# THERMODYNAMICAL APPROACH TO THE HIGHLY EXCITED STATES OF SEMICONDUCTORS

Tomitaro Nagashima, Takeshi Watanabe
and Chuji Horie
Department of Applied Physics
Tohoku University,
Sendai, Japan

## ABSTRACT

In order to understand a general trend of the photoconductivity in a highly excited state of semiconductors, the determination of carrier density against the total excitation has been carried out in a relatively low density region where electrons, holes and excitons coexist. The assumption of chemical equilibrium among electrons, holes and excitons enables one to determine the density of charge carriers. The variation of binding energy of an exciton with the excitation density is taken into account. Carrier density appears to increase abruptly at a certain critical region of total excitation density.

## I. INTRODUCTION

It has been observed that when the density of electron-hole pairs in germanium is increased by illumination of an intense laser light, the photoconductivity shows an abrupt increase at some pair density.[1-2] This phenomenon has been analysed in association with the presence of EHD.[3-4] In the case of tellurium an anomaly in the photoconductivity has also been observed, but has been interpreted as being due to the change in the degree of degeneracy of carriers.[5-6]

In the relatively low excitation densities of about $10^{15}$ $cm^{-3}$ or below in both Ge and Te, there is no quantitative analysis of the photoconductivity, where the presence of bound excitons is taken into account. In order to understand the general trend of photoconductivity at low and intermediate densities of excitation (which will be called the L- and I-region, respectively), we present a thermodynamical investigation of determining the densities of electrons, holes and excitons as functions of a given excitation density. We assume that the system is in

chemical equilibrium. It is shown that the presence of excitons gives rise to significant effects on the screening of the Coulomb force between carriers in the L-region, through the change in the relative densities of carriers and excitons. In the I-region it turns out that the total excitation contributes to the screening. As a result the increase of excitation density proves to increase the carrier density abruptly at a critical density between the L- and I-regions.

In Sec. II we treat the L-region, where particles are considered to be non-degenerate. Whereas the exciton binding energy depends on the carrier density through the screening parameter of a Debye-Hückel type, the chemical equilibrium condition among particles gives the carrier density as a function of the excitation density for a given exciton binding energy. A self-consistent calculation is carried out of the carrier density against the total excitation density.

When the total excitation density is increased, the system is expected to reach the I-region where carriers can be considered degenerate. This region is treated in Sec. III. A model Hamiltonian for the system is constructed by means of the transformation employed by Girardeau.[7] Then, the exciton contribution to the screening and to the self-energy of particles is taken into account diagrammatically besides the usual RPA for the electron and/or hole correlations to obtain the chemical potentials of electrons, holes and excitons. The chemical equilibrium condition among particles is solved numerically for a given temperature and a total excitation density.

Discussion will be made in Sec. IV in connection with an EHD and the exciton condensation.

## II. LOW EXCITATION DENSITY REGION (L-REGION)

It is assumed that there exists a chemical equilibrium among electrons, holes and excitons. Then, the chemical potentials of electrons, holes and excitons, which are denoted by $\mu_e$, $\mu_h$ and $\mu_{ex}$, respectively,

satisfy the relation

$$\mu_e + \mu_h = \mu_{ex}. \tag{1}$$

Denoting the number densities of electrons, holes and excitons by $n_e$, $n_h$ and $n_{ex}$, respectively, and assuming that $n_e$ is equal to $n_h$, the total excitation density n is given by

$$n = n_e + n_{ex}. \tag{2}$$

In the L-region we can assume the Boltzmann distribution for each kind of particle. Combining eqs. (1) and (2), we obtain an equation relating $n_e (= n_h)$ with n for a given temperature and a given exciton binding energy. On the other hand, the exciton binding energy B depends on $n_e$ through the screening parameter $\varkappa$. For the B-$\varkappa$ relation, we use the result of a variational calculation by taking the hydrogen-like trial wave function. The screening parameter is given by

$$\varkappa = \left( \frac{8\pi n_e e^2}{\varepsilon_o kT} \right)^{1/2} \tag{3}$$

where $\varepsilon_o$ is the lattice dielectric constant.

A self-consistent calculation is carried out of the carrier density and the exciton binding energy, by assuming for simplicity that an electron and a hole have an equal effective mass m.

Since we neglect the exciton contribution to the screening as compared to that of electrons and holes, we are confined to the region where the following two inequalities are satisfied:

$$\frac{n_e}{n_{ex}} > 3\left(\frac{kT}{B}\right)^2 , \tag{4}$$

$$B(n_e, T) > kT. \tag{5}$$

These inequalities follow from a simple argument using a generalized dielectric constant and the f-sum rule. Since the left-hand side of the inequality (4) decreases faster than the right-hand side as the temperature decreases, this inequality puts a lower limit on temperature.

On the other hand, the inequality (5) puts a lower limit on the magnitude of $B(n_e, T)$ at given temperatures.

The $n_e$ *vs.* n curves obtained are shown in Fig. 1 together with the

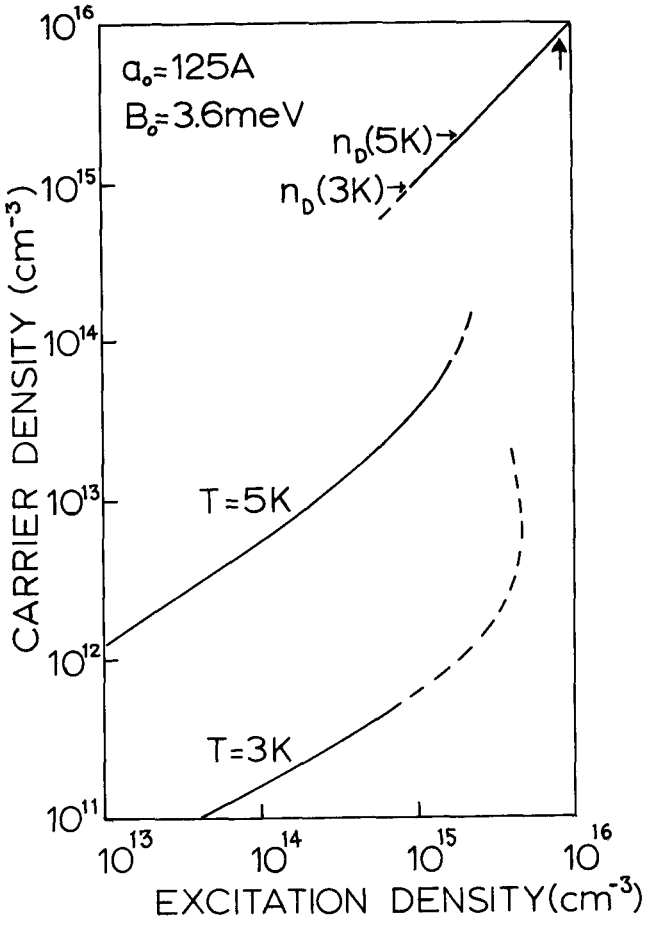


Fig.1. Plot of carrier density $n_e$ against total excitation density n. The lower curves (upper curve) correspond to the lower (intermediate) excitation density region. Parameters denoted by $B_o$ and $a_o$ are, respectively, the exciton binding energy and radius in the absence of screening effect. The arrow in the upper-right corner indicates the point where the exciton binding energy vanishes. For the density of carrier $n_e > n_D$, the carriers can be considered degenerate.

results for the I-region. The parameters chosen are shown in the figure. If we were to extend the lower temperature curve to the region where the above criteria are not satisfied, we would observe an S-shape behavior (dotted portion) which suggests an instability.

## III. INTERMEDIATE EXCITATION DENSITY REGION (I-REGION)

When the excitation density is increased, the system is expected to reach the I-region where the carriers are degenerate and excitons are non-degenerate. This is due to an enormous reduction of the exciton binding energy caused by the increase of screening effect.[8]

The model Hamiltonian for the system is constructed by means of the transformation which replaces the exciton operators by boson operators,[7] and is written as follows:

$$H = H_o + H_c + H_{int}, \tag{6}$$

$$H_o = \sum_k \varepsilon_e(k) c_k^+ c_k + \sum_k \varepsilon_h(k) d_{-k}^+ d_{-k} + \sum E_{ex}(k) a_k^+ a_k , \tag{7}$$

$$H_c = \frac{1}{2} \sum_q v(q)\rho(q)\rho(-q), \tag{8}$$

$$H_{int} = \sum_q \sum_k \{ g(q, k) c_{k+q}^+ d_{-k}^+ a_q + \text{h.c.} \} ,$$

$$g = \tilde{E}_{ex}(q) f(q, k), \quad \tilde{E}_{ex}(q) = E_{ex}(q) - E_G \tag{9}$$

where $c_k$, $d_{-k}$ and $a_k$ are the annihilation operators of electrons, holes and excitons, respectively. $H_c$ represents the Coulomb interaction between carriers, and $H_{int}$ represents the carrier-exciton interaction. $E_G$ represents the energy gap between the conduction and valence bands. $\tilde{E}_{ex}(q)$ is the exciton energy relative to the bottom of the conduction band and $f(q, k)$ is the exciton wave function. Here we have assumed for simplicity that the exciton lies in the lowest levels. In the derivation of the Hamiltonian, we have retained terms up to the order

of $(n_{ex}/n)$.

In order to consider the effect of carrier-exciton interactions, we perform a perturbational calculation by means of the Green's function method. As for the contribution to the screening of the Coulomb potential, we calculate the polarization diagrams represented by (a) and (b) of Fig. 2 in the static and low temperature limit. As for the

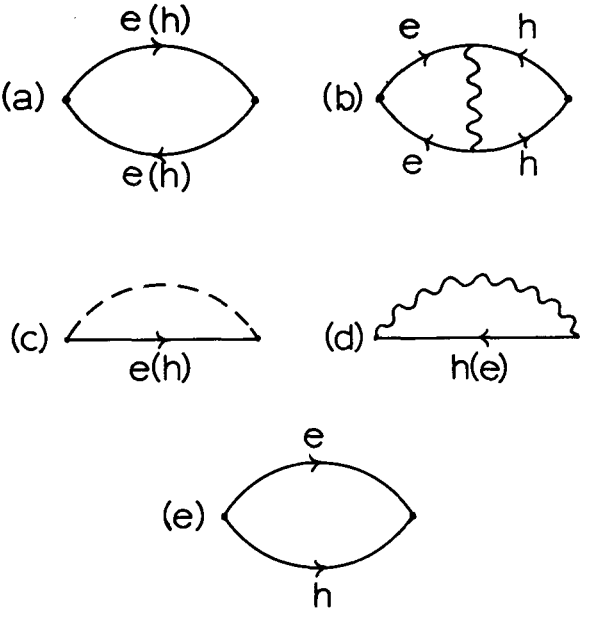


Fig.2. (a) and (b) are polarization diagrams where wavy line represents the exciton propagator. (c) and (d) represent the electron (or hole) self-energies $\Sigma^{c}_{e(h)}$ and $\Sigma^{ex}_{e(h)}$, respectively. Dashed line represents the screened Coulomb interaction. (e) is the self-energy for excitons.

self-energy $\Sigma_e$ ($\Sigma_h$) of an electron (a hole) we take diagrams represented by (c) and (d) of Fig. 2. For the self-energy $\Pi$ of an exciton we evaluate the diagram (e) in Fig. 2.

In terms of the self-energies the chemical potentials of the

respective components are defined by

$$\mu_e = \frac{p_o^2}{2m_e} + \mathrm{Re}\,\Sigma_e\,(p_o,\ 0) + E_G,$$

$$\mu_h = \frac{p_o^2}{2m_h} + \mathrm{Re}\Sigma_h(p_o,\ 0),$$

$$\mu_{ex} = \mu_{ex}^{(o)} + \mathrm{Re}\,\Pi(0,\ 0) - B + E_G,$$

$$\mu_{ex}^{(o)} = kT\ell n\,(n_{ex}\lambda_{ex}^3),$$

where $p_o = (3\pi^2 n_e)^{1/3}$, and $\lambda_{ex}$ is the thermal de Broglie wavelength of an exciton.

The exciton binding energy B is calculated by the method mentioned in Sec. II. As for $\varkappa$, we use the Thomas-Fermi screening parameter reduced by a factor $\delta\,(<1)$. The factor $\delta$ accounts for the fact that the carriers are not fully degenerate in the I-region.

The chemical equilibrium condition is solved numerically to give $n_e$ for a given temperature and for a total excitation density. We have again assumed that $m_e = m_h$. The result is plotted in Fig. 1. It should be noted that in the I-region the exciton concentration $n_{ex}$ is found to be extremely small so that $n_e$ is almost equal to n. It appears from the figure that the carrier density increases abruptly at a critical density between the L- and I-regions.

## IV. DISCUSSION AND CONCLUSION

The calculation is carried out of the chemical potential $\mu$ of electron-hole pairs which are in chemical equilibrium with excitons. The result is shown in Fig. 3. The arrow in the figure indicates the excitation density at which the exciton binding energy vanishes. Because of a large negative value of the self-energy the chemical potential is greatly reduced in the I-region. On the other hand, in

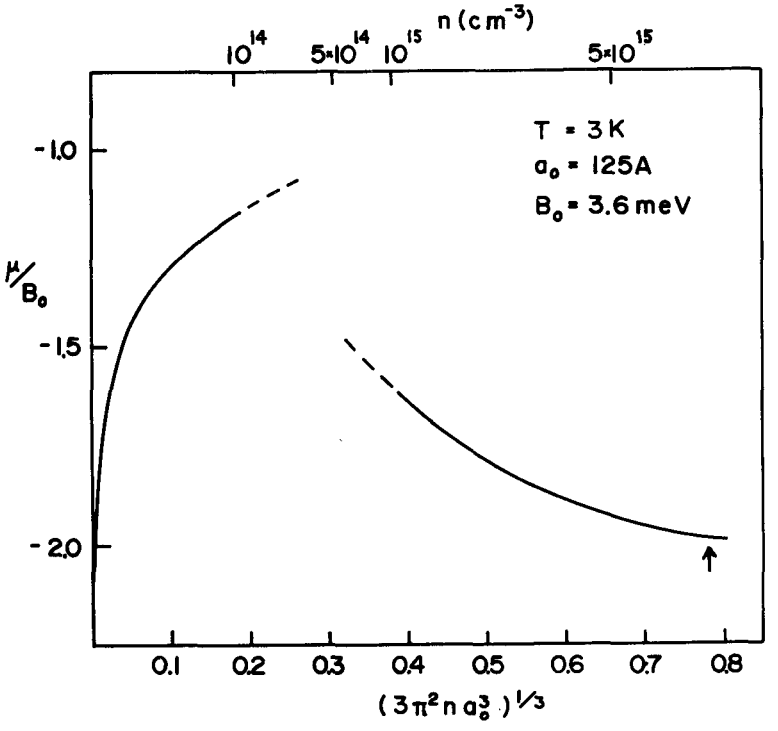


Fig.3. Chemical potentials in the low and intermediate density regions. The arrow indicates the excitation density at which the exciton binding energy vanishes.

the L-region the entropy term in the free energy is sufficiently large to guarantee the chemical equilibrium between carriers and excitons.

Since the appearance of the negative gradient of $\mu$ *vs.* n curve (T = 3K) in the I-region suggests the occurrence of a gas-liquid transition as discussed by Mahler[9] and by Combescot[10] in association with the possibility of EHD, we have to reconsider how the carrier density behaves after the EHD condensate is formed. However, even if the temperature is sufficiently high so that there exists no EHD condensate, it seems that there still exists a sharp increase of $n_e$ at some critical density between the L- and I-regions.

It should be noticed that at sufficiently low temperatures there appears a critical region between the L- and I-regions, in which the

approximation adopted in this paper is no longer valid. In this region, the carriers are neither degenerate nor non-degenerate, and excitons become degenerate and might undergo the exciton condensation.[9] However, even if the exciton condensation occurs, the exciton binding energy continues to decrease as the total excitation increases.[8] As a result, the exciton density begins to decrease with the increase of the total excitation and excitons again become non-degenerate while the carriers become degenerate as assumed in Sec. III. The critical region is not treated in the present paper and is a subject of further investigation.

In conclusion, the thermodynamical investigation of the system composed of electrons, holes and excitons has shown that there is an abrupt increase of carrier density when a total excitation density n increases from the L-region to the I-region, and that the n-dependence of the chemical potential of an electron-hole pair or an exciton is different in those two regions.

## REFERENCES


1) A. A. Rogachev: *Proc. 9th Int. Conf. Phys. Semiconductors, Moscow* 1968 ed. S. M. Ryvkin (Nauka, Leningrad, 1968) p.409.

2) M. N. Gurnee, M. Glicksman and P. W. Yu: Solid State Commun. 11 (1972) 11.

3) A. Nakamura and K. Morigaki: Solid State Commun. 14 (1974) 41.

4) J. C. Hensel, T. G. Phillips and T. M. Rice: Phys. Rev. Letters 30 (1973) 227.

5) Y. Nishina, T. Nakanomyo and T. Fukase: *Proc. 10th Int. Conf. Phys. Semiconductors, Cambridge* 1970 ed. S. P. Keller *et al.* (NBS, Springfield, Va., 1970) p.493.

6) Y. Miura and C. Horie: J. Phys. Soc. Japan 33 (1972) 1522.

7) M. D. Girardeau: Phys. Rev. Letters 27 (1971) 1416.

8) T. Nagashima and C. Horie: J. Phys. Soc. Japan 37 (1974) 614.

9) G. Mahler: Phys. Rev. B11 (1975) 4050.

10) M. Combescot: Phys. Rev. Letters 32 (1974) 15.