Trapping and Annihilation of Electrons and Positive Holes in KCl-TlCl[†]

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(Received 31 May 1966)

During γ irradiation at 77°K, Cl_2^- and thallium atoms (Tl^0) are formed in KCl-TlCl crystals. On warming the irradiated crystals, two glow peaks are observed. The low-temperature glow peak at 208°K is caused by the diffusion of Cl_2^- and the subsequent electron-hole annihilation involving nearby pairs of Cl_2^- and Tl^0. In addition to diffusing into the neighborhood of Tl^0, a Cl_2^- can diffuse into the neighborhood of a Tl^+ and become retrapped to form Tl^{++}. The high-temperature glow peak at 300°K results when electrons are thermally released from thallium atoms into the conduction band and recombination of these electrons and Tl^{++} takes place. Spectral analysis of the low-temperature glow peak shows that it consists of two emission bands with peaks at 410 and 298 nm while the high-temperature glow peak consists only of the 298-nm band. The processes which give rise to these emissions are discussed. The optical absorption of Tl^0 and Tl^{++} has been measured. The absorption spectrum of Tl^0 consists of very weak bands at 1500 and 1260 nm, a strong band at 380 nm, and weak bands at 250, 300, and 640 nm. Tl^{++} has strong absorption bands at 220, 262, 294, and 364 nm. The concentrations of Tl^0 and Tl^{++} produced by irradiation were determined by measuring the decrease in height of the A band of Tl^+ and thus determining the decrease in the concentration of Tl^+. From the concentration of Tl^0 and Tl^{++} and the optical-absorption spectra of these species it was possible to calculate the oscillator strengths of the Tl^0, Tl^{++}, and Cl_2^- bands.

1. INTRODUCTION

CONSIDERABLE work has been reported on the optical absorption and luminescence properties of alkali-halide crystals containing thallous-ion impurity.[1–7] The effects of x-ray or ultraviolet irradiation on these crystals has also been investigated.[8–12] In particular, Johnson and Williams[9] observed that on warming a KCl-TlCl crystal, after ultraviolet irradiation at liquid-nitrogen temperature, glow peaks appeared at 205 and 300°K. They also reported that both glow peaks showed emission bands at 305 and 475 nm, but with varying relative intensities. It was proposed that as a result of ultraviolet irradiation, thallous ions are excited to $^1P_1$ or $^3P_1$ bound states from which they then decay into the metastable $^3P_0$ and $^3P_2$ states. They further proposed that on warming the crystal, thallous ions in these metastable states are thermally raised to states from which radiative transitions to the ground state are possible. The weak infrared absorptions, reported to lie at 1150 and 1550 nm by Bünger and Flechsig[8] from

stimulated luminescence studies, were attributed to $^3P_0 \rightarrow {}^3P_1$ and $^3P_0 \rightarrow {}^1P_1$ transitions in the thallous ions. Delbecq, Smaller, and Yuster,[13,14] while studying the optical spectrum of Cl_2^-, reported that after x-ray or γ-ray irradiation at liquid-nitrogen temperature, KCl-TlCl crystals showed thermoluminescence glow peaks at 208 and 300°K. The first of these peaks was associated with the disappearance of Cl_2^- molecule ions, as shown by ESR measurements. The present work[15] using optical absorption, ESR, thermoluminescence, and stimulation techniques, was undertaken in order to study the products formed during x-ray or γ-ray irradiation and the subsequent changes which produce thermoluminescence. From the results obtained in the present investigation, it is concluded that the two thermal glow peaks in KCl-TlCl result from recombination of electrons and holes. These ideas are in contradiction to those postulated by Johnson and Williams.[9]

2. EXPERIMENTAL PROCEDURE

Crystals for these experiments were grown in air from the melt by the Kyropoulos method. The melt consisted of 100 g of reagent grade KCl to which 0.75 g of TlCl had been added. One of the resulting crystals contained $(1.28\pm0.06)\times10^{-2}$ mole % Tl^+, as determined by neutron-activation analysis. The concentration of Tl^+ ions in the remaining crystals was determined by optical measurement of the absorption coefficient at the maximum of the A band and assuming that the concentration of Tl^+ varies linearly with the absorption coeffi-

† Based on work performed under the auspices of the U. S. Atomic Energy Commission.
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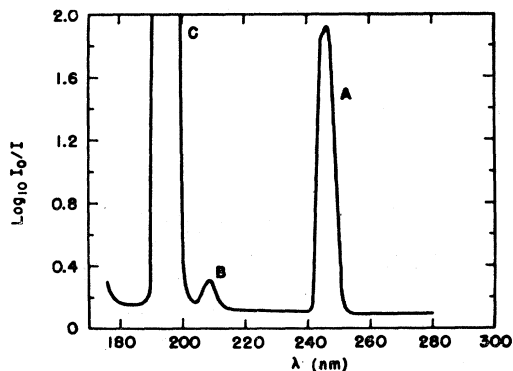
[13] C. J. Delbecq, B. Smaller, and P. H. Yuster, Color Center Symposium at Argonne National Laboratory, 1956 (unpublished).
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FIG. 1. Absorption spectrum, at 77°K, showing the A, B, and C bands of Tl⁺ in a 0.21-mm-thick KCl-TlCl crystal containing 1.28×10^{-2} mole % Tl⁺.

cient.[16] These crystals were exposed, at 77°K, to ionizing radiation from a 2000 Curie Co[60] γ-ray source or a Machlett x-ray tube operated at 50 kV and 50 mA (x rays were filtered through a 1-mm-thick silica plate).

In order to ascertain whether the presence of certain impurities influenced our results, two special crystals were grown. (1) A KCl-TlCl crystal was grown in vacuum using reagent grade KCl which had been treated with HCl at high temperature in order to remove OH⁻. The TlCl, while molten, was also treated separately wlth HCl. After these treatments the two components were mixed together. All of these procedures were carried out under high vacuum conditions. (2) A KCl-TlCl crystal was grown in air using zone-refined KCl which contained approximately 10 to 50 times less Br⁻ than is present in reagent grade KCl. The experiments reported in this paper showed no difference in behavior between these special crystals and those grown as described above.

Optical-absorption spectra were recorded with a Cary Model 14R spectrophotometer; slide wires measuring 0 to 1 or 0 to 0.1 optical density units full scale were used, depending on the strength of the absorption. Emission spectra were taken with an automatic scanning monochromator described elsewhere.[17] The combination of the entrance lenses, the monochromator, and the detector (an EMI 9558QB photomultiplier tube), was calibrated between 250 and 670 nm using a National Bureau of Standards standard lamp. In luminescence work it was generally necessary to use crystals having very low color center absorption in order to minimize the effects of reabsorption of luminescence on the shape of an emission band or the production of extraneous processes.

A Bausch and Lomb (33-86-25) grating monochromator, with a grating blazed at $1\,\mu$, was coupled with a filament lamp and used as a light source in the investigation of the stimulated emission. The band pass of the system was from 50 to 150 Å depending upon the resolution desired in the experiment. The light emitted during stimulation was focused on the slit of the scanning monochromator and studied as a function of wavelength, or the monochromator was set at a fixed wavelength (the peak of one of the emission bands) and the intensity studied as a function of the stimulating wavelength and temperature. The band pass of the scanning monochromator was 100 Å.

3. EXPERIMENTAL RESULTS

A. Optical Absorption Spectra

Figure 1 shows the optical absorption spectrum, at 77°K, of a potassium chloride crystal containing 1.28 $\times 10^{-2}$ mole % thallous chloride; the well-known A, B,
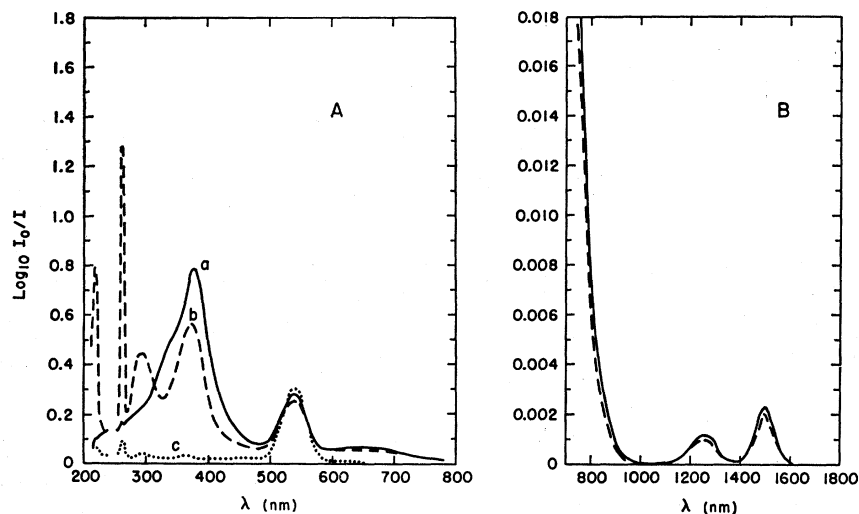

FIG. 2. Net Absorption of a KCl-TlCl crystal at 77°K after (a) a 15-min exposure to Co[60] γ rays at 77°K, (b) warming the crystal to 233°K for 5 min, and (c) warming the crystal to 320°K for 5 min.

[16] W. Wagner, Z. Physik **181**, 143 (1964).
[17] A. K. Ghosh, Appl. Opt. **3**, 243 (1963).

and C absorption bands of Tl^+ are observed at 247, 209, and 196 nm, respectively.

Figures 2(A) and 2(B) show net[18] absorption spectra, measured at 77°K, of a KCl-TlCl crystal which has been exposed to γ-ray radiation and given subsequent treatments. The spectra in part (a), because of relatively strong absorption, were taken on a 4-mm-thick crystal. Those in part B, because of weak absorption, were taken on a 22-mm-thick crystal, using the sensitive slidewire of the Cary spectrophotometer. The spectra in part B are normalized to correspond to the absorption which would be observed in a 4-mm-thick crystal. Curve (a) shows the net absorption after a 15-min exposure to Co^{60} γ rays at 77°K and subsequent optical bleaching to remove F' centers. After the irradiation, a very weak F' band was present and was bleached out by exposure to light of 1.0-μ wavelength. It was shown that this bleaching treatment was specific for the F' center. The removal of F' centers was necessary to avoid interference with the 640 and 1260 nm bands of Tl^0 (Fig. 3). The spectrum, curve (a), is complicated and consists of bands with peaks at 367 nm (Cl_2^- centers), 540 nm (F centers), and Tl^0 bands with peaks at ~300, 380, 640, 1260, and 1500 nm. In addition, a weak 262-nm band is observable indicating the formation of a low concentration of Tl^{++} ions (Fig. 4). Curve (b) shows the net absorption after warming to 233°K for 5 min. This treatment eliminates Cl_2^-; it has been shown that Cl_2^- in KCl becomes thermally unstable near 173°K.[14] In KCl-TlCl, Cl_2^- has a maximum rate of decay and a half-life of about 2 min at 208°K.[13,14] Similar to the case of KCl-AgCl,[19] a fraction of the Cl_2^- are annihilated by radiative recombination with electrons from Tl^0, a very small fraction are annihilated by recombination with electrons from F centers, and the remainder are trapped at Tl^+ to form Tl^{++}. Curve (b), therefore, consists of a combination of the Tl^{++} bands with peaks at 220, 262, 294, and 364 nm, the above-mentioned Tl^0 bands, and the F band. Curve (c) shows the net absorption after warming to 320°K for 5 min. The thallium atoms become thermally unstable near 288°K, releasing electrons at an appreciable rate into the conduction band; these electrons then recombine with Tl^{++} except for a very small number that are trapped at negative-ion vacancies to form additional F centers. A small fraction of the Tl^{++}, which are thermally stable at 320°K, remain. Because of its relatively small half-width and large oscillator strength, the F-band absorption looks relatively strong in these curves. However, a calculation indicates that the concentration of F centers in curves
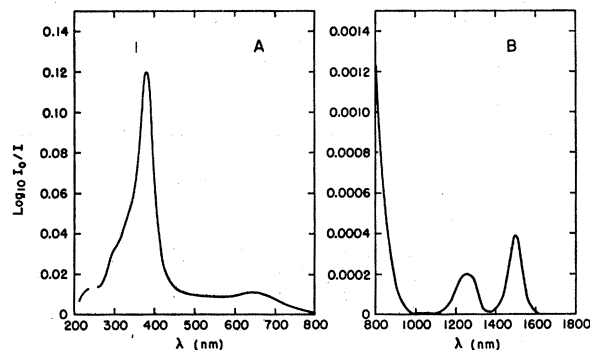

FIG. 3. Absorption spectrum of Tl^0 in a KCl-TlCl crystal at 77°K.

(a) and (b) is less than 10% of the other centers in the crystal.

Figure 3, which shows the optical absorption spectrum of Tl^0 in KCl, with peaks at ~300, 380, 640, 1260, and 1500 nm, was obtained in the following way. A 12-mm-thick crystal was irradiated at 77°K with Co^{60} γ rays for a short time in order to produce a low concentration of Tl^0 and Cl_2^-, and the absorption spectrum, which we will refer to as number 1, was measured. The crystal was warmed to 220°K for 3 min and the absorption spectrum, number 2, was measured at 77°K. The low concentration of Tl^0 and Cl_2^- minimizes the annihilation of trapped electrons and holes during this warmup so that 90% of the holes are retrapped at Tl^+ ions in this experiment. Before warming, the species present are Tl^0, Cl_2^-, and a very small concentration of F centers, and after warming the species present are Tl^0, Tl^{++}, and F centers. At 440 nm the absorption of Tl^0, Tl^{++}, and F centers is small, whereas the absorption of Cl_2^- is relatively strong. Consequently, the total drop in absorption at 440 nm upon warming was assumed to result from the disappearance of Cl_2^-. Since the shape of the Cl_2^- band is known,[14] the intensity of Cl_2^- as a function of wavelength in spectrum number 1 can be determined. Subtracting this Cl_2^- band and the F band from spectrum number 1 gives the first approximation to the absorption spectrum of Tl^0. Once having calculated
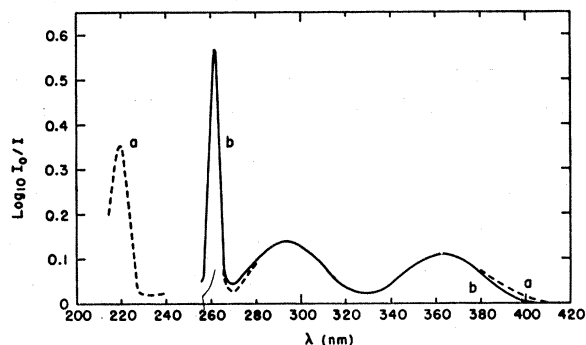

FIG. 4. Absorption spectrum of Tl^{++} in a KCl-TlCl crystal at 77°K.

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[18] The net absorption of a crystal after a given treatment is defined as the total absorption of the crystal minus the absorption of the crystal in its initial state, before any irradiation or heat treatment. Thus the A, B, and C bands of Tl^+ do not appear in Fig. 2. The breaks in the curves in the A band region occur because the optical absorptions are too high to measure.

[19] C. J. Delbecq, W. Hayes, M. C. M. O'Brien, and P. H. Yuster, Proc. Roy. Soc. (London) **271**, 243 (1963).

TABLE I. Characteristics of Tl^0, Tl^+, Tl^{++}, and Cl_2^- measured at 77°K.

	Peak (nm)	Half-width (eV)	Oscillator strength
Tl^0	1500	0.044	8.1×10^{-5}
	1260	0.099	9.3×10^{-5}
	380	a	0.48
	640	0.32	0.03
Tl^+	196	0.23 (0.24)[b] (0.252)[c]	0.48 (0.46)[b] (0.508)[c]
	209	0.11 (0.18)[b] (0.117)[c]	0.0066 (0.015)[b] (0.00832)[c]
	247	0.12 (0.11)[b] (0.124)[c]	0.075 (0.075)[b] (0.0804)[c]
Tl^{++}	220	0.26	0.23
	262	0.091	0.14
	294	0.52	0.22
	364	0.39	0.13
Cl_2^-	367	0.90	0.52[d]

a Because the absorption of Tl^0 is very complicated in this region of the spectrum and obviously consists of several unresolved bands, Fig. 3, no reasonable half-width can be obtained. Therefore, the area under the Tl^0 absorption bands from 200 to 800 nm, minus the area under the 640-nm band, was used in calculating the oscillator strength of the 380-nm band.
b These data, taken at 77°K, were determined by A. Fukuda, Sci. Light 13, 64 (1964).
c These data, taken at 90°K, were determined by W. Wagner, Z. Physik 181, 143 (1964).
d The oscillator strength of Cl_2^- listed above is the maximum f value of the 367-nm band, i.e., for polarized light whose electric vector is parallel to the Cl_2^- molecular axis.

the shape of the Tl^0 absorption by the method described above, a correction was applied to this shape by taking into account the change in absorption at 440 nm resulting from a loss of 10% of the thallium atoms on warming. This second approximation is the absorption spectrum plotted in Fig. 3.

There was some concern initially that since the bands at 1500 and 1260 nm were so weak they might be absorptions connected with some minor center in the crystal. However, irradiation with light into either the 1500 or 1260 nm band at 150°K causes a reduction in intensity of these bands and a proportionate reduction in all the remaining Tl^0 bands. Therefore, these weak infrared bands arise from transitions from the same ground state as the other Tl^0 bands.

The absorption spectrum of Tl^{++}, with peaks at 220, 262, 294, and 364 nm, is shown in Fig. 4. The Tl^{++} spectrum has been determined in two ways. (1) The spectrum indicated by curve (a) was obtained by subtracting 90% of the Tl^0 absorption, Fig. 3, from spectrum number 2 (see above paragraph). (2) The spectrum indicated by curve (b) was obtained from a KCl crystal containing two added impurities, Tl^+ and NO_3^-. A KCl crystal grown from a melt to which KNO_3 has been added contains NO_3^-, NO_2^- and other decomposition products. Some of these species can readily trap electrons, some can trap holes, and some can trap both electrons and holes.[20,21] The absorption bands of none of these species, with or without the electrons or holes, overlap strongly the 262-, 294-, or 364-nm bands of

[20] C. Jaccard, Phys. Rev. 124, 60 (1961).
[21] D. Schoemaker and E. Boesman, Phys. Status Solidi 3, 1695 (1963).

Tl^{++}. Therefore, in a $KCl-TlCl-KNO_3$ crystal, it is possible to trap essentially all of the electrons and some of the holes at the species originating from NO_3^- with the remainder of the holes trapped as Tl^{++}. A 4-mm-thick KCl crystal grown from a melt containing 0.75 weight % $TlCl$ and 0.2 weight % KNO_3 was irradiated at 77°K with Co^{60} γ rays. The crystal was then irradiated at 77°K with light from a filament lamp of wavelength greater than 630 nm to destroy Tl^0, and finally the crystal was warmed to 230°K to remove Cl_2^- and retrap the hole at either Tl^+ or the species derived from NO_3^-. At this point no Tl^0 remains, but the crystal does contain Tl^{++}. The contribution of the NO_3^--derived species to the absorption spectrum of the crystal in this final state was determined by repeating the above experiment with a crystal grown from a melt containing KCl and 0.2 weight % KNO_3; the absorption spectrum of Tl^{++}, indicated by the solid line, was obtained by subtraction of the two spectra. The agreement between the spectra of Tl^{++} obtained by the two methods is very satisfactory.

It is possible to obtain quantitative information regarding the concentration of Tl^0 and Tl^{++} in a crystal of $KCl-TlCl$ by observing the decrease in the height of the A band after irradiation and annealing. After a 15-min exposure, at 77°K, to γ rays, it was observed that the absorption coefficient of the A band in a crystal 0.24 mm thick and containing 0.99×10^{-2} mole % of Tl^+ decreased by 2.3%. If all of the decrease in the A band results from the capture of electrons by Tl^+ to give Tl^0, the concentration of thallium atoms, $[Tl^0]_1$, is equal to the loss in concentration of Tl^+, $\Delta[Tl^+]_1$. If it is also assumed that only Cl_2^- and Tl^0 are formed by the irradiation, $[Cl_2^-]_1 = [Tl^0]_1 = \Delta[Tl^+]_1$. On warming the crystal to 233°K, the A band drops an additional 0.3%. If it is now assumed that the electrons and holes are trapped to form only Tl^0 and Tl^{++}, then $[Tl^0]_2 = [Tl^{++}]_2$. The total loss in Tl^+, $\Delta[Tl^+]_2$ is given by $\Delta[Tl^+]_2 = [Tl^0]_2 + [Tl^{++}]_2$, and therefore, $[Tl^0]_2 = [Tl^{++}]_2 = (\frac{1}{2})\Delta[Tl^+]_2$, where the subscript 2 indicates the values obtained after warming to 233°K. Using the above-mentioned data, one obtains, $[Tl^0]_1 = 3.6 \times 10^{16}/cm^3$ and $[Tl^0]_2 = [Tl^{++}]_2 = 2.0 \times 10^{16}/cm^3$.

The data obtained on a crystal which had the same concentration of Tl^+, but was thicker than the one described in the preceding paragraph, were used along with the data obtained from Figs. 3 and 4 to calculate the oscillator strengths of the Tl^0, Tl^{++}, and Cl_2^- bands. Since the "thick" crystal was irradiated the same length of time and at the same relatively large distance from the Co^{60} source, it was assumed that the concentration of color centers was uniform and was the same as in the crystal discussed above. When Tl^0 and Cl_2^- are the principal color center species present in a crystal, about 75% of the optical absorption at 380 nm is due to Tl^0. Using Fig. 3 to obtain the shape of the Tl^0 absorption, knowing the concentration of Tl^0 from the preceding paragraph, and knowing the absorption coefficient of

Tl⁰ at 380 nm of the "thick" crystal, it is possible to calculate the oscillator strengths of the bands of Tl⁰. Using the shape of the absorption of Tl⁺⁺ obtained from Fig. 4, the absorption coefficient at the maximum of the 262-nm band of the "thick" crystal, and the concentration of Tl⁺⁺, the oscillator strengths of the Tl⁺⁺ bands were obtained. These data are compiled in Table I. The formula

$$ Nf = 0.82 \times 10^{17} \frac{n}{(n^2+2)^2} \int k_E dE $$

was used to calculate the oscillator strengths[22] of the 380- and 640-nm bands of Tl⁰ and the 367-nm band of Cl_2^-. For the remainder of the absorpton bands where half-widths could be measured conveniently, the integrated absorption, $\int k_E dE$, was approximated in the usual fashion assuming a Gaussian shape.

Some of the difficulties involved in obtaining the concentration of Tl⁰ and Tl⁺⁺, as described above, will now be indicated. The A band of Tl⁺ in KCl, when measured at 77°K, has been reported to consist of two unresolved bands.[23,7,16] The A band of the crystal shown in Fig. 1, when studied in more detail, shows similar structure to that obtained previously in crystals with a low concentration of Tl⁺. After the γ-ray irradiation at 77°K, not only did the A band decrease in height but there was a very slight, but measurable, change in shape. Preliminary experiments with KBr-TlBr suggest that this change in shape arises from a relatively sharp Tl⁰ absorption band in this region. Because of the shape change the possible error in the measurement of the decrease in the A band is appreciably increased. Further small errors are introduced by the assumptions that Tl⁺ acts as the only trap for electrons and holes. There are F centers in the irradiated crystals and after removing all the Tl⁰ there remains along with the F centers a slight absorption of Tl⁺⁺. However, calculations indicate that the neglect of F centers and associated holes only introduced errors of between 5–10%. All of these factors contribute to the error which could be as large as 50% for the values of the oscillator strengths of Tl⁰, Tl⁺⁺, and Cl_2^- listed in Table I.

Figures 5(A) and 5(B) show the results of a detailed pulse annealing experiment on a KCl-TlCl crystal which had been irradiated at 77°K with Co⁶⁰ γ rays for 15 min. The temperature rates of change of optical density at the peaks of some Tl⁰ and Tl⁺⁺ absorption bands are plotted as functions of temperature. These curves show the details of the growth and decay of the bands shown in Figs. 3 and 4. The crystal was warmed to an annealing temperature, held there for 3 min, and then cooled to 77°K for measurement of the absorption spectrum. Successive annealing temperatures differed by 15°K. The changes in the optical densities between successive
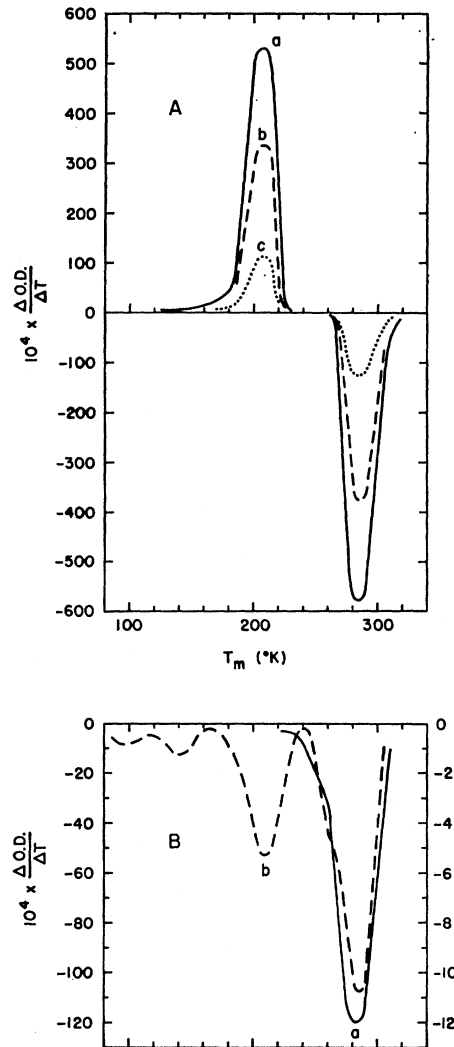
[22] D. L. Dexter, Phys. Rev. **101**, 48 (1956).
[23] D. A. Patterson, Phys. Rev. **112**, 296 (1958).

FIG. 5. A plot of the temperature rate of change of $\log I_0/I$ as a function of temperature: (A) the Tl⁺⁺ bands at (a) 262 nm, (b) 220 nm, and (c) 294 nm; (B) the Tl⁰ bands at (a) 380 nm (scale on left) and (b) 640 nm (scale on right).

anneals were divided by the 15°K difference in annealing temperatures to determine the ordinate values in Fig. 5. The corresponding abscissa values are average values of the temperature for the 15° annealing interval, i.e., $T_m = T_{anneal} - 7.5$. Figure 5(A) presents curves of the rates of growth and decay of the 220-, 262-, and 294-nm Tl⁺⁺ absorption bands; the intensity, sharpness and relative isolation of the Tl⁺⁺ bands allow these data to be obtained readily. Figure 5(B) presents curves of the rates of decay of the 640- and 380-nm Tl⁰ absorption bands; these data were considerably more difficult to obtain since the intensity of the 640-nm band is quite low and the 380-nm band overlaps the 367-nm band of Cl_2^- and the 364-nm band of Tl⁺⁺. Upon warming to 230°K, the Cl_2^- has all decayed so that the absorption in the region of 380 nm results from the 380-nm band of Tl⁰ and the 364-nm band of Tl⁺⁺. The changes in the
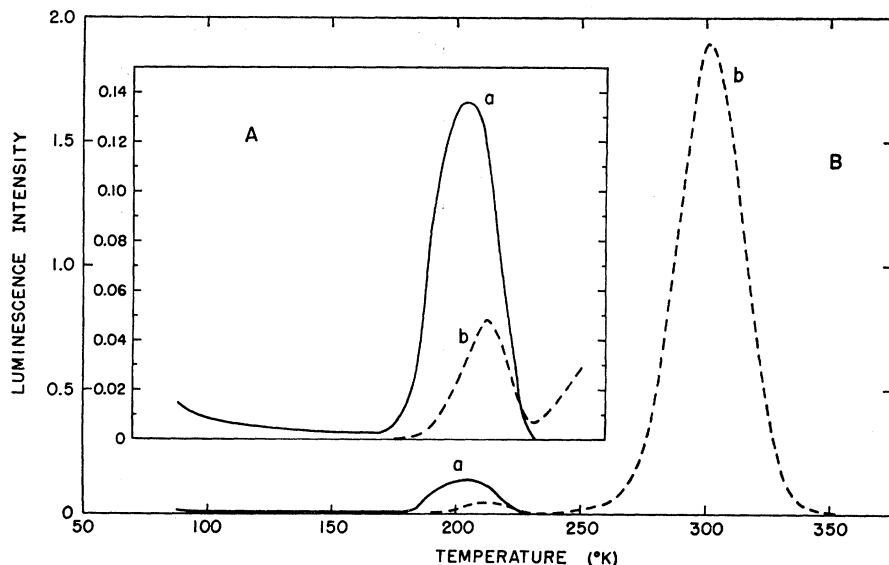
FIG. 6. Glow peaks of a KCl-TlCl crystal which had been exposed to Co[60] γ rays at 77°K. The ordinate indicates the relative intensities of the (a) 410-nm and (b) 298-nm emission bands. The ordinate for part (A) is expanded by a factor of 10.

380-nm band of Tl[0] above 230°K were calculated by subtracting the Tl[++] absorption at 380 nm from the total absorption at 380 nm. The Tl[++] absorption at 380 nm was calculated using the Tl[++] absorption spectrum, Fig. 4, and the height of the 262-nm band as an index of the Tl[++] concentration. As mentioned before, the maximum rate of disappearance of Cl_2^- in KCl-TlCl occurs at about 208°K. This temperature corresponds very well to the temperature at which a minimum occurs in the curve for the 640-nm band of Tl[0] (~210°K), and to the temperature at which maxima occur in the curves for the 220-, 262-, and 294-nm bands of Tl[++] (~207°K). The temperatures of the minima in the curves for the 640-nm band of Tl[0] at about 286°K, the 380-nm band of Tl[0] at about 284°K, and the 220-, 262-, and 294-nm bands of Tl[++] at about 285°K are consistent with each other. These minima at about 285°K arise from the thermal instability of the Tl[0] and the resulting annihilation of electrons at Tl[++] centers. The two low-temperature minima occurring in the 640-nm curve are real but just above the limits of detection. We do not know how they arise, but believe that they are not connected with major reactions occurring in the crystal.

B. Luminescence

Figure 6 shows a plot of the luminescence intensity of a KCl-TlCl crystal, which had been exposed to Co[60] γ rays at 77°K, as it is warmed. The rate of warming was about 3.5°C/min during the low-temperature glow peak and about 6°C/min during the high-temperature glow peak. Two emission bands are observed, one with its peak at 410 nm and the other at 298 nm. The relative intensities of these two bands vary with the temperature. Wavelength sensitivity corrections have been applied so that the ordinate is proportional to the number of photons in either the 410-nm or the 298-nm bands. The afterglow, at 77°K and up to 170°K, shows

only the 410-nm emission band. The low-temperature glow peak is composed of both the 410-nm and 298-nm emission bands, while the high-temperature glow peak consists of only the 298-nm band. The low-temperature glow peak occurs at about 208°K (obtained by adding the two emission components) and the high-temperature glow peak occurs at about 300°K. These temperatures are not identical with the temperatures of the maxima in the rates of change of optical density, Fig. 5. However, the data of Fig. 6 were obtained by a continuous warmup whereas those of Fig. 5 were obtained by a pulsed warmup. Taking into account the experimental procedures used, the pulsed warming is expected to yield a lower glow peak temperature, which is in general agreement with the results.
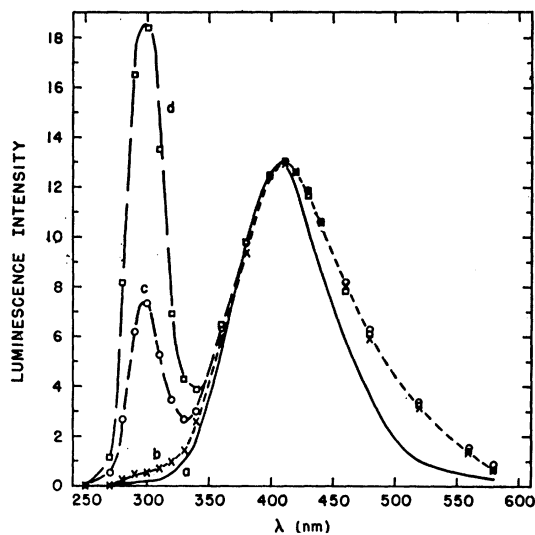

FIG. 7. Emission spectra, taken at (a) 77°K, (b) 184°K, (c) 208°K, and (d) 219°K—characteristic of a KCl-TlCl crystal after exposure to Co[60] γ rays at 77°K.

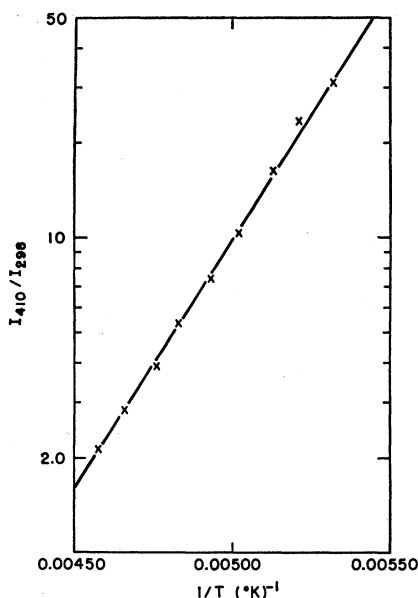FIG. 8. A plot of the logarithm of the ratio of the intensities of the 410-nm band to the 298-nm band versus $1/T$.

Figure 7 shows emission spectra of a KCl-TlCl crystal after exposure to Co^{60} γ rays at 77°K. Curve (a), taken at 77°K, shows the afterglow luminescence spectrum. Curves (b), (c), and (d) represent spectra taken at the low-temperature side (184°K), maximum (208°K), and the high-temperature side (219°K) of the glow peak, respectively. The relative intensities of the 410- and 298-nm emission bands in the region of the low-temperature glow peak depend reversibly on the temperature; e.g., after having warmed the crystal to 219°K, cooling the crystal to 208°K again gives an emission spectrum in which the two bands have the same ratio as shown in curve (c). The 410-nm emission band broadens and shifts only a small amount between 77 and 219°K. The 298-nm emission band, which is the sole component of the high-temperature glow peak, also broadens and shifts little between 200 and 330°K. It is believed that the 410-nm emission arises from the annihilation of an electron and hole of a nearby pair of Tl^0 and Cl_2^-. This process in KCl-TlCl is similar to the one reported for KCl-AgCl.[24] The origin of the 298-nm emission will be discussed in Sec. 4C. Figure 8 shows a plot of the ratio of the intensities of the 410-nm band to the 298-nm band versus $1/T$. The points fall on a good straight line which indicates an activation energy of 0.31 eV.

Figure 9 shows luminescence stimulation spectra, taken at 150°K, for a KCl-TlCl crystal which had been exposed to Co^{60} γ rays at 77°K. The ordinate is proportional to the intensity of the stimulated 298-nm emission per photon of incident stimulating beam; the abscissa is the wavelength of the stimulating light. The

[24] C. J. Delbecq, A. K. Ghosh, and P. Yuster, Bull. Am. Phys. Soc. **9**, 629 (1964).

intensity of the light was sufficiently low that only a very small fraction of the color centers were bleached during the experiment. One set of points shows the stimulation spectrum after γ-ray irradiation, while the other set of points shows the spectrum, normalized at one wavelength, after warming the crystal to 230°K. These two sets of spectra are identical within experimental error and are in good agreement, as to shape and peak position, with the infrared absorption bands of Tl^0 taken at the same temperature. Thus, it may be concluded that excitation of these Tl^0 bands is the first step in the stimulated emission process.

The intensity of emission stimulated by excitation of the 1260- and 1500-nm bands depends on the temperature of the crystal as shown in Fig. 10. The crystal used in obtaining these data was first exposed to ionizing radiation and then warmed to 233°K to produce Tl^{++} before the stimulation experiments were started. The temperature dependence indicated in Fig. 10 is reversible in the temperature range where the Tl^0 and Tl^{++} concentrations remain constant.

Photostimulated electrical conductivity has also been measured, at 150°K, as a function of the wavelength of the stimulating light. The resulting curves are very similar to the curves shown in Fig. 9. Measurements of the intensity of stimulated photoconductivity as a function of temperature also yield the same activation energy as that obtained from the curves in Fig. 10. It is concluded from all the stimulation data that after excitation in the 1260- and 1500-nm bands of Tl^0, at 150°K, electrons are thermally released into the conduction band. The fact that the temperature dependence of the photoconductivity is the same for excitation into the 1260- or 1500-nm band indicates that both excitations lead, by different paths, to the same excited state of Tl^0 from which an electron may be thermally activated to the conduction band with $\Delta E = 0.17$ eV.

The crystals used in the stimulation experiments, before warming to 233°K, contain Tl^0, Cl_2^-, Tl^+, and a low concentration of Tl^{++}. With these species present in the crystal there are three principal processes which can
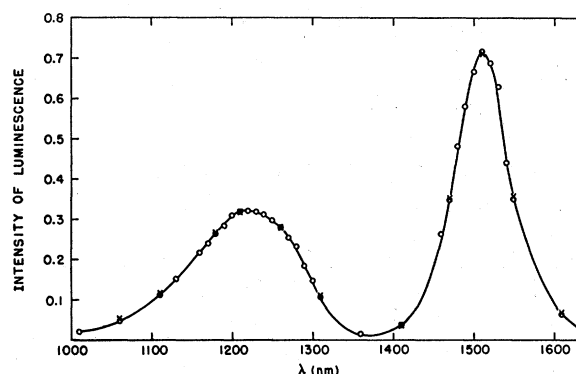

FIG. 9. Stimulation spectra, taken at 150°K, for a KCl-TlCl crystal which had been exposed to Co^{60} γ rays at 77°K. ×-×-× before warming to 233°K. O-O-O after warming to 233°K.
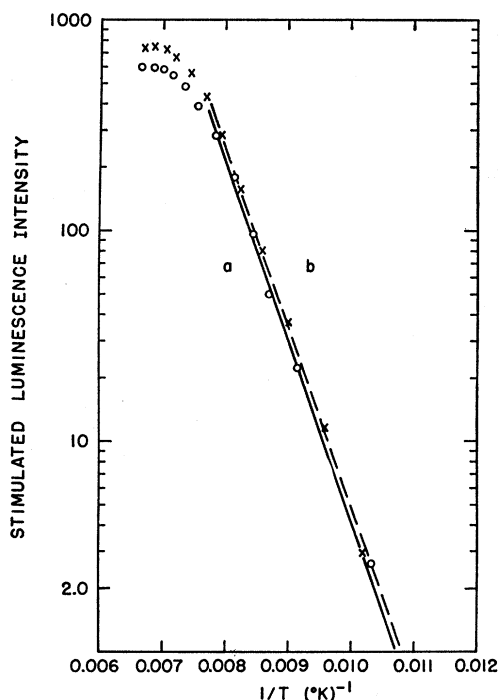
FIG. 10. Temperature dependence of the stimulated 298-nm emission intensity of a KCl-TlCl crystal, which had been exposed to Co^{60} γ rays at 77°K and then warmed to 230°K, upon excitation at (a) 1.25 μ and (b) 1.5 μ.

occur upon the release of electrons from Tl^0. First, electrons can recombine with Tl^{++} to produce 298-nm emission. Second, electrons can be retrapped at Tl^+ to form Tl^0. This second process results in a redistribution of Tl^0 through the crystal and produces an increase in the concentration of nearby Cl_2^--Tl^0 pairs. This increase in the nearby pair concentration in turn causes an increase in the 410-nm afterglow emission. Third, electrons can recombine with Cl_2^-. It has been shown by Kabler[25] that this recombination of electrons and Cl_2^- at 4°K results in an emission with its peak at 2.2 eV; however, the efficiency of this luminescence is so low at 150°K that we do not observe it. After warming the crystal to 230°K, the first and second processes can occur; however, since Cl_2^- is no longer present there is no regeneration of the afterglow. Since the 298-nm emission can be produced both before and after warming to 230°K, this emission was used in the luminescence stimulation experiments.

It is observed in the luminescence stimulation experiments, Fig. 9, that the 298-nm emission intensity per photon absorbed, measured at 150°K, increases by a factor of about 23 on warming the crystal to 230°K, and the Tl^{++} concentration, as indicated by the height of the 262-nm band, increases by a factor of about 24 in the same temperature range. The emission intensity would be expected to be proportional to the concentration of Tl^{++}, as observed, if a large fraction of the

released electrons is retrapped by thallous ions. Evidence for this retrapping is given by the regeneration of the afterglow described above.

4. DISCUSSION

A. Formation of Tl^0 and Tl^{++}

Previous investigations[13,14,19,26] have shown that x irradiation of KCl-TlCl, KCl-AgCl, and KCl-PbCl₂ crystals at 77°K results in the very rapid formation of Cl_2^-. It was proposed that the ions Tl^+, Ag^+, and Pb^{++} in KCl act as very efficient electron traps, thus decreasing the recombination of electrons and holes and allowing a rapid buildup of Cl_2^-. In the system KCl-AgCl it was observed that after x irradiation at 77°K both Cl_2^- and isolated silver atoms, Ag^0, were present in the crystal. Ag^0 results from the capture of an electron by Ag^+ while Cl_2^- results from the capture of a positive hole, Cl^0, by one of the Cl^- ions in the crystal. The optical and ESR absorption of Ag^0 as well as Cl_2^- have been identified. It was shown through disorientation experiments that Cl_2^- begins to undergo a translational motion in the crystal starting at 170°K. As the temperature is raised the rate of diffusion of Cl_2^- increases and results in its disappearance. Upon warming a crystal containing Ag^0 and Cl_2^- a glow peak is observed at about 208°K which corresponds to the maximum in the rate of disappearance of Cl_2^- and Ag^0. This glow peak, with a maximum in the emission spectrum at 550 nm, arises from the recombination of electrons from Ag^0 with Cl_2^- which have migrated into the neighborhood. However, as shown in the ESR and optical absorption spectra, after all the Cl_2^- have disappeared it is observed that 50–90% of the Ag^0 remain and that a new hole center, Ag^{++}, has formed. These Ag^{++} result from the retrapping of positive holes at Ag^+ ions. Upon warming further a second glow peak, with a maximum in the emission spectrum at 275 nm, is observed at about 100°C. In this temperature range the Ag^0 are thermally unstable and release electrons into the conduction band; the luminescence arises from the recombination of these electrons with Ag^{++}. When this process is completed the Ag^0 and all but a small fraction of the Ag^{++} have disappeared.

Although the ESR absorptions of Tl^0 and Tl^{++} have not as yet been observed, it is firmly believed that these species are formed in KCl-TlCl crystals in complete analogy with the formation of Ag^0 and Ag^{++} in KCl-AgCl crystals. Upon warming a KCl-TlCl crystal, there is a glow peak associated with the disappearance of Cl_2^- which arises from recombination of electrons from Tl^0 with Cl_2^- ions that have migrated into the neighborhood. Between 50 and 90% of the Cl_2^- ions are retrapped at Tl^+ ions to form Tl^{++}; the formation of the 220-, 262-, 294-, and 364-nm bands of Tl^{++} coincides

[25] M. N. Kabler, Phys. Rev. 136, A1296 (1964).

[26] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 121, 1043 (1961).

with the disappearance of Cl_2^-. A second glow peak occurs at 300°K, consisting only of the 298-nm emission band. Experiments have shown that this glow peak results from the thermal instability of Tl^0 and the capture of the freed electron by Tl^{++}.

This suggested mechanism for the second glow peak can be confirmed through the use of a KCl-TlCl crystal containing a second electron trap which leads to the formation of an electron excess center having a higher thermal stability than Tl^0, e.g., Ag^0. After x irradiation at 77°K, a KCl-TlCl-AgCl crystal contains Ag^0, Tl^0, and Cl_2^-. After warming to 233°K the crystal contains Ag^0, Ag^{++}, Tl^0, and Tl^{++}. Further warming to 320°K removes Tl^0 completely, reduces Tl^{++} and Ag^{++} somewhat, and increases the concentration of Ag^0 slightly. Thus, it is the thermal instability of Tl^0, not Tl^{++}, which causes the glow peak at 300°K. On raising the temperature of the crystal to 373°K, where Ag^0 is unstable, emissions characteristic of recombination of electrons and Tl^{++} and electrons and Ag^{++} are observed. Thus, independent of the source of electrons, 298-nm emission results from the recombination of electrons and Tl^{++}. The rise in the F band during the high-temperature glow peak is also in agreement with electrons being thermally released into the conduction band by Tl^0.

In addition to the analogous behavior of KCl-AgCl and KCl-TlCl crystals described above, the decrease of the A band of Tl^+ upon γ irradiation at 77°K and warming to 233°K also supports the proposal that electrons and holes are trapped by Tl^+. The complete recovery of the A band of Tl^+, on warming the irradiated crystal to 320°K, is also consistent with the mechanism proposed for the high-temperature glow peak.

B. Absorption Spectra of Tl^0 and Tl^{++}

In the ultraviolet and visible region of the spectrum the absorption of Tl^0 consists of a strong rather sharp absorption band with peak at 380 nm (3.26 eV) and weaker bands at 250 (4.96 eV), 300 (4.13 eV), and 640 nm (1.92 eV). Excitation in any of these bands results in freeing an electron into the conduction band even at temperatures as low as 5°K. In absorption, the lowest energy permitted transition of the free thallium atom is from the $6s^2 6p^1$, $^2P_{1/2}$ ground state to the $6s^2 7s^1$, $^2S_{1/2}$ excited state, with an energy separation of 3.28 eV.[27] It is possible that the strong resonance-like absorption at 380 nm is to be associated with a transition from the $^2P_{1/2}$ ground state to a $^2S_{1/2}$ resonant level in the conduction band and that the remaining absorption results from transitions from the ground state of Tl^0 to conduction-band states. The structure of the remaining absorption may reflect the s-like critical point structure of the conduction band.[28] The agreement in

energy between the observed band at 380 nm and the separation in energy between the $^2P_{1/2}$ and $^2S_{1/2}$ levels is surprisingly good since interactions in the crystal would be expected to shift the levels and change the energy separation. The weak Tl^0 bands at 1260 (0.98 eV) and 1500 mm (0.83 eV) are believed to arise from forbidden transitions between the $^2P_{1/2}$ and $^2P_{3/2}$ levels. The separation between these levels in the free atom is 0.97 eV. M. H. Cohen has suggested to us that the splitting of the $^2P_{3/2}$ level of Tl^0, giving two absorption bands, arises from the dynamical Jahn-Teller effect; this aspect of these transitions will be considered in more detail in a future paper.

Excitation in the 1500-, 1260-, and 640-nm absorption bands of Tl^0 at 5°K with $\langle 100 \rangle$ or $\langle 110 \rangle$ light produces no anisotropy in these bands. Therefore, it is concluded that one, or some combination, of the following conditions obtain, (1) the transitions are not polarized, (2) the ground state is not distorted from cubic symmetry, or (3) the distortion averages to cubic symmetry because it is not frozen in, even at 4.2°K. The ground state of Tl^0 in the crystal probably is in cubic symmetry since no static Jahn-Teller distortion is expected for a $^2P_{1/2}$ state.

The Tl^{++} absorption spectrum shows peaks at 220, 262, 294, and 364 nm. Excitation of the three shorter wavelength transitions, at 77 or 5°K, causes the Tl^{++} ion to decompose and form Cl_2^-. This decomposition can be clearly seen in a crystal originally containing only Tl^0 and Tl^{++} by examining the ESR and optical absorption spectra and also by observing the regeneration of the low-temperature glow peak. The efficiency for decomposition of Tl^{++} into Cl_2^- by excitation in the 364-nm band is much lower. The 294- and 364-nm bands of Tl^{++} and the 338- and 460-nm bands of Ag^{++} behave similarly in that, for both species, excitation of the short wavelength transition produces decomposition much more efficiently than excitation of the long-wavelength transition. In the case of Tl^{++}, as well as in the case of Ag^{++}, we have not established the nature of the transitions associated with these absorption bands. The 220- and 262-nm bands of Tl^{++} show a striking similarity, with respect to relative peak positions, half-widths, and oscillator strengths (Table I), to the C and A bands of Tl^+. It is tempting, therefore, to associate these transitions with Tl^+ transitions which are perturbed by the presence of a positive hole trapped in a near neighbor position. However, the 262-nm band shows a complex structure, consisting of more than three bands, which indicates that this structure cannot be accounted for simply by the splitting of the $^3P_1$ level. In addition the evidence is strong that the species we have indicated as Tl^{++} is in fact a complex ion and, therefore, it is not likely that the 220- and 262-nm bands correspond to absorptions characteristic of Tl^+. The ESR absorption spectrum shows that Ag^{++} is a complex ion in which a Jahn-Teller distortion has taken place producing a square planar configuration. In this con-

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[27] *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington, D. C., 1958).

[28] See for instance J. C. Phillips, *Solid State Physics* (Academic Press Inc., New York, 1966), Vol. 18, pp. 56–161.

figuration a positive hole is shared principally by an Ag^+ and the surrounding four halide ions[19] and is less strongly coupled to the two remaining halide ions. It is believed that a somewhat analogous complex ion forms involving a positive hole, a Tl^+ ion and the neighboring Cl^- ions. In the case of Tl^{++}, however, no Jahn-Teller distortion would be expected if the ground state of Tl^{++} is ^2S; such a state would be produced if Tl^+ ($6s^2$) lost one of its $6s$ electrons to become Tl^{++} ($6s$).

Excitation in the 262-, 294-, and 364-nm transitions of Tl^{++} at $5°K$ with $\langle 100 \rangle$ or $\langle 110 \rangle$ polarized light produces no anisotropy in these bands. The same possible conditions may obtain for Tl^{++} as those enumerated above for Tl^0. However, on the basis of the above discussion in which a ^2S ground state of Tl^{++} is indicated, the most probable choice is that the Tl^{++} has octahedral symmetry.

C. Luminescence Processes

The 298-nm emission band, observed during the low- and high-temperature glow peaks, has the same shape and energy as that observed upon excitation of the A band of Tl^+ and, therefore, is considered to be a characteristic emission of the Tl^+ ion. This emission is generally thought to result from the transition of the thallous ion from the $^3P_1$ excited state to the $^1S_0$ ground state. Edgerton and Teegarden[6] have reported that, at $77°K$, excitation of the B or C band of Tl^+ results in both 301-nm [29] and 247-nm emission. These emissions are also considered to be emissions characteristic of the thallous ion.

It has been reported[30] that an emission band with a peak at 475 nm is also characteristic of the isolated thallous ion; however, Patterson and Klick[31] and Patterson[32] have suggested that it might arise from clusters or pairs of Tl^+. The latter suggestion is supported by recent experiments in this laboratory, which indicate that the 475 nm emission arises from thallous ion pairs.[33] In a KCl crystal containing 10^{-2} mole % Tl^+, the concentration of Tl^+ pairs is very small and only a very feeble 475-nm emission can be detected when exciting at 254 nm.

The 410-nm emission, observed during the afterglow and low-temperature glow peak, is entirely distinct from

the 475-nm emission and is not a characteristic emission of the Tl^+ ion. As will be discussed in detail in a future paper, the 410-nm emission is believed to result from tunneling between a Tl^0 and a nearby Cl_2^- in which the $6p$ electron from Tl^0 and the trapped hole, Cl_2^-, recombine radiatively. The 410-nm emission during the afterglow and during the low-temperature glow peak are both believed to arise from this process. At $77°K$ the concentration of nearby tunneling pairs decreases with time resulting in a decay of the afterglow. However, upon warming the crystal, Cl_2^- starts to diffuse near $170°K$ thus increasing the number of tunneling pairs and, therefore, increasing the intensity of the 410-nm emission. As the temperature is further raised, the mobility of Cl_2^- increases and the rate of production of nearby pairs increases until a maximum is obtained at the glow peak. The probability of the tunneling process, giving rise to the 410-nm emission, is believed to be essentially temperature-independent. The process giving rise to the 298-nm emission during the low-temperature glow peak, however, has a thermally activated step as indicated by Figs. 6, 7, and 8.

The ratio (I_{410}/I_{298}) observed in the low-temperature glow peak is a constant at a given temperature, independent of the concentration of Tl^+ or the length of time the crystal is kept at the given temperature. The release of electrons through reabsorption of the 410-nm luminescence was almost totally eliminated by keeping the color-center concentration very low. Thus, recombination of free electrons and Tl^{++}, which could give 298-nm emission, did not occur. We, therefore, believe that the 298-nm emission observed during the first glow peak arises again from a tunneling process, but in this case a thermal activation is required. The process involves annihilation of one of the $6s^2$ electrons of Tl^0 and the hole of Cl_2^-, and results in a Tl^+ in an excited state ($6s6p, ^3P_1$) from which 298-nm emission occurs. We believe that the two processes which lead to the 410- and 298-nm emissions are competitive and involve nearby $Tl^0-Cl_2^-$ pairs having approximately the same separation. There are two principal differences between these two processes. (1) The 410-nm emission accompanies the annihilation of the $6p$ electron of Tl^0 and the positive hole of Cl_2^-, while the 298-nm emission does not accompany the annihilation of the $6s$ electron of Tl^0 and the positive hole of Cl_2^-, but occurs later with the transition of the excited thallous ion to the ground state. (2) The 410-nm emission process is temperature-independent whereas the 298-nm emission process has a thermal activation energy of 0.31 eV. A simple mathematical treatment shows that the slope obtained from Fig. 8 can be interpreted as the activation energy of the 298-nm emission process. The above considerations can also be used to explain the experimental result, Fig. 6, that the 410-nm emission reaches a maximum at a lower temperature than the 298-nm emission. This result can be accounted for by the fact that the maximum rate of formation of Tl^+ ($^3P_1$), produced by a

[29] R. Edgerton and K. Teegarden report the peak wavelength as 301 nm and P. D. Johnson and F. E. Williams (Ref. 9) as 305 nm. These values are in slight disagreement with the value we obtain of 298 nm.

[30] P. D. Johnson and F. E. Williams, J. Chem. Phys. 20, 124 (1952).

[31] D. A. Patterson and C. C. Klick, Phys. Rev. 105, 401 (1957).

[32] D. A. Patterson, Phys. Rev. 119, 962 (1960).

[33] Earlier work on KI-TlI [P. H. Yuster and C. J. Delbecq, J. Chem. Phys. 21, 892 (1953)] showed that satellite absorption bands of the A and B bands have an intensity which is proportional to the square of the Tl^+ concentration. It was concluded that the satellite bands arise from pairs of Tl^+, in nearest-neighbor cation sites. We have observed satellite bands in KCl-TlCl which show a similar concentration dependence. Excitation in one of these pair bands at 254 nm, on the long-wavelength tail of the A band, produces 475-nm emission. The excitation spectrum for this emission corresponds to the shape of the 254 nm band.

thermally activated process from $Tl^0-Cl_2^-$ pairs, occurs at a higher temperature than the maximum rate of formation of $Tl^0-Cl_2^-$ pairs.

In the case of the high-temperature glow peak, the luminescence process involves the capture of an electron from the conduction band by a Tl^{++} into an excited state which we are unable to specify. The state could be the same as that obtained by excitation in the C band of Tl^+, thought by some to be the $^1P_1$ state, and in this case one might expect to observe both the 298-nm and 247-nm emission bands observed by Edgerton and Teegarden[6] at 80°K and below. The thermal glow peaks occur at relatively high temperatures where the 247-nm emission may not be observable.[6] However, it is possible to obtain the same reaction, i.e., $e^-+Tl^{++} \rightarrow (Tl^+)^* \rightarrow Tl^++$emission, by an optical excitation in the 640-nm band of Tl^0; the asterisk indicates an excited state. The Tl^0 transition at 640 nm, when excited, releases electrons into the conduction band even at 5°K. We have studied the above process at both 77 and 5°K and find the 298-nm emission only. The fact that no 247-nm emission is observed when Tl^{++} captures an electron from the conduction band indicates that capture into the $^3P_1$ state is much more probable than capture into the other states. In particular the $^1P_1$ state of Tl^+, formed by capture of an electron by Tl^{++}, will have the same lattice configuration as Tl^{++}, and hence may lie above the bottom of the conduction band.

SUMMARY

The following are the principal reactions which occur in a KCl-TlCl crystal during x irradiation and subsequent thermal treatment.

(1) Exposure of a KCl-TlCl crystal at 77°K to ionizing radiation results in the formation of free electrons and positive holes which may then be trapped to form Tl^0 and Cl_2^-.

$$Tl^++e^- \rightarrow Tl^0,$$

$$\mathbf{Cl^0}+Cl^- \rightarrow Cl_2^-$$
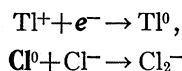
(boldface indicates a mobile species). We believe the lifetime of the free positive hole, Cl^0, to be very short.

(2) There is an afterglow from this crystal at 77°K, consisting of an emission band with a peak at 410 nm, which decreases gradually in intensity after the irradiation. This luminescence results from the annihilation, by tunneling, of a $(6p)$ electron of Tl^0 and the hole of a nearby Cl_2^-.

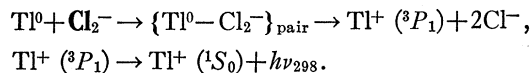$$\{Tl^0-Cl_2^-\}_{pair} \rightarrow Tl^++2Cl^-+h\nu_{410}.$$
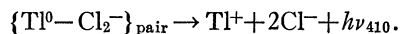
(3) Upon warming the crystal a glow peak is observed, near 208°K, which consists of two emission bands with peaks at 410 and 298 nm. Above 170°K the mobility of Cl_2^- becomes appreciable and increases with increasing temperature.

(a) This 410-nm emission is believed to arise from the process described in (2) above. The increasing mobility of Cl_2^- causes an increase in the concentration of $\{Tl^0-Cl_2^-\}_{pair}$ and therefore an increase in the emission intensity.

$$Tl^0+\mathbf{Cl_2^-} \rightarrow \{Tl^0-Cl_2^-\}_{pair} \rightarrow Tl^++2Cl^-+h\nu_{410}.$$
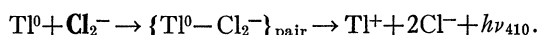
(b) The 298-nm emission is believed to arise from a different tunneling process between thermally activated states of nearby Cl_2^- and Tl^0, the result being the annihilation of the Cl_2^- and a $(6s)$ electron of Tl^0. This results in the formation of a Tl^+ in the $^3P_1$ state which then decays giving the characteristic 298-nm emission.

$$Tl^0+\mathbf{Cl_2^-} \rightarrow \{Tl^0-Cl_2^-\}_{pair} \rightarrow Tl^+ \ (^3P_1)+2Cl^-,$$

$$Tl^+ \ (^3P_1) \rightarrow Tl^+ \ (^1S_0)+h\nu_{298}.$$

The activation energy for the process $\{Tl^0-Cl_2^-\}_{pair} \rightarrow Tl^+ \ (^3P_1)+2Cl^-$ is 0.31 eV.

(c) A large fraction of the Cl_2^- are retrapped at Tl^+ to form Tl^{++}, a complex ion involving also the nearest-neighbor chloride ions.

$$Tl^++\mathbf{Cl_2^-} \rightarrow Tl^{++}+2Cl^-.$$
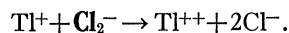
(4) In the neighborhood of 280°K the Tl^0 become thermally unstable and release electrons into the conduction band. These electrons can be retrapped at thallous ions but eventually encounter Tl^{++} ions and produce Tl^+ in the $^3P_1$ state. These excited thallous ions then emit the characteristic 298 nm emission.

$$Tl^0 \rightarrow Tl^++e^-,$$

$$e^-+Tl^{++} \rightarrow Tl^+ \ (^3P_1) \rightarrow Tl^+ \ (^1S_0)+h\nu_{298}.$$
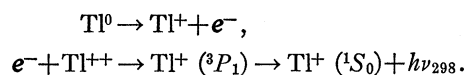
Note added in proof. While this manuscript was in press we found a paper by J. E. A. Alderson, Phys. Status Solidi **7**, 21 (1964) which contains some speculations on the KCl—TlCl system which are similar to conclusions reached in the present work.

ACKNOWLEDGMENTS