quenched from melt.

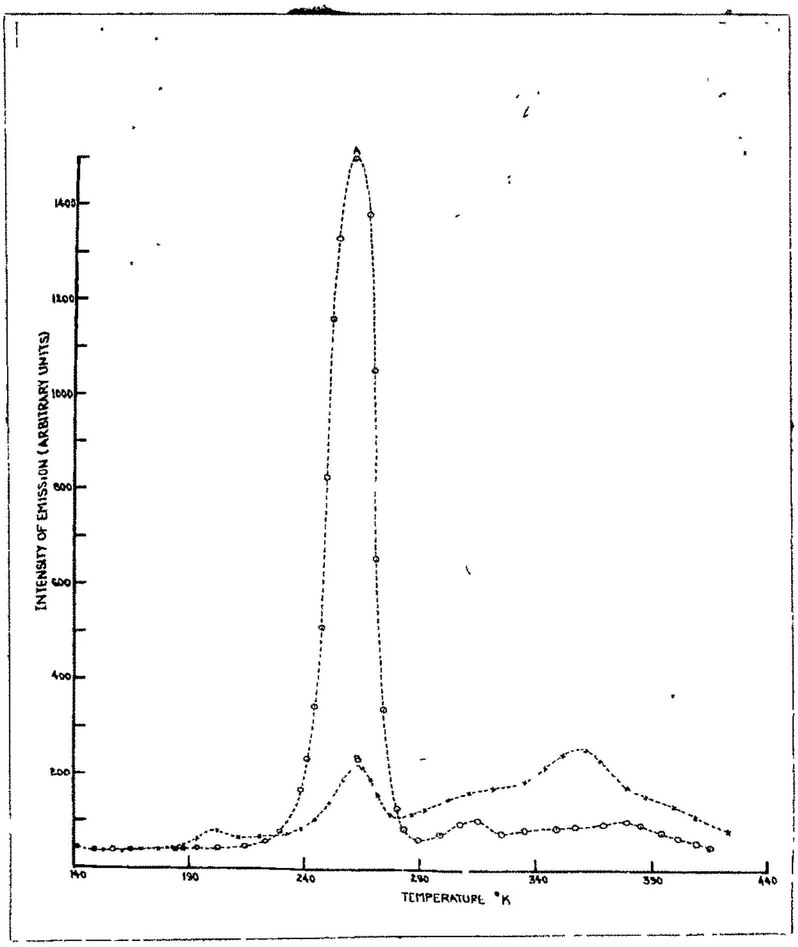


Fig. 13. Thermal glow curve of 'specpure' KCl quenched from melt(A); quenched from melt and compressed(B).

of second heating run. Figure 13 shows that when the quenched specimen is compressed under a pressure of about 2000 kg. $cm^{-2}$, there are large scale changes in the trap distribution. Curve A is for the polycrystalline mass obtained by quenching a given quantity of KCl from the melt to the liquid nitrogen temperature. Curve B shows the effect on the glow curve when another polycrystalline mass, obtained similarly and containing the same amount of KCl, is compressed. It is observed that the peak at $250^{\circ}K$ is considerably suppressed and that at $300^{\circ}K$ is conspicuously enhanced, along with the appearance of a new glow peak at $350^{\circ}K$.

Results reported earlier[61] indicate that the KCl melt, quenched either in air or in vacuum, exhibits the same glow peaks. One may therefore infer that these peaks are not the effects of contamination by air. Further, experiments carried out with 'specpure' and 'Reagent' grade KCl makes a categorical assignment of these effects to impurities alone, improbable. It is suggested that the trapping sites involved at $250^{\circ}K$ are cation-anion vacancy pairs with the cation and anion vacancies residing on two adjacent sites in the lattice.

So far, it has not been possible to obtain experimental evidence to support the existence of vacancy pairs in the alkali halides. However, vacancy pairs have their importance in the understanding of colour centre reactions[14] and anion diffusion[88,90] in alkali halides. Defects present in the alkali halides, at a temperature as high as the melting point, can only be Schottky defects. Theoretical considerations[14,91] indicate that in alkali halides near melting point, approximately 0.1 % of the lattice sites are vacant. At temperatures as high as the melting point, the positive and negative ion vacancies would, as a result of Coulomb attraction, associate into neutral pairs relatively more quickly, thereby eliminating isolated vacancies. Thus, during the quench, most of the vacancies may get associated into pairs and some in higher aggregates. One may then picture the quenched specimen to contain many neutral pairs in equilibrium with dissociated vacancies.

The decrease in the number of 250°K traps, by heating to about 450°K, suggests that the trapping sites are not thermally stable at 450°K. Results reported by Tharmalingam and Lidiard[92] indicate that the mobilities of vacancy pairs in the room temperature region are not much higher than those of single anion vacancies in this region. Since the distance a vacancy pair can move is thus limited by its diffusion coefficient, it is suggested that during the heating, a vacancy pair diffuses to a dislocation site or a sub-boundary situated a few atomic distances away and gets annihilated. Quenching a specimen from melting point to liquid nitrogen temperature imparts a considerable thermal shock to the specimen. Hence the dislocations introduced in the microcrystals of the specimen by thermal stresses should be large in number and their possible effects should be equally significant. The thermal energy provided by heating may be sufficient to stimulate migration of a pair to a nearby dislocation. Since the dislocations act as sinks for vacancies, the vacancy pair gets destroyed at the dislocation site. The decrease in the concentration of vacancy pairs would naturally involve a corresponding decrease in the concentration of free vacancies in equilibrium with the pairs.

In Figure 12 it is observed that the three glow peaks are unequally influenced by the successive runs of heating and cooling. This suggests that these traps do not have the same nature. It is proposed that the

$300^{o}K$ trap is due to single negative ion vacancies and the $400^{o}K$ trap may be due to single negative ion vacancies in a different environment. Since the increase in the number of $400^{o}K$ traps observed at the end of second heating run is not matched by the corresponding decrease in the number of $250^{o}K$ traps, it appears that only a small fraction of the vacancy pairs is involved in the conversion to deeper traps. One may, in general, say that as a result of heating there is decrease in the number of all the traps.

Figure 13 shows that when the quenched specimen is compressed, at room temperature, the $250^{o}K$ traps decrease in number and those at $300^{o}K$ increase considerably. Simultaneously a pronounced new glow peak at $350^{o}K$ appear. In this case the change in trap distribution obviously indicates that a significant number of vacancy pairs takes part in the conversion to deeper traps and a few disappear, probably by diffusion to dislocations. When the specimen is compressed the dislocations will naturally be set in motion. It is proposed that the heat generated by a passing dislocation may be sufficient to cause the removal of the electron from the $Cl^{-}$ ion to the neighbouring negative ion vacancy of the neutral pair.

Trapping of an electron by the pair will break up the pair and the positive ion vacancy will be free to move. Presumably, some of the dissociated positive ion vacancies diffuse away and contribute to form hole-traps at 200°K as indicated by a small rise in the curve at that temperature.

Thus the decrease in the intensity of 250°K glow peak in quenched KCl, by heating or by pressure, is understandable in a general sense on the basis of the vacancy pair model for electron traps at that temperature.

The mechanism suggested for the filling up and the emptying of the traps is as follows. Irradiation with ultraviolet light at liquid nitrogen temperature transfers the electron from a chlorine ion to the adjacent cation-anion vacancy pair. In this case no breaking up of the pair, due to trapping of the electron, is suggested since the mobility of the positive ion vacancy near liquid nitrogen temperature will be almost negligible. Subsequent heating of the phosphor to about 250°K causes the return of the electron to its parent chlorine ion and the resulting electron - hole recombination at the hole centre will be accompanied by the emission of a photon. However, in potassium chloride, the quantum efficiency of such radiative recombination is known to be very low and hence the corresponding luminescence may be observable in the infra-red region. The recording system used in the present measurements did not extend to this region. Therefore, it seems preferable to assume that the emission recorded in the case of quenched 'pure' KCl is not due to luminescent photons emitted during electron - hole recombination; but appears to have its origin in some other process.

It is mentioned in Section 5.1 that 'specpure' KCl contains residual impurities like lead, iron and calcium[84]. The as-received sample must have been cooled extremely slowly, probably over a period of several days, after a high temperature anneal. During the extremely slow cooling of the KCl powder the residual impurities might have precipitated out as a separate phase. Since the quench rate utilised in the present work is sufficiently fast these impurities might have been re-dissolved with even distribution in the bulk of the sample. It is suggested that such re-dissolved impurities, which are mainly divalent, are involved in the occurrence of the glow peak at 250°K. Effects related to such unsuspected impurities, having concentrations below the level of spectrochemical detection, can be observed if the sensitivity of the recording system is sufficiently high. It is suggested that immediately following electron - hole recombination, part of the available excess energy is transferred to the adjacent re-dissolved impurity ion . Absorption of energy by the impurity ion excites it and the subsequent return of the excited ion to the ground state is accompanied by its characteristic emission.

The glow peak at 200°K has been shown to result from the thermal bleach of $V_1$ centres (Seitz's model) [Section 5.1]. If the same hypothesis were to be extended to the present case, one may say that the phosphorescence centre at 250°K in quenched KCl involves a combination of a divalent ion and a cation-anion vacancy pair. Such a configuration would mean that the glow peak at 250°K follows as a consequence of the thermal bleach of one of the Z centres, since these centres are the characteristic of the divalent impurities. In spite of numerous efforts in the past it has not been possible to arrive at a consistent picture of the Z centres either theoretically or experimentally. Hence it is not possible to conclude which of the Z centres is actually involved in the process.

In the light of the proposed vacancy pair model we discuss here the occurrence of a pronounced glow peak at 250°K, reported by Braner and Halperin[51], in x-irradiated KCl. They observed that the glow curve exhibited by virgin KCl crystal undergoes changes in the intensity distribution of the peaks if the crystal is subjected to subsequent cycles of x-irradiation (at liquid nitrogen temperature), heating (to about 500°K) and then cooling. It was observed that 40 cycles of heating and cooling and 5 hours of x-irradiation resulted in enormous increase in the intensity of 250°K glow peak (Figure 4 in Ref. No. 51). This result is consistent with the vacancy pair model as discussed below.

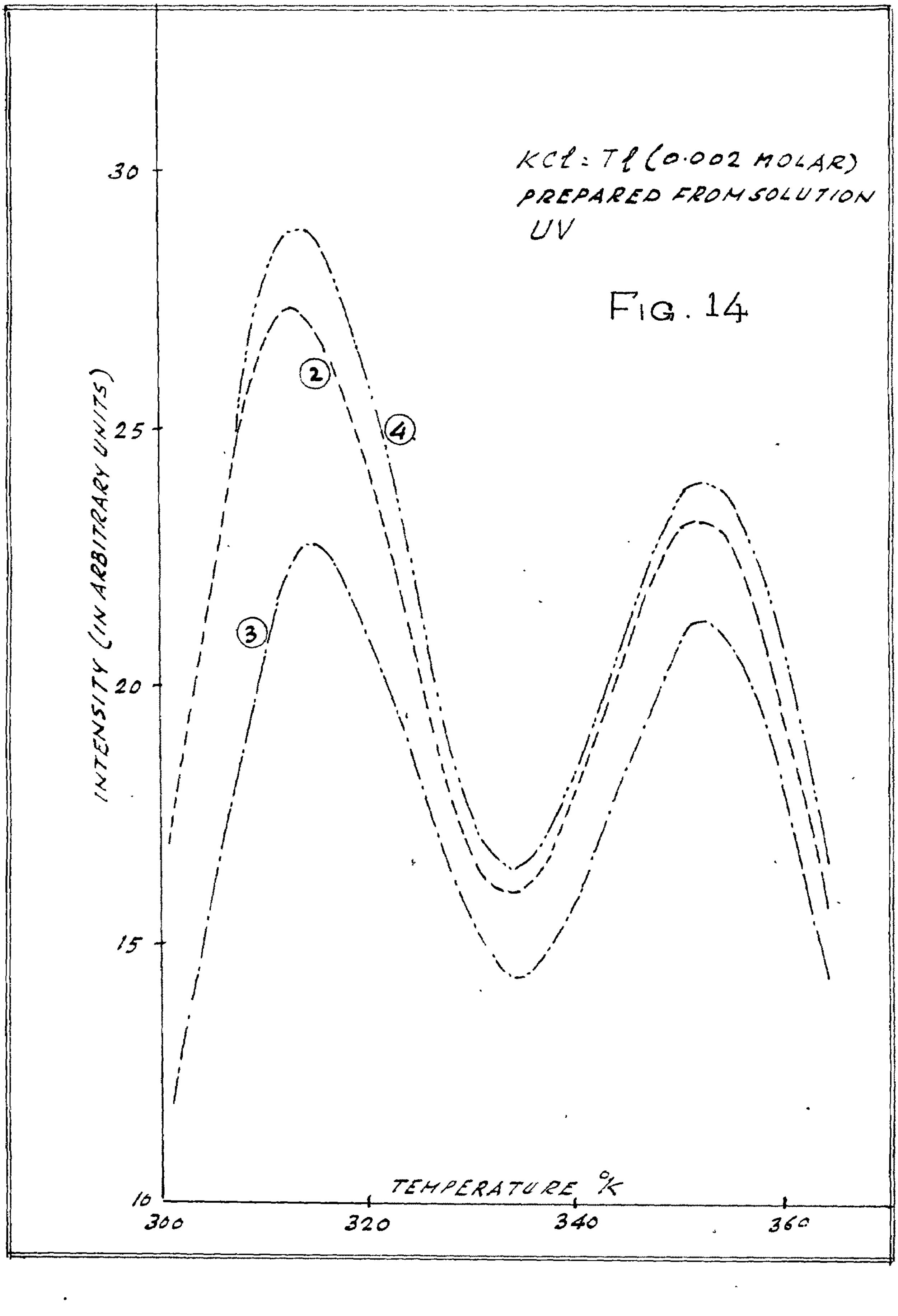
Though the present state of understanding of the nature of the defects formed by x-irradiation at liquid nitrogen temperature is not quite satisfactory, most of the speculations[14] concerning colouration at this temperature assume the production of F centres from Schottky defects. Because of the requirement of electrical neutrality of the crystal, cation and anion vacancies may therefore be continually generated by x-irradiation. After each dose of x-irradiation, Braner and Halperin heated the crystal to about 500°K for the record of the glow curve. The thermal energy provided by heating would be sufficient to stimulate the migration of vacancies. During migration, if a positive ion vacancy and a negative ion vacancy arrive at a distance of few lattice spaces from each other they will, as a result of strong Coulomb attraction, associate themselves to form a neutral pair. Thus, due to cyclical succession of x-irradiation, heating and cooling, the concentration of vacancy pairs in the crystal would increase, which, according to vacancy pair model, would enhance the number of 250°K trapping sites. If the neutral pairs are in the neighbourhood of the impurity ions intrinsically present in the crystal, then, as is to be expected, the strength of the 250°K glow peak would increase.

On the basis of the concept offered to explain the occurrence of 250°K glow peak, the observation of Johnson and Williams[5] can be easily understood. The KCl:Tl phosphors used in their study were prepared by rapid fusion and cooling which would create a high concentration of vacancy pairs in the specimen. Naturally, the electron trapping sites would then be the vacancy pairs and the emission centres would be the $Tl^+$ impurity ions. The excitation of the $Tl^+$ ion would take place by the partial transfer to it of the electron - hole recombination energy.

## 5.3 300°K and 350°K Peaks

In this section the glow peaks at 300 and 350 °K are discussed collectively. This is particularly advantageous since the trapping sites corresponding to these two peaks are suggested to have in common, the same kind of lattice defects. The trapping sites for the two peaks are however differentiated on the basis of the environments of these defects. Another point in discussing these two peaks together is that they are mainly operative in the room temperature decay the results of which, in the case of KCl:Tl, are examined in the next section. The present analysis is based on the study of the effects, on the thermoluminescent properties of KCl:Tl phosphor, of thermal cycling with excitation and without re-excitation and independently of prolonged high temperature anneal followed by slow cooling.

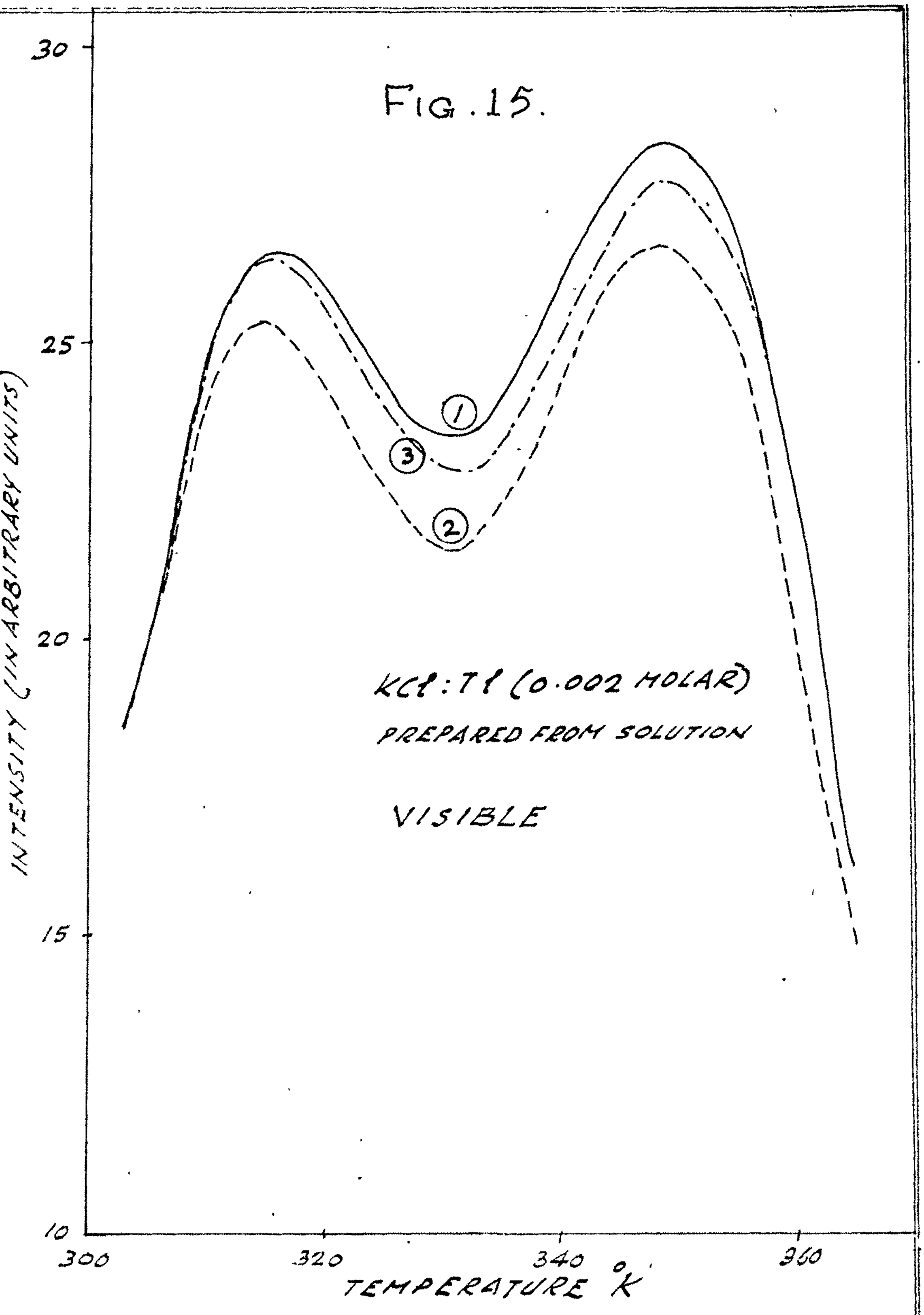
The specimens used were polycrystalline powder obtained by crystallisation from aqueous solution, either in the as-obtained condition or after specific treatment. All the specimens had 0.002 mol. thallium content. The glow curves were recorded at enhanced intensities of the peaks by excitation at room temperature. It is known



KCl : Tl (0·002 MOLAR)
PREPARED FROM SOLUTION
UV

FIG. 14

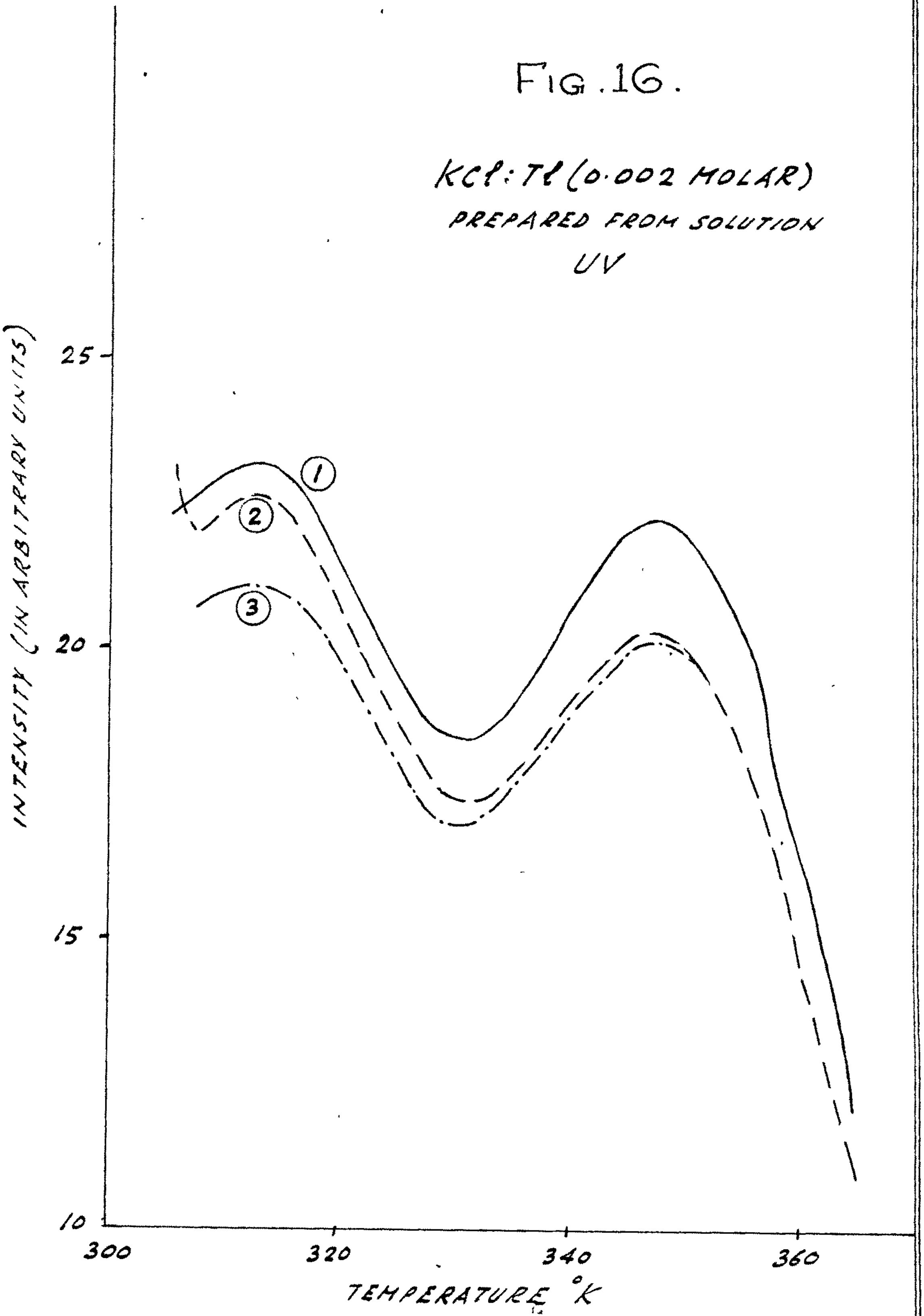
FIG. 15.



KCl : Tl (0.002 MOLAR)
PREPARED FROM SOLUTION

VISIBLE

FIG. 16.



KCl:Tl (0·002 MOLAR)
PREPARED FROM SOLUTION
UV

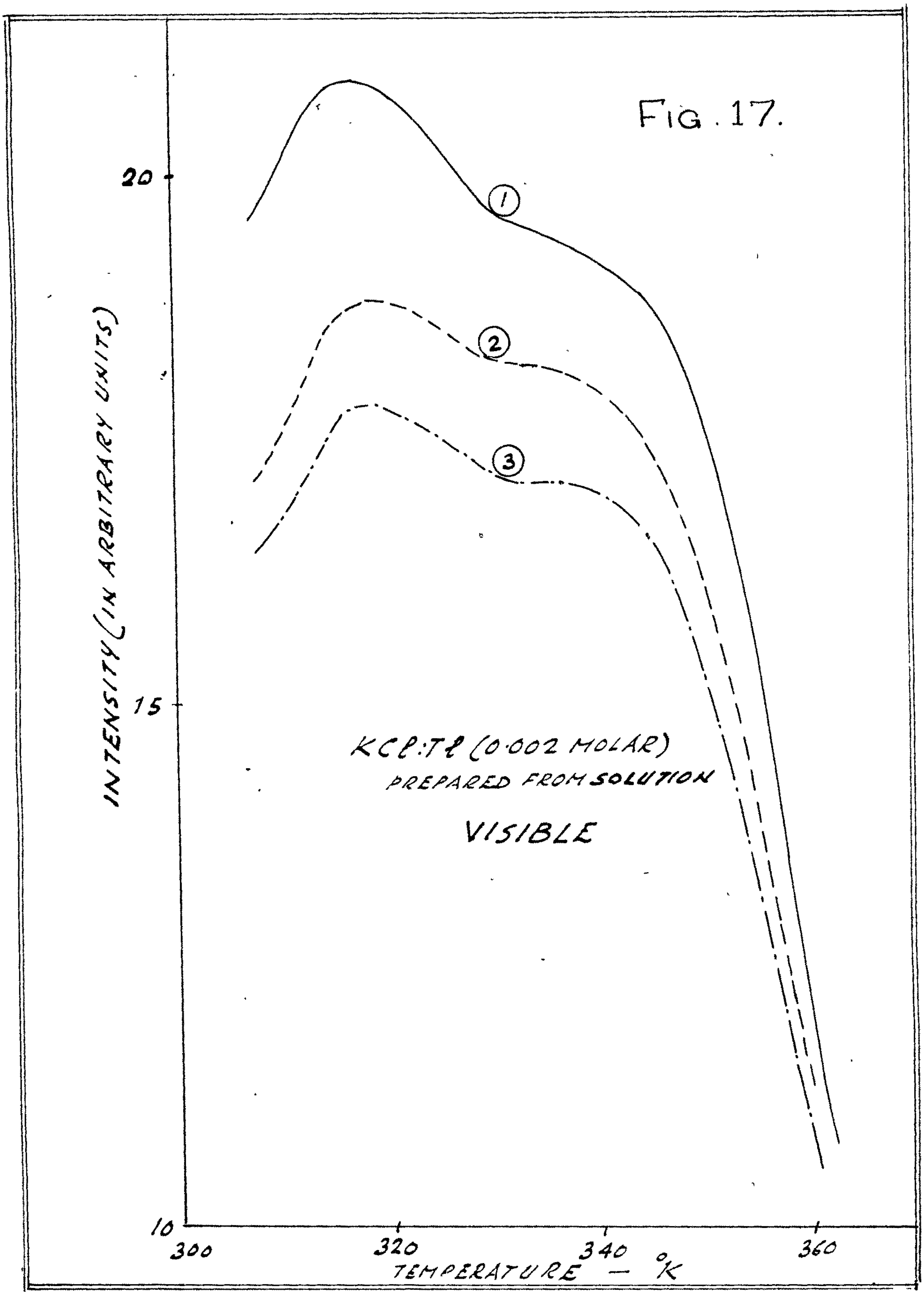


FIG. 17.

INTENSITY (IN ARBITRARY UNITS)
20
15
10
300
320
340
360
TEMPERATURE — °K
①
②
③
KCl:Tl (0·002 MOLAR)
PREPARED FROM SOLUTION
VISIBLE

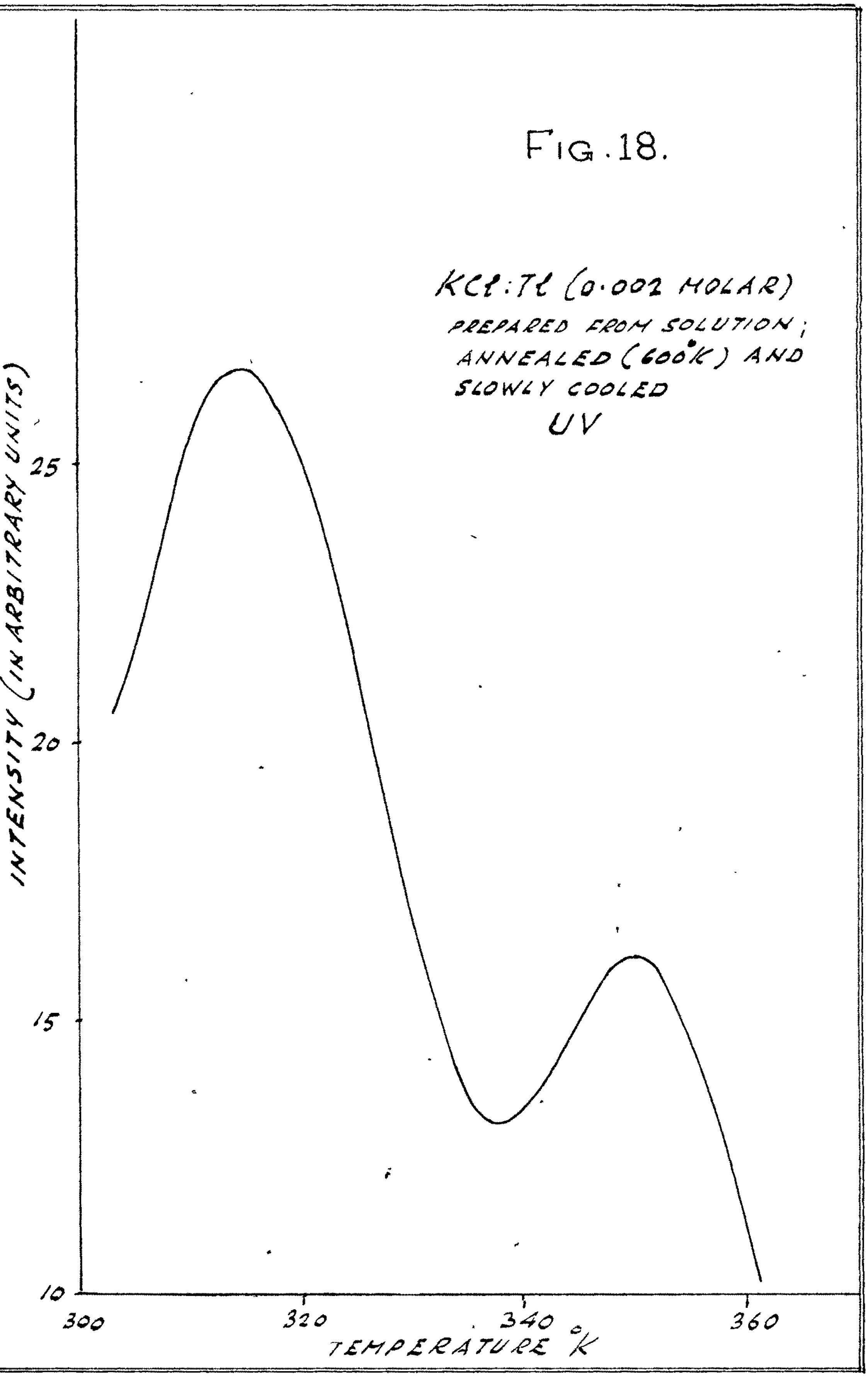
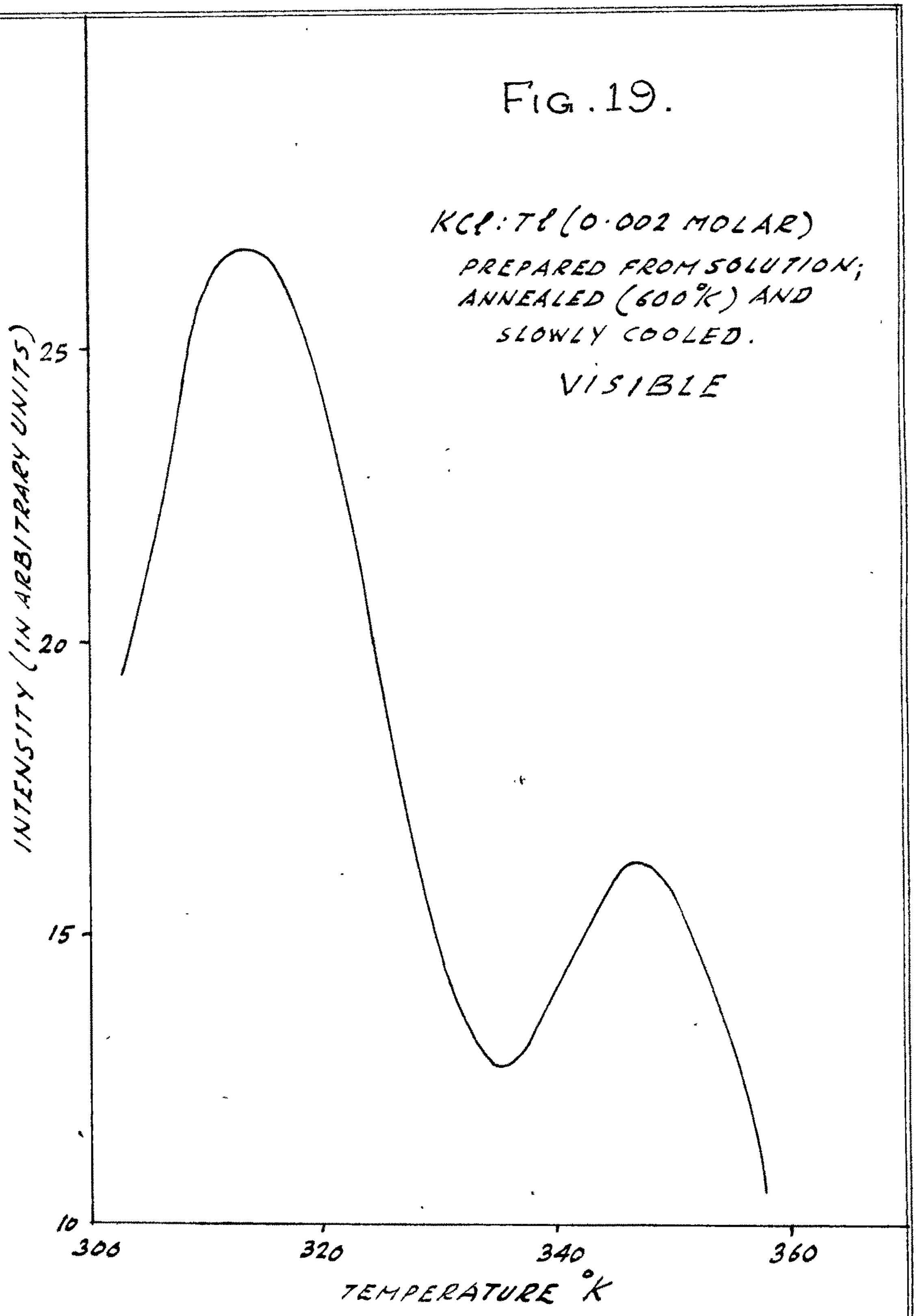


FIG. 18.

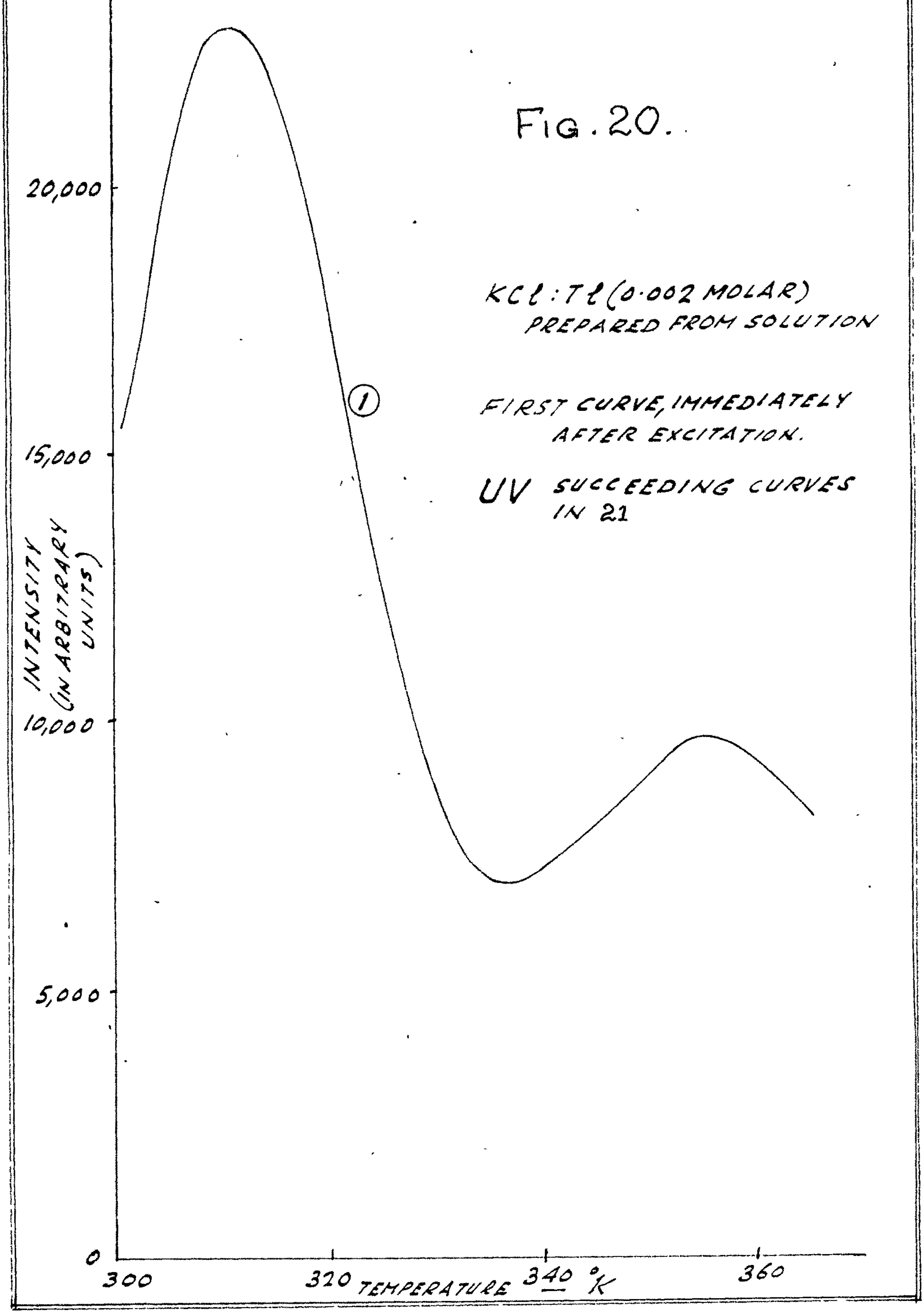
KCl:Tl (0·002 MOLAR)
PREPARED FROM SOLUTION;
ANNEALED (600°K) AND
SLOWLY COOLED
UV

FIG. 19.



KCl:Tl (0·002 MOLAR)
PREPARED FROM SOLUTION;
ANNEALED (600°K) AND
SLOWLY COOLED.
VISIBLE

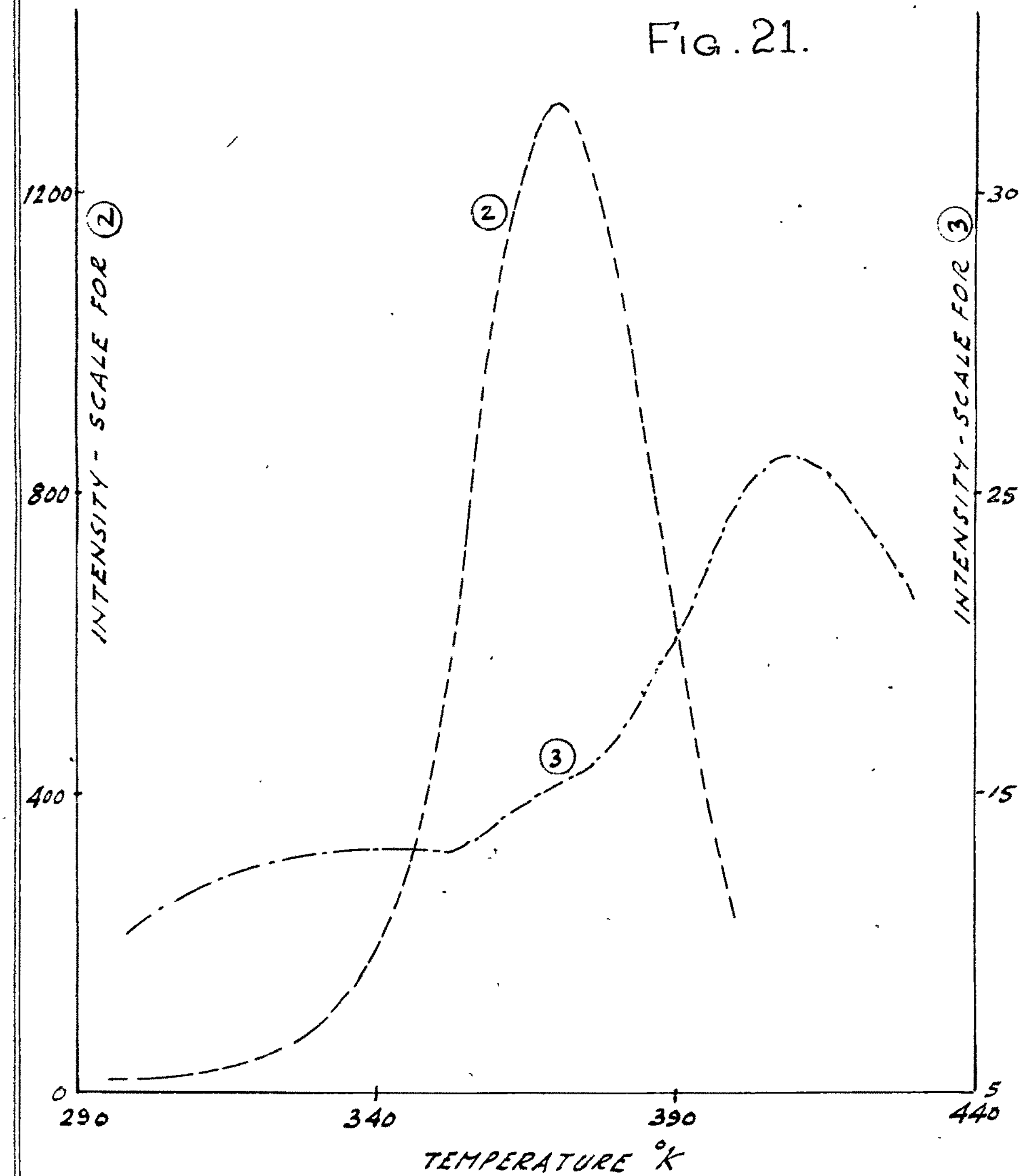
FIG. 20.



KCl : Tl (0·002 MOLAR)
PREPARED FROM SOLUTION

FIRST CURVE, IMMEDIATELY
AFTER EXCITATION.

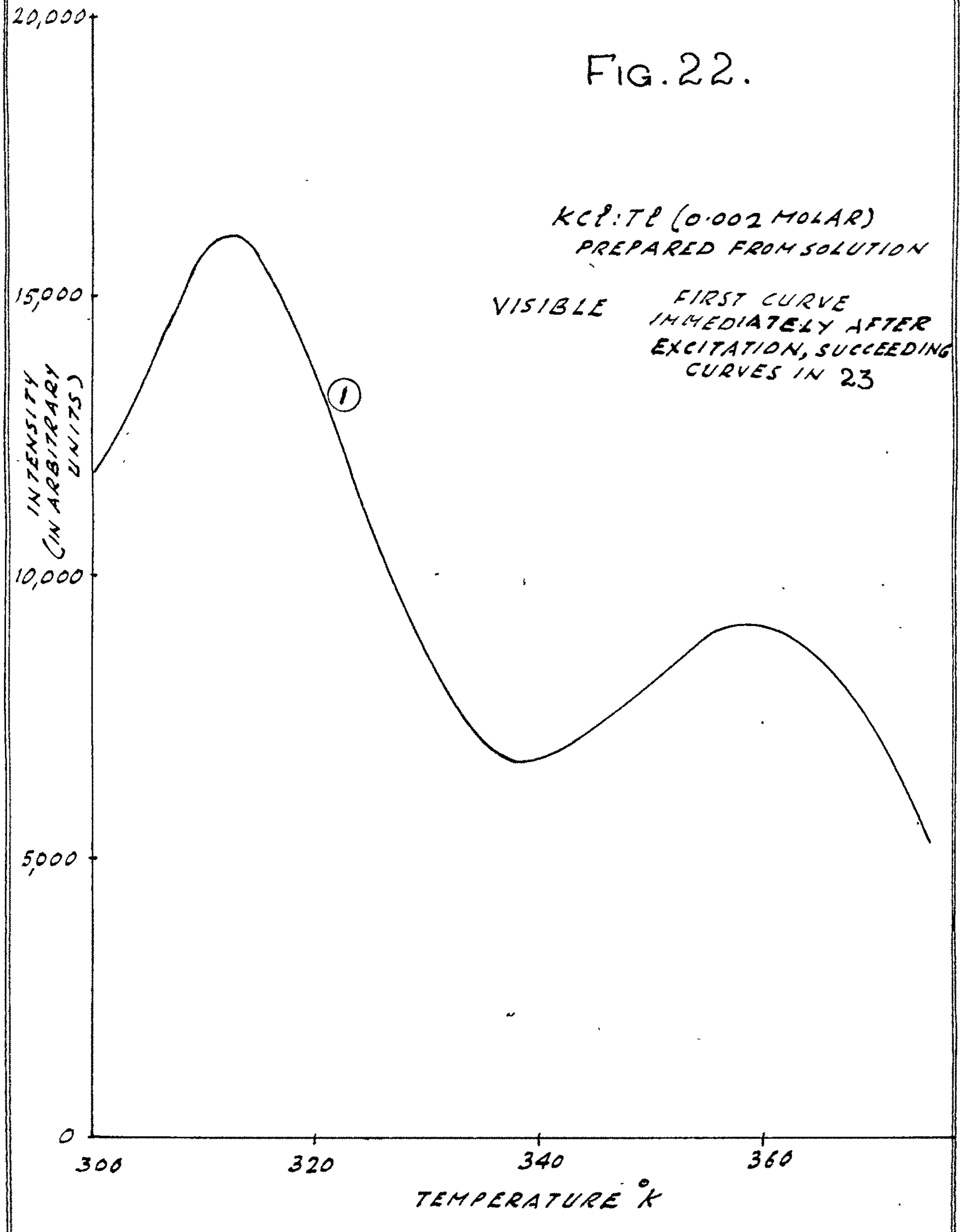
UV SUCCEEDING CURVES
IN 21



INTENSITY - SCALE FOR ②
1200
800
400
0
②
③
INTENSITY - SCALE FOR ③
30
25
15
5
290
340
390
440
TEMPERATURE °K

FIG. 21.

FIG. 22.


KCl:Tl (0·002 MOLAR)
PREPARED FROM SOLUTION
VISIBLE
FIRST CURVE
IMMEDIATELY AFTER
EXCITATION, SUCCEEDING
CURVES IN 23
1
20,000
15,000
10,000
5000
0
INTENSITY
(IN ARBITRARY
UNITS)
300
320
340
360
TEMPERATURE °K

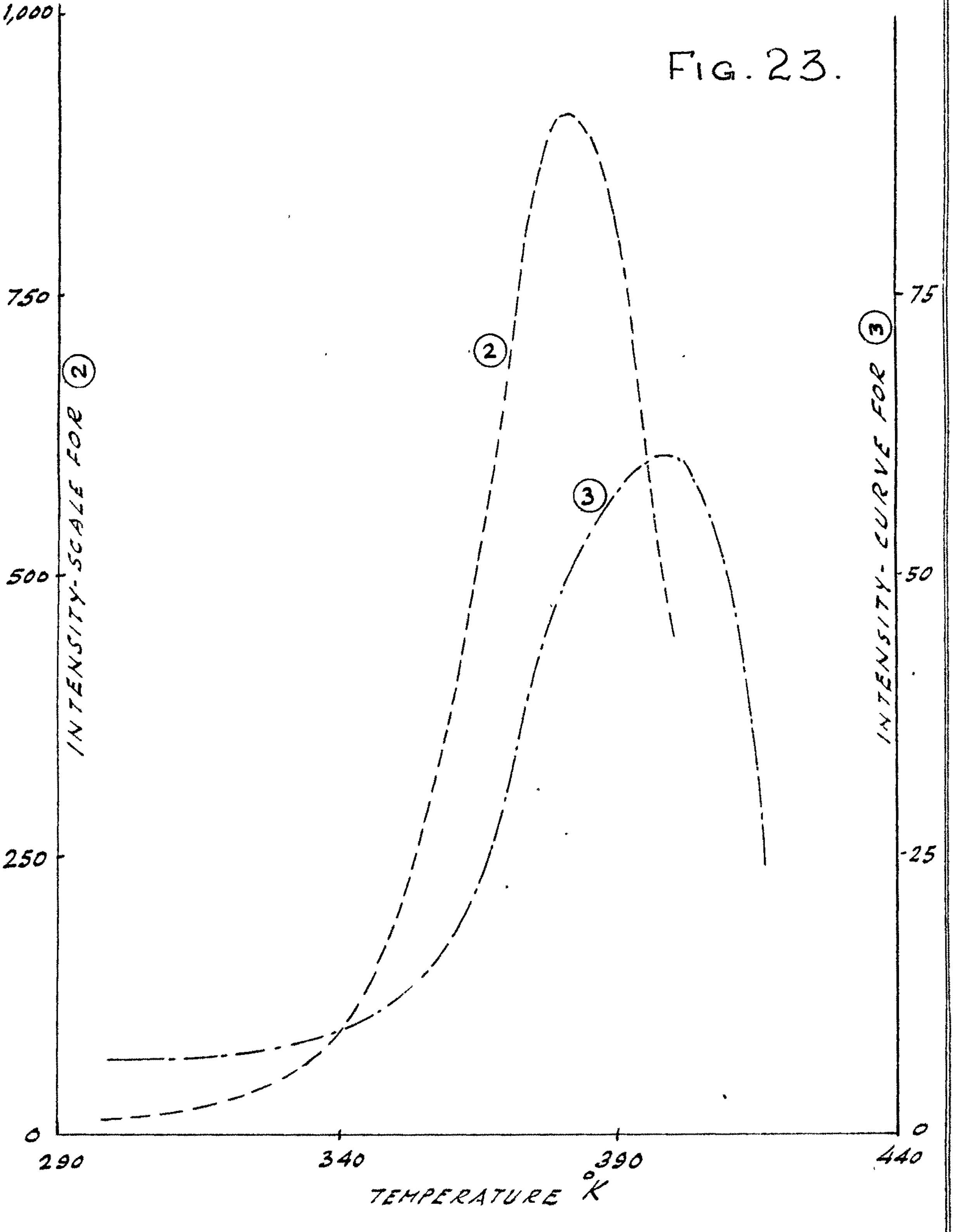

1,000
750
500
250
0
INTENSITY-SCALE FOR ②
②
③
75
50
25
0
INTENSITY-CURVE FOR ③
290
340
390
440
TEMPERATURE °K

FIG. 23.

that glow curve shapes and temperatures of peaks are dependent on the irradiation dose and also on the heating rate. Fixing of the temperature of peak becomes more difficult if the peaks merge irresolvably. The glow peaks observed in the present experiments being in the neighbourhood of 300 and 350 $^{o}$K, these temperature values are used to specify them. Figures 14 and 15 indicate the glow curves for ultraviolet and visible emission respectively, when the KCl:Tl specimen is subjected to the cyclical succession of excitation at room temperature, warming up to about 450$^{o}$K followed by normal cooling i.e., cooling under the conditions prevailing in the laboratory. In both the figures, the consecutive glow curves have been recorded at the interval of about 12 hours. It is observed that the changes for 300 and 350 $^{o}$K peaks, at the end of each heating run, take place in an inconsistent way. However, if the specimen is cooled quickly (within about 15 minutes), by circulating ice-cold water around the specimen holder, the strengths of both the glow peaks decrease progressively at the end of subsequent heating runs. This is exhibited in Figures 16 and 17. The peak at 350$^{o}$K in Figure 17 appears to be spread out. The effect on the glow curves, when the specimen is annealed for 100 hours at 600$^{o}$K and then cooled very slowly at the rate of 0.025$^{o}$/min. is shown in Figures 18 and 19. It is seen that such a treatment selectively suppresses 350°K peak for both the emissions of the phosphor. There are several methods which help to get the individual glow peaks better resolved if they overlap. In one of them, the specimen is subjected to cycles of heating and cooling without re-excitation. Figures 20 to 23 indicate that the use of such a method causes considerable shift in the maximum of the 350°K glow peak to higher temperatures. In the measurement of the glow curves obtained without re-excitation, higher amplification of the recording system had to be used. The first curves obtained immediately after excitation, for ultraviolet and visible emissions of the phosphor are shown in Figures 20 and 22 respectively. The second and third curves for both the emissions obtained without re-excitation are shown in Figures 21 and 23 respectively.

The present analysis makes use of the hypothesis of charged dislocations reported in several recent publications. It has been pointed out, originally by Fishbach and Nowick[93,94] and in greater detail by Eshelby et al[95] that dislocation cores in sodium chloride as well as in some other ionic solids, should be electrically charged. The charge is presumed to arise from the excess of charged jogs on edge components of dislocations. The jogs have been suggested to be produced by the intersection of edge dislocations moving on slip planes which are oblique to each other. By observing the resultant electric field, some workers have suggested that the dislocations in alkali halides behave as if they were positively charged[94], whereas few others have reported negative charge on the dislocations[96,97]. Though the sign of the electrical charge on the dislocations is still uncertain, it has now been established beyond doubt that they carry a net charge. The present discussion relies on the assumption that the dislocations in KCl are negatively charged. The charge on the core of the dislocation is assumed to be small i.e., instead of a model of a compensating charge cloud of ion vacancies around the dislocation line, discrete charges due to these vacancies along the dislocation length has been proposed.

To explain the results obtained, one may consider two categories of phosphorescence centres responsible for thermoluminescence phenomena around room temperature. One of them is presumed to have been formed by a Tl centre - negative ion vacancy complex in the region of the lattice away from dislocations. The other category of phosphorescence centres is proposed to be due to a similar complex but in the vicinity of a charged dislocation. In the second category of phosphorescence centres there may again be various kinds of such centres depending upon the distances of separation between Tl centre - negative ion vacancy complex and the nearby charged dislocation. These phosphorescence centres can then be differentiated on the basis of the degree of electrical interaction between the complex and the charged dislocation. The glow peak at 300°K is suggested to be due to electron - hole recombination in the former category of phosphorescence centre and that at 350°K is presumed to be due to electron - hole recombination in the latter category of phosphorescence centre. The choice as to which type of centre is responsible for which glow peak is mainly based on the qualitative reasoning regarding the ease with which an electron recombines with the hole. For instance, 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 an isolated negative ion vacancy. It will now be shown that the above suggested models for the phosphorescence centres at 300 and 350 °K qualitatively account for all the thermoluminescent features observed in KCl:Tl at these temperatures.

Data presented in Figures 14, 15, 16 and 17 clearly demonstrate that cyclical succession of excitation, heating and cooling of the specimen effects departure from the pre-existing trap distribution. In the alkali halidès, the defects are of the Schottky type, consisting of cation and anion vacancies. Their concentration in the specimen is a function of temperature (vide Section 2.2) given by the relation

$$n = N \exp\left(\frac{-W}{2kT}\right) ,$$

where n is the number of pairs of vacancies per $cm^3$; N is the number of lattice sites of one type per $cm^3$; and W is the formation energy of a pair of vacancies. Changes of the temperature of the specimen will therefore result in the deviation from the equilibrium value of the vacancy concentration. Vacancies can neither be generated nor destroyed within perfect regions of the lattice. It is known that the edge dislocations tend to climb in the presence of a concentration of vacancies differing from the equilibrium concentration. One may therefore say that in the regions of the lattice, remote from free surfaces and grain boundaries, near-equilibrium concentration of vacancies at the temperature of the specimen is maintained through the climb of dislocations. Thus, during warm-up of the specimen, there will be displacement of vacancies i.e., point charges, and also their creation and annihilation at the dislocation sites. At the end of any heating run, when the specimen is cooled to room temperature a re-arrangement must follow to reduce the polarisation effect set up by the displacement of point charges and to restore the equilibrium concentration of vacancies at room temperature. This re-arrangement cannot be instantaneous since it must await the diffusion of vacancies, which would essentially be a slow process. If the lapse of time between two consecutive cycles be sufficiently large (say, 12 hours) then the equilibrium value of the vacancy concentration at room temperature might be re-established. However, the attainment of equilibrium concentration will not necessarily give rise to the same configuration of vacancies at the end of each re-distribution. Hence the changes in the intensity values of the two glow peaks, at the end of successive cycles, would take place in an inconsistent way as seen in Figures 14 and 15. On the other hand, if the specimen is rapidly cooled to room temperature after warm-up, and the glow curve re-measured immediately, then the time gap between two consecutive cycles will not be sufficient for the re-establishment of equilibrium concentration and the subsequent re-distribution. As a result, there will be progressive decrease in the heights of the two glow peaks at the end of each heating run, as exhibited in Figures 16 and 17.

Figures 18 and 19 show that if the specimen is annealed at 600°K for 100 hours and afterwards cooled very slowly, then there is a selective decrease in the strength of 350°K glow peak. Using the etch-pit technique Ueta et al[98] observed no appreciable change in the dislocation density after holding the sample at about 700°K for 24 hours. The etch-pit technique is believed to give a faithful representation of the order of dislocation density. It may therefore be presumed that prolonged anneal at 600°K and the subsequent slow cooling did not appreciably alter the dislocation density. To explain the results obtained, it is suggested that due to the decrease in the potential energy of the lattice in the region of the dislocation, the nearby $Tl^+$ impurity ion might diffuse towards it during high temperature anneal. Since dislocations act as sources and sinks of vacancies, the impurity ion migration can be brought about by the vacancy diffusion mechanism i.e., by changing places with vacancies. The $Tl^+$ ion at the core of dislocation will be energetically unstable and hence may precipitate out as a separate phase at the dislocation site. Such a process will selectively destroy the number of phosphorescence centres responsible for 350°K glow peak.

Excitation, heating, and cooling of the sample followed by cycles of heating and cooling without re-excitation cause a shift in the position of the maximum of the glow peak at 350°K, towards higher temperatures. On the other hand, practically all the traps at 300°K are emptied at the end of the first cycle. This is clear from Figures 20, 21, 22, and 23. It is known that changes in the relative intensities of the components belonging to a complex peak would result in an apparent shift in the position of the maximum. One may therefore conclude that the glow peak at 350°K is composite in nature, formed by the overlap of closely spaced glow peaks. In essence, this could mean that allthe traps at 300°K are unique in nature whereas those at 350°K are not unique. The dissimilarity in the species of traps responsible for 350°K peak can be due to lattice defects common in nature but in different environments giving rise to narrow distribution of trapping levels below the conduction band. This would be in general accord with the concept presented above viz., 300°K peak is due to Tl - negative ion vacancy complex in the perfect region of the lattice whereas, the 350°K peak is due to such complex in the imperfect region of the lattice, distorted due to presence of a dislocation.

Thus, to explain the thermoluminescent process, various types of F centres, depending upon their environments, have to be considered. It has been reported in many earlier publications that the F centre colouration in KCl at room temperature, occurring after the initial first-stage, takes place in different stages. Furthermore, optical bleaching studies near room temperature indicated that F centres in the latter stages are more stable to F light illumination than those formed in the first stage[99 to 101]. Since the thermal glow characteristics of doped and undoped KCl are similar, the models for F centres suggested in this work may shed light on the mechanism of F centre colouration in alkali halides at room temperature.

## 5.4 Room Temperature Phosphorescence Decay

There have been a number of attempts at offering interpretations which would explain the kinetics of the decay processes in KCl:Tl phosphor at room temperature; but without an adequate measure of success. Since it is now almost agreed that the trapping sites for electrons are crystalline imperfections other than the impurity ions[9,10,68,69], it seems indicated that it is worthwhile to study the decay characteristics of the phosphor intensively, under the influence of as many number of different factors as possible. In fact, in all the earlier decay studies of the phosphor no attention has been given to the previous history of the sample. As a result, the interpretations of different observers did not often agree. The shape of the decay curve of KCl:Tl has therefore been a matter of much controversy[46,102 to 107]. The present work, concerned primarily with obtaining necessary data, specifically deals with the effects of thermal treatment, of deformation and of thermal treatment followed by deformation, on the ultraviolet and visible room temperature decay of the phophor. The work also includes the examination of the effect of thallium concentration.

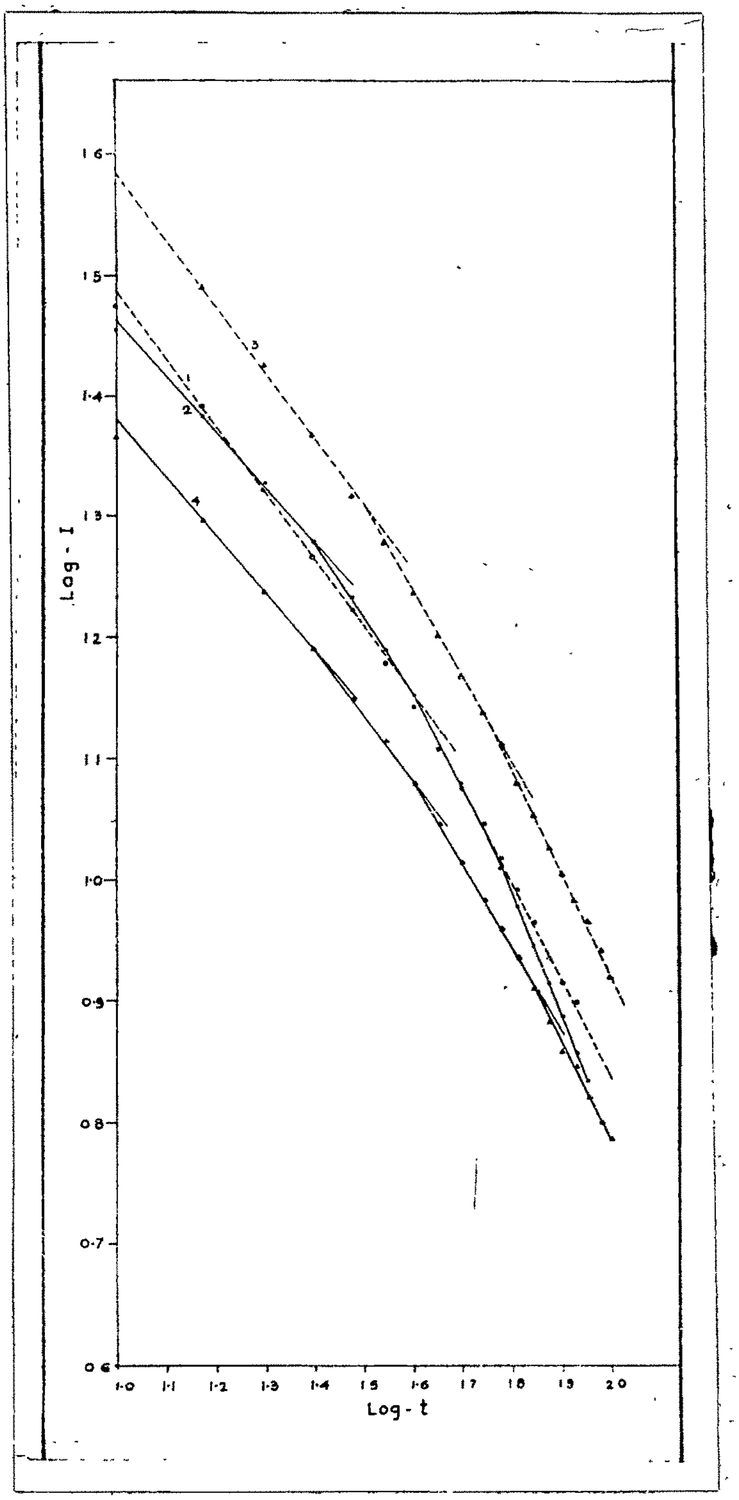


Fig. 24. Decay curves for Sample A (KCl:Tl "as-obtained" from solution)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet( Tl content 0.003 mol. )

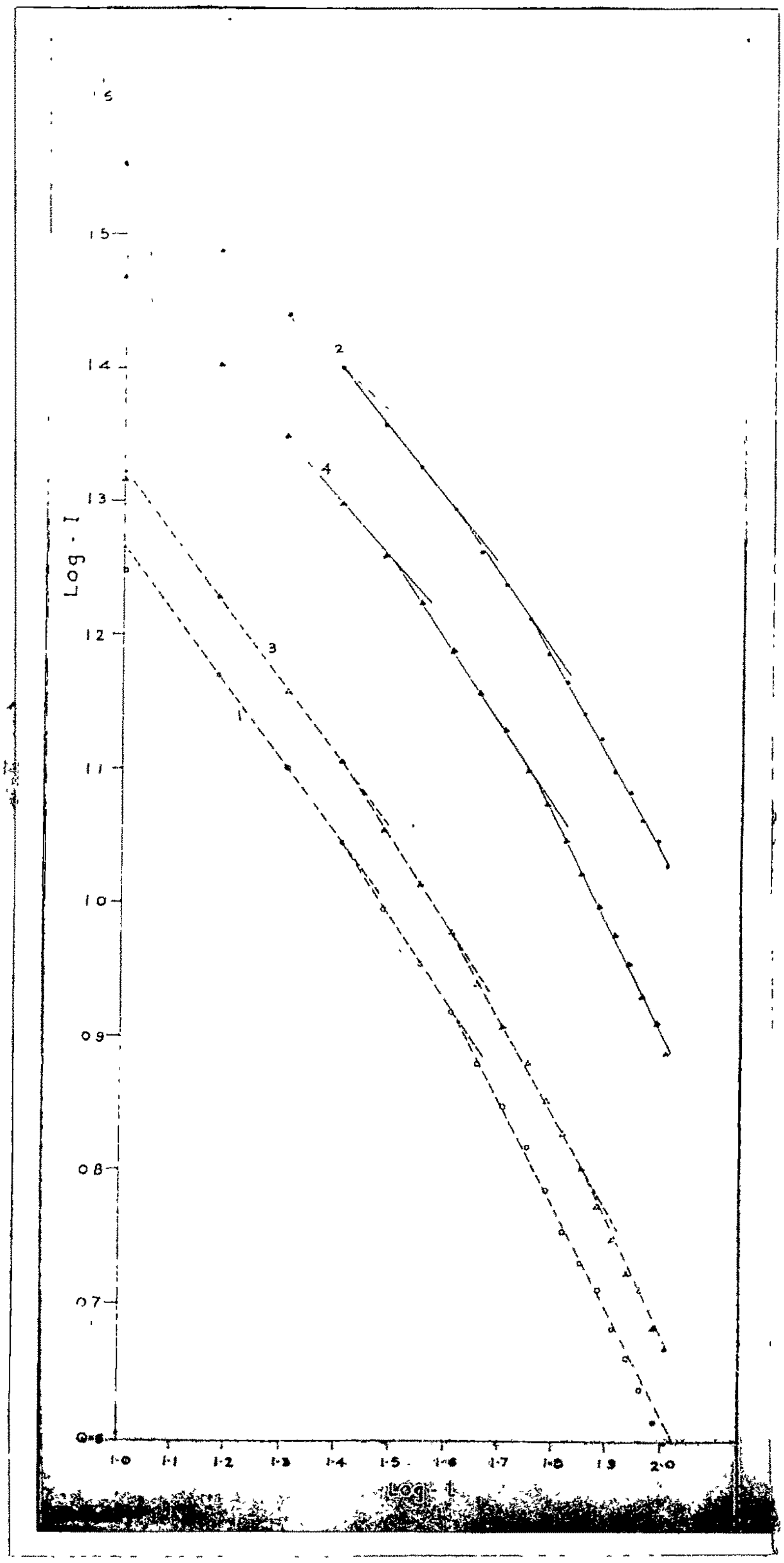


Fig. 25. Decay curves for Sample B (KCl:Tl, annealed at 600°K for 100 hours and slowly cooled)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

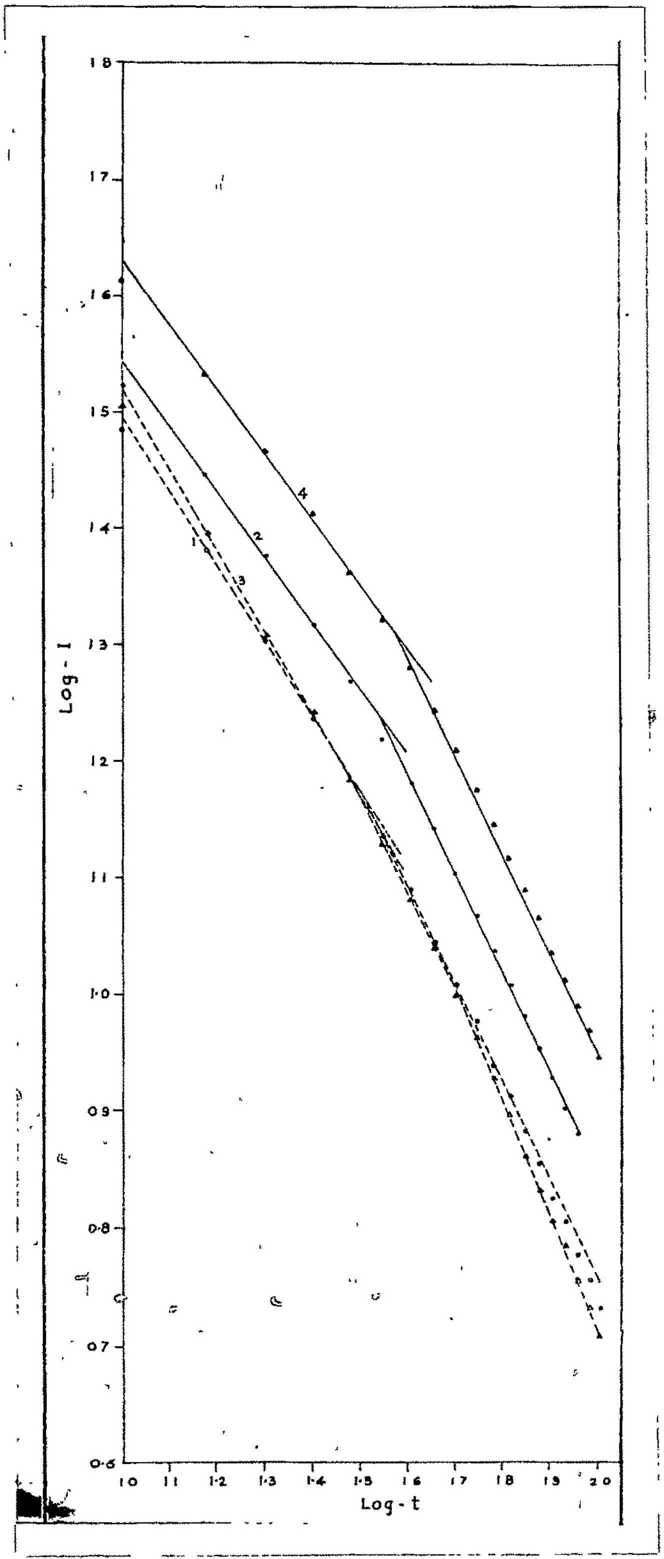


Fig. 27. Decay curves for Sample D ( Sample A, compressed into tablet. )

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

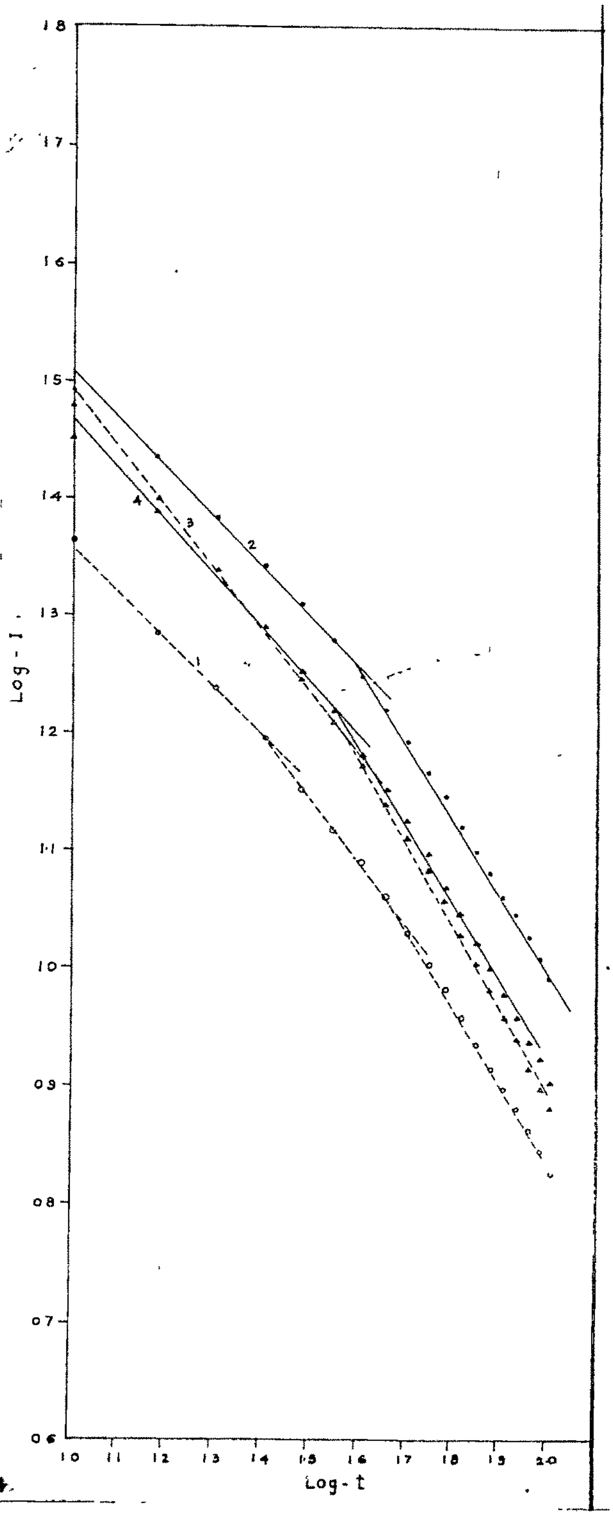


Fig. 28. Decay curves for Sample E ( Sample B, compressed into tablet.)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

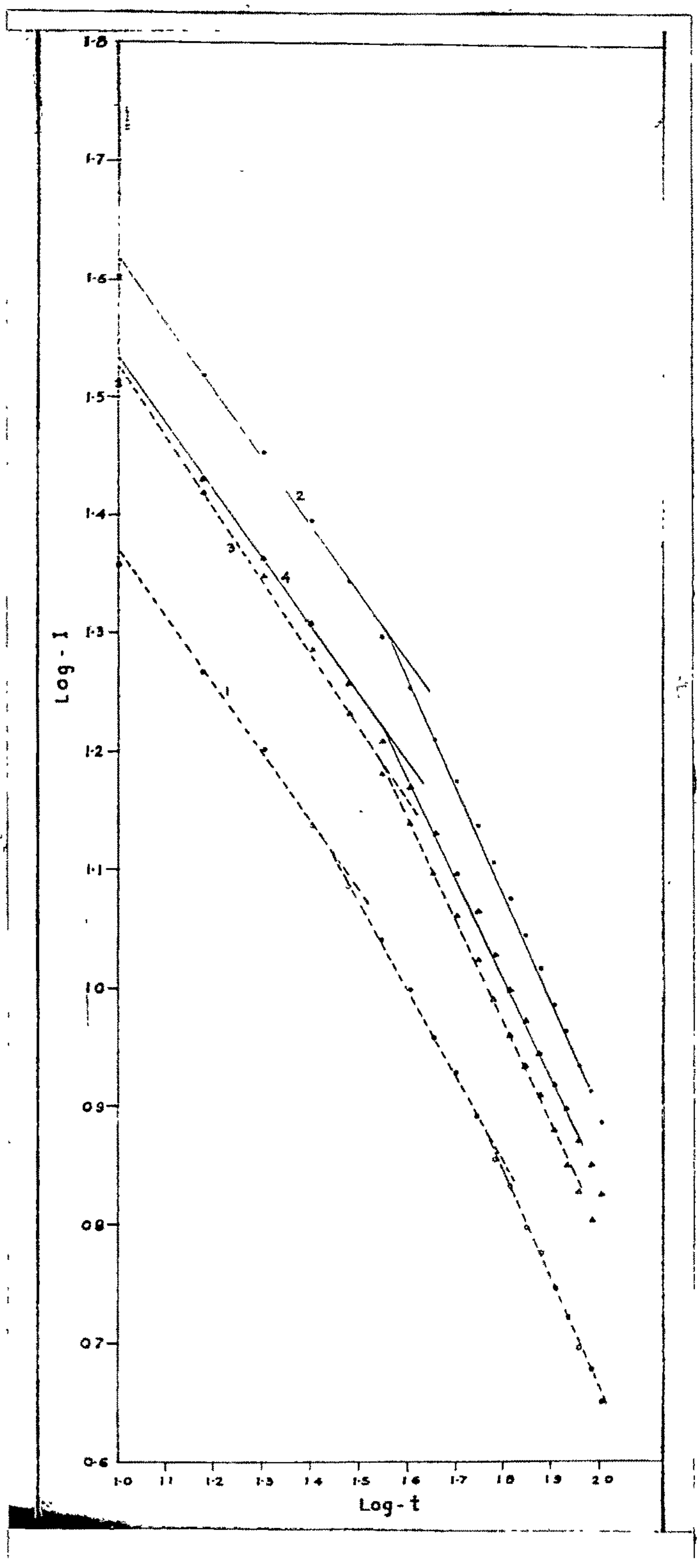


Fig. 29. Decay curves for Sample F ( Sample C, compressed into tablet.)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

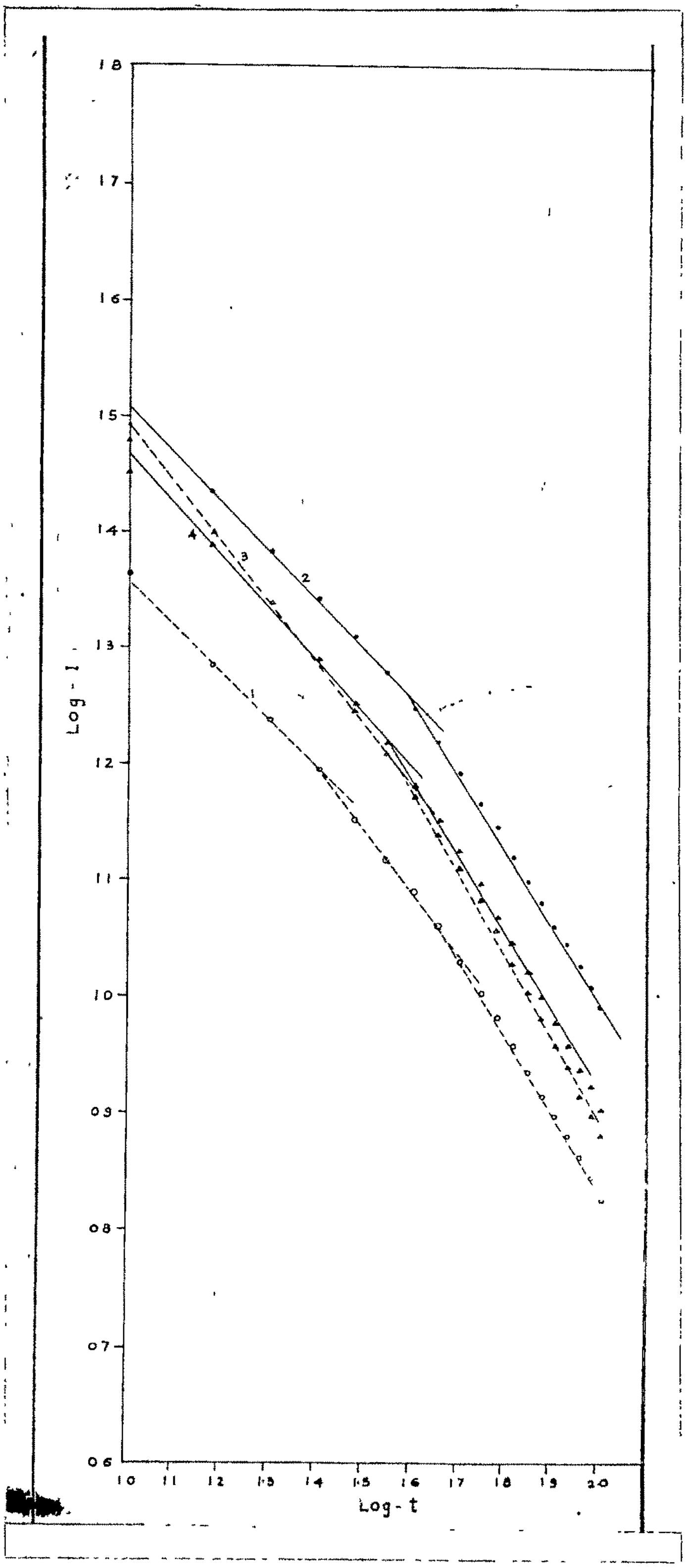


Fig. 28. Decay curves for Sample E ( Sample B, compressed into tablet.)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

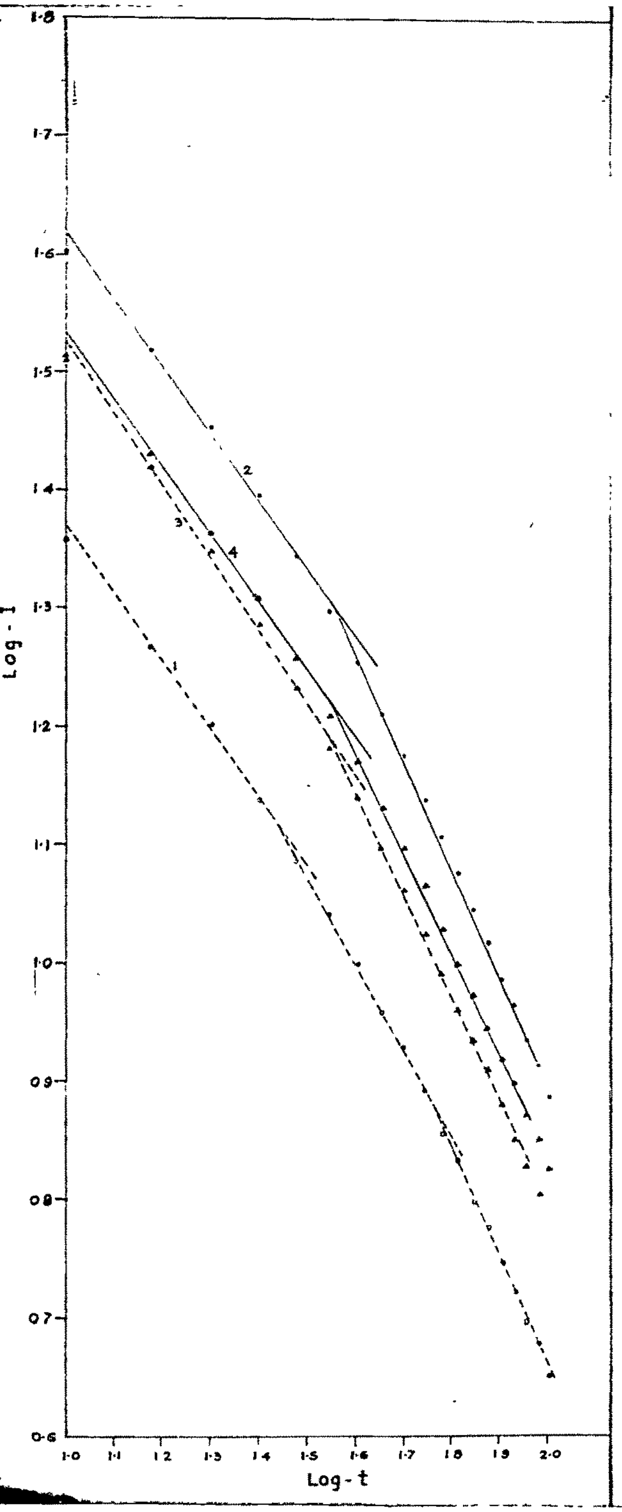


Fig. 29. Decay curves for Sample F ( Sample C, compressed into tablet.)

Curve 1. visible ( Tl content 0.0015 mol. )
Curve 2. ultraviolet ( Tl content 0.0015 mol. )
Curve 3. visible ( Tl content 0.003 mol. )
Curve 4. ultraviolet ( Tl content 0.003 mol. )

The phosphors used in the present work were prepared by crystallisation from aqueous solution containing 0.0015 and 0.003 mol. thallium concentration. The results of the experiments performed with as-obtained and variously pre-treated KCl:Tl phosphors are shown in Figures 24 to 29. In all the figures, the log - log plots of intensity (I) against time (t) show that the results can be fitted very well to the power law decay

$$I = I_o t^{-n} .$$

In order to study the effects of thallium concentration, measurements were made on two KCl:Tl phosphors differing in their Tl content. There is no observable difference in the decay behaviour of the two phosphors. The decay curves for as-obtained or heat-treated samples show distinct curvatures. These curves can be fitted to suggest 3 to 4 independent first order processes. The noteworthy feature of the data presented in the figures is that in general, the number of decay components reduces to two if as-obtained or heat-treated specimen is deformed by stressing. A list of the samples used in the experiments, the nature of the physical treatment received by each sample and the values of the decay constants (n) for ultraviolet and visible emissions are indicated in Table II.

## TABLE II

| Sample | Values of decay constant(n) for different stages | | | |
|---|---|---|---|---|
| | Thallium content 0.0015 mol. | | Thallium content 0.003 mol. | |
| | Ultraviolet | Visible | Ultraviolet | Visible |
| A | 0.46, 0.62,<br>0.82, 1.00 | 0.55, 0.82 | 0.49, 0.55,<br>0.69, 0.82 | 0.55, 0.72,<br>0.86 |
| B | 0.39, 0.51,<br>0.59, 0.72 | 0.55, 0.62<br>0.79 | 0.48, 0.62,<br>0.82 | 0.53, 0.62,<br>0.72, 0.86 |
| C | 0.51, 0.67,<br>0.82 | 0.64, 0.79,<br>0.94 | 0.53, 0.72,<br>0.94 | 0.67, 0.79,<br>0.94 |
| D | 0.57, 0.86 | 0.64, 0.86 | 0.55, 0.86 | 0.69, 0.99 |
| E | 0.43, 0.64 | 0.40, 0.53,<br>0.67 | 0.46, 0.67 | 0.53, 0.69 |
| F | 0.57, 0.90 | 0.57, 0.72,<br>0.90 | 0.57, 0.86 | 0.62, 0.86 |

Sample:

A : As-obtained from solution.

B : Sample A annealed at 600°K for 100 hrs. and slowly cooled.

C : Sample A annealed at 600°K for 100 hrs. and rapidly cooled.

D : Sample A compressed into tablet.

E : Sample B compressed into tablet.

F : Sample C compressed into tablet.

TABLE II

In a recent study it has been suggested by Joshi[64] that the decay of the phosphor is the sum of independent first order processes and that the electron traps are due to single negative ion vacancies in different environments. The trap - emptying process has been suggested to be localised in which the electron is assumed to be raised thermally from the ground state of the trap to the excited state below the conduction band. It then recombines with the hole at the adjacent substitutional parent Tl centre by a tunnelling process, giving rise to an emission characteristic of the impurity ion. The present work is an extension and a more detailed development of the above analysis. It is shown to corroborate the models for the phosphorescence centres presented in Section 5.3 to explain the thermoluminescent characteristics of the phosphor in the room temperature region.

It is seen from the results that the ultraviolet decay characteristics of the phosphor, in relation to the number of decay components before and after various treatments, almost bear a similarity to those in the visible. The decay curve for as-obtained or heat-treated specimen is shown to be resolved into more than two concurrent processes. In general, the number of decay stages for both the emissions reduces to two if as-obtained or heat-treated specimen is compressed by stressing. Similar results have been reported earlier by Morlin[108]. In a log - log plot he observed two linear stages for decay in the case of NaCl:Tl phosphors either in the form of disc prepared from powder or in the form of single crystal deformed by stressing. On the other hand, the plot for an undeformed single crystal phosphor has been observed to be a non-linear curve in the same diagram. As proposed in Section 5.3, these results can be understood if one attempts an explanation in terms of the traps due to single negative ion vacancies in different surroundings. It is suggested that the fastest component of the decay is due to traps formed by isolated negative ion vacancies (first category) and the remaining components are due to traps formed by single negative ion vacancies in the vicinity of edge dislocations presumed, as in Section 5.3, to be negatively charged (second category). The charge on the dislocation is suggested to be due to charged jogs. In the second category, various types of negative ion vacancies are to be considered, depending upon the distances of separation between vacancy and dislocation. In view of the different distances of separation, the elctric field interaction between vacancy and dislocation would vary. This would give rise to variation in the lifetime of the traps belonging to the second category. Since the charge on the core of the dislocation is assumed to be small, a dislocation during its motion, will drag the mobile point charges along with it. Because of the small charge the dislocation will not measurably influence the decay process if the distance of separation is large, say fifty lattice spacings and more. If the vacancy - dislocation separation is only a few lattice spacings, say less than ten, the electric field interaction will be large and will affect the capture and release of an electron considerably. As indicated below, it is likely that after plastic deformation majority of the negative ion vacancies belonging to the second category fall into this type.

It is observed that the number of decay components, for ultraviolet and visible emission, does not depend in an important way, on the heat-treatment to which the specimen has been subjected. Sample heated to 600$^{o}$K and maintained at that temperature for 100 hours, and then cooled rapidly to room temperature will have in its volume an increase in the concentration of randomly dispersed vacancies, relative to that in the slowly cooled one. Since the temperature of quench is not quite high and the quenching rate obtained is not fast enough, the thermal strains produced in the rapidly cooled sample may not be large. Absence of such thermal strains lessens the possibility of dislocation motion and the increase in the dislocation density due to multiple slip. On the basis of the results reported by Ueta et al[98] and mentioned in Section 5.3, the changes in the decay properties of the phosphor that take place after heat treatment at 600°K may be attributed to the diffusion of vacancies, and not to the change in the dislocation density. One may therefore say that annealing in the lower temperature range causes dissociation and re-association of impurity ion - vacancy complex in the vicinity or away from dislocation. This may either increase the number of decay components or change the value of the decay constants or both, depending upon the location of negative ion vacancy, subsequent to heating, with respect to a nearby dislocation. This is clear from Table II.

If the phosphor, as-obtained or heat-treated, is compressed into tablet by stressing, the number of decay components, in general, reduces to two. Compression of the sample causes plastic deformation of the microcrystals forming the phosphorescent powder. During deformation a small stress can give rise to dislocation motion and dislocation multiplication in the microcrystals. The dislocation motion increases the density of dislocation jogs due to their intersections. It is suggested that the dislocations acquire an excess charge during their motion i.e., an excess of jogs of one sign is temporarily formed due to uptake of vacancies situated in the zone swept by the core. The process of acquiring charge during dislocation motion cannot however go on indefinitely. A dislocation, after acquiring some charge, therefore 'boils off' vacancies in clusters or singly to enable further uptake. Evaporation of vacancies from dislocation jogs is suggested to be due to local heating when the dislocation is in motion. During motion, if a dislocation presumed to be negatively charged, comes in the close vicinity of a Tl centre it will be pinned or immobilised by the attachment of the positively charged Tl centre. When the dislocation thus comes to rest a re-arrangement of the jogs and the diffusion of vacancies must follow to reduce the polarisation set up by the displacement of electrical charges. Hence the net result of the deformation would be either an isolated Tl centre or a Tl centre in the close neighbourhood of a dislocation. The phosphorescence centre formed would then involve either the combination of a Tl centre and a negative ion vacancy or a close combination of a Tl centre, negative ion vacancy, and a dislocation. In the latter variety of phosphorescence centres it is likely that in the majority of cases the rate of release of electron from the trap will be affected by dislocation more or less to the same extent due to very close association of the Tl - vacancy complex with a charged dislocation. It is presumed that the two components of the decay observed after deformation are due to the above two types of phosphorescence centres.

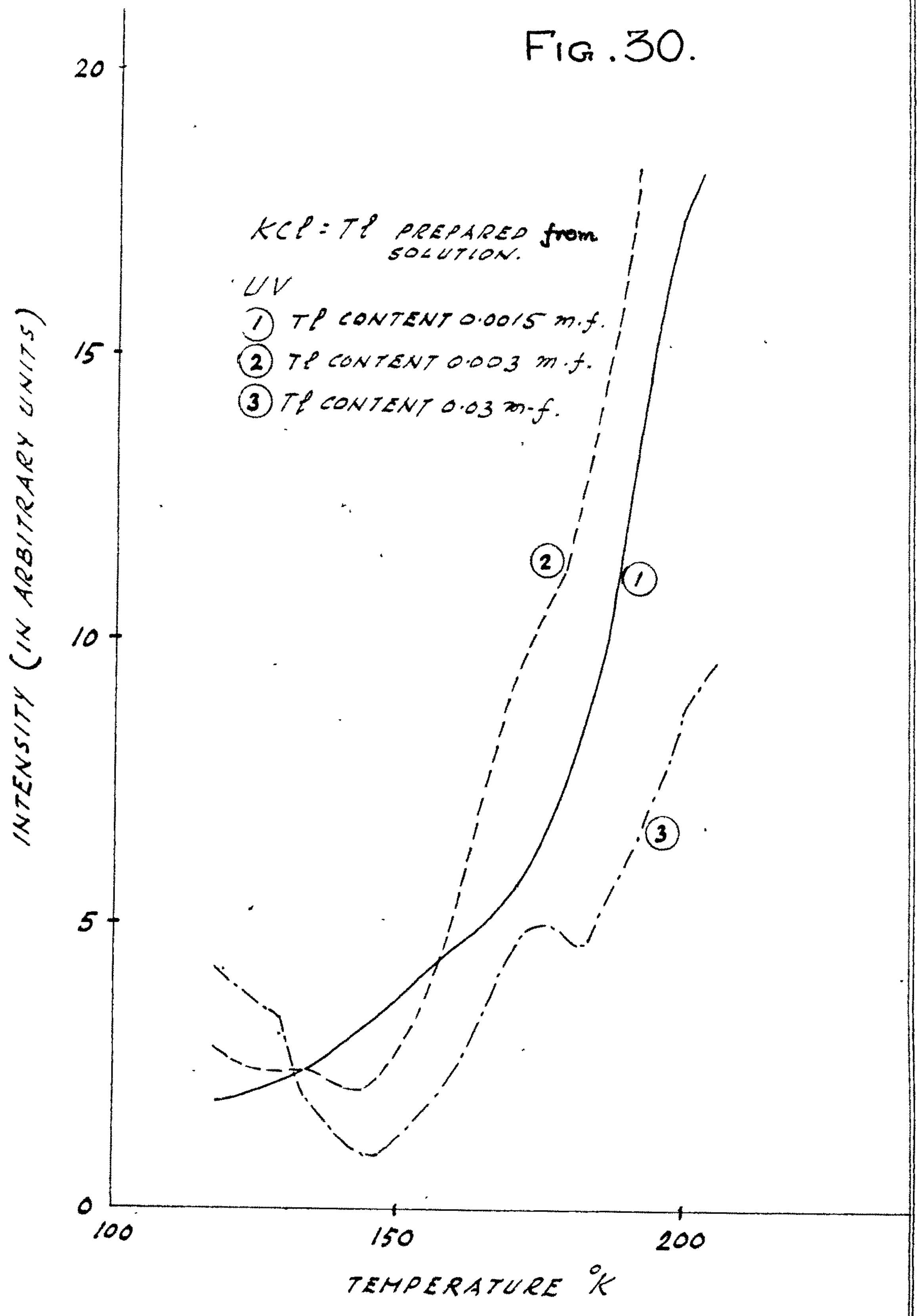
Thus at room temperature, the decay process in KCl:Tl is suggested to involve the thermal bleach of various types of F centres. One of these is due to isolated negative ion vacancies and the rest due to negative ion vacancies in the vicinity of dislocations. In the latter category, F centres are distinguished from one another on the basis of the distance of separation between vacancy and dislocation. Since the negatively charged dislocation exerts a repulsive force on the trapped electron, an F centre in the neighbourhood of dislocation will be more resistant to thermal bleaching than an isolated F centre. The present hypothesis is strengthened by earlier studies wherein on occassions, different types of F centres have been postulated[109]. Further, it has been observed that the F centres produced by additive colouration have a larger half-width value than those produced by x-irradiation[14,110,111]. According to present interpretation, since additive colouration involves rapid cooling from the temperature of colouration, the dislocations may be produced by thermal stresses in the lattice. F centres located in the vicinity of dislocations will therefore give a band whose shape will be different from that of isolated F centres. Thus the hypothesis presented to explain the thermoluminescent properties of the KCl:Tl phosphor around room temperature is in complete accord with that offered to explain its phosphorescent properties at that temperature. It also helps one to understand the non-uniqueness of the F centres reported in many previous publications.

## 5.5 $140^{o}$K and $175^{o}$K Peaks

In the discussions so far, it has been suggested that ion vacancies play an important rôle as trapping sites for electrons and holes. Further, since the colouration phenomena are intimately bound up with the presence of vacancies in KCl:Tl phosphor, it is proposed that at a given temperature, the phosphorescence emission results from the bleaching of a certain species of colour centres and the consequent recombination of the trapped electron or hole. One may therefore expect that the 'self-trapped' hole centres of the type of $V_k$ and H centres, which do not require the presence of ion vacancies, may also in some way be related to the phosphorescence decay in KCl:Tl. Discussion in this section aims at examining such a possibility in relation to 140 and 175 $^{o}$K glow peaks relatively noticeable at high thallium concentration in KCl:Tl.

There had been a long standing discrepancy regarding the centres responsible for luminescence in the alkali halide crystals, containing small amounts of a heavy metal such as thallium. Fromherz, Lih, and Menschik[112 to 115] found that an aqueous solution of TlCl saturated with KCl had a distinct absorption band with a maximum at 241 mμ. On the other hand, a KCl crystal doped lightly with TlCl exhibited an absorption band at 247 mμ. The solid phosphor showed an additional absorption band at 195 mμ and another one at 260 mμ at high thallium concentration, which were not observed in the aqueous solution of KCl:Tl. From their experiments, Fromherz et al concluded that the 241 mμ band observed in aqueous solution and the 247 mμ band in the solid phosphor are identical and hence the luminescence centres in the two are of similar nature. In other wards, the complex ions of the type $(TlCl_n)^-$, presumed to exist in aqueous TlCl solution saturated with KCl, were also suggested to be the luminescence carriers in solid phosphor. Such complexes were assumed to be incorporated in the solid phosphor at the points of lattice defects. According to the complex ion model, during excitation an electron is transferred from the halide ion to the companion $Tl^+$ ion. This model was also supported by Pringsheim[107,116] and Hilsch[117]. However, the complex ion model was relegated into the background soon after Seitz[2] published his substitutional thallous ion model for the luminescence centres in thallium - doped alkali halides. In this model, $Tl^+$ ion excitation with no configuration interaction has been suggested. Using this model, Williams and his co-workers have extensively developed the theory of thallium - activated potassium chloride[3 to 7]. However, it had been observed that the substitutional ion model was not adequate to explain all the experimental data in KCl:Tl phosphor. For instance, Patterson and Klick[45] and Patterson[118] suggested that the visible emission of the phosphor arose either from the clusters of $Tl^+$ ions or $Tl^+$ ions associated with other crystalline imperfections. It is known that every excitation band must be an absorption band. The excitation spectra obtained by Ewles and Joshi[10] gave the clearest evidence that the absorption bands in aqueous TlCl solution saturated with KCl, are additionally observed in the spectra of solid KCl:Tl if the phosphor has very high thallium concentration viz., of the order of 0.03 mol. and above. Furthermore, the parallelism exists not only between absorption spectra of aqueous KCl:Tl solution and solid phosphor but that their emission bands also coincide. Hence they concluded that there should be more than one species of Tl centres in the solid phosphor if the concentration of Tl is high. In such a case, it has been proposed that all of the $Tl^+$ ions may not be in solid solution. Some may be substitutional $Tl^+$ ions either isolated or having other substitutional $Tl^+$ ions, or other crystalline imperfections in the nearest neighbourhood[63] and a small

FIG. 30.


KCl : Tl PREPARED from SOLUTION.
UV
① Tl CONTENT 0·0015 m.f.
② Tl CONTENT 0·003 m.f.
③ Tl CONTENT 0·03 m.f.
INTENSITY (IN ARBITRARY UNITS)
0
5
10
15
20
100
150
200
TEMPERATURE °K
①
②
③

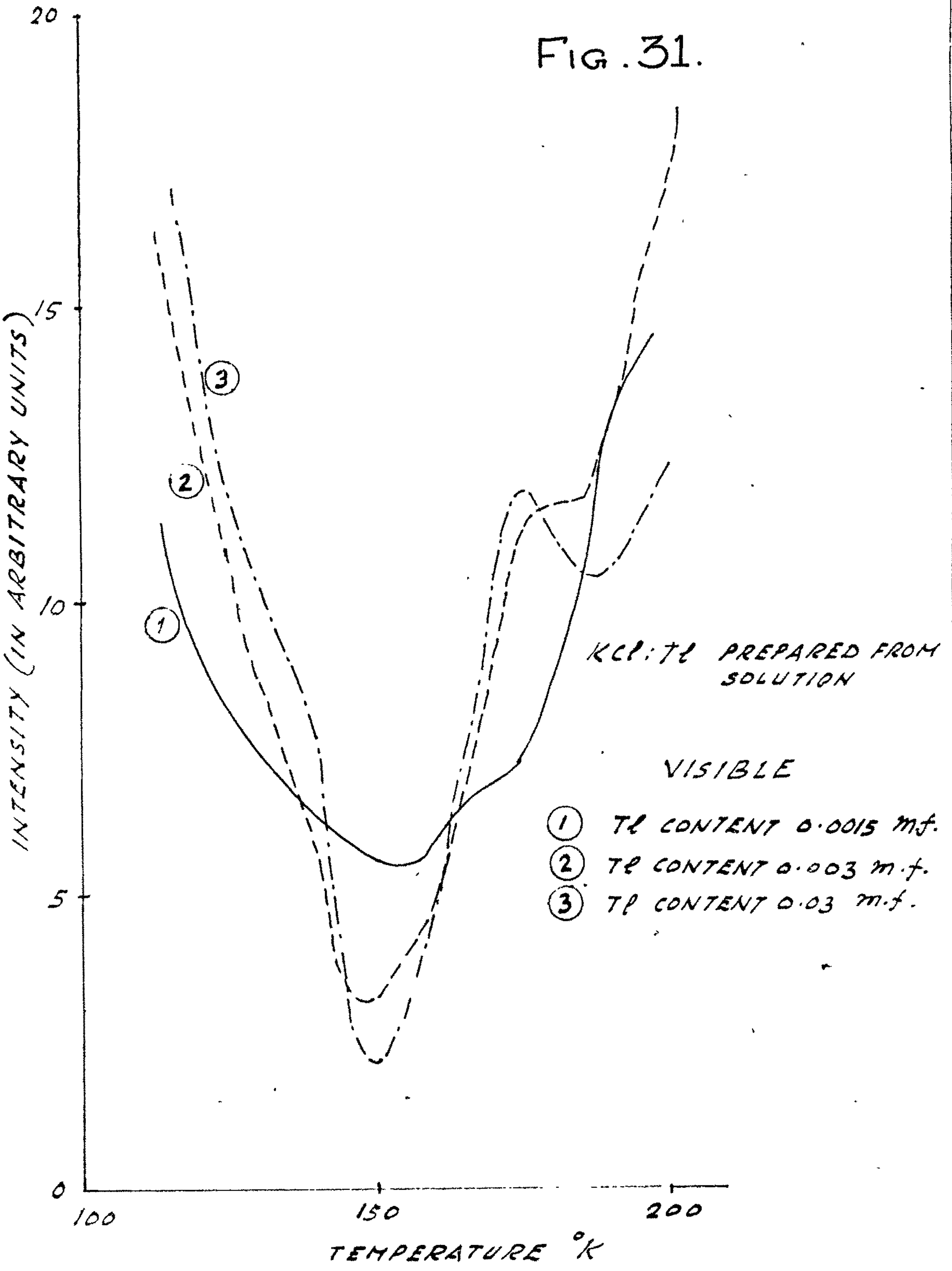

20
15
10
5
0
100
150
200
TEMPERATURE °K
INTENSITY (IN ARBITRARY UNITS)
①
②
③
KCl:Tl PREPARED FROM SOLUTION
VISIBLE
① Tl CONTENT 0·0015 m.f.
② Tl CONTENT 0·003 m.f.
③ Tl CONTENT 0·03 m.f.

FIG. 31.

fraction may be in the aggregated states of the type $TlCl_n$ at special sites such as dislocations or sub-boundaries. There is other corroborating experimental evidence to suggest that undissociated thallous chloride may be present in KCl:Tl when Tl concentration in the phosphor is very high[119]. The concept of the formation of complex ions at points of lattice defects is also in agreement with the suggestion made earlier by Hersh[120] to explain some of the absorption bands in alkali halide crystals.

It is observed from Figures 30 and 31 that for ultraviolet and visible emissions of the phosphor the two glow peaks, about 140 and 175 $^{\circ}$K, are almost absent in the sample with lowest thallium concentration (0.0015 mol.). They are noticeable in the sample with next higher Tl concentration (0.003 mol.) and the peaks further increase in strength at highest Tl concentration used (0.03 mol.). The glow measurements for all the samples were made about three months after their preparation. The experimental conditions in all the measurements were nearly identical. Therefore it seems most reasonable to base the present analysis on the assumption that the occurrence of the two glow peaks directly depends on the thallium concentration. Since, at room temperature, certain

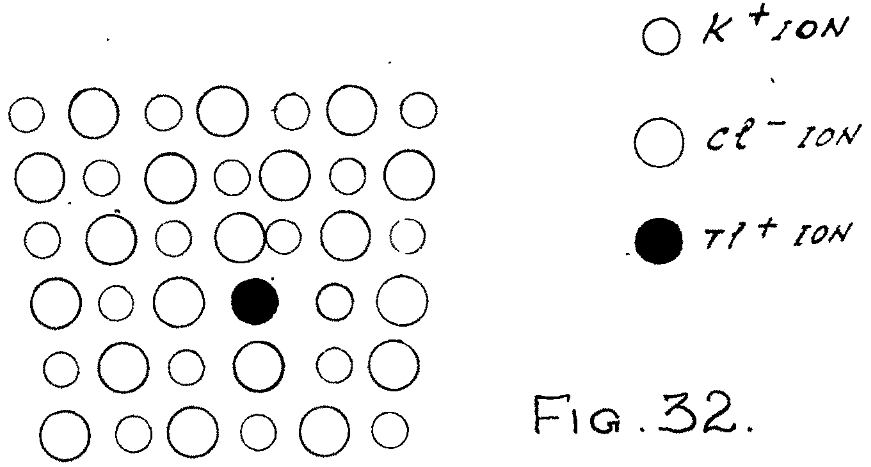


FIG. 32.

AN IMPURITY ION AT THE CORE OF THE EDGE DISLOCATION IN A POTASSIUM CHLORIDE LATTICE.

optimum concentration of Tl should go in solid solution with KCl, the excess Tl would precipitate with the passage of time if the concentration exceeds the equilibrium solubility. It has been observed that precipitates are formed preferentially along dislocation lines or sub-boundaries. In alkali halides, such precipitation effects have been recorded before in the direct observation of 'decorated' dislocation [121 to 124]. Near the core of an edge dislocation in the crystal of an alkali halide, there are halogen ions that do not have the proper number of nearest neighbour alkali ions. Such chlorine ions, which do not have identical environments, may possess different degrees of association with the nearest neighbour $Tl^+$ ion at the core (see Figure 32). It is suggested that the $Tl^+$ ions precipitated along the dislocations are complexed with certain number of $Cl^-$ ions to form two different species of aggregates of the type $(TlCl_n)^-$ say for instance, $(TlCl_2)^-$ and $(TlCl_3)^-$. These may be attributed to the two glow peaks observed. At this stage, it is difficult to speculate on the exact composition of the complexes involved. It is proposed that the thermoluminescence mechanism consists of the transfer in the complex ion of an electron from a chloride ion to the associate $Tl^+$ ion when the phosphor is irradiated with ultraviolet light at liquid nitrogen temperature. Subsequent heating of the phosphor releases the electron from the $Tl^+$ ion, which acts as an efficient electron trap at low temperatures. The liberated electron then recombines with the hole situated at the parent chloride ion. It is believed that the $Tl^+$ ions emit at 140 and 175 °K as a result of this recombination.

It is observed from Figures 30 and 31 that the 140 and 175 °K glow peaks are pronounced in the visible region relative to that in the ultraviolet. This is in agreement with the concept of the presence of complex ions, suggested to form the phosphorescence centres, as follows. It has been observed that the fluorescence of an aqueous TlCl solution saturated with KCl exhibits a continuous emission band extending from the violet to the yellow with a double maximum at 420 and 450 mμ[125]. The Chance OX7 filter, used in the present experiments to separate the ultraviolet component of the glow of the phosphor from the visible, has a cut-off at 420 mμ. Hence the total number of luminescent light quanta reaching the detector will be very less for near ultraviolet than for visible if the emission is assumed to have arisen from complex ions.

In the light of the above hypothesis, it would be relevant to discuss here the results previously obtained by Halperin and Schlesinger[62]. They reported that if KCl crystal is heated in potassium vapour at 500°C, then all the glow peaks in the virgin crystal, observed after x-irradiation, disappear and instead two new glow peaks at 150 and 180 °K appear. Since the peak position on the temperature scale depends on various extraneous factors, it is presumed that these peaks are the same two glow peaks being discussed presently. To explain the effects observed, it is suggested that during high temperature anneal the trace impurities, mainly divalent, inherently present in the crystal will be atomically dispersed in the volume of the crystal. Such impurities in solid solution are able to diffuse, through the vacancy diffusion mechanism, much quicker relative to the monovalent impurities[126]. As a result of their mobility, the impurities keep drifting towards sites, such as dislocations, where they have lowest energy. At room temperature, the drift rate can be accelerated by introducing excess of vacancies. Since during the quench from 500°C in the experiment of Halperin and Schlesinger, a large number of excess vacancies must have been introduced in the crystal, along with numerous dislocations due to thermal stresses, there would be an accelerated diffusion of impurities towards dislocation lines. On this basis, the occurrence of precipitate impurities at dislocations throughout the material can be understood. The precipitated impurity ions, such as lead, may form complexes with the neighbouring chlorine ions thereby giving rise to the observed glow peaks. If a major part of the impurities precipitate at dislocations then it is to be expected that the other glow peaks should disappear, since the trace impurities in the so-called 'pure' crystal, according to the present discussion (Sections 5.1 and 5.2), are believed to act as emitters.

The trapping sites for the holes are suggested to be the polyhalide ions of the type $Cl_n^-$ which form self-trapped hole centres. The phosphorescence centres are attributed to the combination of such polyhalide ions with $Tl^+$ ions along the dislocations where crystallinity of the alkali halides does not play an important role. In this respect the polyhalide ions ($Cl_n^-$)

suggested here are different from the ions of the similar type ($V_k$ and H centres) described by Castner and Känzig[127]. The latter types are the properties of the crystallinity of the alkali halide lattice.

Many of the samples used in the present work have been prepared by crystallisation from aqueous solution. It is well-known that crystallisation from aqueous solution leads to substantial concentration of 'OH' impurity ion (Section 2.4). The maximum of the 'OH' absorption band in KCl is at 204 mμ. Kerkhoff[128] has made detailed study of the photochemical decomposition of $OH^-$ ion in KCl. He observed that illumination into the 'OH' band, near liquid nitrogen temperature, generates the $U_2$ band (band associated with the F centre in the neighbourhood of hydrogen atom). It is therefore suggested that irradiation of doped or 'pure' KCl, at liquid nitrogen temperature in ultraviolet region gives rise to $U_2$ centres. Since the maximum bleaching rate for $U_2$ centres is near 100°K, the OH impurity does not seem to play any role in the occurrence of any of the six glow peaks discussed in this thesis.