

Nonequilibrium thermodynamics of the thermoluminescent process

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The mechanism of the thermoluminescent process in solids is reexamined on the basis of nonequilibrium thermodynamics, thus justifying the kinetic model of Antonov-Romanovskii and Lushchik. By assuming the phosphor to be held in a cavity full of blackbody radiation and applying the principle of minimum entropy production, the electron distribution in the conduction band is found to be in a steady equilibrium with the ones in trapping and recombination levels. This is just the hypothesis which allows for the spoken of model. The same conclusion is attained when the model is generalized by considering luminescent centers constituted by bipolar ions. Even in this case, the electron distribution in high-lying levels, besides the conduction band, is in a steady equilibrium with the one in low-lying levels, so it leaves unchanged the final law for the thermoluminescent emission rate.

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I. INTRODUCTION

When dielectrics or semiconductors are excited at low enough temperature by ionizing radiations, electron-hole pairs are produced, which become trapped in defective regions of the lattice. Thermoluminescent (TL) emission ensues when, by warming up the sample, electrons thermally released from traps enter the conduction band to recombine radiatively with holes bound to luminescent centers. In most experiments, the sample temperature is raised slowly, in general with a constant speed. Under these conditions, it can be assumed that the electron distribution in the conduction band keeps in a steady equilibrium with low-lying levels. Using this hypothesis and taking into account a simple level scheme for the luminescent centers, Antonov-Romanovskii and Lushchik (ARL)^{1,2} devised a kinetic model for explaining the TL emission. It has been systematically applied to TL measurements and, in some cases, its fitness for representing the glow-peak shapes has been quantitatively checked.^{3,4}

We will show that the basic ARL equation still holds true when luminescent centers exhibit a more complex level scheme, provided the electron distribution in all high-lying levels (besides the conduction band) is assumed to be in a steady equilibrium with the ones in low-lying levels. This fact confirms the generality of the ARL kinetic model, but evidences the necessity of substantiating the steady-equilibrium hypothesis with self-supporting arguments. The Onsager and Prigogine's nonequilibrium thermodynamics offers the suitable background. By considering a TL phosphor held in a cavity full of blackbody radiation and assuming that equilibrium is approached keeping at a minimum the rate of entropy production, it will be found that the electron distribution ful-

fills the steadiness conditions in such a way as to allow for the ARL kinetics.

II. KINETICS OF THE THERMOLUMINESCENT PROCESS

According to ARL, the kinetic equations for TL process can be written as

$$\frac{dn_1}{dt} = -s \exp\left(-\frac{E}{kT}\right)n_1 + An^*n_0, \quad (2.1)$$

$$\frac{dn^*}{dt} = s \exp\left(-\frac{E}{kT}\right)n_1 - An^*n_0 - Bn^*m_1, \quad (2.2)$$

$$\frac{dm_1}{dt} = -Bn^*m_1, \quad (2.3)$$

$$n_0 + n_1 = n_t. \quad (2.4)$$

The meaning of symbols is as follows: n_1 and n^* (cm^{-3}) are the concentrations of electrons, respectively, in traps and in the conduction band, n_0 and n_t (cm^{-3}) are, respectively, the empty-trap concentration and total-trap concentration, m_1 (cm^{-3}) is the concentration of holes bound to luminescent centers, s (sec^{-1}) and E (eV) are, respectively, the frequency factor and the activation energy for thermal releasing of electrons from traps, A and B ($\text{cm}^3/\text{sec}^{-1}$) are probability factors, respectively, for the electron retrapping and recombination with holes in luminescent centers. Figure 1(a) shows the level and transition scheme for the concerned process. The steadiness condition for electrons in the conduction band is

$$dn^*/dt = 0. \quad (2.5)$$

Using Eqs. (2.2)–(2.5) and taking into account that the emitted TL light intensity I is proportional to the hole recombination rate, we get

$$I \propto -\frac{dm_1}{dt} = s \exp\left(-\frac{E}{kT}\right) \frac{Bn_1m_1}{A(n_t - n_1) + Bm_1}, \quad (2.6)$$

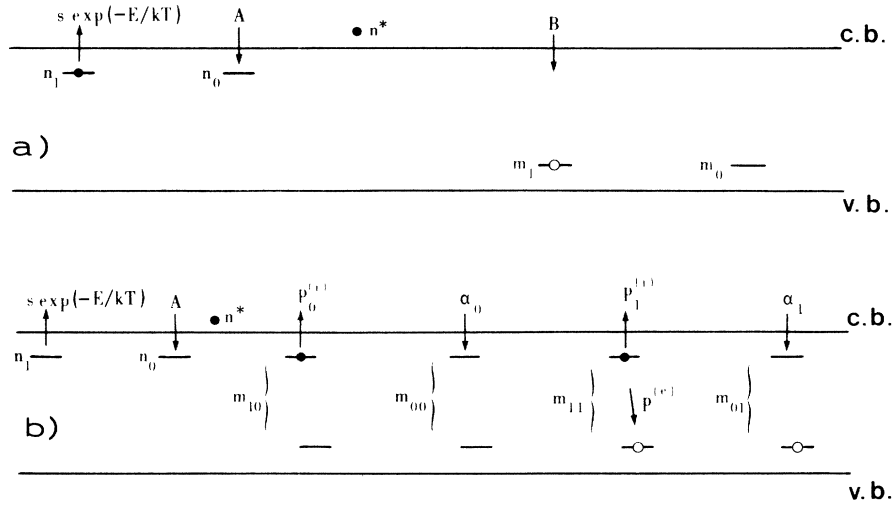


FIG. 1. Level and transition scheme for the thermoluminescent process: (a) concerns the case of luminescent centers constituted by acceptorlike ions, (b) the case of luminescent centers constituted by pairs of acceptorlike and donorlike ions.

which is just the final equation of the ARL model.

The previous picture identifies the luminescent centers with acceptorlike ions constituted by holes bound to lattice defects. But, in some cases, evidence has been obtained that the luminescent centers consist of pairs of acceptor and donorlike ions.⁵⁻⁷ In these cases, electrons of the conduction band, before recombining with bound holes, become trapped in the luminescent centers, so originating bipolar ions. Consequently, the kinetic-equation set takes the form

$$\frac{dn_1}{dt} = -s \exp\left(-\frac{E}{kT}\right)n_1 + An^*n_0, \quad (2.7)$$

$$\frac{dn^*}{dt} = s \exp\left(-\frac{E}{kT}\right)n_1 - An^*n_0 - \alpha_1 n^* m_{01} + p_1^{(i)} m_{11} - \alpha_0 n^* m_{00} + p_0^{(i)} m_{10}, \quad (2.8)$$

$$\frac{dm_{10}}{dt} = \alpha_0 n^* m_{00} - p_0^{(i)} m_{10}, \quad (2.9)$$

$$\frac{dm_{11}}{dt} = \alpha_1 n^* m_{01} - p_1^{(i)} m_{11} - p^{(e)} m_{11}, \quad (2.10)$$

$$\frac{dm_{01}}{dt} = -\alpha_1 n^* m_{01} + p_1^{(i)} m_{11}, \quad (2.11)$$

$$n_0 + n_1 = n_t, \quad (2.12)$$

$$m_{00} + m_{01} + m_{10} + m_{11} = m_t. \quad (2.13)$$

The symbols n_1 , n_0 , n^* , E , and A have the same meaning as before, while m_{00} , m_{01} , m_{10} , and m_{11} (cm^{-3}) stand for the concentrations of luminescent centers according to whether they do not hold either electrons or holes, or, respectively, hold one hole, one electron, or one electron-hole pair; α_1 and α_0 ($\text{cm}^3 \text{sec}^{-1}$) are probability factors for the electron trapping in luminescent centers holding, or not, one hole, $p_1^{(i)}$ and $p_0^{(i)}$ (sec^{-1}) are

probability factors for the opposite ionization process, and finally $p^{(e)}$ (sec^{-1}) is the probability factor for electron-hole recombination, i.e., for TL emission. Figure 1(b) shows the involved level and transition scheme. It is to be remarked that the ionization factors $p_1^{(i)}$ and $p_0^{(i)}$ for electrons bound to luminescent centers depend on the activation energies and frequency factors, respectively, E_1 , E_0 and s_1 , s_0 analogously to what occurs for electrons bound to traps. Thus we have

$$p_1^{(i)} = s_1 \exp(-E_1/kT), \quad (2.14)$$

$$p_0^{(i)} = s_0 \exp(-E_0/kT). \quad (2.15)$$

The steadiness conditions for electrons in high-lying levels are

$$\frac{dn^*}{dt} = 0, \quad \frac{dm_{10}}{dt} = 0, \quad \frac{dm_{11}}{dt} = 0. \quad (2.16)$$

Using Eqs. (2.8), (2.9), and (2.10) and taking into account that the hole recombination rate depends on the term $p^{(e)} m_{11}$, we obtain by straightforward substitutions

$$I \propto p^{(e)} m_{11} = s \exp\left(-\frac{E}{kT}\right) \times \frac{\alpha_0 p^{(e)} (p_1^{(i)} + p^{(e)})^{-1} n_1 m_{01}}{A(n_t - n_1) + \alpha_1 p^{(e)} (p_1^{(i)} + p^{(e)})^{-1} m_{01}}. \quad (2.17)$$

This equation, by letting

$$\alpha_0 p^{(e)} (p_1^{(i)} + p^{(e)})^{-1} = B, \quad (2.18)$$

and considering that m_{01} (as before m_1) represents the trapped hole concentration, actually coincides with Eq. (2.6). The factor B depends, in the present case, on the percentage probability that electrons captured by luminescent centers undergo recombination.

III. ENTROPY PRODUCTION IN THE THERMOLUMINESCENT PROCESS

The rate of entropy production in a complex process involving h transformations (e.g., chemical reactions, phase changes, etc.) is given by^{8,9}

$$\frac{dS}{dt} = \frac{1}{T} \sum_{r=1}^h \mathcal{Q}_r v_r, \quad (3.1)$$

where

$$\mathcal{Q}_r = - \left(\sum_{\gamma} \nu_{\gamma} \mu_{\gamma} \right)_r, \quad (3.2)$$

and v_r are, respectively, the affinity and the velocity of the r th transformation. In Eq. (3.2), ν_{γ} and μ_{γ} stand for stoichiometric coefficients and chemical potentials, respectively. It is to be remarked that, according to Eq. (3.2), the affinities \mathcal{Q}_r are intensive quantities, while the entropy S is an extensive quantity. It follows from Eq. (3.1), that the velocities v_r are extensive quantities as well. This means that velocities concern transformations taking place in the whole extent of the system.

In the case of ARL kinetics, two transformations are to be considered: the releasing of electrons from traps towards the conduction band and their radiative recombination with luminescent centers. The free energy of trapped electrons is given by¹⁰

$$F_1 = -kT \ln \left[2^{N_t} \binom{N_t}{N_1} \right], \quad (3.3)$$

N_t and N_1 standing for, respectively, the total numbers of traps and of trapped electrons. For electrons in the conduction band, we have¹⁰

$$F^* = N^*E - N^*kT \left[1 + \ln \frac{2V}{N^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right], \quad (3.4)$$

in which N^* means the total electron number and V the volume of the phosphor. Using the densities introduced earlier in the kinetic equations [$n_0 = (N_t - N_1)/V$, $n_1 = N_1/V$, $n^* = N^*/V$], we get

$$\mu_1 = \frac{\partial F_1}{\partial N_1} = -kT \ln \left(2 \frac{n_0}{n_1} \right), \quad (3.5)$$

and

$$\mu^* = \frac{\partial F^*}{\partial N^*} = E - kT \ln \left[\frac{2}{n^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right]. \quad (3.6)$$

In the present problem, the stoichiometric coefficients are always ± 1 or -1 , since all transitions involve one electron at a time. We have, therefore,

$$\mathcal{Q}_1 = \mu_1 - \mu^* = kT \ln \left[\frac{n_1}{n_0 n^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{E}{kT} \right) \right], \quad (3.7)$$

which is the affinity of electron releasing. Remem-

bering Eq. (2.1), the corresponding velocity turns out to be

$$v_1 = s \exp \left(-\frac{E}{kT} \right) n_1 V \left(1 - \frac{A}{s \exp(-E/kT)} \frac{n^* n_0}{n_1} \right). \quad (3.8)$$

As the densities n_1 , n_0 , and n^* reach equilibrium values, both the affinity \mathcal{Q}_1 and the velocity v_1 vanish. This leads to

$$s/A = (mkT/2\pi\hbar^2)^{3/2} \quad (3.9)$$

and allows us to write

$$v_1 = s e^{-E/kT} n_1 V (1 - e^{-\mathcal{Q}_1/kT}). \quad (3.10)$$

When, as actually occurs in TL experiments, the transformation takes place slowly, the affinity can be regarded as small in comparison with kT . This allows Eq. (3.10) to be linearized.⁸ By putting

$$L_1 = s \exp \left(-\frac{E}{kT} \right) \frac{\bar{n}_1 V}{kT}, \quad (3.11)$$

where \bar{n}_1 means the equilibrium value of n_1 , we get

$$v_1 = L_1 (\mathcal{Q}_1/T), \quad (3.12)$$

which is the desired phenomenological law for the velocity of electron releasing.

The affinity for the radiative recombination of conduction-band electrons is given by a relation analogous to Eq. (3.7), in which, however, n_1 , n_0 , and E are replaced, respectively, by m_0 , m_1 , and $\hbar\omega$, while the sign is reversed, that is,

$$\mathcal{Q}_2 = -kT \ln \left[\frac{m_0}{m_1 n^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{\hbar\omega}{kT} \right) \right]. \quad (3.13)$$

In this equation m_0 (cm^{-3}) stands for the concentration of luminescent centers deprived of bound holes and $\hbar\omega$ for the energy of the TL photon [see Fig. 1(a)]. The exchange of indexes 1 and 0 between Eqs. (3.7) and (3.13) is an obvious matter, since Eq. (3.7) takes into account electrons, while Eq. (3.13) takes into account holes. As to the recombination velocity v_2 , it depends on both emission and absorption of radiation. Thus, Eq. (2.3) which accounts only for emission is not complete for our purposes. As said in Sec. I, we assume the TL phosphor held in a cavity maintained at uniform temperature, so as to be wet by blackbody radiation at that temperature. Under these conditions, no contribution is brought to the affinity \mathcal{Q}_2 by the black-body radiation, since it remains unchanged during the process. Remembering the detailed-balance argument advanced by Einstein for obtaining the Planck law, we thus get

$$v_2 = [a(\omega) + b(\omega)\rho(\omega)] G_0 N^* M_1 - b(\omega)\rho(\omega) G^* M_0, \quad (3.14)$$

where $a(\omega)$ (sec^{-1}) and $b(\omega)$ ($\text{sec}^{-2} \text{erg}^{-1} \text{cm}^3$) are, respectively, the coefficients for spontaneous and induced transition probabilities, $\rho(\omega)$ (erg sec cm^{-3}) is the blackbody spectral energy density, G_0 and G^* are the degeneracies of final states, respectively, in luminescent centers and the conduction band, while M_1 and M_0 stand for the total numbers of luminescent centers, respectively, with or without a bound hole. We have¹¹

$$a(\omega) = \frac{4e^2\omega^3}{3\hbar c^3} |x_{if}|^2, \quad (3.15)$$

$$b(\omega) = \frac{4\pi^2 e^2}{3\hbar^2} |x_{if}|^2, \quad (3.16)$$

in which x_{if} (cm) is the transition matrix, and

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 [\exp(\hbar\omega/kT) - 1]}. \quad (3.17)$$

In the present problem, x_{if} links initial states of electrons in the conduction band with final states of electrons bound to luminescent centers. It follows that initial states belong to the whole volume of the phosphor, while final states are localized. The respective normalization factors are thus: $V^{-1/2}$ and $(\delta V)^{-1/2}$, δV standing for the volume allowed to electrons localized in the luminescent centers. This enables us to put

$$|x_{if}|^2 = \frac{\delta V}{V} |\xi_{if}|^2, \quad (3.18)$$

where in the matrix ξ_{if} , the same normalization factor $(\delta V)^{-1/2}$ has been applied both to initial and final states. Taking into account Eq. (3.18), the spontaneous-emission probability can be written as

$$a(\omega) = w(\omega)/V, \quad (3.19)$$

in which $w(\omega)$ ($\text{sec}^{-1} \text{cm}^3$), like ξ_{if} , is independent of the volume V . To evaluate the degeneration G^* , only thermally accessible conduction-band states are to be considered. This means that G^* coincides with the partition function for the conduction band,

$$G^* = \sum_{\epsilon} g(\epsilon) \exp\left(-\frac{\epsilon}{kT}\right) = 2 \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} V. \quad (3.20)$$

As to the final states, only spin degeneration contributes. We have thus

$$G_0 = 2. \quad (3.21)$$

In this way, Eq. (3.14) takes the form

$$v_2 = a(\omega) \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right]^{-1} 2n^* m_1 V^2 \times \left[1 - \frac{m_0}{n^* m_1} \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{\hbar\omega}{kT}\right)\right], \quad (3.22)$$

or else, remembering Eqs. (3.13) and (3.19) and disregarding $\exp(-\hbar\omega/kT)$ against unity,¹²

$$v_2 = 2w(\omega) n^* m_1 V \left[1 - \exp\left(-\frac{G_2}{kT}\right)\right]. \quad (3.23)$$

By putting

$$L_2 = 2w(\omega) \bar{n}^* \bar{m}_1 V/k, \quad (3.24)$$

where \bar{n}^* and \bar{m}_1 mean equilibrium values, Eq. (3.23) can be written in the linear form

$$v_2 = L_2 (G_2/T), \quad (3.25)$$

analogously to Eq. (3.12). Remembering Eq. (2.3) and taking into account Eq. (3.19), the recombination probability B turns out to be related to the spontaneous emission probability by

$$B = 2w(\omega), \quad (3.26)$$

where, like in Eq. (3.23), the term $\exp(-\hbar\omega/kT)$ is disregarded.

Using the velocity laws (3.12) and (3.25), we are now able to evaluate the entropy production rate by means of Eq. (3.1). We have

$$\frac{dS}{dt} = L_1 \left(\frac{G_1}{T}\right)^2 + L_2 \left(\frac{G_2}{T}\right)^2. \quad (3.27)$$

On the other hand, the total affinity

$$G = G_1 + G_2 = kT \ln \left[\frac{n_1 m_1}{n_0 m_0} \exp\left(-\frac{E - \hbar\omega}{kT}\right) \right], \quad (3.28)$$

though related to the actual densities of trapped carriers, is independent of the electron density in the conduction band n^* . Therefore, when we search for the minimum entropy production with respect to G_1 and G_2 , the constraint that G behaves as a constant is to be accounted for. In this way, performing straightforward calculations, we obtain

$$G_1 = \frac{L_2}{L_1 + L_2} G \quad (3.29)$$

and

$$G_2 = \frac{L_1}{L_1 + L_2} G. \quad (3.30)$$

By consequence, Eqs. (3.12) and (3.25) lead to

$$v_1 = v_2 = L(G/T), \quad (3.31)$$

where

$$\frac{1}{L} = \frac{1}{L_1} + \frac{1}{L_2}. \quad (3.32)$$

Taking into account that

$$\frac{dn^*}{dt} = \frac{(v_1 - v_2)}{V}, \quad (3.33)$$

the steadiness condition (2.5) is thus vindicated.

We turn now to justify Eq. (2.17). In this case, four transformations participate in the process. They are: the releasing of electrons from traps to the conduction band, the capture of conduction-band electrons in the luminescent centers to form bipolar ions, the capture of conduction-band electrons in luminescent centers deprived of bound holes to form negative ions, and, finally, the radiative recombination of the electron-hole pairs bound to luminescent centers. The affinity and velocity of the first transformation are given, respectively, by Eqs. (3.7) and (3.12). Analogously, the affinities and velocities for the capture of the conduction-band electrons to form bipolar or, respectively, negative ions are

$$\mathcal{G}_2 = -kT \ln \left[\frac{m_{11}}{m_{01} n^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \exp\left(-\frac{E_1}{kT}\right) \right], \quad (3.34)$$

$$\mathcal{G}_3 = -kT \ln \left[\frac{m_{10}}{m_{00} n^*} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \exp\left(-\frac{E_0}{kT}\right) \right] \quad (3.35)$$

and

$$v_r = L_r \frac{\mathcal{G}_r}{T} \quad (r=2, 3), \quad (3.36)$$

in which

$$L_2 = s_1 \exp\left(-\frac{E_1}{kT}\right) \frac{\bar{m}_{11} V}{k} \quad (3.37)$$

and

$$L_3 = s_0 \exp\left(-\frac{E_0}{kT}\right) \frac{\bar{m}_{10} V}{k}. \quad (3.38)$$

The velocity for the radiative recombination is

$$v_4 = [a(\omega) + b(\omega)\rho(\omega)] G_{00} M_{11} - b(\omega)\rho(\omega) G_{11} M_{00}, \quad (3.39)$$

where

$$M_{11} = V m_{11}, \quad M_{00} = V m_{00} \quad (3.40)$$

and

$$G_{00} = G_{11} = 2, \quad (3.41)$$

since only spin degeneration is to be considered. Performing simple transformations, Eq. (3.39) becomes

$$v_4 = a(\omega) \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right]^{-1} 2m_{11} V \times \left[1 - \frac{m_{00}}{m_{11}} \exp\left(-\frac{\hbar\omega}{kT}\right) \right]. \quad (3.42)$$

Proceeding as for Eq. (3.3), the free energy of bipolar ions can be written as

$$F_{11} = M_{11} \hbar\omega - kT \ln \left[2^{M_{11}} \left(\frac{M_{11} + M_{00}}{M_{11}} \right) \right] \quad (3.43)$$

and analogously, after electron-hole recombina-

tion,

$$F_{00} = -kT \ln \left[2^{M_{00}} \left(\frac{M_{11} + M_{00}}{M_{00}} \right) \right]. \quad (3.44)$$

The corresponding chemical potentials are thus

$$\mu_{11} = \frac{\partial F_{11}}{\partial M_{11}} = \hbar\omega - kT \ln \left(2 \frac{M_{11} + M_{00}}{M_{11}} \right) \quad (3.45)$$

and

$$\mu_{00} = \frac{\partial F_{00}}{\partial M_{00}} = -kT \ln \left(2 \frac{M_{11} + M_{00}}{M_{00}} \right), \quad (3.46)$$

which lead to the affinity

$$\mathcal{G}_4 = \mu_{11} - \mu_{00} = -kT \ln \left[\frac{m_{00}}{m_{11}} \exp\left(-\frac{\hbar\omega}{kT}\right) \right]. \quad (3.47)$$

In this way, Eq. (3.42) turns to

$$v_4 = a(\omega) \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right]^{-1} 2m_{11} V \left[1 - \exp\left(-\frac{\mathcal{G}_4}{kT}\right) \right]. \quad (3.48)$$

Disregarding $\exp(-\hbar\omega/kT)$ against unity and putting

$$L_4 = 2a(\omega) \bar{m}_{11} V / k, \quad (3.49)$$

where \bar{m}_{11} means the equilibrium value, Eq. (3.48) takes the form

$$v_4 = L_4 (\mathcal{G}_4 / T), \quad (3.50)$$

which holds for small recombination velocities.

The recombination probability $p^{(e)}$ is given by

$$p^{(e)} = 2a(\omega), \quad (3.51)$$

where again the term $\exp(-\hbar\omega/kT)$ has been omitted.

Taking into account the previous four transformations, the rate of entropy production turns out to be

$$\frac{dS}{dt} = \sum_{r=1}^4 L_r \left(\frac{\mathcal{G}_r}{T} \right)^2. \quad (3.52)$$

On the other hand, we have

$$\mathcal{G} = \mathcal{G}_1 + \mathcal{G}_2 + \mathcal{G}_4 = kT \ln \left[\frac{n_1 m_{01}}{n_0 m_{00}} \exp\left(-\frac{E - (E_1 + \hbar\omega)}{kT}\right) \right], \quad (3.53)$$

which, analogously to Eq. (3.28), depends on the trapped-carrier concentrations, while the concentrations n^* , m_{10} , and m_{11} , concerning electrons in high-lying levels, do not contribute. Therefore we must search for the minimum dS/dt allowed by the constraint that the affinity \mathcal{G} behaves as a constant. Introducing a Lagrangian multiplier λ , we obtain

$$d \left(\frac{dS}{dt} - \lambda \mathcal{G} \right) = \sum_{r=1}^4 \left(2L_r \frac{\mathcal{G}_r}{T^2} - \lambda \right) d\mathcal{G}_r + 2L_3 \frac{\mathcal{G}_3}{T^2} d\mathcal{G}_3 = 0, \quad (3.54)$$

which leads to

$$\alpha_r = \lambda(T^2/2L_r) \quad (r=1, 2, 4) \quad (3.55)$$

and

$$\alpha_3 = 0. \quad (3.56)$$

Eliminating λ by means of Eq. (3.53), it follows that

$$\alpha_r = (L/L_r)\alpha \quad (r=1, 2, 4), \quad (3.57)$$

where

$$\frac{1}{L} = \sum_{r=1}^4 \frac{1}{L_r}. \quad (3.58)$$

Remembering Eqs. (3.12), (3.36), and (3.50), Eq. (3.57) yields

$$v_1 = v_2 = v_4 = L(\alpha/T) \quad (3.59)$$

and

$$v_3 = 0. \quad (3.60)$$

Taking into account that

$$\frac{dn^*}{dt} = \frac{v_1 - v_2 - v_3}{V}, \quad (3.61)$$

$$\frac{dm_{11}}{dt} = \frac{v_2 - v_4}{V}, \quad (3.62)$$

and

$$\frac{dm_{10}}{dt} = \frac{v_3}{V}, \quad (3.63)$$

the steadiness conditions (2.16) are thus justified, so allowing for Eq. (2.17).

IV. DISCUSSION AND CONCLUSIONS

The previous treatment shows that the principle of minimum entropy production works correctly though electronic and radiative processes, rather than chemical reactions, are involved. The TL phosphor plunged in the blackbody radiation constitutes a Markovian system near equilibrium in which the density of electrons in high-lying levels is steady. It follows that all the properties of these systems readily apply, including the steady-state stability.⁸ By consequence, conditions (2.5) and (2.16) and the resulting Eqs. (2.6) and (2.17) remain true even if the phosphor temperature is allowed to increase, as occurs when recording TL glow spectra.

These conclusions concern also TL emission in molecular crystals. In this case, electrons released from traps recombine with ionized molecules to give excited molecules, which come back to the ground state by a radiative transition.¹³

This mechanism, which again leads to an equation like (2.17), has been found active in the TL emission of phenanthrene¹⁴ and naphthacene.¹⁵ It can be derived from Eqs. (2.7)–(2.13) by putting $m_{00}=0$ and $m_{10}=0$. This fact demonstrates the general applicability of the proposed theoretical approach.

Some caution is however necessary to compare the present results with experiment. A first topic concerns the requirement that the phosphor be held in an isothermal cavity full of blackbody radiation, which, indeed, does not occur in practice. But owing to the low temperature of usual TL experiments, the emission rate clearly prevails over that of absorption, which makes the presence of blackbody radiation devoid of an important effect. A more relevant question is raised by the validity of the linear approximation for the velocity laws. The linearity is certainly warranted by a sufficiently small TL emission rate. This, in turn, can be obtained by allowing the phosphor temperature to increase slowly. On the other hand, a slow temperature increase is precisely required in order that glow peaks become well resolved in complex TL spectra. Thus, the linearity requirement actually fits the experimental conditions. This statement can be substantiated by considering, for instance, TL emission in ZnS. This phosphor exhibits a single-glow peak with its maximum near to 200 K.³ Let us give the TL light intensity as a function of the affinity of electron releasing. Using Eqs. (2.1)–(2.6) and Eq. (3.8), we get

$$I \propto -\frac{dm_1}{dt} = \frac{dn_1}{dt} = \frac{v_1}{V}, \quad (4.1)$$

that is, by applying Eqs. (3.11) and (3.12),

$$I \propto s \exp\left(-\frac{E}{kT}\right) \bar{n}_1 \frac{\alpha_1}{kT}. \quad (4.2)$$

On the other hand, Eq. (4.1) shows that the TL light intensity integrated from time t to the peak end is proportional to the density \bar{n}_1 of electrons still kept in traps,

$$\int_t^\infty I dt \propto \bar{n}_1. \quad (4.3)$$

We thus obtain

$$\frac{\alpha_1}{kT} = s^{-1} \exp\left(\frac{E}{kT}\right) \frac{I}{\int_t^\infty I dt}. \quad (4.4)$$

In actual experiments, the TL emission lasts quite a few minutes. Therefore, near the peak's maximum, the ratio $I/\int_t^\infty I dt$ is, in general, of the order of 10^{-2} sec^{-1} . Experiments on ZnS yielded $s \approx 10^3 \text{ sec}^{-1}$, $E \approx 0.15 \text{ eV}$,³ which, using Eq. (4.4), leads to $\alpha_1/kT \approx 6 \times 10^{-2}$. This figure is indeed small enough to allow for a linear velocity affinity relationship. Analogous considerations could be ap-

plied to G_2/kT . Since the ZnS behavior is peculiar to most TL phosphors, it follows that linear-velocity laws hold as a rule in the TL process, differently from what occurs in chemical reactions.

The conclusion can be drawn that nonequilibrium thermodynamics actually supplies a reliable theoretical basis to the ARL model, though different

kinds of TL phosphors are considered. This explains its general suitability to fit experiments.

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¹V. V. Antonov-Romanovskii, *Izv. Akad. Nauk. SSSR Fiz. Ser.* **15**, 637 (1951).

²C. B. Lushchik, *Sov. Phys.-JETP* **3**, 390 (1956).

³V. Maxia, S. Onnis, and A. Rucci, *J. Lumin.* **3**, 378 (1971).

⁴F. Aramu, V. Maxia, and G. Spano, *J. Lumin.* **9**, 104 (1974).

⁵J. S. Prener and F. E. Williams, *J. Phys. Rad.* **17**, 667 (1956).

⁶S. Suzuki and S. Shionoya, *J. Phys. Soc. Jpn.* **31**, 1455 (1971).

⁷A. Suzuki and S. Shionoya, *J. Phys. Soc. Jpn.* **31**, 1462 (1971).

⁸I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1961), Chap. 6.

⁹S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), Chap. 10.

¹⁰N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford U. P., London, 1948), Chap. 5.

¹¹See, for example, W. Heitler, *The Quantum Theory of Radiation* (Oxford U. P., London, 1954), Chap. 5.

¹²For photons in the visible range (i.e. $\hbar\omega \approx 2$ eV), though considering T as high 1000 K, we have:
 $\exp(-\hbar/kT) \approx 8 \times 10^{-11}$.

¹³F. Aramu, V. Maxia, and G. Spano, *J. Lumin.* **10**, 85 (1975).

¹⁴F. Aramu, V. Maxia, and G. Spano, *J. Lumin.* **11**, 153 (1975).

¹⁵F. Aramu, V. Maxia, and G. Spano, *J. Lumin.* **14**, 303 (1976).