Theory and Application of Thermally Stimulated Currents in Photoconductors

Rudolph R. Haering* and Edward N. Adams

Research Laboratory, International Business Machines Corporation, Poughkeepsie, New York

(Received July 30, 1959; revised manuscript received August 24, 1959)

The theory of thermally stimulated currents is investigated in the limits of slow and fast retrapping. A method of obtaining the ionization energy E of the relevant traps is discussed. This method depends on the shift of the conductivity maxima with heating rate and does not involve prior knowledge of the trapping cross sections or of the heating rate.

1. INTRODUCTION

THE problem of determining trap energies is of fundamental importance in the study of luminescence and of photoconductivity. For *luminescent materials*, a possible approach to this problem is a "glow curve" analysis. The phosphor is excited optically at a very low temperature and is then allowed to warm up in the dark at a uniform rate. The resulting curve of luminescent intensity *versus* temperature shows peaks characteristic of the trapping levels. The analysis of such thermoluminescent data is usually based on the original work of Randall and Wilkins,[1] which assumes that carriers which are thermally excited from the traps have a negligible chance of being retrapped. The energies of the trapping levels may be determined from the experimental data in a number of ways. The most widely used approach is that of Garlick and Gibson.[2] These authors observe that the *approach* (from the low-temperature side) to a glow curve maximum is of the form $L = \text{const} e^{E/kT}$, where L is the luminescent intensity and E is the ionization energy of the trap in question. A plot of $\ln L$ *versus* $1/kT$ thus yields E. This method has been criticized by Haake,[3] who points out that the relevant part of the glow curve is generally not observable because of the presence of nearby peaks or because of background noise. An alternate mode of analysis has been proposed by Grossweiner[4] who expresses E in terms of the peak temperature and the temperature at half maximum. Still another method, which employs the shift of the peak with heating rate, is due to Booth.[5]

Recently, Bube[6-11] has studied the energy levels of traps in *photoconductors* by similar techniques. Instead of the luminescent intensity, one measures in this case the thermally stimulated conductivity as a function of temperature. A plot of the conductivity *versus* temperature displays peaks similar to those observed in glow curves. Bube obtains the trap energy from the peak value of the conductivity. If the carrier mobility μ is known, the energy of the traps may be obtained from the peak conductivity $\sigma(T_m)$ and the peak temperature T_m through the relation:

$$E = kT_m \ln[N_c q\mu/\sigma(T_m)], \tag{1.1}$$

where N_c is the density of thermally available states in the conduction band and q is the electron charge.

In this paper we present a theory of thermally stimulated currents. Our theory is an extension of the work of Randall and Wilkins,[1] insofar that explicit solutions will be obtained in the limits of slow *and* of fast retrapping. In order to be specific, we shall refer throughout to conductivity, not luminescence maxima. However, it is clear that with minor modifications our remarks apply equally well to the latter case. In Sec. 2 we present a new method for obtaining trap energies. A critique of the various methods of determining trap energies is included in Sec. 3.

2. THEORY OF THERMALLY STIMULATED CURRENTS

For simplicity, we shall assume a single set of traps with energy E_i (see Fig. 1). These traps are partly filled with electrons by optical excitation at low temperature. During the subsequent heating in the dark, these electrons may be thermally excited to the conduction band. Once in the conduction band, an electron may be retrapped into the states at E_i or may recombine with a hole, either directly or via a recombination center. We assume that: (a) the rate of disappearance of electrons due to recombination may be described by a recombination lifetime τ; and (b) the electrons in the conduction band are nondegenerate, so that Pauli principle effects may be ignored.

* Permanent Address: Department of Physics, McMaster University, Hamilton, Ontario, Canada.

[1] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 366, 390 (1945).

[2] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) A60, 574 (1948).

[3] C. H. Haake, J. Opt. Soc. Am. 47, 649 (1957).

[4] L. I. Grossweiner, J. Appl. Phys. 24, 1306 (1953).

[5] A. H. Booth, Can. J. Chem. 32, 214 (1954).

[6] R. H. Bube, J. Chem. Phys. 23, 18 (1955).

[7] R. H. Bube, Phys. Rev. 99, 1105 (1955).

[8] R. H. Bube, Proc. Inst. Radio Engrs. 43, 1836 (1955).

[9] R. H. Bube, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge et al. (John Wiley and Sons, New York, 1956), pp. 575–590.

[10] R. H. Bube, Phys. Rev. 101, 1668 (1956).
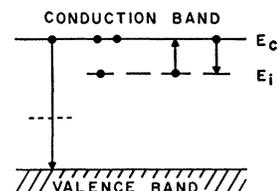
[11] R. H. Bube, Phys. Rev. 106, 703 (1957).

Fig. 1. Energy levels and transitions appropriate to Eqs. (2.1a) and (2.1b).

Under these conditions, we may write down the following rate equations:

$$\frac{dn_i}{dt} = -n_i N_c S v e^{-E/kT} + n_c(N_i - n_i)Sv, \quad (2.1a)$$

$$\frac{dn_c}{dt} = \frac{n_c}{\tau} - \frac{dn_i}{dt}. \quad (2.1b)$$

The notation is the following: N_i, N_c = concentration and effective concentration of trapping and conduction states, respectively, n_i, n_c = concentrations of electrons in traps and in the conduction band, S = cross section of a trap for an electron, v = thermal velocity of electrons in conduction band, $E = E_c - E_i$ (see Fig. 1), k = Boltzmann's constant, and T = temperature in °K. The resulting conductivity is:

$$\sigma = n_c q \mu. \quad (2.2)$$

The solution of Eqs. (2.1a) and (2.1b) is straightforward in the limits of slow and fast retrapping. We shall now investigate these limits.

Slow Retrapping [$(N_i - n_i)Sv \ll \tau^{-1}$]

In this case, every electron in the conduction band recombines with a hole, retrapping being negligible. If it is assumed that the temperature is a linear function of time

$$T = T_0 + bt,$$

the solution to Eqs. (2.1) is:

$$n_i = n_0 \exp\left[-\frac{1}{b}\int_{T_0}^{T} N_c S v e^{-E/kT} dT\right], \quad (2.3a)$$

$$n_c = -\int_{T_0}^{T} dT' \frac{dn_i}{dT'} \exp\left[\frac{T'-T}{b\tau}\right] \simeq -b\tau \frac{dn_i}{dT}, \quad (2.3b)$$

where n_0 is the number of electrons in the traps at time $t=0$. The conductivity is therefore:

$$\sigma(T) = n_c q \mu = N_c S v q \mu \tau n_0$$

$$\times \exp\left[-\frac{E}{kT} - \frac{1}{b}\int_{T_0}^{T} N_c S v e^{-E/kT} dT\right]. \quad (2.4)$$

Differentiating $\ln[\sigma(T)]$ to find the maximum of $\sigma(T)$, one obtains:

$$\exp\left[\frac{E}{kT_m}\right] = \frac{N_c v S k T_m^2}{bE}, \quad (2.5)$$

where T_m is the temperature at which $\sigma(T)$ is a maximum. In differentiating (2.4), the slow variations of N_c, μ, v, S, and τ have been ignored.[12] It has been assumed that $E/kT_m \gg 1$.

---

[12] In the case of direct recombination τ may depend on the electron concentration, hence indirectly on the temperature. In
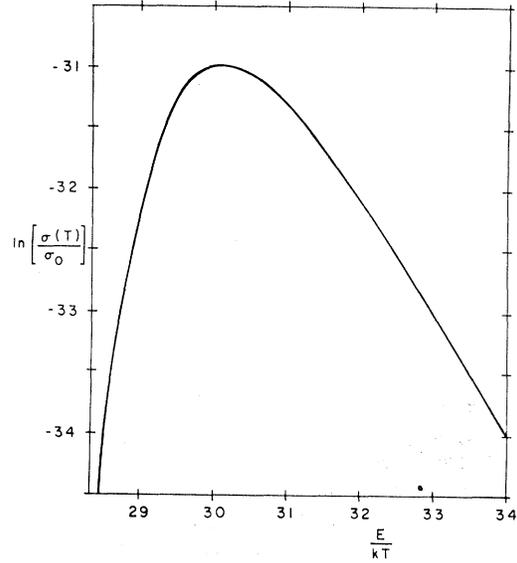

FIG. 2. Shape of a typical conductivity peak. E/kT_m has been taken to be 30, but the shape of the curve is not sensitive to the value of E/kT_m provided this value is large.

Equation (2.5) is not suitable for finding the energy E, unless the cross section S is known. Additional information may, however, be obtained from the maximum conductivity $\sigma(T_m)$. Since E/kT_m is generally large (for Bube's samples this parameter was about 30), we may use an asymptotic expansion for the integral in the exponent of Eq. (2.4). One then obtains [using (2.8)]:

$$\sigma(T_m) = \sigma_0 \exp\left[-\frac{E}{kT_m} - 1\right], \quad (2.6)$$

where $\sigma_0 = N_c v \mu q S \tau n_0$. The quantity σ_0 is virtually independent of the temperature T_m. We shall see shortly how the above result may be used to determine the energy E.

It is instructive to study the shape of a conductivity peak. By arguments similar to those leading to Eq. (2.6), one readily finds:

$$-\ln\left[\frac{\sigma(T)}{\sigma_0}\right] \sim \epsilon + \left(\frac{\epsilon_m}{\epsilon}\right)^4 \exp[\epsilon_m - \epsilon]$$

$$\sim \epsilon + \exp[\epsilon_m - \epsilon] \quad \text{when} \quad \epsilon \sim \epsilon_m, \quad (2.7)$$

where $\epsilon = E/kT$; $\epsilon_m = E/kT_m$.

It is easily verified that the maximum conductivity predicted by (2.7) occurs very nearly at $\epsilon = \epsilon_m$. In a typical case, the error made in using (2.7) instead of (2.4) to find T_m is less than 1°K. Figure 2 shows a plot of Eq. (2.7) with $\epsilon_m = 30$. When $\epsilon \gg \epsilon_m$ (i.e., $T \ll T_m$), the plot is linear. The existence of this linear region is the basis of the method of Garlick and Gibson.[2]

---

that case the development we present below must be modified somewhat.

Fast Retrapping $[(N_i - n_i)Sv \gg \tau^{-1}]$

In this case the time required for thermal equilibrium to be established between electrons in traps and electrons in the conduction band is much shorter than the recombination lifetime. For this reason, there is effective thermal equilibrium between the traps and the conduction band. Let us denote the *total* number of electrons by $n = n_i + n_c$. Then:

$$\frac{dn}{dt} = -\frac{n_c}{\tau} = -\frac{n}{\tau}\left(\frac{N_c}{N_i}\right)\exp\left[-\frac{E}{kT}\right], \qquad (2.8)$$

where it has been assumed that $N_i \gg N_c \exp[-E/kT].$[13] The solution of Eq. (2.8) is

$$n = n_0 \exp\left[-\frac{1}{b}\int_{T_0}^{T} N_c N_i^{-1}\tau^{-1}e^{-E/kT}dT\right], \qquad (2.9)$$

and the resulting conductivity is:

$$\sigma(T) = n_c q\mu = \frac{N_c\mu}{N_i}qn_0$$

$$\times \exp\left[-\frac{E}{kT} - \frac{1}{N_i b\tau}\int_{T_0}^{T} N_c e^{-E/kT}dT\right]. \qquad (2.10)$$

Differentiating $\ln[\sigma(T)]$ to find the maximum, one obtains (for $E/kT_m \gg 1$):

$$\exp\left[\frac{E}{kT_m}\right] = \frac{N_c kT_m^2}{N_i b\tau E}. \qquad (2.11)$$

The maximum conuctivity becomes:

$$\sigma(T_m) = \sigma_0 \exp\left[-\frac{E}{kT_m} - 1\right] \qquad (2.12)$$

where $\sigma_0 = (N_c\mu/N_i)\,qn_0$ and the shape of the conductivity curve is:

$$-\ln\left[\frac{\sigma(T)}{\sigma_0}\right] \sim \epsilon + \left(\frac{\epsilon_m}{\epsilon}\right)^{7/2}\exp[\epsilon_m - \epsilon]$$

$$\sim \epsilon + \exp[\epsilon_m - \epsilon] \quad \text{when} \quad \epsilon \sim \epsilon_m. \qquad (2.13)$$

Equations (2.11), (2.12), and (2.13) are to be compared with Eqs. (2.5), (2.6) and (2.7), respectively.

Determination of Trap Energy

Two important results emerge from the preceding analysis.

---

[13] If the initial occupancy of the traps is very large, the above treatment should be modified somewhat to take account of degeneracy. This modification may be made by introducing on the right-hand side of each of Eqs. (2.11) and (2.12) a factor $[N_i/N_i - n_i(T_m)]^2$. This change has no effect on the determination of trap energies by the method of the text. However, a high degree of degeneracy does change the shape of the conductivity peak somewhat from that given in the text.

(1) The shape of a conductivity peak is virtually independent of the retrapping rate. In the immediate vicinity of the peak there exists a universal curve of the form

$$-\ln\left[\frac{\sigma(T)}{\sigma_0}\right] = \frac{E}{kT} + \exp\left[\frac{E}{kT_m} - \frac{E}{kT}\right]. \qquad (2.14)$$

σ_0 is, to a very good approximation, independent of temperature.

(2) There exists a universal relation between the conductivity and the temperature at the maximum of the form

$$-\ln\left[\frac{\sigma(T_m)}{\sigma_0}\right] = \frac{E}{kT_m} + 1, \qquad (2.15)$$

where σ_0 is to a good approximation independent of T_m.

This suggests a convenient method for obtaining the trap energy E. From Eqs. (2.5) or (2.11), we note that T_m depends on the heating rate b. In a typical case, the heating rate might be 1°K/sec with $T_m \sim 200°K$. Changing the heating rate by a factor of two will shift T_m about 5°K. If then $\sigma(T_m)$ and T_m are measured for *different* heating rates, and $\ln[\sigma(T_m)]$ is plotted *versus* $1/kT_m$, the slope of the resulting straight line will yield E.

The success of this method of measuring trap energies depends on how much the position of a conductivity peak can be shifted by a change in the heating rate. Heating rates varying from 0.03°K/sec to 3.0°K/sec have been reported in the literature.[5] For a typical trap this implies a variation in T_m of about 30°K. If T_m can be measured to within 1°K, the method will be accurate to better than 5%.

3. DISCUSSION

It is worthwhile to compare the proposed method for determining E with that of Bube.[6-11] Bube's formula for the energy [see Eq. (1.1)] is deduced by assuming that the number of conduction electrons at maximum, $n_c(T_m)$, is

$$n_c(T_m) = N_c e^{-E/kT_m}. \qquad (3.1)$$

Equation (3.1) is an *ad hoc* relation, which is used without theoretical foundation; on the basis of the preceding analysis we can determine how well it succeeds in the limits of slow and fast retrapping. For slow retrapping

$$n_c(T_m) \sim \tau\frac{n_i}{\tau_{ej}},$$

where $\tau_{ej} = [(N_i - n_i)/N_c]\tau_{tr}e^{+E/kT_m}$, and $\tau_{tr}^{-1} = (N_i - n_i)Sv$. Therefore

$$n_c(T_m) \sim N_c e^{-E/kT_m}\left[\frac{n_i\tau}{(N_i - n_i)\tau_{tr}}\right]. \qquad (3.2)$$

On the other hand, for fast retrapping

$$n_c(T_m) \sim N_c e^{-E/kT_m}[n_i/(N_i - n_i)]. \qquad (3.3)$$

On the basis of Eqs. (3.2) and (3.3) we might expect by interpolation that for an intermediate retrapping rate:

$$n_c(T_m) \sim N_c e^{-E/kT_m}\left[\frac{n_i \tau}{(N_i - n_i)(\tau + \tau_{tr})}\right]. \qquad (3.4)$$

From Eq. (3.4) we estimate that the energy E, as determined by the use of Eq. (3.1), will be in error by the amount:

$$\Delta E \sim kT_m \ln\left[\frac{n_i \tau}{(N_i - n_i)(\tau + \tau_{tr})}\right]. \qquad (3.5)$$

Clearly, the error given by Eq. (3.5) depends on both the amount of retrapping and the degree of initial saturation of the trap under consideration. The most favorable situation obtains when there is very fast retrapping and the trap states are initially saturated. In that case, it can be shown that $n_i(T_m) \sim 0.37 N_i$ and that the error in the energy is only $\sim -\frac{1}{2}kT_m$. In other cases the error will always be negative and larger than $-\frac{1}{2}kT_m$. How important this error is depends on what the value of E is used for. We will see that it is not necessarily negligible. As a case in point, we will examine Bube's application of this method to the determination of trapping cross sections. In Bube's procedure, the energy is determined from the peak conductivity [see Eq. (1.1)] and is inserted into Eq. (2.5) to determine the cross section S. As we have seen, Eq. (2.5) is valid only in the slow retrapping limit; in the fast retrapping limit the exponential in Eq. (2.5) should be replaced by the expression (2.11). Combining these various equations in the appropriate limits we obtain formulas for the error in Bube's cross section which can be represented by the interpolation formula:

$$S_{\text{Bube}} = S_{\text{True}}\left(\frac{n_i}{N_i - n_i}\right)\left(\frac{\tau \tau_{tr}}{(\tau + \tau_{tr})^2}\right). \qquad (3.6)$$

The logarithms have disappeared in Eq. (3.6) because the error ΔE [see Eq. (3.5)] enters into an exponent. It is clear from Eq. (3.6) that Bube's procedure for obtaining energy values leads to very considerable errors in the cross sections in either the fast or the slow retrapping limit.

If the energies in Bube's procedure for calculating cross sections were determined by the method we propose, there would still be large uncertainties in the cross sections because of the great sensitivity of the exponential in (2.5) to an error ΔE in the energy value. In a favorable case ($E \sim 0.35$ ev, $\Delta E \sim 0.016$ ev) the calculated cross section would be in doubt about a factor of 3, in an unfavorable case by about an order of magnitude. On the average we think the error would

be smaller than the error made using Bube's estimate of the energy since there is no reason to suppose that the recombination and trapping times will ordinarily agree within a factor of 10. In any case, the error, ΔE, made using our procedure should be a random error, uncorrelated to the trapping or recombination rates. We cannot make an empirical comparison of the two methods on the basis of the data available in the literature since most of the reported experimental data does not include all of the necessary information. In one case reported by Bube,[6] sufficient data are reported so that our procedure of analysis may be used although we have no means of knowing whether the experimental conditions were such that our analysis is relevant (see our discussion below). However, if we assume that it is relevant, we obtain an energy value in agreement with that found by Bube.

Haake's criticism[3] of the method of Garlick and Gibson[2] has already been mentioned in the Introduction. This method requires for its application a peak which stands a factor of 10 or more above the background. The method has the disadvantage that it does not make use of the data near the peak (which are the most accurate data) but derives the trap energy from the "wings" of the peak.

The method of Grossweiner[4] involves the measurement of the half-width of the peak. In a typical case this half-width may be $5°-10°K$. Since the trap energy E is inversely proportional to the half-width,[4] very precise temperature values are required for accurate values of E. For instance, if temperatures can be measured with an experimental uncertainty of $1°K$, the resulting trap energy will be uncertain by about 25%.

The method of Booth[5] makes use of the shift of the peak with heating rate. In this respect it is similar to the method proposed here. However, the present method makes use of the peak conductivity values while Booth employs known heating rates. In either case an experimental difficulty arises which is absent in other methods. The use of different heating rates requires the repetition of the experiment, starting from the same initial trap population. In order to ensure this, the conditions of excitation must be such that the degree of saturation of trap population may be accurately reproduced. In a typical case, the method of Booth[5] and the present method should yield comparable accuracy.

The advantage of a method based on the use of different heating rates over that of Grossweiner is that for a given precision of temperature measurement one can obtain more precise values for the trap energies. Thus, for a typical case in which the shift of the temperature maximum is $30°K$ and the uncertainty of a temperature measurement is $1°K$, the error in the energy is of the order of 5%, as compared with 25% for the method of Grossweiner.