Field Formulation of Rate Processes in Photoconductors*

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The conventional field approach, used to describe the dynamic equilibrium of gases and solid-state masers, is applied to photoconducting solids. The dynamics of such systems can be treated with none of the inherent limitations of the traditional phenomenological approach. The significance of capture cross sections and attempt-to-escape frequencies can be appreciated, stimulated recombination evaluated, and phenomenological quantities can be given physical significance. A correlation between optical cross sections and capture coefficients is simply derived, which is absent in earlier models.

INTRODUCTION

THE dynamic behavior of charge carriers in photoconductors is generally discussed in terms of the phenomenological theory principally developed by Rose and Bube.[1,2] This formalism, which is carried over to some degree to describe semiconductors, involves concepts such as the "attempt-to-escape" frequency, Boltzmann factors, and capture cross sections. Though this approach has been highly developed, there are several difficulties which a systematic analysis can clarify. As a convenient example, the equilibrium between a density N_1 of imperfections and the conduction band level N_c will be considered. The traditional rate equation is

$$n_1 v^* e^{-E/kT} = n_2(N_1 - n_1)Sv, \qquad (1)$$

where n_1 and n_2 are the electron densities in the appropriate levels, as illustrated by Fig. 1(a).

The quantity on the left of Eq. (1) is the rate of thermal excitation from the imperfections to the conduction band. It is invariably taken to be excitation by lattice vibrations. The quantity v^* is the "attempt-to-escape" frequency, defined as the product of the maximum lattice frequency and a factor, equal to or less than 1, describing the probability of the electron entering the conduction band after receiving sufficient energy. The Boltzmann factor represents the thermal activation energy for the transition. This expression was derived by Williams and Eyring on thermodynamic grounds.[3]

The terms on the right of Eq. (1) describe the rate of recombination between free electrons n_2 and empty imperfections $(N_1 - n_1)$. The capture probability for a free electron is expressed as the product of a capture cross section S and the average thermal velocity of an electron v. The model is that of a free electron, moving with velocity v, intersecting an area S associated with each imperfection.

Equilibrium considerations consistent with Eq. (1) show that

$$v^* = N_c Sv, \qquad (2)$$

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

It is the purpose of this discussion to consider in more detail the basic system. This produces a fundamental formulation with physical significance attached to the above-described parameters. The basic theoretical framework is then available to accurately describe the rate processes in photoconductors. In some respects the phenomenological approach gives equivalent results.

Specific criticism can be leveled against the traditional model in the following areas:

1. The "attempt-to-escape" frequency remains a catch-all phenomenological quantity without physical significance.

2. The role of radiative and nonradiative transitions is not clear.

3. The description of recombination in terms of a capture cross section and a thermal velocity is devoid of any rate-limiting process describing the equilibrium steady state.

Some clarification of the last point is worthwhile. Consider a crystal isolated in an evacuated cavity. The steady state, and hence the temperature of the crystal and that appropriate to the electron distribution, is governed by radiative transfer with the walls of the cavity, i.e., they will both be in equilibrium with the blackbody energy density within the cavity. This steady state is not expressed in the phenomenological theory; the equations only describe a closed system.

To these specific criticisms, one could add the general criticisms that the range of applicability is not clear, and that stimulated recombination is neglected.

The basic argument of the current formulation is that in a system at constant temperature the net balance of rates can be described solely in terms of radiative processes. In the case of the cavity discussed above, this is the only way a steady state may be reached and maintained. With additional photo-excitation on the crystal there will typically be net luminescence from electron transitions to the walls of the cavity and additional emission from the lattice as

[1] A. Rose, *Concepts in Photoconductivity and Allied Problems* (Interscience Publishers, Inc., New York, 1963).
[2] R. H. Bube, *Photoconductivity* (John Wiley & Sons, Inc., New York, 1960).
[3] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).

its temperature reaches a steady state above the temperature of the walls. The net exchange of energy from the electrons to the lattice and from the lattice to the walls can be described in terms analogous to those about to be formulated. This point is referred to later when the basic outline has been described. For convenience, the electrons will be considered isolated from the lattice.

The approach is that conventionally used to describe rate processes in gases, plasmas, and in the microwave and laser branches of solid-state physics.[4–6] Apart from considerations of noise,[7] it does not appear to have been extended in any general sense to photoconductors.

A FIELD FORMULATION

Consider the interaction between a radiation field, composed of the blackbody energy density of temperature T, and the two levels already discussed. The equilibrium situation is illustrated by Fig. 1(b). The thermal-equilibrium rate equation is

$$(\omega_{sp}+\omega_{21})n_2\frac{N_1-n_1}{N_1}=\omega_{12}n_1\frac{N_c-n_2}{N_c}, \qquad (3)$$

where the ω's are the spontaneous and induced total transition probabilities per unit time between one initial state and all the final states. They may be written as

$$\omega=\text{const}\times|X_{12}|^2, \qquad (4)$$

where X_{12} is the appropriate matrix element for the transition summed over the final density of states. This approach is adopted in the absence of specific information concerning the initial- and final-state wave functions. The remaining terms in Eq. (3) are the density of initially occupied states, and the probability the final state is empty, to give the required total rate per unit time per unit volume. The significance of the probability term on the right of Eq. (3) is discussed below.

Defining transition probabilities per pair of states as W_{12}, W_{21}, W_{sp}, where

$$\omega_{12}=N_cW_{12}, \quad \omega_{21}=N_1W_{21}, \quad \omega_{sp}=N_1W_{sp}, \qquad (5)$$

Eq. (3) becomes

$$(W_{sp}+W_{21})n_2(N_1-n_1)=W_{12}n_1(N_c-n_2). \qquad (6)$$

The transition probabilities are now characteristic of the transition and $W_{12}\equiv W_{21}$, since both these transitions are induced by the same background

[4] A. Einstein, Physik Z. 18, 121 (1917).
[5] M. Garbuny, *Optical Physics* (Academic Press Inc., New York, 1965).
[6] A. E. Siegman, *Microwave Solid State Masers* (McGraw-Hill Book Company, Inc., New York, 1964).
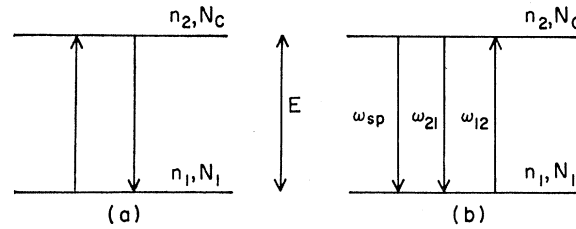[7] K. M. van Vliet, Proc. IRE 1004 (1958).

FIG. 1. (a) Phenomenological equilibrium. (b) Equilibrium in the field formulation.

radiation fields. Equation (6) can now be written as

$$\frac{W_{sp}+W}{W}=\frac{n_1N_c(1-n_2/N_c)}{n_2N_1(1-n_1/N_1)}=e^{E/kT}, \qquad (7)$$

since

$$\frac{n_1}{N_1}=\frac{1}{e^{(E_F-E)/kT}+1} \quad \text{and} \quad \frac{n_2}{N_c}=\frac{1}{e^{E_F/kT}+1}$$

at an equilibrium temperature T.[8]

The significance of the probability term on the right of Eq. (3) can now be discussed conveniently. The picture so far presented is one of a discrete conduction band in which the occupation n_2/N_c can be described in terms of a Fermi-Dirac function. In any practical solid, this is invalid, and N_c would not have its conventional significance. However, attention can be restricted to nondegenerate photoconductors where $n_2/N_c=e^{-E/kT}$ and the n_2 term can be dropped from right-hand side of Eqs. (3) and (6). Under these circumstances the identity expressed by Eq. (7) is rigorous, the n_2/N_c being omitted. This presentation emphasizes the physical origin of the rate equation. For the remainder of this paper it is assumed $n_2\ll N_c$.

Inspection of Eq. (7) shows that W_{sp} is identical to the Einstein A coefficient whereas $W=\rho B$, with B the induced transition coefficient and ρ the blackbody energy density appropriate to the energy E. The energy density ρ is given by

$$\rho=\frac{8\pi h\nu^3}{c^{*3}}\frac{1}{e^{E/kT}-1} \qquad (8)$$

per unit frequency interval, where c^* is the velocity of light in the crystal and the dispersion is assumed small. This should be integrated over the absorption band, or approximated by assuming that the change in ρ is small between E and $E+dE$ at the energy under consideration. In any case, ρ may be expressed as

$$\rho=\rho(q)(e^{E/kT}-1)^{-1}, \qquad (9)$$

and is the product of the energy density of states, and the probability of having a quantum in a given state of the radiation field.

[8] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, London, 1938).

Substitution of (9) into (7), with $W=\rho B$ gives the conventional relationship between the Einstein coefficients

$$W_{sp}=A=(8\pi h\nu^3/c^{*3})B. \tag{10}$$

COMPARISON OF THE FORMULATIONS

The two equilibrium equations (1) and (6) can now be compared to attribute physical significance to phenomenological quantities. Equation (1) may be written as

$$n_1 N_c e^{-E/kT}=n_2(N_1-n_1), \tag{11}$$

and Eq. (6) may be written as

$$n_1(N_c)e^{-E/kT}=n_2(N_1-n_1). \tag{12}$$

The two equations are found to be identical for the general nondegenerate situation where $n_2 \ll N_c$. The appearance of the exponential term in Eq. (12) is interpreted as the ratio of the stimulated transition probability to the total (spontaneous plus stimulated) relaxation probability [Eq. (7)].

Physical significance can be attributed to ν^* by identifying the capture probability $\beta=Sv$ with W_{sp}, the transition probability per pair of states for spontaneous recombination. Then from Eqs. (2) and (7) we have

$$\nu^*=N_c\beta=N_cW(e^{E/kT}-1)=\omega_{12}(e^{E/kT}-1). \tag{13}$$

Thus the "attempt-to-escape" frequency is identified as the total transition probability per unit time divided by the probability of having a photon of the required energy in a state of the radiation field. From Eq. (11), ν^* is a rapidly varying function of the energy of the transition for a constant total transition probability. Traditionally, it is assumed constant.[9] This variation does not contradict general consideration of detailed balance,[10] but is a consequence of it. Since $\beta=Sv$, this parameter also reflects the interaction with the background photons.

The electron-lattice interaction, giving rise to radiationless transitions, can be described in similar terms.[6] An "attempt-to-escape" frequency can be defined which will be identical to Eq. (13), with an appropriate total transition probability. An energy-density of phonon states will replace $\rho(q)$ in Eq. (9), which will be characteristic of the lattice under consideration.

PHOTOEXCITATION EFFECTS

The effects of additional photoexcitation will now be considered in terms of the background excitation ρ_1 and an additional excitation ρ_2. The steady-state rate

[9] D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963).
[10] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948).

equation is

$$[(\rho_1+\rho_2)B+W_{sp}]n_2^*(N_1-n_1^*)$$
$$=(\rho_1+\rho_2)Bn_1^*[N_c], \tag{14}$$

where

$$n_2^*=n_2+\Delta n_2, \quad n_1^*=n_1+\Delta n_1, \quad W=\rho_1 B, \quad \text{and} \quad n_2^* \ll N_c.$$

The traditional way of writing this steady state is

$$n_2^*(N_1-n_1^*)\beta=n_1^*N_c\beta e^{-E/kT}+S_{opt}n_1^*f, \tag{15}$$

where S_{opt} is the optical cross section for absorption of a photon to make the transition from the imperfection level to the conduction band, and f is the excitation intensity per unit area per unit time. To compare the two formulations, Eq. (14) is rewritten as

$$(\rho_1+\rho_2)Bn_2^*(N_1-n_1^*)+W_{sp}n_2^*(N_1-n_1^*)$$
$$=Wn_1^*(N_c)+\rho_2 Bn_1^*(N_c). \tag{16}$$

The first term on the left of Eq. (16) represents stimulated emission resulting in recombination of an electron in the conduction band at the imperfection level; this has no counterpart in the phenomenological approach.

The second term on the left of Eq. (16) represents spontaneous recombination. This term is the same in both formulations, since $\beta \equiv W_{sp}$ on the left of Eq. (15).

The first term on the right of Eq. (16) is approximately equal to the first term on the right of Eq. (15), since

$$W=\beta(e^{E/kT}-1)^{-1}\approx\beta e^{-E/kT} \tag{17}$$

for $E \gg kT$. This represents the background excitation to the conduction band.

The second term on the right of both Eq. (15) and Eq. (16) is due to the additional photoexcitation. From these two equations we have

$$fS_{opt}=\rho_2 BN_c. \tag{18}$$

Thus, if $f/d\nu=\rho_2 c^*$ per unit frequency range, we obtain

$$c^*S_{opt}d\nu=BN_c. \tag{19}$$

From Eq. (10), $\beta \equiv W_{sp}=\rho(q)B$, and we finally have

$$\frac{c^*S_{opt}d\nu}{\beta}=\frac{N_c}{\rho(q)}. \tag{20}$$

This gives the relationship between the optical cross section for excitation out of a center and the capture probability for capture by the center. Furthermore, since $\beta N_c=\nu^*$ and $\nu^*=\rho(q)$ times the transition probability per quantum per unit time, c^*S_{opt} reduces to this transition probability in accordance with the picture of a photon of velocity c^* intercepting an area of S_{opt} cm². That is,

$$W_{12}=\rho_1 c^*S_{opt}d\nu, \tag{21}$$

from Eqs. (13) and (20).

It is useful to put typical values in Eq. (20) to clarify the dimensions. The significance of these values will not be discussed here but they are typical of models generally used in photoconductivity in the visible region.[2] They are $c^* = 10^{10}$ cm sec^{-1}, $\rho(q) = \frac{1}{10}$ eV cm^{-3} sec, and $d\nu = 10^{13}$ sec^{-1}. $S_{opt} = 10^{-16}$ cm^2 and $N_c = 10^{19}$ cm^{-3}, to give a capture coefficient β of 10^{-13} eV cm^3 sec^{-1}.

STIMULATED RECOMBINATION

The condition for stimulated recombination to be significant, in the simple two-level system, can be expressed as

$$(\rho_1 + \rho_2)B \approx W_{sp} \qquad (22)$$

from inspection of the left-hand side of Eq. (14). For $\rho_1 \ll \rho_2$, using Eq. (10), we have

$$(e^{E/kT_1} - 1)^{-1} \approx 1,$$

where T_1 is the effective temperature of the lamp giving rise to ρ_2. Thus for a tungsten lamp at 3000°K, stimulated recombination can be significant for energy separations of the order of 0.2 eV, though the problem of the geometry of any given situation is dominant. Similarly, stimulated phonon recombination becomes significant for $E \approx 0.02$ eV, when T_1 is the lattice temperature of 300°K. This condition expresses the relative probability of having a zero-point quantum and a quantum of the radiation field. Though these are not typical conditions encountered in, say, the II–VI compounds, they are significant with regard to photoconductivity in silicon and germanium. This will be discussed elsewhere.

SATURATION

Equation (14) can be written as

$$(W_{12} + W_{sp})n_2^*(N_1 - n_1^*) = W_{12}n_1^*(N_c) + F, \qquad (23)$$

where F is the net rate of generation of electrons given by

$$F = \rho_2 B[n_1^*(N_c) - n_2^*(N_1 - n_1^*)]$$

on comparison of Eq. (14) and Eq. (23). This can be written in terms of the excess densities as

$$F = \rho_2 B[(N_c + n_2^*)n_1^* - N_1 n_2^*]. \qquad (24)$$

For the general case $N_c \gg n_2^*$, the photoconductor will be saturated when the densities in the two levels are in the ratio of the density states, and F will go to zero.

CONCLUSIONS

It is possible to write down a consistent formulation for the dynamics of charge carriers in photoconductors with none of the deficiencies inherent in the conventional approach. The significance of capture cross sections can be clarified, stimulated recombination to shallow states can be described, and the typical models postulated in the field of photoconductivity can be critically analyzed. This will be done elsewhere.

ACKNOWLEDGMENTS