

## Photoconductor Performance, Space-Charge Currents, and the Steady-State Fermi Level

A. ROSE AND M. A. LAMPERT  
*RCA Laboratories, Princeton, New Jersey*

(Received September 29, 1958)

The performance of a photoconductor is analyzed, via the concept of the steady-state Fermi level, and shown to be limited by the injection of space charge. Using the gain-bandwidth product  $G/\tau_0$  as a measure of performance, it is found that  $G/\tau_0 = M/\tau_r$ , where  $\tau_r$  is the dielectric relaxation time under operating conditions, and  $M = \mathcal{N}_A/\mathcal{N}_T$ , with  $e\mathcal{N}_A$  the total charge on the anode and  $e\mathcal{N}_T$  the total volume charge, free plus trapped, effectively in thermal contact with the free charge. Generally  $M > 1$  is achieved only concomitantly with space-charge-limited currents varying steeply with voltage. An important exception is the case where recombination centers control the onset of injected space charge.

### I. INTRODUCTION

THE performance of a photoconductor is generally determined by the properties of its localized defect states—their density, their locations in energy in the forbidden gap, and their cross sections for capture of free carriers. These properties, which are of quite general interest in the physics of solids, are not easily accessible by direct measurement. On the other hand, the performance of a photoconductor is macroscopically characterized by the measurement of such simple observables as (i) the ratio of the current of photoelectrons through the photoconductor to the current of photons incident upon it, (ii) the time required, at a fixed applied voltage, for the photocurrent to rise or decay to a steady-state value following a change in the incident light intensity, and (iii) the resistance and capacitance of the photoconductor under operating conditions.<sup>1</sup>

The first of these observables defines the gain of the photoconductor, and the second the speed of response, or its reciprocal, the band width. The product of the pair of observables in (iii) is the  $RC$  time constant or “the dielectric relaxation time under operating conditions.”<sup>1</sup> A particular combination of these observables, namely the gain-band width product, has proven especially valuable in characterizing the performance of a photoconductor.

It is the purpose of this paper to investigate the relationships of the macroscopic observables to the properties of the defect states<sup>2</sup> of the photoconductor.

<sup>1</sup> In the range of space-charge-limited currents, the  $I$ - $V$  (current-voltage) characteristic is nonlinear, and it is necessary to define the “resistance  $R$  under operating conditions.” Throughout this report we take  $R = V/I$ . Because of the injected space charge,  $R$  may be orders of magnitude smaller than the ordinary bulk resistance measured in the Ohm’s-law range of voltages. On the other hand, the capacitance  $C$ , under conditions of injected space charge, does not differ substantially from the “geometric” capacitance measured in the Ohm’s-law range of voltages (for proof of this see reference 6), and therefore may be taken as this latter quantity. We call the quantity  $RC$  “the dielectric relaxation time under operating conditions” since it has the same meaning as is ordinarily understood in the Ohm’s-law range of voltages.

<sup>2</sup> This paper concerns itself only with volume-distributed defect states. The possible special effects of defect states in the neighborhood of the contact are examined in the following paper: M. A. Lampert and A. Rose, *Phys. Rev.* **113**, 1236 (1959).

It will be shown that space-charge-limited currents play a decisive role in these relationships. Also the analysis will bring out the considerable usefulness of the concept of the steady-state Fermi level for the study of photoconductivity.

In earlier work<sup>3-6</sup> it was shown that the density of free carriers could be increased by application of a sufficiently high voltage (space-charge-limited currents) in the same crystal in which the carrier density was increased by optical excitation. The increased carrier densities in both cases were described, in a purely formal way, by a steady-state Fermi level  $E_F$  lying closer to the band edge than the thermal-equilibrium Fermi level  $\bar{E}_F$ . If  $n$  is the free carrier density under excitation conditions, the corresponding steady-state Fermi level  $E_F$  is formally defined by

$$n = N_c \exp[(E_F - E_c)/kT],$$

where  $N_c$  is the effective density of states in the energy band under consideration. The significant question is whether the steady-state Fermi level properly describes the altered occupancy of the discrete states in the forbidden energy gap. For a shift in Fermi level caused solely by the voltage-induced injection of excess carriers of one sign, one should clearly expect the answer to be “yes” and to be independent of the capture cross sections of the discrete states.<sup>7</sup> On the other hand, when the Fermi level is shifted by optical excitation alone the occupancy of only part of the discrete states is properly described by the steady-state Fermi level, namely those states that can be considered to be in thermal equilibrium with the free carriers. The occupancy of the other states will be dominated by the kinetics of the recombination processes. The distinction

<sup>3</sup> R. W. Smith, *Phys. Rev.* **97**, 1525 (1955).

<sup>4</sup> R. W. Smith and A. Rose, *Phys. Rev.* **97**, 1531 (1955).

<sup>5</sup> A. Rose, *Phys. Rev.* **97**, 1538 (1955).

<sup>6</sup> M. A. Lampert, *Phys. Rev.* **103**, 1648 (1956).

<sup>7</sup> Here we are assuming that the free carriers are not significantly heated by the applied field. If they are, and the capture cross sections are velocity-sensitive, then the Fermi-Dirac occupation function is altered in functional form from its thermal-equilibrium form. The results presented here would not, in any case, be drastically altered by this effect except at fields sufficiently high to cause collision ionization.

between thermally and kinetically controlled occupancies<sup>8</sup> is an essential factor in the determination of the gain-band width product for a photoconductor. Conversely, measurements of the gain-band width product can give information about the fraction of discrete states in thermal equilibrium with the conduction band. The correlation of independent measurements of space-charge-limited currents and of photoconductivity is a particularly potent means to disentangle the kinetically occupied (recombination) centers from the thermally occupied (trapping) centers. Such knowledge is needed to interpret other nonequilibrium measurements such as phosphorescent decay and glow-curve data.

The performance of photoconductors has recently been analyzed under restricted conditions by Stöckmann,<sup>9</sup> Rose,<sup>10</sup> and Redington.<sup>11</sup> Stöckmann<sup>9</sup> showed that for the special conditions: neutral contact, trap-free material, and photocurrents less than the dark current, the maximum gain-band width product is given by the reciprocal of the dielectric relaxation time. The term "neutral contact" is used here to describe a contact for which the bands at the metal-semiconductor interface remain flat. Stöckmann's conclusion is still valid when shallow traps are introduced. The neutral contact is, however, a restrictive condition. Most sensitive photoconductors have ohmic contacts, that is, contacts that can freely supply electrons to the volume of the photoconductor. The bending of bands at an ohmic contact is opposite to that customarily assumed for a blocking contact.

Rose<sup>10</sup> obtained the same relation as Stöckmann's for the conditions: ohmic contact, arbitrary distributions of traps, and photocurrents less than the dark current. An implicit assumption in his analysis was that the recombination centers be located well below the dark Fermi level. As will be discussed later in this paper, if the recombination centers are located near the dark Fermi level, the gain-band width product need not be restricted to the value obtained by Rose and Stöckmann. A further correction on the Rose paper is that the advent of space-charge-limited currents does not necessarily cause the gain to decrease. The gain is more likely to increase linearly with applied voltage or, in the case of large space-charge-limited currents, to remain constant.

Redington<sup>11</sup> analyzed photoconductor performance under the conditions: ohmic contact, shallow traps, and large photocurrents—and reached conclusions similar to Rose.<sup>10</sup>

The present paper extends these earlier analyses to include arbitrary light levels and arbitrary trap distributions. Under certain conditions an important

correction, expressed in the factor  $M$  of Eq. (5), is made on the earlier results. The analysis is carried out for a one-carrier model, namely electron conduction, for the sake of definiteness. The results are equally valid for hole conduction. In either case it is assumed that the contacts are injecting for the majority carrier, that is, capable of supplying space-charge-limited currents to the photoconductor. Further, it is assumed that the minority carriers are mostly trapped in recombination centers and therefore do not themselves make a significant contribution to the photocurrent. Possible effects of the electric field on the number and distribution of minority carriers are neglected.<sup>12</sup>

In the following section the gain-band width product is expressed in terms of inherent properties of the photoconductor. The resulting formula, Eq. (5), is then applied, in Sec. III, to several different cases by way of illustration. Some questions bearing on response time are examined in the appendix.

For convenience a list of symbols is given at the end of the paper.

Before proceeding to the detailed analysis, the authors wish to emphasize two aspects of this work. On the one hand, this report endeavors to correlate and explain a large body of currently available experimental data pointing toward photoconductive gain-band width products which approach zero for highly insulating materials. On the other hand, it is shown that this is not a universal phenomenon, that with special distributions of traps or recombination centers the gain-bandwidth product can be high even at high resistivity. Some precision has been sacrificed in order to clarify the major ideas. A precise, rigorous analysis of photoconductivity embodying its known complexities would be entirely too unwieldy—buried in the details would be the underlying, common features which are of real interest. With this in mind, the authors do not consider it important, for example, in the discussion of response time, to distinguish between a factor of 2 or  $e = 2.718 \dots$ . Accordingly, the results stated are understood to be valid only to within a factor of approximately two.

<sup>12</sup> Actually, at sufficiently high fields drastic effects may be expected. Thus if the positive contact is blocking for the minority carriers, high fields will extract the minority carriers before they are captured by recombination centers. For sensitive photoconductors, this process can be looked upon, at least qualitatively, as effectively reducing the number of incident photons, since those minority carriers that are drawn out before being captured in a recombination center have negligible influence on the photocurrent. If the positive contact is injecting for the minority carrier, high fields may be expected to produce double-injection, breakdown-like currents, such as observed by Smith in CdS and Tyler in Ge [R. W. Smith, Phys. Rev. **105**, 900 (1957) and W. W. Tyler, Phys. Rev. **96**, 226 (1954)]. In this connection it has often been observed that a contact which is blocking at low fields may be "broken down" at sufficiently high fields and then serve as an injecting contact.

<sup>8</sup> A. Rose, Phys. Rev. **97**, 322 (1955).

<sup>9</sup> F. Stöckmann, Z. Physik **147**, 544 (1957).

<sup>10</sup> A. Rose, Helv. Phys. Acta **30**, 242 (1957).

<sup>11</sup> R. W. Redington, J. Appl. Phys. **29**, 189 (1958).

## II. GAIN-BAND WIDTH PRODUCT

The current-gain of a photoconductor is<sup>13</sup>

$$G = \Delta I / eF = \tau_l / T'; \quad (1)$$

$\Delta I$  is the steady-state photocurrent, i.e., the change in current from its "dark" value, produced by light. The dark current can be either the thermal equilibrium value or a much higher value corresponding to space-charge currents.  $F$  is the incident current of photons (i.e., the number of excitations per second),  $\tau_l$  is the mean life of a free carrier, and  $T'$  is the transit time of a free carrier between cathode and anode.

The rise, or decay, time of photocurrents is, in general, greater than the mean life of a free carrier owing to the need to fill, or empty, trapping states that are in thermal equilibrium with the free carriers. This fact is noted formally by the relation<sup>14</sup>

$$\tau_0 = (\mathfrak{N}_T / \mathfrak{N}) \tau_l; \quad (2)$$

$\tau_0$  is the response time,  $\mathfrak{N}$  is the total number of free electrons, and  $\mathfrak{N}_T$  is a quantity determined by the dynamical relationships between free and trapped charge. Actually, we find it convenient to regard the relation (2) as the formal definition of  $\mathfrak{N}_T$ .

For the sake of definiteness we shall consider the response time defined with reference to photoconductive decay, namely as the time it takes for the photocurrent to decay to one-half of its steady-state value after the light is removed.

The transit time in Eq. (1) is given by

$$T' = L^2 / V\mu \quad (3)$$

where  $L$  is the spacing between electrodes,  $V$  the applied voltage, and  $\mu$  the mobility of free carriers.

$\tau_0$  and  $T'$  from Eqs. (2) and (3) are inserted in Eq. (1) to give

$$G = \tau_0 (\mathfrak{N} / \mathfrak{N}_T) (V\mu / L^2). \quad (4)$$

Equation (4) can be rewritten  $G / \tau_0 = (\mathfrak{N}e\mu / L^2C) \times (VC / e\mathfrak{N}_T) = (1/RC) (\mathfrak{N}_A / \mathfrak{N}_T)$ , giving finally

$$G(1/\tau_0) = (1/\tau_r) M, \text{ with } \tau_r = RC \text{ and } M = \mathfrak{N}_A / \mathfrak{N}_T. \quad (5)$$

$\mathfrak{N}_A$  is the total number of positive charges on the anode due to the applied voltage.<sup>15</sup>  $R$  and  $C$  are the resistance and capacitance of the photoconductor *under the conditions of operation*.<sup>1</sup>

It is to be emphasized that Eq. (5) is purely a formal relationship. It is valid for any homogeneous photo-

<sup>13</sup> A. Rose, RCA Rev. 12, 362 (1951).

<sup>14</sup> The mean life is defined by the relation  $\tau_l = \Delta\mathfrak{N} / F$ , where  $\Delta\mathfrak{N}$  is the steady-state increment in  $\mathfrak{N}$  produced by the incident photon current  $F$ . Hence, for the case that the incident light just doubles  $\mathfrak{N}$ , one has  $\Delta\mathfrak{N} = \mathfrak{N}$ , and Eq. (2) can also be written  $\tau_0 = \mathfrak{N}_T / F$ .

<sup>15</sup> Even without applied voltage there will be positive charge on the anode if there is an ohmic contact for electrons at the anode. This anode charge is the positive component of the dipole layer needed to match the insulator to the anode material. Throughout this report  $\mathfrak{N}_A$  refers to the *additional* positive charges on the anode due to an applied voltage.

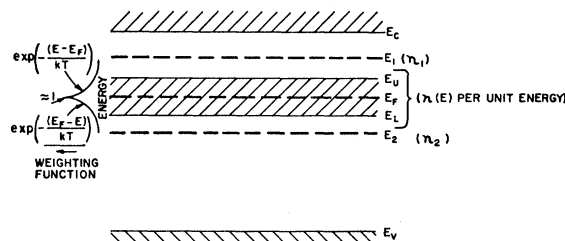


FIG. 1. Weighting function for calculation of  $\mathfrak{N}_T$ .  $E_c$  is the conduction-band energy minimum,  $E_v$  the valence-band energy maximum.  $E_F$  is the steady-state Fermi level.  $E_1$  and  $E_2$  are the energy levels of discrete traps, of total numbers  $\mathfrak{N}_1$  and  $\mathfrak{N}_2$ , respectively. There is a continuous distribution of traps, of total number  $\mathfrak{N}(E)$  per unit energy at  $E$ , between levels  $E_U$  and  $E_L$ .

conductor having a uniform cross section and for all voltages, excluding only fields that give rise to collision ionization. The virtue of Eq. (5) is that its entire physical content lies in the interpretation of the factor  $M$  or, in particular,  $\mathfrak{N}_T$ . Even if formally possible, it would be of dubious value to give a general, physical characterization of  $\mathfrak{N}_T$  valid for all photoconductive phenomena. This problem is briefly discussed in the appendix where, for example, the difficulties associated with such complex phenomena as supralinearity are pointed out. However, for relatively simple photoconductive phenomena (see the appendix),  $\mathfrak{N}_T$  can be precisely characterized as being equal to  $\mathfrak{N}$  plus the total number of trapped electrons which are "effectively in thermal equilibrium" with the free carriers. Referring to Fig. 1, the latter number is computed as follows. Traps of total number  $\mathfrak{N}(E)$  per unit energy and located in energy near  $E_F$  contribute to  $\mathfrak{N}_T$  the number  $\mathfrak{N}(E_F)kT$ . Traps of total number  $\mathfrak{N}_1$ , located at energy  $E_1 > E_F$  contribute to  $\mathfrak{N}_T$  the number  $\mathfrak{N}_1 \exp[(E_F - E_1)/kT]$ . This is the same as the number of electrons in  $\mathfrak{N}_1$ . Traps of total number  $\mathfrak{N}_2$  located at energy  $E_2 < E_F$  contribute to  $\mathfrak{N}_T$  the number  $\mathfrak{N}_2 \exp[(E_2 - E_F)/kT]$ . This is the same as the number of holes in  $\mathfrak{N}_2$ . This prescription for calculating  $\mathfrak{N}_T$  is obtained simply and directly by calculating the change in the total number of trapped electrons when the number of free electrons is doubled. The net result, as illustrated in Fig. 1, is an exponential weighting function centered sharply at the Fermi level, so that in the many cases where the trap distribution in energy varies more slowly than the Boltzmann factor at the operating temperature, the significant term is  $\mathfrak{N}(E_F)kT$ . In the evaluation of  $\mathfrak{N}_T$  only those traps contribute which are in thermal contact with the conduction band, that is, whose electron occupancy is determined by  $E_F$ . Recombination centers, whose occupancy is determined by the kinetics of recombination, do not contribute to  $\mathfrak{N}_T$ .

The importance of injected, excess carriers (i.e., carriers producing space charge in the bulk of the solid) for photoconductive performance can be seen directly in the following way. If excess carriers were not injected

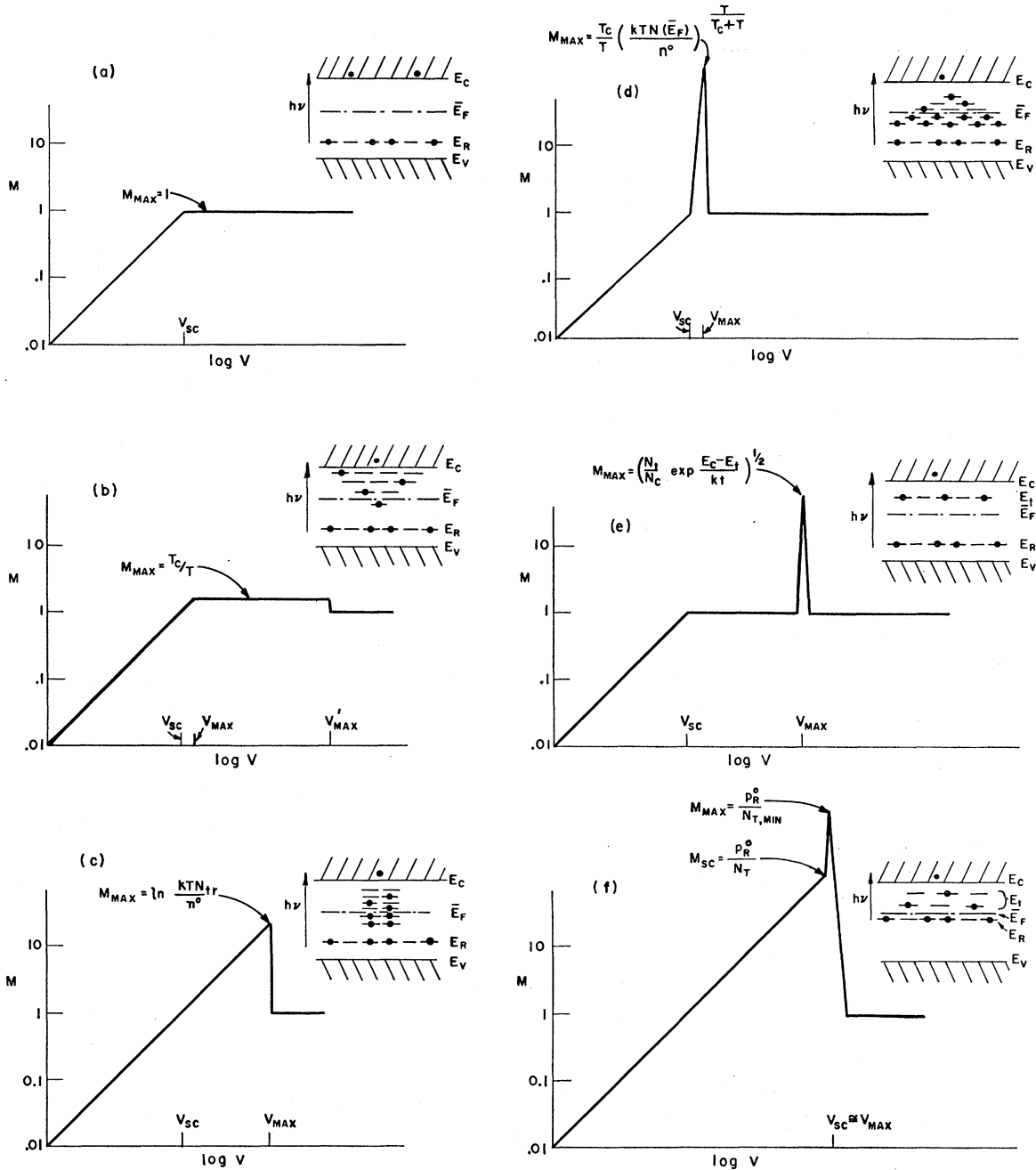


FIG. 2. Dependence of  $M$  on applied voltage  $V$  for different trap distributions.  $V_{sc}$  is the voltage at the onset, in the dark, of space-charge-limited currents. For all cases but (f),  $M=1$  at  $V=V_{sc}$ .  $V_{max}$  is that voltage at which  $M$  attains its maximum value,  $M_{max}$ .  $\bar{E}_F$  is the thermodynamic-equilibrium Fermi level and  $E_R$  the energy level of the recombination centers. (a) Trap-free case. (b) Decreasing density of traps (characterized by an effective "temperature"  $T_c$ );  $V_{max}'$  is the voltage at which  $M$  drops back to unity. (c) Uniform distribution of traps (of density  $N_t$  per unit energy  $\bar{n}$  is the thermal-equilibrium density of free electrons). (d) Increasing density of traps [of density  $N(E) = N(\bar{E}_F) \exp((\bar{E}_F - E)/kT_c)$  per unit energy at  $E$ ]. (e) Single, discrete trap level (of density  $N_t$  at energy  $E_t > \bar{E}_F$ ,  $N_c$  is the effective density of states in the conduction band). (f) Recombination centers located close to  $\bar{E}_F$ . ( $p_R^0$  is the thermal-equilibrium density of holes in these centers.  $N_T$  is the total density of electrons, free plus trapped, at a given light level, effectively in thermal contact with the free electrons.  $N_{T,min}$  is the minimum value of  $N_T$  obtained through the injection of space-charge.)

at any voltage, then  $\mathcal{N}_T$  would be independent of voltage and the factor  $M$  could be increased without limit by either an increase in voltage or a decrease in

spacing. Much of the interest in Eq. (5) would then vanish since arbitrarily large gain-band width products, even for insulators, could be obtained by arranging for

arbitrarily large values of  $M$ . What makes Eq. (5) of significance is that for a large variety of trap distributions the maximum value of  $M$  is limited to unity either absolutely or effectively. This comes about precisely because as the voltage is increased, space-charge-limited currents must set in, and, for a variety of trap distributions, the number of charges  $\mathfrak{N}_A$  on the anode can be physically interpreted to be equal to the number of charges  $\mathfrak{N}_T$  that control the response time. For practical applications there is particular interest in those special properties of a photoconductor which make possible values for  $M$  greatly exceeding unity. Furthermore, measurements of  $M > 1$  may be expected to give information about the occupancy of defect states in the crystal.

### III. GAIN-BAND WIDTH PRODUCT FOR PARTICULAR TRAP DISTRIBUTIONS

In this section the voltage dependence of the gain-band width product is studied for the several representative trap distributions shown in Fig. 2 and discussed in Secs. IIIa–IIIc. The interesting and novel features of this dependence are contained in the voltage dependence of the  $M$  factor and we therefore focus our attention on this feature of the problem. The voltage dependence of  $\tau_r$  is straightforward. In the Ohm's-law range of currents there is no dependence at all. In the space-charge-limited range of currents,  $\tau_r$  decreases with voltage roughly as the inverse of the current. (Space-charge-limited current-voltage characteristics have been discussed in some detail in the literature.<sup>5,6</sup>)

For all cases discussed below it is assumed that  $\mathfrak{N}_T$  is simply the sum of the total number of free electrons  $\mathfrak{N}$  and the total number of trapped electrons effectively in thermal equilibrium with the free carriers. The prescription for calculating  $\mathfrak{N}_T$  is given in the preceding section. As to notation, the densities corresponding to the total numbers  $\mathfrak{N}$ ,  $\mathfrak{N}_T$ ,  $\mathfrak{N}(E)dE$ ,  $\mathfrak{N}_{tr}dE$ ,  $\mathfrak{N}_i$ ,  $\mathfrak{N}_R$ ,  $\mathcal{P}_R$  which appear in the following discussion are denoted, respectively by  $n$ ,  $N_T$ ,  $N(E)dE$ ,  $N_{tr}dE$ ,  $N_i$ ,  $N_R$ ,  $p_R$ . Further,  $n^0$ ,  $\mathfrak{N}^0$ ,  $N_T^0$ ,  $\mathfrak{N}_T^0, \dots$  denote the values of the corresponding quantities in thermal equilibrium. (See the list of symbols at the end of the paper.)

For all cases below, excepting (f), the onset of space-charge-limited currents is controlled by the trapping states and not by the recombination centers. This requires that  $p_R^0/2 < N_T^0$ ,  $p_R^0$  being the thermal-equilibrium density of holes in the recombination centers, of density  $N_R$ . For  $N_R > N_T^0$ , this condition is met by assuming the recombination centers sufficiently "deep-lying," i.e.,  $(\bar{E}_F - E_R)/kT$  sufficiently greater than unity, where  $E_R$  is the energy level of the recombination centers. In the diagrams of Fig. 2 the light is shown as exciting electrons directly from the recombination centers into the conduction band. This is, of course, equivalent to the situation where the light excites free electron-hole pairs directly across the band

gap and the holes are quickly captured by the recombination centers.

The various cases, (a)–(f), have several features in common. At the low voltage end,  $M < 1$ , the linear increase of  $M$  with voltage is straightforward. The lines of force of the anode charges end on negative charges close to the cathode. The increase in anode voltage does not affect the density of free electrons or the density of trapped electrons in the volume. Hence,  $\mathfrak{N}_T$  remains constant while  $\mathfrak{N}_A$  increases linearly with voltage. This continues at least until  $\mathfrak{N}_A$  equals  $\mathfrak{N}_T$ , hence until  $M = 1$ , providing dielectric breakdown does not intervene.

At the onset of space-charge-limited currents, the lines of force of the anode charge end on injected free and trapped electrons distributed throughout the volume of the photoconductor. In general, with case (f) excepted, this is the same distribution of free and trapped charge that would be generated by photoexcitation alone. That is, let the density of carriers be doubled in one case by voltage alone and in another case by light alone. In each case the Fermi level is raised approximately  $kT$ . In the case of voltage alone, the extra free and trapped electrons are injected from the cathode and hence are not compensated by positive charge. In the case of light alone, the same distribution of extra free and trapped electrons are injected, so to speak, from deep-lying recombination centers and are now charge-compensated by the holes left behind in the centers. Under these conditions  $M = 1$  at the onset of space-charge-limited currents, at the voltage  $V = V_{sc}$ . Note that here, and in the following,  $V_{sc}$  denotes the voltage threshold for the injection of space charge in the dark. By the use of a bias light this threshold can be pushed to higher voltages.

The detailed behavior of  $M$  for  $V > V_{sc}$  depends on the particular trap distribution, as is evident from inspection of Fig. 2. Nevertheless certain general observations can be made. It is seen that  $M$  values exceeding unity can be realized in the range of space-charge-limited currents, i.e., at voltages  $V > V_{sc}$ . However, so long as the same trapping centers control both the response time and the space-charge-limited currents, cases (b)–(e) below,  $M > 1$  is realized only in a range of voltages over which the current-voltage characteristic, in the absence of a biasing light, is quite steep. For all cases, at a sufficiently high voltage (again, providing dielectric breakdown has not intervened)  $M$  returns to unity, and thereafter remains equal to unity. This is the voltage range over which the free-carrier density is so large that trapping is negligible:  $\mathfrak{N}_T \simeq \mathfrak{N} \simeq \mathfrak{N}_A$  and  $\tau_0 = \tau_i$ . In this range the current is proportional to the square of the voltage.

We now discuss the different cases separately.

#### (a) Trap-Free Photoconductor

It is clear from Fig. 2(a) that the response time of the photoconductor is equal to the mean life of the free

electrons—that is, the time required for the light to excite the extra density of electrons. Since there are no traps, there are no trapped electrons contributing to  $\mathfrak{N}_T$ :  $\mathfrak{N}_T = \mathfrak{N}$ . Therefore the factor  $M$  can be written  $M = \mathfrak{N}_A / \mathfrak{N}$ .

For this case, clearly,  $V_{so} = e\mathfrak{N}^0/C$ . For  $V > V_{so}$ , excess charge is injected into the crystal. Since all the excess charge must be free,  $\mathfrak{N} = \mathfrak{N}_A$ . Further the current is proportional to the square of the voltage. The effect of space-charge-limited currents is to restrict the maximum value of  $M$ , as shown in Fig. 2(a), to unity. At the same time the gain-band width product increases linearly with voltage (in the space-charge-limited range) since the reciprocal of the dielectric relaxation time is proportional to voltage. The gain itself remains constant since the mean life of a free carrier is inversely proportional in this model to the density of free carriers.

### (b) Decreasing Density of Traps

In Fig. 2(b) the trap density is shown schematically as decreasing as one departs from the conduction band. Assuming that the density distribution  $N(E)$  of traps in energy does not vary faster than the Boltzmann factor at the operating temperature, then the major contribution to  $N_T$  comes from the trapping states with  $kT$  of the Fermi level  $E_F$ . This is true both for  $E_F \simeq \bar{E}_F$  (low lights) and for  $E_F > \bar{E}_F$  (higher lights). Therefore  $N_T \simeq N(E_F)kT$ . Space-charge-limited currents set in at the voltage  $V_{so} = ekT\mathfrak{N}(\bar{E}_F)/C$ , and at this voltage  $M = 1$ .

Figure 2(b) shows  $M$  increasing beyond unity to  $T_c/T$  at higher voltages. This value is obtained by first applying a voltage in the dark sufficient to raise the Fermi level at least several  $kT$  above its dark value. The excess charge on the anode required to raise the Fermi level will then be given approximately by the number of states lying between the initial and final positions of the Fermi level. Here it is assumed that the trap distribution can be described by a Boltzmann distribution with a temperature  $T_c$ , i.e., that  $N(E) = N(E_F) \times \exp[(E - \bar{E}_F)/kT_c]$ . Therefore the number of states in question will be approximately  $kT_c\mathfrak{N}(\bar{E}_F) = \mathfrak{N}_A$ . After applying the voltage, the photoconductor is exposed to light and the response time is determined. From the above it is clear that  $M_{\max} = T_c/T$ , first reached at the voltage  $V_{\max} = ekT_c\mathfrak{N}(\bar{E}_F)/C$ .

$M$  breaks from its plateau (and thereafter rapidly returns to unity) when the excess free charge density  $n$  equals the excess trapped charge density in effective thermal contact with the free charges, that is when  $E_F$  is located such that  $n = N_c \exp[(E_F - E_c)/kT] = kTN(E_F)$ . The voltage  $V_{\max}'$  at which this takes place is given by

$$V_{\max}' = \{ekT_c\mathfrak{N}(\bar{E}_F)[kTN(\bar{E}_F)/\bar{n}]T/(T_c - T)\} \times C^{-1}.$$

Throughout the entire region of the  $M$  plateau, the current-voltage characteristic is quite steep<sup>3</sup>:

$I \propto V^{(T_c+T)/T}$ ; correspondingly the dielectric relaxation time drops quite steeply:  $\tau_r \propto V^{-(T_c+T)/T}$ . If  $T_c < T$ , the density of traps  $N(E)$  varies faster than the Boltzmann factor. This is the case of "shallow traps," discussed by Redington,<sup>11</sup> for which the maximum value of  $M$  is unity.

### (c) Uniform Trap Density

The behavior of  $M$  as a function of voltage for a uniform distribution of traps in energy,  $N(E) = N_{tr} = \text{constant}$ , is generally similar to that for the decreasing density of traps just discussed. The chief difference is that, in the space-charge-limited current range, the approximation previously used for  $\mathfrak{N}_A$  is no longer valid. That is, the characteristic temperature  $T_c$  of a uniform distribution of traps is infinite and would lead to an infinite value of  $kT_c\mathfrak{N}(E)$ .

Injection of space-charge takes place at the voltage  $V_{so} = ekT\mathfrak{N}_{tr}/C$ . For  $V > V_{so}$ ,  $M$  is computed in Fig. 2(c) by taking  $\mathfrak{N}_A$  equal to the total number of traps between  $\bar{E}_F$  and  $E_F$ , where the injection of extra charge by the applied voltage has raised the Fermi level from  $\bar{E}_F$  to  $E_F$ . The value of  $\mathfrak{N}_T$  is, as before, equal to the total number of traps within  $kT$  of the steady-state Fermi level  $E_F$  plus the number of free carriers. At the onset of space-charge-limited currents  $M = 1$ . Further increase in voltage causes the current to increase exponentially as  $e^{\alpha V}$ , where  $\alpha$  is a function of the trap density and dimensions of the photoconductor.<sup>5</sup> Correspondingly  $\tau_r \propto e^{-\alpha V}$ . In this range,  $\mathfrak{N}_A$  increases linearly with applied voltage while  $\mathfrak{N}_T$  remains constant until the number of free carriers equals the number of traps within  $kT$  of the Fermi level. This takes place at the voltage

$$V_{\max} = e\mathfrak{N}_{tr}kT[\ln(N_{tr}kT/n^0)]/C.$$

Here  $M$  takes on its maximum value [Fig. 2(c)], but abruptly and within a factor of two in voltage drops back to unity.

### (d) Increasing Density of Traps

The density of trapping states is assumed to increase as one departs from the conduction band. The chief difference between the behavior of  $M$  here and in the two previous cases, (b) and (c), are: (1)  $M$  can achieve a higher maximum value, and (2) the space-charge-limited current increases even more steeply with voltage than in either of the previous two cases.

The maximum value of  $M$ , following the reasoning of Secs. (b) and (c), is given approximately by the ratio of the density of traps at the thermal equilibrium Fermi level  $\bar{E}_F$  to the density of traps at the steady-state Fermi level  $E_F$  when the latter is raised to such a value that the density of free electrons equals the density of electrons trapped within  $kT$  of  $E_F$ . For the case that the trap distribution can be described by a Boltzmann distribution with a temperature  $T_c$ , i.e.,

that  $N(E) = N(\bar{E}_F) \exp[(\bar{E}_F - E)/kT_c]$ , the value for  $M_{\max}$  is given in Fig. 2(d). It occurs at the voltage  $V_{\max} = ekT_c \mathfrak{N}(\bar{E}_F)/C$ . The voltage region over which  $M > 1$  is so narrow as to give this portion of the  $M$ -curve the appearance of a spike.

#### (e) Single, Discrete Trap Level

It is assumed that the traps, of density  $N_t$ , are located at an energy  $E_t > \bar{E}_F$  and that the trapped electrons are more numerous than the free ones.

The significant difference between this case and the preceding one is the displacement of the "spike" in the  $M$ -curve along the  $M=1$  plateau to a higher voltage. The onset of the spike coincides with the Fermi level  $E_F$  passing through the trap level  $E_t$ . This occurs at the voltage  $V \simeq e \mathfrak{N}_t / 2C$ . The top of the spike occurs at  $V_{\max} \simeq e \mathfrak{N}_t / C$ ,  $M_{\max}$  being given in Fig. 2(e).

So long as  $E_F < E_t$ , this is simply a shallow-trap situation.<sup>11</sup> The  $M=1$  plateau is reached at  $V_{sc} = e \mathfrak{N}_t \times \exp[(\bar{E}_F - E_t)/kT]/C$ .

As with the preceding case, the current-voltage curve in the region of the  $M$  spike is extremely steep—indeed, so steep as to have the appearance of a breakdown. The dielectric relaxation time is, of course, correspondingly steep with voltage.

#### (f) Recombination Centers near the Fermi Level

In the previous cases (a)–(e), the onset of space-charge-limited currents coincided with a value of unity for  $M$ . This was because the same trapping centers controlled the response time and the space-charge-limited currents. Where higher values of  $M$  were obtainable, the accompanying current-voltage characteristic was inevitably very steep, provided the space-charge-limited current exceeded the photocurrent. Where a steady bias light produces a photocurrent exceeding the space-charge-limited current, the current-voltage characteristic remains ohmic (see Fig. 4, reference 4). The price paid for this however is substantially lowered resistivity from the dark value.

If the (empty) recombination centers are numerous enough to control the onset of space-charge-limited currents; i.e., if  $p_r^0/2 > \bar{N}_T$  as stated in the introductory comments to this section, then large  $M$  values can be obtained prior to the onset of space-charge-limited currents and without the use of bias light.<sup>16</sup> This is illustrated in Fig. 2(f) where the recombination centers are shown sharply localized near (within  $kT$  of) the dark Fermi level  $\bar{E}_F$ . It is assumed that their density  $N_R$  dominates other states in the neighborhood of  $\bar{E}_F$ . Space-charge-limited currents set in at voltage  $V_{sc}$

$= e \mathcal{P}_R^0 / C$ , with  $\mathcal{P}_R^0$  the total number of empty recombination centers in the dark ( $\mathcal{P}_R^0 = p_r^0 \times \text{volume}$ ). At this voltage  $M = p_r^0 / N_T$ , where  $N_T$  is determined by where the light excitation has brought the Fermi level  $E_F$ . (Here we have assumed that the exciting light has not appreciably changed  $p_R$  from  $p_R^0$ .) At low lights,  $M_{sc} = p_r^0 / N_T^0$ . Through an increase in voltage beyond  $V_{sc}$ , the Fermi level can be moved further towards the conduction band, to a position where  $N_T = N_{T,\min}$  giving  $M_{\max} = p_r^0 / N_{T,\min}$ . This puts a spike, similar to the one of Figs. 2(d) and (e), on top of  $M_{\max}$ . The spike occurs, as with cases (d) and (e), in the region of extreme steepness of the current-voltage curve.

From the examination of particular models, it is seen that values of  $M$  exceeding unity are associated with an injected space charge which exceeds the trapped charge controlling the response time of the photoconductor. Looked at in this way, there are other ways of achieving  $M > 1$  than by selected energy distribution of traps. For example, if there are states (other than recombination centers) that exchange carriers with the conduction band very slowly, these states will not be counted as part of  $\mathfrak{N}_T$  since they will not retard the rise or decay of photocurrents. These states will, however, be counted among those that must be filled before the onset of space-charge-limited currents. The filling of these states under space-charge flow is a steady-state phenomenon and does not depend on their capture cross section, while their filling and emptying during the rise and decay of photocurrents is a transient phenomenon and requires a cross section at least as large as that of the recombination centers.

This possibility may arise in the case of thin films or needles, where the total number of trapping states at or near the surface can exceed the total number in the volume. This is suggested by the fact, for example, that high photocurrents usually come from volume-absorbed light, the sensitivity to strongly absorbed light being generally smaller by a factor of two or three and sometimes of ten or more. The rise and decay of photocurrents will be controlled by the volume density of traps while the onset of space-charge flow will be controlled by the volume plus the surface density of traps. If the total number of surface states is larger than the total number of volume states (both near the Fermi level) the value of  $M$  can be expected to exceed unity by the same ratio.<sup>17</sup> The slow exchange of electrons between the conduction band in the volume and the surface states is likely to be insured by the Demmer field set up when light causes the volume to be more conducting than the surface.

Another possible source of states effective in space-charge flow but not in photoresponse can be associated

<sup>16</sup> During the course of this work,  $M$  values as high as 50 were observed at low lights by R. W. Smith in single crystals of CdS. The currents were pure volume currents. Independent measurements by Smith verified that the centers controlling the response time were different from the centers controlling the onset of space-charge-limited currents.

<sup>17</sup> H. B. DeVore has reported [Meeting of the American Institute of Electrical Engineers, February, 1958 (unpublished)].  $M$  values approaching 50 at low lights for thin sintered films of CdSe. It is not yet known whether this result can be assigned to a favorable energy distribution of recombination states in the volume or to a large density of surface traps.

with physical voids in the lattice. Foreign atoms located in these voids will have a smaller coupling with the lattice than normal impurity states.

A not altogether trivial means for getting values of  $M > 1$  is to hang an external capacitance across the photoconductor. The external capacitance increases both the  $RC$  time constant of the photoconductor and the anode charge  $\mathfrak{N}_A$  by the same factors. The increase in  $\mathfrak{N}_A$  means, of course, a corresponding increase in  $M$ . While the addition of a capacitance has no bearing on the physics of the photoconductor, it does serve to illustrate in simple fashion how the charge that must be put on the anode to initiate space-charge flow can be different from and greater than the trapped charge  $\mathfrak{N}_t$  in thermal equilibrium with the free carriers.

In conclusion, our analysis has established an intimate connection among space-charge-limited currents, the steady-state Fermi level and photoconductive performance. This connection has been examined by studying the gain-band width product, and in particular the ratio  $M = \mathfrak{N}_A / \mathfrak{N}_T$ , as a function of applied voltage. Because of the connection, separate measurements of space-charge-limited currents and photoconductive performance provide a powerful combination for the study of defect states in solids. Obviously there are far-reaching device implications in the gain-band width relation expressed by Eq. (5). We hope to report on this aspect of the work elsewhere.

#### ACKNOWLEDGMENTS

The writers wish to express their gratitude to R. H. Bube, H. B. DeVore, and R. W. Smith for informative discussions of their work in progress and to D. O. North for a critical reading of the manuscript.

#### LIST OF SYMBOLS

$\mathfrak{N}_A$  is the total number of positive charges on the anode due to the applied voltage.

$\mathfrak{N}_T, N_T$  are the total number and density, respectively, of volume charges, free plus trapped, effectively in thermal contact with the free charges.

$N_c$  is the effective density of states in the conduction band.

$\mathfrak{N}, n$  are the total number and density, respectively, of free charges.

$\mathfrak{N}(E), N(E)$  are the total number and density, respectively, of traps per unit energy at the energy  $E$  for a distribution (in energy) of traps.

$\mathfrak{N}_{tr}, N_{tr}$  are the total number and density, respectively, of traps per unit energy for a uniform distribution (in energy) of traps.

$\mathfrak{N}_t, N_t$  are the total number and density, respectively, of traps at a discrete energy.

$\mathfrak{N}_R, N_R$  are the total number and density, respectively, of recombination centers.

$\mathfrak{P}_R, p_R$  are the total number and density, respectively, of holes in recombination centers.

$p_t, n_t$  are the densities of holes and electrons, respectively, in traps.

A superscript "0" on a quantity denotes the thermal-equilibrium value of that quantity.

$\tau_0$  is the response time.

$\tau_l$  is the free-electron lifetime.

$\tau_r$  is the dielectric relaxation time under operating conditions.

#### APPENDIX

The response-time parameter  $\mathfrak{N}_T$  defined by Eq. (2) plays an essential role in our evaluation of photoconductor performance. Generally we have taken  $\mathfrak{N}_T$  to be the sum of the total number of free electrons and the total number of trapped electrons effectively in thermal contact with the free electrons. The prescription for calculating  $\mathfrak{N}_T$  was given in Sec. II. Underlying this interpretation of  $\mathfrak{N}_T$  are two assumptions:

(i) Throughout the response-time period  $\tau_0$  the occupancy of the recombination centers by holes does not change drastically, i.e., by more than a factor of about two. It follows directly from this assumption that throughout the period  $\tau_0$  the decay of the excited electrons takes place through the same recombination centers which control the steady-state lifetime  $\tau_l$ .

(ii) The probability of capture of free electrons by traps is substantially greater than the probability of their capture by recombination centers:  $\sigma_{nt} p_t > \sigma_{nR} p_R$ , where  $\sigma_{nt}$  and  $\sigma_{nR}$  are the cross sections for capture of free electrons by empty traps (density  $p_t$ ) and empty recombination centers (density  $p_R$ ), respectively.

Neither of the two assumptions is valid for all conceivable cases of photoconductivity. For example, if the variation of the steady-state photocurrent with light intensity is observed to be more rapid than linear, then it is likely that two physically distinct classes of recombination centers are involved. In this case conceivably assumption (i) would be violated over some range of light levels. However, it is more than likely valid even for this case. Generally assumption (i) may be regarded as reasonable and probable. Where it is violated this would be indicated by the complex form of the decay, even within the first decay period  $\tau_0$ . Assumption (ii) insures that a free electron will be emitted and captured by a trap many times before its life is terminated by capture into a recombination center, i.e., that the free and trapped electrons maintain thermal contact during the first decay period. Violation of assumption (ii), which would make possible  $M$ -values greater than unity, as discussed in the text, would be revealed not only by a complex decay structure but also by overshoot in the transient photoconductive rise. The validity of this assumption clearly depends on the density of traps,  $N_t$ . With all other parameters of the crystal held constant, if  $N_t$  is reduced, a value will be reached where (ii) is no longer valid and accordingly  $M > 1$  at sufficiently high voltage (e.g., at  $V = V_{sc}$ ).



With further reduction of  $N_t$ , the point will finally be reached where the traps play no role in photoconductivity, i.e., most of the excited electrons are free, and the maximum value of  $M$  will be unity (trap-free case).

With assumptions (i) and (ii), a single differential equation governs the decay:

$$\frac{d}{dt}(n+n_t) = -n/\tau_t, \quad (\text{A1})$$

with the trapped and free electrons,  $n_t$  and  $n$ , respectively, in quasithermal equilibrium; i.e., for example, for a set of discrete traps of density  $N_t$  at energy  $E_t$ ,

$$n_t = N_t \left( \frac{n}{n+N} \right), \quad \text{with } N = \frac{1}{2} N_c \exp\left( \frac{E_t - E_c}{kT} \right). \quad (\text{A2})$$

$N_c$  is the effective density of states in the conduction band, and a statistical weight of two, corresponding to spin-degeneracy, is assigned to the traps.

Setting  $dn_t/dn = K'$  and  $K' + 1 = K$ , and regarding  $K$  as a constant, (A1) reduces to  $Kdn/dt = -n/\tau_t$ , with solution  $n = n_0 \exp(-t/\tau_0)$ , where  $\tau_0 = K\tau_t$ . Furthermore,

$$K' = \frac{dn_t}{dn} = \frac{N_t N}{(n+N)^2} = \frac{n_t N}{n(n+N)^2} = \frac{p_t}{n+N},$$

with

$$p_t = N_t - n_t. \quad (\text{A3})$$

For deep traps, one has  $(E_F - E_t)/kT > 1$  and  $n > N$ , giving  $K' \simeq p_t/n$  and  $K \simeq (n + p_t)/n$ .

For shallow traps, one has  $(E_t - E_F)/kT > 1$  and  $N > n$ , giving  $K' \simeq n_t/n$  and  $K \simeq (n + n_t)/n$ .

For  $E_F = E_t$ , one has  $N = n$ ,  $K' = n_t/2n = p_t/2n = N_t/4n$ , and  $K = (n + \frac{1}{4}N_t)/n$ .

These results are essentially our prescription, Sec. II, for the calculation of  $N_T$ .

We have not been concerned with precision in this discussion. Strictly speaking,  $K'$  is not a constant, and the exact result (A3) should be substituted into (A1) and the resulting differential equation solved in the separate ranges of  $E_F$ . Although indeed the form of the decay is sensitive to this change in  $K'$  (an exponential becoming hyperbolic, for example), the response time  $\tau_0$ , as defined by decay of  $n$  to one-half of its initial value, is not significantly changed by a more accurate treatment.

Likewise we have regarded  $p_R$ , the density of holes in the recombination centers, as constant during the decay. Actually,  $p_R = N_t + n$  is not an unlikely relationship in many cases. Here again the form of the decay would be changed somewhat, but  $\tau_0$  would again be essentially unchanged.

Finally, in writing Eq. (A1) we have neglected thermal emission of electrons from the recombination centers back into the conduction band. This approximation becomes rapidly valid for recombination states well within the demarcation levels as discussed in reference 8. Further, even where the approximation is not valid, at very low light intensities the current treatment gives exactly the same results as obtained above, so long as  $\Delta n_t/\Delta n$  remains constant throughout the decay period, where  $\Delta n_t = n_t - n_t^0$  and  $\Delta n = n - n^0$ .