# Properties of the electron-hole drop in *n*-doped germanium and silicon<sup>†</sup>

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The gas-liquid transition of an electron-hole plasma is studied under the influence of a donor electron system of density  $n_D^-$ . It is found that the density of holes within the drop decreases with increasing  $n_D^-$ . The width of the electron-hole recombination line calculated from the joint density of states, is found to go through a minimum in agreement with experiment. It is further shown that the behavior of the linewidth reflects the nature of the impurity-induced semiconductor-metal transition. It is therefore possible to construct the underlying change of the free-carrier density with doping which is demonstrated for Si:P. Condensation seems to occur up to high doping levels. It might also be expected in a number of heavily doped (metallic) semiconductors, for which the metallic phase is not stable with respect to exciton formation under normal conditions.

#### I. INTRODUCTION

The occurrence of a metallic condensate in pure Ge and Si under high excitation is very well established, experimentally and theoretically (see, e.g., Ref. l). Recently, the influence of doping on prop erties of the electron-hole drop (EHD) has been studied in<sup>2,3</sup> Ge, and<sup>4</sup> Si. It seems that condensation is not suppressed even for very high doping levels, but significant- changes of the luminescence properties have been observed. Up to the present no theoretical investigation of this experimental situation has been carried out.

In this paper we will try to show that the majority of the EHD properties can readily be understood by an extension of existing theories appropriate for pure samples. This may supplement our knowledge of the metallic condensation, in general, as well as of the nature of the semiconductor-metal transition induced by doping,

### II. SYSTEM

The system under consideration is basically a free-carrier plasma, for which the numbers of electrons  $N_e$  and holes  $N_h$  may generally be different:  $N_e - N_h = N_D^*$ . Of course,  $N_D^*$  cannot exceed the number of donor centers  $N_D$ . The respective number densities are  $n_h$ ,  $n_e$ , and  $n_D^*$ . Our model calculation will be based on  $T = 0$  and the following assumptions: (a) The donor centers are distributed homogeneously over the sample. (b) The band structure is taken into account within the framework of the effective-mass theory with anisotropy and multivalley structure approximately included. The effective energy gap  $E_{\epsilon}(n_{\rm D})$  may be changed, but the effective masses are assumed independent of doping. (c}The donor electrons are supposed to be either localized and then neglected  $(i.e.,$  removed from the free-carrier system), or freeand then described by the properties of the respective conduction band. Complications due to the occurrence of an impurity band are thus neglected. (d) Any explicit influence of excitons (free or bound) is not considered here, which is justified for highcarrier densities (i. e, , high excitation and/or doping).

#### III. HAMILTONIAN

Let us assume that the single-particle energies of momentum  $\bar{q}$  are given by

$$
E_j^0(\vec{q}) = \bar{n}^2 q^2 / 2m_j + \text{const},\tag{1}
$$

where  $j$  is the band index. Bands included are the upper valence bands (holes) and the lower conduction bands (electrons). All energies are measured from the conduction-band minimum. The Hamiltonian for the N-particle system, consisting of  $N_{\alpha}$ pairs and  $N_D^*$  excess electrons, may then be written

$$
H(N_{p}, N_{D}^{-}) = H_{\text{kin}}(N_{p}, N_{D}^{-}) + H_{x}(N_{p}, N_{D}^{-})
$$
  
+  $H_{c}(N_{p}, N_{D}^{-})$ , (2)

with

$$
H_{\text{kin}}(N_p, N_p^-) = \sum_{\substack{\vec{q}, \sigma \\ j}} E_j^0(\vec{q}) n_{\vec{q}, \sigma}^{(j)} \tag{3}
$$

 $n_{q,\sigma}^{(j)} = c_{\bar{q},\sigma}^{\dagger(j)} c_{\bar{q},\sigma}^{(j)}$ ,  $c_{\bar{q},\sigma}^{\dagger(j)}$  are the creation operators of a single particle in a state  $(\bar{q}, j)$  with spin  $\sigma$ .  $H_x$  is the exchange part given by

$$
H_{x}(N_{p}, N_{D}^{-}) = -\frac{2\pi e^{2}}{V \epsilon_{0}} \sum_{\vec{k}, \vec{q}, \sigma} \frac{1}{k^{2}} n_{\vec{q}, \sigma}^{(j)} n_{\vec{q} + \vec{k}, \sigma}^{(j)}.
$$
 (4)

 $H_c$  represents the correction due to correlation. Following a model proposed by Overhauser, <sup>5</sup> we describe the correlation by a coupling of the single particles to an effective plasmon mode  $\omega_k$  which approximates the dielectric response of the system

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$$
H_c(N_p, N_p^-) = \sum_{\substack{\vec{k}, \vec{q}, \sigma \\ j}} \hbar \omega_{\vec{k}} n_{\vec{k}} \qquad \text{we m} \qquad \text{from} \qquad \text{from} \qquad \text{from} \qquad \text{to} \qquad \text{to}
$$

$$
+\sum_{\substack{\vec{k},\vec{q},\sigma\\j}}M^j(\vec{k})\left(a^{\dagger}_{\vec{k}}+a^{\star}_{\vec{k}}\right)c^{\dagger(j)}_{\vec{q}+\vec{k},\sigma}c^{\,(j)}_{\vec{q},\sigma}.
$$

Here  $n_{\mathbf{k}}^* = a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}^*$  and  $a_{\mathbf{k}}^{\dagger}$  is the creation operator of an effective plasmon.  $M^j$  is determined by requiring the single mode  $\omega_{\mathbf{k}}$  to fulfill the f sum rule, and  $\omega_{\mathbf{k}}$  by requiring the model to reproduce the appropriate dielectric function  $\varepsilon(k, 0)$ .

This dielectric function is assumed to be

$$
\epsilon(\vec{k}, 0) = 1 + \frac{1}{k^2} \sum_j k_c^{(j)2} Q_j\left(\frac{k}{2k_F^{(j)}}\right),\tag{6}
$$

where

$$
Q_j(x) = F(x) / [1 + S_j(x)F(x)],
$$
\n(7)

$$
F(x) = \frac{1}{2} + \left[ (1 - x^2)/4x \right] \ln \left| (1 + x)/(1 - x) \right| \quad . \tag{8}
$$

 $k_{c}^{(j)}$  is the Thomas-Fermi screening wave vector

$$
k_c^{(j)^2} = 6\pi n^{(j)} e^2 / \epsilon_0 E_F^{(j)} . \qquad (9)
$$

 $k_{F}^{(j)}$  is the Fermi vector and  $E_{F}^{(j)}$  is the Fermi energy. With  $S_i = 0$ , we would get the Lindhard formula.  $S_i$  describes the exchange and correlation corrections to the dielectric response. According to Singwi et  $al.$   $6$  we choose

$$
S_j(x) = 2x^2/(1+4x^2+\beta_j) , \qquad (10)
$$

with

$$
\beta_j = k_c^{(j)}/k_F^{(j)} \tag{11}
$$

Then the form factor  $M^{(j)}$  is found to be (cf. Ref. 6)

$$
M^{(j)}(\vec{\mathbf{k}}) = \left(\frac{2\pi e^2 \hbar \omega_p}{\epsilon_0 k^2 \omega_k V}\right)^{1/2} \left[1 - S_j\left(\frac{k}{2k_F}\right)\right],
$$
 (12)

$$
\omega_p^2 = \frac{4\pi e^2}{\epsilon_0} \sum_j \frac{n^{(j)}}{m_j} \,. \tag{13}
$$

 $\omega_{p}$  is the plasma frequency for  $k-0$ , while the dispersion relation is given by

$$
\omega_k^2 = \omega_p^2 \epsilon(k, 0) / [\epsilon(k, 0) - 1]. \qquad (14)
$$

We may now treat  $H_c$  as a perturbation, and calculate its influence by second-order perturbation theory. Assuming no plasmons to be present we get

$$
E_c = -\sum_{\vec{a}, \vec{k}, \sigma_s} \int \frac{M^{(j)}(\vec{k})^2 (1 - n_{\vec{a}}^2 \cdot \vec{k}, \sigma) n_{\vec{a}, \sigma}^{(j)}}{\hbar \omega_{\vec{k}} + E_j^0(\vec{k} + \vec{q}) - E_j^0(\vec{q})} . \tag{15}
$$

From the total exchange-correlation energy of the system,

$$
E_{xc}(N_{p}, N_{D}^{-}) = E_{x}(N_{p}, N_{D}^{-}) + E_{c}(N_{p}, N_{D}^{-}) , \qquad (16)
$$

ay easily derive the mean energies per electron and per hole,  $\overline{E}_{xc}^{a,h}(n_b, n_b)$ . These are obd by restricting the j summation in Eqs. (15) and (4) to the hole or electron bands, respectively, and then dividing by the respective particle numbers.  $\overline{E}_{xc}^{e,h}$ , by definition, only depends on the densities, but is otherwise independent of the momentum of the particle under consideration. This local approximation turns out to be well justified, as shown previously by Overhauser<sup>5</sup> for a one-component plasma, and can be used to simplify the calculations.

To get the total energy per particle, one has to add the kinetic energy

$$
E^{\mathbf{e},h}(\vec{\mathbf{q}}) = E_{\mathbf{xi}\,n}^{\mathbf{e},h}(\vec{\mathbf{q}}) + \overline{E}_{\mathbf{xc}}^{\mathbf{e},h}(n_{\rho}, n_{D}^{-}) \tag{17}
$$

The mean values are

$$
\overline{E}^{\mathbf{e},h}(n_{\mathbf{p}}, n_{D}^{-}) = \frac{3}{5} E^{\mathbf{e},h}_{F} + \overline{E}^{\mathbf{e},h}_{xc}(n_{\mathbf{p}}, n_{D}^{-})
$$
 (18)

Et is also convenient to introduce the mean energy per pair

$$
\overline{E}_p(n_p, n_D^-) = \overline{E}^e(n_p, n_D^-) + \overline{E}^h(n_p, n_D^-) \ . \tag{19}
$$

Then the total energy of the free-carrier system with respect to the conduction-band edge may be written for a given homogeneous density  $n_D = N_D^2/V$ , as

$$
E_{\text{tot}}(N_p^{\bullet}, N_D^{\bullet}) = N_p \left[ \overline{E}_p(n_p, n_D^{\bullet}) + R + E_g \right] + N_D^{\bullet} \overline{E}^{\theta}(0, n_D^{\bullet}) . \tag{20}
$$

 $E_{r}$  is the energy gap and the last term is the energy of the excess-electron system as for  $N_{p} = 0$ .  $N_{p}\,R$  is the change of this energy induced by the electron-hole pairs of density  $n_{p}$  in the volume  $V_{p}$  $=N_{\rho}/n_{\rho}$ ,

$$
R = (n_D^-/n_p) \left[ \overline{E}^e(n_p, n_D^-) - \overline{E}^e(0, n_D^-) \right]. \tag{21}
$$

Obviously, for fixed  $N_p$  and total volume V, the modified pair energy as given by

$$
E(n_{p}, n_{D}^{-}) = E_{p}(n_{p}, n_{D}^{-}) + R , \qquad (22)
$$

and likewise  $E_{\text{tot}}$  is still a function of  $n_{p}$ . This free parameter is now fixed by the condition that Eq. (20) should describe the stable state at  $T=0$ , which means the state of lowest internal energy. This minimum condition

$$
\partial E(n_{p}, n_{D}^{-})/\partial n_{p} = 0 , \qquad (23)
$$

determines the density  $n_a^0(n_a)$  and the chemical potential

$$
\mu(n_p^0) = \left(\frac{\partial E_{\text{tot}}}{\partial N_p}\right)_V = E(n_p^0, n_D^-) + E_g
$$
\n(24)

of the pairs in the condensed phase [provided there is a finite density  $n_{p}$  fulfilling condition (23)]. Condition (23) establishes the stability of the condensed phase within the present approximation, which ne-

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glects excitons. This is justified for high excesscarrier densities  $n_n$ . Since no excitons can exist, condensation might occur in any semiconductor (if thermal equilibrium can be reached). But for  $n_{\rm p}$   $\rightarrow$  0, we may think of the free-carrier system as being in thermal equilibrium with an exciton gas.<sup>11</sup> Then the condensate will only be stable if<sup>1</sup>

$$
\varphi(n_{D}^{-})=E(n_{P}^{0}, n_{D}^{-})+E_{b}(n_{D}^{-})<0 , \qquad (25)
$$

where  $E<sub>b</sub>$  is the binding energy of the exciton. This condition has so far resulted in the restriction of condensation for  $n_D^{\dagger} = 0$  to Si and Ge.

## IV. INFLUENCE OF THE SEMICONDUCTOR-METAL **TRANSITION**

We considered so far a condensation process within a homogeneous excess-electron gas of given density  $n_{\rho}$ . Now  $n_{\rho}$  will also be influenced by the electron-hole condensate. We may assume that the carrier density inside the drop is always high enough to guarantee that  $n_{\mathbf{p}} = n_{\mathbf{p}}$  even for very lowdoping levels. But outside the drop  $n<sub>p</sub>$  will be related to  $n<sub>p</sub>$ , the density of donor centers. This relation characterizes the semiconductor -metal transition

$$
n_D^- = f(n_D) \tag{26}
$$

Above a critical value  $n_c,$ <sup>7</sup>

$$
n_c^{1/3} = 0.25/a_B^*,
$$
 (27) 
$$
I(s) = \alpha
$$

where  $a_B^*$  is the Bohr radius of the donor centers at  $n<sub>D</sub>$  ~ 0; all donor electrons are delocalized (which means in our simplified model that they are in the conduction band). Below  $n_c$ ,  $n_D^{\dagger}$  outside the drop will go to zero. If it was a discontinuous Mott transition<sup>7</sup> we would expect, for  $T = 0$ .

$$
n_D^{\bullet} = \begin{cases} n_D & \text{for } n_D \ge n_c , \\ 0 & \text{for } n_D < n_c . \end{cases} \tag{28}
$$

In any case, this means that for  $n_p < n_c$ , the density of the excess-electron system will be smaller outside than inside. Mechanical equilibrium requires the pressure in both phases to be equal. At  $T=0$ , the pressure of a system of density  $n$ , characterized by the internal energy  $E^N = NE(n)$ , is given by

$$
P(n) = -\left(\frac{\partial E^N}{\partial V}\right)_N = n^2 \left(\frac{\partial E(n)}{\partial n}\right)_V.
$$
 (29)

Assuming the electron density outside the drop to be  $n_{\rm D} = f(n_{\rm D})$ , the balance for the pressure reads

$$
P_{\text{pair}}(n_{p}) + P_{e}(n_{D}) = P_{e}(n_{D}^{-}) , \qquad (30)
$$

which leads to the condition

$$
P_{\text{pair}}(n_{p}) + P_{e}(n_{D}) = P_{e}(n_{D}), \qquad (30)
$$
\nch leads to the condition

\n
$$
\frac{\partial E(n_{p}, n_{D})}{\partial n_{p}} = \frac{1}{n_{p}^{2}} \left( (n_{D}^{2})^{2} \frac{\partial E^{e}(0, n_{e})}{\partial n_{e}} \Big|_{n_{D}^{2}} - n_{D}^{2} \frac{\partial E^{e}(0, n_{e})}{\partial n_{e}} \Big|_{n_{D}} \right). \qquad (31)
$$

For  $n_D = n_D$  (i. e.,  $n_D \ge n_c$ ) we get back Eq. (22).

It turns out that for  $n_D < n_c$ , condition (31) tends to increase  $n_{p}^{0}$  over the value obtained from Eq. (22), depending on  $f(n_D)$ . As  $n_b^0$  strongly influences the linewidth of the electron-hole recombination line, the function  $f(n_p)$  can be studied from the behavior of the linewidth as a function of  $n_{\rm b}$ . More details are presented with the application to Si and Ge.

#### V. LINE SHAPE

We assume that the luminescence intensity is proportional to the joint density of states of the electron and the hole subsystem.

$$
I(h\nu) = \alpha \int_0^{\infty} \int_0^{\infty} n(E_{\text{kin}}^{\theta}) n(E_{\text{kin}}^{\hbar}) f(E_{\text{kin}}^{\theta}) f(E_{\text{kin}}^{\hbar})
$$
  
 
$$
\times \delta(h\nu - E_{\epsilon} - E^{\theta} - E^{\hbar} + \hbar \Omega) dE_{\text{kin}}^{\theta} dE_{\text{kin}}^{\hbar}, \qquad (32)
$$

where  $\alpha$  is a constant,  $n(E_{\text{kin}}^{\theta,h})$  are the respective densities of states, and  $f(E_{\text{kin}}^{\theta,h})$  are the distribution functions.  $E^e$ ,  $E^h$  are the total energies per particle according to Eq. (17) and  $\hbar\Omega$  is the energy of a phonon involved.

For  $T = 0$ , we get with

$$
s = h\nu - E_g - E_{\infty}^{\theta} - E_{\infty}^h + \hbar\Omega \t{,} \t(33)
$$

$$
I(s) = \alpha \int_A^B (E_{\text{kin}}^e)^{1/2} (s - E_{\text{kin}}^e)^{1/2} dE_{\text{kin}}^e , \qquad (34)
$$

where

$$
A = \begin{cases} 0 & \text{for } s \le E_F^h, \\ s - E_F^h & \text{for } s > E_F^h; \end{cases}
$$
\n
$$
B = \begin{cases} s & \text{for } s \le E_F^g, \\ E_F^g & \text{for } s > E_F^g. \end{cases}
$$
\n
$$
(35)
$$

The halfwidth  $\Delta$  of the line, and the position of the maximum with respect to the high-energy edge  $d$ are given in Fig. 1, as a function of

$$
t = \left| E_F^e - E_F^h \right| / (E_F^e + E_F^h) \tag{36}
$$

This approach does not include possible effects due to potential flucutations.

## VI. LINE SHIFT

The energy released by the recombination of one electron and one hole is given by the difference of the total energy of the system in its initial and final state

$$
h\nu = E_{\text{tot}}(N_p, N_p) - E_{\text{tot}}(N_p - 1, N_p)
$$
 (37)

If both states are drops (in their ground state), as studied above, then  $hv$  corresponds to the high-energy edge of the recombination line,  $\delta$  and the two states only differ by the number of pairs. We can then write

 $\overline{c}$ 

 $\equiv$ 



FIG. 1. Combined density of states of an EH-plasma: half width  $\Delta$  and position of the maximum with respect to the high-energy edge d as a function of t; (1)  $\Delta/E_F$ , (2)  $1+d/E_{F}$ .

$$
h\nu_{\max} = \left(\frac{\partial E_{\text{tot}}}{\partial N_p}\right)_V,
$$
\n(38)

which is identical to the chemical potential [compare Eg. (24)]. Under the general condition (31), and allowing for a phonon  $h\Omega$  to be emitted, we get

$$
h\nu_{\max} = E(n_p^0, n_p) + n_p^0 \frac{\partial E(n_p, n_p)}{\partial n_p} + E_g - \bar{\hbar}\Omega \quad . \quad (39)
$$

The second term is zero for  $n_D > n_c$ . For these high doping levels the shift of the high-energy edge  $h\nu_{\text{max}}$  with respect to its position at  $n_p = 0$  is given by

$$
\Delta h \nu_{\text{max}} = \Delta E(n_p^0, n_p) + \Delta E_{\ell}(n_p) , \qquad (40)
$$

where

$$
\Delta E(n_p^0, n_p) = E(n_p^0, n_p) - E(n_p^0, 0) ; \qquad (41)
$$

$$
\Delta E_{g}(n_{D}) = E_{g}(n_{D}) - E_{g}(0) . \qquad (42)
$$

Note that  $\Delta E_{\epsilon}(n_{D})$  does *not* contain the influence of particle-particle interactions, as these are included in  $\Delta E$ .  $\Delta E$ <sub>*f*</sub> is due to any other influence of the donor centers (compare, e.g., Ref. 9). Instead of the high-energy edge, we may as well study the peak position  $E_{\text{peak}}$ ,

$$
E_{\text{peak}} = h\nu_{\text{max}} - d \tag{43}
$$

Given  $t$  and  $E_F$ ,  $d$  can be read from Fig. 1.

# VII. APPLICATION TO Si AND Ge

The Fermi energies in these cases are given  $by<sup>10</sup>$ 

$$
E_F^e = \hbar^2 k_F^{e^2} / 2m_{\text{de}} \,, \tag{44}
$$

$$
m_{\rm de} = (m_t)^{2/3} (m_t)^{1/3} \,, \tag{45}
$$

$$
E_F^h = \hbar^2 k_F^{h^2} / 2m_{\rm hh} (1 + \gamma^{3/2})^{2/3} \,, \tag{46}
$$

$$
\gamma = m_{1h} / m_{hh} < 1 \tag{47}
$$

For the exchange-correlation correction we as-

TABLE I. Input data.<sup>a</sup>

1.58 Ge					
	0.082	0.042	0.347	15.36	2.66
Si 0.9163	0.1905	0.154	0.523	11.4	13

sume g isotropic conduction bands of mass  $m_{\infty}$ ,

$$
m_{\mathbf{0}\bullet}^{-1} = \frac{1}{3} \left( 2/m_t + 1/m_t \right) , \tag{48}
$$

and two isotropic valence bands of mass  $m_{\rm oh}$ ,

$$
m_{\rm oh}^{-1} = \frac{1}{2} \left( 1/m_{\rm hh} + 1/m_{\rm 1h} \right) \,. \tag{49}
$$

 $g = 6$  for Si and  $g = 4$  for Ge. The input data used are given in Table I.

The energy  $E(n_p, n_p)$  following Eq. (23) is calculated as a function of  $n<sub>p</sub>$  for a homogeneous excess electron density  $n_D^*$ . Part of the results are shown in Fig. 2. We see that this function has (at least a local) minimum at  $n_b^0(n_p)$ . The values for  $n<sub>D</sub> = 0$  are given in Table II and agree well with experiment. (Compare also Ref. 11.)

Figure 3 shows the contribution  $\Delta E(n_p^0, n_p)$  to the shift of the high-energy edge of the electron-hole



FIG. 2. Energy  $E(n_p, n_p)$  as a function of  $n_p$  for various homogeneous excess-electron densities  $n_D$ , (1)  $n_E$ = 0, (2)  $n_D^-$  = 10<sup>16</sup> cm<sup>-3</sup>, (3)  $n_D^-$  = 10<sup>17</sup> cm<sup>-3</sup>, (4)  $n_D^-$  = 10<sup>18</sup> cm<sup>-3</sup>, (5)  $n_D^-$  = 10<sup>19</sup> cm<sup>-3</sup>, (6)  $n_D^-$  = 10<sup>20</sup> cm<sup>-3</sup>; (a) Ge, (b) Si.





<sup>a</sup> Assuming  $E_5^{\text{gpt}} = 3.8 \text{ meV (Ge)}$ , 14.7 meV (Si). <br><sup>b</sup>T. K. Lo, Solid State Commun. <u>15</u>, 1231 (1974). <sup>c</sup>C. Benoit à la Guillaume, Solid State Commun. 12, 1257 (1973).

tion line according to  $\mathbf{Eq.}$  (40). For high doping levels, this shift rapidly becomes positive, which recalls the well-known Burstein shift.<sup>12</sup> As we do not know  $\Delta E_{\ell}(n_p)$ , we cannot give a theoretical account of the total shift  $\Delta h\nu_{\text{max}}$ , it is possible, however, to use experimental values for  $\Delta h\nu_{\text{max}}$  to determine  $\Delta E_{g}(n_{D})$ .

For moderate doping levels  $\Delta E$  is negative, indicating that it is energetically favorable for the drop to form in such doped regions. This is someextension of the nucleation hypothesi cently investigated further by Silver.<sup>13</sup>

h of the electron-hold In Fig. 4, we give the equilibre in Fig. 5, the halfwidth of the electron bination line as a function of



t of the ground-state energy,  $\Delta E (n_p^0, n_p^0)$ as a function of the homogeneous excess-electron density  $n_D^{\bullet}$ ; (a) Ge, (b) Si.



4.  $n^0_p$  as a function of the doping level  $n_D$ ; capita letters refer to the assumptions  $n_D^- = f (n_D)$ , defined in<br>the text. (a) Ge:As,  $\Delta$  expt (As) Ref. 3, expt (As) Ref. 2, + expt (Sb) Ref. 2. (b) Si: P,  $\Delta$  expt Ref. 4.



of the doping level  $n_D$ , capital letters refer to the assumptions  $n_D^- = f(n_D)$ <br>defined in the text (a) Ge,  $\nabla$  expt. Ref. 2,  $\Delta$  expt. Ref. 16. (b) Si, o expt. Ref. 4.

Ge



FIG. 6.  $n_{D}^{-} = f(n_{D})$  for Si, o, expt, Ref. 14.

 $n<sub>D</sub>$ . This is done for the following three assumptions:

(A) 
$$
n_D^- = n_D
$$
,  
\n(B)  $n_D^- = \begin{cases} n_D & \text{for } n_D \ge n_c \\ 0 & \text{for } n_D < n_c \end{cases}$ 

(C)  $n_{\rm n} = f(n_{\rm n})$  taken from expt (only for Si).

All three assumptions are identical for  $n_p \geq n_c$ . Below  $n_c$ , condition (31) leads to different values  $n_{\rm h}^{0}(n_{\rm n})$ , and therefore to different halfwidths. A and  $\overline{B}$  represent the two extreme cases; any experimental result is therefore expected to lie between them, reflecting a specific function  $f(n<sub>p</sub>)$ . This can be seen for Si, when  $n_D^{\dagger}$  is taken from experiment<sup>14</sup> (compare Fig. 6). Furthermore, in this case there is a striking agreement between calculated and measured halfwidth.

It will also be clear that  $n_{p}^{0}$  and  $\Delta(n_{p})$  will depend on the chemical nature of the donor center, in that  $n_c$  and  $f(n_p)$  are changed. Even without knowing details about  $f(n<sub>p</sub>)$ , one will expect that the minimum occurring in the linewidth as a function of  $n<sub>p</sub>$  gets deeper with decreasing  $n_c$ , i.e., decreasing ionization energy of the donors. Similarly, the reduction at  $n_{\rm b}^0$  with  $n_{\rm D}$ , sets in already at smaller  $n_{\rm D}$ , if donors with a smaller ionization energy are used.

The latter finding is in qualitative agreement with experiments in Ge [cf. Fig.  $4(a)$ ]. The measured linewidth, too, shows the expected behavior, except for the bump around  $3 \times 10^{12}$  cm<sup>-3</sup>. This may be due to the influence of potential fluctuations.<sup>15</sup> It is not clear why this influence is apparently stronger in Ge than in Si.

So far there is no definite indication of a breakdown of the assumption of parabolic bands. It is expected, however, that deviations from this theory will occur at very high-doping levels: In this case the line-shape should no longer be determined by Eq. (34).

## VIII. SUMMARY AND CONCLUDING REMARKS

In order for condensation to occur, the condensed state should be the ground state, i.e., the state of lowest energy, of the free-carrier system. Within our approach we found that this is the case for Ge and Si even for high doping levels, i.e., in metallic samples, though one might expect that the EHD lifetime<sup>2</sup> will be reduced. The change of the critical temperature remains to be studied.

Because in the metallic samples the ground state of the carrier system is necessarily a plasma state (not the exciton state), condensation effects may even occur in a number of other semiconductors, for which in the pure case the exciton state is the stable state.

Below a critical density  $n_c$ , the excess electrons outside the condensate start to localize, resulting in a change of pressure in that phase. We then have to study the drop under pressure: It has been demonstrated that the variation of the equilibrium pair density and the linewidth as a function of  $n<sub>D</sub>$ can be understood on the basis of our simplified approach, which neglects all complications due to the occurrence of an impurity band. The nature of the semiconductor-metal transition is reflected by these functions, so that it is possible to construct the free-carrier density as a function of doping from linewidth measurements. Insofar as  $n_{p} (n_{p})$ also depends on the chemical nature of the donor centers, so will the properties of the EHD: It seems that the drop can be used as an internal detector of the impurity-induced semiconductor -metal transition, signaling the situation around it by a characteristic linewidth.

Note added in proof. A theoretical study of the high-doping region was recently published by B. Bergerson, P. Jena, and A. J. Berlinsky, J. Phys. C 8, 1377 (1976).

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