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THEORY OF TEMPERATURE AND INTENSITY DEPENDENCE OF PHOTOCONDUCTIVITY IN AMORPHOUS SEMICONDUCTORS

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Abstract.- The generation and recombination kinetics of non-equilibrium charge carriers under illumination is studied in order to obtain the temperature and intensity dependence of the steady state energy distribution of photo-induced carriers in the range of energies contributing to the electrical transport. The results are applied to a model of transport in amorphous solids developed previously. Comparison with experimental data on photoconductivity of glow-discharge silicon provides further support for this model.

Introduction.—In two recent publications (1,2) a model for the transport near the band edge in amorphous semiconductors has been developed. This model is based on Kubo-Greenwood formulae for the conductivity and the thermoelectric power taking into account contributions of the entire energy range extending from localized tail states to delocalized states above the mobility edge. The experimentally observed discrepancy between the 'activation energies' for conductivity and thermopower which had been a puzzle for quite a while has found a natural explanation in our theory. The model is also able to split the temperature dependence of conductivity and thermopower activation energy unambiguously into a contribution due to the 'statistical shift' of the Fermi level and another one due to a shift of the average energy at which the transport takes place. Finally it is possible to deduce the differential conductivity $\sigma(\varepsilon)$ by Laplace transformation of the results obtained from a combined analysis of conductivity and thermopower data.

In this paper we are extending our model to transport under nonequilibrium conditions for the case of photoconductivity. The major part of the paper will be devoted to a discussion of the temperature and intensity dependent carrier distribution function under illumination. We will show that the expression for the photoconductivity under certain conditions may be expressed as a product of a temperature dependent and an intensity dependent factor. The temperature dependent factor is related in a simple way to the temperature dependent 'prefactor' of the dark conductivity. The implications of this relation between dark and photoconductivity will be tested by comparison with experimental results from the literature.

1. Theory of photoconductivity
1.1 Expressions for the conductivity under illumination.—In our previous papers the dark conductivity was expressed as the integral over all the contributions of a differential conductivity $\sigma(\varepsilon)=\epsilon\sigma(\varepsilon)N(\varepsilon)$ weighted with the probability that the (localized or extended) states at that energy are occupied (1,2)
The occupation probability in the case of dark conductivity is the Fermi distribution function

\[ f^0(\varepsilon; T) = \frac{1}{\exp\left(\frac{(\varepsilon - \varepsilon_F(T))}{kT} + 1\right)} \]

\( \varepsilon_F(T) \) = Fermi level at temperature \( T \). Under non-equilibrium conditions \( f^0(\varepsilon; T) \) in equ. (1) has to be replaced by the appropriate steady state non-equilibrium distribution function

\[ \sigma^{\text{ph}}(T; I) = \int d\varepsilon \, \epsilon \mu(\varepsilon) N(\varepsilon) \, f^{\text{ph}}(\varepsilon; T; I) \]

It should be noted that our \( \sigma^{\text{ph}} \) represents the total non-equilibrium conductivity and not the conventional excess photoconductivity \( \sigma^{\text{photo}} \) which is related to our \( \sigma^{\text{ph}} \) by

\[ \sigma^{\text{photo}}(T; I) = \sigma^{\text{ph}}(T; I) - \sigma^d(T) \]

The distribution function \( f^{\text{ph}}(\varepsilon; T; I) \) depends in a complicated manner on the temperature \( T \) and intensity \( I \). The distribution function, in particular, is a functional of the whole density of states distribution \( N(\varepsilon') \), of the transition probability \( w(\varepsilon \rightarrow \varepsilon') \) for transitions from and to states at the energy \( \varepsilon' \) and, finally, of the real space statistics if the states are localized.

As there is no hope to solve this problem exactly we will try to obtain information about the general structure of \( f^{\text{ph}}(\varepsilon; T; I) \) which will enable us to evaluate the intensity and temperature dependence of \( \sigma^{\text{ph}} \) at least qualitatively.

1.2 Distribution function at \( T = 0 \). - The assumption of zero temperature reduces the problem of determining \( f^{\text{ph}}(\varepsilon; I) \) considerably because we have to consider only energy dissipating processes in the kinetics of the photo-excited electrons and holes. The reciprocal lifetime of a carrier at the energy \( \varepsilon \) is given by the probability per time \( w(\varepsilon) \) to perform a transition into any other state at some lower energy \( \varepsilon' \)

\[ \tau(\varepsilon) = w(\varepsilon) = \int_0^d d\varepsilon w(\epsilon \rightarrow \epsilon')N(\epsilon')(1-f^{\text{ph}}(\epsilon')) \]

The contributions to the integrand in eqn. (5) may be classified into relaxation and recombination processes. For electrons it is reasonable to consider those transitions as relaxation processes whose final energy \( \varepsilon' \) is above midgap \( \psi \) (or above the ground state Fermi level) and to call them recombination processes for any energy below

\[ \tau_{\text{relax}}(\varepsilon) = \int_0^d d\varepsilon w(\epsilon \rightarrow \epsilon')N(\epsilon)(1-f^{\text{ph}}(\epsilon')) \]

\[ \tau_{\text{rec}}(\varepsilon) = \int_0^d d\varepsilon w(\epsilon \rightarrow \epsilon')N(\epsilon)(1-f^{\text{ph}}(\epsilon')) \]

At high electron energies above the mobility edge \( E_c \) the relaxation processes are very fast: Both, the density of states \( N(\varepsilon) \) and the probability \( w(\varepsilon \rightarrow \varepsilon') \) for energy dissipating relaxation processes by phonon emission are large and \( 1-f^{\text{ph}} \) is close to unity. Below the mobility edge, however, the average values of \( w(\varepsilon \rightarrow \varepsilon') \) for relaxation processes decrease more and more to lower energies because of the increasingly localized character of the wave functions and the decreasing density of states. Therefore, \( \tau_{\text{relax}}(\varepsilon) \) qualitatively increases on an exponential scale below \( E_c \).
The lifetime for recombination processes $\tau_{n,\text{rec}}(E)$ depends much less on energy than for relaxation: There are always photo-excited holes in extended or weakly localized states available for recombination with an electron even if itself is trapped in a strongly localized state. In Fig. 1 the energy dependence of $\tau_{n,\text{relax}}(E)$, $\tau_{n,\text{rec}}(E;I)$ and of $\tau_0(\epsilon;I)$ is shown qualitatively. From equ(6) and (7) it can be seen easily that $\tau_{n,\text{rec}}(\epsilon)$, in contrast to $\tau_{n,\text{relax}}(\epsilon)$, is intensity dependent because of the strongly intensity dependent hole distribution function $1-f_{\text{ph}}^0(\epsilon;I)$. Nearly no electrons are lost by recombination at energies sufficiently above $\epsilon_f$. Therefore $f_{\text{ph}}^0(\epsilon;I)\propto 1/\tau_{n,relax}(\epsilon)$ holds approximately and $f_{\text{ph}}^0(\epsilon;I)$ increases by many orders of magnitude when the energy of the relaxing carriers approaches $\epsilon_f$. The recombination channel, however becomes very efficient at energies close to $\epsilon_f$ and below of it because of the large values of $f_{\text{ph}}^0(\epsilon;I)$ which follow from the long lifetimes $\tau_{n}(\epsilon;I)$ in this energy range. In Fig. 2 a qualitative picture of the zero temperature $f_{\text{ph}}^0(\epsilon;I)$ and of $1-f_{\text{ph}}^0(\epsilon;I)$ (for holes) is given.

1.3 Distribution function at $T \neq 0$. At finite temperatures the situation differs into major points from the previously discussed kinetics: i) The condition of detailed balance requires that

$$f_{\text{ph}}^0(\epsilon;T;I) = \exp\left(-\frac{(\epsilon-\epsilon_f)}{kT}\right)f_{\text{ph}}^0(\epsilon_f;T;I)$$

or, expressed in another way, the distribution function never decreases faster than $\exp\left(-\frac{(\epsilon-\epsilon_f)}{kT}\right)$. This condition affects the distribution function strongly for $\epsilon$ above $I$.

In this range

$$f_{\text{ph}}(\epsilon;T;I) = \exp\left(-\frac{(\epsilon-\epsilon_f)}{kT}\right)f_{\text{ph}}^0(\epsilon_f;T;I)$$  (9) 

is a reasonable approximation as the fast relaxing carriers can induce only minor deviations from (9). ii) The recombination lifetime, in general, will be modified. The probability $w(\epsilon'\rightarrow\epsilon)$ in (6) and (7) may change considerably with temperature if there are configurational shifts involved in the recombination processes. If this is not the case, the temperature dependence of the factor $1-f_{\text{ph}}^0(\epsilon_f;T;I)$ for $\epsilon_f$ below $\epsilon_f$ may still influence $\tau_{n,\text{rec}}(\epsilon)$ (see equ. (7)). It is, however, at least plausible to assume that this temperature dependence of the recombination lifetimes is rather weak for electron and hole energies around $\epsilon_{c,I}$ and $\epsilon_{v,I}$, which will turn out to be the energies of major importance for our following discussion.

![Fig.1](image1.png) Relaxation, recombination, and total lifetime $\tau_n(I)$ of electrons as a function of energy. At $\epsilon_f$ there is a sharp change from dominant relaxation to dominant recombination.

![Fig.2](image2.png) Electron and hole distribution function under illumination at zero temperature (dashed lines) and at finite temperatures $T_1$ and $T_2$ (full lines)
of the photoconductivity. We assume that the overlap of localized electron states near $E$ and hole states near $E'$, with other electron states at lower energy is comparable to that one. With this condition we expect that recombination processes, also at higher temperatures, occur predominantly with the relatively large number of moderately localized holes near $E'$ rather than with an exponentially smaller number of holes closer to $E$, although their probability $w(E-E')$ will be larger because of weak localization.

We may summarize: At the energies $E$ and $E'$ the occupation probabilities $f_{ph}(E,I;I)$ and $1-f_{ph}(E',I;I)$ depend on the intensity but only moderately on temperature. At the energies above $E$ and below $E'$ where the transport takes place the occupation factors are related to those values by Boltzmann factors (see equ. (9)). Under these conditions the expressions (1) and (3) for the dark conductivity and for the conductivity under illumination become quite similar. In our previous papers (1,2) we had introduced an arbitrary reference energy $E_0$ in order to rewrite equ. (1) in the form

$$\sigma_0(T) = \sigma_o(T) \exp[-(E_o-E_F(T))/kT] \text{ with } \sigma_o(T) = \int \text{d}E N(E) \exp[-(E-E_o)/kT]$$

$$\sigma_0(T)$$

(10)

where $\sigma_0(T)$ can be determined by a combined analysis of conductivity and thermopower data. Using the same energy $E_0$ we may also rewrite equ. (3) as

$$\sigma_{ph}(T;I) = \sigma_o(T) \exp[-(E_o-E_c,I)/kT] f_{ph}(E_c,I)$$

(11)

Due to the simple relation between $\sigma_o(T)$ and $\sigma_{ph}(T;I)$ it is easy to test whether our assumptions are compatible with experimental results.

2. Comparison with experiment.- The samples investigated in the photoconductivity experiments of Rehm, Fischer, Stuke, and Wagner (3) on phosphorus-doped glow-discharge Si were prepared under similar conditions as those in the thermopower and dark conductivity studies by Beyer, Mell, and Overhof (4). From the systematic changes of $\sigma_o(T)$ with doping as deduced from our previous analysis we can attribute corresponding values of the quantities $T_0$, $n$, and $V_0$ (page 2089 of Ref.1) also to the samples used in the photoconductivity experiments (see inset-table in Fig.3). The experimental points in Fig.3 represent the total conductivity under illumination (see equ. (4)) for the set of samples obtained from Fig.1 in Ref.3. The full lines are calculated from equ.(11) with $E_o-E_c,I$ as fitting parameter (see last column of the table in Fig.3). The (experimental) dark conductivity is shown as dashed lines in the range where $\sigma_d(T)$ exceeds the values calculated from (11). It should be noted that the good agreement between the experimental data could only be obtained when the changes of $\sigma_o(T)$ with increasing doping level are taken into account. The increase of $E_o-E_c,I$ with higher doping, which corresponds to a shift of $E_c,I$ to lower energies, is fully consistent with the doping induced broadening of the differential conductivity function $\sigma(E)$ to lower energies as found previously (see Fig.7. of Ref.1).

Conclusions.- In our study of relaxation and recombination kinetics we have derived an expression for the total conductivity under illumination. The agreement of our theory with experimental results is excellent. A discussion including previous work (5) will be given elsewhere.