Nonequilibrium thermodynamics of luminescent processes in solids

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The kinetic mechanism of luminescent processes in solids is discussed on the grounds of linear nonequilibrium thermodynamics. By applying the principle of minimum entropy production, the densities of electrons in the conduction band and holes in the valence band are found to remain steady during the thermoluminescent emission, while, during the thermoluminescence buildup and the accompanying photoluminescent emission, they increase with a rate equal to half the rate of pair production by ionizing radiation. Analogously, the densities in intermediate levels lying in the forbidden energy gap are found to behave always steadily. In this way, simple equations are derived to represent these processes both in the case of single-level luminescent centers and when they are constituted by two-level states for localized electron-hole pairs. It is shown that the linear approximation for nonequilibrium thermodynamics becomes more reliable the more the thermoluminescent process approaches its end. On the contrary, for thermoluminescent buildup and photoluminescent emission the best reliability is found at the beginning, while it gets worse as these processes go on, thus removing the system from the initial state of thermodynamic equilibrium.

I. INTRODUCTION

Dielectrics or semiconductors whose forbidden energy gap holds localized levels capable of originating radiative transitions behave as luminescent materials. In fact, when they are excited with ionizing radiations, electron-hole pairs are produced which then recombine through the localized levels, thus giving rise to light emission. At the same time, some electrons or holes become stored in traps, provided these are also present and the temperature is kept low enough. This builds up the thermoluminescent (TL) emission which ensues when, as the ionizing radiation is removed, the temperature is allowed to increase. Depending on the nature of the luminescent centers, that is, the lattice defects or impurities which originate the recombination levels, three basic emission schemes are to be considered. They are: The Schön-Klasens (SK) scheme, in which a conduction-band electron recombines with a hole kept in a localized level, the opposite Lamb-Klick (LK) scheme, in which a valence-band hole recombines with a localized electron, and the Prener-Williams (PW) scheme, in which both electron and hole are localized within a two-level center. All these schemes are actually found in luminescent materials.[1]

For studying the aforementioned luminescent processes, kinetic models are to be considered which take into account the actual situation of recombination and trapping levels. However, even if crude simplifications are introduced, the direct solution of the resulting equations is hardly practicable. For this reason, it becomes reasonable to resort to nonequilibrium thermodynamics, which provides general methods for irreversible transformations such as those intervening in luminescent processes.[2,3] More precisely, linear nonequilibrium thermodynamics will be applied. It concerns systems near to equilibrium characterized by linear-flux laws with constant phenomenological coefficients. A general feature of these systems is the fact that entropy production takes place at the minimum rate compatible with the system constraints. This allows for some subsidiary conditions which greatly simplify the problem. Although the validity of this approach is restricted by the closeness-to-equilibrium requirement, it can be properly used when dealing with various time-dependent phenomena. In previous papers, the TL emission was investigated in this way.[4,5] An analogous treatment will be developed here, concerning the kinetics of photoluminescence (PL) and of TL buildup.

II. KINETIC EQUATIONS

Let us consider at first the case in which a single kind of electron-trapping level is present and the SK scheme applies to the luminescent centers. Moreover, in order to deal with a definite radiation field, let us assume a phosphor kept in an isothermal cavity full of blackbody radiation, in such a way as to allow the exchange of energy between electron levels and the radiation field. It is clear that this assumption does not imply any limitation of generality as far as the luminescent processes are concerned. On this ground, the kinetic set can be written as

$$\frac{dn^*}{dt} = \gamma\Phi + \nu_T \exp(-E_G/kT) - \sigma n^* m^*$$

$$- A_e n^* n_0 + s_e \exp(-E_e/kT)n_1$$

$$- B n^* m_1 + s_R \exp(-\hbar\omega/kT)m_0, \qquad (2.1)$$

$$\frac{dn_1}{dt} = A_e n^* n_0 - s_e \exp(-E_e/kT)n_1, \qquad (2.2)$$

$$\frac{dm^*}{dt} = \gamma\Phi + \nu_T \exp(-E_G/kT) - \sigma n^* m^* - A_h m^* m_0$$

$$+ s_h \exp(-E_h/kT)m_1, \qquad (2.3)$$

$$\frac{dm_1}{dt} = A_h m^* m_0 - s_h \exp(-E_h/kT)m_1 - B n^* m_1$$

$$+ s_R \exp(-\hbar\omega/kT)m_0, \qquad (2.4)$$

$$n_0 + n_1 = n_t, \qquad (2.5)$$

$$m_0 + m_1 = m_t. \qquad (2.6)$$

The meaning of the symbols is as follows [see Fig. 1(a)]: n^* and m^* (cm^{-3}), the densities of electrons in the conduction band and holes in the valence band, respectively, n_0 and n_1 (cm^{-3}), the densities of empty traps and of traps with a bound electron, respectively, m_0 and m_1 (cm^{-3}), the densities of empty recombination levels and of levels occupied by a hole, respectively, n_t and m_t (cm^{-3}), the total densities of electron traps and recombination levels, respectively, Φ (erg sec^{-1} cm^{-2}), the incident flux of ionizing radiation, γ (erg^{-1} cm^{-1}), the efficiency factor for the pair production, ν_T (sec^{-1} cm^{-3}) and σ (sec^{-1} cm^3), the probability factors for the thermal pair production and recombination, respectively, E_G (erg), the gap energy, A_e (sec^{-1} cm^3) and s_e (sec^{-1}), the probability factors for the electron trapping and releasing from traps, respectively, E_e (erg), the depth of electron traps below the conduction band, B (sec^{-1} cm^3) and s_R (sec^{-1}), respectively, the probability factors for the radiative pair recombination in the luminescent centers and for the opposite process, in which a photon of frequency ω regenerates the pair, finally, A_h (sec^{-1} cm^3) and s_h (sec^{-1}), the probability factors for the capture and releasing of a hole by a recombination level, respectively.

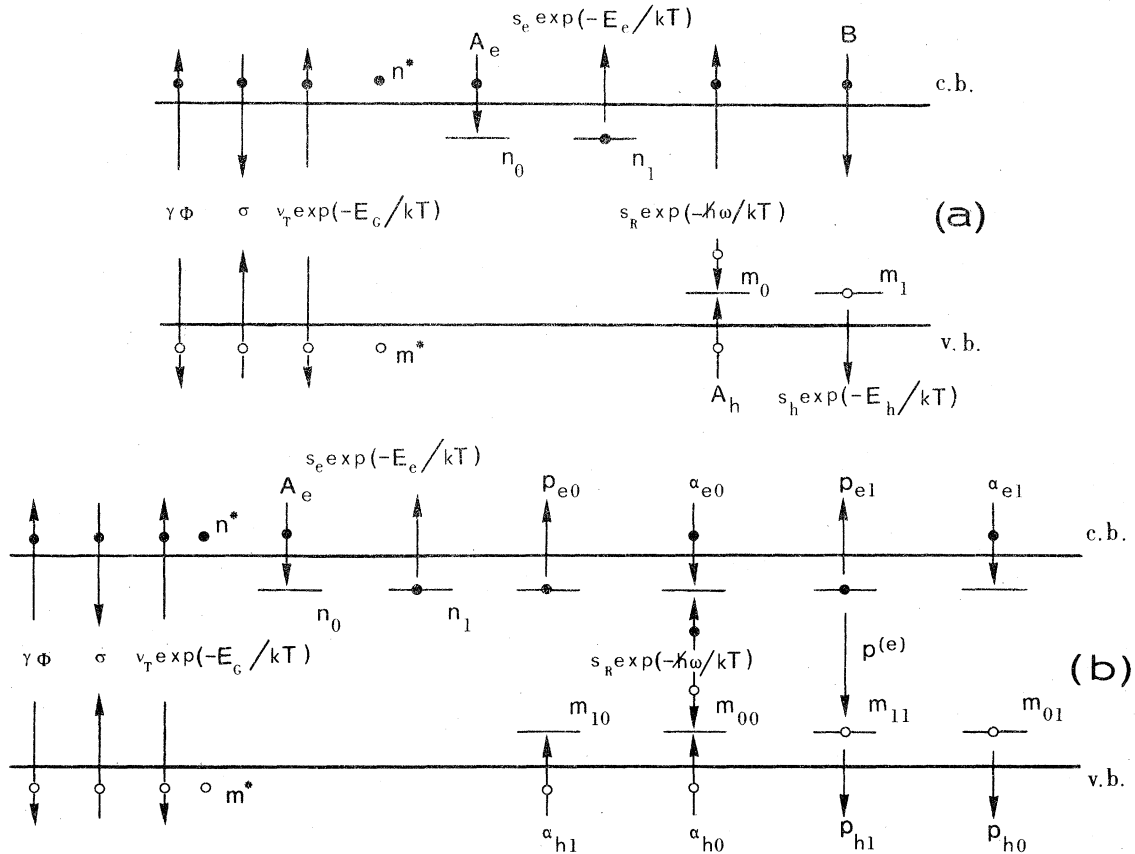All these factors, as is usually done in kinetic

FIG. 1. Level and transition schemes for luminescent processes in solids: (a) concerns the case of single-level luminescent centers, (b) the case of two-level luminescent centers.

models, can be regarded as empirical paramet-
ers. However, some simple equations can be
readily established which restrain their values.
In fact, remembering the mass law for carrier
concentrations in dielectrics or semiconductors,
we have[6]

$$v_T/\sigma = 4(m_e kT/2\pi\hbar^2)^{3/2}(m_h kT/2\pi\hbar^2)^{3/2}, \qquad (2.7)$$

m_e and m_h standing for the effective masses of
electrons and holes, respectively. Similar con-
siderations concerning electrons in the conduction
band and trapping levels lead to[5]

$$s_e/A_e = (m_e kT/2\pi\hbar^2)^{3/2}; \qquad (2.8)$$

analogously for holes:

$$s_h/A_h = (m_h kT/2\pi\hbar^2)^{3/2}. \qquad (2.9)$$

As for the exchange of energy between electron
levels and the radiation field, it must be kept in
mind that luminescent processes usually take
place at temperatures low enough that the black-
body spectral density at luminescent photon energy
is very small. Consequently, the emission is
governed mainly by spontaneous probability.
According to Ref. 5, we have thus

$$B = a(\omega)G_0 V \qquad (2.10)$$

and

$$s_R \exp(-\hbar\omega/kT) = b(\omega)\rho(\omega)G^*, \qquad (2.11)$$

where $a(\omega)$ (sec^{-1}) and $b(\omega)$ (sec^{-2} erg^{-1} cm^3) mean,
respectively, the coefficients for spontaneous and
induced transition probabilities, $\rho(\omega)$ (erg sec cm^{-3}),
the blackbody spectral energy density, G_0 and G^*,
the degeneracies of final states, respectively, in
luminescent centers and conduction band. In this
way, using the actual expressions of $a(\omega)$, $b(\omega)$,
$\rho(\omega)$, G^*, and G_0, we obtain

$$s_R/B = (m_e kT/2\pi\hbar^2)^{3/2}. \qquad (2.12)$$

When the LK level scheme is to be considered,
and a single kind of hole-trapping level is present,
Eqs. (2.1) and (2.6) still hold, except that all
quantities concerning electrons are to be exchanged
with quantities concerning holes. This leaves
unchanged the mechanism of the luminescent pro-
cess and therefore does not require a special
discussion. We omit more complex cases in
which both electron and hole traps are present
and turn to the PW level scheme. Using the same
assumptions as for Eqs. (2.1) and (2.6), the
kinetic set takes the form

$$\frac{dn^*}{dt} = \gamma\Phi + v_T \exp(-E_G/kT) - \sigma n^* m^* - A_e n^* n_0$$
$$+ s_e \exp(-E_e/kT)n_1 - \alpha_{e1} n^* m_{01} + p_{e1} m_{11}$$
$$- \alpha_{e0} n^* m_{00} + p_{e0} m_{10}, \qquad (2.13)$$

$$\frac{dn_1}{dt} = A_e n^* n_0 - s_e \exp(-E_e/kT)n_1, \qquad (2.14)$$

$$\frac{dm_{10}}{dt} = \alpha_{e0} n^* m_{00} - p_{e0} m_{10} - \alpha_{h1} m^* m_{10} + p_{h1} m_{11}, \qquad (2.15)$$

$$\frac{dm_{01}}{dt} = \alpha_{h0} m^* m_{00} - p_{h0} m_{01} - \alpha_{e1} n^* m_{01} + p_{e1} m_{11}, \qquad (2.16)$$

$$\frac{dm_{11}}{dt} = \alpha_{e1} n^* m_{01} - p_{e1} m_{11} + \alpha_{h1} m^* m_{10}$$
$$- p_{h1} m_{11} - p^{(e)} m_{11} + s_R \exp(-\hbar\omega/kT) m_{00}, \qquad (2.17)$$

$$\frac{dm^*}{dt} = \gamma\Phi + v_T \exp(-E_G/kT) - \sigma n^* m^* - \alpha_{h1} m^* m_{10}$$
$$+ p_{h1} m_{11} - \alpha_{h0} m^* m_{00} + p_{h0} m_{01}, \qquad (2.18)$$

$$n_0 + n_1 = n_t, \qquad (2.19)$$

$$m_{00} + m_{10} + m_{01} + m_{11} = m_t. \qquad (2.20)$$

The symbols already used in Eqs. (2.1) to (2.6)
have the same meanings as before, while m_{00},
m_{01}, m_{10}, and m_{11} (cm^{-3}) stand for the densities
of luminescent centers according to whether they
hold neither electrons nor holes, or, respectively,
hold one hole, one electron, or one electron-hole
pair; α_{e1} and α_{e0} (cm^3 sec^{-1}) are probability factors
for the electron trapping in luminescent centers
holding, or not, one hole; p_{e1} and p_{e0} (sec^{-1}) are
probability factors for the opposite releasing pro-
cesses; α_{h1} and α_{h0} (cm^3 sec^{-1}) have the same
meanings as α_{e1} and α_{e0} except for the mutual
exchange of electrons and holes; likewise p_{h1} and
p_{h0} (sec^{-1}) have meanings analogous to p_{e1} and p_{e0};
finally, $p^{(e)}$ (sec^{-1}) is the probability factor for the
electron-hole recombination in the luminescent
centers. Figure 1(b) shows the level and transi-
tion scheme concerned. It is to be remarked that
the ionization probabilities p_{e1}, p_{e0} and p_{h1}, p_{h0} for
electrons and holes bound to luminescent centers
depend on activation energies and frequency fac-
tors, respectively, E_{e1}, E_{e0}, E_{h1}, E_{h0} and s_{e1}, s_{e0},
s_{h1}, s_{h0}, analogously to that which occurs for
electrons bound to traps. We have therefore

$$p_{e1} = s_{e1} \exp(-E_{e1}/kT), \qquad (2.21)$$

$$p_{e0} = s_{e0} \exp(-E_{e0}/kT), \qquad (2.22)$$

$$p_{h1} = s_{h1} \exp(-E_{h1}/kT), \qquad (2.23)$$

$$p_{h0} = s_{h0} \exp(-E_{h0}/kT). \qquad (2.24)$$

The frequency factors s_{e1}, s_{e0}, s_{h1}, and s_{h0} can be
related to the corresponding factors α_{e1}, α_{e0}, α_{h1},
and α_{h0} by equations such as Eqs. (2.8) and (2.9).
As for the recombination and pair-regeneration

probabilities, we have[5]

$$p^{(e)} = a(\omega) G_0 \qquad (2.25)$$

and

$$s_R \exp(-\hbar\omega/kT) = b(\omega)\rho(\omega)G_{11} , \qquad (2.26)$$

which hold under the same conditions as in Eq. (2.10). The degeneracy G_{11} belongs to luminescent centers holding one electron-hole pair. Taking into account the actual expressions of the probabilities concerned,[5] we obtain

$$s_R/p^{(e)} = 1 . \qquad (2.27)$$

The previous equations allow us, in principle, to evaluate as functions of time and flux Φ all the densities of electrons and holes in the various levels. Consequently, the light emission intensity I (sec^{-1} cm^{-3}) can be written in the form

$$I(t) = Bn^*(t)m_1(t) , \qquad (2.28)$$

for the SK and LK schemes, or

$$I(t) = p^{(e)}m_{11}(t) , \qquad (2.29)$$

for the PW scheme. On this basis, the PL output is represented by intensity I when flux Φ is active. Likewise, the TL buildup, that is, the storage of carriers in trapping levels, is represented by the increase of $n_1(t)$ when the temperature is low. Finally, the TL output is given by the value of I when flux Φ is switched off and temperature is increased. Since the complete solution of the kinetic equations constitutes a very arduous task even if numerical procedures are accounted for, we will face the problem by introducing the criterion of a minimum rate of entropy production.

III. ENTROPY PRODUCTION IN THE LUMINESCENT PROCESSES

According to Gibbs's general formula, the entropy production rate depends bilinearly on the transformation velocities and the correspondent affinities.[2,3] In the case of the SK scheme, the following transformations are to be considered:

(1) The thermal generation and recombination of pairs through the forbidden energy gap.

(2) The exchange of electrons between conduction band and traps.

(3) The exchange of holes between valence band and luminescent centers.

(4) The exchange of energy between electron levels and the radiation field.

We must take into account, moreover, the production of pairs by ionizing radiation. We have thus

$$\frac{dS}{dt} = \sum_{i=1}^{4} \frac{\alpha_i}{T} v_i + \frac{\alpha_1}{T} \gamma \Phi V + \left(\frac{dS}{dt}\right)_{\text{ext}} , \qquad (3.1)$$

v_i (sec^{-1}) and α_i (erg) standing for, respectively, the velocities and the affinities of the above quoted transformations. It is to be remarked that in Eq. (3.1) entropy S and velocities v_i are regarded as extensive quantities concerning the whole phosphor volume V (cm^3). For this reason, a factor V has been introduced in the term representing the production of pairs by ionizing radiation. The last term takes into account the contribution due to the generation of ionizing radiation in the external world and its transfer into the phosphor. Remembering a well-known thermodynamic equation,[2] the affinities concerned can be written as

$$\alpha_1 = kT \ln \frac{\bar{n}^* \bar{m}^*}{n^* m^*} , \qquad (3.2)$$

$$\alpha_2 = kT \ln \frac{n^* n_0}{n_1} \frac{\bar{n}_1}{\bar{n}^* \bar{n}_0} , \qquad (3.3)$$

$$\alpha_3 = kT \ln \frac{m^* m_0}{m_1} \frac{\bar{m}_1}{\bar{m}^* \bar{m}_0} , \qquad (3.4)$$

$$\alpha_4 = kT \ln \frac{n^* m_1}{m_0} \frac{\bar{m}_0}{\bar{n}^* \bar{m}_1} , \qquad (3.5)$$

where the bars mean the equilibrium values. As for the velocities v_i, Eqs. (2.1)–(2.6) lead to

$$v_1 = [v_T \exp(-E_G/kT) - \sigma n^* m^*]V , \qquad (3.6)$$

$$v_2 = [A_e n^* n_0 - s_e \exp(-E_e/kT)n_1]V , \qquad (3.7)$$

$$v_3 = [A_h m^* m_0 - s_h \exp(-E_h/kT)m_1]V , \qquad (3.8)$$

$$v_4 = [Bn^* m_1 - s_R \exp(-\hbar\omega/kT)m_0]V . \qquad (3.9)$$

When the system is in thermodynamic equilibrium all affinities and velocities vanish. It follows that the equilibrium densities are related to the level energies and probability factors by

$$\bar{n}^* \bar{m}^* = (v_T/\sigma) \exp(-E_G/kT) , \qquad (3.10)$$

$$\bar{n}_1/\bar{n}^* \bar{n}_0 = (A_e/s_e) \exp(E_e/kT) , \qquad (3.11)$$

$$\bar{m}_1/\bar{m}^* \bar{m}_0 = (A_h/\sigma_h) \exp(E_h/kT) , \qquad (3.12)$$

$$\bar{m}_0/\bar{n}^* \bar{m}_1 = (B/s_R) \exp(\hbar\omega/kT) . \qquad (3.13)$$

It is worthwhile to point out that, by using Eqs. (2.7)–(2.12), the probability factors can be eliminated so that equilibrium densities turn out related only to level energies. Taking into account Eqs. (3.2)–(3.5) and (3.10)–(3.13), the velocities v_i can be written as functions of the affinities. Moreover, by assuming the luminescent system near to equilibrium so as to keep all affinities small with respect to kT, the velocity laws take the usual linear form[2]

$$v_i = L_i \frac{\alpha_i}{T} \quad (i = 1, 2, 3, 4) , \qquad (3.14)$$

where

$$L_1 = \nu_T \exp(- E_G/kT)V/k , \qquad (3.15)$$

$$L_2 = A_e \bar{n}^* \bar{n}_0 V/k , \qquad (3.16)$$

$$L_3 = A_h \bar{m}^* \bar{m}_0 V/k , \qquad (3.17)$$

$$L_4 = B \bar{n}^* \bar{m}_1 V/k , \qquad (3.18)$$

are phenomenological coefficients dependent on the level energies and probability factors concerned.

Equations (3.14)–(3.18) allow the entropy production rate to be written as

$$\frac{dS}{dt} = \sum_{i=1}^{4} L_i \left(\frac{\mathcal{Q}_i}{T}\right)^2 + \frac{\mathcal{Q}_1}{T} \gamma \Phi V + \left(\frac{dS}{dt}\right)_{\text{ext}} . \qquad (3.19)$$

This expression is to be made minimum with respect to the affinities. These quantities, however, are not mutually independent. Keeping in mind Eqs. (3.2), (3.4), and (3.5), we found, indeed,

$$\mathcal{Q}_1 + \mathcal{Q}_3 + \mathcal{Q}_4 = 0 . \qquad (3.20)$$

This relation takes into account the fact that transformations (1), (3), and (4) constitute a closed Markovian chain which corresponds to a vanishing total free-energy variation, that is, a vanishing total affinity [see Fig. 2(a)]. On the other hand,

we have

$$-\mathcal{Q}_2 + \mathcal{Q}_4 = \mathcal{Q}_T , \qquad (3.21)$$

where

$$\mathcal{Q}_T = kT \ln \frac{n_1 m_1}{n_0 m_0} \frac{\bar{n}_0 \bar{m}_0}{\bar{n}_1 \bar{m}_1} \qquad (3.22)$$

is the affinity for the releasing of electrons from traps and their recombination with holes in luminescent centers, that is, the affinity for the TL process. It appears from Eq. (3.22) that $\mathcal{Q}_T$ depends only on the actual densities of trapped electrons and holes. Therefore, when searching for the affinities which minimize dS/dt, $\mathcal{Q}_T$ is to be regarded as a constant quantity. Introducing the Lagrangian multipliers λ and μ, we have thus

$$d\left(\frac{dS}{dt} - \lambda \frac{\mathcal{Q}_1 + \mathcal{Q}_3 + \mathcal{Q}_4}{T} - \mu \frac{-\mathcal{Q}_2 + \mathcal{Q}_4}{T}\right) = 0 , \qquad (3.23)$$

which, using Eq. (3.19), yields

$$L_1 \frac{A_1}{T} = \tfrac{1}{2}(\lambda - \gamma \Phi V) , \qquad (3.24)$$

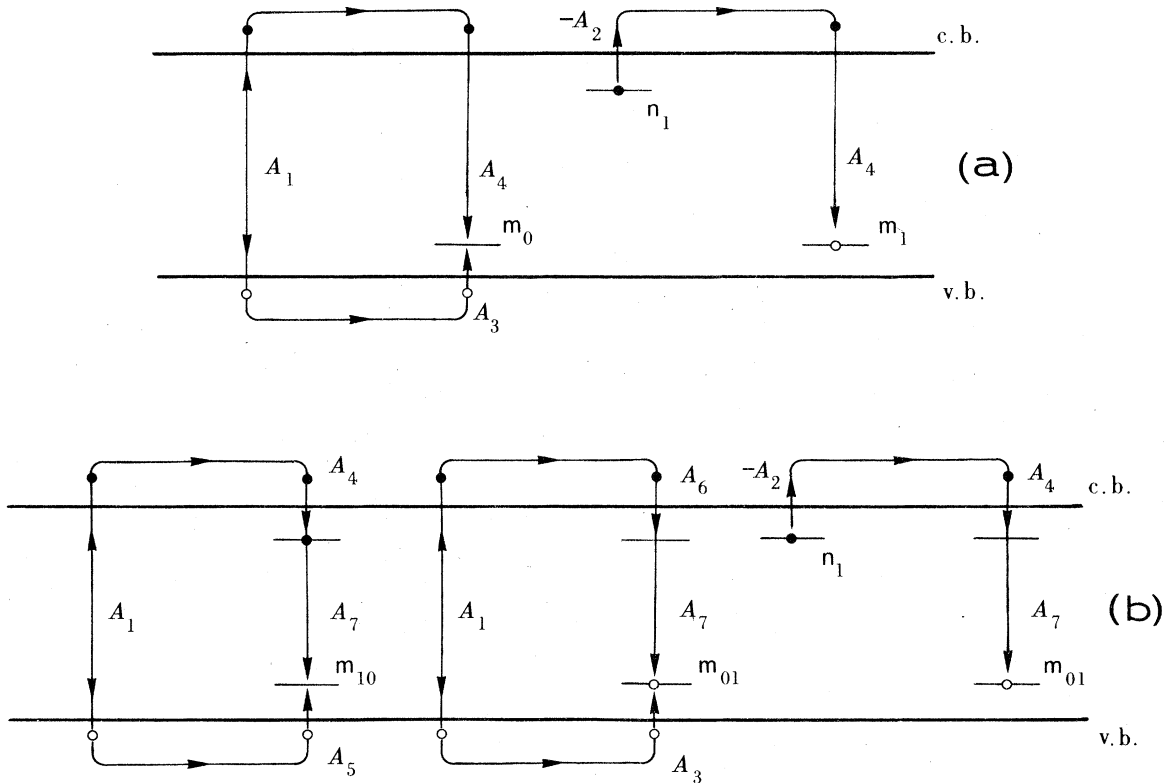$$L_2 \frac{\mathcal{Q}_2}{T} = -\tfrac{1}{2}\mu , \qquad (3.25)$$

FIG. 2. Chains of Markovian transformations in luminescence: (a) concerns the case of single-level luminescent centers, (b) the case of two-level luminescent centers. Chain 1367 differs from chain 1457 in that of electron capture in the luminescent center follows the hole capture.

$$L_3 \frac{\mathcal{Q}_3}{T} = \tfrac{1}{2}\lambda, \tag{3.26}$$

$$L_4 \frac{\mathcal{Q}_4}{T} = \tfrac{1}{2}(\lambda + \mu). \tag{3.27}$$

Substituting in Eqs. (3.20) and (3.21), the multipliers could be evaluated as functions of $\mathcal{Q}_T$, $\gamma \Phi V$, and the phenomenological coefficients. However, as far as the simplification of the kinetic problem is concerned, this is unnecessary. In fact, remembering Eqs. (3.6) to (3.9), the kinetic Eqs. (2.1)–(2.4) can be rewritten as

$$\frac{dn^*}{dt} = \gamma \Phi + (v_1 - v_2 - v_4)/V, \tag{3.28}$$

$$\frac{dn_1}{dt} = v_2/V, \tag{3.29}$$

$$\frac{dm^*}{dt} = \gamma \Phi + (v_1 - v_3)/V, \tag{3.30}$$

$$\frac{dm_1}{dt} = (v_3 - v_4)/V. \tag{3.31}$$

Introducing the velocities obtained from Eqs. (3.14) and (3.24)–(3.27), the multipliers are eliminated, yielding

$$\frac{dn^*}{dt} = \frac{dm^*}{dt} = \tfrac{1}{2}\gamma \Phi, \tag{3.32}$$

$$\frac{dn_1}{dt} = \frac{dm_1}{dt}. \tag{3.33}$$

This result holds independently of the actual values of phenomenological coefficients and of the parameters appearing in the kinetic equations. It will be seen in the next section that the subsidiary conditions (3.32) and (3.33) allow the kinetic equations to be readily solved.

Since the previous results apply also to the LK level scheme, we proceed at once to the PW scheme. In this case, besides pair production caused by ionizing radiations, the following transformations intervene in the process:

(i) The thermal generation and recombination of pairs through the forbidden energy gap.

(ii) The exchange of electrons between conduction band and traps.

(iii) The exchange of holes between valence band and luminescent centers devoid of electrons.

(iv) The exchange of electrons between conduction band and luminescent centers devoid of holes.

(v) The exchange of holes between valence band and luminescent centers holding an electron.

(vi) The exchange of electrons between conduction band and luminescent centers holding a hole.

(vii) The electron-hole recombination within the luminescent centers.

On this ground and taking into account the same assumptions as for Eq. (3.1), the entropy production becomes:

$$\frac{dS}{dt} = \sum_{i=1}^{7} \frac{\mathcal{Q}_i}{T} v_i + \frac{\mathcal{Q}_1}{T} \gamma \Phi V + \left(\frac{dS}{dt}\right)_{\text{ext}}, \tag{3.34}$$

in which the affinities are given by

$$\mathcal{Q}_1 = kT \ln \frac{\overline{n}^* \overline{m}^*}{n^* m^*}, \tag{3.35}$$

$$\mathcal{Q}_2 = kT \ln \frac{n^* n_0}{n_1} \frac{\overline{n}_1}{\overline{n}^* \overline{n}_0}, \tag{3.36}$$

$$\mathcal{Q}_3 = kT \ln \frac{m^* m_{00}}{m_{01}} \frac{\overline{m}_{01}}{\overline{m}^* \overline{m}_{00}}, \tag{3.37}$$

$$\mathcal{Q}_4 = kT \ln \frac{n^* m_{00}}{m_{10}} \frac{\overline{m}_{10}}{\overline{n}^* \overline{m}_{00}}, \tag{3.38}$$

$$\mathcal{Q}_5 = kT \ln \frac{m^* m_{10}}{m_{11}} \frac{\overline{m}_{11}}{\overline{m}^* \overline{m}_{10}}, \tag{3.39}$$

$$\mathcal{Q}_6 = kT \ln \frac{n^* m_{01}}{m_{11}} \frac{\overline{m}_{11}}{\overline{n}^* \overline{m}_{01}}, \tag{3.40}$$

$$\mathcal{Q}_7 = kT \ln \frac{m_{11}}{m_{00}} \frac{\overline{m}_{00}}{\overline{m}_{11}}. \tag{3.41}$$

Remembering the kinetic Eqs. (2.13)–(2.18), the velocities become:

$$v_1 = [v_T \exp(-E_G/kT) - \sigma n^* m^*]V, \tag{3.42}$$

$$v_2 = [A_e n^* n_0 - s_e \exp(-E_e/kT)n_1]V, \tag{3.43}$$

$$v_3 = (\alpha_{h0} m^* m_{00} - p_{h0} m_{01})V, \tag{3.44}$$

$$v_4 = (\alpha_{e0} n^* m_{00} - p_{e0} m_{10})V, \tag{3.45}$$

$$v_5 = (\alpha_{h1} m^* m_{10} - p_{h1} m_{11})V, \tag{3.46}$$

$$v_6 = (\alpha_{e1} n^* m_{01} - p_{e1} m_{11})V, \tag{3.47}$$

$$v_7 = [p^{(e)} m_{11} - s_R \exp(-\hbar\omega/kT)m_{00}]V. \tag{3.48}$$

By using the same procedure as for the SK case, these velocities can be written in linear form as in Eq. (3.14). The phenomenological coefficients concerned are

$$L_1 = v_T \exp(-E_G/kT)V/k, \tag{3.49}$$

$$L_2 = A_e \overline{n}^* \overline{n}_0 V/k, \tag{3.50}$$

$$L_3 = \alpha_{h0} \overline{m}^* \overline{m}_{00} V/k, \tag{3.51}$$

$$L_4 = \alpha_{e0} \overline{n}^* \overline{m}_{00} V/k, \tag{3.52}$$

$$L_5 = \alpha_{h1} \overline{m}^* \overline{m}_{10} V/k, \tag{3.53}$$

$$L_6 = \alpha_{e1} \overline{n}^* \overline{m}_{01} V/k, \tag{3.54}$$

$$L_7 = p^{(e)} \overline{m}_{11} V/k. \tag{3.55}$$

In this way, Eq. (3.34) becomes

$$\frac{dS}{dt} = \sum_{i=1}^{7} L_i \left(\frac{\mathcal{Q}_i}{T}\right)^2 + \frac{\mathcal{Q}_1}{T} \gamma \Phi V + \left(\frac{dS}{dt}\right)_{\text{ext}}, \tag{3.56}$$

which, analogously to Eq. (3.19), is to be made

minimum with respect to the affinities. It appears, from Eqs. (3.35)–(3.41), that these quantities fulfil the equations

$$\alpha_1 + \alpha_4 + \alpha_5 + \alpha_7 = 0, \tag{3.57}$$

$$\alpha_1 + \alpha_3 + \alpha_6 + \alpha_7 = 0, \tag{3.58}$$

$$-\alpha_2 + \alpha_6 + \alpha_7 = kT \ln \frac{n_1 m_{01}}{n_0 m_{00}} \frac{\overline{n_0} \overline{m_{00}}}{\overline{n_1} \overline{m_{01}}} = \alpha_T. \tag{3.59}$$

The first and the second correspond to closed Markovian chains yielding vanishing total affinity; the last corresponds to an open chain, yielding, as Eq. (3.22), the affinity of the TL process [see Fig. 2(b)]. By proceeding as for Eq. (3.23), we get

$$d\left(\frac{dS}{dt} - \lambda \frac{\alpha_1 + \alpha_4 + \alpha_5 + \alpha_7}{T}\right.$$
$$\left. - \mu \frac{\alpha_1 + \alpha_3 + \alpha_6 + \alpha_7}{T} - \nu \frac{-\alpha_2 + \alpha_6 + \alpha_7}{T}\right) = 0, \tag{3.60}$$

where λ, μ, and ν are Lagrangian multipliers. Using Eq. (3.56), the equations follow:

$$L_1 \frac{\alpha_1}{T} = \tfrac{1}{2}(\mu + \lambda - \gamma\Phi V), \tag{3.61}$$

$$L_2 \frac{\alpha_2}{T} = -\tfrac{1}{2}\nu, \tag{3.62}$$

$$L_3 \frac{\alpha_3}{T} = \tfrac{1}{2}\mu, \tag{3.63}$$

$$L_4 \frac{\alpha_4}{T} = \tfrac{1}{2}\lambda, \tag{3.64}$$

$$L_5 \frac{\alpha_5}{T} = \tfrac{1}{2}\lambda, \tag{3.65}$$

$$L_6 \frac{\alpha_6}{T} = \tfrac{1}{2}(\mu + \gamma), \tag{3.66}$$

$$L_7 \frac{\alpha_7}{T} = \tfrac{1}{2}(\lambda + \mu + \gamma), \tag{3.67}$$

which relate the affinities to the multipliers. The substitution of this result in Eqs. (3.57), (3.58), and (3.59) would allow the multipliers to be evaluated. However, as in the SK case, this is unnecessary. In fact, taking into account the velocities (3.42)–(3.48), the kinetic set (2.13)–(2.18) can be rewritten as

$$\frac{dn^*}{dt} = \gamma\Phi + (v_1 - v_2 - v_4 - v_6)/V, \tag{3.68}$$

$$\frac{dn_1}{dt} = v_2/V, \tag{3.69}$$

$$\frac{dm_{10}}{dt} = (v_4 - v_5)/V, \tag{3.70}$$

$$\frac{dm_{01}}{dt} = (v_3 - v_6)/V, \tag{3.71}$$

$$\frac{dm_{11}}{dt} = (v_6 + v_5 - v_7)/V, \tag{3.72}$$

$$\frac{dm^*}{dt} = \gamma\Phi + (v_1 - v_3 - v_5)/V. \tag{3.73}$$

The elimination of velocities by means of Eqs. (3.14) and (3.61)–(3.67) yields

$$\frac{dn^*}{dt} = \frac{dm^*}{dt} = \tfrac{1}{2}\gamma\Phi, \tag{3.74}$$

$$\frac{dn_1}{dt} = \frac{dm_{01}}{dt}, \tag{3.75}$$

$$\frac{dm_{10}}{dt} = \frac{dm_{11}}{dt} = 0. \tag{3.76}$$

Even in this case, these conditions, which hold independently of the actual values of parameters, will allow the simplification of the kinetic problem.

IV. EQUATIONS FOR THE LUMINESCENT PROCESSES

Let us first investigate the TL emission. In this case, the term $\gamma\Phi$ for the pair production caused by ionizing radiation is set equal to zero and the system is assumed to hold some initial densities of trapped electrons and holes so as to be out of equilibrium. Remembering Eqs. (3.32) and (3.74), it follows that both the densities n^* of electrons in the conduction band and m^* of holes in the valence band remain steady. Therefore, by considering the SK or LK level schemes, Eqs. (2.1) and (2.3) become

$$\nu_T \exp(-E_G/kT) - \sigma n^* m^* - A_e n^* n_0$$
$$+ s_e \exp(-E_e/kT)n_1 - B n^* m_1$$
$$+ s_R \exp(-\hbar\omega/kT)m_0 = 0 \tag{4.1}$$

and

$$\nu_T \exp(-E_G/kT) - \sigma n^* m^* - A_h m^* m_0$$
$$+ s_h \exp(-E_h/kT)m_1 = 0, \tag{4.2}$$

which allow the density n^* to be evaluated. In TL phosphors the energies E_G and $\hbar\omega$ are, in general, on the order of some eV.[1] As a consequence, the exponential terms $\exp(-E_G/kT)$ and $\exp(-\hbar\omega/kT)$ are seen to be very small and can be at once omitted. It is known, moreover, that the rate of the band-to-band electron-hole recombination is small when compared with the rate of recombination in luminescent centers and the rates of electron and hole trapping.[7,8] On this basis, the density n^* can be written as

$$n^* = \frac{s_e \exp(-E_e/kT)m_1}{A_e n_0 + B m_1}\left\{1 - \frac{\sigma}{A_h m_0}\frac{s_h \exp(-E_h/kT)m_1}{A_e n_0 + B m_1} + O\left[\left(\frac{\sigma}{A_h m_0}\frac{s_h \exp(-E_h/kT)m_1}{A_e n_0 + B m_1}\right)^2\right]\right\}. \tag{4.3}$$

It is to be remarked, on the other hand, that the probability for the thermal releasing of holes from luminescent centers [i. e., $s_h \exp(- E_h/kT)$] is to be regarded as small with respect to the probability for the releasing of electrons from traps. In a different way the TL emission would be quenched. For these reasons, the terms in braces can be disregarded, so that, remembering Eq. (2.28), the TL emission intensity takes the usual form

$$I_{\text{TL}} = s_e \exp\left(- \frac{E_e}{kT}\right) \frac{B n_1 m_1}{A(n_t - n_1) + B m_1} . \qquad (4.4)$$

Thus the result of Ref. 5 is confirmed on the ground of the current more detailed kinetic model.

An analogous equation is derived with the same approximations for the PW level scheme. In fact, remembering the condition (3.74) and bearing in mind that the terms depending on E_G and σ can be disregarded, Eq. (2.18) leads to

$$m^* = \frac{p_{h1} m_{11} + p_{h0} m_{01}}{\alpha_{h1} m_{10} + \alpha_{h0} m_{00}} . \qquad (4.5)$$

Therefore assuming as before the probabilities p_{h1} and p_{h0} for the thermal releasing of holes from luminescent centers to be small when compared with the probabilities α_{h1} and α_{h0} for the opposite trapping process, the valence-band-hole density m^* turns out negligible. Using these approximations and omitting the term dependent on $\hbar\omega$, Eqs. (2.13), (2.15), and (2.17) together with conditions (3.74) and (3.76) yield

$$s_e \exp(- E_e/kT) n_1 - A_e n^* n_0 - \alpha_{e1} n^* m_{01}$$
$$- p_{e1} m_{11} - \alpha_{e0} n^* m_{00} + p_{e0} m_{10} = 0, \quad (4.6)$$

$$\alpha_{e0} n^* m_{00} - p_{e0} m_{10} = 0 , \qquad (4.7)$$

and

$$\alpha_e n^* m_{01} - p_{e1} m_{11} - p^{(e)} m_{11} = 0 . \qquad (4.8)$$

In this way, remembering Eq. (2.29), straightforward substitutions allow the TL emission intensity to be written as

$$I_{\text{TL}} = s_e \exp(- E_e/kT) \frac{\alpha_{e1} p^{(e)} (p_{e1} + p^{(e)})^{-1} n_1 m_{01}}{A_e(n_t - n_1) + \alpha_{e1} p^{(e)}(p_{e1} + p^{(e)})^{-1} m_{01}} . \qquad (4.9)$$

This equation, by letting

$$\alpha_{e1} p^{(e)} (p_{e1} + p^{(e)})^{-1} = B \qquad (4.10)$$

and considering that m_{01} represents as does m_1 the trapped hole concentration, coincides in form with Eq. (4.4).

We turn now to the TL buildup. For this purpose the phosphor temperature is assumed sufficiently low to prevent TL emission. In these conditions, all exponential terms depending on thermal activation energies can be omitted. By considering the SK or LK schemes and remembering the condition (3.32), it follows that Eqs. (2.1) and (2.3) become

$$\tfrac{1}{2}\gamma\Phi = \sigma n^* m^* + A_e n^* n_0 + B m_1 \qquad (4.11)$$

and

$$\tfrac{1}{2}\gamma\Phi = \sigma n^* m^* + A_h m^* m_0 . \qquad (4.12)$$

Taking into account, as for Eq. (4.3), the smallness of the term for band-to-band pair recombination, density n^* turns out related to the pair production rate by

$$n^* = \frac{1}{2} \frac{\gamma\Phi}{A_e n_0 + B m_1} \left\{ 1 - \frac{1}{2} \frac{\sigma}{A_h m_0} \frac{\gamma\Phi}{A_e n_0 + B m_1} \right.$$
$$\left. + O\left[\left(\frac{\sigma}{A_h m_0} \frac{\gamma\Phi}{A_e n_0 + B m_1}\right)^2\right] \right\} . $$
$$(4.13)$$

Disregarding the term in curly braces, Eq. (2.2) allows the rate of electron storage in trapping levels to be written as

$$\frac{dn_1}{dt} = \tfrac{1}{2}\gamma\Phi \frac{A_e n_0}{A_e n_0 + B m_1} . \qquad (4.14)$$

Since the process starts with vanishing densities of both trapped electrons and holes (i. e., $n_1 = m_1 = 0$), Eq. (3.33) yields $n_1 = m_1$. Therefore, using Eq. (2.5), we obtain

$$\frac{dn_1}{dt} = \tfrac{1}{2}\gamma\Phi \frac{A_e(n_t - n_1)}{A_e(n_t - n_1) + B n_1} , \qquad (4.15)$$

or, integrating,

$$\left(1 - \frac{B}{A_e}\right)n_1 - \frac{B}{A_e} n_t \ln\left(1 - \frac{n_1}{n_t}\right) = \tfrac{1}{2}\gamma\Phi t , \qquad (4.16)$$

which actually represents the TL buildup. A similar result holds for the PW scheme. In fact, disregarding as before band-to-band pair recombination and using the condition (3.74), we have from Eq. (2.13)

$$n^* = \frac{1}{2} \frac{\gamma\Phi}{A_e n_0 + \alpha_{e1} m_{01} + \alpha_{e0} m_{00}} , \qquad (4.17)$$

which, substituting in Eq. (2.14), leads to

$$\frac{dn_1}{dt} = \tfrac{1}{2}\gamma\Phi \frac{A_e n_0}{A_e n_0 + \alpha_{e1} m_{01} + \alpha_{e0} m_{00}} . \qquad (4.18)$$

Remembering Eq. (2.20) and condition (3.76), we

get

$$\frac{d}{dt}(m_{00} + m_{01}) = 0 .$$ (4.19)

As, at the beginning of the process, a trapped-hole density does not exist, that is, $m_{00} = m_t$ and $m_{01} = 0$, Eq. (4.19) yields $m_{00} = m_t - m_{01}$. Keeping in mind condition (3.75) and also the fact that the initial density of trapped electrons is zero, we have $m_{01} = n_1$. In this way, using Eq. (2.19), Eq. (4.18) can be rewritten as

$$\frac{dn_1}{dt} = \frac{1}{2}\gamma\Phi \frac{A_e(n_t - n_1)}{A_e(n_t - n_1) + (\alpha_{e1} - \alpha_{e0})n_1 + \alpha_{e0}m_t} ,$$ (4.20)

or, performing integration,

$$\left(1 - \frac{\alpha_{e1} - \alpha_{e0}}{A_e}\right)n_1 - \left(\frac{\alpha_{e1} - \alpha_{e0}}{A_e}n_t + \frac{\alpha_{e0}}{A_e}m_t\right)$$
$$\times \ln\left(1 - \frac{n_1}{n_t}\right) = \frac{1}{2}\gamma\Phi t, \quad (4.21)$$

which allows for the TL buildup in the PW case.

The TL buildup at low temperature is accompanied by the PL emission. Consequently, the previous approximations apply to this process as well. In particular, all terms depending on activation energies and band-to-band pair recombinations will be omitted. In these conditions, it follows from Eqs. (2.28) and (4.13) that

$$I_{PL} = \frac{1}{2}\gamma\Phi \frac{Bm_1}{A_e n_0 + Bm_1} .$$ (4.22)

That is, by performing the same transformations as for Eq. (4.14),

$$I_{PL} = \frac{1}{2}\gamma\Phi \frac{Bn_1}{A_e(n_t - n_1) + Bn_1} ,$$ (4.23)

which, taking into account the time dependence of n_1 given by Eq. (4.16), represents the PL output for the SK or LK level schemes. When the PW scheme is considered, remembering Eq. (2.29) and using Eq. (2.17) together with condition (3.76), we have

$$I_{PL} = p^{(e)} m_{11} = \alpha_{e1} n^* m_{01} + \alpha_{h1} m^* m_{10} .$$ (4.24)

On the other hand, Eq. (2.18) and condition (3.74) lead to

$$m^* = \frac{1}{2} \frac{\gamma\Phi}{\alpha_{h1}m_{10} + \alpha_{h0}m_{00}} .$$ (4.25)

Substituting this result and Eq. (4.17) in Eq. (4.24), we get

$$I_{PL} = \frac{1}{2}\gamma\Phi\left(\frac{\alpha_{e1}m_{01}}{A_e n_0 + \alpha_{e1}m_{01} + \alpha_{e0}m_{00}}\right.$$
$$\left. + \frac{\alpha_{h1}m_{10}}{\alpha_{h1}m_{10} + \alpha_{h0}m_{00}}\right).$$ (4.26)

To simplify this expression, Eqs. (2.14) and (2.16) together with condition (3.75) can be used. We have in fact

$$A_e n^* n_0 = \alpha_{h0} m^* m_{00} - \alpha_{e1} n^* m_{01} ,$$ (4.27)

that is, eliminating n^* and m^* by means of Eqs. (4.17) and (4.25),

$$\frac{A_e n_0 + \alpha_{e1}m_{01}}{A_e n_0 + \alpha_{e1}m_{01} + \alpha_{e0}m_{00}} = \frac{\alpha_{h0}m_{00}}{\alpha_{h1}m_{10} + \alpha_{h0}m_{00}} .$$ (4.28)

In this way, Eq. (4.26) becomes

$$I_{PL} = \frac{1}{2}\gamma\Phi \frac{\alpha_{e1}m_{01} + \alpha_{e0}m_{00}}{A_e n_0 + \alpha_{e1}m_{01} + \alpha_{e0}m_{00}} ,$$ (4.29)

or, proceeding as for Eq. (4.18),

$$I_{PL} = \frac{1}{2}\gamma\Phi \frac{(\alpha_{e1} - \alpha_{e0})n_1 + \alpha_{e0}m_t}{A_e(n_t - n_1) + (\alpha_{e1} - \alpha_{e0})n_1 + \alpha_{e0}m_t} ,$$ (4.30)

which, by allowing for the values of $n_1(t)$ given by Eq. (4.21), yields the PL output for the PW level scheme.

It is worthwhile to remark that, considering the pairs of Eqs. (4.15) and (4.23) or (4.20) and (4.30), we always obtain

$$\frac{dn_1}{dt} + I_{PL} = \frac{1}{2}\gamma\Phi ,$$ (4.31)

which therefore holds for all the level schemes. According to Eq. (4.31), the TL buildup plus the PL emission take up half the electron-hole pairs produced at the instant t. This constitutes an obvious result. In fact, the remaining half raises, as stated by conditions (3.32) or (3.74), the carrier densities in the conduction and valence bands. It appears from Eq. (4.23) that in the case of the SK or LK level schemes the PL intensity I_{PL} starts with a vanishing value, which afterwards grows larger to the detriment of the trapping rate dn_1/dt. Owing to Eq. (4.30), an analogous behavior applies also for the PW scheme, but, in this case, the initial value of I_{PL} is different from zero.

V. DISCUSSION AND CONCLUSIONS

The foregoing theoretical results deserve some comments. We found that during the TL emission the carrier densities in conduction and valence bands remain steady, while they grow larger during the TL buildup and the simultaneous PL emission. This behavior can be explained by bearing in mind that the TL emission takes place when the phosphor holds some initial densities of trapped carriers, so that all level densities are initially out of equilibrium. This allows the process to go on without having to change the den-

sities in the conduction and valence band. On the contrary, the TL buildup and PL emission start from an initial state of equilibrium. This implies that the ionizing radiation raises the carrier densities in conduction and valence bands, thus removing the system from equilibrium and originating the trapping and recombination processes. Linear nonequilibrium thermodynamics establishes that this rise of densities takes place at the very rate $\frac{1}{2}\gamma\Phi$. For this reason, the behavior concerned turns out quite reasonable.

But the main question, as far as the reliability of the present results is concerned, is the applicability of the linear approximation. In Ref. 5 this matter has been discussed in the case of the TL emission. It was found that, in experimental situations in which the phosphor was weakly excited, the linear approximation works correctly. It is to be remembered, on the other hand, that Eq. (4.4) for the TL emission was advanced on a semiempirical basis about a quarter of a century ago.[7,8] Since then, it has turned out to be in agreement with the experiments even of especially quantitative nature.[9,10] This circumstance gives evidence in favor of the steadiness of electron density in the conduction band. The conclusion ensues that in significant cases the linear approximation is suited for representing the behavior of the TL emission. For this reason, we do not dwell further on this subject. As for the TL buildup and the accompanying PL emission, it is to be remarked that at the beginning of these processes the phosphor is in thermal equilibrium. In these conditions, all affinities vanish. Therefore, the requirement that affinities remain small with respect to kT is at once fulfilled. This allows for the initial applicability of the linear approximation. Such a circumstance is the opposite of what occurs in the TL emission. In this case, in fact, the phosphor, initially out of equilibrium, approaches equilibrium as the emission comes to an end. This means precisely that the linear approximation is applicable, at least at the end of the process. In order to settle more extensively the applicability of the linear approximation for the TL buildup and the simultaneous PL emission, let us point out first that, owing to the smallness of the factor $\exp(-E_G/kT)$, Eqs. (3.15) and (3.49) allow us to set $L_1 = 0$. It follows that the corresponding velocity v_1 is also a vanishing quantity which, therefore, is not subject to the linear law (3.14). We must thus consider only the affinities for the exchange of carriers between the conduction or valence band and levels lying in the forbidden gap, analogous to what occurs for the TL emission. For this purpose, taking into account the SK scheme and using Eqs. (3.29), (3.14), and (3.16),

the electron trapping rate during the TL buildup can be written as

$$\left(\frac{dn_1}{dt}\right)_{BU} = A_e \bar{n}^* \bar{n}_0 \left(\frac{\alpha_2}{kT}\right)_{BU}. \tag{5.1}$$

On the other hand, Eqs. (2.28) and (2.4) allow the TL emission intensity to be set in the form

$$I_{TL} = B n^* m_1 = -\left(\frac{dm_1}{dt}\right)_{TL}. \tag{5.2}$$

Therefore, remembering the condition (3.33),

$$I_{TL} = -\left(\frac{dn_1}{dt}\right)_{TL} = -A_e \bar{n}^* \bar{n}_0 \left(\frac{\alpha_2}{kT}\right)_{TL}. \tag{5.3}$$

As the factor $A_e \bar{n}^* \bar{n}_0$ is to be regarded as a constant quantity, we get

$$\left(\frac{\alpha_2}{kT}\right)_{BU} = -\frac{(dn_1/dt)_{BU}}{I_{TL}} \left(\frac{\alpha_2}{kT}\right)_{TL}. \tag{5.4}$$

In this way, the ratio $(\alpha_2/kT)_{BU}$ for the TL buildup turns out to be related to the analogous ratio for the TL emission. According to Eq. (5.4), their relative magnitudes depend on the ratio between the rates of electron trapping and electron releasing from traps, which, in turn, is related to the intensity of the ionizing radiation flux Φ and the actual TL temperature. Anyhow, in usual experiments, both these processes last in general some 10^2 sec.[11] This means that the rates of electron trapping and releasing range in the same order of magnitude. Consequently, the same occurs for the corresponding affinities. It can readily be seen that the same approach leads to analogous results for the other affinities and for all the level schemes considered. The conclusion can be safely drawn that the linear approximation can be applied to processes induced by ionizing radiation with the same degree of confidence expected for the TL emission.

It must be kept in mind, however, that the previous arguments by no means allow for a general applicability of the linear approximation. In fact, according to Eqs. (3.32) and (3.74), the carrier densities n^* and m^* increase unlimitedly if the ionizing flux Φ remains active. The system, therefore, is progressively removed from equilibrium until affinities large with respect to kT are originated. It follows that the linear approximation fails and a situation clearly is reached in which the carrier densities n^* and m^* become steady, that is,

$$\frac{dn^*}{dt} = \frac{dm^*}{dt} = 0. \tag{5.5}$$

In the nonlinear region, the behavior of the luminescent system is ruled by the general inequality[2,12]

$$\delta_x\left(\frac{dS}{dt}\right) = \frac{1}{T}\sum_{i=1}^{n}\frac{\delta A_i}{T}v_i \le 0 \,.$$ (5.6)

It does not allow for the minimum of a potential, as occurs when the system is near to equilibrium, and therefore is not suited for disentangling the kinetic problem. It is worthwhile to point out,

however, that in the limiting case in which Eq. (5.5) is fulfilled, all the results obtained in Sec. IV remain true, provided that in all equations the quantity $\frac{1}{2}\gamma\Phi$ is replaced by $\gamma\Phi$. Thus, the behavior of the luminescent system in the nonlinear region is expected to be intermediate between these limiting cases.

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