charge release. It is therefore probable that line B indicates the temperature of a hole release and line C indicates the temperature at which an electron is released in the various alkali halides. A more detailed discussion of the defects associated with lines B and C in Fig. 11 would be too speculative to include at the present time.

VI. SUMMARY

The glow-curve measurements from a variety of LiF samples have been described. These have been used to determine the activation energies and pre-exponential (frequency) factors describing the untrapping processes for the majority of the glow peaks. In many cases it has been determined if a particular glow peak is related to electron or hole release.

An attempt has been made to relate specific peaks to charge release from known defect centers. The peak at 115°K ($E=0.32$ eV) is associated with the H center; the peak at 133°K ($E=0.26$ eV) has been attributed to the V_K center and the 194°K ($E=0.53$ eV) peak to the V_t center. Despite the similarity of the annealing temperature for the V_F center with the glow peak at 225 or 255°K, the glow peaks arise from different defects.

Finally, the annealing temperatures associated with a variety of processes, observed for different alkali halides, have been compared. Trends, similar to the Ivey-Mollwo relation, are observed and indicated that the annealing temperatures associated with a variety of processes can be correlated with the lattice parameter.

ACKNOWLEDGMENT

We are grateful to Miss E. Wolfson for performing some of the numerical integrations used in the activation-energy analysis.

PHYSICAL REVIEW VOLUME 155, NUMBER 3 15 MARCH 1967

Numerical Analysis of Charge-Redistribution Processes Involving Trapping Centers*

P. J. KEMMEY† AND P. D. TOWNSEND†
Explosives Laboratory, Picatinny Arsenal, Dover, New Jersey

AND

P. W. LEVY
Brookhaven National Laboratory, Upton, New York

(Received 1 September 1966)

A method for calculating charge-transfer processes in solids has been developed which is particularly suited for use with a computer. In this instance it has been applied to the computation of thermoluminescent glow curves. The concentrations of all defects in the crystal, which enter into the calculations, and all normal lattice sites in the host crystal are specified. Also, the initial electron, hole, and exciton, i.e., excited-state, populations are specified. The computation proceeds in arbitrarily small time steps. During each step the concentrations of trapped charge, the carrier concentrations, the radiative relaxations of excited centers, etc. are adjusted in accord with the physical processes involved. The temperature is fixed during each computational time increment, but may be made an arbitrary function of time. When used to analyze experimental data, some initial conditions usually are fixed and a process of successive approximations is used to determine the remaining parameters, e.g., activation energies and preexponential factors. The method is designed to analyze data in cases which cannot be described by tractable analytical expressions or when a closed expression cannot be applied readily. It has been used for analyses of measurements of thermoluminescence in lithium fluoride by Townsend, Clark, and Levy. As an example, the analysis of one of their glow peaks is included.

THERMOLUMINESCENCE is a useful tool for studying the nature, thermal stability, concentrations, etc., of shallow-electron and hole-trapping centers in luminescent materials. The thermoluminescent process involves the thermal release of trapped charges, the possible retrapping of these charges in the original or in other traps, and their ultimate trapping by recombination and/or luminescent centers. Recombination may or may not involve the emission of light. Experimental results are usually presented as light intensity as a function of temperature or time. Curves of such results are referred to as thermoluminescence spectra or glow curves.

In a few cases the equations describing the physical processes which give rise to the glow curves can be

* Research performed at Brookhaven National Laboratory and supported jointly by Picatinny Arsenal and the U. S. Atomic Energy Commission.

† Guest scientist at Brookhaven National Laboratory, Upton, New York.

solved directly.[1] In most cases, however, one has to resort to treating only oversimplified physical cases, or to the use of solutions involving approximations.[2] In many cases the physical processes being considered are quite simple, but the differential equations describing them are not integrable. A numerical method for dealing with such cases will be described below.

The initial step in the method is to assume that for charge-transfer processes, or thermoluminescence processes in particular, the crystal consists of a large number of normal lattice sites and a set of defects of different types. An initial concentration of trapped holes, electrons, and of free carriers is also assumed. After fixing initial concentrations, the temperature either remains constant or is varied as some function of time. The changes in occupancy of the defect centers and the carrier concentrations are calculated for arbitrarily small time intervals, and a system of bookkeeping is used to keep track of the concentrations. This calculation is most conveniently done using a digital computer, and this method is developed in a form suitable for that purpose.

The concentrations of defects are described by the quantities P_{nj}, where j labels the type of defect and n refers to the electronic state. Defects may be considered neutral, electron-occupied, hole-occupied, or in an excited, or exciton-occupied, neutral state corresponding to $n=1$, 2, 3, and 4, respectively. The reason for this particular choice of labels is given below. It may not be possible for a given defect to exist in all of these states, and certain states, for example doubly charged states, are not considered in this calculation.

The concentrations of free charges and normal lattice sites are described in the same way as the defect concentrations and are assigned a particular value of j, say l. The lattice sites may also be in one of four states: normal, electron, hole, or exciton occupied, again corresponding to $n=1$, 2, 3, and 4, respectively. Note that it is unnecessary to include separate terms for free-carrier concentrations since they are being described as charged states of normal lattice sites.

The calculation proceeds as a function of time, and in each small time interval δ_v the temperature T is taken to be a constant. In each time interval, the first step is to calculate the net rate of trapping of carriers at each trap. This net rate is the difference between the rate for carrier trapping and the rate at which the carriers are thermally released. The trapping rate is equal to the product of the carrier concentration, the trap concentration, and a trapping parameter. The untrapping rate is given by an Arrhenius expression of the form (const) $\times\exp(-E/kT)$, where the constant is the product of a "frequency factor" and the concentration of traps containing carriers, and E is an activation energy. The net rate of trapping of a carrier at a particular center is the difference between these two rates as expressed by the following equation:

$$A_{nmj}=X_{nmj}P_{hl}P_{nj}-Y_{nmj}P_{mj}\exp(-E_{nmj}/\mathrm{kT})\cdots, \quad (1)$$

where $m>n$ and $h=m-n+1$.

In this expression A_{nmj} is the net rate of a process in which the jth defect in an initial-state n traps a carrier and is left in state m. The term $X_{nmj}P_{hl}P_{nj}$ gives the rate of trapping by a center whose concentration is P_{nj}. The concentration of the carriers being trapped is P_{hl}, where l is the index assigned to the lattice and h indicates which carrier is being trapped. The use of the expression $h=m-n+1$ ensures that the concentration of the appropriate carrier is used in the calculation. The validity of this expression is demonstrated in Table I.

TABLE I. Relation between indices describing trapping processes and indices specifying required carrier.

Initial state of trap	Final state of trap	Carrier required	$h=m-n+1$
n	m		
1 neutral	2 electron-occupied	electron	2
1 neutral	3 hole-occupied	hole	3
1 neutral	4 exciton-occupied	"exciton"	4
2 electron-occupied	4 exciton-occupied	hole	3
3 hole-occupied	4 exciton-occupied	electron	2

The X_{nmj} is the trapping parameter, and has the dimensions of the product of a cross-section and a carrier velocity. In the second term in Eq. (1), P_{mj} is the concentration of centers of the jth type in state m, the final state of the trapping process. Y_{nmj} is the pre-exponential factor and E_{nmj} is the appropriate activation energy for untrapping.

For any defect, one or more of X_{nmj}, Y_{nmj}, and E_{nmj} may be zero. For example, when no retrapping effects are being considered, X_{nmj} is zero and A_{nmj} would be negative.

The net trapping rates A_{nmj} are used to calculate the concentration changes in the initial and final states of the individual defects as follows:

$$\delta P_{nj}=-\delta P_{mj}=-A_{nmj}\delta t. \quad (2)$$

Note that this ensures that the sum of the concentrations for all charge states of a defect remains a constant.

When (1) and (2) have been evaluated for all values n, m, and j in a particular time interval, it is still necessary to adjust the lattice charge concentrations to reflect the transfer of charge to or from the defects.

[1] For discussions of the theoretical treatment of glow curves, see G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, New York, 1949); D. Curie, *Luminescence in Crystals* (Methuen and Company Ltd., New York, 1963); and a recent review by K. H. Nicholas and J. Woods, Brit. J. Appl. Phys. **15**, 783, 1964.

[2] P. Townsend, C. D. Clark, and P. W. Levy, preceding paper, Phys. Rev. **155**, 908 (1967).

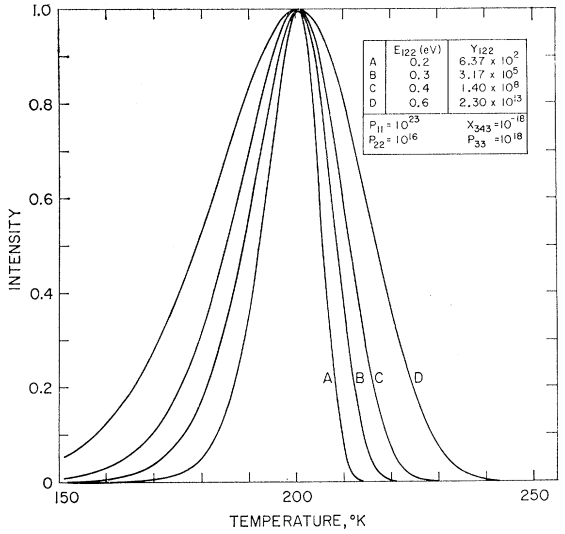

FIG. 1. Calculated glow peaks using the indicated activation energies, adjusted to have their maxima at the same temperature by varying the frequency factor Y_{122}.

The change in lattice charge concentrations is given by

$$\delta P_{il}=\sum_j \sum_n A_{nqj}\delta t, \tag{3}$$

where $q=n+i-1$ and $n\neq i$, $i\neq 1$.

Expression (3) gives the total number of electrons, holes, and excitons which are released from defects during the time interval δt, and are to be added to the lattice states. The corresponding change in the number of neutral lattice states is given by

$$\delta P_{1l}=-\sum_i \delta P_{il},$$

or

$$=-\sum_i \sum_j \sum_n A_{nqj}\delta t; \tag{4}$$

again $q=n+i-1$, $n\neq i$, $i\neq 1$.

The expression for the index q ensures that, in dealing with a particular carrier, only those processes involving that carrier are included. The expression $q=n+i-1$ is, in fact, the same as that for h following Eq. (1). This correspondence and the validity of the relation can be seen by substituting q for m and i for h in Table I.

When the increments given in Eqs. (2), (3), and (4) have been calculated, they are added to the appropriate concentrations and the calculation proceeds to the next time interval.

To calculate the thermoluminescent spectra, i.e., glow curves, the luminescent intensity must be determined for each time interval. The light is emitted during radiative relaxation of the excited states of one or more recombination centers. The number of light quanta L_r emitted from the rth center is given by

$$L_r=P_{4r}M_r\delta t, \tag{5}$$

where M_r is the radiative-recombination probability. In the examples given below, $M_r=1/\tau_r$ is used where τ_r is a constant lifetime. The changes in excited-state and ground-state concentrations are given by

$$\delta P_{4r}=-\delta P_{1r}=P_{4r}\delta t/\tau_r.$$

From a few arbitrarily chosen examples, one can show that large changes in the shapes of glow curves may be obtained by varying some of the trapping and untrapping parameters and the relative concentrations of defects. This facilitates the selection of reasonably good parameters in the analysis of experimental data. For example, consider a case where untrapping occurs from a single electron trap. It is possible to construct any number of glow curves with maxima at the same temperature by using a variety of E and Y values of the activation energy E and the frequency factor Y. Figure 1 shows four such curves having the indicated activation energies.[3] The other parameters are fixed and are given in the figure. In all the following examples, temperature is taken to be a linear function of time and a heating rate of 0.1° K/sec is used.

Consider a further case where retrapping is made an important parameter. This is done by making the electron-trap cross section comparable to the cross section of the recombination center.

In this case, the concentration of recombination centers has an important effect on the shape of the glow curve. In constructing Fig. 2, the recombination-center concentration has been varied from a value equal to that of the electron trap to a value two orders of magnitude

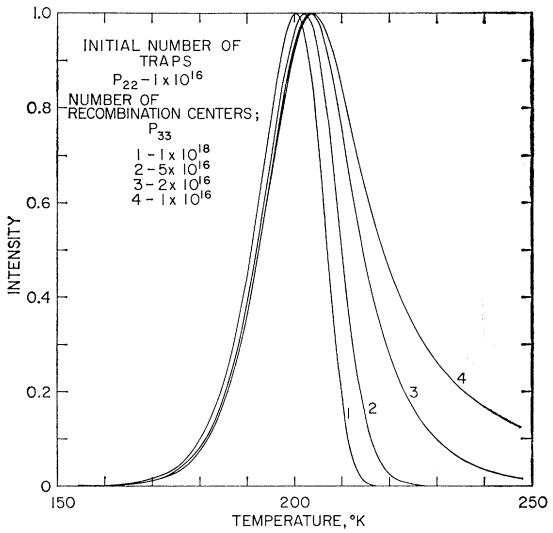

FIG. 2. Calculated glow curves for cases where retrapping occurs showing that the curve shape depends on the number of recombination centers. $E=0.5$ eV, $Y=0.58\times 10^{11}$ sec^{-1}.

[3] Values of E were assumed and those of Y were calculated from $Y=\text{const}\ E\exp(E)$ in order to have all the peak maxima occur at the same temperature. The relationships between the activation energy, frequency factor, and peak temperature are discussed in Ref. 2.

greater. The curves have been computed for the following conditions: a lattice containing 10^{23} sites, i.e., $P_{11}=10^{23}$, the initial number of electron occupied traps is $P_{22}=10^{16}$, the number of recombination centers P_{33} was varied from 10^{16} to 10^{18}, and the capture cross sections for trapping by the recombination center P_{33} or by an empty trap P_{12} were both given the value 10^{-18}, i.e., $X_{343}=X_{122}=10^{-18}$. It is evident from the set of curves in Fig. 2 that any analysis using only the leading edges of the glow peaks would yield similar energies; however, the high temperature sides of the peaks are sufficiently different to be useful in determining the retrapping contribution occurring experimentally. An illustration of the variation of the different concentrations as a function of time is shown in Fig. 3. These curves give the variations in concentrations which occur during the computation of the fourth curve of Fig. 2. This figure shows the change from an initial condition in which filled electron traps and filled hole traps, i.e., the recombination centers, are populated, P_{22} and P_{33}, respectively. Towards the end of the process they become completely empty. During the emission of light, the concentrations of free electrons, P_{12}, and excited recombination centers, P_{43}, have finite values.

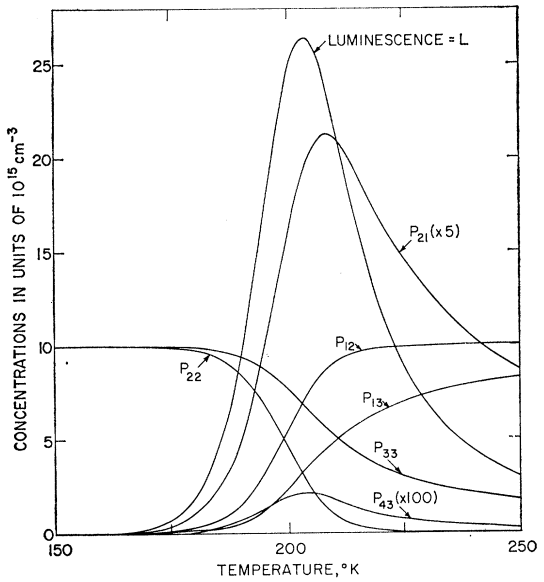

FIG. 3. The charge-state populations and luminescent emission as a function of temperature during the calculation of curve 4 of Fig. 2. The different curves refer to neutral lattice sites, P_{11}; free electrons, P_{21}; empty electron traps, P_{12}; filled electron traps, P_{22}; hole-filled recombination centers, P_{33}; excited recombination centers, P_{43}; and empty recombination centers, P_{14}.

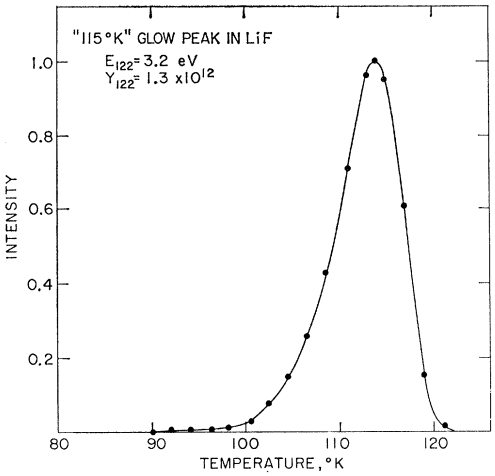

FIG. 4. Experimental points taken from the previous paper (Ref. 2) for the 115°K glow curve in LiF and the computed curve for a model in which only simple untrapping is occurring.

An example of the application of the calculation to experimental data is shown in Fig. 4. The data points are those for the 115°K peak taken from the preceding paper.[2] For the analysis of experimental data, the values for E and Y are not fixed. Initial approximate values are chosen, and they are varied by the computer program to determine the values giving the best least-squares fit to the experimental data. In this instance, initial concentrations used were the same as those used to compute Fig. 3, except that an excess of recombination centers is assumed,[4] namely, $P_{33}=10^{18}$. The agreement between the calculated curve and the data indicates that these data can be described adequately in terms of a simple untrapping process. There seems, in this case, to be no need to consider either retrapping processes or exhaustion of recombination centers.

This method has also been applied to the glow peaks obtained from KN_3 and $CaCO_3$. In the latter case, retrapping effects must be considered; however, it is still possible to fit the data with an appropriate choice of trapping cross sections.

Finally, errors which arise in the numerical integrations have been found to be negligibly small by computing glow-peak temperatures for cases in which an analytic expression for the peak temperature is available.

[4] The excess of recombination centers has the result that the retrapping process becomes unimportant.