

## SUMMARY

(1) Deformation of an irradiated crystal causes a reappearance of the "first-stage" coloration for the  $F$  centers. Moreover, the coloring curve can be separated into the same stages as those present for the undeformed samples. This verifies the effect reported by Agulló-Lopez and Levy.<sup>7</sup>

(2) The deformation induced enhancement of the colorability can be annealed out by heat treating the samples in air at 450°C for 20 min. After this treatment reirradiation yields the same coloring curve as that characteristic of an undeformed sample. A longer heat treatment in air results in an increase in the colorability of the sample. This is possibly due to oxygen since no increase in colorability was noted for an Isomet sample

cleaved from the center of a large block which had been held at 575°C for 2 h.<sup>9</sup>

(3) The incremental increase in the  $F$ -center colorability due to deformation is different for crystals obtained from different sources for the same amount of deformation.

(4) In samples where the 195- and 212-m $\mu$  absorption bands grow more slowly than the  $V_2$  band it is observed that the coloration curves for the  $V_2$  band are very similar to those for the  $F$  band, and are affected by deformation and heat treatment in the same way.

## ACKNOWLEDGMENTS

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## Nonthermal Equilibrium Fluctuations of Electrons and Holes\*

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A discussion is presented on the behavior of electron and hole fluctuations under steady-state conditions. The differences between steady-state and thermal-equilibrium systems, associated with microscopic reversibility, are briefly discussed. It is concluded that so far all calculations pertained to conditions valid for (quasi-) thermal equilibrium. To illustrate the features for a nonequilibrium state, an academic model involving cyclic transitions through one set of electron traps is analyzed. The variance is shown to be super-Poissonian in the range where the photoconductance is superlinear and sub-Poissonian in the range where all traps are filled. The connection with presently accepted two-center models for phosphors and photoconductors is also indicated.

## 1. INTRODUCTION

DURING the past decade several methods have been developed to obtain the variances and covariances of electron and hole fluctuations in solids.<sup>1-4</sup> These fluctuations arise from spontaneous or induced transitions between the various energy levels in a particular solid material. A specification of these various transition rates together with the applicable constraints (e.g., charge neutrality) and *a priori* probabilities for the quantum states (generally governed by the Pauli exclusion principle) is sufficient to obtain the variances  $\langle \Delta n_i^2 \rangle$  and covariances  $\langle \Delta n_i \Delta n_j \rangle$ . In the past two completely different procedures have been employed for materials which are in thermal equilibrium with the surroundings.

(a) Burgess<sup>1</sup> has shown that carrier variances are

easily calculated from the expression for the free-energy function  $F(n_1, n_2, \dots, n_s)$ , where  $n_1 \dots n_s$  represent the carrier densities in the various electronic levels close to the equilibrium state. If  $n_1 \dots n_{s-1}$  are unconstrained variables (i.e., the charge-neutrality equation has been used to eliminate  $n_s$ ), then we have simply for the variances and covariances

$$\sum_j \langle \Delta n_i \Delta n_j \rangle (\partial^2 F / \partial n_j \partial n_k) = kT \delta_{ik},$$

or, in matrix notation,

$$\langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle = kT [\partial^2 F / \partial \mathbf{n} \partial \mathbf{n}]^{-1}. \quad (1.1)$$

This result could also be obtained using irreversible thermodynamics, compare Ref. 3.

(b) A purely stochastic procedure was first employed by van Vliet and Blok<sup>2</sup> and later on by Lax<sup>4</sup> by solving the Fokker-Planck equation or master equation, respectively. The kinetic equations are written in the form

$$\frac{dn_i}{dt} = \sum_{j=1}^s [\dot{p}_{ji}(\mathbf{n}) - p_{ij}(\mathbf{n})], \quad (1.2)$$

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<sup>1</sup>R. E. Burgess, Proc. Phys. Soc. (London) **B68**, 661 (1955); **B69**, 1020 (1956).

<sup>2</sup>K. M. van Vliet and J. Blok, Physica **22**, 231 (1956).

<sup>3</sup>K. M. van Vliet, Phys. Rev. **110**, 50 (1958).

<sup>4</sup>M. Lax, Rev. Mod. Phys. **32**, 25 (1960).

or, in linearized form, expanding about  $\langle \mathbf{n} \rangle = \mathbf{n}_0$

$$\frac{d\Delta n_i}{dt} = \sum_{k=1}^{s-1} a_{ik}(\mathbf{n}) \Delta n_k; \quad (1.3)$$

here  $\mathbf{n}$  stands for all the independent variables and

$$a_{ik} = \sum_i^s \left\{ \left[ \frac{\partial p_{ji}}{\partial n_k} \right]_{\mathbf{n}=\mathbf{n}_0} - \left[ \frac{\partial p_{ij}}{\partial n_k} \right]_{\mathbf{n}=\mathbf{n}_0} \right\}. \quad (1.4)$$

The result of the solutions referred to above yields the "generalized  $g$ - $r$  theorem"

$$\mathbf{a} \cdot \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle + \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle \cdot \mathbf{a}^T = -\mathfrak{B}, \quad (1.5)$$

where  $\mathbf{a}$  is the rate-coefficients matrix defined by (1.3),  $\mathbf{a}^T$  its transpose, and  $\mathfrak{B}$  is composed of the second-order Fokker-Planck moments:

$$B_{ii} = 2 \sum_i^s p_{ij}(\mathbf{n}_0), \quad (1.6)$$

$$B_{ij} = -p_{ij}(\mathbf{n}_0) - p_{ji}(\mathbf{n}_0) \quad (i \neq j).$$

The equivalence of both procedures *under thermal equilibrium conditions* was proven by Burgess and by van Vliet for special cases<sup>1,5</sup> and later on quite generally employing arguments based on irreversible thermodynamics by van Vliet<sup>3</sup> and by Lax.<sup>4</sup> However, the result (1.5) is more general in that it also applies to nonthermal equilibrium, i.e., in a steady state in which stationary driving forces are present. Though, even then, under some conditions the result (1.5) is still identical with (1.1), this is not generally true. It is the purpose of this paper to investigate the fluctuations in a genuine nonthermodynamic state, and the conditions for which this occurs. Particularly, we shall explore the possibility of obtaining large variances ( $\langle \Delta n^2 \rangle \gg n_0$ ), such as have been found in some photoconductors.<sup>6,7</sup>

## 2. THERMAL EQUILIBRIUM VERSUS STEADY-STATE PROCESSES

Rate equations such as (1.2) can generally be written down for any stationary state that is attained as a balance between gain and loss processes. We shall assume that the linearized fluctuations from the steady state are Gaussian in character and, moreover, that the process as a whole is Markoffian random. This requires first of all that the specification of the stochastic variables  $\mathbf{n}(t)$  is complete and, furthermore, that Smoluchowski's integral relation for the conditional probabilities  $P(\mathbf{n}, t | \mathbf{n}_0)$  holds. This latter relation is

equivalent with the master equation<sup>8,9</sup>

$$\frac{\partial P(\mathbf{n}, t | \mathbf{m})}{\partial t} = \sum_{\mathbf{k}}' P(\mathbf{k}, t | \mathbf{m}) Q(\mathbf{n}; \mathbf{k}) - \sum_{\mathbf{k}}' P(\mathbf{n}, t | \mathbf{m}) Q(\mathbf{k}; \mathbf{n}), \quad (2.1)$$

where  $\mathbf{k}$  and  $\mathbf{m}$  have been used as additional symbols to represent the set  $\mathbf{n}$ ;  $Q(\mathbf{n}; \mathbf{k})$  is the transition probability

$$Q(\mathbf{n}; \mathbf{k}) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} P(\mathbf{n}, \Delta t | \mathbf{k}), \quad (2.2)$$

providing this limit exists.

The central feature of thermodynamic equilibrium is expressed by the principle of microscopic reversibility (see Refs. 10 and 11), which, in a simple form, states

$$W_2(\mathbf{k}, \mathbf{m}) = W_2(\mathbf{m}, \mathbf{k}); \quad (2.3)$$

here  $W_2$  refers to the joint probability for  $\mathbf{n}(t_1)$  and  $\mathbf{n}(t_2)$ . The consequences of this principle are manifold, of which we mention here:

(i) The postulate (2.3) leads to detailed balance. An easy proof (compare, e.g., Bowen and Meyer<sup>12</sup>) is as follows. Let  $\mathbf{n}(0) = \mathbf{k}$  and  $\mathbf{n}(\Delta t) = \mathbf{m}$ . Then (2.3) means:

$$W_1(\mathbf{k}) P(\mathbf{m}, \Delta t | \mathbf{k}) = W_1(\mathbf{m}) P(\mathbf{k}, \Delta t | \mathbf{m}), \quad (2.4)$$

where  $W_1(\mathbf{n})$  is the single probability distribution of the set  $\mathbf{n}$ . Dividing by  $\Delta t$  we have

$$W_1(\mathbf{k}) Q(\mathbf{m}; \mathbf{k}) = W_1(\mathbf{m}) Q(\mathbf{k}; \mathbf{m}). \quad (2.5)$$

In particular, let us now consider the transitions determined by

$$\{m_1, \dots, m_i, m_j, \dots, m_s\} = \{k_1, \dots, k_i + 1, k_j - 1, \dots, k_s\}. \quad (2.6)$$

Then for the transition probabilities we have

$$\begin{aligned} Q(\mathbf{m}; \mathbf{k}) &= p_{ji}(\mathbf{k}), \\ Q(\mathbf{k}; \mathbf{m}) &= p_{ij}(\mathbf{m}). \end{aligned} \quad (2.7)$$

Summing Eq. (2.5) over all  $\mathbf{k}$ , we have, using Eq. (2.6),

$$\begin{aligned} &\sum_{k_1=0}^{\infty} \dots \sum_{k_i=0}^{\infty} \sum_{k_j=1}^{\infty} \dots \sum_{k_s=0}^{\infty} W_1(\mathbf{k}) p_{ji}(\mathbf{k}) \\ &= \sum_{k_1=1}^{\infty} \dots \sum_{k_i=0}^{\infty} \sum_{k_j=1}^{\infty} \dots \sum_{k_s=0}^{\infty} W_1(\mathbf{m}) p_{ij}(\mathbf{m}) \\ &= \sum_{m_1=1}^{\infty} \dots \sum_{m_i=1}^{\infty} \sum_{m_j=0}^{\infty} \dots \sum_{m_s=0}^{\infty} W_1(\mathbf{m}) p_{ij}(\mathbf{m}). \end{aligned} \quad (2.8)$$

<sup>8</sup> This equation is also known as the Chapman-Kolmogoroff equation in the mathematical literature.

<sup>9</sup> A. N. Kolmogoroff, *Math. Ann.* **104**, 415 (1931).

<sup>10</sup> H. B. G. Casimir, *Rev. Mod. Phys.* **17**, 343 (1945).

<sup>11</sup> S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1962).

<sup>12</sup> J. I. Bowen and P. N. Meyer, *Physica* **26**, 485 (1960).

<sup>5</sup> K. M. van Vliet, *Physica* **23**, 248 (1957).

<sup>6</sup> K. M. van Vliet, J. Blok, C. Ris, and J. Steketeet, *Physica* **22**, 723 (1956).

<sup>7</sup> J. J. Brophy and R. J. Robinson, *Phys. Rev.* **117**, 738 (1960); also J. J. Brophy, *ibid.* **119**, 591 (1960); J. J. Brophy and R. J. Robinson, *J. Appl. Phys.* **31**, 1343 (1960).

The sum in the left-hand side is  $\langle p_{ji}(\mathbf{n}) \rangle$ . Likewise, the summations in the right-hand side yield immediately  $\langle p_{ij}(\mathbf{n}) \rangle$ . If  $\langle n_i \rangle \equiv n_{i0}$  are large numbers, it is easily shown that the above result is equivalent to

$$p_{ij}(\mathbf{n}_0) = p_{ji}(\mathbf{n}_0) + O(\Delta n^2) \quad (2.9)$$

which expresses the principle of detailed balance.

(ii) It has been shown before<sup>8</sup> that the kinetic equations can be written in the standard form of irreversible thermodynamics,

$$\frac{d\Delta n_i}{dt} = \sum_{j=1}^s (R^{-1})_{ij} (\mu_s - \mu_j), \quad (2.10)$$

where  $(\mu_s - \mu_j)$  are generalized driving forces,  $(R^{-1})_{ij}$  are generalized conductances. These conductances are directly related to the  $p_{ij}(\mathbf{n})$  and obey the Onsager relations, i.e.,  $(R^{-1})_{ij} = (R^{-1})_{ji}$ . The general proof of Onsager's relations, following from microscopic reversibility, is, of course, well known. (For original proof see, e.g., Ref. 10, for a modern proof, Ref. 11.)

(iii) A more peculiar result, based on microscopic reversibility, and of prime importance in the present paper, is the fact that  $\mathbf{a} \cdot \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle$  is a symmetrical matrix, i.e.,

$$\mathbf{a} \cdot \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle = \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle \cdot \mathbf{a}^T. \quad (2.11)$$

This means that now the covariance matrix [see Eq. (1.5)] can be explicitly expressed as

$$\langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle = -\frac{1}{2} \mathbf{a}^{-1} \cdot \mathfrak{B}. \quad (2.12)$$

This result and its complete equivalence with (1.1) was first proven by the author<sup>13</sup>; later on, a very direct proof of (2.11) was given by Lax.<sup>14</sup> The essential parts of this proof are as follows. From microscopic reversibility we have, noticing

$$\langle \Delta \mathbf{n}(t) \Delta \mathbf{n}(0) \rangle = \sum_{\Delta \mathbf{n}(0)=\mathbf{n}} \sum_{\Delta \mathbf{n}(t)=\mathbf{n}'} \Delta \mathbf{n} \Delta \mathbf{n}' W_2(\mathbf{n}, \mathbf{n}'), \quad (2.13)$$

the well-known result

$$\langle \Delta \mathbf{n}(t) \Delta \mathbf{n}(0) \rangle = \langle \Delta \mathbf{n}(0) \Delta \mathbf{n}(t) \rangle. \quad (2.14)$$

The linearized master equation solution using the Stozahlansatz (2.7) is easily shown to result in

$$\langle \Delta \mathbf{n}(t) \Delta \mathbf{n}(0) \rangle = [\exp(\mathbf{a}t)] \cdot \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle. \quad (2.15)$$

For small  $t$  this yields

$$\langle \Delta \mathbf{n}(\Delta t) \Delta \mathbf{n}(0) \rangle - \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle = \mathbf{a} \cdot \langle \Delta \mathbf{n} \Delta \mathbf{n} \rangle \Delta t. \quad (2.16)$$

Since the left-hand side is symmetrical, the right-hand side must be symmetrical also, thereby establishing (2.11).

Let us now consider a nonthermodynamic steady state. Microscopic reversibility does not necessarily exist. From the master equation we easily get the

macroscopic equations by various procedures (cf. Refs. 15, 16).

$$\frac{\partial \langle \mathbf{n}_i(t) | \mathbf{m} \rangle}{\partial t} = \sum_j' \langle p_{ji}(\mathbf{n}) | \mathbf{m} \rangle - \sum_j' \langle p_{ij}(\mathbf{n}) | \mathbf{m} \rangle, \quad (2.17)$$

which leads to the stationary state equations ( $t \rightarrow \infty$ )

$$\sum_j' p_{ij}(\mathbf{n}_0) = \sum_j' p_{ji}(\mathbf{n}_0) + O(\Delta n^2). \quad (2.18)$$

In case transitions occur between two states only this is equivalent to (2.9). These cases can be considered as quasithermal equilibrium cases. Also, in several photoconductors it has been assumed that a set of traps exists in quasithermal equilibrium with the conduction band (i.e., having a common quasi-Fermi level) and a set of activation centra, in quasithermal equilibrium with the valence band. The variances in these cases are similar as for thermal equilibrium conditions.<sup>17</sup> In particular, it can be shown that the simplified result (2.12), holding under (quasi-) thermal equilibrium conditions, always yields sub-Poissonian variances, i.e.,  $\langle \Delta n_i^2 \rangle / n_{i0} \leq 1$ .

### 3. A NONEQUILIBRIUM MODEL

Though noise has been calculated in various photoconductive materials, unfortunately so far all applications referred to a quasithermal equilibrium state. In this paper we shall consider an academic model of a three-level photoconductor, being in a steady state (sometimes referred to as driven equilibrium) and in which detailed balance is completely lacking. It will be shown that in certain regions large, i.e., super-Poissonian, fluctuations can occur. Though the model—when properly amended, see Sec. 4—may have some bearing to “giant noise” as observed in CdS, (Refs. 6 and 7) this will not be pursued in this paper, particularly since experiments on indium-doped CdS by Zijlstra<sup>18</sup> may point to an alternative explanation.<sup>19</sup>

<sup>13</sup> N. G. van Kampen, *Physica* **23**, 707 (1953).

<sup>14</sup> J. R. Fassett, Ph.D. thesis, University of Minnesota, 1962 (unpublished); also K. M. van Vliet, *Phys. Stat. Solidi* (to be published).

<sup>17</sup> In connection with the experimental work in CdS it may further be emphasized here that a quasithermal equilibrium model involving relatively shallow traps, such as discussed previously [K. M. van Vliet and J. Blok, *Physica* **22**, 525 (1956)] will not lead to super-Poissonian fluctuations. This was pointed out to me by Dr. A. Rose of RCA Laboratories.

<sup>18</sup> R. J. Zijlstra, *Physica* (to be published).

<sup>19</sup> The experimental situation about CdS noise is not completely clear at present. Van Vliet *et al.*, reported  $g$ - $r$  noise in silver- and self-activated CdS crystals, for which the shape of the spectra was shown to be in agreement with the measured response to alternating light (Ref. 6). The estimated magnitude of the variance  $\langle \Delta n^2 \rangle / \bar{n}$  was below 10 in most cases, and as high as 50 in some curves (if the mobility is evaluated at 100 cm<sup>2</sup>/V sec). Brophy and Robinson (Ref. 7) on the contrary report relative variances as high as 5000. Even larger magnitudes were found recently by Pai in this department. It is by no means sure in all these cases that the noise is  $g$ - $r$  noise. Zijlstra showed that similar spectra as reported by Brophy occur in indium-doped CdS layers

<sup>13</sup> K. M. van Vliet, see Ref. 3, Sec. 8.

<sup>14</sup> M. Lax, Ref. 4, Sec. 6.

The simple model is depicted in Fig. 1(a). We assume that recombination levels are filled by electrons from the conduction band, which in turn only release their carriers to the valence band. Thus the transitions can be labeled  $p_{31}$ ,  $p_{12}$ ,  $p_{23}$ . The opposite transitions are absent (simply because traps are too "deep"). We assume that  $p_{31}$  is induced by light. The advantage of this model is that, though detailed balance is lacking, the rate constants do not enter explicitly into the expression for the variances, as shown below.

The rate equations are in this case

$$\begin{aligned} dn/dt &= \alpha Z - \delta n(I-i), \\ di/dt &= \delta n(I-i) - \kappa i(n+i), \end{aligned} \quad (3.1)$$

where  $n$ ,  $i$ ,  $p = n+i$  are the carrier concentrations in conduction band, traps and valence band, respectively.  $I$  is the number of traps,  $\alpha$  is an absorption efficiency,  $\delta$  and  $\kappa$  are rate constants, related to the cross sections for electron and hole trapping. Linearizing in the form (1.3) we obtain:

$$\left. \begin{aligned} a_{11} &= -\delta(I-i_0) & a_{12} &= \delta n_0 \\ a_{21} &= \delta I - \delta i_0 - \kappa i_0 & a_{22} &= -(\delta n_0 + \kappa n_0 + 2\kappa i_0) \end{aligned} \right\}. \quad (3.2)$$

For the  $B$  matrix we find from (1.6) in conjunction with Fig. 1(a):

$$\left. \begin{aligned} B_{11} &= 2(p_{12}^0 + p_{13}^0) = 2\delta n_0(I-i_0) \\ B_{12} &= B_{21} = -p_{12}^0 - p_{21}^0 = -\delta n_0(I-i_0) \\ B_{22} &= 2(p_{12}^0 + p_{32}^0) = 2\delta n_0(I-i_0) \end{aligned} \right\}. \quad (3.3)$$

The coefficients  $\kappa$ ,  $\alpha$ , and  $\delta$  are related to each other, since in the steady state

$$\alpha Z = \delta n_0(I-i_0) = \kappa i_0(n_0+i_0). \quad (3.4)$$

It is then possible to express the  $a$ 's and  $B$ 's in  $\delta$  only (besides  $n_0$ ,  $i_0$ ,  $I$ ) and, since the matrix equation (1.5) is homogeneous in  $a_{ij}$  and  $B_{ij}$ , the variance is determined by the concentrations only. One then obtains

$$\frac{\langle \Delta n^2 \rangle}{n_0} = \frac{(I-i_0)^2 2i_0 + 3n_0 i_0 (I-i_0) + i_0^2 n_0}{(I-i_0)^2 2i_0 + 3n_0 i_0 (I-i_0) + 2n_0^2 (I-i_0) + i_0 n_0^2}. \quad (3.5)$$

It is easily verified that this solution differs from that of a quasithermal equilibrium state in which (2.10) and (2.11) are supposed to hold. If the traps are being filled  $I-i_0 \rightarrow 0$ . Then

$$\langle \Delta n^2 \rangle / n_0 \rightarrow i_0 / n_0. \quad (3.6)$$

This may be several orders of magnitude larger than unity. More specifically, let us put

$$(I-i_0)/i_0 = k, \quad n_0/i_0 = q. \quad (3.7)$$

on an insulating CdS substratum. In this case the fluctuations are clearly to be attributed to diffusion of the carriers from the semi-conducting layer into the insulating substratum. The possibility that similar effects occur in regular insulating CdS platelets should not be excluded and is being investigated.

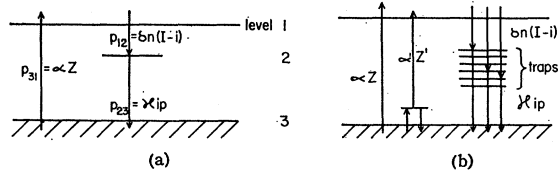


FIG. 1. Noise due to cyclic transitions. (a) Academic model. (b) More realistic model.

Then,

$$\frac{\langle \Delta n^2 \rangle}{n_0} = \frac{2k^2 + (3k+1)q}{2k^2 + 3kq + (1+2k)q^2}. \quad (3.8)$$

Large variances can occur in a narrow range where  $k \ll 1$  and  $q \ll 1$ . To discuss the feasibility of this situation, we investigate the photoconductivity exhibited by the model, following from the steady-state equations (3.4).

(a) For very low light intensities,  $n_0 \ll i_0$ ,  $i_0 \ll I$  or  $k \gg 1$ ,  $q \ll 1$ . This yields immediately

$$n_0 = \alpha Z / \delta I, \quad (3.9)$$

i.e., the photoconductance is linear with  $Z$ .

(b) High light intensity. From the second relation of (3.4) we have

$$i_0 = \frac{-n_0(\kappa + \delta)}{2\kappa} + \frac{1}{2\kappa} [(\kappa + \delta)^2 n_0^2 + 4\delta n_0 I \kappa]^{1/2}. \quad (3.10)$$

If  $\delta n_0 \gg 4I\kappa$ , the square root can be expanded, yielding  $i_0/I \simeq \delta/(\kappa + \delta)$ . Substitution of this into the first relation of (3.4) yields

$$n_0 = \frac{\alpha Z}{\delta I} \frac{\kappa + \delta}{\kappa}. \quad (3.11)$$

Again, the photoconductance is linear with  $Z$ ; the proportionality constant is larger than in the low light case. Thus, the photoconductor is superlinear, and the more so when  $\delta/\kappa$  increases.

(c) In the intermediate region approximations are not appropriate. From (3.4) we have the relations

$$kq/(q+1) = \kappa/\delta \equiv y, \quad (3.12)$$

$$qk/(k+1)^2 = \alpha Z / \delta I^2 \equiv \mathcal{L}, \quad (3.13)$$

$$P \equiv n_0/I = q^2/[q(1+y)+y]; \quad (3.14)$$

here  $k$  and  $q$  were defined before [Eq. (3.7)],  $y$  is a dimensionless parameter involving the ratio of the capture cross sections,  $\mathcal{L}$  is the normalized light intensity,  $P$  is a measure for the photoconductance. Equations (3.12) and (3.13) lead to a cubic equation for  $k$  and  $q$ , which was solved for varying  $\mathcal{L}$  and  $y$  using a Control Data 1604 computer. The results are shown in Fig. 2 (computed photoconductance), Fig. 3 (computed filling of traps  $i_0/I$  versus  $\mathcal{L}$ ) and Fig. 4 [computed relative variance according to Eq. (3.8)].

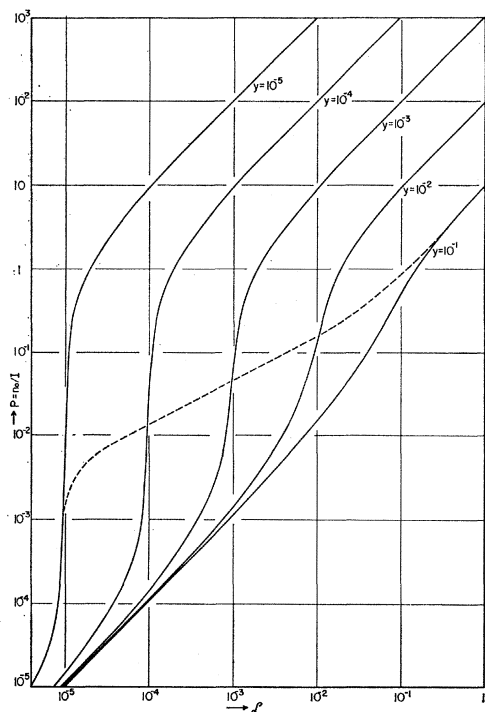


FIG. 2. Relative photoconductance  $n_0/I$  versus normalized light intensity  $\mathcal{L} = \alpha Z/\delta I^2$  for various  $y = \kappa/\delta$  (Control Data 1604 computer results).

First of all, it is noted that the photoconductance is extremely strongly superlinear, particularly for low  $\kappa/\delta$  (which is physically most feasible, see Sec. 4). This superlinearity occurs due to the filling of traps, which do not release their carriers to the conduction band and thus are "ground states" in Rose's sense; a comparison of Fig. 2 with Fig. 3 clarifies this point.

The variance is indeed quite large in the superlinear region (the largest value in Fig. 4 is  $\langle \Delta n^2 \rangle/n_0 = 75$ ). More clearly, we show the relative variance versus the number of photoexcited carriers in the superlinear region in Fig. 5, taking  $\kappa/\delta = 10^{-5}$ . It will further be noted that the noise drops to zero in the high light region due to the absence of shallow traps in the present model.

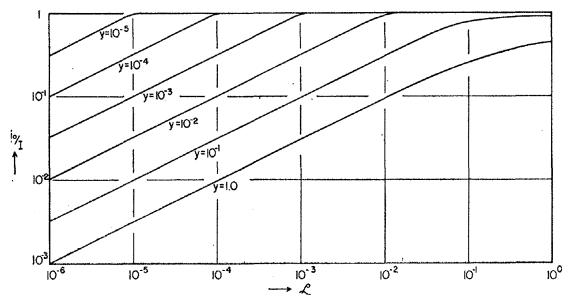


FIG. 3. The filling of the traps (computed).

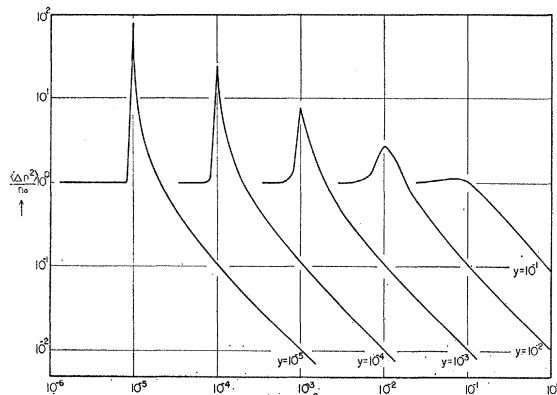


FIG. 4. The relative variance  $\langle \Delta n^2 \rangle/n_0$  versus  $\mathcal{L}$  (computed results).

A final peculiarity of the model is that the addition of a distribution of traps with the same  $\delta$  and  $\kappa$ , throughout the forbidden gap does not affect the noise power, nor the lifetime. This is so, because the kinetic equations remain of the form (3.1), where now  $i = \sum i_k$ ,  $I = \sum I_k$ .

#### 4. MORE SOPHISTICATED MODELS

The above described three-level model is academic in that only one fixed electron-trapping level has been assumed. Most photoconductive phenomena have been explained, however, on the basis of a two-center model, see, e.g., Rose,<sup>20</sup> and H. A. Klasens.<sup>21</sup> The basic reason for this stems from the chemistry of phosphors: The principle of "controlled valency" requires generally that both donors and acceptors be incorporated. Nevertheless, the absence of appreciable hole conductivity in materials like CdS, indicates a preference for hole trapping by the occupied acceptor states (in the chemical sense) above the valence band.<sup>22</sup> The quasithermal equilibrium between these states and free holes is indicated

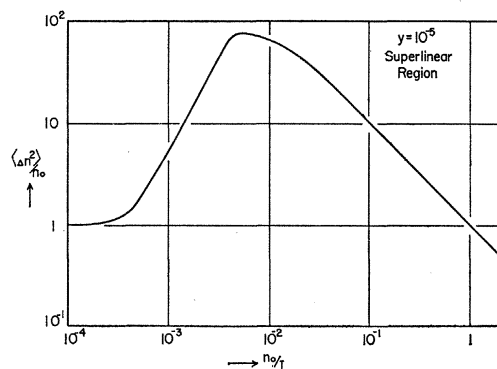


FIG. 5. Relative variance as a function of the free carrier concentration in the superlinear region for  $y = 10^{-5}$ .

<sup>20</sup> A. Rose, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), pp. 3-48.

<sup>21</sup> H. A. Klasens, *Phys. Chem. Solids* 7, 175 (1958).

<sup>22</sup> F. A. Kröger, H. J. Vink, and J. van den Boomgaard, *Z. Physik. Chem.* 203, 1 (1954).

by the usual equation [compare Fig. 1(b)]

$$da_k/dt = \gamma p(A_k - a_k) - \gamma p_{k1} a_k = 0, \quad (4.1)$$

where  $A_k$  is the number of acceptors of kind  $k$ ,  $a_k$  the number of trapped holes,  $p_{k1}$  the Shockley-Read quantity (i.e., the number of free holes if the quasi-Fermi level of the centers coincides with the trapping level). At low light intensities and times large compared to the hole-acceptor relaxation times we have  $a_k \ll A_k$ , and  $p = p_{k1}(a_k/A_k)$ . Since also  $p = n + \sum_j i_j - \sum_k a_k$ , we find, denoting by  $i$  the total electron trap population,

$$p = (n+i)/[1 + \sum_k (A_k/p_{k1})]. \quad (4.2)$$

Thus, the recombination through the electron trap—assuming that all traps are still characterized by one  $\delta$  and  $\kappa$ —can be written as

$$R_1 = \delta n \sum_j (I_j - i_j) = \delta n(I - i) \quad (4.3)$$

$$R_2 = \sum_j \kappa i_j p = \kappa i(n+i)/F, \quad (4.4)$$

where  $F$  is the denominator in (4.2). Clearly  $F \gg 1$ ; hence, the apparent recombination constant  $\kappa' = \kappa/F \ll \kappa$ . Thus, even if  $\delta$  and  $\kappa$  are of the same order of magnitude, the apparent  $y = \kappa'/\delta$  is a very small quantity. This leads to superlinearity and large variances. Moreover, the abundant hole trapping reduces the free hole concentration to such an extent that the electrons become the majority carriers, i.e.,  $n_0 \gg p_0$ , even though  $n_0 < p_0 + a_0$ , thus making the electron fluctuations  $\langle \Delta n^2 \rangle$  observable (no contribution from  $\langle \Delta p^2 \rangle$  in the conductance fluctuations).

The previous model concentrated the superlinearity in a very small light range. If the small value of the parameter  $y = \kappa'/\delta$  is attributed to hole trapping, however, this is no longer the case. If a set of acceptor levels fills up, i.e.,  $a_{k0} \rightarrow A_k$ , the apparent  $\kappa'$  starts to rise. Thus, the presence of acceptors in the forbidden gap will make the photoconductance to rise much more gradual than before, particularly if these acceptors are distributed in energy. If, e.g., this distribution were such that  $\kappa'$  would rise linearly with  $\mathcal{L}$  for  $\mathcal{L} \gtrsim 10^{-5}$  the photoconductance would behave as indicated by the dashed line in Fig. 2. It may be noted that in this case the photoconductor shows superlinearity in the transition

range, whereas the effect of the distribution of states is to make the overall photoconductivity large but sub-linear, with  $n_0$  proportional to  $\mathcal{L}^{0.53}$  over nearly four decades. (The whole situation becomes quite analogous to that presented by Rose; see, e.g., Ref. 20, Fig. 4.)

Unfortunately, the behavior of the variance under these more realistic conditions cannot be predicted with certainty. If the acceptor-valence band interactions were extremely fast and noiseless, the effect of these states indeed would be to spread the super-Poissonian variance region along with the photoresponse over a wide light-intensity range. However, the possibility of negative correlations which would reduce the noise cannot be excluded. Thus, to obtain reliable results, the matrix equation (1.5) has to be solved for the entire multilevel system. Though a formulation in terms of integral equations is feasible—in case one assumes continuous trap distributions—an alternative is to invert (1.5) directly by computer techniques, which is presently being programmed.

### 5. CONCLUSIONS

It has been shown that the computation of the variances and covariances in a multilevel electron system in a steady state is more involved and entirely different from that in a thermal equilibrium (or quasi-thermal equilibrium) state.

The academic model presented here shows a relative variance  $\langle \Delta n^2 \rangle / n_0$  not bounded by unity as is the case for thermodynamic fluctuations.

More realistic models involving two kinds of centers are likely to retain several of these features.

Along with the variance the photoconductivity has been evaluated and the results are shown to be consistent with current understanding.

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