Decay of Phosphorescence in $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, and $CaSO_4$

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The decay of phosphorescence in $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, and $CaSO_4$ obeys the relation $I = I_0 [b/(b+t)]^m$, where the parameters b and m are functions of the temperature of decay and the fraction of initially filled traps (i.e., the excitation time). This result can be derived from the usual model for second-order decay, and the results predicted for the behavior of b and m with temperature and excitation time are the same whether it is assumed that the traps and luminescent centers are independent of each other or are due to the same defect or impurity center. It is shown, however, that in both cases the predicted behavior is not in agreement with the experimental results for the crystals studied here.

I. INTRODUCTION

THE decay of emission in thermoluminescent materials is generally referred to as a first- or second-order process depending on whether the electrons involved in the various transitions are confined to a localized center or spend part of their time in the conduction band. The first-order decay is exponential in form whereas the form of the second-order process involves a power law relation.

Various models have been proposed which predict the observed form of the second-order decay and make it possible to duplicate mathematically the decay of some phosphors such as ZnS. However, further verification of the models has been lacking; in particular, there has been no effort to verify the dependence of such parameters as temperature and fraction of initially filled traps. This paper describes the results of an investigation of these parameters in the decay curves of some common thermoluminescent minerals including $CaCO_3$ (calcite and aragonite), $MgCO_3$ (magnesite), $CaMg(CO_3)_2$ (dolomite), and $CaSO_4$ (anhydrite). All of these minerals exhibit thermoluminescent decay features which are characteristic of the second-order mechanism. It will be shown that none of the models proposed for second-order decay predict the observed dependence on temperature and initial filling of traps except at temperatures well above the glow peak.

II. THEORY

Figure 1 illustrates the various transitions which occur during second-order decay. The traps are considered as discrete levels denoted by F. The levels at L are luminescent centers and x, y, and z denote the numbers of empty luminescent centers, empty traps, and filled traps, respectively; α, γ, and β are the probabilities of filling empty traps, emptying filled traps, and filling empty luminescent centers, respectively. It should be pointed out that retrapping of an electron at the same center where it was originally confined can be neglected, since it can be considered that the electron had never left the trap, which only has the effect of reducing the value of γ. This case is analogous to retrapping in first-order decay.

It is clear that the decay of emission for the second-order process is proportional to the number of empty luminescent centers and the number of filled traps, the latter being determined by the rate at which the traps are emptied and by the rate at which retrapping and recombination takes place. On the basis of this model, which has been described and elaborated upon by a number of authors,[1-4] it is possible to obtain an expression for the decay of phosphorescence as a function of time. Two cases must be considered: (1) where the luminescent centers are independent of the traps, and (2) where the luminescent centers and traps are different valence states of the same impurity ion or defect site.

The case where the luminescent centers are independent of the traps will be considered first. With reference to Fig. 1, the following equations can be written:

$$dz/dt = -dy/dt = -\gamma z + \alpha n y, \qquad (1)$$

$$dx/dt = -\beta n x, \qquad (2)$$

$$dn/dt = \gamma z - \alpha n y - \beta n x, \qquad (3)$$

$$N = y + z, \qquad (4)$$
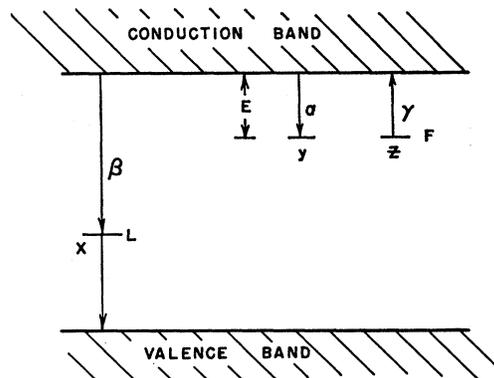
where n is the number of electrons in the conduction

FIG. 1. Energy levels involved in second-order decay.

[1] M. P. Lord, A. L. G. Rees, and M. E. Wise, Proc. Phys. Soc. (London) **59**, 473 (1947).
[2] R. T. Ellickson and W. L. Parker, Phys. Rev. **70**, 290 (1946).
[3] H. A. Klasens and M. E. Wise, Nature **158**, 483 (1946).
[4] E. I. Adirovitch, J. phys. radium **17**, 49 (1956).

band and N is the total number of traps. Only three of the above equations are independent. A fourth independent equation is obtained by assuming that

$$dn/dt \approx 0, \qquad (5)$$

which is a good approximation as long as $x \gg n$.

Combining Eqs. (3), (4), and (5) gives

$$n = \gamma z / [\alpha(N-z) + \beta x], \qquad (6)$$

and combining Eqs. (1), (2), and (3) gives

$$dn/dt = dx/dt - dz/dt. \qquad (7)$$

From Eqs. (4), (5), and (7), it follows that

$$z \approx x - x_0 + z_0 = x + N - y_0 - x_0, \qquad (8)$$

where x_0, y_0, z_0 are the values of x, y, and z when $t = t_0$, the time when the exciting radiation ceases and the decay of emission begins. When (8) is substituted into (6) and the resulting equation in n is substituted into Eq. (2), a relation involving only x and t is obtained,

$$-\frac{dx}{dt} = \frac{\gamma x(x + N - y_0 - x_0)}{\zeta(y_0 + x_0 - x) + x} = I(x), \qquad (9)$$

where $\zeta = \alpha/\beta$ is the ratio of the probability of retrapping to the probability of capture by luminescent centers. This can be integrated to give

$$\frac{x}{x_0}\left[\frac{N - y_0 - x_0 + x}{N - y_0}\right]^{-\{1 + [(\zeta - 1)(N - y_0 - x_0)]/[\zeta(y_0 + x_0)]\}}$$
$$= \exp\left[\frac{-(N - y_0 - x_0)}{\zeta(y_0 + x_0)}\gamma(t - t_0)\right]. \quad (10)$$

It is reasonable to assume that the rate constants α and β are independent of the temperature of decay, whereas γ is related to the temperature T through the Boltzman factor,

$$\gamma = \nu e^{-E/kT}. \qquad (11)$$

The rate constant, ν, is the rate at which a trapped electron attempts to escape and E is the trap depth shown in Fig. 1. Since Eq. (10) cannot be solved for x in terms of t, it is not possible to obtain an equation for the intensity of emission, I, as an explicit function of t. Instead, I must be calculated by approximation methods from Eqs. (9) and (10) for given values of $t - t_0$.

In many thermoluminescent crystals a simple relation exists between the number of luminescent centers, x, and the number of trapped and free electrons. This is a result of the part played by the holes created in the valence band when electrons are raised to the conduction band and captured by traps during excitation. In many cases an impurity or defect center cannot act as a luminescent center until it has captured one of these holes from the valence band. An example of this is CdS containing monovalent silver as the activator.[5]

In this case the number of luminescent centers will be equal to the number of holes created by the excitation process, or

$$x_0 = z_0 + n_0 \approx z_0.$$

If nonradiative transitions occur at a negligible rate, then the rate of emptying traps will be equal to the rate of filling luminescent centers and $x \approx z$. When this relation is substituted into Eq. (6) and the resulting equation substituted into (2) a much simpler relation for I is obtained:

$$I = -\frac{dx}{dt} = \frac{\beta\gamma x^2}{\alpha(N-x) + \beta x} = \frac{\gamma x^2}{\zeta(N-x) + x}. \qquad (12)$$

Equation (12) can be integrated to give

$$\gamma(t - t_0) = (1 - \zeta)\log_e\left(\frac{z_0}{x}\right) + \zeta N\left(\frac{1}{x} - \frac{1}{z_0}\right). \qquad (13)$$

Equations (12) and (13) must again be solved by approximation methods to obtain values of I corresponding to various values of $t - t_0$.

The case where the luminescent centers are a different valence state of the impurity or defect which serves as the trapping level has been worked out by Lehovec.[6] In this case the result for n is given by

$$n = \frac{\gamma(x + aA - B)}{\alpha[B - (a+1)x] + \beta x}, \qquad (14)$$

where a is the valence number of the tapping centers, A is the total number of ions or defects, and B is the number of negatively charged centers present in the crystal which do not participate in the phosphorescent transitions but still contribute to the charge in the crystal. For a discussion regarding the validity of independently varying the values of A and B the reader is referred to the original paper by Lehovec. From Eq. (14) the intensity of emission is given by

$$I = -\frac{dx}{dt} = \beta nx = \frac{\beta\gamma x(aA - B + x)}{\alpha(a+1)[B/(a+1) - x] + \beta x}. \qquad (15)$$

Although it has not been pointed out by previous authors, Eq. (15) is of the same form as (9). In fact, if α in (15) is replaced by $\alpha/(a+1)$ and the substitutions,

$$A = y_0 + x_0 + N/a,$$
$$B = (a+1)(y_0 + x_0),$$

are made, the result will be identical with (9). Furthermore, for the special case where $B/a = A$, Eq. (15) reduces to (12) with the above substitutions. The result is that the decay curve has the same form regardless of whether the luminescent centers are independent of the traps. Also, when the number of

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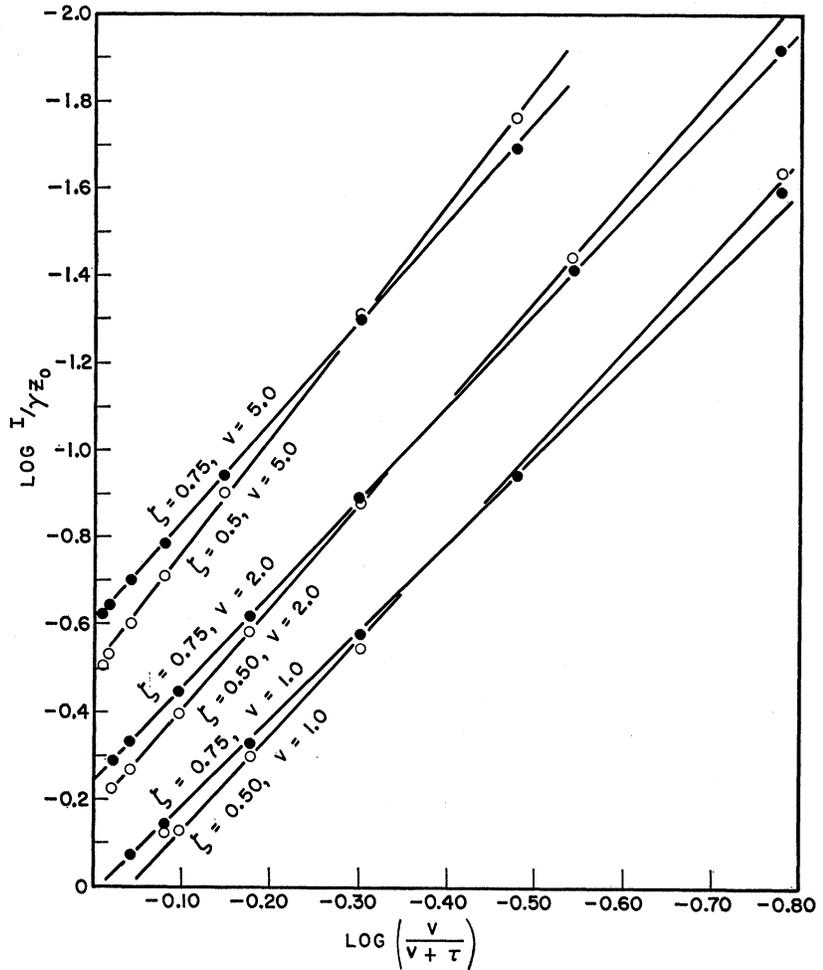[6] K. Lehovec, J. Opt. Soc. Am. 45, 219 (1955).

FIG. 2. Theoretical decay curves with points computed from Eqs. (12) and (13) for $v = N/z_0$ and $\tau = \gamma(t - t_0)$.

charges due to centers participating in thermoluminescence is equal to the number of all other charges, the result for the dependent case is equivalent to the result for the independent case in which the luminescent centers interact with holes from the valence band.

Equation (15) is based on the assumption that a luminescent center is formed by removing an electron from a trapping center. This appears to be the most likely condition but it is interesting to consider the alternate case where a trap is formed by removing an electron from a luminescent center. In this case,

$$I = -\frac{dx}{dt} = \frac{\beta\gamma x(aA - B - x)}{\alpha(1-a)[B/(1-a) + x] - \beta x}.$$

This result can be obtained from Eq. (15) by replacing $(a+1)$ by $(1-a)$ and x by $-x$. Therefore, the form of the decay curve is the same in both cases.

Equation (12) reduces to the bimolecular decay expression when $\zeta = 1$. In this case the probability of retrapping is equal to the probability of capture by a luminescence center and

$$dx/dt = -\gamma x^2/N,$$

or

$$x = \frac{N}{\gamma}\left[\frac{1}{(N/\gamma z_0) + (t - t_0)}\right],$$

so that

$$I = -\frac{dx}{dt} = \frac{\gamma z_0^2}{N}\left[\frac{V}{V + (t - t_0)}\right]^2, \qquad (16)$$

where $V = N/\gamma z_0$ is inversely proportional to the fractional number of traps filled at $t = t_0$ when the exciting radiation is removed.

III. COMPARISON WITH EXPERIMENT

All of the common thermoluminescent minerals such as calcite, dolomite, magnesite, anhydrite, and aragonite have decay curves which can be fitted to the expression,

$$I = I_0[b/(b + t)]^m, \qquad (17)$$

during the early part of their decay. In general, decay curves of the form of Eq. (17) have been attributed to the second-order mechanism discussed earlier. The
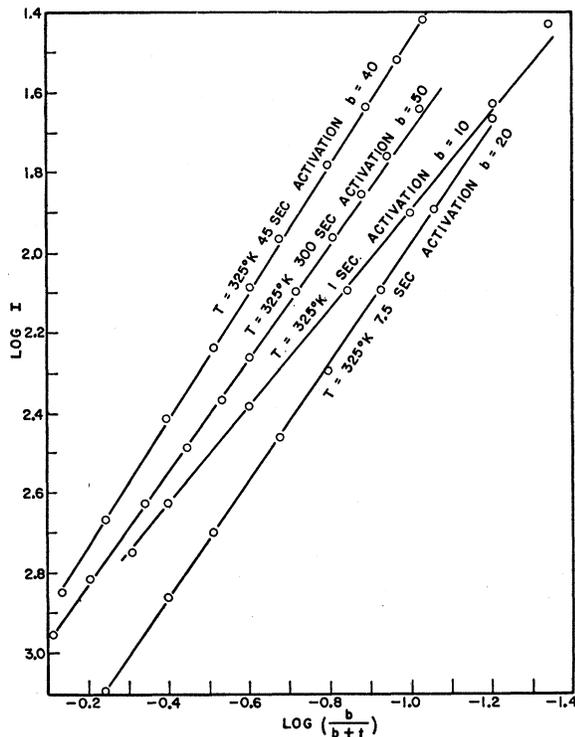
FIG. 3. Experimental decay curves for a calcite sample containing 100 ppm Mn^{++}

ture T, activation energy E, and frequency factor ν. For values of E, ν, and T representative of those for calcite, dolomite, etc., the curves of Fig. 2 fit Eq. (17) for periods in excess of 10^3 seconds. In most experimental observations the periods for which (17) is applicable are of the same order of magnitude. This is illustrated in Fig. 3 where some experimental decay curves are shown for a calcite sample. Although the curves of Fig. 2 were calculated by assuming that the luminescent centers are independent of the traps, it is clear from the earlier discussion that these curves can be duplicated for the case where the luminescent centers and traps are due to the same ion or defect (when $B/a=A$).

It can also be shown by carrying out a sufficient number of calculations that Eqs. (9) and (10) can be fitted to Eq. (17). The results in this case are based on the assumption that the number of filled traps is not related to the number of luminescent centers. Some decay curves computed from Eqs. (9) and (10) are illustrated in Fig. 4 and the following observations can be made: (1) The curves fit Eq. (17) over a shorter range of $\gamma(t-t_0)$ than before; (2) b still decreases with z_0/N but not in a linear fashion except when ζ is close to 1; and (3) m still increases with excitation time when

parameters b and m are functions of temperature and length of activation time for an isolated glow peak.[7]

Equation (16), which corresponds to the case of bimolecular decay ($\zeta=1$), fits the experimental relation for all time and gives $b=v=N/\gamma z_0$ and $m=2$. This means that b should decrease with excitation time for this particular case.

It can be shown, by carrying out a sufficient number of calculations, that the more general Eqs. (12) and (13) can also be fitted to Eq. (17) over periods of time as long as those observed experimentally. The best fit is obtained by taking $b=N/\gamma z_0$ which means that b should still decrease with excitation time. For values of ζ much larger or much smaller than 1 the fit is very poor [actually for $\zeta \to 0$, Eq. (12) reduces to an exponential decay]. The values of m obtained graphically from these results increase above 2 as ζ becomes smaller than 1 and approach zero as ζ becomes larger than 1. For $\zeta<1$, m decreases with z_0/N and for $\zeta>1$, m increases with z_0/N. Therefore, when it exceeds 2, m should increase with excitation time and when it is less than 2, it should decrease with excitation time. To illustrate these results, some decay curves computed from Eqs. (12) and (13) are shown in Fig. 2 for some representative values of z_0/N and ζ. For simplification, the time variable used in Fig. 2 is multiplied by γ which can be calculated from Eq. (11) for a given tempera-

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[7] W. L. Medlin, J. Phys. Chem. Solids (to be published).

FIG. 4. Theoretical decay curves with points computed from Eqs. (9) and (10) for $\tau=\gamma(t-t_0)$.

TABLE I. Experimental values of b and m.

Sample	Impurity	Glow peak	Activation time (sec)	Temperature (deg. K)	b (sec)	m
Calcite	100 ppm Mn⁺⁺	350°K	45	273	20	0.72
Calcite	100 ppm Mn⁺⁺	350°K	45	300	30	0.84
Calcite	100 ppm Mn⁺⁺	350°K	300	300	60	0.70
Calcite	100 ppm Mn⁺⁺	350°K	1800	300	100	0.57
Calcite	100 ppm Mn⁺⁺	350°K	1.0	325	10	1.19
Calcite	100 ppm Mn⁺⁺	350°K	7.5	325	20	1.44
Calcite	100 ppm Mn⁺⁺	350°K	45	325	40	1.63
Calcite	100 ppm Mn⁺⁺	350°K	300	325	50	1.41
Calcite	100 ppm Mn⁺⁺	350°K	1800	325	50	0.81
Calcite	100 ppm Mn⁺⁺	350°K	45	350	15	1.81
Calcite	100 ppm Mn⁺⁺	350°K	300	350	2	0.97
Calcite	100 ppm Mn⁺⁺	350°K	1800	350	2	0.91
Calcite	100 ppm Mn⁺⁺	350°K	45	375	0	1.04
Calcite	100 ppm Mn⁺⁺	350°K	300	375	0	0.60
Calcite	40 ppm Mn⁺⁺	470°K	45	500	10	1.6
Calcite	40 ppm Mn⁺⁺	470°K	300	500	12	1.3
Calcite	40 ppm Mn⁺⁺	470°K	45	540	35	1.2
Calcite	40 ppm Mn⁺⁺	470°K	300	540	60	1.1
Calcite	500 ppm Pb⁺⁺	410°K	45	390	200	1.4
Calcite	500 ppm Pb⁺⁺	410°K	300	390	300	1.7
Calcite	500 ppm Pb⁺⁺	410°K	45	420	40	2.6
Calcite	500 ppm Pb⁺⁺	410°K	300	420	100	2.9
Calcite	500 ppm Pb⁺⁺	410°K	45	440	12	2.3
Calcite	500 ppm Pb⁺⁺	410°K	300	440	12	2.0
Calcite	500 ppm Pb⁺⁺	410°K	45	455	0	1.5
Calcite	500 ppm Pb⁺⁺	410°K	300	455	0	0.90
Anhydrite	680 ppm Mn⁺⁺	390°K	45	300	30	0.92
Anhydrite	680 ppm Mn⁺⁺	390°K	300	300	60	0.78
Anhydrite	680 ppm Mn⁺⁺	390°K	45	335	150	1.74
Anhydrite	680 ppm Mn⁺⁺	390°K	300	335	200	1.59
Anhydrite	680 ppm Mn⁺⁺	390°K	45	360	40	1.57
Anhydrite	680 ppm Mn⁺⁺	390°K	300	360	50	1.34
Anhydrite	680 ppm Mn⁺⁺	390°K	45	390	20	1.54
Anhydrite	680 ppm Mn⁺⁺	390°K	300	390	25	1.35
Anhydrite	680 ppm Mn⁺⁺	390°K	45	420	5	1.36
Anhydrite	680 ppm Mn⁺⁺	390°K	300	420	10	1.07
Anhydrite	680 ppm Mn⁺⁺	390°K	45	455	5	1.12
Anhydrite	680 ppm Mn⁺⁺	390°K	300	455	10	1.06
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	300	40	0.51
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	300	150	0.62
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	325	30	0.88
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	325	60	0.90
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	355	30	1.25
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	355	50	1.23
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	390	25	1.88
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	390	15	1.43
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	420	15	1.16
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	420	10	0.84
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	45	455	10	1.22
Anhydrite	950 ppm Sb⁺⁺⁺	355°K	300	455	10	0.82
Aragonite	80 ppm Mn⁺⁺	250°K	45	245	15	1.1
Aragonite	80 ppm Mn⁺⁺	250°K	45	273	20	1.5
Aragonite	80 ppm Mn⁺⁺	250°K	300	273	30	1.3
Aragonite	80 ppm Mn⁺⁺	250°K	45	300	25	2.1
Aragonite	80 ppm Mn⁺⁺	250°K	300	300	25	1.7
Dolomite	1100 ppm Mn⁺⁺	330°K	45	273	40	0.91
Dolomite	1100 ppm Mn⁺⁺	330°K	300	273	70	0.71
Dolomite	1100 ppm Mn⁺⁺	330°K	45	300	70	1.4
Dolomite	1100 ppm Mn⁺⁺	330°K	300	300	110	1.0
Dolomite	1100 ppm Mn⁺⁺	500°K	45	480	50	0.94
Dolomite	1100 ppm Mn⁺⁺	500°K	300	480	130	1.1
Dolomite	1100 ppm Mn⁺⁺	500°K	45	530	10	1.1
Dolomite	1100 ppm Mn⁺⁺	500°K	300	530	40	1.1
Magnesite	260 ppm Mn⁺⁺	220°K	45	250	5	1.2
Magnesite	260 ppm Mn⁺⁺	220°K	300	250	5	1.3
Magnesite	260 ppm Mn⁺⁺	470°K	45	480	5	1.1
Magnesite	260 ppm Mn⁺⁺	470°K	300	480	30	0.93

$m>2$ and decreases when $m<2$. These results also apply to the case where the luminescent centers are due to the same ion or defect and $B/a \neq A$.

The results of Figs. 2 and 4 show that the same behavior is predicted for b and m in all cases: (1) b should decrease with excitation time, and (2) m should increase with excitation time if it is greater than 2 and decrease with excitation time if it is less than 2.

In order to test these results, a large number of decay curves were measured after various excitation times for the prominent glow peaks in thermoluminescent samples of calcite,[8] dolomite,[9] anhydrite,[7] aragonite, and magnesite.[7] The samples were prepared synthetically by coprecipitating activator impurities such as Mn^{++}, Pb^{++}, Zn^{++}, etc., with the matrix material. The decay curves for all of these minerals can be fitted to Eq. (17) over periods of the order of 10^3 seconds. Some representative values of b and m determined graphically from the decay curves of these samples are given in Table I. In most cases it was impossible to measure the decay curves over a very large range of temperatures because of interference from neighboring glow peaks. Some exceptional cases for which the glow peaks are fairly well isolated are anhydrite with Mn^{++} and Sb^{+++} activators, calcite with Pb^{++} activator, and aragonite with Mn^{++} activator.

The results of Table I show that the predicted increase in b is not observed in any of the samples except at temperatures well above the glow peak. Also, the results for m agree with the predicted behavior in less than half of the cases studied. It can be concluded that none of the models described in the previous section account for the experimental results at temperatures near the glow peak during the early part of the decay period.

For very long decay times, Eq. (13) reduces to the exponential form,

$$I \approx \left[\frac{x_0 \gamma (y_0 + x_0 - N)}{\zeta(y_0 + x_0) + (\zeta - 1)(N - y_0 - x_0)} \right]$$

$$\times \exp\left[-\frac{(y_0 + x_0 - N)\gamma(t - t_0)}{\zeta(y_0 + x_0) + (\zeta - 1)(N - y_0 - x_0)} \right],$$

but it is questionable whether this result is valid since the approximation $z \approx x$ is probably not very good at long decay times. Equation (15) which should be valid for all times, reduces to a bimolecular form for long decay times,

$$I \approx \frac{x_0^2}{\zeta(y_0 + x_0)} \left\{ \frac{[\zeta(y_0 + x_0)/x_0]}{[\zeta(y_0 + x_0)/x_0] + \gamma(t - t_0)} \right\}.$$

Decay curves for several of the samples listed in Table I were measured for long decay periods (up to 3 hours) and in all cases the curves did not assume either a bimolecular or exponential form. The results for long period decay provide further evidence that the second-order mechanism does not account for the observed results.

It should be noted that other decay mechanisms involving nonlocalized transitions are possible[10] and therefore the results obtained here do not conclusively rule out the second-order process. The possibility of distributions of trapping levels must certainly be considered in this regard.[11] Also, the effect of nonradiative transitions which has been neglected here may be important since the number of these may be a strong function of temperature.

IV. CONCLUSIONS

The second-order decay process leads to a decay curve of the form

$$I = I_0 \left(\frac{b}{b+t} \right)^m,$$

during the early part of the decay. This result applies to the case where the traps and luminescent centers are independent of each other as well as the case where they are not. The decay curves for the common thermoluminescent minerals, calcite, dolomite, anhydrite, aragonite, and magnesite, are all of this form during the early part of their decay and both b and m are functions of the temperature and activation time. However, the behavior predicted for b and m as functions of these conditions for the second-order process is not observed in any of the crystals studied here except at temperatures well above the glow peak. It is concluded that some other mechanism is necessary to explain the decay curves of these minerals at temperatures near and below the glow peak.

ACKNOWLEDGMENTS

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