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Two carrier temperatures non-equilibrium generalized Planck law for semiconductors

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ABSTRACT

Planck's law of radiation describes the light emitted by a blackbody. This law has been generalized in the past for the case of a non-blackbody material having a quasi Fermi-level splitting: the lattice of the material and the carriers are then considered in an isothermal regime. Hot carrier spectroscopy deals with carriers out of the isothermal regime, as their respective temperatures ($T_H^e \neq T_H^h$) are considered to be different than that of the lattice (T_L). Here we show that Fermi–Dirac distribution temperature for each type of carrier still determine an effective radiation temperature: an explicit relationship is given involving the effective masses. Moreover, we show how to determine, in principle with an additional approximation, the carrier temperatures (T_H^e, T_H^h) and the corresponding absolute electrochemical potentials from photoluminescence measurements.

1. Introduction

The spectral distribution of light emitted by any piece of matter brings a wealth of information. At thermal equilibrium, it is described by Planck's radiation law [1] and it informs on the absorptivity (hence the electronic structure of the material) and temperature. This law has been generalized by Lasher and Stern [2], De Vos and Pauwels [3] and Würfel [4] for materials in quasi-equilibrium. This so called "generalized Planck's law" describes the emitted photon flux from electron and hole populations, where carriers can still be described by a Fermi Dirac distribution (i.e. temperature and chemical potentials can be defined) and which are at the same temperature. This equation has been applied with success to determine absorption [5–7], quasi-Fermi level splitting [8,9] or temperature [10–12] with direct applications in photovoltaic research [13–15].

This law is currently being used to measure the quasi-Fermi level separation in excited semiconductors and has therefore a considerable potential to be used in, e.g., investigations on photovoltaic effect by luminescence analysis [9,16–18]. Photoluminescence experiments are often carried out under high excitation, conditions where thermal equilibrium of carriers with the lattice is not always valid, and, because they relax at different rates, the thermal equilibrium between the electrons subsystem and the holes subsystem is not always valid either. Such situations are commonly encountered in recent scientific studies (transistors, diodes, hot carrier solar cells, etc.) [19–23] including hot topics such as carrier relaxation in 2D materials such as graphene [24–27] and dichaocogenides [28].

In order to investigate the properties of hot carriers in a wide range of different semiconducting devices, luminescence analysis has been widely used to estimate the energy distribution of the carrier population [10,12,29–35].

In luminescence experiments, a light beam generates electron–hole pairs in the material and the light emitted by the sample by carrier recombination is recorded as a photoluminescence spectrum. Assuming a constant temperature and electrochemical potential in the probed region of the sample, this photoluminescence spectrum obeys the generalized Planck's law [2,4]:

$$I_{PL}(\hbar\omega) = A(\hbar\omega)\frac{\Omega n_{op}^2(\hbar\omega)^2}{4\pi^2\hbar^3 c_0^2}\left[\exp\left(\frac{\hbar\omega - \Delta\mu}{k_B T}\right) - 1\right]^{-1} \tag{1}$$

where $\hbar\omega$ is the energy of the emitted photon, $A(\hbar\omega)$ the energy and excitation [13] dependant absorption of the semiconductor, Ω the solid angle for emission, n_{op} the optical index of the semiconductor, c_0 the velocity of the light in vacuum, k_B the Boltzmann

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constant, T the temperature of the semiconductor and $\Delta\mu$ the quasi-Fermi level splitting written as an electrochemical potential difference.

From the photoluminescence spectrum, a spectral shift indicates a change in the lattice temperature, the intensity is related to the quasi-Fermi level splitting and the slope at energies close but higher than that of the peak shows the emission temperature variation. Indeed, Planck indicates [1] that the temperature included in his radiation law is an emission temperature, defined as that of a body in equilibrium with the radiation.

The temperature of the carrier is a true challenge for the community, theoretically and experimentally. While some consider that a same temperature describes the electrons and the holes that are in thermal equilibrium [21,36–39], others think that the holes, having a higher effective mass, are always close to the lattice temperature [40] and that only electrons are hot, or that the majority carriers are fully thermalized whereas only the minority ones are hot [21]. Apart from the value of these temperatures, it remains a hard task to know the meaning of the temperature in the generalized Planck's law in non-equilibrium conditions, and especially to determine which carrier is mostly affected by hot carrier effects.

Here we propose a more complete analysis, where the radiation law is written with electron and hole populations which are not at the same temperature.

Indeed we show the expression of the generalized Planck's law for different electron and hole temperatures. This law enables us to verify the different assumptions made about the nature of the individual hot carrier population and offers new perspectives in advanced optical characterization of materials. The effective mass ratio appears to be the critical parameter that relates the radiation temperature to the two carrier temperatures. The usefulness of the developed expression is discussed for the case of hot carrier solar cells since the knowledge of the two carrier temperatures is a key point towards the development of energy selective contacts.

2. Theory

2.1. General expression

The transition from Planck's law to its generalized expression has been done by Lasher and Stern [2] and later by de Vos and Pauwels [3] and Würfel [4]: their method roots on the balance between the absorption, spontaneous and stimulated emission of the semiconductor. These general expressions depend only on the transition matrix element and on the Fermi–Dirac distribution of carriers. In the presence of hot carriers, as the lattice remains constant and close to ambient temperature, the transition matrix elements are the same as in the absence of hot carriers, as the density of states is the same. Using very general expressions of Fermi–Dirac distributions, namely f_V^e, f_C^e as the distributions of the electrons in the valence and in the conduction band respectively, Würfel [41] gives the expression of the photoluminescence intensity:

$$I_{PL}(\hbar\omega) = A(\hbar\omega)\frac{\Omega n_{op}^2(\hbar\omega)^2}{4\pi^3\hbar^3c_0^2}\frac{[1 - f_V^e(E^h)]f_C^e(E^e)}{f_V^e(E^h) - f_C^e(E^e)},$$

where the general distributions for electron and for holes are respectively:

$$f_V^e(E^h) = \left[1 + \exp\left(\frac{E^h - E_{F_p,H}}{k_BT_H^h}\right)\right]^{-1} f_C^e(E^e) = \left[1 + \exp\left(\frac{E^e - E_{F_n,H}}{k_BT_H^e}\right)\right]^{-1}$$

where $E^{e,h}$ is the energy of the electron (hole), $\mu^{e,h}$ the electrochemical potential and $T^{e,h}$ the temperature.

Using these distributions leads to the general expression of Planck's law with two temperatures:

$$I_{PL}(\hbar\omega) = A(\hbar\omega)\frac{\Omega n^2(\hbar\omega)^2}{4n^2\hbar^3c^2} \times \left[\exp\left(\frac{E^e(\hbar\omega) - E_{F_n,H}}{k_BT_H^e} - \frac{E^h(\hbar\omega) - E_{F_p,H}}{k_BT_H^h}\right) - 1\right]^{-1} \tag{2}$$

where $A(\hbar\omega)$ is considered to be the same spectral absorptivity than that appearing in Planck's law, as can be inferred by setting $T_H^e = T_H^h = T$, $E_{Fn} = E_{Fp}$ and $E^e - E^h = \hbar\omega$.

If $T_H^e = T_H^h = T$ and $E^e - E^h = \hbar\omega$, expression (1) is recovered. In expression (2) because of the different temperatures, the energy of the electron E^e and hole E^h have to be expressed explicitly.

Rather than using quasi-Fermi levels, the energies of the carriers will be expressed relatively to their electrochemical potential μ_H^e, μ_H^h [41]. In order to express the energies of the electron E^e and hole E^h, a known energy reference has to be determined. This reference is classically the vacuum energy; for the semiconducting materials considered here, the middle of the energy gap seems to be much more appropriate. The different energies are shown relative to this reference in Fig. 1.

Since an energy reference has been defined, it is possible to determine the energy of the electrons and holes for different material structures, and therefore write a generalized Planck's law for non-equilibrium carrier for semiconductor in permanent regime [42].

In this work, we suppose that the bands are isotropic and parabolic and the energy reference is taken at the mid-gap around Γ in the Brillouin zone. So the energy of the conduction and valence band edges are $E_c = E_G/2$ and $E_v = -E_G/2$ respectively.

2.2. Generalized Planck's law expressions

The dispersion relation of a bulk semiconductor gives the energy of the electron in the conduction band E^e and that of the hole in the valence band E^h, with m^e, m^h the effective mass of the electron in the conduction band and of the hole in the valence band respectively, $\mathbf{k}$ the wavevector for the considered radiative transition:

$$E^e = \frac{E_G}{2} + \frac{\hbar^2\mathbf{k}^2}{2m^e} E^h = -\frac{E_G}{2} - \frac{\hbar^2\mathbf{k}^2}{2m^h}$$

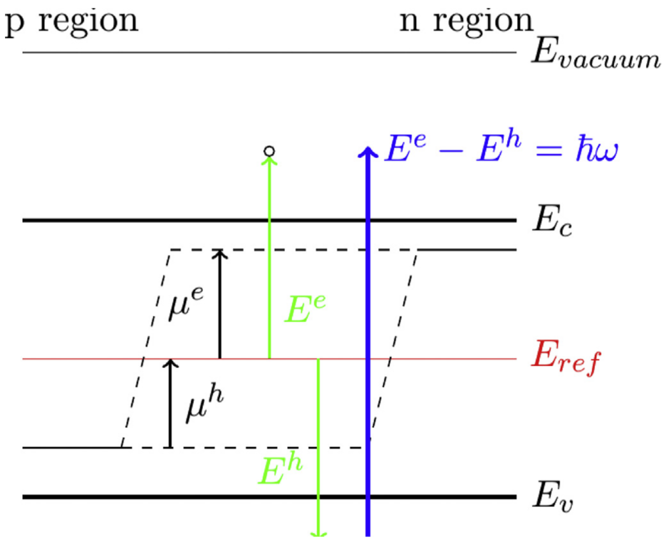

Fig. 1. Energy reference used in this work.