Original Papers

Centre National d'Etudes des Télécommunications, Issy-les-Moulineaux, Seine

Laser Conditions in Semiconductors

By

MAURICE G. A. BERNARD and GEORGES DURAFFOURG

On considère la possibilité d'obtenir dans les semiconducteurs des émissions stimulées par des transitions entre bande de conduction et bande de valence, ou entre une des bandes et un niveau d'impureté de la bande interdite. Si on caractérise l'état d'occupation des bandes et des niveaux par des pseudo-niveaux de Fermi, la condition nécessaire pour qu'il y ait émission stimulée est $\Delta F > h\nu$ oú ΔF est la différence entre les pseudo-niveaux de Fermi de l'état initial et de l'état final de la transition, et ν la fréquence émise. L'existence des pseudo-niveaux de Fermi est discutée et on montre que la relation obtenue est équivalente à l'expression du deuxième principe de la Thermodynamique. On en déduit que les transitions bande à bande directe dans InAs et InSb et les transitions entre bande de conduction et niveaux accepteurs de Zn et de In respectivement dans Ge et dans Si sont assez intéressantes pour justifier une étude expérimentale.

The possibility of obtaining stimulated emissions in semiconductors has been considered for transitions between the conduction band and the valence band, or between one band and an impurity level. If the occupation of the bands and of the impurity levels is taken into account by quasi-Fermi levels, the necessary condition for stimulated emission to be possible turns out to be simply: $\Delta F > h\nu$ where ΔF is the difference of the quasi-Fermi levels of the initial and final state, and ν is the emitted frequency. The existence of such quasi-Fermi levels is discussed, and it is shown that the above condition is due to the second law of thermodynamics. Direct interband transitions in InAs or InSb, and transitions between the conduction band and Zn and In acceptor levels, respectively, in Ge and Si are thought to be sufficiently attractive to be studied experimentally.

Many papers[1]) have been recently published on lasers but, most of them consider only stimulated emission between localized levels. Thus it is well known that the necessary condition to obtain amplification of electromagnetic waves by stimulation of emitted radiation is the so called "population inversion" between the two localized levels of the transition. However in 1958, P. AIGRAIN[2]) has shown that this condition was not necessary in the case of the emission of two bosons, one being stimulated, the other thermalized.

Actually, in the one-particle approximation an electronic state in a solid may be represented by a Bloch wave defined over the whole crystal; let us assume two such states: one with a wave vector k_i and energy $E_v(k_i)$, the other with a wave vector k_j and energy $E_c(k_j)$. Let us suppose that the first of these states belong to a group of states (v) and the second to a group of states (c); we shall first suppose that these two groups are respectively the valence band and the conduction band of a semiconductor.

---

[1]) For a recent bibliography on lasers see, for instance, review articles by A. AUTHIER (to be published in NUCLEUS) and by N. G. BASOV, O. N. KROKHIN and YU. M. POPOV [1].

[2]) P. AIGRAIN, unpublished lecture at the "International Conference on Solid State Physics in Electronics and Telecommunications", Bruxelles 1958. The same idea has been suggested recently and independently by N. G. BASOV, O. N. KROKHIN and YU. M. POPOV, Second International Conference on Quantum Electronics.

Under equilibrium conditions the occupation probability of any state of energy $E(k)$ is given by the Fermi-Dirac function

$$f = \frac{1}{1 + \exp\left[E(k) - F_0\right]/k_0 T}$$

where k_0 is the Boltzmann constant and F_0 the Fermi level or chemical potential for electrons. If the crystal is no longer in equilibrium, W. SHOCKLEY [2] has shown that, under certain conditions, which we shall discuss later, the occupation probability of any state of the conduction band is given by

$$f_c = \frac{1}{1 + \exp\left[E(k) - F_c\right]/k_0 T}$$

where F_c is the "quasi Fermi level" for the electrons of the conduction band; in the same way we can define a "quasi Fermi level" F_v for the holes of the valence band; at equilibrium $F_c = F_v = F_0$.

A state $E_v(k_i)$ of the valence band is in general connected to a state $E_c(k_j)$ of the conduction band by a direct radiative transition; let W_v^c be the probability per unit time of such a process; in a radiation field containing a density $P(\nu)$ of photons of energy $h\nu$, the number N_a of quanta absorbed per unit time is

$$N_a = A \, W_v^c \, f_v(k_i) \, [1 - f_c(k_j)] \, P(\nu) \tag{1}$$

The number N_e of quanta emitted per unit time by stimulated emission is

$$N_e = A \, W_c^v \, [1 - f_v(k_i)] \, f_c(k_j) \, P(\nu) \tag{2}$$

where the proportionnality coefficient A includes the densities of states of the valence band and of the conduction band; taking into account $W_v^c = W_c^v$, the necessary condition for amplification to be possible, $N_e > N_a$, can be written

$$f_c(k_j) \, [1 - f_v(k_i)] > f_v(k_i) \, [1 - f_c(k_j)]$$

that is to say

$$\exp\left(F_c - F_v\right)/k_0 T > \exp\left[E_c(k_j) - E_v(k_i)\right]/k_0 T \tag{3}$$

and as

$$E_c(k_j) - E_v(k_i) = h\nu$$

the above conditions simply reduces to

$$F_c - F_v > h\nu . \tag{4}$$

This condition can be generalized in different ways. First, let us consider an indirect transition in which one or several phonons are emitted or absorbed; the expressions (1) and (2) should be modified; by a straightforward calculation it is shown that, if the phonons are thermalized, the inequality (3) is replaced by

$$\exp\left(F_c - F_v\right)/k_0 T > \exp\left[E_c(k_j) - E_v(k_i) - \sum_q \varepsilon_q \hbar \omega_q\right]/k_0 T \tag{5}$$

where $\hbar \omega_q$ is the energy of the qth phonon involved and where $\varepsilon_q = \pm 1$ (+ 1 if the phonon is emitted during the stimulated process and —1 if the phonon is absorbed); but the frequency of the radiation we want to stimulate is given by

$$h\nu = E_c(k_j) - E_v(k_i) - \sum \varepsilon_q \hbar \omega_q$$

and again the laser condition is given by relation (4).

Secondly, let us consider a radiative transition, direct or indirect, between one of the bands, say, for instance, the conduction band, and a given impurity level

of the forbidden energy gap. The statistics of occupation of defect centers of different charge conditions and various degeneracies [3] and the statistics of recombination on such centers [4, 5] have been treated by different authors; an equivalent treatment has been made by one of us [5] using the concept of a "quasi Fermi level" associated with each impurity level; let N_s be the number of centers in charge condition s, N_{s+1} the number of centers in charge condition $s + 1$; the energy $E_{s+1/2}$ of the level $(s, s + 1)$ is defined by [4, 5]

$$E_{s+1/2} = k_0 \, T \log Z_s/Z_{s+1}$$

where Z_s and Z_{s+1} are two partition functions.

At thermal equilibrium we have

$$N_{s+1}/N_s = \exp \, (F_0 - E_{s+1/2})/k_0 \, T \tag{6}$$

where F_0 is the Fermi level. Under non-equilibrium conditions the ratio N_{s+1}/N_s is no longer equal to that given by equation (6); under certain conditions which we shall discuss later, we may define a "quasi-Fermi level" $F_{s+1/2}$ for the level $(s, s + 1)$ by the relation

$$N_{s+1}/N_s = \exp \, (F_{s+1/2} - E_{s+1/2})/k_0 T \, .$$

Now a simple calculation show that the laser condition for the transition between a state of the conduction band $E_c(k_j)$ and a state of the defect level $(s, s + 1)$ is

$$F_c - F_{s+1/2} > h \, \nu \tag{7}$$

which is again equivalent to relation (4).

Thus, under the assumption that, for different groups of electronic states in a semiconductor (conduction band, valence band, impurity levels) we may define a "quasi Fermi-level" associated with each group, the necessary condition for electromagnetic waves to be amplified by stimulation of emitted radiation is given by the simple formula (4). The concept of a "quasi Fermi level" for a group of states is valid if the electrons of the group exchange energy with a heat reservoir, or thermostat, in a time short compared to the time necessary for the population to come back to equilibrium by transitions between states of the different groups; this is apparently the case in most semiconductors. In other words, we may look at any semiconductor laser as a collection of a very large number of three-level masers (or even more than three) having nearly the same signal frequency but a wide spectrum of "idler frequencies"; to admit the existence of a "quasi Fermi level" is equivalent to express that the corresponding "idler frequencies" are strongly coupled to a thermostat. If the pump transitions are provided, through a filter, by a good contact of the semiconductor with the radiation of a black body at a temperature T_p, a simple calculation [6], based upon a detailed balance argument applied to the continuous pumping action, shows that

$$F_c - F_v = h \, \nu_p \left(1 - \frac{T}{T_p} \right) = h \, \nu_p \, \eta_c$$

where $\eta_c = 1 - (T/T_p)$ is the Carnot efficiency of a heat engine working between temperatures T and T_p; but the efficiency of the laser is $\eta = h \, \nu/h \, \nu_p = \nu/\nu_p$ and the laser condition (4) can now be rewritten

$$\eta < \eta_c$$

which shows that the efficiency of a heat engine giving coherent light must be less than the Carnot efficiency.

The interest of such an approach is emphasized by the following remarks:

i) The actual operation of a semiconductor laser needs not only the necessary condition (4) to be fulfilled but also requires the net emission to be greater than the losses: diffraction, reflexion, free carrier absorption etc. . . But this sufficient condition should be calculated in each particular case; thus relation (4) is a useful step in predicting what are the most favourable cases to be more carefully studied.

ii) For a direct transition, $h\nu = E_G$ (where E_G is the width of the energy gap) and condition (4) requires that the number of carriers injected be so large that both the electron and hole populations are degenerate or nearly degenerate; low effective mass materials at low temperature should be favourable; as an example it is proposed to use, say, an n type InSb or InAs crystal at liquid Helium temperature with a pump transition ν_p between the top of the valence band and the Fermi surface in the conduction band and a stimulated emission ν_s between the bottom of the conduction band and the top of the valence band[3] (Fig. 1).

iii) For an indirect transition $h\nu$ is less than the energy gap

$$h\nu = E_G - h\omega$$

where $h\omega$ is the energy of an emitted phonon; this must reduce greatly the pump power necessary for laser effect; we find a result which had been anticipated by AIGRAIN who was the first, to propose in 1958 the indirect recombination radiation in Germanium to obtain an emission of coherent light[2].

iv) For an impurity transition, again, $h\nu$ is less than E_G; let us consider, for instance, the radiative transition on the second acceptor level of Zn in Germanium (Fig. 2): the capture of an electron of the conduction band by a Zn⁻ ion is anti-
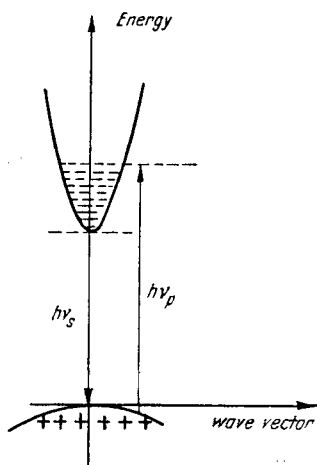

Fig. 1. Pump and signal transitions in the band structure of InSb or InAs (degeneracies in the band structure have been omitted for simplicity)
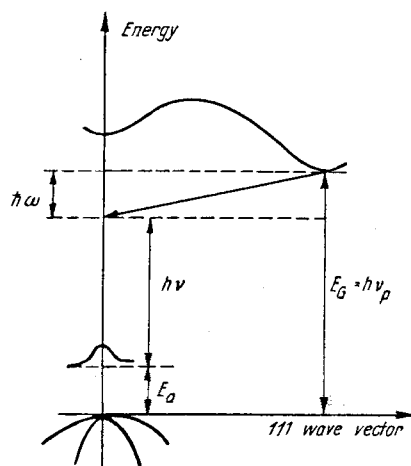
Fig. 2. Band structure of Ge with the different involved transitions. The Fourier transform of the wave function of the 2nd acceptor level of zinc is estimated to be important only in the vicinity of k (000); the first acceptor zinc level, which should also offer interesting possibilities has been omitted for clarity

[3]) The same proposal has also been made independently by C. BENOÎT à LA GUILLAUME and C. TRIC.

cipated to be a slow radiative process while the capture of a hole by a Zn^{--} ion should be very fast; thus the quasi Fermi level for electrons F_c will rise up with injection while the "quasi Fermi level" $F_{3/2}$ for the Zn level will be close to the "quasi Fermi level" for holes F_v and thus close to the valence band. On the other hand the energy of the emitted photon $h\,\nu$ is much less than the energy gap and given by

$$h\,\nu = E_G - E_a - \hbar\,\omega$$

where E_a is the ionisation energy of the 2nd acceptor level of Zn ($E_a = 0,09$ eV) and $\hbar\,\omega$ is the energy of a phonon emitted by the radiative transition which should be indirect.

Another interesting case is that of Indium in Silicon; according to recent data [7] the capture of an electron on a neutral Indium atom is a slow radiative process while the capture of a hole on a negatively charged Indium atom is faster by six orders of magnitude.

A detailed paper on the subject will be soon published; experiments on InSb, InAs, Zn in Ge and In in Si are under progress.

References

[1] N. G. BASOV, O. N. KROKHIN and YU. M. POPOV, Soviet Physics Uspekhi 3, 702 (1961).

[2] W. SHOCKLEY, B. S. T. J. 28, 435 (1949).

[3] P. T. LANDSBERG, Proc. Phys. Soc. B 69, 661 (1956).
C. H. CHAMPNESS, Proc. Phys. Soc. B 69, 1335 (1957).
W. SHOCKLEY and J. T. LAST, Phys. Rev. 107, 392 (1957).

[4] R. N. HALL, Phys. Rev. 83, 228 (1951) and 87, 387 (1952).
W. SHOCKLEY and W. J. READ, Phys. Rev. 87, 835 (1952).
P. T. LANDSBERG, Proc. Phys. Soc. B 70, 282 (1957).
M. BERNARD, J. of Electronics and Contr. 4, 15 (1958).
C. T. SAH and W. SHOCKLEY, Phys. Rev. 109, 1103 (1958).

[5] M. BERNARD, Défauts dans les semiconducteurs, Cours du 3e cycle de Physique des Solides, Faculté des Sciences d'Orsay.

[6] H. E. D. SCOVIL and E. O. SCHULZ-DUBOIS, Phys. Rev. Letters 2, 262 (1959).

[7] Y. E. POKROVSKY and K. J. SVISTUNOVA, International Conference on Photoconductivity, Ithaca, USA., Août 1961.