

Luminescent Decay of KI:Tl, KBr:Tl, and KCl:Tl†

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(Received 15 May 1964)

The luminescent decay of single crystals of KI:Tl excited in the *A*, *B*, *C*, and *D* absorption bands has been investigated over the temperature range 10→300°K. A quantitative description of the decay of luminescence excited in the *A* band is given. Four of the emission bands have decay times consistent with the Seitz model, but the decay of the 4300-Å band does not agree with this model. Measurements of the luminescent decay of KBr:Tl and KCl:Tl excited in the *A* absorption band are presented, and the results are compared with those obtained for KI:Tl. The results support the hypothesis that the 3000-Å emission band in KCl:Tl at 10°K is double.

I. INTRODUCTION

THE emission spectra of KI:Tl excited in the *A*, *B*, *C*, and *D* absorption bands have been investigated by Edgerton and Teegarden.^{1,2} They found five emission bands at 12°K, at least two of these five bands being excited in each absorption band. As had been known previously,^{3,4} only two of the emission bands were present at 80°K and only one was present at 300°K.

Edgerton and Teegarden^{1,2} discussed their experimental data in terms of the model for the luminescence center in the thallium-activated alkali halides first proposed by Seitz,⁵ and identified each emission band with an electronic transition from one of the excited states to the ground state of the Tl⁺ ion. Since transitions from two of the excited states to the ground state were "allowed" on the Seitz model, Edgerton and Teegarden suggested that the lifetimes of two of the excited states should be short, of the order of 10⁻⁸ sec, but the lifetimes of the other excited states might be expected to be appreciably longer.

The original purpose of the present work was to measure the lifetimes of the excited states of the luminescence center in KI:Tl at low temperatures to check the above prediction. Early in the work, however, experimental data were obtained which could not be fitted to the simple model. For this reason, a detailed investigation of the emission spectra and luminescent decay of KI:Tl over the whole temperature range 10→300°K was undertaken. The results are presented in this paper and the extent to which they are consistent with the Seitz model is discussed. Although the work was primarily concerned with the properties of KI:Tl, some preliminary measurements carried out on KBr:Tl and KCl:Tl will be presented at the end of the paper.

† Research supported by the National Aeronautics and Space Administration, Goddard Space Flight Center, under contract NASW-107, and completed under a N.A.T.O. Research Fellowship at the University of Reading.

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¹ R. F. Edgerton and K. Teegarden, *Phys. Rev.* **129**, 169 (1963).

² R. F. Edgerton, Ph.D. thesis, University of Rochester, 1962 (unpublished).

³ K. Teegarden, *Phys. Rev.* **105**, 1222 (1957).

⁴ M. Tomura and Y. Kaibe, *J. Phys. Soc. Japan* **15**, 1295 (1960).

⁵ F. Seitz, *J. Chem. Phys.* **6**, 150 (1938).

II. EXPERIMENTAL

a. Samples

Single crystals of KI:Tl were taken from the ingot previously used by Edgerton and Teegarden.^{1,2} The absorption spectrum⁶ indicated a Tl⁺ concentration of 0.002 mole %.

b. Temperature Control and Measurement

Basically, the cryostat consisted of a liquid-helium reservoir thermally isolated from the crystal holder. Cold helium gas from the boiling liquid circulated through the crystal holder, and a small heater behind the crystal was used to control the temperature.

The temperature of the crystal was measured with a thermocouple (Au:2.1% Co-Ag:0.37% Au) soldered with indium to a thin strip of copper pressed against the front surface of the crystal but thermally isolated from the crystal holder. Between 80°K and room temperature, the measurements were accurate to within ±1°K. At lower temperatures, however, the measurements were less precise. Since the back surface of the crystal was cooled by thermal conduction to the crystal holder and the front surface was heated by radiation, a temperature gradient was formed because of the poor thermal conductivity of the crystal at low temperatures. For example, when the measured temperature of the crystal holder was 5°K, the temperature of the front face of the crystal was found to be 10°K. Since this temperature difference was less at higher temperatures, a systematic error of uncertain magnitude was introduced.

c. Emission Spectra

Emission spectra were obtained when the sample was excited separately in the *A*, *B*, *C*, and *D* absorption bands with light from a hydrogen lamp and a prism monochromator. The light emitted by the sample at right angles to the incident beam was collected by a spherical, front-surfaced mirror and focused on the entrance slit of a motor-driven Bausch and Lomb grating monochromator. The luminescence was detected

⁶ P. Yuster and C. Delbecq, *J. Chem. Phys.* **21**, 892 (1953).

with an EMI 9426B photomultiplier and the photocurrent amplified and then recorded on a Brown $\frac{1}{4}$ -sec pen recorder. The bandpass of the detecting monochromator was usually 20 Å and that of the exciting monochromator usually 50 Å. After making a correction for the response of the photomultiplier, the product of the maximum photocurrent and the half-width (in eV) was measured as a function of temperature for each emission band. Throughout the paper, this product (which is proportional to the number of photons emitted in each band) is called the intensity. We shall refer to each emission band by giving the wavelength of its maximum at 10°K, although it is known^{1,2} that, for some of the emission bands, the positions of the maxima change slightly as the temperature is varied.

d. Decay Times

To measure the decay time of each emission band, a pulse of light from a spark source was passed through the prism monochromator and focused on the crystal. The spark was formed between pointed steel electrodes connected across a small condenser to which a voltage of 5 kV was applied. With the spark gap contained in a nitrogen atmosphere at a pressure of 30 cm Hg, light pulses as short as 3×10^{-8} sec could be obtained. Pulses of duration greater than 10^{-7} sec were formed with a simple air gap. The light emitted by the crystal at right angles to the exciting light passed through a second monochromator and was detected with the photomultiplier. The photocurrent was amplified and displayed on an oscilloscope, and the oscilloscope traces of single pulses were photographed using Polaroid film. The rise time of the detecting system was 3×10^{-9} sec. When the photocurrent was plotted against time on semilog paper for times greater than the duration of the spark, a single straight line could usually be drawn through the points on the graph, indicating that the photocurrent at time t was proportional to $\exp(-t/\tau)$. τ is the "decay time" obtained by measuring the gradient of the straight line.

It is important now to distinguish between the terms "radiative lifetime," "lifetime," and "decay time." Throughout this paper, the lifetime τ_i of an excited state (i) of a luminescence center is defined as the reciprocal of the probability/unit time that an electron may leave state (i), either by a radiative transition to the ground state (g) or by a nonradiative transition to other excited states (j). The radiative lifetime τ_{ig} , which is the quantity we wish to evaluate, is defined as the reciprocal of the probability/unit time that an electron initially in state (i) undergoes a spontaneous radiative transition (i) \rightarrow (g). Then, if τ_{ij} is the probability/unit time for the nonradiative transition (i) \rightarrow (j), τ_i and τ_{ij} are related by the equation

$$\tau_i = [1/\tau_{ig} + \sum_j (1/\tau_{ij})]^{-1}. \quad (1)$$

There are two simple decay schemes which may give rise to an exponential decay:

(a) When electrons are raised to level (i), either by a radiative transition from the ground state or by nonradiative transitions from other excited states within a time much less than τ_i , the rate at which electrons return to the ground state depends only on τ_i . Hence, the measured decay time for the emission band corresponding to the transition (i) \rightarrow (g) is equal to τ_i .

(b) If electrons arrive in level (i) from some other excited state (k) during a time much greater than τ_i , the rate at which electrons return to the ground state is determined by the probability of a nonradiative transition from (k) to (i). In this case, the measured decay time for the emission band corresponding to the transition (i) \rightarrow (g) is equal to τ_{ki} and is independent of τ_i .

From these two examples, it is apparent that the magnitude of the measured decay time of an emission band can be different when excited in each absorption band, and may not be related to the lifetime of the level from which the radiative transition takes place.

No attempt was made to correct for the shape of the exciting pulse from the spark. Hence, decay times greater than 3×10^{-7} sec could be measured with some degree of accuracy. Decay times between 5×10^{-8} and 3×10^{-7} sec were estimated roughly, and decay times less than 5×10^{-8} sec could not be measured.

III. RESULTS FOR KI:Tl

a. Excitation in the A Band

The emission spectrum of KI:Tl excited in the A band at 10°K is shown in Fig. 1(a), and the intensities of the two emission bands are plotted against $1/T$ in Fig. 2, where T is the absolute temperature. At low temperatures, the 3356 Å band predominates, but as the temperature is raised, the relative intensity of the 4300-Å band is increased. The total intensity of the two bands is constant over the whole temperature range.

The decay time of the 3356-Å band was less than the limits of measurement ($< 5 \times 10^{-8}$ sec). The decay of the 4300-Å band, however, was found to be complex. Part of the 4300-Å band was emitted within a short time ($< 5 \times 10^{-8}$ sec) after excitation with the spark, and the rest was emitted over a longer period with an exponential decay. Figure 3 shows the "fast" and "slow" components of the 4300-Å band following excitation at 80°K by a spark of half-width 10^{-7} sec. The decay time τ_{4300}^s of the slow component and the intensities I_{4300}^f and I_{4300}^s of the fast and slow components were found to depend on temperature. In Fig. 4, τ_{4300}^s is plotted against $1/T$. At low temperatures, τ_{4300}^s is equal to $(3.0 \pm 0.2) \times 10^{-3}$ sec but falls off at higher temperatures. I_{4300}^f and I_{4300}^s are plotted against $1/T$ in Fig. 5. At low temperatures, both I_{4300}^f

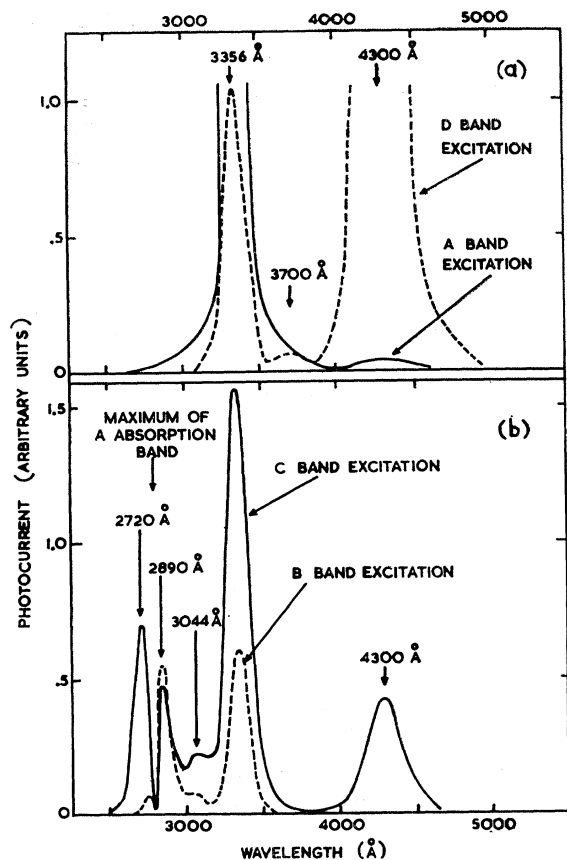


FIG. 1. Emission spectra (Refs. 1 and 2) of KI:Tl at 10°K. (a) Excited in the *A* and *D* bands. (b) Excited in the *B* and *C* bands. The minimum at 2830 Å in (b) coincides with the maximum of the *A* absorption band.

and I_{4300}^s are weak, but as the temperature is raised, they increase in magnitude. At higher temperatures, I_{4300}^f falls off again and is not detectable for $T > 170^\circ\text{K}$. The curves drawn through the experimental points in Figs. 2, 4, and 5 are given by Eqs. (7), (8), (9), (10), and (12), as described later.

The accuracy of the values of I_{4300}^f and I_{4300}^s for $T < 30^\circ\text{K}$ in Fig. 5 is rather poor, because of the difficulty of measuring the intensity of the fast component, when the total emission is very weak. Exciting radiation scattered by the crystal through the analyzing monochromator and thence into the photomultiplier was, of course, detected immediately following excitation with the spark. Scattered light thus enhanced the fast component but not the slow exponentially decaying component. At temperatures less than 30°K, scattered light was comparable in intensity to I_{4300}^f .

Careful examination of the emission spectra showed that the wavelengths of maximum emission and the half-widths of the 4300-Å band were constant within 5 Å over the temperature range 10–30°K.

b. Excitation in the *B* Band

When excited in the *B* band, emission bands were observed at 2890, 3044, 3356, and 4300 Å. Three of the bands, shown in Fig. 1(b), were present at 10°K. The intensities of the four emission bands are plotted against $1/T$ in Fig. 6. As Fig. 6 shows, the total intensity in all four emission bands is considerably less at liquid-helium temperature than at liquid nitrogen temperature. The 2890-Å band overlaps the *A* absorption band.

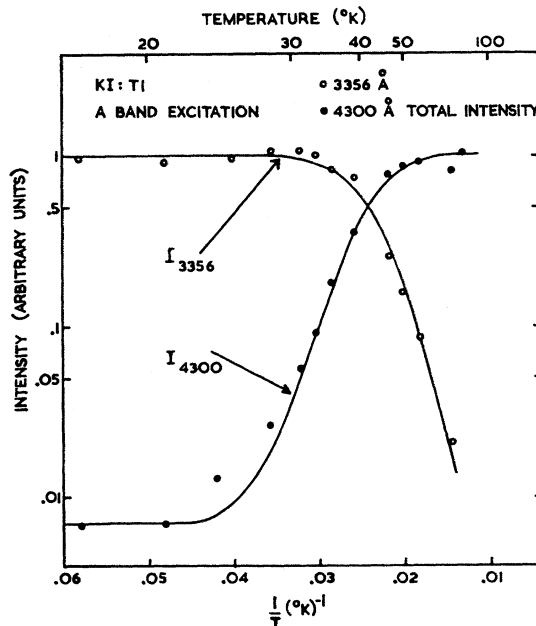


FIG. 2. Temperature dependence of the intensities of the 3356–4300-Å bands excited in the *A* absorption band. The curves through the experimental points are described by Eqs. (7) and (12).

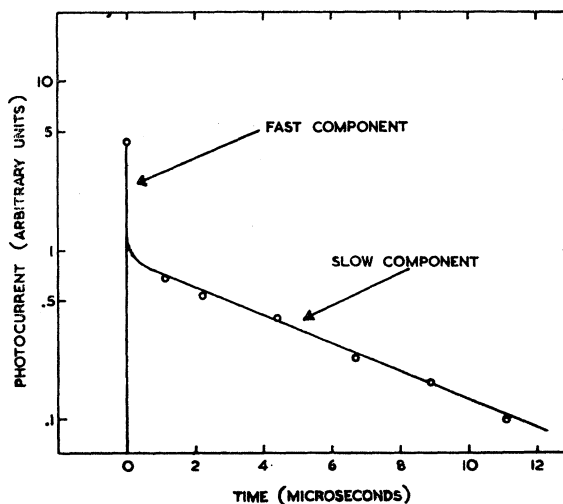


FIG. 3. Decay of the 4300-Å emission band in KI:Tl at 80°K following excitation in the *A* band with a pulse of light of half-width 10^{-7} sec.

The 3044-Å band, which is weak at low temperatures, predominates in the temperature range 35 to 120°K, but falls off at higher temperatures. The 4300-Å band

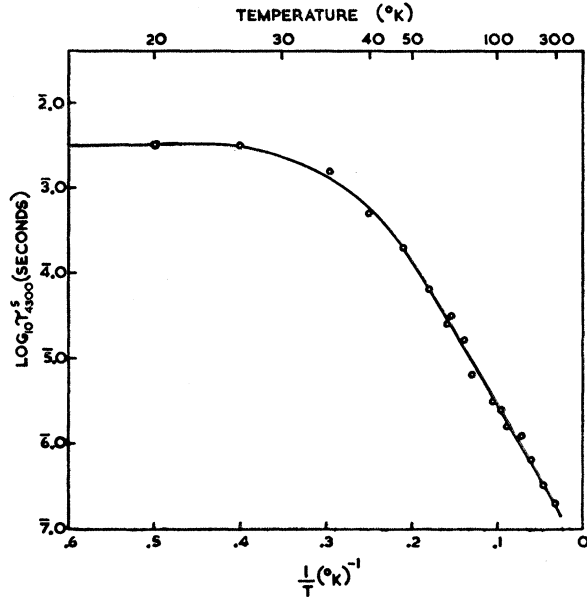


FIG. 4. Temperature dependence of the decay time τ_{4300} of the slow component of the 4300-Å emission band in KI:Tl excited in the *A* band. The circles are experimental values. The curve is described by Eq. (10).

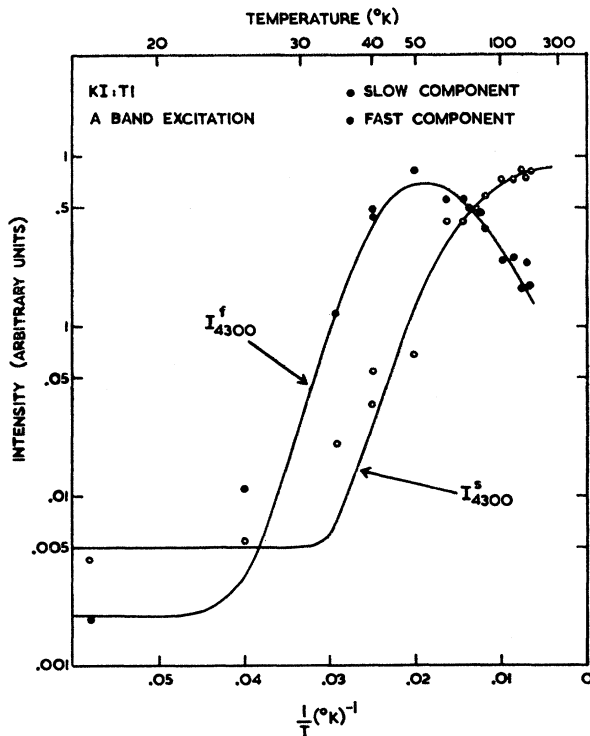


FIG. 5. Temperature dependence of the intensities of the fast and slow components of the 4300-Å emission band in KI:Tl excited in the *A* band. The curves through the experimental points are given by Eqs. (8) and (9).

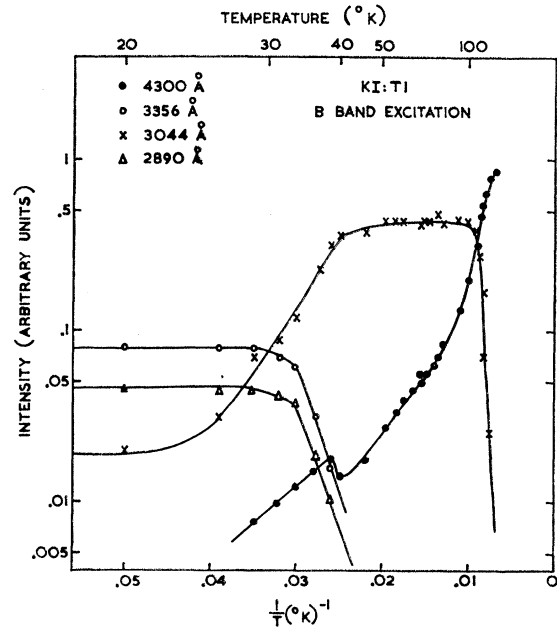


FIG. 6. Temperature dependence of the intensities of the four emission bands in KI:Tl excited in the *B* band. The points on the figure are experimental values.

increases in intensity as the temperature is raised from 10–40°K, but at 40°K it suddenly becomes weaker. The discontinuity in the curve in Fig. 6 at 40°K was found to be quite reproducible. Above 40°K, the 4300-Å band continues to increase in intensity, and at about 100°K the intensity suddenly increases at a greater rate as the 3044-Å band becomes weaker.

Both the 2890- and 3356-Å bands were found to have the identical decay time (within the limits of accuracy of the measurements) of $1.6 \pm 0.4 \mu\text{sec}$. The decay of the 4300-Å band was exponential, with decay time the same as for the slow component of the 4300-Å band when excited in the *A* band (Fig. 4). The fast component observed with *A*-band excitation was not found with *B*-band excitation. The decay time of the 3044-Å emission band had a constant value of $1.2 \pm 0.2 \mu\text{sec}$ for temperatures less than 100°K, but fell off as the temperature was increased above 100°K. Measurements of the decay times of the 4300- and 3044-Å bands were not possible below 40°K because of low intensities.

c. Excitation in the *C* Band

The emission spectrum of KI:Tl when excited in the *C* band at 10°K is given in Fig. 1(b). Since the *A* absorption band lies on top of the high-energy end of the spectrum, it is not immediately clear from Fig. 1(b) how many emission bands there are. It will be shown below that there are actually five bands: the 2890-, 3044-, 3356-, and 4300-Å bands also found with *B*-band excitation, and an additional band at 2720 Å. The temperature dependences of the five emission bands are

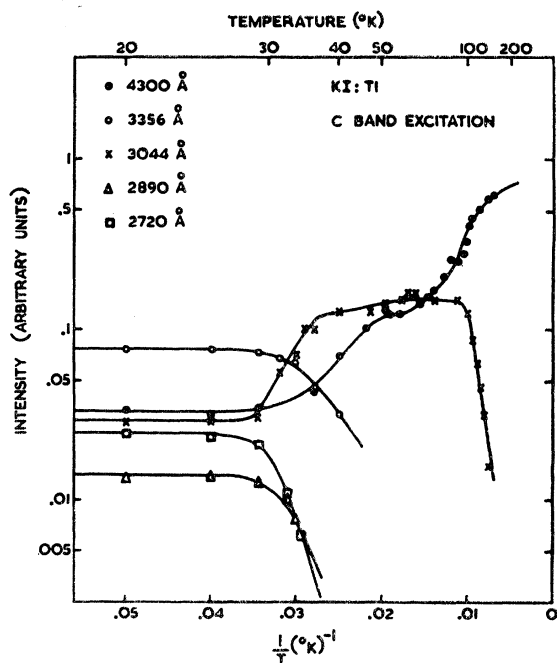


FIG. 7. Temperature dependence of the intensities of the five emission bands in KI:Tl excited in the C band. The points on the figure are experimental values.

given in Fig. 7. As the temperature is increased from liquid-helium temperature, the 2720-Å band decreases as the 3044-Å band increases, and the 3356-Å band decreases as the 4300-Å band increases. The excitation spectrum for the 4300-Å band showed that the 4300-Å band at 10°K was due to absorption in the D band, which overlaps the C band at all temperatures. However, the increase in intensity of the 4300-Å band above 35°K, shown in Fig. 7 may be attributed to absorption of light in the C band.

The decay time of the 2720-Å band was found to be less than the limits of measurement ($<5 \times 10^{-8}$ sec). However, the decay time of the 2890-Å band was 1.6×10^{-6} sec as for B excitation, indicating that the 2720- and 2890-Å bands are indeed separate emission bands and not parts of a single strong emission band centered on the A absorption band.

d. Excitation in the D Band

Figure 1(a) shows the emission spectrum of KI:Tl excited in the D band at 10°K. There are two main bands. One at 4300 and 3356 Å and, in addition, a very weak band at 3700 Å. The temperature dependences of the two main bands are given in Fig. 8.

The decay time of the 3356-Å band was less than 4×10^{-8} sec. Measurements of the decay of the 4300-Å band showed that the fast and slow components, mentioned previously for A-band excitation, were present. When excited in the D band, however, at 10°K, more than 50% of the 4300-Å band was emitted within

a period of less than 5×10^{-8} sec after excitation with the spark. The decay of the slow component was exponential with decay time having the temperature dependence given previously in Fig. 4.

The decay time and the temperature dependence of the 3700-Å band, which was not observed for $T > 30^\circ\text{K}$, were not measured because of the low intensity.

IV. DISCUSSION

a. Excitation in the A Band

As described previously, when KI:Tl is excited in the A band, two emission bands may be observed. One of the emission bands (4300 Å) exhibits two types of decay. Therefore, at least three excited states of the luminescence center, in addition to the ground state, are involved in the processes which follow excitation in the A band. Two of the excited states must have short lifetimes and the third must have a long lifetime (to account for the slow component of the 4300-Å band). A decay scheme constructed from these three excited states which is consistent with the experimental data given in Figs. 2, 3, 4, and 5 is described in the following paragraphs.

Figure 9 illustrates the proposed decay scheme. The potential energies of the three excited states, arbitrarily labeled (1), (2), and (3), and the ground state (*g*), are drawn as functions of some single, fictitious, configurational coordinate. The curves are completely qualitative in origin. Absorption in the A band corresponds to the transition (*g*) \rightarrow (1). After absorption, the luminescence

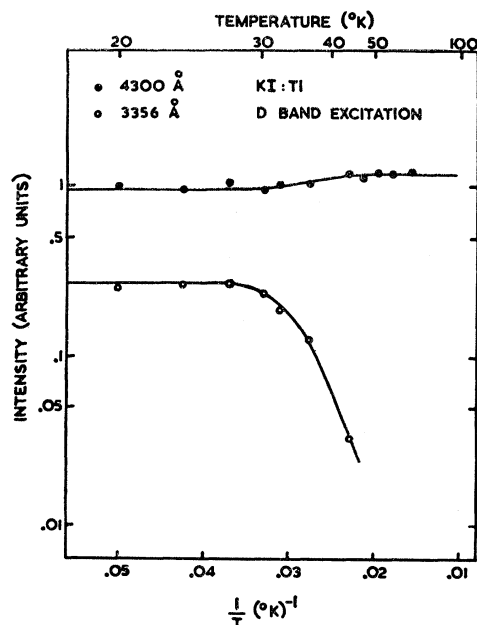


FIG. 8. Temperature dependence of the intensities of the two main emission bands in KI:Tl excited in the D band. The points on the figure are experimental values.

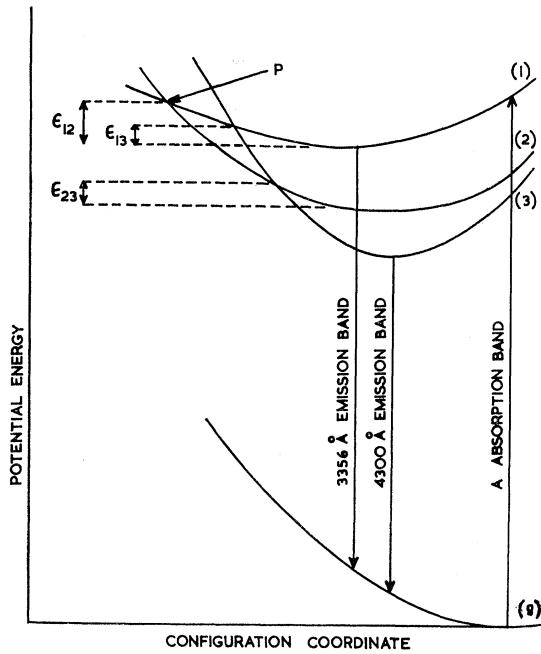


Fig. 9. Configuration coordinate diagram illustrating the luminescent decay of KI:Tl excited in the *A* band.

center reaches thermal equilibrium by the loss of potential energy to the surrounding lattice. At some later time, electrons in (1) return to the ground state (g) with the emission of radiation in the 3356-Å band, or go into levels (2) or (3) by nonradiative transitions. The 4300-Å emission band corresponds to the transition (3) → (g). Both levels, (1) and (3), have lifetimes less than 5×10^{-8} sec corresponding to the measured upper limit to the decay times of the 3356-Å band and fast component of the 4300-Å band when excited in the *A* band. Level (2) in Fig. 9 is long-lived with the radiative transition (2) → (g) completely forbidden. However, we assume that electrons may go into level (2) from level (1) by a nonradiative transition, and may at some later time go from (2) → (3). On this model, therefore, the intensity of the slow component of the 4300-Å band depends on the probability/unit time that an electron may go from (1) → (2), and the decay time τ_{4300^s} is equal to the lifetime of level (2). Then we have the following expressions:

$$I_{3356} = (1/\tau_{1g})[1/\tau_{1g} + 1/\tau_{12} + 1/\tau_{13}]^{-1}, \quad (2)$$

$$I_{4300^f} = (1/\tau_{13})[1/\tau_{1g} + 1/\tau_{12} + 1/\tau_{13}]^{-1}, \quad (3)$$

$$I_{4300^s} = (1/\tau_{12})[1/\tau_{1g} + 1/\tau_{12} + 1/\tau_{13}]^{-1}, \quad (4)$$

$$\tau_{4300^s} = \tau_2 = \tau_{23}, \quad (5)$$

where, as previously, $1/\tau_{ij}$ = probability/unit time for the transition (i) → (j).

On the decay scheme illustrated in Fig. 9, the nonradiative transition (1) → (2) will be most likely to

occur when electrons initially occupy the upper vibrational levels of (1); for which the configuration coordinate curves (1) and (2) are close together (point *P* in Fig. 9). According to the simple theory for thermal quenching,⁷ if we assume that transitions (1) → (2) can only take place at point *P* in Fig. 9, $1/\tau_{12}$ is proportional to $\exp(-\epsilon_{12}/kT)$, where k = Boltzmann's constant, T = absolute temperature, and ϵ_{12} = energy difference between the minimum of (1) and point *P*. This description of thermal quenching predicts that as $T \rightarrow 0$, the probability of a nonradiative transition also tends to zero. Hence, only one emission band should be observed at low temperatures when luminescence is excited by absorption of light in a single absorption band. As the experimental data show, however, this is not the case. Therefore, we conclude that, in addition to transitions from the upper vibrational levels of (1), nonradiative transitions also occur, with low probability, from the lower vibrational levels. If we assume that these latter transitions occur with probability/unit time $1/\tau_{012}'$, which is independent of temperature, we can write $1/\tau_{12}$ in the form

$$1/\tau_{12} = 1/\tau_{012}' + 1/\tau_{012} \exp(-\epsilon_{12}/kT), \quad (6)$$

where τ_{012} = constant. In Eq. (6), a triple subscript commencing with a zero indicates a constant, independent of temperature, and the primed decay time refers to the constant low-temperature value of the decay time not explained by the simple model for thermal quenching. If Eq. (6) and similar expressions for $1/\tau_{13}$ and $1/\tau_{23}$ are substituted into Eqs. (2), (3), (4), and (5), we obtain

$$I_{3356} = \tau_1/\tau_{1g}, \quad (7)$$

$$I_{4300^f} = \tau_1[1/\tau_{013}' + (1/\tau_{013}) \exp(-\epsilon_{13}/kT)], \quad (8)$$

$$I_{4300^s} = \tau_1[1/\tau_{012}' + (1/\tau_{012}) \exp(-\epsilon_{12}/kT)], \quad (9)$$

$$\tau_{4300^s} = [1/\tau_{023}' + (1/\tau_{023}) \exp(-\epsilon_{23}/kT)]^{-1}, \quad (10)$$

where

$$\tau_1 = \left[\frac{1}{\tau_{1g}} + \frac{1}{\tau_{012}'} + \frac{1}{\tau_{013}'} + \frac{1}{\tau_{012}} \exp\left(-\frac{\epsilon_{12}}{kT}\right) + \frac{1}{\tau_{013}} \exp\left(-\frac{\epsilon_{13}}{kT}\right) \right]^{-1}. \quad (11)$$

Addition of Eqs. (8) and (9) then gives the total intensity of the 4300 Å band as a function of temperature.

$$I_{4300} = [1 - \tau_1/\tau_{1g}]. \quad (12)$$

Equations (7), (8), (9), (10), and (12) are fitted to the

⁷D. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

experimental points in Figs. 2, 4, and 5, using the values

$$\begin{aligned}\epsilon_{13} &= 0.032 \pm 0.003 \text{ eV,} \\ \epsilon_{12} &= 0.054 \pm 0.003 \text{ eV,} \\ \epsilon_{23} &= 0.030 \pm 0.003 \text{ eV,} \\ \tau_{023}' &= (3.0 \pm 0.2) \times 10^{-3} \text{ sec,} \\ \tau_{023} &= (5 \pm 2) \times 10^{-8} \text{ sec,} \\ \tau_{10}/\tau_{013}' &= (2 \pm 2) \times 10^{-3}, \\ \tau_{10}/\tau_{012}' &= (5 \pm 2) \times 10^{-3}, \\ \tau_{10}/\tau_{013} &= (7 \pm 2) \times 10^3, \\ \tau_{013}/\tau_{012} &= 30 \pm 5.\end{aligned}$$

The errors given here have been estimated assuming an uncertainty of $\pm 3^\circ\text{K}$ in the temperature measurement in the range $20 \rightarrow 40^\circ\text{K}$. The curves fit the experimental points over the whole temperature range, indicating that the proposed decay scheme is consistent with the experimental results.

On the Seitz model for luminescence in the thallium-activated alkali halides, the *A* absorption band is identified with the electronic transition of the Tl^+ ion, ${}^1\Gamma_1^e \rightarrow {}^3\Gamma_4^0$, where we use the spectroscopic notation given by Seitz and by Edgerton and Teegarden. Thus, level (1) of the decay scheme may be identified with the ${}^3\Gamma_4^0$ state of the Tl^+ ion. The corresponding emission band (3356 Å) has a decay time less than 5×10^{-8} sec, confirming that the transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$ is allowed. It is proposed that level (2) may be identified with the ${}^3\Gamma_1^0$ excited state. Since no emission or absorption bands corresponding to this level have been observed, the transition ${}^3\Gamma_1^0 \rightleftharpoons {}^1\Gamma_1^e$ is completely forbidden, in agreement with the Seitz model. However, as described above, the decay time of the fast component of the 4300-Å band was found to be short ($< 5 \times 10^{-8}$ sec), indicating that the transition (3) \rightarrow (g) is an allowed transition. There is, apparently, no short-lived excited state of the Tl^+ ion which corresponds to level (3). It will be shown later that this important conclusion is applicable to KCl:Tl and KBr:Tl .

b. Excitation in the *B* Band

According to Yuster and Delbecq,⁶ the area under the *B* absorption band in KI:Tl is reduced by 40% as the temperature is lowered from liquid-nitrogen temperature to liquid-helium temperature. This change in the absorption band is sufficient to account for the change in the total intensity of the four emission bands (Fig. 6), assuming that the total quantum yield is independent of temperature.

The electronic transitions thought to occur at the luminescence center after excitation in the *B* and *C* absorption bands are illustrated in Fig. 10. The diagram includes the three energy levels discussed previously for excitation in the *A* band, but no attempt is made in Fig. 10 to represent the lattice relaxation. Each energy

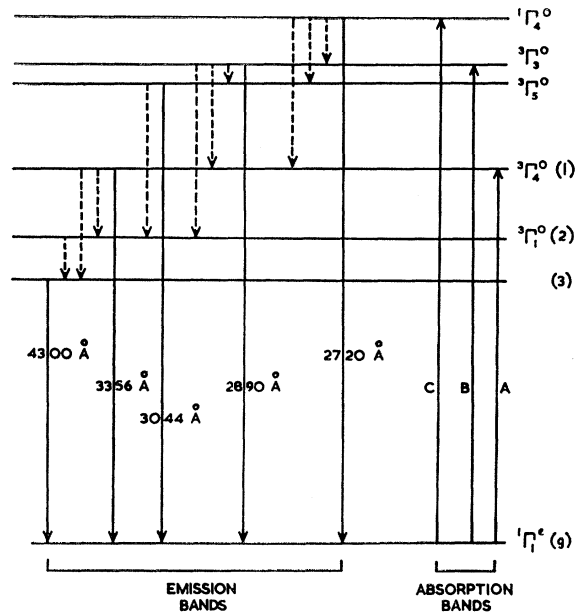


FIG. 10. Energy level diagram illustrating the luminescent decay of KI:Tl excited in the *A*, *B*, and *C* bands. The solid vertical lines represent radiative transitions. The dashed vertical lines represent nonradiative transitions.

level, with the exception of level (3), is identified with one of the excited states of the Tl^+ ion. Radiative transitions are represented by solid vertical lines, and nonradiative transitions are drawn as dashed lines. In Fig. 10, absorption in the *B* band corresponds to the transition ${}^1\Gamma_1^e \rightarrow {}^3\Gamma_3^0$, and the 2890-Å band is associated with the reverse transition ${}^3\Gamma_3^0 \rightarrow {}^1\Gamma_1^e$. The 3044-Å emission band is attributed to the transition ${}^3\Gamma_5^0 \rightarrow {}^1\Gamma_1^e$.

The measured decay time ($1.6 \pm 0.4 \mu\text{sec}$) of the 2890-Å band at 10°K represents the lifetime of the ${}^3\Gamma_3^0$ state. The decay time ($1.2 \pm 0.2 \mu\text{sec}$) of the 3040-Å band, measured between 40 and 80°K , is assumed to be equal to the radiative lifetime of the ${}^3\Gamma_5^0$ state. Thus, the radiative lifetimes of the ${}^3\Gamma_3^0$ and ${}^3\Gamma_1^0$ states (corresponding to the 3P_2 level of the free Tl^+ ion) are of the same order of magnitude and are characteristic of "forbidden" transitions, in agreement with the Seitz model. The decrease in the decay time of the 3044-Å emission band above 100°K is associated with thermal quenching of this emission band.

At 10°K , we assume that most of the electrons raised to the ${}^3\Gamma_3^0$ state return to the ground state with the emission of light in the 2890-Å band. This emission band overlaps the *A* absorption band (Fig. 1) and is partly absorbed in the *A* band, resulting in the emission of the 3356- and 4300-Å emission bands (Fig. 2). As the temperature is increased from 10°K , the proportion of light re-emitted in the 4300-Å band increases (Figs. 2, 6). However, as the temperature is increased further, the 2890-Å band is thermally quenched (Fig. 6) and the intensities of the 3356- and 4300-Å bands are therefore

reduced. This accounts for the sudden drop in the intensity of the 4300-Å band at 40°K, shown in Fig. 6.

The nonradiative transitions from ${}^3\Gamma_3^0$ occurring after absorption of light in the *B* band are indicated in Fig. 10. At 10°K, there is a small probability that the nonradiative transition to ${}^3\Gamma_5^0$ may occur with subsequent emission of the 3044-Å band. As the temperature is raised, this probability increases, the 2890-Å band is thermally quenched, and the 3044-Å band becomes strong (Fig. 6). At higher temperatures ($T > 40^\circ\text{K}$) nonradiative transitions ${}^3\Gamma_3^0 \rightarrow {}^3\Gamma_1^0$ become more probable, and the slow component of the 4300-Å band increases in intensity. The fast component of this emission band is not observed for excitation in the *B* band, indicating that the transition ${}^3\Gamma_3^0 \rightarrow (3)$ does not occur. Above 100°K, transitions ${}^3\Gamma_3^0 \rightarrow {}^3\Gamma_1^0$ become probable, leading to thermal quenching of the 3044-Å band and a sudden increase in the intensity of the slow component of the 4300-Å band. From the appearance of Fig. 6, it seems likely that each of the nonradiative transition probabilities may be represented in the form of Eq. (6), given previously for excitation in the *A* band. However, because of the change in the magnitude of the *B* band and the effect of reabsorption of the 2890-Å band, it is not possible to describe the temperature dependence of the emission bands in a quantitative manner.

c. Excitation in the C Band

The decay time of the 2720-Å band, which is only excited in the *C* band, was found to be less than 5×10^{-8} sec. Thus (Fig. 10), we associate this emission band^{1,2} with the allowed transition ${}^1\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$. Apparently, nonradiative transitions may take place from ${}^1\Gamma_4^0$ to other excited states of the Tl^+ ion, resulting in the emission of all the other bands (Fig. 1). Some of the nonradiative transitions are indicated in Fig. 10. Since both the 2720- and 2890-Å bands overlap the *A* absorption band, and the *D* absorption band overlaps the *C* absorption band, a detailed interpretation of the temperature dependence of the intensities of the emission bands (Fig. 7) has not been attempted.

d. Excitation in the D Band

According to Yuster and Delbecq,⁶ the *D* absorption band in KI:Tl may be attributed to an electronic transition in the I^- ions adjacent to the Tl^+ impurity. As described above, the 3356-Å band has a decay time of less than 5×10^{-8} sec when excited in the *D* band. Since the 3356-Å band has already been identified with the transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$ of the Tl^+ ion, it is apparent that energy must be transferred to the Tl^+ ion within this time.

It is, perhaps, significant that at 10°K, it is only in the *D* band that the fast component of the 4300-Å band is strongly excited. This part of the emission band, with a decay time of less than 5×10^{-8} sec, has already

TABLE I. Summary of the radiative lifetimes of the excited states of the luminescence center in KI:Tl.

Emission band (Å)	Excited state of Tl^+ impurity	Radiative lifetime of excited state (sec)	Excited state of free Tl^+ ion
2720	${}^1\Gamma_4^0$	$< 5 \times 10^{-8}$	1P_1
2890	${}^3\Gamma_3^0$	$(1.6 \pm 0.4) \times 10^{-6}$	3P_2
3044	${}^3\Gamma_5^0$	$(1.2 \pm 0.2) \times 10^{-6}$	3P_2
3357	${}^3\Gamma_4^0$	$< 5 \times 10^{-8}$	3P_1
4300	?	$< 5 \times 10^{-8}$?
None	${}^3\Gamma_1^0$...	3P_0

been associated with a transition from an excited state [level (3) of the previous discussion], which was not one of the excited states of the Tl^+ ion. We may speculate, therefore, that level (3) may be identified with an excited state of the I^- ions surrounding the Tl^+ impurity.

The origin of the weak emission band at 3700 Å, which was observed at low temperatures when luminescence was excited in the *D* band, is not clear. It would be interesting to know whether this weak emission band in KI:Tl is of the same origin as the strong emission band found at the same wavelength when pure KI is excited in the exciton absorption band.^{3,4}

e. Summary

Table I summarizes the radiative lifetimes of the excited states of the luminescence center in KI:Tl. The first column of the table lists each emission band resulting from a radiative transition from the excited state given in column 2. Column 3 gives the radiative lifetimes of the excited states. The corresponding levels of the free thallous ion are given in column 4.

V. LUMINESCENCE OF KBr:Tl EXCITED IN THE A ABSORPTION BAND

a. Results

It has been shown above that a decay scheme involving three excited states can account for the observed luminescence properties of KI:Tl when excited in the *A* band. The experimental work on KBr:Tl and KCl:Tl, now to be described, was undertaken specifically to determine whether a similar decay scheme might also be applicable to other thallium-activated potassium halides.

Previous workers^{1,2,8} have found that when KBr:Tl is excited in the *A* band at 300°K, two unresolved emission bands, with maximum intensities at 3630 Å, and at about 3200 Å, are observed. At 80°K the two emission bands are resolved with maximum intensities at 3630 and 3103 Å.

Figure 11 shows the temperature dependence of the intensities of the emission bands. At 10°K, the 3103-Å band is strong, but as the temperature is raised, the

⁸ W. von Meyeren, *Z. Physik* **61**, 321 (1930).

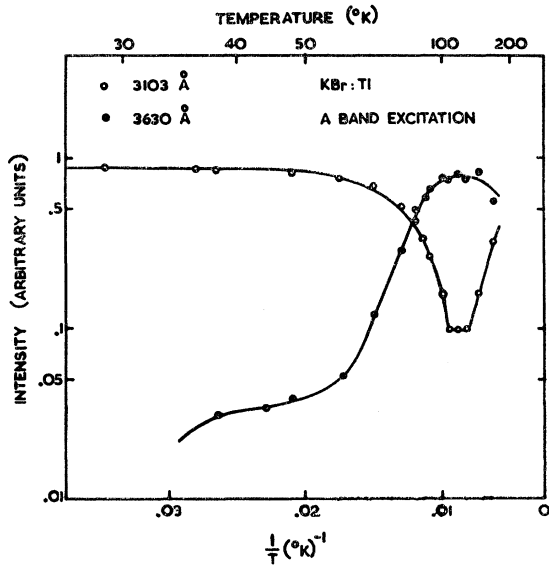


FIG. 11. Temperature dependence of the intensities of the emission bands in KBr:Tl excited in the *A* band. The points on the figure are experimental values.

3103-Å band is quenched, and the intensity of the 3630-Å band is increased. At higher temperatures, an emission band appears at the high-energy side of the 3630 Å band and increases in intensity as the temperature is raised. The two emission bands are not resolved at temperatures greater than 120°K and it is difficult to measure the half-width and wavelength of maximum intensity of the high-energy band. For this reason, it is

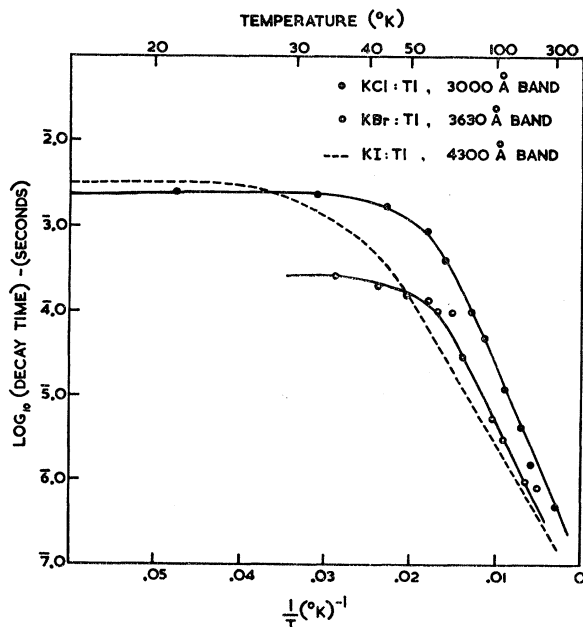


FIG. 12. Temperature dependence of the decay times of the 4300-Å band in KI:Tl, 3630-Å band in KBr:Tl, and 3000-Å band in KCl:Tl when excited in the *A* absorption band.

not clear whether the high-energy emission bands at 10 and 300°K are the same emission band with a wavelength of maximum intensity which changes slightly with temperature, or are different emission bands which happen to lie in the same part of the spectrum.

The decay time of the 3630-Å band is shown as a function of temperature in Fig. 12. Measurements were not made at temperatures less than 30°K, because of the low intensity of the band. At 10°K, the decay time of the 3103-Å band was less than 5×10^{-8} sec.

b. Discussion

The experimental results for KBr:Tl show some remarkable similarities with the data obtained previously for KI:Tl when excited in the *A* band. The 3103-Å band in KBr:Tl, which has a decay time of less than 5×10^{-8} sec at 10°K and is quenched at higher temperatures, corresponds to the 3356-Å band in KI:Tl. The 3103-Å band may therefore be attributed to the allowed transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$. As Fig. 12 shows, the temperature dependence of the decay time of the 3630-Å band in KBr:Tl closely resembles the temperature dependence of the decay time τ_{4300}^0 of the slow component of the 4300-Å band in KI:Tl. Therefore, we associate the 3630-Å band in KBr:Tl with a radiative transition from an excited state [equivalent to level (3) of the previous discussion for KI:Tl], which is not one of the Tl^+ excited states. Similarly, it is proposed that the decay time of the 3630-Å band is determined by the probability of a thermal transition from the ${}^3\Gamma_4^0$ excited state into the equivalent of level (3). No "fast" component of the 3630-Å band has been observed, indicating that the nonradiative transition ${}^3\Gamma_4^0 \rightarrow (3)$ does not occur in KBr:Tl. However, the high-temperature, high-energy emission band in KBr:Tl has no counterpart in KI:Tl, and its origin is not understood.

VI. LUMINESCENCE OF KCl:Tl EXCITED IN THE *A* BAND

a. Results

Work on KCl:Tl was limited to a study of the decay time of the prominent emission band at 3000 Å when luminescence was excited in the *A* band. It was found that at low temperatures, less than 20% of the light was emitted within a period of less than 5×10^{-8} sec after excitation with the spark. More than 80% of the light, however, was emitted over a longer period with an exponential decay. Figure 12 shows the temperature dependence of the decay time of this part of the luminescence emission. The relative proportions of the two parts of the decay were apparently constant as the temperature was raised from 10°K up to about 80°K. At temperatures above 90°K, however, only the long-lived exponential part of the decay could be detected.

b. Discussion

Previous workers^{1,2,9} have shown that at 10°K the 3000-Å band in KCl:Tl is asymmetric, and that as the temperature is raised from 10 to about 80°K, the peak position of the band moves slightly to longer wavelengths. Between 80 and 300°K, the position of the maximum is constant. Edgerton and Teegarden^{1,2} suggested that this behavior could be explained by assuming that the emission band consisted of two overlapping bands with relative intensities dependent on the temperature. The present data support this hypothesis. At low temperatures, more than 80% of the luminescence emission has a decay time (Fig. 12) characteristic of the long-wavelength emission bands in KBr:Tl and KI:Tl. This suggests that the main part of the 3000-Å band in KCl:Tl may be associated with a radiative transition from an excited state, which corresponds to level (3) of the decay scheme for KI:Tl, and which is not an excited state of the Tl⁺ ion. The decay time (Fig. 12) is then determined by the probability of the nonradiative transition ${}^3\Gamma_1^0 \rightarrow (3)$. At low temperatures, less than 20% of the 3000-Å emission band in KCl:Tl has a decay time less than 5×10^{-8} sec. As the temperature is raised above 80°K, this part of the emission is thermally quenched in a manner similar to the 3103- and 3356-Å bands in KBr:Tl and KI:Tl, respectively. Therefore, in analogy with KI:Tl, we associate the short-lived part of the 3000-Å emission band in KCl:Tl with the allowed transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$.

There are two previous experimental investigations which are relevant to the present work. First, Klick and Compton¹⁰ found that, at liquid-helium temperature, when KCl:Tl was excited in the *A* absorption band with polarized light, the 3000-Å emission band was polarized with degree of polarization equal to 0.2. From the present work, it is likely that the polarized part of the emission band is emitted within a period of less than 5×10^{-8} sec following excitation, and that the unpolarized part corresponds to the slow exponential decay. Second, Patterson¹¹ has shown that at high temperatures, the *A* absorption band is split into three components indicating electronic transitions from the ground state of the luminescence center to three excited states. It would be interesting to know whether the three excited states found by Patterson could be identified with the three excited states proposed above for KCl:Tl.

VII. CONCLUSION

The decay times of four of the emission bands in KI:Tl have values consistent with those expected on

⁹ D. Patterson and C. Klick, *Phys. Rev.* **105**, 401 (1957).

¹⁰ C. Klick and D. Compton, *Phys. Chem. Solids* **7**, 170 (1958).

¹¹ D. Patterson, *Phys. Rev.* **119**, 962 (1960).

the Seitz model as predicted by Edgerton and Teegarden. The 2720- and 3356-Å bands have decay times less than 5×10^{-8} sec and are associated with the transitions ${}^1\Gamma_4^0, {}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$. The 2890- and 3044-Å bands at low temperatures have decay times 1.6 ± 0.4 and 1.2 ± 0.2 μ sec, respectively, and are associated with the "forbidden" transitions ${}^3\Gamma_{3,5}^0 \rightarrow {}^1\Gamma_1^e$.

The luminescent decay of KI:Tl excited in the *A* band has been examined in detail. It has been found that the well-known simple model for thermal quenching is not applicable at low temperatures, but is apparently valid as the temperature is raised. From the temperature dependence of the decay of the 4300-Å emission band excited in the *A* absorption band, it has been shown that this emission band must be attributed to an "allowed" transition from an excited state which is not characteristic of the Tl⁺ ion. Transitions between the lowest excited state (${}^3\Gamma_1^0$) of the Tl⁺ ion and the ground state do not occur. At 10°K, the 4300-Å emission band is excited strongly only in the *D* absorption band, and it has been speculated that the emission band may therefore be attributed to an electronic transition in the I⁻ ions adjacent to the Tl⁺ impurity.

When KBr:Tl is excited in the *A* band, at least three excited states are involved in the decay scheme. The 3630-Å emission band in KBr:Tl is similar to the 4300-Å band in KI:Tl, and is attributed to the same unidentified electronic transition. The 3103-Å band in KBr:Tl resembles the 3356-Å band in KI:Tl, and is therefore attributed to the allowed transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$. The origin of the high-energy emission band observed at temperatures greater than 120°K is not understood.

More than 80% of the strong 3000 Å band in KCl:Tl excited in the *A* absorption band has the decay time characteristic of the long-wavelength emission bands in KBr:Tl and KI:Tl, and is attributed to the same unidentified electronic transition. Less than 20% of the emission band has a short decay time corresponding to the high-energy emission bands excited in the *A* absorption bands in KI:Tl and KBr:Tl. This short-lived part of the emission band, which is quenched at temperatures greater than 80°K, is attributed to the allowed transition ${}^3\Gamma_4^0 \rightarrow {}^1\Gamma_1^e$. The results support the hypothesis that the 3000-Å emission band in KCl:Tl at 10°K is actually double.

ACKNOWLEDGMENTS

The author thanks Dr. K. J. Teegarden and Dr. R. F. Edgerton for many discussions in connection with this work. Thanks are also due to Dr. G. Baldini and Dr. G. R. Huggett for advice on low-temperature techniques.