PHYSICAL REVIEW B VOLUME 8, NUMBER 12 15 DECEMBER 1973

Kinetics of Self-Trapped Holes in Alkali-Halide Crystals: Experiments in NaI(Tl) and KI(Tl)†

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(Received 25 June 1973)

A previous model calculation of the kinetics of hole diffusion in thallium-activated alkali iodides led to predictions concerning the role of binary electron-hole diffusion in the energy transport associated with the scintillation process. In this paper we report the results of time-resolved emission and absorption measurements on KI(Tl) and NaI(Tl) at various temperatures and compare these results with the model calculation. By absorption spectroscopy we recorded the growth and decay of the Tl^{++} absorption band following excitation by pulse of electrons. The characteristic diffusion time of the self-trapped hole was obtained from the growth curve, and recombination kinetics (due to electrons thermally excited from Tl^0) were obtained from the decay curve. The luminescence intensity was also recorded as a function of time and this function was correlated with the diffusion and recombination processes. Experimental results are in accord with the principal conclusions of the diffusion calculation, and permit definitive statements regarding the mechanism of energy transport. In particular, it is concluded that nearly all of the energy transport in KI(Tl) occurs by electron-hole diffusion.

I. INTRODUCTION

Excitation of a thallium-activated halide phosphor by ionizing radiation produces a luminescence characteristic of the Tl^+ impurity ion. Since the Tl^+ concentration in a scintillation crystal such as NaI(Tl) is about 0.1 mole%, it is clear the the energy deposited by the incident radiation is lost predominately to the host lattice. Thus an energy transfer process must occur in which part of the incident energy is transferred to create excited states of Tl^+ ions. Experiments have shown that one mechanism of energy transfer that results in Tl^+ luminescence is the sequential capture of both an electron and a hole, in either order. These experiments, however, do not exclude other modes of energy transfer, e.g., exciton diffusion. A brief review of the evidence is given elsewhere.[1]

In alkali halide crystals the hole does not move in valence-band states with a well-defined momentum. Instead the hole occurs in a "self-trapped" configuration as a localized molecular ion, I_2^-, in the alkali iodides and jumps from one site to another in a diffusive motion. As a consequence of this type of motion the hole is characterized by a very small mobility and moves relatively slowly through the lattice.[2] This raises the question of whether the hole can participate in energy transfer processes prior to a microsecond scintillation pulse. This question of the kinetics of hole diffusion was studied in a model calculation by Dietrich and Murray.[1] They estimated the time required for sequential capture of the hole and electron at thallium sites in four crystals, NaI(Tl), KI(Tl), RbI(Tl), and KCl(Tl). Three processes were considered, each involving a different characteristic time:

(a) The first process is the prompt ($\lesssim 10^{-9}$ sec) creation of an excited state, $(Tl^+)^*$, by any of sevseveral mechanisms, including exciton capture or electron inelastic scattering.

(b) The second process is the prompt capture of electrons to form Tl^0, followed by diffusion of holes and hole capture at Tl^0 to form $(Tl^+)^*$. The luminescence-pulse decay time will be a composite of the hole diffusion time and the $(Tl^+)^*$ lifetime.

(c) The third process is the prompt capture of electrons to form Tl^0, followed by hole diffusion and capture to form Tl^{++}. Then at a later time, electrons are thermally excited from the Tl^0 traps and subsequently retrapped or captured at Tl^{++} to form $(Tl^+)^*$. The luminescence-pulse decay time will be largely determined by the characteristic time for thermal release of electrons from the Tl^0.

The principal results of the previous model calculation were order-of-magnitude estimates of the hole diffusion time and the Tl^0 lifetime in the four crystals studied. In the iodides it was found that the hole diffusion time was short compared to the luminescence-pulse decay time, confirming that the hole can participate in energy transfer preceding a scintillation pulse. It was also predicted that the Tl^0 lifetime is much longer than the hole diffusion time, so that process (c) occurs with a much longer time constant than (a) or (b).

In this paper we report experiments on NaI(Tl) and KI(Tl) performed to measure some of the time constants predicted in the model calculation.[1] In particular, we have measured at various temperatures the hole diffusion time, the time-constant characteristic of electron release from Tl^0, and the scintillation-pulse intensity as a function of time.

The terms "self-trapped hole" and "V_k center" are used interchangeably.

II. EXPERIMENT

The basic experiment consisted of making time-resolved measurements of the emission and absorption spectra of KI(Tl) and NaI(Tl) single crystals subsequent to a 3-nsec-wide electron pulse from a 600-kV Febetron. Figure 1 is a schematic diagram of the experimental configuration. A detailed description of the apparatus can be found elsewhere.[3] For those measurements which required a time resolution of 1 μsec or longer, an analyzing light beam was obtained by passing the light from a dc xenon light source through monochromator M_1. When a resolution of less than 1 μsec was required the dc xenon source was replaced by an EG & G xenon flash lamp with a 100-J input, and monochromator M_1 was removed. A wide-band filter was placed between the flash lamp and the crystal to eliminate long-wavelength visible and ir radiation which might produce photostimulation of the trapped electrons. Photomultipler 1 measured the light intensities from which the absorption and emission data were obtained. Photomultiplier 2 measured the luminescence following each electron burst. The intensity of this luminescence was used to correct for fluctuations in the strength of the electron pulses.

Crystals were mounted in a standard cold-finger Dewar. The temperature was monitored by a copper-constantan thermocouple attached to the sample block. The NaI(Tl) was cleaved and mounted in a dry-box atmosphere in order to avoid fogging of the surfaces.

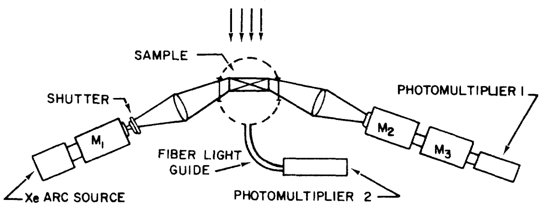

FIG. 1. Experimental arrangement.

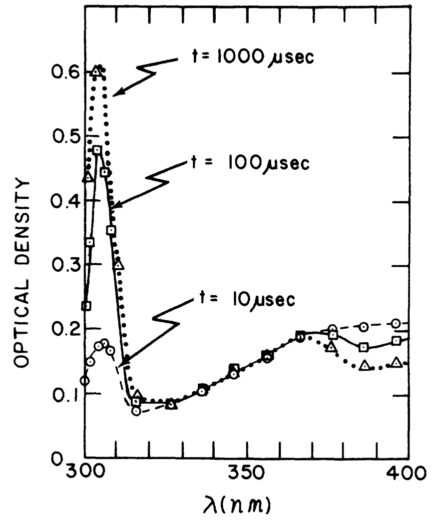

FIG. 2. Absorption spectrum of KI(Tl) at 10 μsec, 100 μsec, and 1 msec after electron pulse. Sample was at 195 °K.

The mean electron energy used in these experiments was 420 ± 20 keV, and the average electron dose at the surface of the crystal was $(7 \pm 3) \times 10^{16}$ $\mathrm{eV/cm^2}$ per pulse. From the known range of these electrons, and assuming 20 eV is necessary to create an electron-hole pair, the initial concentration of electrons and holes was approximately 1×10^{17} $\mathrm{cm^{-3}}$ in both KI and NaI.

Crystals were obtained from Harshaw Chemical Co. The specimens used in the experiments were analyzed by emission spectroscopy. The results gave a thallium concentration of 0.12 mole% in the KI(Tl) crystal and 0.07 mole% in the NaI(Tl).

III. RESULTS AND ANALYSIS

The most straightforward method of observing the hole-capture kinetics would be to measure the optical absorption due to V_k centers as a function of time following the electron burst. This is not feasible because the regions of V_k absorption are overlapped by the absorption bands of various other point defects. However, a sharp and well-resolved absorption band due to Tl^{++} centers has been identified in KI(Tl) at 306 nm[4,5] and in NaI(Tl)[6,7] at 312 nm. The absorption spectrum of KI(Tl) in the region of the Tl^{++} absorption is shown in Fig. 2 at several times with the crystal at 195 °K. Analysis shows that a study of the Tl^{++} absorption as a function of time provides the desired information on hole-capture kinetics; therefore, all of the absorption measurements were concerned with the Tl^{++} absorption band.

The Tl^{++} absorption band was observed over the time range extending from nanoseconds to milliseconds by making successive measurements which overlapped in time, and normalizing the different

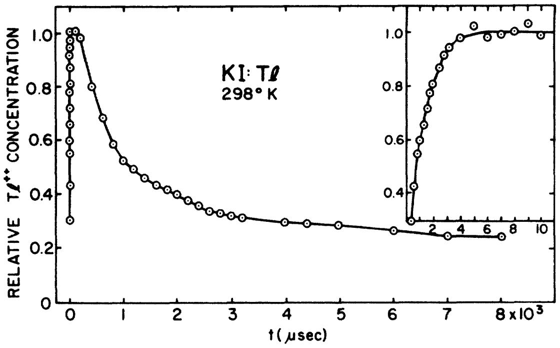

FIG. 3. Relative Tl^{++} concentration as a function of time in KI(Tl) at 298 °K. The inset shows data at early time (0–10 μsec).

measurements in the regions of overlapping times. An example of these data is given in Fig. 3, showing the relative Tl^{++} concentration over most of the measured time range, with the crystal at 298 °K. It is seen in this figure that the Tl^{++} concentration initially rises and reaches a maximum value at $t \gtrsim 5$ μsec. This behavior is due principally to the formation of isolated V_k centers at the time of the electron burst, followed by their diffusion and capture at Tl^{+} sites. The Tl^{++}concentration decays in the millisecond region when electrons are thermally excited from trapping centers and subsequently captured at Tl^{++} sites.

In order to facilitate the discussion of Tl^{++} concentrations we will break up the time scale into three regions according to the physical processes of interest: (a) early time (nanoseconds or less) when some Tl^{++} are formed by the creation of a hole in the vicinity of a Tl^{+} ion; (b) intermediate time, characterized by diffusion of holes to Tl^{+} sites and capture to form Tl^{++}; (c) later time, when Tl^{++} are destroyed by thermally excited release of electrons from Tl^{0}.

A. Early Time

In studies of luminescence processes in KI(Tl) and NaI(Tl), Kaufman *et al.*[7] found that some Tl^{++} centers were formed during x-irradiation at a temperature below that where V_k centers are mobile. Their analysis showed that any hole created within a volume of 25 unit cells around the Tl^{+} ion will form Tl^{++}, and this is a nonthermal (i.e., nondiffusive) process. This leads to the prediction that, in a crystal of 0.1-mole% Tl^{+} concentration 10% of the holes initially created during irradiation will be promptly trapped at Tl^{+} sites to form a Tl^{++} ion. "Prompt" here means a time short compared to any thermally activated process.

In all measurements of Tl^{++} absorption in KI(Tl) an initial sharp rise was observed, followed by a slower increase in Tl^{++} concentration. In order to examine the time dependence of this prompt Tl^{++} signal, we recorded the 306-nm absorption as a function of time in the range 0–200 nsec, with the KI(Tl) crystal at 195 °K. Results are shown in Fig. 4. The absorption signal continues to rise at longer times and reaches a maximum at about 400 μsec. Two pieces of information can be derived from Fig. 4. First, the initial sharp rise of the signal is limited by the rise time of the oscilloscope preamplifier, 8 nsec. Thus the initial rise of Tl^{++} concentration in KI(Tl) occurs in a time $\lesssim 10^{-9}$ sec. This is consistent with the concept of a "prompt" localization of the hole to form a Tl^{++} species if it is initially created within a characteristic distance of a Tl^{+} ion.

Also implicit in Fig. 4 is the fraction of holes that undergo prompt localization to form Tl^{++}. The ordinate of Fig. 4 is normalized to 1.0 at the saturation value of the Tl^{++} absorption signal. The smooth curve in Fig. 4 is a least-squares fit (using a second-order polynomial) to the data points between 0.02 and 0.20 μsec, a time region where the Tl^{++} concentration increases by V_k diffusion. This smooth curve intercepts the ordinate at a value of 0.131 at $t = 0$, so that ≈ 13% of the final number of Tl^{++} centers were created directly by prompt trapping. Some of the initially formed holes will annihilate at Tl^{0} centers rather than diffuse to Tl^{+} sites to form Tl^{++}. This effect can be taken into account by knowing approximate values of the hole-capture cross section at Tl^{0} and Tl^{+} as outlined in Ref. 1. Correcting for this effect, we conclude that 12% of the initial holes are promptly trapped as Tl^{++}. This result is in excellent agreement with the results of Kaufman *et al.*[7] giving a sensitive volume for prompt trapping of 25 unit cells, corresponding to a fraction of 12% for 0.12-mole% thallium.

We did not obtain a quantitative estimate of the fraction of holes trapped promptly as Tl^{++} in NaI(Tl).

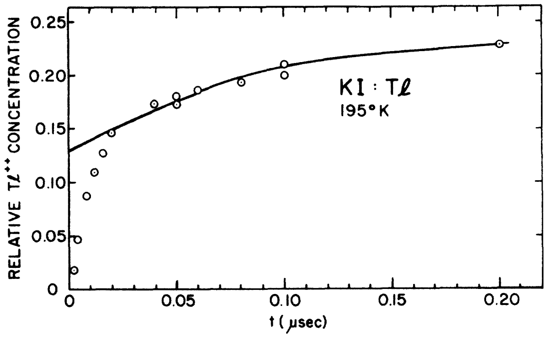

FIG. 4. Relative Tl^{++} concentration as a function of time in KI(Tl) at 195 °K. Solid curve is least-squares fit to data between 0.02 and 0.20 μsec.

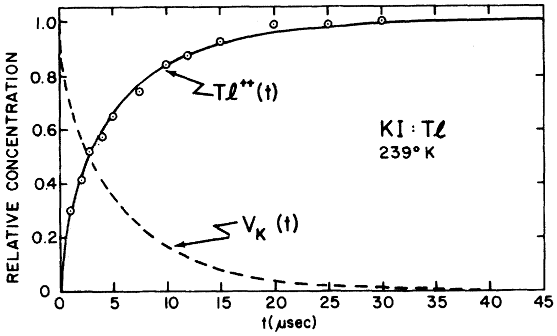

FIG. 5. Relative Tl^{++} concentration and V_k concentration in KI(Tl) at 239 °K. Circles are measured data points for Tl^{++} concentration. Curves represent calculated relative concentrations.

However, the appearance of the NaI(Tl) traces was qualitatively similar to those from KI(Tl).

B. Intermediate Time

In this time region the Tl^{++} absorption increases in time with a characteristic time constant that is temperature dependent. This behavior is attributed to the thermally excited diffusion of self-trapped holes, followed by capture at Tl^+ sites. The observed behavior can be compared directly with the predictions of the model calculation.[1] In KI(Tl) the best agreement between experiment and calculation occurs near 240 °K. Figure 5 shows the calculated and measured Tl^{++} concentration as a function of time at 239 °K. The dashed curve represents the calculated concentration of V_k centers, and the solid curve is the calculated Tl^{++} concentration. Both curves represent relative values, and the saturation value for the Tl^{++} concentration does not have the same absolute value as the initial V_k concentration. In fact calculation predicts that, at this temperature, 91% of the V_k centers will be trapped by Tl^+ to form Tl^{++}, and 9% will be trapped by Tl^0 to form $(Tl^+)^*$.

The circles in Fig. 5 represent measured data points of relative Tl^{++} concentration, normalized to their saturation value at $t = 30$ μsec, and corrected for the contribution of Tl^{++} formed by prompt capture of holes at $t < 10^{-9}$ sec. The data of Fig. 5 thus represent only the Tl^{++} concentration due to hole diffusion and capture. The agreement between experiment and calculation is excellent for this temperature.

In the previous model calculation[1] the characteristic time for V_k diffusion and capture was taken as the time required for the initial V_k concentration to fall by a factor of 3. Calculations show that for all cases reported in this paper this characteristic time differs from the time required for the Tl^{++} concentration to reach $\frac{2}{3}$ of its maximum value by 2% or less. We will therefore discuss the V_k diffusion time as the time necessary to reach $\frac{2}{3}$ of the maximum Tl^{++} concentration, denoted $t_{2/3}$.

Figure 6 shows measured values of $t_{2/3}$ at various temperatures for KI(Tl). Error bars correspond to an estimated uncertainty of ± 25%, arising from random errors due to signal noise, width of scope trace, and determination of Tl^{++} saturation signal. The uncertainty in the temperature scale is estimated as ± 2 °K. Also shown in Fig. 6 is the calculated V_k diffusion time from the previous calculation.[1] It is seen that agreement is good around 240 °K, with significant disagreement at both lower and higher temperatures. In assessing the agreement between calculation and experiment, it is important to recognize that the calculated curve is significant only as to order of magnitude, as noted previously.[1] The rather large uncertainty in the calculated function arises from the fact that it is based on experimental data obtained at low temperature and extrapolated over many orders of magnitude to the temperature region in which the present experiments were performed. The calculated curve is based on the validity of the Song function[8] for the V_k reorientation rate over the entire temperature range, and further assumes the correctness of the Waite diffusion-controlled re-

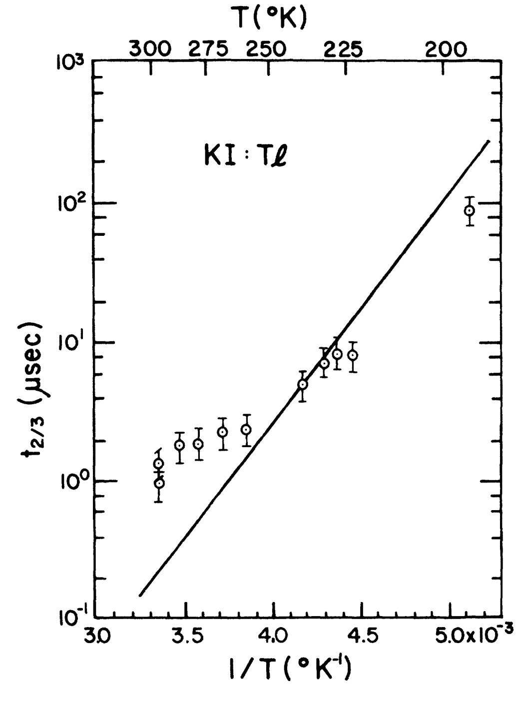

FIG. 6. Measured and calculated $t_{2/3}$ for KI(Tl) as a function of T^{-1}. The calculated curve is significant only as to order of magnitude; see text.

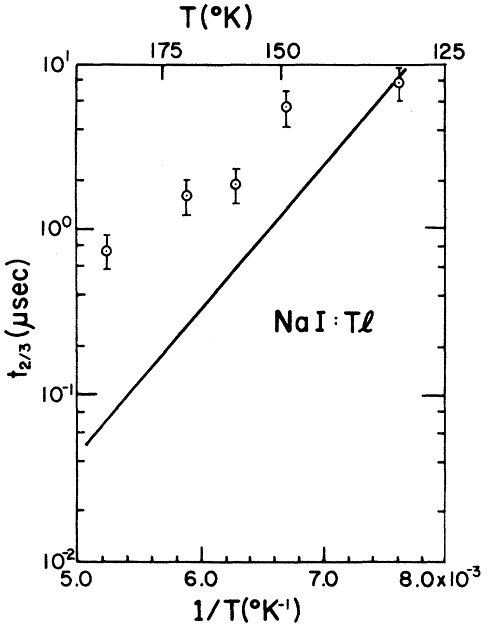

FIG. 7. Measured and calculated $t_{2/3}$ for NaI(Tl) as a function of T^{-1}. The calculated curve is significant only as to order of magnitude; see text.

action theory and various input parameters. Within this order-of-magnitude criterion we feel that the comparison between experiment and calculation, Fig. 6, is reasonable. One point of interest is the fact that the temperature dependence of the calculated curve is different from that of the data points. This may be associated with the fact that the calculation assumes a $1/T$ dependence for r_0 (capture radius of a Tl^0 for a diffusing hole) and assumes a temperature-independent value of r_+ (capture radius of a Tl^+ for a diffusing hole). These assumptions are surely over-simplifications.

Similar experiments in NaI(Tl), at a somewhat lower temperature, lead to the measured values of $t_{2/3}$ presented in Fig. 7. Agreement with the calculated curve from Ref. 1 is good at the lowest temperature, and the data points exhibit a slope different from that of the calculated curve similar to the case of KI(Tl). Comments on the comparison between experiment and calculation in the preceding paragraph on KI(Tl) apply to the case of NaI(Tl) as well.

C. Later Time

Reference to Fig. 3 shows that at a later time (after the V_k diffusion process) the Tl^{++} concentration drops. This behavior is attributed to the thermal excitation of electrons from electron-trapping defects, followed by their migration to Tl^{++} centers to produce $(Tl^+)^*$ states. There exists a large amount of low-temperature data (see Ref. 1) which establishes the Tl^0 as the primary electron trap in 0.1-mole% thallium-activated alkali iodide crystals. On the basis of this work we identify the Tl^0 as the predominant source of thermally excited electrons. Previous thermoluminescence observations have been interpreted as due to this process.[1,5] Estimates of the Tl^0 lifetime at room temperature indicate that it is substantially longer than the V_k diffusion time in both KI(Tl) and Na(Tl).[1]

We note in Fig. 3 that the Tl^{++} concentration in KI(Tl) at room temperature decays with a time constant of several milliseconds, although the data do not strictly follow an exponential function. This characteristic time is in reasonable agreement with the previously estimated[1] Tl^0 lifetime of ~ 10^{-2} sec. The process of Tl^{++} annihilation therefore occurs much slower than the hole diffusion, for which the time constant at room temperature is measured to be about 1 μsec. For purposes of describing the Tl^{++} decay we can therefore consider the hole diffusion as a process occurring "instantaneously", i.e., at $t=0$.

A similar situation exists for NaI(Tl). Figure 8 shows the Tl^{++} concentration as a function of time for NaI(Tl) at room temperature. In this case the data are well described by an exponential function with time constant 0.35 μsec. This is faster than the Tl^0 lifetime previously estimated from thermoluminescence.[1] The V_k diffusion time was not measured at room temperature, but extrapolation of the measured data to room temperature indicates a diffusion time below 0.35 μsec.

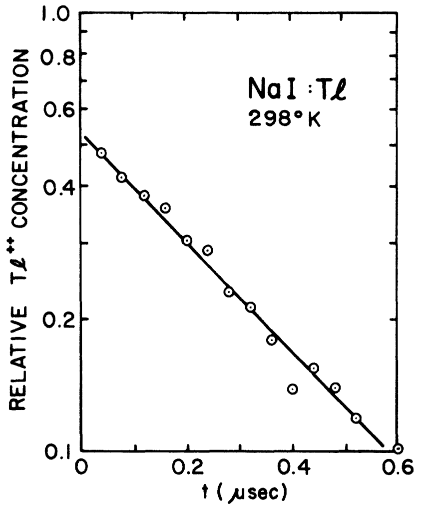

FIG. 8. Relative optical density of Tl^{++} absorption band in NaI(Tl) as a function of time, during the Tl^{++} decay. Crystal at room temperature. The straight line corresponds to an exponential decay with 0.35-μsec time constant.

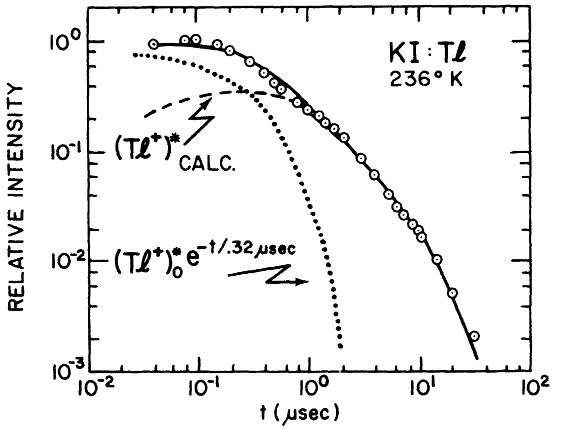

FIG. 9. Relative luminescence intensity of KI(Tl) at 236 °K. The initial sharp rise was not recorded. Broken curve: $(Tl^+)^*$ concentration calculated from Ref. 1 normalized to data at 4 μsec. Dotted curve: calculated $(Tl^+)^*$ based on exponential decay from prompt excitation. Solid curve: Sum of two calculated curves normalized to data at 0.2 μsec. Circles are experimental points.

D. Low-Temperature Luminescence

As indicated in Sec. I, the characteristic thallium luminescence arises from the radiative decay of a Tl^+ excited state, denoted $(Tl^+)^*$. Previous experiments have shown that the excited state can be produced both by electron capture at Tl^{++} or by hole capture at Tl^0. (Other mechanisms are direct excitation of Tl^+ by inelastic electron scattering or by exciton migration.) The lifetime of the $(Tl^+)^*$ state is temperature-dependent and has been measured by Pliavin.[9] Having measured the hole-diffusion kinetics and the decay of Tl^{++}, as discussed above, it should now be possible to relate these results to the luminescence kinetics.

We measured the luminescence intensity (at 430 nm) as a function of time for KI(Tl) at various temperatures; results at 236 °K are shown in Fig. 9 as data points. At this temperature thallium luminescence arises from two processes: (i) hole diffusion to Tl^0 sites to produce $(Tl^+)^*$, and (ii) direct excitation at $t \approx 0$. (The lifetime of Tl^0 is too long to see a contribution from $Tl^0 \rightarrow Tl^+ + e^-$, followed by electron capture at Tl^{++}.) The luminescence intensity from process (i) was calculated as a function of time using the methods of Ref. 1. The calculated function was normalized to the data at 4.0 μsec. Process (ii) gives rise simply to an exponentially decaying luminescence intensity with lifetime τ,

$$(Tl^+)^*_t = (Tl^+)^*_0 e^{-t/\tau} . \qquad (1)$$

The amplitude $(Tl^+)^*_0$ was obtained by setting $(Tl^+)^*_t$ equal to the difference between the calculated function for process (i) and the data at 0.2 μsec. The lifetime τ was taken from the experimental results of Pliavin as 0.32 μsec. The calculated curves from (i) and (ii) are shown as broken and dotted curves in Fig. 9, and their sum is presented as a solid curve. It is seen that the solid curve provides a good fit to the data over the entire range of time from 0.04 to 30 μsec; we note that 30 μsec is approximately six times the measured value of $t_{2/3}$. It should be noted that the lifetime τ is taken from experiment, and the V_k diffusion kinetics are taken from the previous model calculation.[1] The only curve fitting in Fig. 9 involves normalization of the calculated curves to the data.

A similar fit was generated for the data obtained at 195 °K, using the measured value of $t_{2/3}$. These data spanned a time from 0.04 to 30 μsec, and 30 μsec is approximately two and one-half times the measured $t_{2/3}$ (195 °K). Here again, the calculated curve fitted the data within experimental error over the entire range.

One can find the light output associated with processes (i) and (ii) by integration of the calculated curves which have been fitted to the data. Such integrations show that at both 195 and 236 °K only about 20% of the light emitted in the time period from 0.04 μsec to $2.5 t_{2/3}$ is the result of "prompt" excitation of the thallium. However, the energy transport associated with "prompt" processes is far less than this 20% because on the time scale considered above a significant fraction of the energy transported by electron-hole diffusion is stored at the Tl^0 and Tl^{++} sites.

We did not obtain data on the low-temperature luminescence of NaI(Tl).

E. Room-Temperature Luminescence

At room temperature, the KI(Tl) luminescence exhibits a qualitatively new feature, viz., a long tail extending to milliseconds, see Fig. 10. We identify this luminescence as arising from thermally excited release of trapped electrons at Tl^0 sites, followed by electron capture at Tl^{++} to produce $(Tl^+)^*$. This identification can be confirmed by comparing the luminescence intensity at long times with $-dTl^{++}/dt$ taken from experiment (Fig. 3). The basis for this comparison is given in the Appendix. Comparison of the luminescence intensity and $-dTl^{++}/dt$ is shown in Fig. 11: the smooth curve is the luminescence intensity (from Fig. 10) and the points represent $-dTl^{++}/dt$ obtained from the data of Fig. 3. The curve was normalized to the points at 0.9 μsec. It is seen that the agreement is good, confirming the correlation between the long-time luminescence and the Tl^{++} annihilation.

In the case of NaI(Tl) at room temperature, no luminescence is observed in the millisecond range, see Fig. 10. This arises from the fact that the

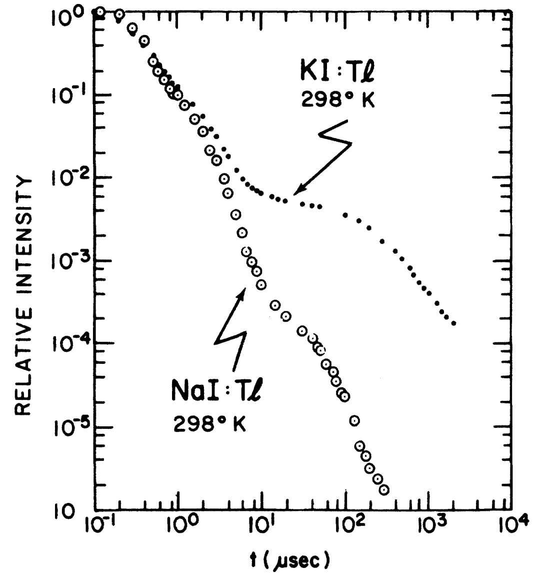

FIG. 10. Relative luminescence intensity of KI(Tl) and NaI(Tl) at room temperature. The initial sharp rise was not recorded.

Tl^{++} centers are annihilated with a time constant of 0.35 μsec as shown in Fig. 8. The (Tl^{+})* lifetime is 0.25 μsec.

Thus in KI(Tl) the "fast" component arises from hole diffusion in about 1 μsec and the "slow" component occurs in the msec range, producing the distinct hump at long times in Fig. 10. On the other hand, in NaI(Tl) the "fast" component of the luminescence at room temperature arises from hole diffusion and capture (in ~10^{-7}–10^{-8} sec) to produce an excited state of lifetime 0.25 μsec. The slow component, arising from electron release at Tl^{0}, occurs with a time constant of 0.35 μsec. It is not possible to resolve these components in the measured luminescence kinetics.

Another way to look at the data of Fig. 10 is to plot the light sum as a function of time. Integrating under the two curves of Fig. 10 produces the light sums shown in Fig. 12. For KI(Tl) we have plotted the relative light sum normalized to its value at 2 msec. The NaI(Tl) light sum reaches a saturation value at ~10 μsec. One can see a substantial difference in the behavior of the two crystals. At 1 μsec the NaI(Tl) has already emitted about 90% of the total light, but KI(Tl) has released only about 25%. The KI(Tl) value of 25% represents an upper limit because we have neglected the light emitted from this crystal beyond 2 msec. This marked difference in the behavior of the two crystals is the result of the long-lived Tl^{0} trap in KI(Tl). This point is discussed further below.

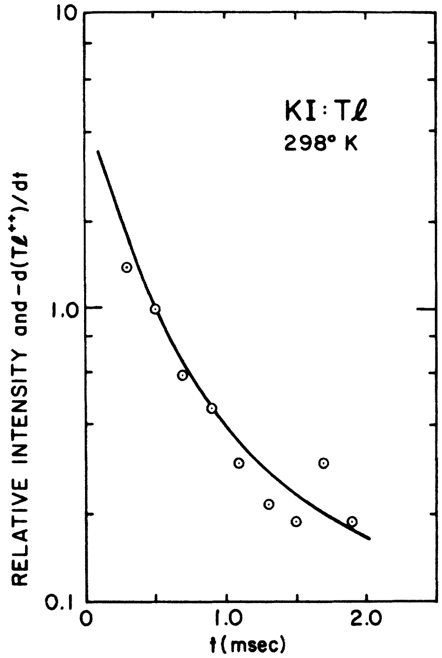

FIG. 11. Measured luminescence intensity (solid curve) and values of $-d\,\mathrm{Tl}^{++}/dt$ obtained from experiment (circles) for KI(Tl) at room temperautre.

Referring to Fig. 12, we see that at room temperature 75% or more of the total light output of KI(Tl) is correlated with the thermal release of electrons from the Tl^{0} (or other long-lived traps). This fraction of the light is emitted on a time scale which is long compared to 1 μsec and hence does not contribute to the scintillation pulse when 1 μsec clipping is used in the pulse amplifier. These results are in sharp contrast to the case of NaI(Tl) where anneal of the Tl^{++} was found to occur on the time scale of 0.1–1 μsec. It was further observed that in NaI(Tl), ~90% of the light was emitted prior to 1 μsec. On the basis of these observations we

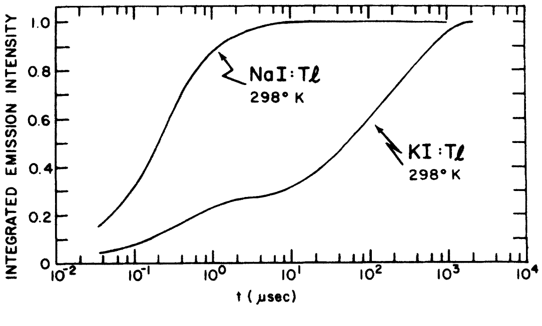

FIG. 12. Measured light sum as a function of time for KI(Tl) and NaI(Tl) at room temperature. Both curves normalized to 1.0. The KI(Tl) curve continues to rise beyond 2 msec.

conclude that the long-lived Tl^0 trap in KI(Tl) is the primary reason that the pulse height from KI(Tl) is approximately 25% of that from NaI(Tl) at a typical clipping time of 1 μsec.

IV. SUMMARY

The principal results of this work are the following:

(a) In KI(Tl) a fraction of the initially produced holes are trapped promptly ($\lesssim 10^{-9}$ sec) at Tl^+ sites to produce Tl^{++} centers. The characteristic capture volume is 25 unit cells. Qualitatively similar effects occur in NaI(Tl).

(b) Holes diffuse to Tl^+ sites with a temperature-dependent time constant that is predicted in order of magnitude by a previous model calculation.

(c) Tl^{++} centers are annihilated at "long" times by electrons thermally excited from Tl^0 centers.

(d) The luminescence kinetics of KI(Tl) at low temperatures is quantitatively described in terms of two processes: A prompt excitation to the radiative state at $t \approx 0$, and hole diffusion followed by capture at Tl^0 sites. About 80% of the light emitted at low temperatures results from hole diffusion to Tl^0 sites. Thus at least 80% of the energy transport from host lattice to thallium sites occurs by binary electron-hole diffusion. In fact, since electrons trapped at Tl^0 are immobile at these low temperatures, some energy is stored at Tl^0 and Tl^{++} sites, and we conclude that nearly all ($\approx 95\%$) of the energy transport takes place by electron-hole diffusion.

(e) The luminescence intensity of KI(Tl) at room temperature extends into the millisecond region, where radiative states are excited by the thermal release of electrons from Tl^0 followed by their capture at Tl^{++}. The analogous process in NaI(Tl) occurs in the range 10^{-7}–10^{-6} sec.

Finally, it should be noted that the conclusions of this work regarding the dominant role of electron-hole diffusion in energy transport are based on experiments in which the excitation occurs by energetic ionizing radiation which creates electron-hole pairs. These conclusions should not be extrapolated to experiments in which excitation occurs by optical absorption in the fundamental band to create excitons, for example, the recent work of Hattori *et al.*[10]

ACKNOWLEDGMENTS

This work was performed at the Naval Research Laboratory, with three of the authors as guest scientists. We wish to express our thanks to M.N. Kabler for his interest and helpful conversations.

APPENDIX

We consider the creation of $(\mathrm{Tl}^+)^*$ by the thermal excitation of trapped electrons and their subsequent capture at Tl^{++}. For KI(Tl) at room temperature the time scale is in the millisecond range, a time very long compared to either the V_k diffusion time or $(\mathrm{Tl}^+)^*$ lifetime (microseconds). The equation describing the process is

$$\frac{d}{dt}(\mathrm{Tl}^+)^* = -\frac{d}{dt}\mathrm{Tl}^{++} - \frac{(\mathrm{Tl}^+)^*}{\tau} \quad . \tag{2}$$

The solution to Eq. (2) is given by

$$(\mathrm{Tl}^+)^*_t = (\mathrm{Tl}^+)^*_0\, e^{-t/\tau} - e^{-t/\tau}\int_0^t e^{t'/\tau}\frac{d}{dt'}\mathrm{Tl}^{++}(t')\,dt' \ . \tag{3}$$

In view of the time scale of milliseconds, $t=0$ in Eq. (3) refers to a time when the V_k diffusion is complete, and not the time of the electron burst. For the same reason $(\mathrm{Tl}^+)^*_t$ refers only to the concentration of excited states from electron capture at Tl^{++}, and thus $(\mathrm{Tl}^+)^*_0 = 0$. To obtain an analytical solution to (3) requires an analytical form for $d\mathrm{Tl}^{++}/dt$. For present purposes it is adequate to take $\mathrm{Tl}^{++}(t)$ as an exponential function with decay time τ_{++}, which is of order 10^{-3} sec. Then (3) becomes

$$(\mathrm{Tl}^+)^*_t = \frac{\mathrm{Tl}_0^{++}}{\tau_{++}/\tau - 1}\left(e^{-t/\tau_{++}} - e^{-t/\tau}\right) \quad . \tag{4}$$

At room temperature τ for KI(Tl) has been measured[9] as 0.28 μsec and $\tau_{++} \approx 10^{-3}$ sec so that $(\tau_{++}/\tau) \gg 1$. For t greater than a few microseconds the second exponential term of (4) is negligible and we obtain

$$(\mathrm{Tl}^+)^*_t = \mathrm{Tl}_0^{++}(\tau/\tau_{++})\, e^{-t/\tau_{++}} \ , \tag{5}$$

or

$$\frac{(\mathrm{Tl}^+)^*_t}{\tau} = \frac{\mathrm{Tl}_0^{++}}{\tau_{++}}\, e^{-t/\tau_{++}} = \frac{-d}{dt}\mathrm{Tl}^{++}(t) \ . \tag{6}$$

The left-hand side of (6) is proportional to the luminescence intensity $I(t)$, so $I(t) \propto -d\,\mathrm{Tl}^{++}(t)/dt$.

[†] Work supported in part by the National Science Foundation under a grant to the University of Delaware.

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