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The Long-Lived Phosphorescent Components of Thallium-Activated Sodium Iodide

C. R. Emigh and L. R. Megill*
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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Using a cobalt-60 source as a means of primary irradiation, the long-lived phosphorescent decay of thallium-activated sodium iodide crystal has been studied at several crystal temperatures. The results have been interpreted assuming that the different trap levels act independently of each other and that each trap decays according to the monomolecular process. Values for the experimental trap depths and vibrational frequency factors are given.

INTRODUCTION

The monomolecular theory generally has been accepted as that which accounts for the extremely long-lived phosphorescent decay of the heavy-metal activated alkali halides.[1,2] As these crystals usually have a complex decay scheme, a thorough investigation of the decay characteristics must be made to substantiate convincingly the presence of the monomolecular decay process for the different trap levels. This decay is characteristic of a phosphor which shows no photoconductivity. Therefore, the luminescence may be thought of as being produced as a result of excitation and subsequent delayed optical emission arising from the transition characteristics of the heavy activator. In thallium-activated sodium iodide, which is assumed to be an ionic crystal, the emission spectrum will be that of the thallium ion which is substituted in dilute concentrations for the sodium ion in the lattice structure.[3]

The results of experiments[4–6] on the thermoluminescence of KI(Tl) and NaI(Tl) crystals indicate that these alkali halides probably have many traps which take part in the decay. These traps are considered to be in the neighborhood of the thallium ions; consequently the electrons, on escaping, are captured by the same luminescent centers from which they were originally emitted.[7]

The decay curves necessarily will be complex because of the many traps. If the primary decay process were of a bimolecular nature, the procedure for finding the components due to various traps by an analysis of the decay characteristics would be indeed most difficult, if not impossible. However, the monomolecular process for the different traps gives a mixture of exponential decay components. Therefore, the phosphorescent decay is subject to simple analysis by a "peel-off" of these components. It might be argued that any monotonically decreasing curve can be represented by a superposition of exponential components. This of course is true. However, if the initial intensities of the exponential components are varied relative to each other and if all the resulting decay curves can be resolved into terms with a consistent set of mean lives for the exponential components, then considerable support is given to the exponential decay hypothesis. Furthermore, if the initial intensities of the different traps behave in a manner consistent with a simple exponential theory in their relationship to the exposure times, then added support is obtained. The initial intensities may be varied relative to each other by varying the irradiation time of the crystal. This effect will be made clear by the experimental results which are explained in a later section.

THE MONOMOLECULAR THEORY

The monomolecular theory for phosphorescence decay is reviewed here to bring out some of the underlying assumptions which are made in its development. As retrapping and radiationless transitions between traps are to be considered negligible, each trapping process will act independently of all the other traps. For each trap level the decay process can be considered identical and the following remarks will apply to all the trap levels.

We need not go into detail about the nature of the traps themselves or about their relationships with the lattice structure. It is assumed that the trap exists, that a transitional state through which a trapped electron must pass to reach an excited state of the luminescent center exists, and that in order to free an electron from a trap an energy of activation is required to raise the trapped electron to the transitional state. Whether or not this transitional state is a localized conduction band has no effect, as the entire process is assumed to occur in the region of the luminescent center. After making these simplifying assumptions, the absolute rate theory[8] can be applied. Therefore, the specific reaction rate k_i is

$$k_i = s_i e^{-\epsilon_i/kT}. \qquad (1)$$

In this expression, s_i is the frequency factor for transi-

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* Now at the University of Colorado, Boulder, Colorado.

[1] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 347 (1945).

[2] F. Seitz, J. Chem. Phys. 6, 150 (1938).

[3] J. E. Mayer, J. Chem. Phys. 1, 270, 327 (1933).

[4] B. Smaller and E. Avery, Phys. Rev. 85, 766 (1952).

[5] Smaller, May, and Freedman, Phys. Rev. 79, 94 (1950).

[6] J. Bonanomi and J. Rossel, Helv. Phys. Acta 24, 310 (1951).

[7] F. Seitz, in *Preparation and Characteristics of Solid Luminescent Materials* (Cornell Symposium of the American Physical Society, John Wiley and Sons, Inc., New York, 1948), Paper 1, p. 14.

[8] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

tions from the trap, or the metastable state, to the emitting state and ϵ_i is the experimental trap depth.

Under the condition of constant irradiation, the buildup of electrons in a given trap can be expressed approximately by the differential equation

$$dn_3/dt = -k_1n_3 - k_2n_3 + B_3n_1, \tag{2}$$

where n_3 represents the number of electrons in the metastable state at a given time t_0, B_3n_1 is the number of electrons raised into the metastable state per unit time, k_1 is the specific reaction rate for the radiationless transition to the normal state, and k_2 is the specific reaction rate for the transition to the emitting state (Fig. 1). This equation is based on n_3 being at all times much smaller than the total number of unfilled traps.

The buildup of electrons in the emitting state can be expressed approximately by the differential equation

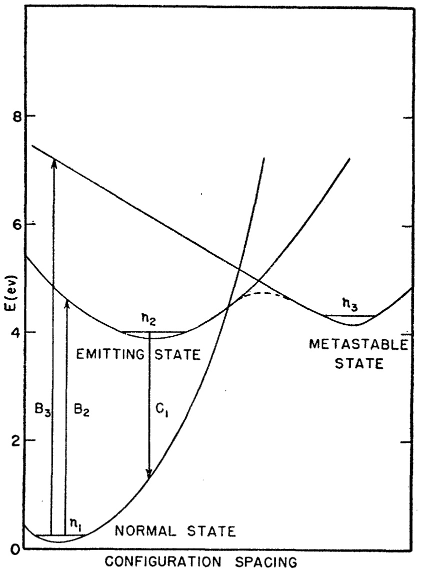

FIG. 1. Configurational coordinate diagram for NaI(Tl).

$$dn_2/dt = -C_1n_2 + B_2n_1 + \mu_1k_1n_3 + (1-\mu_2)k_2n_3, \tag{3}$$

where n_2 is the number of electrons in the emitting state at the time t_0, B_2n_1 is the number of electrons raised into the emitting state per unit time, μ_1 is the fraction of trapped electrons which go over the nonradiative barrier into the normal state but are captured by the emitting state before losing their energy by elastic waves, μ_2 is the fraction of trapped electrons which go over the barrier into the emitting state and are captured immediately by radiationless transitions into the normal state, and C_1 is the optical transition rate from the emitting state to the ground state.

As the measured phosphorescent intensity is assumed proportional to the optical transition rate, the buildup intensity due to one given trap at a given exposure time, t_0, in terms of the solutions to Eqs. (2) and (3) is

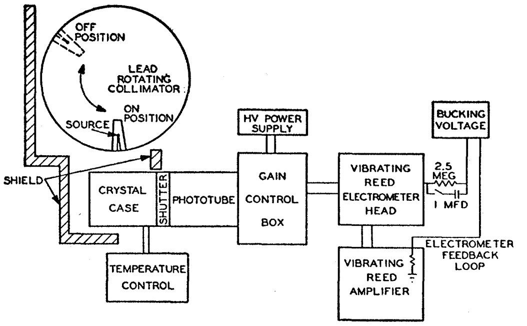

FIG. 2. Schematic diagram of experimental setup.

$$I_0(t_0) = DC_1n_2(t_0)$$
$$= DB_3n_1\frac{\mu_1k_1 + (1-\mu_2)k_2}{k_1+k_2}(1-e^{-(k_1+k_2)t_0}), \tag{4}$$

where D is a constant relating the observed intensity to the electron transition rate from the emitting state to the normal state. When the crystal exposure is terminated, the phosphorescent intensity due to each trap will fall off exponentially from the initial intensity $I_0(t_0)$ and can be expressed approximately by

$$I(t) = I_0(t_0)e^{-(k_1+k_2)t}. \tag{5}$$

The irradiation time is given by t_0 while the time of decay after cessation of irradiation is given by t.

It is the primary purpose of this experiment to analyze decay curves obtained from various irradiation exposure times, t_0, into a series of terms of the type given by Eq. (5), then to apply the experimentally determined mean lives and initial intensities for the different traps to equations of type (4) to show the internal consistency of these experimentally determined constants.

EXPERIMENTAL SETUP

A thallium-activated sodium iodide crystal was obtained from the Larco Nuclear Instrument Company for this experiment. The crystal has a thallium-activator concentration of 0.20 percent by weight. It has a square

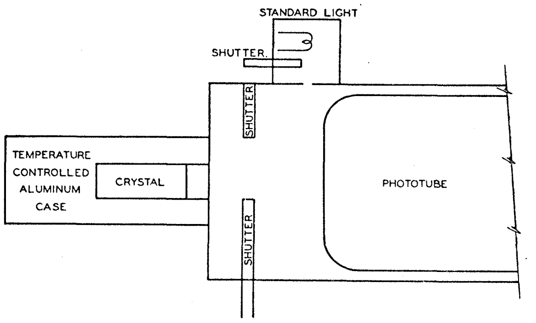

FIG. 3. Detailed schematic diagram of the crystal container.

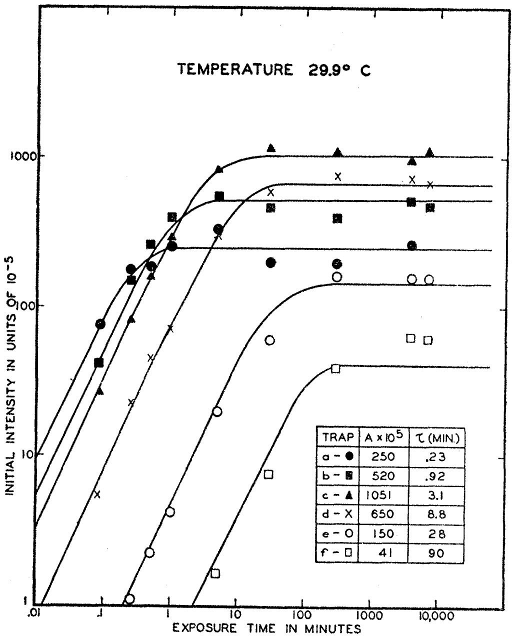

FIG. 4. Experimental equilibrium intensity curves for NaI(Tl) at a temperature of 29.9°C.

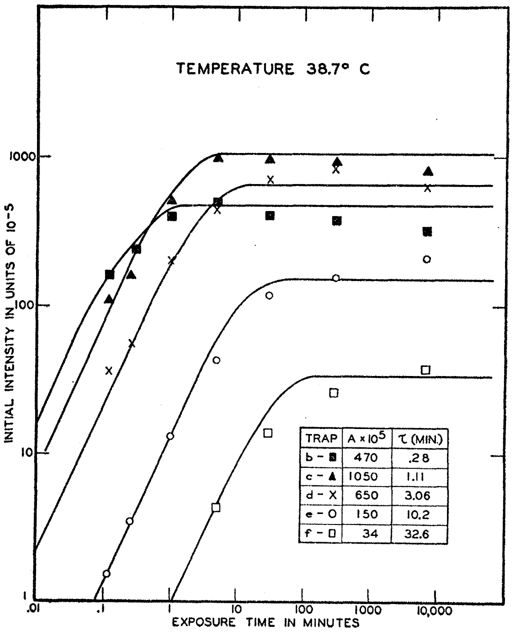

FIG. 5. Experimental equilibrium intensity curves for NaI(Tl) at a temperature of 38.7°C.

cross section of 2.5 cm on a side and is 1 cm thick. The temperature of the crystal was controlled throughout the experiment to ±0.03°C.

A cobalt-60 source was used to irradiate the crystal. The source is kept in a collimator which can be rotated into position for irradiation of the crystal (Fig. 2). The collimator is 7 cm long and has a 1.25-cm aperture. The crystal was placed 28 cm from the source and was oriented so that the radiation was incident normally on the larger surface. The time required to direct the radiation onto or off the crystal was less than 0.1 second, allowing the time of irradiation to be determined to this degree of accuracy.

A 5819 photomultiplier was used to detect the light from the crystal. The signal from the photomultiplier was fed into a vibrating reed electrometer used as a current measuring device. The circuit used is discussed in greater detail elsewhere in regard to another application.[9] The electrometer operates a recording millivoltmeter so that data may be obtained automatically.

The gain of the system was checked occasionally by use of a standard light. The dark current from the photomultiplier was measured periodically by closing a modified camera lens shutter between the crystal and the photomultiplier (Fig. 3). The background from the crystal due to extraneous radiation—cosmic rays and scattered radiation from the cobalt-60 source—was determined before a run was made. The value of this background remains quite constant. The data are corrected for small variations in gain, dark current, and background before analysis. The accuracy of the corrected data is somewhat better than 3 percent except at signals which are of the same order of magnitude as the background and dark current.

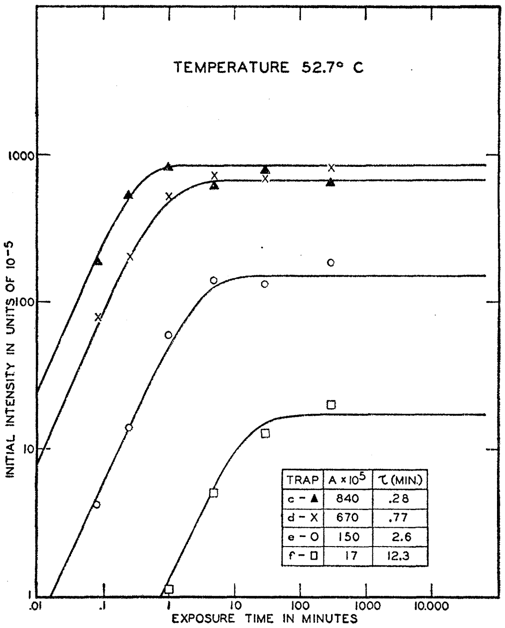

FIG. 6. Experimental equilibrium intensity curves for NaI(Tl) at a temperature of 52.7°C.

RESULTS

The phosphorescent decay data for a given temperature and for various exposure times were analyzed by

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[9] C. R. Emigh and L. R. Megill, Non-Destructive Testing **11**, No. 3, 30 (1953).

the exponential "peel-off" procedure into a series of terms of the type given by Eq. (5). A set of values for the initial intensities and mean lives of the various traps involved are obtained by a preliminary peel-off cut through the data. This entire analyzing procedure is repeated in a slightly different manner. Before the constants for each trap are determined, the exponential term which represents the next shallower trap and which is obtained from the preliminary cut is subtracted out of the data. This results in a longer straight line on a log intensity *versus* time plot. Consequently, a somewhat better determination of the constants for each trap is obtained. Repetition of this procedure two or three times results in a set of values which do not change by successive cuts through the data.

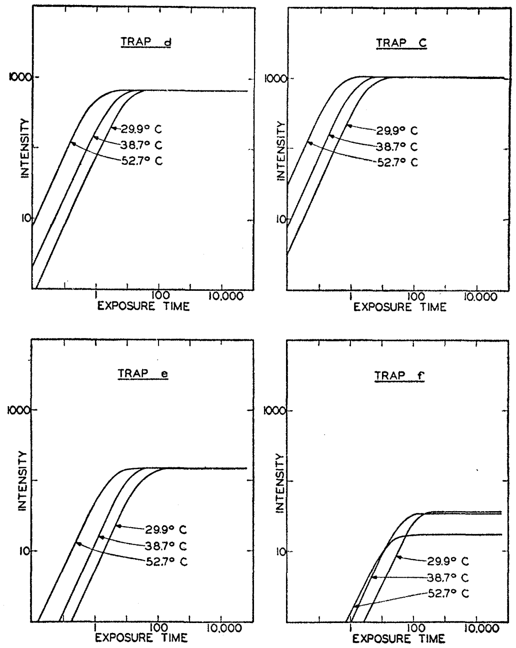

Fig. 7. Equilibrium intensity curves grouped as to trap designations.

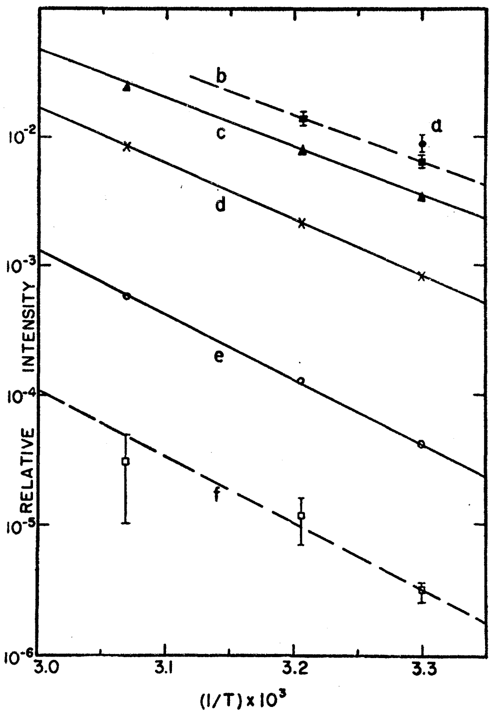

Fig. 8. Semilogarithmic plot of relative intensity *versus* reciprocal temperature.

The results of such analysis are shown in Figs. 4, 5, and 6 for crystal temperatures of 29.9°C, 38.7°C, and 52.7°C, respectively. Here, the initial intensities relative to the total intensity from the crystal during irradiation are plotted *versus* the irradiation exposure time. For each trap and at all three temperatures, the initial intensity levels off with increasing exposure times indicating an equilibrium between the rate of trapping electrons and the rate of losing electrons from each trap. The experimental mean lives τ's and the equilibrium intensities A's are given in the tables accompanying the figures. The τ's are the averaged values obtained for each trap by averaging the values of τ obtained at the various exposure times. The solid curves through the experimental points are obtained by using the experimentally determined τ's and the values of A which best fit all the experimental points in equations of the type given by Eq. (4), where τ is set equal to $1/(k_1+k_2)$, and the equilibrium intensity is set equal to

$$A=DB_3n_1\frac{\mu_1k_1+(1-\mu_2)k_2}{k_1+k_2}. \tag{6}$$

Figure 7 shows the equilibrium curves grouped as to trap designation for the traps *c*, *d*, *e*, and *f*. For traps *c*, *d*, and *e* the equilibrium intensities are temperature independent within the experimental error. It is felt that the same is probably true for the *a* and *b* traps although the experimental evidence is not conclusive. If indeed these equilibrium intensities are temperature independent, then the relation (6) implies that only one specific reaction rate is employed in the decay process for each trap. It is therefore assumed that radiationless transitions from either the emitting state or the metastable state directly to the ground state play a negligible role in the decay process at these temperatures. Therefore, the equilibrium intensity can be expressed by

$$A=DB_3n_1(1-\mu_2)=\text{constant}. \tag{7}$$

In the case of trap *f*, a temperature dependence in the equilibrium intensity is definitely indicated. This same temperature dependence also appears in the intensities for very small exposure times, which is, for exposure times much less than $1/k_2$,

$$I=DB_3n_1(1-\mu_2)k_2t_0. \tag{8}$$

TABLE I. Trap characteristics.

	Trap *a*	Trap *b*	Trap *c*	Trap *d*	Trap *e*	Trap *f*	Temp in °C
Mean lives in minutes	0.23	0.92	3.1	8.8	28	90	29.9
	···	0.28	1.11	3.06	10.2	32.6	38.7
	···	···	0.28	0.77	2.6	12.3	52.7
Trap depth in ev	···	0.7±0.2	0.75±0.05	0.88±0.05	1.00±0.05	1.1±0.2	···
Vibrational frequency	···	$(1\pm0.8)\times10^{10}$	$(2.2\pm1)\times10^{10}$	$(7.3\pm3)\times10^{11}$	$(2.2\pm1)\times10^{13}$	$(3\pm2)\times10^{14}$	···
Relative equilibrium amplitudes	1.7	3.5	7.0	4.3	1.00	0.27	29.9
	···	3.1	7.0	4.3	1.00	0.23	38.7
	···	···	5.6	4.5	1.00	0.11	52.7
$B_3n_1(1-\mu_2)$ (relative)	1.5	4.6	8.1	5.5	0.90	0.22	29.9
	···	3.6	6.8	5.0	1.00	0.22	38.7
	···	···	5.4	5.0	1.16	0.12	52.7

The conclusion is that either the coefficient μ_2 or B_3 is the temperature dependent parameter in Eq. (7) for this trap in this temperature range. It is more likely that μ_2 contains this temperature dependence rather than B_3, which is proportional to the capture cross section for a given trap.

From the decay data the experimental activation energy (trap depth, ϵ) can be calculated in two different ways. One, by using the experimental mean lives, the trap depth can be found from the slope of the $\ln\tau$ *versus* $1/T$ plot (see Eq. (1)]. Two, by using the equation for the intensity for very small exposure times, Eq. (8), the trap depth can be found from the slope of the $\ln I$ *versus* $1/T$ plot, suitable corrections being made for the temperature dependence of μ_2 in the case of the f trap. Of the two methods, the latter appears to give a more consistent set of results. This is probably because in the peel-off analysis the initial intensities are percentage-wise more accurately determined than the mean lives. Figure 8 is a plot of $\ln I$ *versus* $1/T$. The values of intensities which were used were obtained by extrapolating the linear portion of the intensity curves at low exposure times to the 1-minute exposure time. The values of the trap depths with an estimate of their probable errors are tabulated in Table I. Using these values for the trap depths, the values for the frequency factor s_i in Eq. (1) are calculated from the experimental τ's. These are also tabulated in Table I.

The experimental trap depths are in essential agreement with those values obtained by Smaller[5] in his experiment on KI(Tl). This is not surprising as the luminescent center consists of a thallium ion whose nearest neighbors are iodine ions for both the NaI(Tl) and KI(Tl) crystals. As the traps are probably formed by a displacement of the thallium ion with respect to an iodine neighbor,[10] the relatively distant Na or K ions will have little influence on the configurational potential relationships.

The *a priori* probability for electrons to fall into any given trap is generally considered to be constant, that is, $I\tau$ or I/k_1 is equal to a constant. From Eq. (8) this would imply that $DB_3n_1(1-\mu_2)$ be constant for all traps. The experimental values for $DB_3n_1(1-\mu_2)$ for the different traps calculated both from Eq. (8) and from the equilibrium intensity Eq. (7), are tabulated in Table I. Although all these values are of roughly the same order of magnitude, the variation implies that either the cross section for capture, which is proportional to B_3, or the cross-over coefficient μ_2 varies slightly with trap depth.

Because of the low intensity due to traps other than those which are herein reported, no consistent data were obtained for shorter or longer mean lives. However, definite indications of shorter mean lives were in evidence as well as mean lives of the order of several days.

Our interpretations of the results of this experiment indicate that the process is fundamentally a monomolecular one and that retrapping and radiationless transitions to the ground state are negligible, or at least, they do not change the process into one of a bimolecular nature.

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[10] F. E. Williams, in *Preparation and Characteristics of Solid Luminescent Materials* (Cornell Symposium of the American Physical Society, John Wiley and Sons, Inc., New York, 1948), Paper 20, pp. 338, 339.