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The Shape of Thermoluminescence Glow Peaks in Molecular Solids

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Abstract—Existing physical models predicting the profile of thermoluminescence glow peaks are critically examined and extensions of these models are tested against experimental data for one glow peak from the organic solid hexamine. It is pointed out that gross departures of the experimental data from the Randall and Wilkins curve must lead to the rejection of models based on the annealing of isolated centres such as self-trapped excitons. All reasonable departures from this model introduce the concept of retrapping and so are applicable to a physical situation involving electrons and positive holes trapped in physically separated centres. A simple test for departure from the Randall and Wilkins model is found in the comparison of experimental activation energies derived from the initial rise of the luminescence intensity with those given by other methods based on peak shifts or peak widths.

1. Introduction

Thermoluminescence provides a technique for studying certain types of defects in solids with a directness not usual with other methods. Experimental studies of this phenomenon are relatively straightforward and can be used to ascertain the nature of some of the centres produced during irradiation with X-rays or ultra-violet light. There are several likely candidate models for the defects responsible for glow peaks found in molecular crystals. They could arise from a centre somewhat of the nature of a charge transfer exciton, or they may be due to the thermal annealing of a long lived excited state. Also owing to the fact that many studies have been done on semiconductors and alkali halides, thermoluminescence glow peaks have usually been regarded as being due to the thermal release of trapped

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electrons (or holes) during warming, and their subsequent recombination. However it would appear unwarranted to assume from the outset that this is necessarily the case in organic crystals and one should initially allow the hypothesis that they arise from trapped electron-hole pairs (charge transfer excitons) or some other thermally annealable long-lived excited state, perhaps related to the centres which give the long lived afterglow often found in organic materials. The work outlined in this paper arose from the desire to ascertain the nature of the defects responsible for the glow curves observed during warming of organic crystalline materials after low-temperature X-irradiation. It was decided to investigate in detail a suitable glow peak from an organic material and find what features the experimental peak shape forced on a number of suggested kinetic models.

2. Early Models Predicting Glow Peak Shapes

The general form of the variation of the light intensity in a glow peak is determined by two physical processes, namely the stored damage being annealed out at a rate governed by an Arrhenius factor, and the depletion of the finite number of centres available leading to the eventual exhaustion of the stored damage. Other authors have shown that the shape of the glow peak may be modified by additional complications.[1-4]

In considering the first of the above mentioned processes we note that the probability per unit time of any damage centre being destroyed by annealing is given by an Arrhenius factor i.e.

$$p = s \exp(-E/kT) \tag{1}$$

where k is Boltzmanns constant and T the absolute temperature. For our purposes we may regard s as a factor with the dimensions of reciprocal time, and note that in most postulated models moderate changes in it have the effect of shifting the peak to higher or lower temperatures. E is a parameter with the dimensions of energy and is identifiable with features of proposed models. If we explain the glow peaks in terms of the capture and subsequent thermally stimulated release of electrons by traps, E corresponds to the " trap depth ", while if trapped electron hole pairs are postulated it repre-

sents the height of the potential barrier which must be overcome in order for them to recombine. E is generally referred to as the " activation energy ".

The most fundamental technique for measuring E involves an examination of the initial portion of the curve in the region where very little depletion of the number of available centres has taken place.[1] Since the shape of this portion of the plot is determined solely by the Arrhenius expression (1), E may be determined from the slope of log (intensity) versus $1/T$ (°K). If the sample is warmed sufficiently that only the initial portion of the curve is observed and then is rapidly cooled the procedure may be repeated a number of times and the value of E found over a range of temperatures without introducing the inaccuracies discussed by Haake.[5] This procedure also determines whether defects with a unique activation energy are responsible for the glow peak.

The earliest and most general model giving a theoretical prediction of the shape of a glow peak using the measured value of E was that proposed by Randall and Wilkins.[6] These authors assumed that if there were no damage centres initially capable of giving rise to light emission, and at any time t, n of these remained, the intensity of light at that time would be given by

$$I = -a\,\mathrm{d}n/\mathrm{d}t \tag{2}$$

$$= -a\,n\,p \tag{3}$$

where a is an efficiency factor. On making the substitution

$$\mathrm{d}T = \beta \mathrm{d}t \tag{4}$$

where β is the rate of warming of the sample, integrating and substituting in (2) we find that the shape of the predicted peak is given by

$$I = an_0 s \exp\left(-\int_0^T (1/\beta)\, s \exp(-E/kT)\mathrm{d}T \right) \cdot \exp(-E/kT) \tag{5}$$

It will be noted that in deriving this expression no assumption has been made concerning the nature or mechanism of the process, and so this formulation is applicable to both models involving electrons and holes held in physically separate centres, and models involving trapped electron-hole pairs.

There are a number of ways of determining the value of E when

one has a peak of this shape. The activation energy may be calculated using the initial portion of the curve, since in this region the first exponential of expression (5) is nearly equal to unity. E may also be found from two curves obtained using different heating rates β and β' which have their maximum intensities at temperatures T_0 and T_0' through the use of an expression derived by Booth,[7] viz.

$$E = k\,T_0\,T_0'\,(\ln(\beta/\beta') + 2\ln(T_0'/T))/(T_0 - T_0') \tag{6}$$

Hoogenstraaten[8] showed that for a peak of the shape described by Eq. (5)

$$\ln(T_0^2/\beta) = \ln(E/ks) + E/k\,T_0 \tag{7}$$

Thus E may be calculated from the slope of a plot of $\ln(T_0^2/\beta)$ versus $1/T$ obtained using a number of different heating rates. Grossweiner[9] showed how the activation energy may be derived from the temperatures at which the maximum luminosity occurs and at which the emission has half this intensity on the low temperature side of the peak. These are the most commonly used methods of measuring the value of E. It should be noted that all but the initial rise technique rely on the peak having exactly the shape predicted by the well known Randall and Wilkins expression, and if they are to be used in the interpretation of experimental results one must ensure that they are applicable.

The other simple model for describing the shape of a glow peak commonly cited in the literature is that of Garlick and Gibson.[1] This model differs from the one proposed by Randall and Wilkins in that it allows the retrapping of mobile charges in the same variety of centre after they have been thermally excited into the conduction band and have become mobile. It should be noted that this is only applicable to a physical situation in which electrons and holes are trapped at physically separate centres. This implies that the model of Garlick and Gibson is not applicable in any physical situation involving electron hole pairs trapped at the same site.

In the treatment of Garlick and Gibson the probability of an electron being excited into the conduction band is given by expression (1). Assuming there are N trapping sites available and $N-n$ of these are empty at any given time and the empty sites have the same capture cross-section for electrons as the positive centres,

the fraction of the electrons in the conduction band which enter recombination sites is

$$n/((N - n) + n) = n/N. \tag{8}$$

If we multiply the right hand side of Eq. (3) by this factor and follow the same algebraic steps as used in the previous model we find that the shape of the glow peak is given by

$$I = \frac{n_0^2 S \exp(-E/kT)}{N[1 - (n_0/N)\int_0^T (S/\beta)\exp(-E/kT)\mathrm{d}T]^2} \tag{9}$$

This expression describes a somewhat broader peak whose width depends on the values of E and n_0/N. This implies that Grossweiner's method for the determination of E is no longer applicable. On differentiating the right hand side of Eq. (9) and equating the result to zero we find that for β constant

$$\ln(T_0^2/\beta) = \ln(E/ks) + (E/kT_0) + \ln\left[(N/2n_0)\left(1 + (n_0 s/N\beta)\int_0^T \exp(-E/kT)\mathrm{d}T\right)\right] \tag{10}$$

If this is compared with Eq. (7) it will be seen that a new term whose value is not easily found has been introduced. Thus it can be seen that Hoogenstraatens' method of determining the activation energy is inapplicable, as is of course the essentially similar technique advocated by Booth. However during the initial rise in the light intensity the integral in Eq. (9) is approximately zero and hence the shape of this portion of the glow peak is described by an Arrhenius expression so one may still use this to calculate the activation energy.

3. Experimental Results

The experimental glow peak selected for detailed study and comparison with the predictions of existing and proposed models was found at 160.5 °K when a sample of hexamine was warmed at 0.338 °K/sec after irradiation with $M_0K\alpha$ X-rays at liquid air temperature. This feature was chosen because it was the brightest isolated peak found in the glow curves of 42 organic compounds studied and it was possible to determine its shape accurately and

repeatably without difficulty. The experimental plot is illustrated in Fig. 1. This feature arose as a consequence of the annealing of a unique species of defect, as could be shown by partially annealing the peak, cooling the sample and warming it again. The shape of the

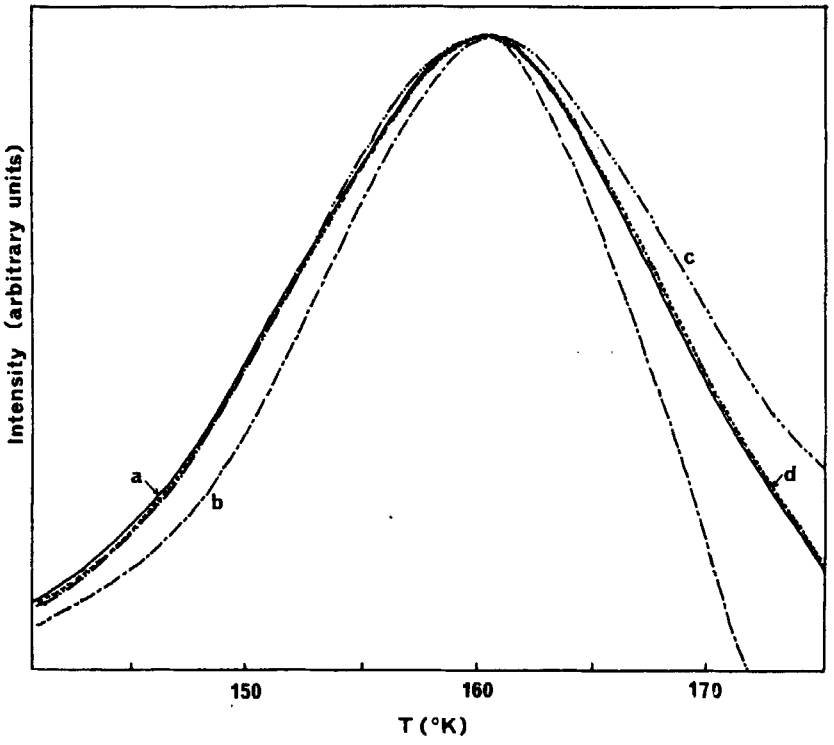

Figure 1. A comparison between the experimental and predicted peak shapes for the hexamine glow peak which has its maximum intensity at 160.5 °K when the sample is warmed at 0·330 °K/second. (*a*) experimental curve, (*b*) Randall and Wilkins Model, $E = 0.35$ eV, $s = 1.87 \times 10^{11}$, (*c*) Garlick and Gibson Model, $E = 0.35$ eV, $N = 2n_0$, $s = 1.17 \times 10^{10}$, (*d*) Unequal Cross Section Model, $E = 0.35$ eV, $N = 9n_0$, $b = 0.1$, $s = 9.01 \times 10^{8}$.

peak remained unchanged showing that it could not be resolved into species annealing at slightly different temperatures. Also repeated determination of the activation energy with the initial rise technique outlined in the previous section invariably gave the same value of E throughout the temperature range studied.

Using this method a value of $E = 0.35 (\pm 0.01)$ eV was found.

while Hoogenstraaten's and Grossweiner's techniques gave 0.20 (± 0.01) eV and 0.29 (± 0.01) eV respectively, implying that the peak was not of the shape predicted by the Randall and Wilkins model. In computing the predicted shape of the peak it is apparent that one must use the value of E obtained from the initial rise in order that the early portion of the plot might have the same shape as the experimental curve. A CDC 6400 computer was used to perform this task and the result is shown in Fig. 1. When the Randall and Wilkins function was used with $E = 0.35$ eV the resultant prediction was a much narrower peak than that found experimentally, confirming the suggestion that this model is not applicable here. The shape of the peak predicted by the Garlick and Gibson expression (10) can be altered slightly by varying the ratio n_0/N and making appropriate changes to the value of s to compensate for the resulting shift in the temperature of the maximum emission intensity. It can be seen in Fig. 1 that quite a good fit can be obtained to the low temperature side of the peak while at later stages the predicted emission is far too bright. Since the shape of this portion of the curve is largely controlled by the depletion of the number of charged traps available it is to this that we must look to produce a better fit.

4. Unequal Cross-section Model

In the last model we have assumed that the electron capture cross-sections are the same for both empty traps and recombination centres. This is of course not necessarily the case, especially if the luminescent centres are charged and therefore capable of influencing the motions of electrons at a distance, while the empty traps are uncharged and can only interact at close range.

If the capture cross-section of an empty trap is b times that of a luminescent site, the probability of an electron reaching such a site is given by

$$p'' = n/[b\,(N - n) + n] \tag{10}$$

Equations (1), (2) and (10) imply

$$I = \frac{an^2\, s \exp(-E/kT)}{bN + (1 - b)\, n} \tag{11}$$

On separating variables in (2) and (11) and integrating we find

$$-(1-b)\ln(n/n_0) + bN/n = \int_0^T (S/\beta)\exp(-E/kT)\,dT + bN/n_0. \tag{12}$$

This cannot be solved analytically to yield a solution for n. However if it is rewritten in the form

$$n = bN(1-b)\left[\ln(n/n_0) + \int_0^T (S/\beta)\exp(-E/kT)\,dt + bN/n_0\right]^{-1} \tag{13}$$

numerical values of n may be found by iteration and then substituted in (11) to give values of the emission intensity at any temperature. A computer program was used to perform this calculation.

In order to determine the effect of changing the heating rate (β) upon the temperature at which the maximum light intensity is emitted we differentiate the right hand side of Eq. (11) with respect to T and equate it to zero. If one substitutes the expression for dn/dT found by differentiating (13) into this equation one finds, after some simplification

$$\ln(T_0^2/\beta) = \ln(E/ks) + \ln[(bN + (1-b)n)^2/bNn^2] \tag{14}$$

The above expression implies that a plot of $\ln(T_0^2/\beta)$ versus $(1/T_0)$ will not be linear, and therefore methods of determining the value of the activation energy based on the shift of the maximum of the peak with variation of the heating rate are no longer applicable. The shape of the glow peak predicted by this model (Fig. 1) is very different from that obtained in the Randall and Wilkins model and hence one would not expect Grossweiner's method for the determination of E to be applicable.

A computer program was written to obtain the values of n by iteration from Eq. (13) and hence calculate the emission intensity from Eq. (11). It was found that varying the ratio n_0/N (i.e. postulating various degrees of filling of the traps) had little effect on the shape of the plot, and that good fits to the experimental curve were found whenever b was less than 0.2 (i.e. when the recombination sites had larger capture cross-sections than the empty traps).

Although variations in the value of b did not produce sufficient effect on the shape of the curve to enable one to find a unique value of this parameter, the unequal cross-sections model predicted a curve which gave the best fit to the experimental curve with values of b in a physically acceptable range.

5. Conclusions

We have shown in some detail that the hexamine glow peak examined is inconsistent with the model proposed by Randall and Wilkins and a better fit between the predicted peak shape and the experimental plot can only be obtained using more elaborate models. This provides evidence which rules out the possibility of the glow peak arising from the annealing of single centres such as trapped charge transfer excitons. It appears impossible to suggest a model which satisfactorily explains the shape of the observed peak without assuming the existence of physically separated positively and negatively charged centres, as one is unable to make any reasonable elaborations to the model of Randall and Wilkins on the basis of a physical situation involving only a single centre. Experimental evidence rules out the hypothesis of a distribution of trap depths.

It is clear that one must accept the value of the activation energy obtained from the early portion of the curve using the method suggested by Garlick and Gibson as this value is determined when the kinetics are simplest. With E constrained to this value we have obtained a fit to the later portion of the curve by elaborating the kinetic model essentially by the introduction of reasonable hypotheses regarding retrapping. The activation energy E is of importance since it may be measured directly and is independent of the kinetic model of the annealing and because it can be interpreted physically either as a trap depth or as the height of an energy barrier to the annealing process. The other oft-mentioned parameter of the peak, the pre-exponential s, is not so useful as it cannot be directly measured and its value depends on the kinetic model chosen, as do the values of the ratios b and N/n_0.

A simple test to determine whether a glow peak departs from the Randall and Wilkins model may be made by comparing the value of the activation energy obtained using the initial rise with that found

from Grossweiner's or Booth's methods or any elaboration of these (e.g. Refs. (8),(10) and (11)).

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