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## Random-Walk Model of Energy Transfer in Cathodoluminescence

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The probability  $S$  of energy transfer from excited host lattice to activator ions can be calculated from experimental concentration-dependence data. It is 0.66 for  $Y_2O_2S:Eu$ ,  $S$  is the quantum efficiency for host-excited luminescence and can be used to calculate cathodoluminescence efficiency.

The mechanism of cathodoluminescence (CL) in inorganic phosphors is not completely understood. This is because the concepts of energy transfer from host lattice to the activator ions have so far been inadequate.<sup>1-3</sup> In this Letter, we shall report a new approach to determining the probability of the energy transfer from excited host lattice to activator ions.

Energy-transfer mechanisms in luminescent materials have been studied extensively by measuring luminescence intensities and lifetimes.<sup>4</sup> A point commonly overlooked in the measurements of luminescence intensities is the volume in which the excitation energy is contained. For phosphors in which the activator ions are excited only directly by the incident electrons (including internally generated secondary electrons<sup>5</sup>) the active volume  $V_a$  for directly excited phosphors is defined by the penetration depth of the incident electrons.  $V_a$  is thus a constant for a given cathode-ray (CR) voltage; the penetration depth of 10-kV electrons is  $0.4 \mu\text{m}$ .<sup>6</sup> If the energy of the incident electrons is scattered uniformly in  $V_a$  all of the lattice sites in  $V_a$  will have an equal chance of excitation. Therefore, the number of activator ions excited in  $V_a$ , which is proportional to the CL intensity, will be proportional to the activator concentration. Consequently, we expect the luminescence intensity as a function of activator concentration, i.e., the concentration dependence (CD), to have unit slope in a log-log plot at low activator concentrations where self-quench-

ing is negligible.<sup>7</sup> As an example of a directly excited phosphor, Fig. 1 shows the CD curves of  $Y_2O_2S:Ho$  under continuous (dc) CR excitation (10 kV,  $0.5 \mu\text{A}/\text{cm}^2$  were used throughout this report) and under direct  $Ho^{+3}$  excitation using 423-nm radiation. It is found that the slope is, as anticipated, unity.

For phosphors whose activator ions are excited by both incident electrons and excited host lattice (host excitation), the active volume ( $V_a$ ) is defined by the subsequent migration of the energy carriers<sup>8</sup> (ECs) created by the incident electrons in  $V_a$

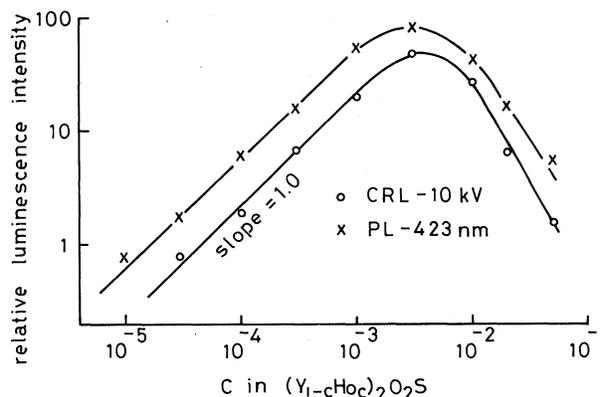


FIG. 1. Concentration-dependence curves of time-averaged  $Ho^{+3}$  luminescence at 544 nm of  $Y_2O_2S:Ho$  under continuous cathode-ray (CRL) and direct photoexcitation with 423-nm radiation (PL).

(on the assumption that the crystal volume is greater than  $V_d$ ). If the migration of an EC terminates on the first visit to an unexcited activator ion, the migration length  $L$  (i.e.,  $L^3 = V_d$ ) increases as the activator concentration decreases or as the electron beam density increases. Increase in the beam density introduces uncertainty in the experiments because of heating of the crystals. It is, therefore, preferable to study the change in  $L$  with activator concentration rather than with electron beam density. Because  $V_a$  is an inverse function of activator concentration, qualitatively different CD curves from the curves in Fig. 1 are expected for host-excited phosphors: If  $V_a \gg V_d$ , the CD curves will have two characteristic activator concentration regions corresponding to  $L$  greater than, and  $L$  less than, the crystal size. Figure 2 shows the CD curves for  $Y_2O_3S:Eu$  of different average crystal sizes (3, 10, and 20  $\mu m$  by the sedimentation weight method) under dc CR excitation.  $Y_2O_3S:Eu$  is a host-excited phosphor. It is found that there are two slopes, 0.66 and 0.22 ( $=0.66/3$ ). As will be confirmed quantitatively later in this report, the inflection points of CD curves show that  $L$  equals the crystal size. In the activator concentration region below the inflection point,  $L$  is greater than the crystal size, and  $V_a$  is limited by the crystal size. This crystal-size-limited volume will hereafter be referred to as  $V_h$ . We have used the CD curves in  $V_h$  of  $Y_2O_3S:Eu$  to study the EC motion in the crystals. The fact that the slope

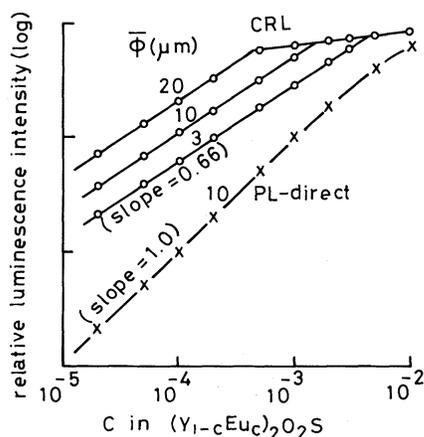


FIG. 2. Concentration-dependence curves of time-averaged luminescence intensity  ${}^5D_0 \rightarrow {}^7F_2Eu^{+3}$  of  $Y_2O_3S:Eu$  phosphors of different crystal sizes (3, 6, and 20  $\mu m$  by sedimentation weight method) under continuous cathode-ray (CRL) and direct photoexcitation with 330-nm radiation (PL-direct).

of the CD curves in Fig. 2 is 0.66 rather than 1 indicates that the motion of the ECs in  $V_h$  differs quite strongly from the motion of the incident electrons in  $V_d$ .

As a simple, approximate model of the EC motion in  $V_h$  ( $\gg V_d$ ), we make the following assumptions: (1) Each EC has its own domain in  $V_h$  and has a probability  $S$  of exciting an activator ion in this domain. If the domains overlap, a lattice site will be common to many, say  $n$ , domains. This lattice site has a probability  $S'$  to be visited by the ECs from the  $n$  different domains. This probability  $S'$  is given by

$$S' = 1 - (1 - S)^n. \quad (1)$$

For large  $n$ ,  $S'$  approaches unity. Consequently, unit slope would be expected for the CD curves in the region where the number of activator ions is less than the number of ECs. As already demonstrated, this is not true for the EC motion in  $V_h$ . (2) The EC migrates to lattice points in its domain by a random walk, and migration of the EC terminates on the first visit either to an unexcited activator ion or to the surface layer. (3) The crystals are covered with a de-excitation layer<sup>9</sup>; in a domain containing no activators, the EC ultimately disappears at the de-excitation layer. (4) The intrinsic lifetime of the EC is longer than its transit time across the crystal. (5) The concentration of internal sinks, e.g., crystal imperfections, is negligible compared to the activator concentration.

Consider first the excitation of activator ions under short-pulsed CR excitation. Let  $\nu$  be the number of the ECs created in  $V_d$  by pulsed CR excitation,  $K$  be the number of lattice points in  $V_h$ , and  $N$  be the number of activator ions in  $V_h$ . We assume that the activator ions are excited only once by the  $\nu$  ECs, which means, in terms of probability theory, that the excitation of activators is an excitation without replacement. Then we may derive the average number  $E_p$  of activator ions in  $V_h$  excited by the  $\nu$  ECs as follows: Any one of the  $\nu$  domains may contain a particular activator ion which is excited by the EC with the probability  $S$ . Hence, there are  $\nu S$  possible ways to excite an activator ion. It follows that there are  $N\nu S$  possible ways to excite  $N$  activator ions in  $V_h$ . In this calculation, however, we have counted the excitation of each ion  $\nu$  times. We can remove this duplication by dividing by  $\nu$ . Then we have

$$E_p = \nu NS / \nu = NS, \quad (2)$$

with the boundary condition  $NS/\nu \leq 1$ . Saturation of luminescence begins when  $N \leq \nu/S$ . Since  $N$  is proportional to the activator concentration, this defines the critical activator concentration  $C_p^*$  (in mole fraction). Below  $C_p^*$ , the active volume  $V_a$  is constant and limited by crystal size but above  $C_p^*$ ,  $V_a$  changes with the activator concentration. In  $Y_2O_3S$ , two of the five ions can be activator ions. Thus  $C_p^*$  for  $Y_2O_3S:Eu$  is given by  $C_p^* = 5\nu/2KS$ , because  $N = 2KC/5$  where  $C$  is the activator concentration in mole fraction.

Consider next dc excitation. Each excited activator ion, after remaining some time in its excited state, emits a photon and returns to the ground state. This de-excited activator ion may be re-excited if another EC is present. Thus, the excitation of activators under dc excitation is, in terms of probability theory, excitation with replacement. We assume that under dc excitation,  $\nu'$  ECs per second are created in  $V_d$ . Hence,  $\nu't$  domains are created in time  $t$  ( $\gg$  lifetime of excited activator ions) in  $V_h$  and an activator in each domain is excited with probability  $S$  by the EC. Because any one of  $\nu't$  domains may contain a particular activator ion, there are  $\nu'St$  possible ways to excite an activator ion. With  $N$  activator ions (with replacement), there are  $N^{\nu'St}$  possible ways to excite  $N$  activator ions.<sup>10</sup> In the calculation of  $N^{\nu'St}$  we have counted the duplicate excitations of activator ions to the  $\nu't$ th power. We can remove this duplication from  $N^{\nu'St}$  by raising the product to the  $(1/\nu't)$ th power. Then we have the average number  $E_D$  of the excitation of the  $N$  activator ions in  $V_h$  excited by  $\nu't$  ECs:

$$E_D = (N^{\nu'tS})^{1/\nu't} = N^S. \quad (3)$$

Assuming that the activator ions are excited only once in their average lifetime  $\tau$ , the boundary condition for Eq. (3) is determined by the number of activator ions excited and the number of the ECs created during  $\tau$  (i.e.,  $NS/\nu'\tau < 1$ ). Saturation of luminescence under dc excitation begins when  $N < \nu'\tau/S$ . This defines the critical activator concentration  $C_D^*$  in mole fraction; for  $Y_2O_3S:Eu$

$$C_D^* = 5\nu'\tau/2KS. \quad (4)$$

We have determined that  $\tau = 1$  msec for  $Y_2O_3S:Eu$  ( $^5D_0$  luminescence).

The time-averaged luminescence intensity,  $I$ , from the excited activator ions in  $V_h$  under given CR excitation conditions is proportional to the average number of the activator ions which are

TABLE I. Determined and calculated optimum activator concentration  $C_D^*$  in mole fraction.

Particle size ( $\mu m$ )	Experimental (mole)	Calculated (mole)
3	$4.5 \times 10^{-3}$	$5.2 \times 10^{-3}$
5	$2.7 \times 10^{-3}$	$3.1 \times 10^{-3}$
10	$1.6 \times 10^{-3}$	$1.5 \times 10^{-3}$
20	$4.6 \times 10^{-4}$	$7.6 \times 10^{-4}$

excited in  $V_h$  (neglecting direct excitation because  $V_h \gg V_d$ ). Thus we have

$$I_p \sim E_p = NS = K_1 SC \quad (5)$$

for pulse excitation,

$$I_D \sim E_D = N^S = K_2 C^S \quad (6)$$

for dc excitation, where  $K_1 = 2K/5$  and  $K_2 = (2K/5)^S$  for  $Y_2O_3S:Eu$ . If  $S = 1$ , both  $I_p$  and  $I_D$  are proportional to  $N$ , which is the case usually considered in CL studies. Thus, we can experimentally determine  $S$  from the slope of the CD curves, plotted on log-log basis, under dc CR excitation.

As already shown in Fig. 2, all of the curves under the dc CR excitation have two slopes where the inflection points depend on the crystal sizes. Table I shows  $C_D^*$  values determined from the inflection points in Fig. 2 together with the values calculated from Eq. (4), using  $S = 0.66$ ,  $\tau = 1$  msec, and  $2E_g$  for the creation energy of an electron-hole pair in  $V_d$  (where  $E_g$  is the band-gap energy of the host crystal).<sup>11</sup> There is good agreement. The fact that  $C_D^*$  shifts to lower activator concentration as the crystal size increases shows that the intrinsic lifetime of the ECs in  $Y_2O_3S:Eu$  crystal is longer than the transit time of the ECs across the crystal. The straight lines for concentrations below and above  $C_D^*$  indicate that the sink concentration in  $Y_2O_3S:Eu$  is negligible. One can thus determine  $S$  from the slope in the activator concentration region below the inflection points; for  $Y_2O_3S:Eu$ ,  $S$  is 0.66.

In the random-walk model of Soos and Powell,<sup>12</sup> the probability  $S(A)$  that a particle visit a trap after a large number of steps has been derived mathematically.  $S(0)$  for a point center<sup>12</sup> is 0.66 for an isotropic random walk on a simple cubic lattice.<sup>13</sup> Thus  $S$  can be identified with  $S(A)$ .

Because  $S$  is interpretable as the quantum efficiency for host-excited luminescence (which is often difficult to determine experimentally) one can compute theoretical efficiency  $\eta_{ct}$  from the

measured value of  $S$  and the equation

$$\eta_{cr} = (E_m/2E_g)S, \quad (7)$$

where  $E_m$  is emitted photon energy. We compute  $\eta_{cr} = 0.13$  for  $Y_2O_3S:Eu$ , using  $E_m = 2.0$  eV,  $E_g = 5.0$  eV, and  $S = 0.66$ , which is in agreement with the experimental  $\eta_{cr} = 0.13$  reported by Ludwig and Kingsley.<sup>2</sup>

Thus, all the experimental results on the energy transfer from host lattice to activators are consistent with a random-walk model in the domain.

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## COMMENTS

### Comment on "Self-Consistent Solution for an Axisymmetric Pulsar Model"

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Implications of the results described in the paper by Kuo-Petravic, Petravic, and Roberts are further discussed and reasons are put forward for the observed breakdown of the force-free assumption. An earlier attempt by Michel to reconcile our results with that of the force-free model is discussed.

In 1974 we reported on our self-consistent, numerical, time-dependent solution for a model of the pulsar magnetosphere.<sup>1</sup> The basic features of our solution, which are described in more detail elsewhere,<sup>2</sup> are the following: (a) space-charge limited emission and currents at small radii  $r \ll R_L$ , where  $R_L$  is the light radius; (b)  $\vec{E} \cdot \vec{B} \neq 0$  and flow across the field lines at large radii  $r \geq R_L$ ; (c) closed magnetic field lines everywhere in the magnetosphere. These results are in serious disagreement with the expectations from the approaches using the assumption  $\vec{E} \cdot \vec{B} = 0$ .<sup>3-6</sup> We would like to note that although no force-free solution valid in the region around the light radius exists at present, it follows