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A Theoretical Property of Relaxation Curves in Luminescence and Photoconductivity

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The universally accepted concepts concerning the recombination mechanism of phosphors and photoconductors are not suitable to describe the kinetics of concentration or temperature extinguished phosphorescence and of photoconductivity, although from a priori considerations, applicability of these concepts to extinction phenomena seems most natural.

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1. INTRODUCTION

THE kinetic equations used to describe luminescence and conductivity in crystals excited by light are generally based on the assumption that the probability of the excited electron returning to its initial state is either proportional to n, i.e., the number of excited electrons (monomolecular or pseudomonomolecular reaction)[*] or proportional to n^2 (bimolecular reaction). Opinions of different writers concerning the degree of correspondence between equations of this type and the actual mechanism of the processes in semiconductors vary considerably and depend on the nature of the experiments, the results of which are being compared with the theory. In general, the simpler the experiments the closer are the results in agreement with the theory. It is customary to justify non-agreement of experimental results with the theory, especially where the shape of relaxation curves is concerned, by references to complications arising from the principles or methods employed in the experiment which were not reflected in the theoretical equations. Thus, the question as to whether or not the initial theoretical premises (for example, monomolecular or bimolecular nature of the reaction) are justified does not generally receive a final answer. At the same time a criterion of applicability can be established for the assumed theoretical solutions, a criterion that is not so sensitive to the secondary complications of the processes but which depends strongly on the type of the mechanism of excitation and recombination accepted by the theory. We are referring to the ratio L_p/L_3, the value of which can be different in different theories[1], and which will be designated by the letter s. L_p is the area above the curve of increasing light emission or conductivity, L_3 is the area under the quenching curve (Fig.1). We shall present in this paper the computation of s for a very important general case and compare the result with experiment.

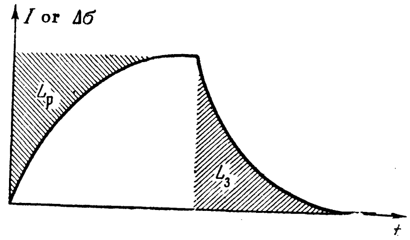

FIG. 1

2. FUNDAMENTAL EQUATION

Nail, Pearlman and Urbach[2] proposed the kinetic equation

$$dn/dt = E - \beta n^2 - \gamma n, \tag{1}$$

where n is the number of excited electrons, E the intensity of exciting light, β and γ the probabilities of bimolecular and monomolecular recombinations. The brightness of illumination I, according to the assumption of the authors, is equal to

$$I = \varepsilon\beta n^2 + \eta\gamma n, \tag{2}$$

where $0 \leqslant \varepsilon \leqslant 1$, and $0 \leqslant \eta \leqslant 1$. The quantity ϵ denotes the fraction of the total number of electrons, recombining according to the bimolecular law, that combine with emission of radiation. The quantity η is a similar quantity for the monomolecular process.

By means of Eqs. (1) and (2), the authors of reference 2 explained the various relationships between the background brightness I_{st} and the inten-

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[*] We shall refer in this paper to both of these reactions as simply the monomolecular reaction.

[1] N. A. Tolstoi and I. A.Litvinenko, J. Exper. Theoret. Phys. USSR **29**, 507 (1955); Soviet Phys. JETP. **2**, 420 (1956)

[2] N. R.Nail, D. Pearlman and F. Urbach, *Solid Luminescent Materials*, Cornell Symposium, 1948, p. 190.

sity of the exciting light E, especially the "greater-than-linear" dependence ($I_{st} \sim E^2$) observed at strong quenching, and also the experimentally observed weaker-than-linear relationships.

3. RISE OF LUMINESCENCE

We rewrite Eq. (1) in the form

$$\frac{dn}{dt} = \beta\left[\frac{E}{\beta} + \left(\frac{\gamma}{2\beta}\right)^2\right]\left[1 - \frac{(n + \gamma/2\beta)^2}{(E/\beta) + (\gamma/2\beta)^2}\right] \qquad (3)$$

and designate

$$(E/\beta) + (\gamma/2\beta)^2 = A. \qquad (4)$$

The solution of Eq. (3) for the luminescent rise process has the form

$$n = n_{st} - \sqrt{A}\,\frac{2ce^{-\tau}}{1 + ce^{-\tau}}, \qquad (5)$$

where

$$n_{st} = n_{t=\infty} = \sqrt{A} - \gamma/2\beta, \qquad (6)$$

$$\tau = 2\beta\sqrt{A}t, \quad c = \frac{\sqrt{A} - \gamma/2\beta}{\sqrt{A} + \gamma/2\beta}.$$

The quantity which interests us,

$$L_p = \int_0^\infty (I_{st} - I)\,dt$$

is computed by means of (2) and (5). By performing substitutions and integrating we obtain:

$$L_p = \left[\frac{\gamma}{\beta}(\varepsilon - \eta)\ln u + \frac{2\varepsilon\sqrt{A}}{u}\right]_{t=0}^{t=\infty}, \qquad (7)$$

where

$$u = 1 + ce^{-\tau}.$$

4. QUENCHING

Solving Eq. (1) with $E = 0$, we have

$$n = \frac{\gamma}{\beta}\,\frac{ce^{-\gamma t}}{1 - ce^{-\gamma t}}, \qquad (8)$$

where c again is obtained from (6). The quantity of interest., L_3, turns out to be equal to

$$L_3 = \int_0^\infty I\,dt = -\left[\frac{\gamma}{\beta}(\varepsilon - \eta)\ln v - \frac{\gamma\varepsilon}{\beta}\frac{1}{v}\right]_{t=0}^{t=\infty}, \qquad (9)$$

where

$$v = 1 - ce^{-\gamma\tau}.$$

5. THE QUANTITY $s = L_p/L_3$

By computing the limits in (7) and (9) and forming the ratio s we obtain, upon transformation,

$$s = \frac{\Delta\delta - 2\ln\left(\frac{1 + \Delta}{1 + (\Delta/2)}\right)}{\Delta\delta - 2\ln(1 + (\Delta/2))}, \qquad (10)$$

where there are introduced symbols

$$\Delta = \sqrt{1 + 4\beta\gamma^{-2}E} - 1, \quad \delta = \varepsilon/(\varepsilon - \eta). \qquad (11)$$

Thus

$$c = \Delta/(\Delta + 2) \quad (c \geqslant 0).$$

The variable Δ can vary within limits $0 \leqslant \Delta \leqslant \infty$. The limits of δ are determined by the fact that ϵ and η are both positive, and can have values from zero to unity. Therefore, either $-\infty \leqslant \delta \leqslant 0$,or $1 \leqslant \delta \leqslant \infty$, , i.e., δ cannot have values within the interval (0, 1).

6. VARIATION OF THE QUANTITY S

(a) Let $\Delta \to \infty$. Then, if $\delta \neq 0$, we have $s \to 1$. If, however, $\delta = 0$, $s \to 0$

(b) Let $\Delta \to 0$. Expanding the logarithmic terms into series up to terms of the order Δ^2, we find

$$s \approx \frac{(\delta - 1) + {}^3\!/_4\Delta}{(\delta - 1) + {}^1\!/_4\Delta}.$$

Then, if $\delta = 1$, we have*: $s \to 3$, and if $\delta \neq 1$, $s \to 1$

(c) Let us compute the partial derivative of s with respect to Δ for $\Delta \to 0$:

$$\frac{ds}{d\Delta} = \frac{(\delta - 1)\,\Delta^2}{[\Delta\delta - 2\ln(1 + \Delta/2)]^2} \qquad (12)$$

(the logarithmic terms in the numerator were expanded up to the order Δ^2).

When $\delta > 1$, $ds/d\Delta > 0$, and when $\delta \leq 0$, $ds/d\Delta < 0$, i.e., for the case of $\delta > 1$ s begins to increase with the increase of Δ (becomes > 1) and for the case of $\delta \leq 0$, s becomes < 1. When $\delta = 1$, as can be confirmed by a separate computation, $ds/d\Delta$ is negative in the region of small Δ, i.e., $s < 3$.

(d) Let us compute $ds/d\Delta$ for $\Delta \to \infty$:

$$\frac{ds}{d\Delta} \to \frac{2\delta\,[\ln(1 + \Delta) - \ln(1 + \Delta + \Delta^2/4)]}{[\Delta\delta - 2\ln(1 + \Delta/2)]^2}. \qquad (13)$$

It can be seen from (13) that $ds/d\Delta \to 0$ since the denominator approaches ∞ faster than the numerator.

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* This special case was examined previously in the paper by Tolstoi[3].

[3] N. A. Tolstoi, Dokl. Akad. Nauk SSSR 95, 249 (1954).

The structure of the numerator in (13) shows that when $\delta \geq 1$, $ds/d\Delta \leq 0$, and when $\delta < 0$, $ds/d\Delta \geq 0$. When $\delta = 0$, as can be shown, $ds/d\Delta \leq 0$ for all values of Δ from 0 to ∞.

Thus the variations of s with Δ have a maximum (if $\delta > 1$) or a minimum (if $\delta < 0$). When $\delta = 1$ or $\delta = 0$, these variations are of the same kind: s decreases with the increase of Δ.

(3) Let us compute the derivative of s with respect to δ:

$$\frac{ds}{d\delta} = \frac{2\Delta \ln\left(\frac{1+\Delta}{1+\Delta+\Delta^2/4}\right)}{[\Delta\delta - 2\ln(1+\Delta/2)]^2}. \tag{14}$$

It is not difficult to see that $ds/d\delta$ is negative for all values of δ. Therefore, for any Δ, smaller values of s will correspond to larger δ. The curves $s(\Delta)$ will nowhere intersect and will coincide only at points $\Delta = 0$ and $\Delta = \infty$.

7. LIMITS OF VARIATION OF S

In order to evaluate the maximum possible values of s, let us rewrite (10) in the form:

$$\Delta\delta = 2\frac{s+1}{s-1}\ln(1+\Delta/2) - \frac{2}{s-1}\ln(1+\Delta), \tag{15}$$

and differentiate both sides with respect to Δ. Let us agree to differentiate only at those points where s (as a function of Δ) has a maximum or a minimum. It can then be considered that s and δ do not depend on Δ, and they can be treated as constants in the differentiation process:

$$\delta = \frac{s+1}{s-1}A - \frac{2}{s-1}B, \tag{16}$$

where $A = 1/(1 + \Delta/2)$, $B = 1/(1 + \Delta)$. Let $\delta = 0$. Then since $A > B$ and the right part must be negative, $s < 1$. Let $\delta > 1$ Then, by transformation of (16) we have:

$$(\delta - 1) = \frac{\Delta}{1+\Delta}\left[\frac{1}{(s-1)(1+\Delta)} - \frac{1}{2}\right]. \tag{17}$$

Since the expression in parentheses must be positive, $s < 3$. It is evident from this expression that $s \geq 1$.

For curves $s(\Delta)$ corresponding to the cases of $\delta = 0$ and $\delta = 1$ we know the values of $s(0)$ and $s(\infty)$. If these curves had maxima at $\Delta > 0$ the evaluations $s < 1$ (when $\delta = 0$) and $s < 3$ (when $\delta = 1$) would apply. If they have no maxima, i.e., s decreases uniformly with increase of Δ, then the following evaluations would apply: $s \leq 1$ (when $\delta = 0$) and $s \leq 3$ (when $\delta = 1$).

Summarizing, we have: for the case $1 \leq \delta \leq \infty$, $1 \leq s \leq 3$ and for the case $0 \geq \delta \geq -\infty$, $0 \leq s \leq 1$.

Figure 2 shows the general appearance of the family of curves $s(\Delta)$ for various values of δ. The table contains a summary of all results; the symbols 0-1, etc , indicate the limits of variations for the corresponding quantities.

TABLE

No.	Excitation	Quenching	β	γ	ε	η	$\Delta_{\varepsilon > 0}$	δ	$s = L_p/L_3$	$s\vert_{E\to 0}$	$s\vert_{E\to\infty}$
1	Any	None	+	+	1	1	+	$\pm\infty$	1	1	1
2	Mono	Mono	0	+	—	0—1	0	—	1	1	1
3	”	Bi	+	+	0	1	+	0	0—1	1	0
4	”	Mono-Bi	+	+	0	0—1	+	0	0—1	1	0
5	Bi	Mono	+	+	1	0	+	1	1—3	3	1
6	”	Bi	+	0	0—1	0	∞	1	1	1	1
7	”	Moro-Bi	+	+	0—1	0	+	1	1—3	3	1
8	Mono-Bi	Mono	+	+	1	0—1	+	>1	1—3	1	1
9	” ”	Bi	+	+	0—1	1	+	<0	0—1	1	1
10	” ”	Mono-Bi	+	+	0—1	0—1	+	<0 >1	0—1 1—3	1 1	1 1

Mono - Monomolecular
Bi - Bimolecular

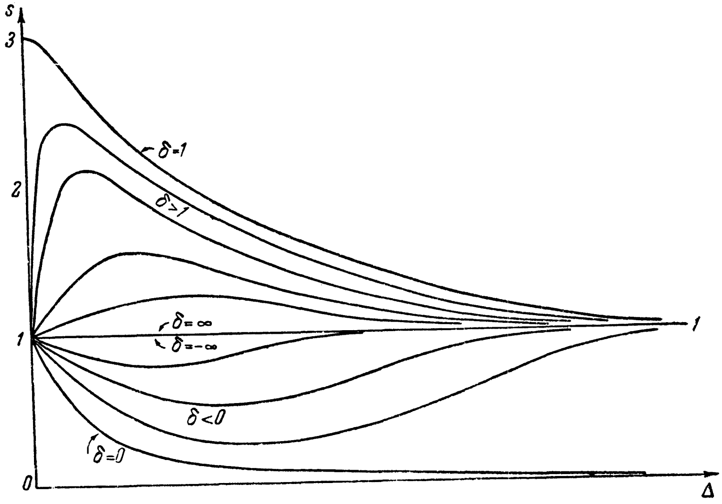

FIG. 2. General Shape of curves $s(\Delta)$ for different values of δ.

8. DISCUSSION

The most important result of the above computations is that in all cases the value of s remains less than 3. However, experiments indicate that under conditions of strong temperature and concentration quenching, the luminescence of sulphide type phosphors is characterized by values of s far in excess of 3 (for example, $s = 10$ – to 12, see reference 1). It is therefore necessary to conclude that even such a flexible and universal kinetic equation, which was assumed in reference 2 and which well describes the regular order of steady luminescence) cannot be adequate for the kinetics of luminescence of quenched phosphors of the sulphide type. It is natural to suppose that the reason why experimental results do not agree with the theory is that Eqs. (1) and (2) describe excited states singularly characterized by the number n of excited electrons.

In substance, this indicates that among the various energy levels of excitation (conduction band, levels of sticking) there exists also exchange equilibrium. Under ordinary conditions, the existence of such exchange equilibrium is more than doubtful. However, at a higher temperature under conditions of strong temperature quenching, for example i.e., exactly when values of $s > 3$ are observed, thermal exchange equilibrium becomes highly probable . Moreover, all other complications which are usually ascribed to kinetic processes in phosphors should, it seems, disappear at high temperatures[3] (for example, filling of local levels close to saturation, luminescent action of the exciting light, etc.). Such lack of agreement between experiment and theory, based on the application of the general criterion (value of s), must be considered as significant and compels a review of the widespread concepts concerning the mechanism of luminescence for sulphide phosphors.

The mechanism of photoconductivity is also generally described by type (1) equations with the difference that the value of photoconductivity $\Delta\sigma$, as distinguished from the brightness of luminescence I, is expressed as $\Delta\sigma = \alpha n$.

It is not difficult to see that it is possible to make use of the above results when one determines the value s for photoconductivity. Formally, the case of photoconductivity corresponds to monomolecular luminescence, and therefore, as seen from the table (Nos. 2, 3, 4) s for photoconductivity should be ≤ 1. Roughly speaking, this means that in the case of photoconductivity the curve of the current rise can only be "faster" than the decay curve; or, in the extreme case, equal to it. It follows that the appearance in photoconductivity experiments of values $s > 1$ also indicates sharp disagreement with accepted concepts. Nevertheless, such values are observed in experiments (for example, in CdS-Cu with high concentration of copper)

It is known that unequal excitation of the phosphor or the photoconductor in depth, connected with the absorption of light in the thickness of the sample, leads to additional complications in the case of non-linearly or non-exponentially relaxing substances. These complications, however, cannot influence the evaluated limits we have found for s, since any superposition of relaxation curves, for which these limits hold, cannot result in an integral curve for which s is outside the evaluated limits (above as well as below).

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