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Analytical and experimental check of a model for correlated thermoluminescence and thermally stimulated conductivity

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We consider the simple trapped-carrier–free-carrier recombination model often used to describe thermoluminescence (TL) and thermally activated current (TAC) experiments. Both TL and TAC and thermogram shapes depend sensitively on parameter values in the model and general solutions for them have not been derived. We show, however, that one can derive a correlation expression for TL and TAC signals. This correlation expression is exact and can be studied experimentally to check the validity of the model. Experiments in LiF demonstrate, for two pairs of correlated TL/TAC peaks, that the model fails to describe adequately the experimental results. We present arguments that the actual system probably possesses significant spatial correlation between trapped carriers and optically active recombination centers.

I. INTRODUCTION

When an insulating material is exposed to ionizing radiation, some of the charge carriers (electrons and holes) liberated by the radiation will, instead of returning immediately to their ground state, be captured at trapping sites where they are immobile. If the temperature is maintained at a sufficiently low value, the carriers will remain essentially immobile.

When the temperature rises, however, these trapped charge carriers are thermally mobilized and may diffuse some distance through the material before returning to their ground state, possibly with the emission of light to yield thermoluminescence (TL). Under the proper experimental conditions, one may also observe a transient thermally activated current (TAC). Other investigators[1–8] have studied this effect and have called it thermally stimulated conductivity (TSC). Unfortunately, this term TSC often causes confusion as it has been used by investigators of electret-state depolarization[9–11] to signify "thermostimulated current." Also, it is possible that the externally measured current might be a polarization displacement rather than a conductive thruput current in the sample.

We see that TL and TAC are closely related phenomena. The relationships between correlated TL and TAC have been studied experimentally and theoretically by Bohm and Scharmann[1–3] while theoretical work has been done by Kelly and Braunlich,[6] Braunlich and Kelly,[7] and Kelly, Laubitz, and Braunlich.[8] Other studies by Zimmerman[12] have focused on similar correlations between TL and the related thermally stimulated exoelectron emission (TSEE) effect.

In describing these effects, the system is modeled by a set of kinetic equations describing population dynamics of trapped charge carriers and released mobile carriers. Kelly *et al.*[8] have considered one simple model and obtained exact solutions by numerical methods. Their results show that the approximation normally used to solve the equations and analyze experimental data for trapping parameters can easily become highly invalid and give very erroneous results. They conclude that isolated measurements of thermally activated processes are virtually useless for obtaining trap parameters.

This conclusion leaves open the question of whether the model itself offers a reasonably good description of actual TL/TAC systems. Analysis of experimental data by Bohm and Scharmann, based upon approximate solutions to model equations, shows that simultaneous TAC and TL measurements do not correlate as predicted. In view of the work by Kelly and Braunlich,[6–8] however, this may easily result from invalidity of the assumptions made in obtaining the approximate solutions.

Our interest is in the correlation between TAC and TL in thermally-isolated-carrier-release peaks. We wish to determine if the normally used model is at all satisfactory, quite apart from our ability to generate exact solutions to the model equations. We have found that the model equations yield directly a simple analytic expression for the correlation between TAC and TL curves. No approximate solution is necessary. One can therefore experimentally examine the extent to which the model is appropriate in describing the system's behavior.

We shall first develop the theory for TL/TAC correlations appropriate to this simple model. A

description of our experiments on two pairs of well-resolved correlated TL/TAC peaks is next given, followed by a discussion of the application of model predictions to the experimental data.

II. THEORY

We shall use the notation introduced by Kelly, Laubitz, and Braunlich.[8] Considering a single isolated TL/TAC "glow peak," let n_c be the density of mobile charge carriers and n be the density of trapped charge carriers associated with the particular glow peak of interest. We let $f = n_c + n$ be the net density of charge carriers associated with the glow peak of interest, M be the density of deep traps associated with thermally disconnected peaks having higher activation energies, N be the net trap density associated with the peak of interest, p be the temperature-dependent rate associated with carrier release from traps, where E is the activation energy and T is temperature, and p_0 is temperature independent ($p = p_0 e^{-E/kT}$). p_0 is the temperature- and time-independent capture coefficient of an empty trap for a free-charge carrier, γ the temperature- and time-independent capture coefficient of a recombination center for a free-charge carrier, μ the charge mobility, and η the optical-efficiency factor relating luminescence output to recombination rate.

By "thermally disconnected" we refer to all higher-temperature peaks whose detrapping rate is negligibly small at the temperature attained during the readout of the isolated peak under consideration. In our model the decay of trapped carriers is governed by the equation

$$\partial_t n = -pn + \beta n_c (N - n), \tag{1}$$

while the density of charge carriers diminishes according to

$$\partial_t (n + n_c) = \partial_t f = -\gamma n_c (n + n_c + M) \tag{2a}$$

or

$$\partial_t f = -\gamma n_c (f + M). \tag{2b}$$

The next model assumption is that the magnitudes of the TAC (σ) and TL (φ) as functions of time and of temperature may be expressed by

$$\sigma = \mu e n_c, \tag{3}$$

$$\varphi = -\eta \partial_t f, \tag{4}$$

where μ is the carrier mobility and η is the probability that the decay of a free-charge carrier results in the emission of a photon.

Equations (1) and (2) have been solved numerically for special cases by Kelly, Laubitz, and Braunlich.[8] Their calculations demonstrate that (a) the location of TL and TAC peaks is a function of p_0, E, M, N, and f; (b) the shape of TL and TAC peaks is determined chiefly by β/γ, M, and N; (c) the TL magnitude depends on N, f, M (weakly), and η; and (d) the TAC magnitude is a function of γ, M, N, f, and μ. M and N are not independent. They conclude that the only quantity one may in general hope to determine uniquely using only TL/TAC data is the activation energy E.

We are interested here in determining what conclusions may be drawn from quantitative TL/TAC correlations where both effects are simultaneously monitored. In our approach to the above model we need use only Eqs. (2)–(4). Combining these equations leads directly to the relation

$$\sigma = (e\mu/\eta\gamma)[\varphi/(M + f)]. \tag{5}$$

In the simple model, the quantities e, μ, η, and γ are temperature independent; thus, if we take the temperature derivative of Eq. (5) and evaluate at the TAC peak $T_{max}(\mathrm{TAC})$, where $\partial_t \sigma = 0$, we have

$$0 = \left(\partial_t \varphi - \frac{\varphi \partial_t f}{M + f}\right)\Bigg|_{T = T_{max}(\mathrm{TAC})}. \tag{6}$$

Using the facts that $\partial_t f < 0$ always and $(M + f) > 0$, one sees from Eq. (6) that

$$\partial_t \varphi < 0 \quad [T = T_{max}(\mathrm{TAC})]. \tag{7}$$

This expression indicates that the TL is decreasing at the TAC peak; i.e., that the TAC peak is at a higher temperature than the TL peak. Substituting Eq. (2) into Eq. (6), we have the relation

$$\frac{\partial_t \varphi}{\varphi} = -\gamma n_c \quad [T = T_{max}(\mathrm{TAC})]. \tag{8}$$

These same conclusions may be reached by evaluating Eq. (5) at the TL peak temperature.

We need not assume above that the quantities γ and μ are individually temperature independent; indeed, it is sufficient for our purposes in deriving Eqs. (6)–(8) that the ratio μ/γ is not a function of temperature. This is certainly true if we assume a single-charged-particle recombination picture. We compute the time rate of decrease of f, the recombination center density for the isolated peak due to the current of free carriers, n_c, which diffuse to within a distance R from the recombination center. Designating $E(R)$ the electric field at the effective recombination radius R, and taking $(M + f)$ as the density of recombination centers, we have

$$\partial_t f = -(f + M)\mu E(R) n_c 4\pi R^2. \tag{9}$$

This is physically just the "recombination current" which, from Eq. (2), is equal to $[-\gamma n_c (f + M)]$. Consequently,

$$\gamma = \mu E(R) 4\pi R^2, \tag{10}$$

and by substituting $E = q/R^2$, where q is the effec-

tive recombination center charge, we find

$$\gamma/\mu = 4\pi q . \tag{11}$$

Thus the ratio (γ/μ) depends only upon the recombination-center effective charge q, which must be temperature independent for Eq. (8) to be valid.

We can extract still more useful results from these equations. Integrating Eq. (4) over time from an initial time 0, to a measurement time t, we have

$$\int_0^t (\varphi/\eta)\, dt' = -\int_0^t (\partial_t f)\, dt' = f_0 - f , \tag{12}$$

where f_0 is the value of f prior to initiating readout. Solving Eq. (5) for f and substituting the result into Eq. (12) gives us

$$\int_0^t \varphi dt'/\eta = M_0 - (e\mu/\eta\gamma)(\varphi/\sigma) , \tag{13}$$

where $M_0 = M + f_0$; this is the initial net concentration of recombination centers. We now accept the usual model assumption that η is temperature and time independent, which allows us to factor it from the integral. In contrast to the expressions in Eqs. (6)–(8), however, we may allow $(e\mu/\gamma)$ to be temperature dependent. Using the recombination-center effective-charge expression in Eq. (11), we find

$$\int_0^t \varphi(T)\, dt' = \eta M_0 - (e/4\pi q)[\varphi(T)/\sigma(T)] . \tag{14}$$

Equation (14) gives the final form of the correlation expression relating the integrated TL at any time to the ratio of TL and TAC signals at that time. We have made no approximations other than those embodied in the detrapping-diffusion-recombination mode. Equation (14) allows us to relate experimental data to the parameters ηM_0 and $(4\pi q/e)$. We see that it is independent of detrapping rate $W(T)$, concentration of filled traps (n) and unfilled traps (N_0), and retrapping cross section (β).

Another useful relation, which allows us to evaluate the effective recombination-center charge, is obtained by combining Eqs. (2b), (8), and (11):

$$(q/e) = -(\partial_t \varphi/\varphi)(1/4\pi\sigma) \quad [T = T_{max}(\mathrm{TAC})] . \tag{15}$$

III. EXPERIMENTAL

These preliminary experiments were designed to test the validity of Eq. (14) as a check of the usefulness of the simple model we have described. Our apparatus is similar to that used by Podgorsak *et al.*,[13] with the addition of sample-contact electrodes to permit measurement of TAC. A more detailed description is provided elsewhere.[14] We used a single-crystal sample of commercial lithium fluoride dosimetric material, *TLD*-100, purchased from the Harshaw Chemical Co. The dominant dopants in this material are divalent ions, particularly the alkaline earths, together with some aluminum and titanium activators.

The LiF system was chosen for these studies due to its having been well studied; Bohm and Scharmann[2,3] were able to derive a theoretical fit to TL/TAC shapes for a pair of correlated peaks observed at 140 °K based upon approximate phenomenological solutions.

The sample was a chip roughly 1 cm^2 in area and 0.1 cm thick. Immediately prior to irradiation, the sample was heated to 700 °K and cooled rapidly to approximately 80 °K. The sample was then irradiated with 2-mm-Al-filtered x rays from a molybdenum-target x-ray tube operated at 75 kV and 50 mA. Typical irradiation levels in these experiments were in the range of 10^3 rad. A voltage source and a Keithley 610C electrometer were connected in series to the sample electrodes. We could attain more than adequate signal-to-noise ratios with 30 V applied to the sample and with the system heated at a roughly constant rate of approximately 0.5 °K/sec. The sample temperature was monitored by a thermocouple hard soldered to the copper sample block. This sample block served as a mounting point for the sample, thermocouple, and heater, and was also the common electrode for TAC experiments. Sample current and light output, which was monitored by a photomultiplier, were plotted simultaneously as functions of temperature using two X-Y plotters. Synchronous timing marks were recorded along with the data on each recorder to allow accurate superposition of TL and TAC data.

Among the recorded data were two sets of quite well-resolved correlated TL/TAC peaks. The first, with a peak temperature around 160 °K, is shown in Fig. 1. Using the relation[15]

$$E/kT_m \approx \ln W_0(\partial_t T/T)^{-1} , \tag{16}$$

one may show that this peak is the same as that seen by Bohm and Scharmann[2,3] at 140 °K at a heating rate of 0.05 °K sec^{-1} and by Podgorsak *et al.*,[13] at 150 °K. The TL/TAC signals were well above noise from 135 to about 185 °K. The second TL/TAC set studied is shown in Fig. 2; this set has a peaking temperature at about 270 °K. We discuss first the behavior of the 160 °K peaks. We note that the temperature shift of TAC to higher temperature than TL, as predicted in Eq. (7), is very pronounced in Fig. 1. From our measured values at the TAC peak, $\sigma = 2.3\times10^{-4}$ sec^{-1} (cgs units) and $(\partial_t\varphi/\varphi) = -2.9\times10^{-2}$ sec^{-1}, we use Eq. (15) to calculate the ratio of recombination-center effective charge to electronic charge. This yields the value $(q/e) \simeq 10$.

To study the full correlation expression of Eq. (14), the data sets were digitized manually as presented in Figs. 1 and 2. A least-squares fit of each data set to Eq. (14) was made using a PDP-10 computer and a modified Householder linear-least-squares procedure.[16,17] ηM_0 was assumed constant,

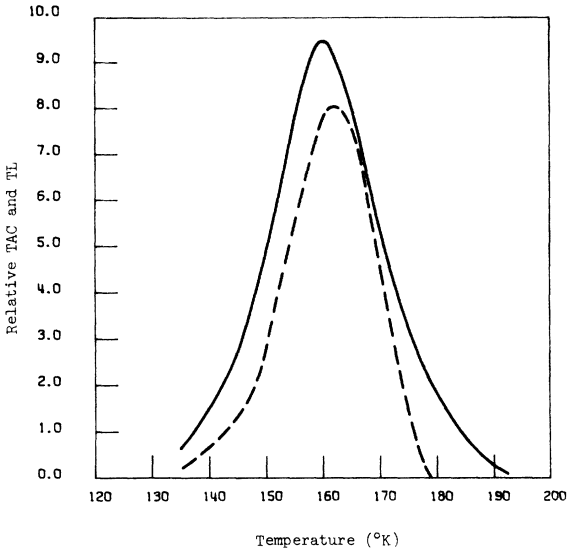

FIG. 1. Relative thermally activated conductivity (dotted line) and thermoluminescence (solid line) for 160 °K peaks in LiF (*TLD*-100).

whereas the factor $e/4\pi q$ was fit to a general third-order temperature function $a+bT+cT^2+dT^3$, where T represents temperature and the other variables were determined. From this procedure we obtained a value of $\eta M_0 = (0.89 \pm 1.0) \times 10^{13}$ cm^{-3} for the 160 °K feature. This value was then substituted back into Eq. (14) and the ratio $e/4\pi q$ was computed and plotted along with the TL signal in Fig. 3. An alternate specification of ηM_0 is obtained from the time interval of TL; by this process a value of $\eta M_0/\varphi_{max} = 300 \pm 60$ sec is obtained.

The charge ratio $(e/4\pi q)$ not only shows a large temperature variation, but even changes algebraic sign. This behavior is roughly indicated by the solid line in Fig. 3 for the 160 °K TAC/TL peaks. Obviously, these experimental results grossly disagree with the assumptions of the simple trapped-charge–free-charge recombination model which led to the correlation expression of Eq. (14). In particular, negative values of (q/e) are unphysical. In the initial rise region, from 135 to 155 °K, $(e/4\pi q)$ is reasonably constant at about $(3.3 \pm 0.5) \times 10^{-2}$, or $(q/e) \sim 4$. This value, considering the observed behavior, is in reasonable agreement with the value $(q/e) \sim 10$ obtained previously from Eq. (15).

The observed variation in and the negative going behavior of this ratio are experimentally real. The signal to noise is sufficiently high to ensure goos statistics; we have made no assumptions such as a single-trap "glow peak," and we have verified that the observed effects could not be due to departures from our assumed heating rate. The temperature dependence of q/e is qualitatively the same whether we perform our least-squares fit using a constant "average" heating rate or a rate that is a moderately strong function of temperature.

Our second pair of correlated peaks, shown in Fig. 2 was above the noise level from 225 °K through around 300 °K. When analyzed in a manner

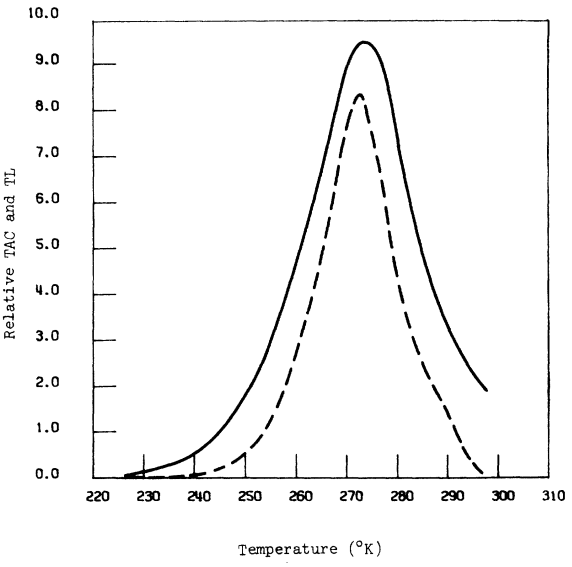

FIG. 2. Relative thermally activated conductivity (dotted line) and thermoluminescence (solid line) for 270 °K peaks in LiF (*TLD*-100).

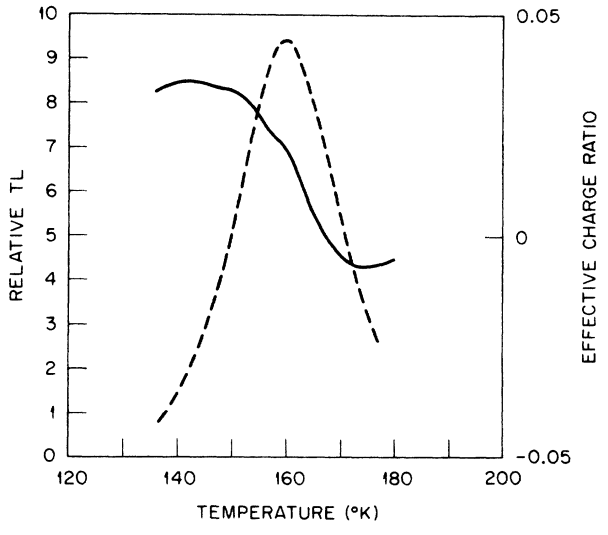

FIG. 3. Solid line shows the behavior of the effective-charge ratio $(e/4\pi q)$ for the 160 °K peaks from Eq. (14). The TL results (dashed line) are shown for comparison. The value of $(e/4\pi q)$ varies from a maximum of 0.0346 to a minimum of -0.0063 (dimensionless in cgs units).

identical to that described for the 160 °K peaks, the value $\eta M_0 = (3.4 \pm 2.4) \times 10^{13}$ cm^{-3} was found. The factor $e/4\pi q$ has an initial value 2.4 ± 0.5 and is plotted to show its variations along with TL in Fig. 4. This TL/TAC behavior exhibits an even greater departure from anticipated behavior than does the 160 °K peak. Equation (8) is not verified. The TL and TAC maxima lie at apparently the same temperature. The function representing $e/4\pi q$ obtained for this data set had an even larger negative (nonphysical) region than that for the 160 °K peak. It does, however, exhibit behavior rather similar to that of the 160 °K data set in having an initial "positive" portion followed by a negative going peak. Our leading-edge estimation of ηM_0 in this case yields a value $\eta M_0/\varphi_{max} = (1.0 \pm 0.6)\ 10^3$ sec.

A striking feature of the relative magnitudes of the TL and TAC effects at 160 and 270 °K is that, whereas the 270 °K TL feature was down from the 160 °K feature by more than an order of magnitude (an effect also observed by Podgorsak *et al.*[13]); the 270 °K TAC signal was up by two orders of magnitude from its 160 °K counterpart.

IV. DISCUSSION

For neither of the two LiF (*TLD*-100) TL/TAC structures analyzed in these experiments can we obtain correlation behavior between TL and TAC that has reasonable agreement with the expression in Eq. (14) for the simple model. Consequently, further discussion of the detailed numerical values derived would be of little value.

We note that our TL/TAC correlation expression, Eq. (14), rests only on Eq. (2b), which relates the time rate of change of the probability that a given recombination site remains active to the average free-carrier concentration, and Eq. (4), which relates the TL to the optical-recombination efficiency and the density of recombination centers associated with the peak of interest. In order to reconcile the simple model to our results, one might assume that the optical efficiency η is some complicated sharply breaking function of temperature. By such an assumption, one could always force the data to fit Eq. (14). On physical grounds, however, such a procedure is difficult to justify. We believe a consideration of the qualitative results gives an improved insight into the system's behavior.

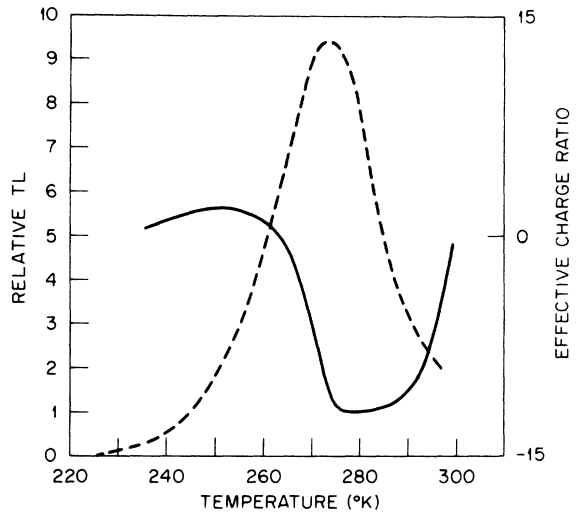

FIG. 4. Solid line shows the $(e/4\pi q)$ effective-charge ratio for the 270 °K peak. This ratio varies from a maximum of 2.4, through a minimum of -12.6. The TL (dashed line) behavior is shown for comparison.

First of all, the effective charge of a recombination center, q, in an insulating lattice would be expected to be an electronic charge divided by the material's dielectric constant. For LiF, $\epsilon = 9.0$; we therefore expect $(q/e) \sim 0.1$. This is, for example, a factor of 30–90 smaller than the values derived either from the leading slope TL/TAC correlation fit to Eq. (14) or from Eq. (15) for the 160 °K TL/TAC results. This suggests to us that the local concentration of carriers near optically active recombination (TL) centers may be much higher than the average bulk-carrier concentration, which is measured in the TAC experiment. We speculate, therefore, that, at least in this highly doped TL material, trapped carriers and associated TL recombination centers are spatially correlated to a substantial degree.

We also observed that the ratio of TL to TAC throughout the 270 °K feature is less than that ratio for the 160 °K feature; that is, a given charge carrier contributes relatively more to TL than TAC for the 160 °K peak but more to the TAC than to the TL for the 270 °K peak. We might expect this behavior from a system of spatially correlated trapped carriers and recombination centers in which those carriers trapped closest to the recombination centers have a lower activation energy and are therefore observed at a lower temperature than those carriers trapped further from recombination centers.

In the simple model earlier described, the TAC on the high-temperature side should fall relatively more slowly than the TL. The reason is that as recombination depletes the TL recombination centers, the detrapped carriers remain free a relatively longer time. Therefore, with respect to the TL output, they contribute relatively more to the TAC on the high-temperature than on the low-temperature side of the peaks. Experimentally, we find this behavior violated; the high-temperature TL does not decrease more rapidly than the TAC. As a result, we derive from Eq. (14) apparent

negative values for (q/e) on the high-temperature side of the measured peaks. On the other hand, if the TL-active recombination centers are spatially correlated with trapped carriers, then the high-temperature TL need not decrease more rapidly than the TAC tails. Such behavior is compatible with the experimental results.

V. SUMMARY

Our experimental results on correlated TL/TAC peaks in LiF are in striking disagreement with a TL/TAC correlation expression which can be derived exactly from the simple trapped carrier-free carrier-recombination model. We conclude that this model, which is the one normally used to describe TL and TAC measurements, does not provide an adequate description of the system's behavior. These experimental results complement the conclusions of Kelly, Laubitz, and Braunlich[8] that the approximations often used in analyzing correlated thermally activated data are theoretically unwarranted.

From the observed TL/TAC results, in contrast with the predicted TL/TAC correlation expression, we feel that the real system has substantial spatial correlation between trapped carriers and TL-active recombination centers. This could easily account for the discrepancies we observe between experiment and the theoretical expressions which are based upon the assumption of active recombination centers distributed randomly with respect to trapped charges.

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