MIXED FIRST AND SECOND ORDER KINETICS IN THERMALLY STIMULATED PROCESSES

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A kinetic equation of the "mixed order" form

$$I(t) = -\mathrm{d}n/\mathrm{d}t = s'n^2 \exp(-E/kT) + s'Cn \exp(-E/kT)$$

is considered and shown to govern thermoluminescence (TL), thermally stimulated conductivity (TSC) and ionic thermoconductivity (ITC) under certain conditions. The present equation is compared to the previously accepted "three parameters" general order equation, namely

$$I(t) = -\mathrm{d}n/\mathrm{d}t = s'n^b \exp(-E/kT),$$

where b is the "effective order" of the kinetics. The mixed order equation is shown to result from the more general set of three differential equations governing the "traffic" of carriers between a trap, the conduction band and a recombination center under certain physical assumptions. Also, the applicability of this equation is discussed as an empirical approximation to the more general case. The solution of this equation is investigated, and methods for experimentally extracting the three parameter E, s' and C are introduced. The advantages of this presentation as compared to the "general order" one are discussed. As a different case where the mixed order equation seems to accurately describe the physical situation, we discuss TL and conductivity attributed to ionic transport.

1. Introduction

The theory of thermoluminescence (TL) started with the introduction by Randall and Wilkins [1] of the first order equation

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = sn \, \exp\left(-\frac{E}{kT}\right), \tag{1}$$

which shows the expected evolution of $I(t)$, the intensity of emission with the

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time. This can be replaced by $I(T)$, the evolution with the temperature, when the heating function $T(t)$ is given. $E(\text{eV})$ is the activation energy, $s(\text{s}^{-1})$ the frequency (or pre-exponential) factor, and $k(\text{eV K}^{-1})$ the Boltzmann constant. Physically, the Randall and Wilkins equation implicitly assumes that retrapping of a thermally released carrier is practically impossible. Garlick and Gibson [2] introduced the case of strong retrapping, which brought about the second order kinetics

$$I(t) = -\frac{dn}{dt} = s'n^2 \exp\left(-\frac{E}{kT}\right). \tag{2}$$

Here the pre-exponential factor is $s'(\text{cm}^3 \text{ s}^{-1})$.

From this point on, the theoretical investigation of the TL effect took two routes. Halperin and Braner [3] adopted a set of three simultaneous differential equations, previously used by Adirovitch [4] to deal with phosphorescence decay, and showed that with a proper adjustment they could be used for TL. This set of equations deals with the "traffic" of charged carriers during the heating of the sample, when one trapping state (say, of electrons) and one kind of recombination center (of holes) are involved. These equations are

$$I(t) = -\frac{dm}{dt} = A_m m n_c, \tag{3}$$

$$-\frac{dn}{dt} = sn \exp\left(-\frac{E}{kT}\right) - A_n n_c(N - n), \tag{4}$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt}, \tag{5}$$

where $m(\text{cm}^{-3})$ is the concentration of holes in centers, $n(\text{cm}^{-3})$ that of electrons in traps, $N(\text{cm}^{-3})$ the concentration of traps of the kind responsible for the peak being considered, $n_c(\text{cm}^{-3})$ the concentration of electrons in the conduction band, and $A_m, A_n(\text{cm}^3 \text{ s}^{-1})$ the probabilities of recombination and retrapping respectively. This set of equations includes eight parameters, namely $s, E, A_m, A_n, N, m_0, n_0$ and n_{c0} (initial values of m, n and n_c). Even this degree of complication does not entirely cover all the possible physical cases (see below). It is obvious, however, that one can, at least in principle, fit with no difficulty an experimental TL peak to an eight parameter theoretical one by an adjustment of this set of parameters. Actually, it seems that the difficulties lies in the fact that more than one set of eight parameters may be found to yield a good fit to a desired accuracy. In practice, the use of eight parameters is very difficult and one would always like to reduce the number of parameters involved before starting an analysis such as a curve fitting. In the eight parameter case n_{c0} can be assumed to be equal to zero, and only the ratio n_0/m_0 is to be considered. The number of parameters is thus reduced by two, while the problem loses only very little of its generality. However even six free parameters to handle are too many in this case. Halperin and Braner [3] made

the two physical assumptions

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right|; \qquad n_c \ll n, \tag{6}$$

which essentially mean that electrons are not accumulating in the conduction band in substantial amounts, and they got the approximate expression

$$I(t) = -\frac{dm}{dt} = sn \exp\left(-\frac{E}{kT}\right) \frac{A_m m}{A_m m + A_n(N-n)}. \tag{7}$$

Since it includes two unknown functions, m and n, eq. (7) cannot be solved, and additional assumptions are needed. One simple assumption is that recombination dominates, i.e. $A_m m \gg A_n(N-n)$, which results in

$$I(t) = -\frac{dm}{dt} = sn \exp\left(-\frac{E}{kT}\right). \tag{8}$$

In the framework of one trap and one center, the equality

$$\frac{dm}{dt} = \frac{dn}{dt} \qquad (\text{or } m = n + \text{const.})$$

necessarily occurs, which reduces eq. (8) to eq. (1).

The second order eq. (2) can be derived from eq. (7) by two different sets of assumptions, both including the quite restrictive assertion $m = n$. Firstly, Garlick and Gibson's [2] "strong retrapping case" can be written as: $A_n(N-n) \gg A_m m$; and secondly if the trap is assumed to be far from saturation, $N \gg n$, eq. (7) results in

$$I(t) = -\frac{dn}{dt} = \left(\frac{sA_m}{NA_n}\right) n^2 \exp\left(-\frac{E}{kT}\right), \tag{9}$$

thus, the pre-exponential factor here is $s' = sA_m/NA_n$.

An alternative suggested by Wrzesinska [5] is to assume $A_m = A_n$ (which is also quite a particular assumption) in addition to $m = n$, which results in eq. (7) becoming

$$I(t) = -\frac{dn}{dt} = \left(\frac{s}{N}\right) n^2 \exp\left(-\frac{E}{kT}\right). \tag{10}$$

This is eq. (2) with s' being equal to s/N. It is to be emphasized that both the first and second order kinetics are rather extreme cases, and that eq. (7) includes mostly "intermediate" situations, which are neither of first nor of second order.

2. General order kinetics

Although numerical solutions of the set of three simultaneous differential eqs. (3)–(5) have been carried out for given sets of the eight parameters [6,7],

the availability of such solutions has not been of much help in the more important inverse problem, of analysing a given glow curve to derive the values of the parameters from it. To deal with this problem, early investigators assumed only first and second order kinetics, namely a two parameter case (E and s or s'), but later authors [8–15] suggested a three parameter equation of the form

$$I(t) = -\frac{dn}{dt} = s'n^b \exp\left(-\frac{E}{kT}\right), \tag{11}$$

where b is the "effective order" of the kinetics, which could be between 1 and 2 and somewhat beyond this range. The fourth parameter n_0 must not be considered as being of equal importance, since its main influence is on the total intensity of the glow peak rather than on its shape. This approach of using eq. (11) can account for various symmetries observed on the glow peaks. Following Halperin and Braner [3] the symmetry factor μ_g of a peak can be defined by $\mu_g = \delta/\omega$ where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$, and where T_m is the temperature of the maximum and T_1 and T_2 are the low and high half intensity temperatures. Computations show a first order peak to be characterized by $\mu_g \simeq 0.42$ and a second order one by $\mu_g \simeq 0.52$ [16]. The third parameter b results in the theoretical three parameter curve having intermediate values of μ_g, as well as values out of the range 0.42 to 0.52, for $b < 1$ or $b > 2$, which may be observed experimentally. As shown by Chen [10], the parameter μ_g can be used in formulae deriving the activation energy from half intensity measurements as an interpolation parameter. These formulae are of the form

$$E = c_\alpha\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m), \tag{12}$$

where α stands for $\tau(= T_m - T_1)$, δ or ω, and where, for example

$$c_\tau = 1.51 + 3(\mu_g - 0.42); \qquad b_\tau = 1.58 + 4.2(\mu_g - 0.42). \tag{13}$$

Similar expressions for c_δ and b_δ as well as c_ω and b_ω were given by Chen [10]. The measured value of μ_g can also be used to evaluate the effective kinetic order b and the pre-exponential factor s' [10]. Eqs. (1) have been successfully used by a number of investigators [17–19] for various experimental TL peaks.

There are, however, two obvious disadvantages to the approach of eq. (11), beside its approximate nature (its being dependent on three parameters only). One is that it is entirely empirical, in the sense that no approximation can be found which would enable us to derive eq. (11) from the three differential eqs. (3)–(5). (Possibly with the one exception mentioned by May and Partridge [8,9].) An intermediate power appears typically much more phenomenological than physical. The other disadvantage is that s' has the "strange" units of $cm^{3(b-1)}$ s^{-1}. Instead of s', the parameter $s'n_0^{(b-1)}$ may be used; it has frequency units like $s(s^{-1})$ but then this new frequency factor is occupancy-dependent-rather than being a constant.

Another approach to a "general order" description of glow curves may be found in a recent paper by Kanunnikov [20]. The following identities are well known:

$$\beta \frac{E}{kT_m^2} = b \frac{I_m}{n_m} \tag{14}$$

for first or second order glow curves; with b equals 1 for first order, 2 for second order; T_m the temperature of the maximum of glow peak; I_m the intensity at this maximum; n_m the number of charges still trapped at $T = T_m$ and β the heating rate.

Kanunnikov writes eq. (7) with the assumption $n = m$; which results in the single variable kinetic equation

$$I(t) = -\frac{dn}{dt} = \frac{A_m n^2}{(A_m - A_n)n + A_n N} s \exp\left(-\frac{E}{kT}\right). \tag{15}$$

At the glow peak maximum, it results in the identity

$$\beta \frac{E}{kT_m^2} = b' \frac{I_m}{n_m}. \tag{16}$$

The parameter b' thus introduced does have the values one or two respectively for the limiting cases were eq. (15) is reduced to a first or second order kinetic equation, but also other values in the range 1 to 2 for all other cases. Besides, b' has a very clear physical interpretation (as opposed to b), which makes it (associated with eq. (15)) an attractive substitute to b as a "general order" parameter to describe a wide range of glow curves. A drawback could be found in the fact that b' does not appear as such in eq. (15). Another, more basic, objection to this approach is as follows.

3. Mixed first and second orders

In all sets of assumptions leading to higher order kinetics, a common one is $m = n$. This assertion seems actually the least probable to occur since in all real samples, many kinds of defects and impurities are present. (To have only one kind of trap and one kind of center acting in a certain temperature range, may already be considered as a stroke of good luck.) In this case, $m = n + n_c + C$ where C is a constant (positive or negative) [22]. This relation represents the conservation of charge in the range of temperature in which the peak occurs and it is equivalent to eq. (5). C represents the number of trapped electrons or holes not taking part in the TL process in the temperature range being considered due to their being in deep traps or in low probability recombination centers. (More accurately, C is the difference between the concentrations of

these trapped electrons and holes.) As is usually assumed, n_c can be neglected as compared to m or n. But, additionally, taking C to be equal to zero seems much more implausible.

When $C \neq 0$, in the case of equal probabilities for recombination and retrapping ($A_m = A_n$), eq. (7) becomes

$$I(t) = -\frac{dn}{dt} = \left(\frac{s}{C+N}\right)n(n+C)\exp\left(-\frac{E}{kT}\right) \tag{17}$$

instead of eq. (10), derived for C equals zero.

When the situation is that of the already considered dominating retrapping $A_n(N-n) \gg A_m m$, and if the trap is far from saturation, $N \gg n$, eq. (7) becomes

$$I(t) = -\frac{dn}{dt} = \left(\frac{sA_m}{NA_n}\right)n(n+C)\exp\left(-\frac{E}{kT}\right) \tag{18}$$

instead of eq. (9), when C equals zero.

Both eqs. (17) and (18) can be written as

$$I(t) = -\frac{dn}{dt} = s'n(n+C)\exp\left(-\frac{E}{kT}\right), \tag{19}$$

where s' is a constant with units of $cm^3\ s^{-1}$. It is to be noted that an equation similar to eq. (18) for the case of phosphorescence ($T = const.$) has already been suggested by Mott and Gurney [21]. Eq. (19) can simply be considered as a combination of the well known first and second order kinetics.

Eq. (19) may also be derived directly from the more general eq. (7) by combining it with the assumption that in a certain temperature range, only one trap and one center are involved, i.e. $m = n + C$, eq. (7) is then written as

$$I(t) = -\frac{dn}{dt} = \frac{sA_m\exp(-E/kT)n(n+C)}{A_m(n+C)+A_n(N-n)}, \tag{20}$$

which can be written as

$$I(t) = -\frac{dn}{dt} = s\exp\left(-\frac{E}{kT}\right)F(n). \tag{21}$$

Under appropriate mathematical conditions, $F(n)$ can be developed into a power series

$$F(n) = C_1 n + C_2 n^2 + C_3 n^3 + \ldots \tag{22}$$

No constant additive term is included, since $F(0) = 0$. In some cases (but not always) taking the first two term may give a reasonable approximation, which brings us back to eq. (19) [22].

It is to be noted that the solution of eq. (19) is not a combination of the first and second order solutions. In this respect, the present treatment differs from that of Schlesinger and Menon [23] who assumed, in an empirical way, a

weighted combination of first and second order solutions.

To solve eq. (19), we introduce the parameter

$$\alpha = \frac{n_0}{(n_0 + C)}.$$

Eq. (19) may be written as

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = s'n\left(n - n_0 + \frac{n_0}{\alpha}\right)\exp\left(-\frac{E}{kT}\right). \tag{23}$$

The solution, starting from temperature T_0 with the constant heating rate β is

$$I(T) = \frac{s'C^2\alpha \exp\left[(Cs'/\beta)\int_{T_0}^{T}\exp(-E/kT')\,\mathrm{d}T'\right]\exp(-E/kT)}{\left\{\exp\left[(Cs'/\beta)\int_{T_0}^{T}\exp(-E/kT')\,\mathrm{d}T'\right] - \alpha\right\}^2}. \tag{24}$$

Similarly to the first, second and general order cases, initially, i.e. at the lower temperatures, this expression behaves like $\exp(-E/kT)$. At higher temperatures, the shape characteristic to the particular value of α is obtained. This solution appears to be intermediate between the first and second order expressions in the sense that for $\alpha = 0$ ($n_0 \ll C$) it tends to first order, and for $\alpha = 1$ ($n_0 \gg C$), to second order. To derive, from eq. (24), numerical values of T_{m}, T_1 and T_2 for given values of E, s', β, α and n_0 a computer program has been prepared and executed. Values of μ_{g} have been readily obtained from T_{m}, T_1 and T_2. The symmetry factor μ_{g} as a function of α appears to gradually change from the value 0.42 characteristic of first order when α equals zero, to the value 0.52 of the second order when α equals one, as shown by curve (a) of fig. 1.

Only the values of α from zero to one, i.e. for $n_0 \leqslant m_0$ are shown in fig. 1. As for the case $n_0 > m_0$, i.e. $\alpha > 1$, let us change in eq. (19) the variable n into $m = n + C$, and, instead of α, use the parameter: $\alpha' = \alpha^{-1} = m_0/n_0$. Eq. (19) readily becomes

$$I(t) = -\frac{\mathrm{d}m}{\mathrm{d}t} = s'm\left(m - m_0 + \frac{m_0}{\alpha'}\right)\exp\left(\frac{-E}{kT}\right), \tag{25}$$

which is strictly the same as eq. (23), hence has the same solution [22]. μ_{g} as a function of α' here will be the same as μ_{g} vs. α in eq. (23). Thus, for the cases where $n_0 > m_0$, μ_{g} will be obtained by the same curve (a), fig. 1, but using $\alpha^{-1} = m_0/n_0$ instead of α as the variable (and $C' = |C|$).

It is interesting to note in this context the results by Halperin and Braner [3] related to the case of $n_0 \geqslant m_0$. They show that when the recombination probability is very large ($A_{\mathrm{m}} \approx \infty$), δ (and therefore, μ_{g}) may be very small, and while increasing n_0 as compared to m_0, they may reduce to zero and even attain effective negative values. We are not concerned, however, with this case

since neither eq. (17) nor eq. (18) results from the assumption that A_m is very large, on the contrary, eq. (17) is related to the case of equal probabilities whereas eq. (18) results from the assumption of low recombination.

The main point regarding the curve μ_g vs. α is that, although it has been calculated by choosing certain values for E and s', we have verified that changing E and s' modifies the graph but slightly, in other words, μ_g is a relatively strong function of α and a very weak function of E and s'. This and the shape of curve (a) bring to mind the suggestion to use experimental values of μ_g to compute the interpolation coefficients of eqs. (13) and similar equations based on δ and ω, and then the activation energy E by the half intensity formulae (12) as given by Chen [10].

The point is that both in the "general order" case then considered, and in the "mixed order" case presently studied, eqs. (13) are empirical and the condition for their being useful is that μ_g is a slowly varying function of b in the general order case of eq. (11) and of α in the mixed order case of eq. (10).

The half intensity formulae have been actually tested for "synthetic" glow peaks, computer calculated with eq. (24) for given parameters. The values for e thus derived were found to be within 3% of the given values, which represents just as good a fit as with curves computed with the general order model [10]. As for the value of α itself, it can be deduced from the experimental value of μ_g directly with curve (a) in fig. 1.
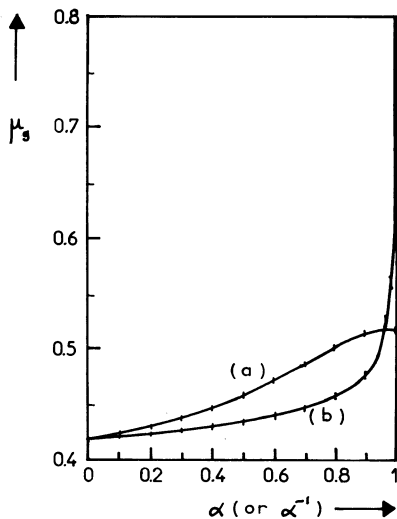

Fig. 1. The geometrical factor μ_g calculated as a function of $\alpha = n_0/(n_0 + C) = n_0/m_0$ (or m_0/n_0); (a) for the TL peak, according to eq. (24), (b) for the TSC peak, according to eq. (30).

4. Measurements of TSC and TL due to ionic conductivity

Fuchs and Taylor [24,25] suggested that conductivity peaks observed during a linear heating of irradiated KBr at low temperatures (10 to 35 K) are due to displacements of ions in the process of complementary centers annihilation by recombination. It has been found [26] also in other alkali halides that conductivity peaks in the low temperature range are due to ionic motions, and that such conductivity peaks are usually accompanied by TL ones.

Fuchs and Taylor proposed for this recombination the rate equation

$$-\frac{dn}{dt} = nn_R K \exp\left(-\frac{E}{kT}\right), \tag{26}$$

when n and n_R are the concentrations of interstitials and ionic recombination centers respectively, and $K(\text{cm}^3 \text{ sec}^{-1})$ the rate constant. They identified n with the mobile interstitials and n_R with the immobile vacancies. If the recombination is radiative, the term dn/dt corresponds to the intensity of luminescence. The ionic conductivity is given by

$$\sigma_i(T) = en(T)\mu(T), \tag{27}$$

the mobility $\mu(T)$ being for ions

$$\mu(T) = \left(\frac{\mu_0}{T}\right) \exp\left(-\frac{E_m}{kT}\right). \tag{28}$$

The expression for $\sigma_i(T)$ thus obtained is quite similar to the well-known expression for $\sigma_e(T)$, the conductivity due to electrons (TSC) [24–28].

Fuchs and Taylor [24] use in eq. (26) an activation energy E and in eq. (28) a motion energy E_m, and then assume "for simplicity" that $E = E_m$. We tend to believe that the same energy E should be used in both equations not only as a matter of convenience but rather since in this model both E and E_m are physically the heights of potential barriers for the motion of the ion [22]. In eq. (26) the rate of recombination $(-dn/dt)$ is described as being proportional to n and n_R as well as to $\exp(-E/kT)$; this can be accounted for by the fact that $\exp(-E_m/kT)$ appears in the expression for the mobility μ; the higher the temperature is, the more mobile are the ions and therefore they recombine more, thus producing thermoluminescence. By such a recombination, a mobile interstitial ion and a vacancy mutually annihilate and restore the normal lattice.

We now denote by C the concentration of interstitials trapped by other defects [26], which cannot participate in the mobility and recombination effects. We can thus write $n_r = n + C$ where C is constant during a glow peak, following a given irradiation. Eq. (26) can now be rewritten as

$$I = -\frac{dn}{dt} = Kn^2 \exp\left(-\frac{E}{kT}\right) + KCn \exp\left(-\frac{E}{kT}\right), \tag{29}$$

which is actually eq. (19) with K replacing s'. Thus the suggestion already made above to use eq. (12) with coefficients given by eq. (13) to evaluate E, can be applied here as well.

The expression for the ionic thermoconductivity σ_i related to the same process can be found by combining eqs. (27) and (28). This yields

$$\sigma_i(T) = \frac{eC(\mu_0/T)\exp(-E/kT)}{\exp\left[(CK/\beta)\int_{T_0}^{T}\exp(-E/kT')\,\mathrm{d}T'\right] - \alpha} \tag{30}$$

with $\alpha = n_0/(n_0 + C)$ or $(n_0 + C)/n_0$, whichever is the smaller, as we saw above (and the absolute value of C in both cases).

Again, the initial behavior, at the lower temperatures, is the regular initial rise one, $\sigma(T) \propto \exp(-E/kT)$. Curve (b) in fig. 1 shows the variation of the symmetry factor μ_g for the conductivity curve given by eq. (30) vs. the parameter α (resp. α^{-1}). In the same way as in curve (a), the results are rather insensitive to the particular values chosen for E and K. The variation of μ_g with α is seen to be rather mild, up to $\alpha \simeq 0.9$. However, between $\alpha = 0.9$ and $\alpha = 1$, μ_g changes very quickly and reaches values up to ~ 0.8. This prevents any attempt to use a simple interpolation formula for the evaluation of the parameters from the conductivity curve. The high value of $\mu_g \sim 0.8$ corresponds to conductivity related to pure second order TL. This has been already investigated by Saunders [27] and Chen [28] in the similar case of TSC.

5. Summary and discussion

We have presented in this paper an equation that should replace, under certain conditions, the formulae used presently for the description of the thermally-stimulated phenomena. This eq. ((19) above) includes three free parameters, the activation energy E, the pre-exponential factor s' (or K), and the excess concentration C (or alternatively, the parameter α). As in the "general order" case mentioned in section 2 above, we disregard the additional parameter n_0 since it only influences the scale (or total intensity) rather than the shape of the peak. As far as the number of parameters is concerned, the present "mixed order" is thus similar to the "general order" case, therefore, both may be equally well fitted to describe a general glow peak. Also, the two are similar in the sense that they tend to the first or second order cases when the appropriate values are chosen for the parameters. As shown above, the same interpolation equations can be used for evaluating the activation energy for both, and a similar diagram to evaluate the "third parameter" (b or α) from the symmetry μ_g factor. The present mixed order approach has, however, the following advantages:

(1) The pre-exponential factor s' (or K) has units of $cm^3\ s^{-1}$ in the present case, as against the "strange" units of $cm^{3(b-1)}\ s^{-1}$ in the "general order" case.

(2) As explained above, simple assumptions lead from the three differential equations describing a glow peak in a general way to the "mixed order" equations. No similar derivation can result in the "general order" equation.

(3) In particular cases, such as TL resulting from recombination of mobile ions, the mixed order equation seems to be the natural one derived straightforward from the physical model without additional assumptions being made.

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