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Relaxation of highly excited carriers in wide-gap semiconductors

V G Tyuterev\textsuperscript{1,2,4}, V P Zhukov\textsuperscript{3,4}, P M Echenique\textsuperscript{4,5} and E V Chulkov\textsuperscript{2,4,5}

\textsuperscript{1} Tomsk State Pedagogical University, Kievskaya st. 60, Tomsk 634041, Russia
\textsuperscript{2} National Research Tomsk State University, Lenin st. 36, Tomsk 634050, Russia
\textsuperscript{3} Institute of Solid State Chemistry, Urals Branch of the Russian Academy of Sciences, Pervomayskaya st. 91, Yekaterinburg 620990, Russia
\textsuperscript{4} Donostia International Physics Center (DIPC), P Manuel de Lardizabal 4, 20018 San Sebastian, Spain
\textsuperscript{5} Departamento de Fisica de Materiales, Facultad de Ciencias Quimicas, UPV/EHU and CFM-MPC, Apartado 1072, 20080 San Sebastian, Spain

E-mail: tyuterev@gmail.com

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Abstract

The electron energy relaxation in semiconductors and insulators after high-level external excitation is analysed by a semi-classical approach based on a kinetic equation of the Boltzmann type. We show that the non-equilibrium distributions of electrons and holes have a customary Fermi-like shape with some effective temperature but also possess a high-energy non-Fermian ‘tail’. The latter may extend deep into the conduction and valence bands while the Fermi-like component is localized within a small energy range just above the edge of the band gap. The effective temperature, effective chemical potential, and the shape of the high-energy component are governed by the process of electron–phonon interactions as well as by the rates of carrier generation and inter-band radiative recombination.

Keywords: wide-gap semiconductors, high-level excitation, electron–phonon interactions, radiative recombination, non-equilibrium distribution

1. Introduction

The effects of high-energy irradiation on the carrier distribution in semiconducting crystals and their structures were widely investigated in recent decades \cite{1,2}. The studies of electron excitation from a crystal ground state and subsequent relaxation processes in various ultrashort timescales can elucidate the fundamental physics of ultra-fast processes in solids and micro-structures and point out a way to enhance the processing speed of microelectronic devices. The analysis of the characteristic features of energy and momentum relaxation of non-equilibrium carriers in experiments with high-energy electron beams and powerful femtosecond lasers may elucidate the traits of high-field electric transport in crystals and nano-materials \cite{3–5}. It may also help in understanding the carriers’ behaviour in strong electric fields, including those which are close to the electric breakdown fields \cite{6,7}. The effects of abrupt thermal impact \cite{8,9} and other extremal exposures can also be more clearly understood. The study of energy relaxation is essential for understanding phenomena like the laser ablation \cite{10}, ultra-fast phase transformations \cite{11}, photocatalysis \cite{12} and solar energy conversion in the UV frequency range \cite{13,14}. To date, the energy relaxation in highly excited carriers has been investigated quite thoroughly in silicon \cite{1,15}, GaAs \cite{14,16–18}, GaP \cite{19}, InP \cite{19,20}, and CdSe \cite{21}. With regard to the large band-gap materials, the dynamics of the relaxation processes have been studied in selected publications only: ZnS \cite{5}, ZnO \cite{12,22,23}, TiO\textsubscript{2} \cite{23}, SiO\textsubscript{2} \cite{10}.

The evolution of the non-equilibrium distribution of charged carriers in wide band gap semiconductors was investigated in \cite{12,22,23}. Here the first-principle calculation of so called ‘quasi-stationary’ distributions of electrons \cite{12,22}, and holes \cite{23} in ZnO and TiO\textsubscript{2} have been performed. It was shown that a non-equilibrium distribution spreads over wide energy intervals inside the valence and conduction bands. The key role of this kind of distribution in the explanation of the photocatalytic properties was discussed and a relationship with the characteristics of photo-excitation was studied. The approach developed in the papers \cite{12,22,23}...
2. The physics of relaxation processes

In this section we discuss the effect of high-energy electron beam or powerful laser source exposure on semiconductors or insulators.

In the first step, due to the external ionization processes, a significant quantity of electrons are thrown up from the valence bands to the highly excited states in the conduction bands. Thereby an initial distribution of charge carriers, electrons and holes, is created. At this first stage there are a considerable number of electrons that have an energy sufficiently large for the act of band-to-band impact ionization. These electrons are capable of knocking the secondary electrons from the valence band and creating the holes. Thus these primary electrons are capable of producing the avalanche-like increase in the secondary carriers’ concentration.

The act of impact ionization goes along with the exchange of energy between the primary and secondary electrons. So the average energy of the primary carriers in the ensemble decreases. The threshold of the impact ionization $E_{\text{imp}}$ roughly equals the value of the forbidden gap above the bottom of the conduction band. Once the energy of a primary electron becomes lower than $E_{\text{imp}}$ the production of secondary electrons and holes is prohibited by the energy conservation law. The order of a characteristic time for the electrons’ energy exchange process is about several tens of femtoseconds. After the impact ionization terminates, an electron distribution arises in the conduction band and is concentrated below the threshold $E_{\text{imp}}$ (hereafter ‘instant distribution’). In the valence bands the ‘instant distribution’ of holes appears below the band gap.

For the sake of certainty, in what follows we shall discuss the evolution of electrons’ energy distribution, but any conclusions can be generalized straightforwardly for holes. In the energy region below the impact ionization threshold the main energy loss mechanism is connected with the electron–phonon inelastic scattering with a characteristic time of the order of hundreds of femtoseconds. The size of a phase area for scattering increases considerably. Therefore in the current paper we perform a theoretical research of the carrier non-equilibrium distribution on a more broad foundation which helps us to clarify the effect of the electron–hole recombination processes, to specify the distribution function near the band gap edges and to associate the obtained results with the generic quasi-Fermi distribution.

essentially differs from those employed formerly for the analyses of the excited carriers’ dynamics in semiconductors, see e.g. [17, 18, 21], where a quasi-Fermi distribution of excited electrons near the bottom of the conduction band was conjectured. However, the shape of the carrier distribution function near the edges of the band gap was disregarded in the proposed approach. Furthermore, the effect of the interband radiative recombination on the distribution function was neglected. Therefore in the current paper we perform a theoretical research of the carrier non-equilibrium distribution on a more broad foundation which helps us to clarify the effect of the electron–hole recombination processes, to specify the distribution function near the band gap edges and to associate the obtained results with the generic quasi-Fermi distribution.

3. General expressions

During the first stage the randomization of momentum occurs within several femtoseconds due to the electron–electron scattering [1]. Therefore the occupation number of an electron’s band state can be regarded as a function of an energy only.

We proceed from a kinetic equation for the occupation number of an electron state with energy $E_{ik}$ in the conduction band:

$$\frac{dn(t, E_{ik})}{dt} = (1 - n(t, E_{ik})) \sum_{k'} W_{ik'k}^{el-ph} n(t, E_{ik'}) - n(t, E_{ik}) \sum_{i} W_{ik}^{el} n(t, E_{i}) + (1 - n(t, E_{ik})) \sum_{i} W_{ik}^{ph} (1 - n(t, E_{i}))$$

$$- n(t, E_{ik}) \sum_{i} W_{ik}^{ph} (1 - n(t, E_{i}))$$

(1)

$E_i$ indicates all other electron states lying below the bottom of the conduction band. $W_{ik}^{el}$ and $W_{ik}^{ph}$ denote the probabilities...
describing the processes of electron generation from the valence band and the inverse processes of band-to-band recombination respectively. $W^{\text{el-ph}}_{\epsilon_k\kappa'}$ is the probability per unit time of the electron–phonon transition within the conduction band. Here we take into account one-phonon processes only because the probabilities of multiphonon processes manifest themselves in the higher orders of perturbation theory and so are exponentially small.

$$W^{\text{el-ph}}_{\epsilon_k\kappa'} = \sum_{\sigma} P^{\text{el-ph}}_{\epsilon_k\kappa'} \delta (E_{\epsilon_k} - E_{\epsilon_k'} + \varepsilon_{\sigma})$$

(2)

$P^{\text{el-ph}}_{\epsilon_k\kappa'} = \sum_{\sigma} \left| \langle c_k | H^{\text{el-ph}}_{\sigma} | c_{\kappa} \rangle \right|^2$ is the matrix element of the electron–phonon interaction operator. $\varepsilon_{\sigma}$ is the energy of a phonon of $\sigma$th branch with the wave vector $\mathbf{q}$. The phonon occupation number $N (\varepsilon_{\sigma})$ is also considered to be energy-dependent. It is convenient to introduce a spectral function of electron–phonon interaction as:

$$F^{\text{el-ph}} (\epsilon, E, E') = \frac{1}{\pi} \sum_{\sigma} \delta (E - E_{\epsilon_k}) P^{\text{el-ph}}_{\epsilon_k\kappa'} \delta (\epsilon - \varepsilon_{\sigma})$$

(3)

After summing with the delta-function $\delta (E - E_{\epsilon_k})$ by $\mathbf{k}$ and all $c$ from the conduction bands, one comes to the following equation for the distribution function $f (t, E) = G (E) n(t, E)$ of electrons in the conduction band.

$$\frac{df (t, E)}{dt} = \int_{0}^{E_n} d\epsilon \{ F (\epsilon, E, E + \epsilon) (N (\epsilon) + 1) (1 - n(t, E))$$

$$\times n(t, E + \epsilon) + F (\epsilon, E, E - \epsilon) N (\epsilon) (1 - n(t, E))$$

$$\times n(t, E - \epsilon) - F (\epsilon, E, E + \epsilon) N (\epsilon) n(t, E)$$

$$(1 - n(t, E + \epsilon)) - F (\epsilon, E, E - \epsilon) (N (\epsilon) + 1)$$

$$\times n(t, E)(1 - n(t, E - \epsilon)) + [df (t, E)/dt]_{\text{ext}} - f (t, E) \gamma_0 (E)$$

(4)

Here $G (E) = \sum_{\epsilon_k} \delta (E - E_{\epsilon_k})$ is the density of electron states, the energy taken with respect to the bottom of the conduction band (hereafter 'excess energy'). The range of integration by $\epsilon$ extends from zero up to the maximal phonon energy $\varepsilon_m$. The term $[df (t, E)/dt]_{\text{ext}}$ describes the distribution created by generation processes (the aforesaid 'instant distribution'). The expression $f (t, E) \gamma_0 (E)$ takes into consideration the flow of electrons from the conduction band to the valence bands and to the impurity levels because of the radiative recombination.

For holes one can introduce the usual definitions of hole occupation numbers and the energy reference level. Then the equation for the hole distribution can be reduced to the form similar to equation (4) by straightforward mathematical manipulation. So any results regarding the dynamics of excited electrons can be rewritten for the excitation inside the valence bands.

As a phonon energy is a small quantity relative to the band energy one can expand equation (4) by parameter $\epsilon$. Retaining the terms linear and quadratic in $\epsilon$ one obtains:

$$\frac{df (E)}{d\epsilon} = \frac{d}{dE} [n(t, E) (1 - n(t, E)) \Phi_1 (E) + \frac{dn(t, E)}{dE} \Phi_2 (E)] + [dn(t, E)/dT]_{\text{ext}} - n(t, E) \gamma_0 (E)$$

(5)

Hereafter

$$\Phi_0 (E) = \int_{0}^{E_n} \Phi (\epsilon, E, E') d\epsilon; \quad \Phi_1 (E) = \int_{0}^{E_n} \Phi (\epsilon, E, E') d\epsilon$$

(6)

$$\Phi_2 (E) = \int_{0}^{E_n} \phi (E, E', E) d\epsilon$$

(7)

$\Phi (\epsilon, E)$ is defined as $F (\epsilon, E, E')$ at coinciding arguments $E = E'$. $\Phi (\epsilon, E)$ is:

$$\Phi (\epsilon, E) = \sum_{\sigma} \delta (E - E_{\epsilon_k}) E^{\text{el-ph}}_{\epsilon_k\kappa'} \delta (\epsilon - \varepsilon_{\sigma})$$

(8)

In deriving equation (5) we have used the identity

$$[df (\epsilon, E, E') /d\epsilon]_{E=E'} = 1/2 [d\Phi (\epsilon, E) /dE]$$

(9)

Obviously the function

$$w (E) = G^{-1} (E) \Phi_0 (E)$$

(10)

specifies the probability per unit time for an electron to leave a given excess energy level $E$. Consequently the average lifetime of a single electron at the excess energy level $E$ can be assigned as

$$\tau (E) = w^{-1} (E) = G (E) / \Phi_0 (E)$$

(11)

4. The electron–phonon relaxation time

A velocity of energy losses due to the inter-band transition of an electron from a single state with excess energy $E$ to every possible level inside the conduction bands due to inelastic scattering by phonons should be naturally defined as

$$dE/dt = G^{-1} (E) \sum_{\epsilon_k} \delta (E - E_{\epsilon_k}) (E_{\epsilon_k} - E_{\epsilon_k'}) W^{\text{el-ph}}_{\epsilon_k\kappa'}$$

(12)

In the foregoing notations this expression is rewritten as

$$dE/dt = G^{-1} (E) \int_{0}^{E_n} [N (\epsilon) F (\epsilon, E, E + \epsilon)$$

$$-(N (\epsilon) + 1) F (\epsilon, E, E - \epsilon)] d\epsilon$$

(13)

Accurate within a first-order in terms of $\epsilon$ one has:

$$dE/dt = -G^{-1} (E) \Phi_1 (E)$$

(14)

Formally

$$\frac{dE}{d\epsilon} = -G (E) / \Phi_1 (E)$$

(15)
Hence the time of the electron’s downfall from a certain highest excitation level $E_{\text{max}}$ to some given $E$ is

$$t(E) = \int_{E}^{E_{\text{max}}} \frac{G(E')/\Phi_1(E')}{\epsilon_0(E')} \, dE'$$ \hspace{1cm} (17)

Let us define an average energy loss by an individual electron in the process of a single transition act from an excess level $E$ as

$$\epsilon_0(E) = \Phi_1(E)/\Phi_0(E)$$ \hspace{1cm} (18)

Using equations (5) one has for the velocity of energy losses

$$dE/dt = -\epsilon_0(E)/\tau(E)$$ \hspace{1cm} (19)

Thereafter the dropping down time from the level $E_{\text{max}}$ to the bottom of the conduction band can be written as:

$$t_{\text{max}} = \int_{0}^{E_{\text{max}}} \tau(E) \epsilon_0^{-1}(E) \, dE$$ \hspace{1cm} (20)

5. Stationary solution for the distribution function

A stationary solution of equation (5) satisfies the condition $df(t, E)/dt = 0$ and is reduced itself to the time-independent equation for the occupation number $n(E)$. It is convenient to look for its solution in the form $n(E) = n_0(E) + n_1(E)$, where $n_0(E)$ is the solution for the stationary equation without sources and sinks. A direct substitution checks that the particular solution has a form

$$n_0(E) = (1 - \tanh \frac{R(E)}{2})$$ \hspace{1cm} (21)

where

$$R(E) = \int_{0}^{E} \Phi_1(E')/\Phi_2(E') \, dE' + C$$ \hspace{1cm} (22)

Here $C$ is an integration constant.

Under conditions of low intensity of external exposure one has to regard $n_0(E)$ as a small quantity. In this case neglecting by terms $n^2$ and $n \, dn/dE$ we come from equation (5) in a stationary regime without sources and sinks to the linearized equation with a stationary solution

$$n_0(E) = A \exp(-R(E))$$ \hspace{1cm} (23)

Both (21) and (23) should be localized in the energy region where the electron–phonon relaxation is inefficient, i.e. at $E \lesssim \epsilon_{\text{max}}$, where $\epsilon_{\text{max}}$ is the upper bound of the phonon spectrum. An equation for the high-order correction $n_1(E)$ comes out by substitution of $n_0(E)$ into the master equation (5). We restrict ourselves by the examination of excitation regimes when $n_1(E)$ can be treated as a small quantity. In that case we have to consider $n_1^2$, $n_1 \, dn_1/dE$, $\epsilon^2_0 \, dn_1/dE$, $\epsilon^2 \, d^2 n_1/dE^2$, $n_1 \gamma_n$ as small quantities as well. The equation for the correction term in the stationary regime acquires then the following form:

$$\frac{d}{dE} \left[ (1 - 2n_0(E)) n_1(E) \Phi_1(E) \right] + \left[ dn(t, E)/dr \right]_{\text{ext}} - n_0(E) G(E) \gamma_n(E) = 0$$ \hspace{1cm} (24)

A solution which satisfies the condition $n_1(E) = 0$ at $E \gtrsim E_{\text{max}}$ can be written as

$$n_1(E) = [[1 - 2n_0(E)] \Phi_1(E)]^{-1}$$

$$\times \int_{E}^{E_{\text{max}}} \left[ \left[ \frac{dn(t, E')}{dr} \right]_{\text{ext}} - n_0(E') G(E') \gamma_n(E') \right] dE'$$ \hspace{1cm} (25)

In the limit of small values of energy near the bottom of the conduction band the dispersion law is a quadratic one, as a consequence the quantity $\Phi_1(E)$ appears to be proportional to $E$. The divergence of (25) at $E \to 0$ can be excluded using a condition:

$$\int_{E}^{E_{\text{max}}} \left[ \frac{dn(t, E')}{dr} \right]_{\text{ext}} dE = \int_{0}^{E_{\text{max}}} n_0(E) G(E) \gamma_n(E) dE$$ \hspace{1cm} (26)

In other words $n_1(E)$ has a finite limit at the bottom of the conduction band when the total amount of electrons generated per unit time by the external source compensates those that left a conduction band during the same time due to the inter-band recombination and trapping by the impurity levels. Equation (26) determines the integration constants $C$ and $A$ in the solutions (21) and (23) of $n_0(E)$. Applying equation (26) one can rewrite (25) as

$$n_1(E) = [[1 - 2n_0(E)] \Phi_1(E)]^{-1}$$

$$\times \int_{0}^{E_{\text{max}}} \left[ n_0(E') G(E') \gamma_n(E') \right] dE' - \left[ \frac{dn(t, E')}{dr} \right]_{\text{ext}} dE'$$ \hspace{1cm} (27)

As $n_0(E)$ is strongly localized in a small region in the vicinity of order $E \lesssim \epsilon_{\text{max}}$ at the bottom of the band, then one can neglect the value of $n_0(E) \ll 1$ beyond. In addition we have

$$\int_{0}^{E_{\text{max}}} n_0(E') G(E') \gamma_n(E') dE' \approx \int_{0}^{E_{\text{max}}} n_0(E') G(E') \gamma_n(E') dE'$$

$$= \int_{0}^{E_{\text{max}}} \left[ \frac{dn(t, E')}{dr} \right]_{\text{ext}} dE'$$ \hspace{1cm} (28)

The non-equilibrium distribution function in this high energy region can be expressed as

$$f_1(E) \approx G(E)/\Phi_1(E) \int_{E}^{E_{\text{max}}} \left[ \frac{dn(t, E')}{dr} \right]_{\text{ext}} dE'$$ \hspace{1cm} (29)

The expression (29) (named as the ‘quasi-equilibrium distribution function’) was formerly obtained in [12, 22, 23] in a different way, where the electron–hole recombination was not formally taken into consideration. One can see from (29) that the electron–hole recombination actually does not affect the shape of the high-energy ‘tail’ which is the most important term connecting the fast electron dynamics and the photo-catalytic properties of ZnO and TiO$_2$ [12, 22, 23].

The conclusion following from our current analyses is that the electron–phonon scattering remains to be the main factor
responsible for the rate of carrier relaxation near the edges of the band gap. This favourable condition, in combination with the ‘effective phonon’ model, to be discussed afterwards, helps us to demonstrate that near the band edges our distribution functions can be approximated by a quasi Fermi-like function.

6. The model of ‘effective phonon’

6.1. Definitions and justification

With the view of a qualitative analysis of the distribution function near the band edges we shall introduce the Einstein-like lattice vibrational model considering the electron scattering by a single ‘effective’ phonon with energy $\varepsilon_0$. In this model we assume that

$$\sum q U_{kq}^{\sigma} \delta (\varepsilon - \varepsilon_{q}) = P_0 \delta (\varepsilon - \varepsilon_0)$$

(30)

Then it follows from a definition (9) that

$$\Phi (\varepsilon, E) = P_0 \delta (\varepsilon - \varepsilon_0) G (E)$$

(31)

Definition (11) implies that

$$w (E) = G (E) P_0$$

(32)

According to (18) the average value of energy loss by an electron in the single electron–phonon scattering act becomes independent of the excess energy level $\varepsilon_{av} (E) = \varepsilon_0$. In our calculations [12, 22, 23] we have shown that for realistic band structures in ZnO and TiO2 this quantity $\varepsilon_{av} (E)$ manifests a weak dependence versus $E$, both for electrons and holes, see figure 1.

Similarly the quantity

$$P_{av} (E) = G^{-1} (E) w (E) = G^{-2} \Phi_0 (E)$$

(33)

displays a weak energy dependence in a wide range.

These observations justify an applicability of the model to the semi-quantitative analysis of carrier dynamics in a high-excitation regime. In the model, the energy loss velocity in a conduction band appears to be proportional to the electron density of states.

$$\frac{dE}{dt} = \varepsilon_0 P_0 G (E)$$

(34)

The downfall time from the level of excitation $E$ to the edge of the band (bottom of the conduction bands for electrons, top of the valence band for holes) is

$$\tau (E) = \varepsilon_0^{-1} P_0^{-1} \int_0^E G^{-1} (E') dE'$$

(35)

The validity of the ‘effective phonon’ approach is well confirmed by means of comparing this data with the results of the ‘exact’ calculations obtained with such an approximation avoided [23, 24].

We see in figure 2 that for both electrons and holes the correspondence between the results of these two approaches is almost perfect.

6.2. Non-equilibrium distribution in the effective phonon model

Solution (22) in the effective phonon model reads

$$R (E) = E / [\varepsilon_0 (N (\varepsilon_0) + 1/2)]$$

(36)

Introducing

$$T_{eff} = \varepsilon_0 (N (\varepsilon_0) + 1/2) / k_B; \quad \mu = -C k_B T_{eff}$$

(37)

where $k_B$ is the Boltzmann constant, we can write down the low-energy term in the shape of a Fermi distribution

$$n_0 (E) = \left( \exp \left( \frac{E - \mu}{k_B T_{eff}} \right) + 1 \right)^{-1}$$

(38)

The effective temperature for the excited electrons’ subsystem $T_{eff}$ and quasi-Fermi level $\mu = -C k_B T_{eff}$ are specified by the effective phonon energy as well as the distribution of phonons generated in the whole process which is also, generally speaking, a non-equilibrium one.

6.3. Strong degeneracy

If the strength of excitation and/or the rate of impact ionization is high enough, then the regime of a strong degeneracy could be implemented meaning that the occupation number at the band bottom is close to unity. The extreme case would be

$$n_0 (E) = \theta (E - \mu),$$

where $\theta (x)$ is the Heaviside step function.

Figure 1. Average loss of energy due to the emission of a phonon by carriers scattered from the excess energy level $E$ in ZnO wurtzite (a) and TiO2 anatase (b) [23].
function. As was noted above, the localization of the low-energy part of the distribution should be restricted by an energy range not exceeding the width of a phonon spectrum above the bottom of the carrier’s band. So we suppose the quasi-Fermi level as a value of order \( \varepsilon_0 \). Inside this energy interval there is a parabolic band dispersion, consequently a density of states has a square root shape \( G(E) = G_0 \sqrt{E} \), where \( G_0 \) is a factor expressed through the effective mass in the usual way \([25]\). One can simplify an analysis by neglecting the energy dependency of the \( \gamma_n \) recombination rate.

\[
\int_0^{E_{\text{max}}} n_0(E) G(E) \gamma_n(E) \, dE = G_0 \gamma_n \int_0^{\mu} \sqrt{E} \, dE = 2/3 G_0 \gamma_n \mu^{3/2} \tag{39}
\]

Taking into account \((26)\) we come to the expression for the quasi-Fermi level

\[
\mu = \left( \frac{3}{2} G_0 \gamma_n^{-1} \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE \right)^{2/3} \tag{40}
\]

At the excess energy \( E > \mu \) due to maximal degeneracy \( n_0(E) = 0 \) hence

\[
\int_0^{E_{\text{max}}} n_0(E') G(E') \gamma_n(E') \, dE' = \int_0^{E_{\text{max}}} n_0(E') G(E') \gamma_n(E') \, dE' = \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' \tag{41}
\]

and equation \((29)\) for the high-energy ‘tail’ \( f_1(E) \) becomes exact.

\[
f_1(E) = P_0^{-1} \varepsilon_0^{-1} G^{-1}(E) \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' \tag{42}
\]

When \( E < \mu \) the maximal degeneracy means \( n_0(E) = 1 \), then we have

\[
\int_0^{E} G(E') \gamma_n(E') \, dE' = 2/3 \gamma_n G_0 E^{3/2} \tag{43}
\]

The downfall times for electrons \((a)\) and holes \((b)\) in ZnO as calculated via the ‘exact’ method \([23, 24]\) and employing the ‘effective phonon’ approach.

\[
f_1(E) = P_0^{-1} \varepsilon_0^{-1} G^{-1}(E) \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' - 2/3 \gamma_n \varepsilon_0^{1/2} \tag{44}
\]

6.4. Weak degeneracy

The case of a weak degeneracy, \( n_0(E) \ll 1 \), seems to be the more realistic one. This occasion corresponds to the linearized equation \((5)\), its solution \((21)\) reduces to the quasi-Boltzmann one.

\[
n_0(E) = A \exp \left( -\frac{E}{\varepsilon_0 (N(\varepsilon_0) + 1/2)} \right) \tag{45}
\]

As is supposed in wide-band-gap semiconductors, we have \( E_{\text{max}} \gg \varepsilon_0 \), then one can replace \( E_{\text{max}} \) by infinity in the right hand side of \((26)\). Keeping in mind a parabolic dispersion at these energies we have

\[
A = 2 \gamma_0^{-1} G_0^{-1} \pi^{-1/2} (k_B T_{\text{eff}})^{-3/2} \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' \tag{46}
\]

When \( E \lesssim k_B T_{\text{eff}} \) we come to the following expression for the high-energy ‘tail’

\[
n_1(E) = (1 - 2 n_0(E))^{-1} P_0^{-1} \varepsilon_0^{-1} G^{-2}(E) \times \left\{ Z \left( \frac{E}{k_B T_{\text{eff}}} \right) \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' + \left( Z \left( \frac{E}{k_B T_{\text{eff}}} \right) - 1 \right) \int_0^{E_{\text{max}}} [dn(t, E')/dt]_{\text{ext}} \, dE' \right\} \tag{47}
\]

Here the function

\[
Z(x) = \text{erf}(\sqrt{x}) - 1/2 \pi^{-1/2} \sqrt{x} e^{-x} \tag{48}
\]

quickly tends to unit at large \( x \), that makes it possible to extend \((47)\) to the high energy region \( E \gtrsim k_B T_{\text{eff}} \) being in accordance with \((29)\).
7. High-energy ‘tail’ of distribution and relevant consequences

The quasi-Fermi shaped phenomenological distributions of form (38) with an effective boundary level (‘chemical potential’) \( \mu \) is often used in the analysis of carrier dynamics in highly excited semiconductors, for instance Si and Ge [1], GaAs [17, 18, 21]. As it concerns an additional high energy component \( f_1(E) \), then to our knowledge it has never been discussed before. Perhaps its influence in the above mentioned materials is less meaningful because in the presence of a low impact ionization threshold, the energy range where \( f_1(E) \) has substantial values is also rather narrow. The situation is different in wide gap semiconductors like ZnO and TiO\(_2\). As was shown for the first time in [12, 22, 23], the ‘tail’ \( f_1(E) \) in these materials spreads over the high-energy region until the values of excess energy are comparable with the magnitude of the forbidden gap. As we see from figure 3 for electrons in ZnO and holes in TiO\(_2\) these ‘tails’ extend from the level of chemical potential \( \mu \) of order 0.1 eV up to the energy 1 eV.

One may expect a nontrivial contribution of non-equilibrium states from tail \( f_1(E) \) into a high-energy conductivity as well as the diffusion coefficients. The consequences would be discussed elsewhere. It was shown that this expansion of the carriers’ non-equilibrium distribution into the depth of conduction and valence bands appears to be a crucially important property from the point of view of the photocatalytic properties of ZnO and TiO\(_2\) compounds [12, 22, 23].

8. Conclusions

We have proposed a quasi-classical theory of energy relaxation in semiconductors and insulators under the condition of a high level of excitation which is based on the kinetic equation of the Boltzmann type. It was shown that in wide-gap materials, the main role in the formation of non-equilibrium distribution belongs to the inelastic scattering processes of electrons by short wave phonons. The non-equilibrium distribution can be separated into two parts: the low-energy part strongly localized near the band edges for electrons and holes and the high-energy term. The low-energy term is localized in the energy region of the order of the phonon spectrum width and its functional dependence has a shape of Fermi distribution with a certain effective temperature which in turn is dependent on the non-equilibrium distribution of phonons generated in the process of electron–phonon relaxation. The value of quasi-Fermi momentum is defined by the rate of the carriers’ generation by an external source. It also depends on the integral characteristics of electron–phonon scattering as well as the inter-band carriers’ recombination. The high-energy ‘tail’ has notably smaller values but extends into a considerably larger energy region in the conduction band for electrons and correspondingly into a valence band for holes. We find, however, that the shape of this tail does not depend on the electron–hole recombination rate. The penetration depth of the tail is defined both by the rates of the carriers’ generation as well as by the integral characteristics of electron-short-wave-phonon interactions. It can achieve values of excess energy apart from the forbidden gap edges comparable to a magnitude of the gap \( E_g \).

In analysis of the dynamics of highly excited electrons and holes in wide gap materials, it is necessary to take into account the existence of high-energy ‘tails’ in their distribution, because in these compounds the range of energy is comparable with the width of the valence band and captures a considerable part of the conduction band. That is why this high energy correction should give the essential contribution to characteristics of the energy and charge transport in the regime of strong external influence.

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