Determination of the band-gap decrease in doped Ge and Si from drop properties*

G. Mahler† and J. L. Birman
Department of Physics, City College of the City University of New York, New York, New York 10031
(Received 4 November 1975)

A theoretical analysis of the shift of the drop recombination line is shown to give direct information about the change of the effective energy gap with doping.

The change of the band structure of a semiconductor with doping has attracted considerable interest.[1-9] More recently, high-excitation experiments have been carried out in[10] Si and[11-13] Ge and the recombination line was subsequently interpreted in terms of a condensation within the charge-carrier system. The purpose of this paper is to discuss the relation between a specific property of the heavily doped semiconductor, namely, the energy gap, and the drop luminescence. It thus supplements a previous paper by the same authors.[14]

Let $n_D = N_D/V$ denote the density of donors and $n_p = N_p/V$ the density of (optically excited) electron-hole pairs. It has been shown[1] that the electrons in the conduction band of density $n_e = n_p + n_D$ (and the holes in the valence band) can approximately be described by respective quasiparticles moving in a screened potential $V^{e,h}$ of randomly distributed ionized donors. The quasiparticle properties are determined by the particle-particle interactions, which lead to self-energy shifts, $E_{xc}^{e,h}(n_p, n_D)$, and a small change in the effective masses, which will be neglected. The potentials $V^{e,h}$ can be decomposed[2,15] into an averaged term $\overline{V}^{e,h}(n_p, n_D)$ and a term $\delta V^{e,h}$, which stands for the potential fluctuations around $\overline{V}^{e,h}$. Assuming a superposition of donor potentials of the type

$$v(r) = -e^2 e^{-k_c r}/\epsilon_0 r \ , \tag{1}$$

where k_c is the appropriate screening constant,[2] we get for[2,3]

$$\overline{V}^e = -4\pi n_D \int_0^\infty v(r) r^2 dr = -\frac{4\pi n_D e^2}{\epsilon_0 k_c^2} = -\overline{V}^h \ . \tag{2}$$

This means that in the Thomas-Fermi approximation the energy per electron-hole pair is not affected by the averaged interaction with the donors. The potential fluctuations then only lead to band tails,[15] but leave the *local* energy gap unchanged.[3] This band tailing will be neglected here, as for the doping levels under consideration the number of states in the tails is comparatively small.[2] The density of states is then parabolic and the energy gap well defined. The total energy of the carrier system with respect to the electronic ground state (i.e., zero excitation) reads[14]

$$E_{\rm tot}(N_p, N_D) = N_p[E_p(n_p, n_D) + E_g^0 + \Delta E_g^D(n_D)] \ . \tag{3}$$

Here ΔE_g^D denotes a shift of the unperturbed energy gap E_g^0, owing to direct influences of the donor centers, such as local strain.[16] This term is supposed to be independent of carrier densities (or at least slowly varying with n_p), but may change with the chemical nature of the impurity.[4] However, ΔE_g^D seems not to be well understood in detail—the contribution from particle-impurity scattering is negligible according to Wolff[1]—so we will treat ΔE_g^D as a parameter to be determined later. Finally,

$$E_p(n_p, n_D) = E^e(n_p, n_D) + E^h(n_p, n_D) + R \tag{4}$$

is the mean energy per pair, where

$$E^{e,h}(n_p, n_D) = \tfrac{3}{5} E_F^{e,h} + E_{xc}^{e,h} \ , \tag{5}$$

$E_F^{e(h)}$ is the Fermi-energy of the electron (hole) system, and $E_{xc}^{e,h}$ is the exchange-correlation energy. R describes the change in energy of the excess electron system due to the presence of the electron-hole pairs

$$R = (n_D/n_p)[E^e(n_p, n_D) - E^e(0, n_D)] \ . \tag{6}$$

Bergerson *et al.*[17] included an additional term, which might be interpreted as the change in the self-energy of the *donor point charges* caused by the interaction with the plasma. We believe, however, that the system under consideration should be restricted to the free carriers.

The high-energy edge of the electron-hole recombination line or the minimum energy required to add an additional pair is given by

$$\epsilon(n_p, n_D) = \frac{\partial E_{\rm tot}(N_p, N_D)}{\partial N_p} \ . \tag{7}$$

Owing to scattering, momentum conservation does not impose any restriction.

Low-excitation limit

For $n_p \to 0$, ϵ is the so-called optical gap[6] and is given by

$$E_g^{\rm opt}(n_D) = \epsilon(0, n_D) = E_F^e + \Delta E_g^c + \Delta E_g^D + E_g^0 \ , \tag{8}$$

where

$$\Delta E_g^c = E_{xc}^h + E_{xc}^e + n_e \frac{\partial}{\partial n_e} E_{xc}^e \ . \tag{9}$$

Also the single hole contributes to ΔE_g^c, as it interacts with the electron plasma.[18]

The effective energy gap can be defined as

$$E_g^*(n_D) = E_g^{\mathrm{opt}}(n_D) - E_F^e \ . \tag{10}$$

It is shifted from its value at $n_D = 0$ by

$$\Delta E_g(n_D) = \Delta E_g^D + \Delta E_g^c \ . \tag{11}$$

$\Delta E_g(n_D)$ has been investigated experimentally in various doped materials. This is usually done by analyzing the absorption coefficient derived from a transmission measurement[6,7] or the recombination radiation from injected carriers.[4]

High-excitation limit

For a high density of electron-hole pairs one might expect a condensation to occur within a free-carriers system, similar to the situation in undoped material.[19] This possibility has been confirmed theoretically in Refs. 17 and 14. Qualitatively, this can be seen from Eq. (3): For given particle numbers and volume, E_{tot} is still a function of the free parameter n_p. At zero temperature the stable state of the system will be that of lowest internal energy, i.e.,

$$\frac{\partial E_p(n_p, n_D)}{\partial n_p} = 0 \ . \tag{12}$$

If a minimum exists (which has to be examined in detail), condition (12) determines the density $n_p^0(n_D)$ and the chemical potential μ of the condensed state:

$$\mu(n_D) = E_p(n_p^0, n_D) \ . \tag{13}$$

Outside that phase $n_p = 0$ for $T = 0$, if Eq. (12) defines an absolute minimum.

For the drop the high-energy edge of the recombination line according to Eq. (7) is given by

$$h\nu_{\max}(n_D) = \epsilon(n_p^0, n_D) = \mu(n_D) + E_g^0 + \Delta E_g^D \ . \tag{14}$$

The recombination line has been measured in[10] Si and[11] Ge for high-doping levels.

Energy gap and drop recombination line

Substituting $\Delta E_g^D + E_g^0$ in Eq. (10) by

$$\Delta E_g^D + E_g^0 = h\nu_{\max}(n_D) - \mu(n_D) \tag{15}$$

from Eq. (13), one gets

$$E_g^* = h\nu_{\max}(n_D) - \mu(n_D) + \Delta E_g^c \ . \tag{16}$$

Having in mind that by definition

$$E_g^0 = h\nu_{\max}(0) - \mu(0) \ , \tag{17}$$

the *shift* of the energy gap is given by

$$\Delta E_g(n_D) = E_g^* - E_g^0 = \Delta h\nu_{\max} - \Delta\mu + \Delta E_g^c \ . \tag{18}$$

Comparison with Eq. (11) finally leads to

$$\Delta E_g^D(n_D) = \Delta h\nu_{\max} - \Delta\mu \ . \tag{19}$$

Equations (18) and (19) constitute the desired relations between the drop property $\Delta h\nu_{\max}$ and ΔE_g, ΔE_g^D of the doped semiconductor. In order to check relation (18) by experimental data, one has to calculate $\Delta\mu(n_D)$ and ΔE_g^c.

As can be seen from Eqs. (9) and (4), this basically means calculating the exchange-correlation energies $E_{xc}^{e,h}(n_p, n_D)$. $E_{xc}^{e,h}$ is usually split into two parts:

$$E_{xc}^{e,h} = E_x^{e,h} + E_c^{e,h} \tag{20}$$

where $E_x^{e,h}$ is the mean exchange energy ($k_F^{e,h}$ the Fermi vectors)

$$E_x^{e,h} = -(3e^2/4\pi\epsilon_0)\, k_F^{e,h} \ . \tag{21}$$

The calculation of $E_c^{e,h}$ is given in more detail in Ref. 14; here we only briefly outline the method: The plasma is treated as a dielectric medium characterized by a single effective plasma mode $\omega(k)$. Any charged particle of type j will interact with this mode resulting in a self-energy shift of that particle. This shift is given in second-order perturbation theory by

$$E_c^j = -\sum_{\vec{q},\vec{k},\sigma} \frac{M^j(\vec{k})^2 (1 - n^{(j)}_{\vec{q}+\vec{k},\sigma}) n^{(j)}_{\vec{q},\sigma}}{\hbar\omega(\vec{k}) + E_j^0(\vec{k}+\vec{q}) - E_j^0(\vec{q})} \ , \tag{22}$$

where $n^{(j)}_{\vec{q},\sigma}$ are the occupation numbers of the unperturbed single particle states $E_j^0(q)$ of spin σ. $M^j(k)$ is the form factor of the interaction, including local-field corrections.[20] Equation (22) could also be used for a single hole ($n_p \to 0$):

$$E_{xc}^h(n_p \to 0) = E_c^h = -\sum_{\vec{k}} \frac{M^j(k)^2}{\hbar\omega(\vec{k}) + E_j^0(\vec{k}+\vec{q}) - E_j^0(\vec{q})} \ . \tag{23}$$

Unfortunately, for this case the correlation correction to the local field acting on that single particle seems not to have been discussed so far, as mentioned previously in Ref. 20. Equation (23) is rather sensitive to such a correction, but we expect from Ref. 18 that E_{xc}^h will be one order of magnitude smaller than E_{xc}^e, so we may neglect E_{xc}^h.

Application to Si and Ge

Experiments in the high-doping range show[10,11] that the line shape can reasonably well be described by the combined parabolic density of states, thus justifying the neglect of band tails. This fact also enables us to relate the peak position to the high-energy edge:

$$\Delta E_{\mathrm{peak}} = \Delta h\nu_{\max} + \delta \ ,$$

where δ can be calculated from the knowledge of the electron and hole-Fermi energies.

Table I summarizes some of the results. The second column shows the equilibrium pair density in the condensate, which goes through a minimum near the Mott density n_c. (n_c is marked in Figs. 1 and 2.) The last column is ΔE_g^D extracted from

TABLE I. All energies in meV. $\Delta\mu\ (n_D)$, E_{xc}^e, E_{xc}^h, and ΔE_g^c [Eq. (9)] from theory; ΔE_g^D derived from experiment using Eq. (19).

	n_D (cm^{-3})	n_p^0 (cm^{-3})	$\Delta\mu\ (n_D)$	E_{xc}^e	ΔE_g^c	ΔE_g^D
	10^{17}	8.1×10^{16}	−0.48	−3.68	−4.51	−1.8
	3.16×10^{17}	2.8×10^{16}	−0.85	−4.86	−6.00	−3.4
Ge	10^{18}	2.4×10^{16}	−0.31	−6.48	−8.05	−6.0
	3.16×10^{18}	2.6×10^{16}	3.16	−8.74	−10.92	−10.5
	10^{19}	3.7×10^{16}	13.96	−11.89	−14.98	−19.1
	3.16×10^{17}	2.3×10^{18}	−0.56	−8.06	−9.78	
	10^{18}	1.5×10^{18}	−1.40	−10.59	−13.00	−2.6
Si	3.16×10^{18}	2.8×10^{17}	−3.26	−14.00	−17.28	−9.7
	10^{19}	3.3×10^{17}	−3.67	−18.68	−24.20	−16.3
	3.16×10^{19}	4.8×10^{17}	2.61	−25.20	−32.50	−21.6

experiment. It generally increases more rapidly with n_D than does ΔE_g^c; in Ge we find $\Delta E_g^D \sim n_D^{1/2}$. The total energy shift as shown in Figs. 1 and 2 can above n_c be approximated by

$$\Delta E_g(n_D) \sim n_D^x ,$$

where $x = 0.3$ for Si and 0.34 for Ge. Although

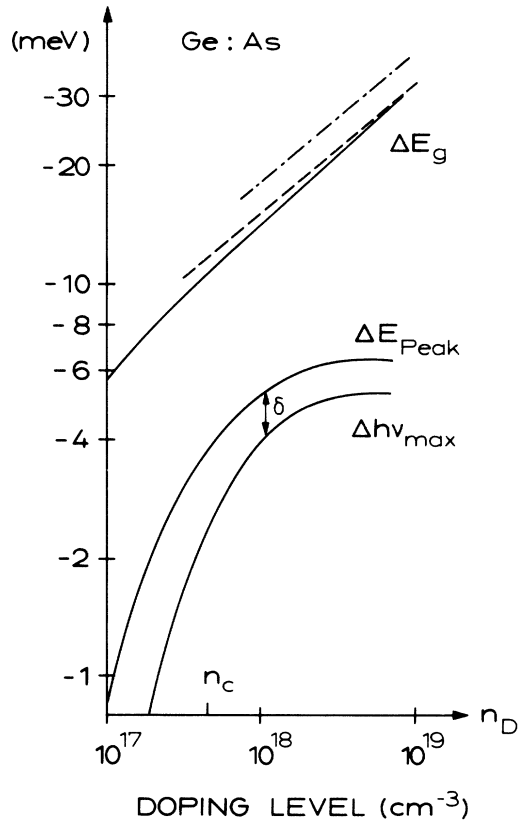

FIG. 1. Measured shift[11] ΔE_{peak} of the electron-hole recombination line in Ge and derived shift $\Delta h\nu_{max}$ assuming the line shape to be determined by the combined density of states. Solid line: ΔE_g from Eq. (18); broken line: experiment, Ref. 5; dotted line: experiment, Ref. 4.

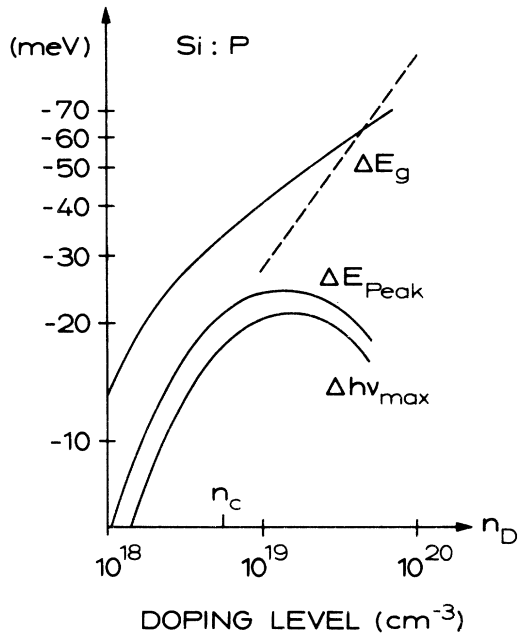

FIG. 2. Measured shift[10] $\Delta h\nu_{max}$ of the electron-hole recombination line in Si and derived shift ΔE_{peak}. Solid line: ΔE_g from Eq. (18); broken line: experiment, Ref. 6.

ΔE_g contains correlation effects and contributions from the donor interaction in addition to the particle exchange energy, this result is very near to $x = \frac{1}{3}$ expected from the exchange contribution alone.[9] The agreement of our result with other experimental data is satisfying for Ge, especially if one takes into account the large experimental uncertainty for ΔE_g. Including of E_{xc}^h should further improve the agreement.

For Si there is unfortunately only one experiment to compare, for which $x \sim \frac{1}{2}$ was found. Our analysis had to be based on few experimental points for $\Delta h\nu_{max}$, so the discrepancy between experiment and theory is not conclusive and could possibly be removed with the help of further data.

The procedure as carried out for Ge and Si can be interpreted as a new method for measuring the energy gap shrinkage in doped semiconductors: it is a direct method, in that it only requires to study the shift of a characteristic recombination line, which should be possible quite precisely. The accuracy further depends on the reliability of the theory, which can easily be checked by its additional predictions, like the halfwidth of the recombination line.[9] An additional advantage is the fact that $\Delta h\nu_{max}$ should within same limits not depend on the excitation power, as a consequence of condensation. This was confirmed experimentally for low doping levels, but seems not to be true at

least for intermediate doping.[12,13] This dependence could be due to surface effects or potential fluctuations both not considered here, but has not yet been reported for the high doping range. In any case it would introduce only a minor error in the derived ΔE_g. Further experiments—also with different impurities—could help to clarify the situation.

---

*Work supported in part by the Deutsche Forschungsgemeinschaft and by the NSF Grant No. DMR74-21991-A0I.

†Present address: Universität Regensburg, Fachbereich Physik, 84 Regensburg, W. Germany.

[1]P. A. Wolff, Phys. Rev. 126, 405 (1962).
[2]C. J. Hwang, Phys. Rev. B 2, 4117 (1970).
[3]H. von Gong and G. Mesnard, Phys. Status Solidi B 52, 553 (1972).
[4]A. P. Shatov and M. S. Murashov, Sov. Phys. Semicond. 1, 476 (1967).
[5]A. A. Rogachev and N. I. Sablina, Sov. Phys.-Solid State 8, 691 (1966).
[6]M. Balkanski, A. Aziza, and E. Amzallag, Phys. Status Solidi 31, 323 (1969).
[7]J. I. Pankove and P. Aigrain, Phys. Rev. 126, 956 (1962).
[8]D. Auvergne, J. Canassel, and H. Mathieu, Phys. Rev. B 11, 2257 (1975).
[9]V. L. Bonch-Bruevich and R. Rozman, Sov. Phys.-Solid State 6, 2016 (1965).
[10]R. E. Halliwell and R. R. Parsons, Solid State Commun. 13, 1245 (1973).
[11]A. Nakamura and K. Morigaki, *Proceedings of the International Conference on the Physics of Semiconductors, Stuttgart*, 1974, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974).
[12]R. W. Martin and R. Sauer, Phys. Status Solidi B 62, 443 (1974).
[13]B. V. Norikov, R. C. Korchazhkina, and N. S. Sokolov, Sov. Phys.-Solid State 15, 326 (1973).
[14]G. Mahler and J. L. Birman, Phys. Rev. B 12, 3221 (1975), Solid State Commun. 17, 1381 (1975).
[15]B. I. Halperin and M. Lax, Phys. Rev. 148, 722 (1966).
[16]W. Shockley and J. Bardeen, Phys. Rev. 77, 407 (1950).
[17]B. Bergerson, P. Jena, and A. J. Berlinsky, J. Phys. C 8, 1377 (1975).
[18]G. D. Mahan, Phys. Rev. 153, 882 (1967).
[19]Ya. E. Pokrovskii, Phys. Status Solidi A 11, 385 (1972).
[20]A. W. Overhauser, Phys. Rev. B 3, 1888 (1971).