the data required for evaluation of thermoelectric power from Eq. (24).

Figure 2 shows a comparison between the measured and calculated thermoelectirc power curves for three n-type, antimony-doped polycrystalline germanium samples and three p-type, aluminum-doped polycrystalline germanium samples. It is apparent that consistently good agreement exists in the transition range, where there is little scatter of the experimental points, and also quite good agreement in the impurity range in view of the rather wide scatter of the experimental points at these lower temperatures.

Figure 3 shows a similar comparison between theory and experiment for two polycrystalline silicon samples, both p type, one (26G) boron-doped and the other (112) aluminum-doped. While there is a fair degree of agreement between theory and experiment, it is not as good as for the germanium samples, perhaps because all measurements on silicon were more difficult than on germanium because pressure contacts were used instead of soldered ones.

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Luminescence Studies of KI-TlI

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The characteristics of the electron traps present in the KI-TlI phosphor have been investigated. Determination of trapping depth and frequency factor yields evidence for representation as a reaction rate process with a division into two distinct trapping systems, while absorption and emission studies indicate a common excited state. Evaluation of concentration and cross section of traps substantiates the above hypothesis.

A. INTRODUCTION

CRYSTALS composed of alkali-halides with small percentages of added thallium-halide have been studied extensively as model impurity-activated phosphors. The original work of Pohl's school[1] and Bünger[2] has been supplemented more recently by that of Garlick[3] and Randall[4] who have also extended studies of the thermoluminescence phenomenon originally investigated by Urbach.[5] The theoretical aspects of the problem, first treated by Seitz,[6] have been advanced quantitatively by Williams.[7] The specific system, potassium iodide-thallium iodide, had been investigated earlier at this laboratory[8] and also by Bonanomi.[9]

A complete analysis of a complex electron-trapping system requires a knowledge of the kinetics involved. For a monomolecular process, the activation energy and frequency factor are required constants for the various trapping levels, as well as the concentration and cross section for trapping under given excitation. Absorption and emission characteristics indicate the processes involved while knowledge of intertrap and nonradiative transitions are necessary to estimate the efficiency of the phosphorescent processes. We have attempted in this investigation to extend the preliminary results previously reported and to discuss certain quantitative aspects of a long-lived phosphorescent system hitherto not mentioned.

B. THERMOLUMINESCENCE STUDIES

If a phosphor is irradiated at a temperature T, the phosphorescent intensity I will be determined by the rate of release of trapped electrons, $-(dn/dt)$, and can be described, for a monomolecular process, by

$$I \propto -(dn/dt) = n/\tau, \tag{1}$$

where the decay time τ is given by

$$\tau = s^{-1} \exp(E/kT). \tag{2}$$

E is the activation energy required to raise the electron from trapped to emitting state, and s is defined as the frequency factor. If the irradiation is stopped after n_0 electrons are trapped and the temperature increased at a rate $\beta = dT/dt$, the emission will continue at a rate

$$dn/dt = -sn_0 \exp\left[-\int_0^T \frac{s}{\beta} e^{-E/kT} dT\right] e^{-E/kT}. \tag{3}$$

[1] See R. Hilsch, Proc. Phys. Soc. (London) **49** (extra part), 40 (1937).
[2] W. Bünger, Z. Physik **66**, 311 (1930); W. Bünger and W. Z. Flechsig, Z. Physik **67**, 421 (1931) and **69**, 627 (1932).
[3] G. F. J. Garlick and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A185**, 408 (1945).
[4] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 347 (1945).
[5] F. Urbach, Wien. Ber. IIa. **139**, 353, 364, 483 (1930).
[6] F. Seitz, J. Chem. Phys. **6**, 150 (1938).
[7] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).
[8] Smaller, May, and Freedman, Phys. Rev. **79**, 940 (1950).
[9] J. Bonanomi and J. Rossel, Helv. Phys. Acta. **24**, 310 (1951); Physica **18**, 486 (1952).

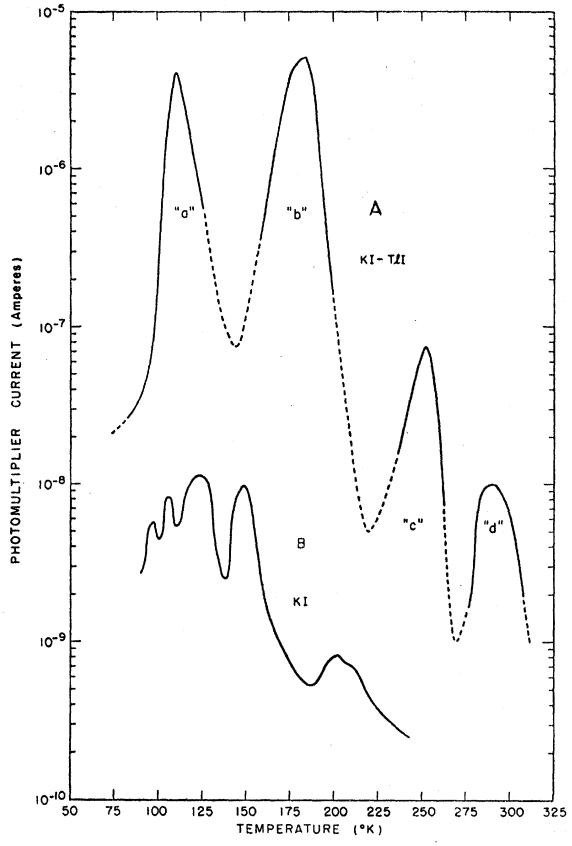

FIG. 1. Glow curves for thallium-activated and pure potassium iodide. A. Glow curve for a crystal containing 0.05 percent of thallium after being subjected to 50-kev x-radiation at 80°K. B. Curve for a control crystal containing less than 3×10^{-7} Tl/K. Heating rate, $\beta=0.22$ deg/sec^{-1}.

The dependence of I on T can be easily seen from the derivative relationship

$$\frac{d\ln I}{d(1/T)}=\frac{s}{\beta}T^2e^{-E/kT}-\frac{E}{k}. \tag{4}$$

Thus, the value of E can be determined from the behavior at low temperature and s then determined from the temperature T_G, where I passes through its maximum.

A representative glow curve for a crystal containing 0.05 percent of thallium (atomic percent of thallium relative to potassium), after being subjected to 50-kev x-radiation at 80°K is shown in Curve A of Fig. 1. The identification of the glow peaks with the thallium impurity can be made by comparison with a glow curve from a control crystal containing less than 3×10^{-7} Tl/K (Curve B, Fig. 1). The residual thermoluminescence may be presumed to be the result of lattice defects and/or F centers formed during irradiation. The heating rate was maintained at 0.22 deg/sec except over the high-temperature peak where an increase in rate was necessary to provide sufficient intensity. The thallium concentration in the crystals was measured by the radioactivity assaying technique[10] which in sensitivity and reliability is superior to spectrographic analysis. Similar results were obtained using the γ-radiation from a 3-millicurie Co^{60} source for the excitation and the single photon counting techniques developed previously for the detection of the luminescence.[8] The photomultiplier used was a cooled RCA 5819 tube. The use of the single photon technique made it possible to test and verify the assumption that saturation effects did not occur.

The absorption and emission spectra of the KI-TlI phosphor have been measured extensively; the correlation of these spectra with the various traps is thus of considerable interest. For these studies ultraviolet light from a monochromator having a 20A band width was used as the exciting agent. The thermoluminescent peaks, "*a*," "*b*," and "*c*," were again reproduced, although the peak intensities for which a saturation condition became evident were much lower than in the experiments using x- or γ-ray excitation. Sensitivity limitations of the recording equipment precluded the verification of Peak "*d*." The spectral dependence of the light-sum (i.e., integrated intensity across the peak) of each trap is shown in Fig. 2. The maximum response at 2310A for all three traps is consistent with the prominent spectral absorption peak at 2330A[11] and thus indicates that the excitation band is a common level for all subsequently trapped electrons. The reverse process, emission following the release of the trapped electrons, was also investigated. With the aid of a Hilger Raman spectrograph and Eastman 103-F emulsion the emission spectra of γ-ray-induced thermoluminescence

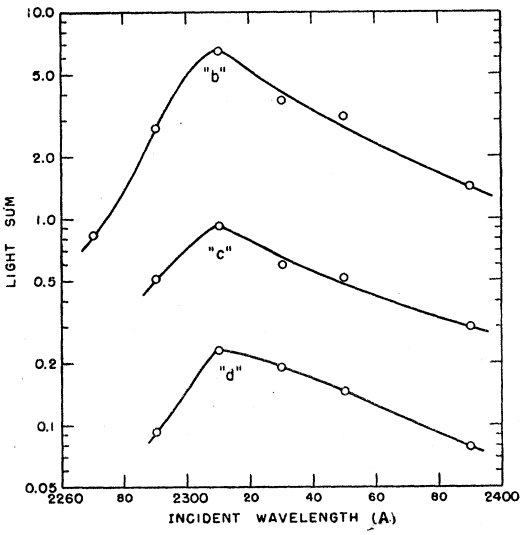

FIG. 2. Glow curve integrated intensity *vs* incident wavelength showing similar dependence of emission of glow peaks "*b*," "*c*," and "*d*" on wavelength of exciting radiation.

[10] Delbecq, Glendenin, and Yuster, Anal. Chem. **25**, 350 (1953).
[11] P. H. Yuster and C. J. Delbecq, Anal. Chem. **25**, 350 (1953).

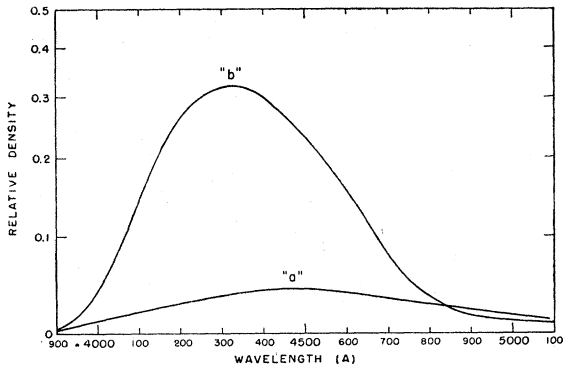

FIG. 3. Densitometer traces of the spectra of glow peaks "*a*" and "*b*" of KI-TlI excited by Co^{60} γ rays.

for the two most prominent peaks "*a*" and "*b*" were observed and are shown in Fig. 3. The other traps, too weak to record photographically, were observed with a pocket spectroscope and showed substantially the same response. The results are in good agreement with those previously reported on the luminescence of KI-TlI following excitation by ultraviolet light by Von Meyeren[12]

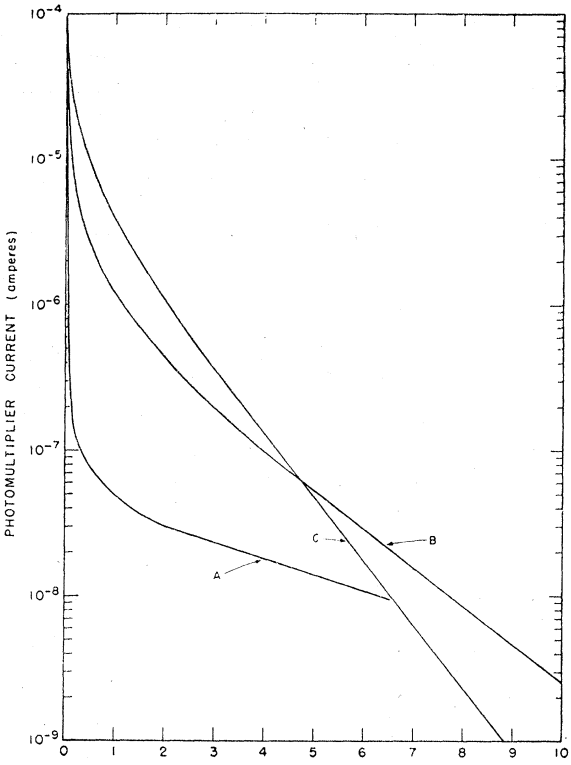

FIG. 4. Phosphorescence decay of KI-TlI for various temperatures.

Curve	T°C	Abscissa scale
A	−16	1 div = 180 min
B	+24	1 div = 300 sec
C	+58	1 div = 2.5 sec.

[12] W. Von Meyeren, Z. Physik **61**, 321 (1930).

and x-rays by Chatterjee.[13] The faint band reported at longer wavelengths by the latter may be related to the usual observation of a green-white emission during thermoluminescence too weak to record on the spectrograph. Thus, the evidence indicates that the photon absorption and emission process is identical for all participating electrons and is independent of the character of the trap.

C. PHOSPHORESCENT DECAY CURVES

A detailed study of the complete phosphorescence permitted the resolution of the composite electron-trapping system into a short-lived and long-lived set.

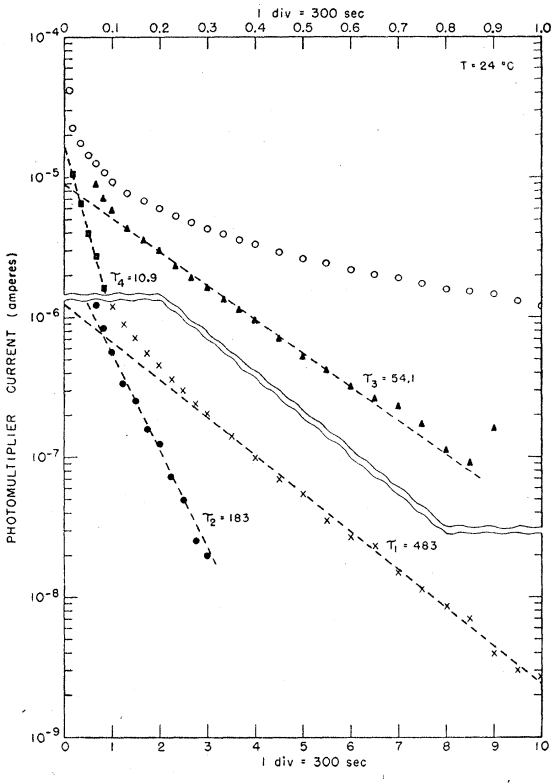

FIG. 5. Resolution of complex decay curve into exponential components.

The long-lived phosphorescence studies were conducted using a 390-curie Co^{60} gamma source as the exciting agent. The KI-TlI crystal, a 10-cc parallelepiped, was secured to the face of a 5819 photomultiplier tube and the excitation source lowered to a position near the opposite face of the crystal. After a given irradiation the source was removed, the photomultiplier high voltage applied and the photocurrent output connected through a direct current amplifier to a recording chart. The entire system was capable of being cooled to −20°C or heated to 100°C. The resultant phosphorescence for typical runs at various temperatures is shown in Fig. 4.

[13] A. Chatterjee, Indian J. Phys. **24**, 331 (1950).

The long stretches of logarithmic response with time indicated that the total response could be resolved into a sum of exponentials. This interpretation as a sum of monomolecular processes involving a set of independent trapping levels, rather than a (diffusion limited) higher order process, was verified by other criteria. A typical resolution into a set of exponentials is shown in Fig. 5 with the indicated decay times τ_i in seconds. From the dependence of the various τ_i's on temperature, as shown in Fig. 6, and using Eq. (2) the activation energy E and frequency factor s were derived. The results are shown in Table I. The traps were arbitrarily

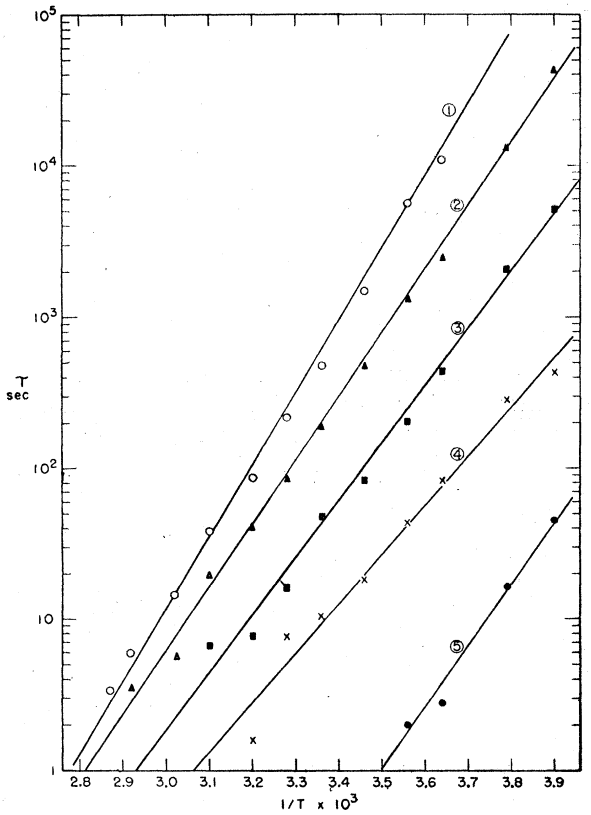

FIG. 6. Decay time *vs* temperature for KI-TlI.

designated 1 to 8 in decreasing decay time while the correspondence with the glow peak designation was derived from further evidence to be presented later. The data for the short-lived set were derived from more indirect investigations. Although the E and s can be determined from the glow curve [Eq. (4)], more reliable values can be secured from phosphorescent studies. Thus for Trap No. 6 the values of Bonanomi have been inserted; while for Trap No. 7, where other data are unavailable, the glow curve values have been used. For Trap No. 8, corresponding to the shortest decay time in KI-TlI of about 0.2 μsec, the values of E and s shown were determined from direct visual observation of the temperature dependence of pulse

TABLE I. Values of the frequency factor and activation energy derived from the temperature dependence of phosphorescence decay times (Fig. 5) and using Eq. (2), $\tau=s^{-1}e^{E/kT}$.

Set	Trap designation	Glow peak designation	Frequency factor $\log_{10}s$	Activation energy, E(ev)
Long-lived	1	*d*	12.81	0.92
	2	*d*	11.83	0.83
	3	*d*	11.25	0.76
	4	*d*	10.01	0.65
Short-lived	5	*c*	14.40	0.82
	6	*b*	12.41[a]	0.535[a]
	7	*a*	10.30[b]	0.26[b]
	8		7.91	0.065

[a] See reference 9.
[b] From glow curve data using Eq. (4).

decay. Substantiating evidence for the monomolecular nature of the electron-trapping process was revealed by the independence of the decay times on intensity or duration of excitation. Also, a recycling of the radiation showed that the phosphorescent intensity from each trap depended only on its own decay time and transitions between traps did not occur.

The distinction between long-lived and short-lived traps was based on the following empirical evidence. The frequency factor has, for chemical processes, been correlated with the entropy of activation, S. From Eyring's[14] Absolute Rate Theory, the decay time

$$\frac{1}{\tau}=\kappa\frac{kT}{h}\exp[\Delta S/R]\exp[-\Delta H/RT], \qquad (5)$$

where $\kappa\equiv$transmission coefficient for activation and $\Delta H=$heat of activation. Assigning a value of unity for κ and assuming, through lack of other evidence, that the zero point energies for metastable and excited states are equal, one can assign an entropy change for each trapping level. Thus for Trap No. 1 the given value of s corresponds to $\Delta S=0$ while for Traps Nos. 2, 3, and 4, $\Delta S<0$. Quantitative interpretation of these

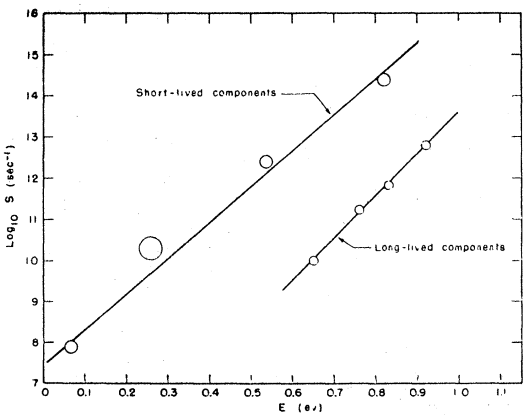

FIG. 7. Showing the separation of the traps of KI-TlI into two sets.

[14] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).

TABLE II. Concentration and cross section of various traps.

Trap number	Cross section $\times 10^{17}$ cm^2	Concentration $\times 10^{-13}$/cc		
		Phosphorescence	Glow data	
			γ ray	x-ray
1	1.8	1.1	$\Sigma=4.0$	$\Sigma=2.0$
2	1.7	1.8		
3	2.4	1.5		
4	1.0	1.0		
5	1.4	11.0	11[a]	11.0[a]
6	1.4[a]	114	785	380
7				171

[a] Indicates assumed value.

values must await a more complete theoretical presentation. Also of interest is the dependence of ΔS on the level depth. From Fig. 7 of log$s$ *vs* E there exists for Traps 1 to 4 and for Traps 5 to 8 an empirical linear relation between ΔS and E. On the basis of these data along with the evidence on the trap concentration and cross section one is led to the division of the trapping system into two sets.

D. TRAP CONCENTRATION AND CROSS SECTION

The rate of filling of the ith kind of trap can be expressed in terms of the concentration of filled traps n_i, its cross section σ_i, and the intensity of excitation I_r by

$$dn_i/dt=I_r\sigma_i(N_i-n_i)-(n_i/\tau_i), \tag{4}$$

where N_i is the concentration of empty traps at the onset of irradiation ($t=0$). It is assumed that I_r is sufficiently low to preclude any significant emptying of traps by the exciting flux. After a time t the number of electrons in the traps will be

$$n_i=I_r\sigma_i N_i\tau_i'[1-\exp(-t/\tau_i')], \tag{5}$$

where τ_i', defined by

$$1/\tau_i'\equiv[(1/\tau_i)+I_r\sigma_i], \tag{6}$$

is the excitation-induced time constant. If one neglects nonradiative transitions, upon removal of excitation the traps will empty with a resultant phosphorescence the intensity of which

$$I\equiv-\alpha dn_i/dt=\alpha n_i/\tau_i. \tag{7}$$

The constants N_i and σ_i can be independently determined from a set of two runs. Thus for the extreme cases of duration of excitation given by a $t=t_a\gg\tau_i'$,

$$I_a\equiv-\alpha(dn_i/dt)_{t=t_a}, \tag{8}$$

and a $t=t_b\ll\tau_i'$,

$$I_b\equiv-\alpha(dn_i/dt)_{t=t_b}. \tag{9}$$

Having defined

$$I_i\equiv I_r[(I_b/I_a)-(t_b/\tau_i)]^{-1}, \tag{10}$$

one can solve for

$$\sigma_i=1/I_i t_b, \tag{11}$$

$$N_i=(I_b/I_r)(I_i\tau_i/\alpha). \tag{12}$$

The cross section could thus be determined from a knowledge of only the excitation flux. It was assumed that the gamma radiation absorbed was converted to a secondary electron flux with an efficiency corresponding to 30 ev per secondary. To determine the trap concentration requires a knowledge of the light geometry and photomultiplier conversion efficiency. The gamma-ray intensity corresponded to an $(I_r\sigma_i)^{-1}=20$ seconds for the long-lived traps, and thus the values of t_b and t_a used were three seconds and 60 seconds, respectively.

The results are shown in Table II. While the absolute values for σ_i and N_i may be in error by as much as 100 percent, the relative values indicate the interrelationships among the various traps. The results are the mean over the temperature range encountered and for Traps 1 to 4 were substantially independent of temperature. One must then assume that nonradiative transitions, involving a different temperature dependence, apparently play no important role. For Trap No. 5 the results were too meager to verify this assumption.

The approximate equality of the N and σ values for the long-lived traps implies that the *a priori* probability for electrons to fall in any given traps is the same for each of the four traps, if nonradiative processes can be neglected. An equivalent statement to $N\sigma=$ constant is that $I_0\tau=$ constant, where I_0 is the initial intensity of luminescence from a trap of cross section σ, and the decay time τ is assumed much longer than the radiation time. In addition to the long-lived set of traps in KI-TlI, a corresponding analysis of the complex decay of thallium activated potassium chloride[15] yields three components having equal $I_0\tau$ values. These long-lived traps thus appear to form a unique set of levels the concentration of which, however, is considerably less than that of the thallium impurity.

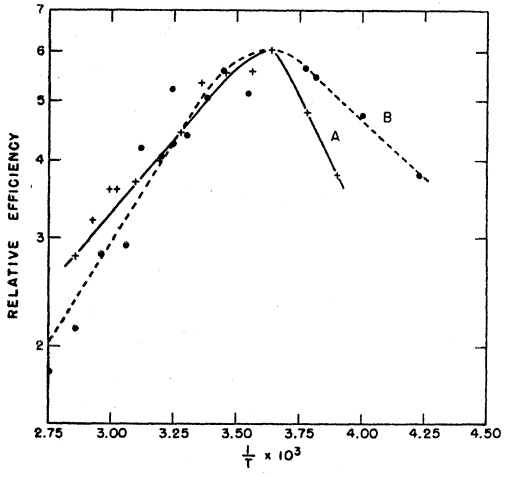

FIG. 8. Temperature dependence of phosphor efficiency.

[15] From decay curves reported by E. H. Hutten and P. Pringsheim, J. Chem. Phys. **16**, 241 (1948).

In a study of the trapping states of KCl-Tl, Johnson and Williams[16] report a low ratio of trap-to-impurity concentration and propose an excitation process in which competition between trapping and de-excitation of traps by the incident radiation accounts for the observed low value of trap concentration.

The characteristics for the short-lived traps can also be evaluated from the intensity of phosphorescence during excitation. For a single (or in our case, very prominent) trap after a time $t \gg \tau_i$ and for $1/\tau_i \gg I_r\sigma_i$ the conditions of dynamic equilibrium yield an emptying rate

$$dn_i/dt = I_r\sigma_i N_i. \quad (13)$$

Assuming the entire process is that of phosphorescence and assuming a value of σ_i as indicated, N_i can be computed. For the short-lived traps, however, dissipative processes cannot be ignored as indicated by the dependence of phosphorescent intensity on temperature. Curve A of Fig. 8 shows the gross phosphorescence during excitation, which may be attributed mainly to Trap No. 6 while in Curve B of Fig. 8 the results are shown for the very short-lived Trap No. 8. A comparison of the relative efficiencies (or $N_i\sigma_i$) of the various traps can be made with the glow-curve results of the light sum. Since only the product $N_i\sigma_i$ can be assigned to each trap, where σ_i could not be directly determined the assumption that $\sigma_i = 1.4\times10^{-17}$ cm^2 was made and the relative number N_i calculated. Thus from the γ-ray glow data, peak "c" corresponding to Trap No. 5 was used as a fiducial value and the values of N_i computed for the composite peak "d" (Traps 1 to 4) and peak "b." A similar assumption was made for the x-ray glow data. Since peak "d" consisting of Traps 1 to 4 remains unresolved, the total N_i for all four traps is indicated.

A check on the consistency of the values derived from the phosphorescence experiments may be made by using these values to compute a theoretical glow curve using Eq. (3) for the contribution to the total intensity from each trap. Comparison between the experimental glow curve of Curve A, Fig. 1 with a computed glow curve for peaks "b," "c," and "d," using the phosphorescent values for E, s, N, and σ, given in Tables I and II, is shown in Fig. 9. Since the dependence of σ on T is not well known, the agreement between results can be considered adequate.

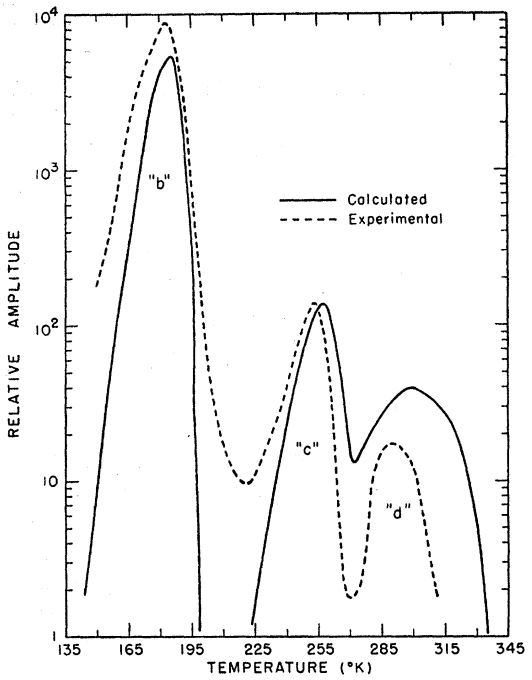

FIG. 9. Comparison of calculated and experimental glow curves for KI-TII. $\beta = 0.22$ deg/sec^{-1} (normalized at "c" peak).

ACKNOWLEDGMENTS

We are greatly indebted to P. H. Yuster for his invaluable cooperation in much of the thermoluminescence work. The spectrographic results were achieved through the assistance of J. K. Brody.

[16] P. D. Johnson and F. E. Williams, J. Chem. Phys. **21**, 125 (1953).