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Abstract. The dose dependence of the concentration of point defects in alkali-halides as well as other crystals, as exhibited by the dependence of the thermoluminescence (TL), optical absorption and ESR on the dose of non-ionizing UV excitation is studied using numerical simulation. The relevant set of coupled rate equations are first written and plausible sets of trapping parameters are chosen. Instead of using simplifying assumptions previously used for reaching conclusions concerning this dose behavior, exact numerical solutions have now been reached. Depending on the parameters chosen, different dose dependencies are seen. In some cases, linear dose dependence is reached in a broad range. Sublinear dose dependence, close to a $D^{1/2}$ dependence when D is the dose of excitation can be reached when retrapping is stronger than trapping in other traps stabilizing the defects. When strong competition between stabilizing traps takes place, an initial linear range is observed followed by strong superlinearity and an approach to saturation. All these behaviors have been observed experimentally in TL measurements as well as ESR and optical absorption in different materials. Similarities and dissimilarities to linear and non-linear dose dependencies obtained experimentally and by simulations when ionizing irradiation is used for excitation are discussed.

1. Introduction

As described by Kelly[1], the simplest types of damage which may be produced by irradiation are the isolated interstitial atom and the isolated vacant lattice site. These may be produced by high energy X-ray or γ-ray photons and by β-rays and high energy particles, and be seen as color centers in optical absorption measurements or in ESR experiments. As explained by Hersh[2] and Pooley[3,4], such color centers may be produced by an excitonic mechanism, which means that UV photons with energy lower than the band gap may produce these point defects. Parker[5] reported on the exciton-induced F-center growth in KI and KBr crystals, where the F-center growth was found to be a volume process and the concentration was found to have a square-root dependence on the number of absorbed photons. Goldstein[6,7] also showed that in KI, the optical density at the F band peak goes like the square root of time of irradiation by deuterium UV light. Later, Kristianpoller and Israeli[8] and Israeli et al.[9] explained the linear and non-linear dose dependencies of thermoluminescence (TL), previously reported in different materials by these excitonic processes. Their assumption was that the

point defects produced by the UV light irradiated samples were stabilized by existing traps in the sample. Using some simplifying assumptions, these authors showed that whereas linear or sublinear dose dependence could be expected when a single type of trap was present, superlinear behavior, sometimes occurring, could be explained by competition between two or more trapping states. An example to this behavior can be seen in the work by Kortov et al.[10] who reported on a very strong superlinear dose dependence ($>D^3$) in non-ionizing UV excited ESR in MgO. Other publications on the dose dependence of point defects should be briefly mentioned. Mitchell et al.[11] reported on the formation of F- and M-centers in KCl by X rays, in which superlinear dose dependence of the optical density took place in certain dose ranges. Popov[12] described the optical production of V_2 centers in KBr and KBr:Tl and reported a quadratic dose dependence of TL, reflecting the dose dependence of the V_2 centers. Wieser et al.[13] found a $D^{1.44}$ dose dependence of the E_1' center in fused silica, based on optical absorption and TL measurements. Israeli and Kristianpoller[14] also described a superlinear dose dependence of UV irradiated KBr. On the other hand, Caldas and Mayhugh[15] reported on a $D^{0.55}$ dose dependence of phototransferred TL (PTTL) in $CaSO_4$:Dy X-irradiated and then illuminated by non-ionizing UV light. A review on the effects of ionizing and non-ionizing radiations on the production of point defects and their stabilization in traps has been given in the book by McKeever[16].

The purpose of the present work is to simulate the dose dependencies, be it linear, sublinear or superlinear, using the basic equations for the production and stabilization of point defects. This work is partially analogous to previous explanations of superlinearity due to different kinds of competition during the excitation and read-out, associated with transitions of charge carriers in a sample by ionizing radiation.

2. Theory

As suggested by Israeli et al.[9], it is assumed that pairs of defects are created in the crystal by UV irradiation, and that the creation rate is proportional to the photon flux of the incident UV radiation. In order to concentrate on the essence of the nonlinear dose dependence, we assume a homogeneous excitation of the whole sample, which means either relatively low absorption coefficient or, alternatively, a rather thin sample (for a discussion on the effect of the absorption coefficient on TL, see Chen et al.[17]). The constituents of such a pair which do not recombine immediately upon creation may be stabilized. It is assumed that one of the constituents is stabilized in a very short time, in a certain configuration specific to the type of the pair. This may be an F-centre in the case of a Frenkel pair. The second constituent of the pair remains mobile for a longer period of time and may be trapped in an existing trap or recombine with a defect of the first type. Several types of traps, T_i, for the mobile constituent are presumed. These traps have generally different trapping probabilities β_i (cm^3s^{-1}) and have different concentrations M_i (cm^{-3}). When more than one kind of trap exists, competition between the traps over the mobile constituents can be expected.
Based on these considerations, the coupled rate equations governing the process can be written as

$$\frac{dn_a}{dt} = X - \alpha n_a n_f, \qquad (1)$$

$$\frac{dm_i}{dt} = \beta_i (M_i - m_i) n_f, \quad i = 1, 2... \quad (2)$$

$$\frac{dn_f}{dt} = \frac{dn_a}{dt} - \sum_i \frac{dm_i}{dt}, \qquad (3)$$

where n_a (cm^{-3}) represents the concentration of the stabilized defects of the first type, n_f (cm^{-3}) is the concentration of the mobile defects which are free at the time t and α (cm^3s^{-1}) is the probability for a free defect to recombine with a stabilized defect. Equation (1) gives the time dependence of the density of the stabilized defects, X ($cm^{-3}s^{-1}$) is the rate of pair production associated with the dose rate,

and the second term represents the rate of recombination. Equation (2) describes the change in the densities of the occupation of the traps at which the mobile defects can be trapped, m_i being the concentration already trapped (out of M_i) at the instant t. Equation (3) gives the rate of change of the mobile defects in terms of the rates of change of the stabilized defects. Note that this presentation differs from that given by Israeli et al.[9] in the definition of m_i and in the assumption (mentioned above) that the absorption coefficient is small. Also, these authors resort from this point on to simplifying assumption whereas we proceed by solving numerically the simultaneous differential equations numerically using specific sets of trapping parameters as described below.
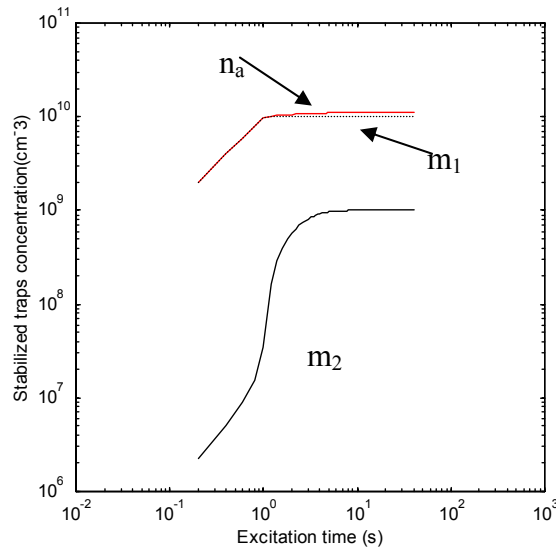
3. Numerical results
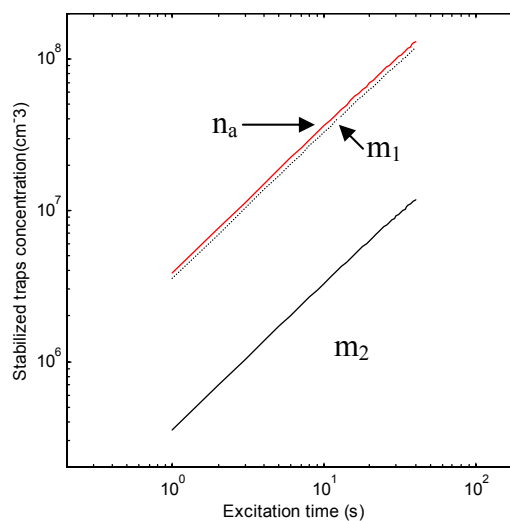
Figure 1. Simulated results of the excitation-time dependence of stabilized traps with parameters: $M_1=10^{10}$ cm^{-3}, $M_2=10^9$ cm^{-3}, $\alpha=10^{-7}$ cm^{3}s^{-1}, $\beta_1=10^{-12}$ cm^{3}s^{-1}, $\beta_2=10^{-12}$ cm^{3}s^{-1}, $X=10^{10}$ cm^{-3}s^{-1}.

In order to see the basic features of the relevant effect, we concentrate on the case with only two kinds of traps, i.e., i=1,2. Figure 1 depicts the dependence of the three concentrations, n_a, m_1 and m_2 on the excitation time which, with the given dose-rate represents the excitation dose. On the log-log scale, the three lines are seen to have a slope of nearly unity, meaning that the dependencies are nearly linear. Note that the difference between the values of n_a and m_1 is rather small, and this small difference represents the values of m_2 as could be expected from the conservation condition. Also, note that the values of n_f are negligibly small, and therefore are not seen on the given scale. It should be added that very similar results are reached if all the probabilities α, β_1 and β_2 are changed by the same factor with one difference. If all these probabilities are small, at the end of irradiation, n_f may not be small, and the values of n_a, m_1 and m_2 may be different, however if one adds a relaxation time, proceeding by solving the same equations but with $X=0$ for a further period of time during which the free defects perform recombination, one ends up with practically the same results as with the set of larger probabilities.

Figure 2 shows the results for the set of parameters given in the caption. Here, β_1 is a hundred times larger than β_2, which means that the filling of m_2 takes place under strong competition with m_1. Here too, n_f is negligibly small, and not seen in the figure. The difference between n_a and m_1 is rather small, but it constitutes the values of m_2 to which either the TL or the optical absorption or the ESR signal are considered to be proportional. m_2 is seen to start linearly, but when m_1 and n_a come close to saturation, m_2 gets very strongly superlinear before going to saturation.

Figure 2. Simulated results of the excitation-time dependence of the stabilized traps with the parameters: $M_1=10^{10}$ cm^{-3}, $M_2=10^9$ cm^{-3}, $\alpha=10^{-12}$ cm^{3}s^{-1}, $\beta_1=10^{-10}$ cm^{3}s^{-1}, $\beta_2=10^{-12}$ cm^{3}s^{-1}, $X=10^{10}$ cm^{-3}s^{-1}.

Figure 3 shows the results with the set of parameters given in the caption. Like before, n_f is negligibly small at the end of each irradiation followed by relaxation time, and is not seen in the graph. Note that α is significantly larger than β_1 and β_2, and that β_1 is 1000 times larger than β_2. Note also that m_2, which is the interesting magnitude as far as the measured quantities are concerned, is multiplied by 100 so as to enable its appearance on the same figure. On the log-log scale given, m_2 which is nearly the same as n_a in this case, is seen as a straight line with a slope of ~0.57. This resembles the experimental results of D$^{0.55}$ in TL of CaSO$_4$:Dy as reported by Caldas and Mayhugh[15], and the D$^{0.5}$ dependence predicted by Israeli et al.[9] using qualitative arguments in cases where α is significantly larger than β_1 and β_2.
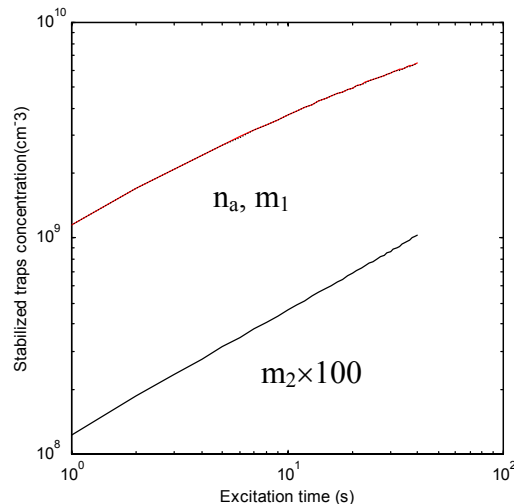
Figure 3. Simulated results of the excitation-time dependence of the stabilized traps with the parameters: $M_1=10^{10}$ cm^{-3}, $M_2=10^{10}$ cm^{-3}, $\alpha=10^{-7}$ cm^{3}s^{-1}, $\beta_1=10^{-9}$ cm^{3}s^{-1}, $\beta_2=10^{-12}$ cm^{3}s^{-1}, $X=10^{10}$ cm^{-3}s^{-1}.

4. Discussion

In the present work, we have solved numerically the simultaneous kinetic differential equations governing the process of stabilization of point defects by competing traps. Effects of linear dependence on the dose as well as sublinear dose dependence, close to a square-root dependence and a very strong superlinear dependence could be reached, which explain known dependencies in different crystals. It should be pointed out that superlinearity of thermoluminescence under different conditions, namely, when the excitation is by ionizing irradiation, and the entities involved in the transitions are electrons or holes, has been described before. This bears some analogy to the present case which deals with the excitation by non-ionizing radiation, where the moving entities are point defects. Kristianpoller et al.[18] gave a theoretical explanation to a dose dependence of TL due to competition with a non-radiative centre during the read-out (heating) of the sample, which resulted in a quadratic dependence on the dose followed by more than quadratic behaviour prior to saturation. Bowman and Chen[19] studied theoretically the dose dependence associated with competition during excitation. Here, using some simplifying assumptions and the electron-band model, initial linear dose dependence was predicted, followed by a superlinear range which, in turn, was followed by an approach to saturation. Chen et al.[20] later combined the two approaches and showed, by numerical simulation, different linear-superlinear dose dependencies of TL associated with competition with inert traps or recombination centres. On the other hand, Lawless et al.[21] have shown that without competition, namely, within the one-trap-one recombination-centre (OTOR) model, a sublinear, square-root dependence can be expected with certain sets of parameters. Further theoretical considerations and the analogy of the results with those of the OTOR model are given in the appendix below.

As pointed out above, the possible effect of a rather strong absorption coefficient of the crystal in hand has not been considered. If this is the case, the excitation by the irradiation is not uniform and the front layers of the sample may approach saturation before the back part. In this case, the superlinear dependence seen in Fig. 2 may not be so steep because of the saturating part.

Appendix

We present here a solution, in parametric form with m_1 as the parameter. Rearranging Eq. (2), we get

$$n_f dt = \frac{dm_1}{\beta_1(M_1 - m_1)} = \frac{dm_2}{\beta_2(M_2 - m_2)} = ... = \frac{dm_N}{\beta_N(M_N - m_N)}. \qquad (A1)$$

This can be readily integrated,

$$-\int_0^t n_f(t')dt' = \frac{\ln(1 - m_1/M_1)}{\beta_1} = \frac{\ln(1 - m_2/M_2)}{\beta_2} = ... = \frac{\ln(1 - m_N/M_N)}{\beta_N}. \qquad (A2)$$

Thus, the concentration of any trap m_i can be related to any other trap m_j. Let us arbitrarily choose trap 1 as a reference and re-write Eq. (A2) as

$$m_i = M_i \left[1 - \left(1 - m_1/M_1\right)^{\beta_i/\beta_1} \right] \qquad for\ i = 1, 2, ..., N. \qquad (A3)$$

Equation (A3) is valid for all times through the excitation and relaxation periods.
From Eq. (3) and the initial conditions, we know that

$$n_a = n_f + \sum_{i=1}^{N} m_i = n_f + \sum_{i=1}^{N} M_i \left[1 - \left(1 - m_1/M_1\right)^{\beta_i/\beta_1} \right]. \qquad (A4)$$

After the excitation ends and after an appropriate relaxation period, n_f decays to zero. Consequently, given m_1, Eq. (A4) can be used to determine the final concentration of n_a.
Let us develop now a relationship between m_i and the dose. Substituting Eqs. (1) and (2) into Eq. (3), we find

$$\frac{dn_f}{dt} = X - \left[\alpha n_a + \sum_{i=1}^{N} \beta_i \left(M_i - m_i\right) \right] n_f. \qquad (A5)$$

From Eq. (A5), it is apparent that n_f has a lifetime of

$$\tau_f = \frac{1}{\alpha n_a + \sum_{i=1}^{N} \beta_i (M_i - m_i)}. \qquad (A6)$$

Laboratory and natural irradiation typically occurs on long time scales, ranging from seconds to millennia. By contrast, the lifetimes of free charges in a solid are typically short compared to the irradiation period, then the concentration of free charges, n_f, will approach its quasi-steady value of

$$n_f = \tau_f X = \frac{X}{\alpha n_a + \sum_{i=1}^{N} \beta_i (M_i - m_i)}. \qquad (A7)$$

Consistent with making the quasi-steady approximation above, we assume $n_f \ll n_a$, so that charge conservation, Eq. (A4), can be approximated as

$$n_a = \sum_{i=1}^{N} m_i. \qquad (A8)$$

To find a relationship between m_1 and dose, we substitute the quasi-steady value of n_f, Eq. (A7), into the m_1 conservation condition, Eq. (2) with i=1, to find

$$\frac{dm_1}{dt} = \frac{\beta_1 (M_1 - m_1)}{\alpha n_a + \sum_{i=1}^{N} \beta_i (M_i - m_i)} X. \qquad (A9)$$

To put Eq. (A9) into a form suitable for integration, we rearrange it

$$X dt = \left[\alpha n_a + \sum_{i=1}^{N} \beta_i (M_i - m_i) \right] \frac{dm_1}{\beta_1 (M_1 - m_1)}. \qquad (A10)$$

Using Eq. (A2), we can replace $dm_1 / [\beta_1 (M_1 - m_1)]$ by $dm_i / [\beta_i (M_i - m_i)]$ for any i. After also using conservation of charge, Eq. (A8), to eliminate n_a in favor of m_i, Eq. (A10) becomes

$$X dt = \sum_{i=1}^{N} \left[\alpha m_i + \sum_{i=1}^{N} \beta_i (M_i - m_i) \right] \frac{dm_i}{\beta_i (M_i - m_i)}. \qquad (A11)$$

This can be readily integrated to find

$$D = \sum_{i=1}^{N} \left[\frac{\beta_i - \alpha}{\beta_i} m_i - \frac{\alpha}{\beta_i} M_i \ln(1 - m_i / M_i) \right], \qquad (A12)$$

where $D = \int X dt$ is the dose. Using Eq. (A3) to eliminate m_i in favor of m_1, we find

$$D = \sum_{i=1}^{N} M_i \left\{ \frac{\beta_i - \alpha}{\beta_i} \left[1 - (1 - m_1 / M_1)^{\beta_i / \beta_1} \right] - \frac{\alpha}{\beta_1} \ln(1 - m_1 / M_1) \right\}. \qquad (A13)$$

Equation (A13) allows us to compute the dose D required to produce any given value of m_1. Eq. (A3) allows us to compute all m_i given the value of m_1. Thus, we have the complete solution in parametric form with m_1 as the parameter. The only approximation used was the quasi-steady assumption for n_f. Considering the special case of N=1, the solution reduces to

$$D = \frac{\beta_1 - \alpha}{\beta_1} m_1 - \frac{\alpha}{\beta_1} M_1 \ln(1 - m_1 / M_1), \qquad (A14)$$

with $n_a = m_1$. This relation is analogous to the equation given by Lawless et al.[21] for the mentioned OTOR case. Therefore, it should show linear then square root dependence for N=1.

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