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Theory of the electron-hole plasma in highly excited Si and Ge†

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In a microscopic-model calculation the electron-hole system is treated as an interacting free-carrier system in thermal equilibrium with a nonideal exciton gas. Renormalization of the excitons is approximately taken into account. The chemical potential as a function of the total electron-hole density is discussed with respect to possible unstable regions also in the low-density regime. Making simplifying assumptions, the phase diagram for the metallic condensation is derived for Ge and Si and compared to experimental data.

I. INTRODUCTION

During the last couple of years the nonequilibrium electron-hole system of highly excited semiconductors has intensively been studied, especially in Ge[1-3] and Si.[4,5] Most investigations in that field have been prompted by the occurrence of a gas-liquid type transition within the system of elementary excitations, known to lead to metallic electron-hole droplets (EHD). The basic mechanism responsible for this cooperative effect can be understood from a Fermi-liquid theory[6-8]: Theoretical values for the equilibrium density and ground-state energy are in fairly good agreement with experiment. Also critical density and critical temperature can be estimated by means of low-temperature expansions[9,10]; a complete Hartree-Fock calculation for finite temperatures has been presented by Silver.[11]

These theories, however, do not allow a full understanding of the coexisting phases, as they are restricted to the high-density limit. In a completely different approach by Reinecke *et al.*[12] the phase diagram has been related to surface properties of the drop, making explicit use of fluctuations. Like the phenomenological models introduced in Refs. 13 and 14, this investigation has to be based on the concept of simple fluids and is, therefore, in principle restricted to the region where the formation of excitons is less important. Furthermore, not even the stability of the EHD can be established, as this requires reference to the properties of excitons in the low-density regime.[2]

To avoid these limitations one might better go back to the microscopically oriented theories, but try to extend their range of validity. In Ref. 15 a model has been introduced, in which thermal equilibrium was assumed between an ionized-carrier system and a screened-exciton system. From the preliminary results it was argued that microscopic properties, especially the band structure, should strongly influence the phase diagram, even qualitatively. The idea of two separate subsystems has been applied by Haug[16] as a consequent extension of Silver's work.[11]

The ionization equilibrium has been more rigorously discussed by Kraeft and co-workers,[17] at the cost of a rather crude approximation of the band structure. They argued that in addition to the high-density condensate, additional instabilities in the intermediate-density regime might occur: This relates to the problem of a separate, discontinuous Mott transition,[18] which is also expected to depend sensitively on microscopic properties of the system. It is, therefore, appealing to use these properties as a starting point.

To the author's knowledge, the electron-hole plasma in semiconductors is, so far, the only system for which a first-principles calculation of the phase diagram can approximately be carried out. This will be the main topic of the present paper. Of course, this does not render the theories based on the universal aspect of critical phenomena redundant. As will be seen, our approach will have to make use of a series of approximations, which limit its reliability because of principle and numerical reasons especially near the critical point.

II. SYSTEM OF ELEMENTARY EXCITATIONS

A. Basic assumptions

The electronic ground state of a semiconductor at $T=0$ is characterized by completely filled valence bands and empty conduction bands. The excited states of this real interacting many-body system of valence electrons will have to be considered now. They can as usual[19] be classified as collective excitations like the plasma oscillation and elementary excitations, which are separated from the ground state by an energy gap E_g.

In the present case the elementary excitations consist of electron-hole pairs, which are both assumed to populate the respective band extrema only. We can therefore apply the effective-mass approximation. As long as the density n_{tot} of the elementary excitations is very small (e.g., at small temperatures), they can be considered as independent particles forming an ideal Boltzmann gas. Appreciably higher densities can be obtained, if the electronic system is coupled to an external photon field of energy $h\nu > E_g$. This will introduce two novel features.

First of all, the system of elementary excitations will no longer be in thermal equilibrium, and the distribution function of electrons and holes might in principle be derived from a Boltzmann equation, in the simplest case within the relaxation-time approximation. Now, the existence of an energy gap allows us to define *two* different relaxation times: the relaxation time of the electrons and holes within their respective bands τ_R and the lifetime τ of the excitations. If the condition

$$\tau_R \ll \tau \tag{1}$$

is satisfied, one can postulate a quasiequilibrium distribution of electrons and holes characterized by an effective temperature T. This temperature will result from the combined effect of excitation and dissipative processes, but will, as usual, be treated as an external parameter here. This concept allows us to use equilibrium thermodynamics. Of course, stable states found in that way can at most be metastable; whether these states will be reached in an actual experiment, cannot be decided on these grounds.

Second, the elementary excitations will no longer be independent, leading to cooperative properties of the system. The correlations between the electrons and holes are of two types: they derive from interparticle forces and from quantum statistics (cf. Ref. 20). The interparticle forces are simply Coulomb type, statically screened by the crystal surroundings. Unfortunately there is a difficult interplay between these correlations and the statistics. As is well known,[21] the electron-hole system is unstable against formation of bound electron-hole pairs. So below a critical density excitons are formed.[6] As a qualitative measure for this critical density the so-called Mott criterion has widely been used[22]

$$n_{\text{Mott}} a_B^{*3} \sim 0.016. \tag{2}$$

Here a_B^* is the Bohr radius of the unperturbed exciton. n_{Mott} is more generally defined by

$$E_b(n_{\text{tot}}, T) = 0 \quad \text{for } n_{\text{tot}} > n_{\text{Mott}}(T), \tag{3}$$

where E_b denotes the screened exciton binding energy. For $n_{\text{tot}} \ll n_{\text{Mott}}$ we expect a system of interacting excitons, which, at least approximately, should obey Bose statistics.[23] Above n_{Mott}, on the other hand, the electron-hole multiple scattering is of less importance,[6] and the system may be viewed as a two-component Fermi system.

This brief survey already indicates that a theory for the correlations of a wide range of densities will be very difficult. In fact, this problem is far from being solved satisfactorily, so a number of approximations are the prerequisites of any theory.

Here the ground state of the many-body system of elementary excitations at low effective temperatures will be studied only. However, one should keep in mind that the highly degenerate condensate will again have excited states such as collective excitations (e.g., plasma oscillations of the electron-hole system) and even elementary excitations. These elementary excitations (of second order) will not be separated from the ground state by an energy gap,[24] so there should be no continuation of this hierarchy.

B. Unstable regions and model assumptions

Phase transitions are typical examples of cooperative effects. There are various possibilities to define such transitions in terms of characteristic functions. For convenience, we choose the particle density n_{tot} as a function of the chemical potential μ. A gas-liquid type transition is then characterized by a discontinuity of $n_{\text{tot}}(\mu)$ for a given temperature. Our investigation will therefore require the approximate calculation of that function or its inverse, $\mu(n_{\text{tot}}, T)$. Thermodynamic stability imposes the condition[25]

$$\left(\frac{\partial \mu(n_{\text{tot}}, T)}{\partial n_{\text{tot}}}\right)_{V,T} \geq 0. \tag{4}$$

Violation of this condition also indicates a phase transition. We will assume now that the system decomposes into two subsystems: an exciton gas of density n_{ex} and a two-component plasma of density n, for which electron-hole multiple scattering will be neglected

$$n_{\text{tot}} = n + n_{\text{ex}}. \tag{5}$$

This assumption considerably simplifies the treatment of the ionization equilibrium. Thermal equilibrium between the subsystems requires

$$\mu_{eh}(n, n_{\text{ex}}, T) = \mu_{\text{ex}}(n_{\text{ex}}, n, T), \tag{6}$$

where μ_{eh} and μ_{ex} are the chemical potentials of the plasma and the exciton system, respectively. Mutual interactions between the subsystems have been formally included by letting the potentials depend on both densities.

Equations (5) and (6) implicitly define $n(n_{\text{tot}})$ and $n_{\text{ex}}(n_{\text{tot}})$ for any T, with

$$\left(\frac{\partial n}{\partial n_{\mathrm{tot}}}\right)_T + \left(\frac{\partial n_{\mathrm{ex}}}{\partial n_{\mathrm{tot}}}\right)_T = 1. \tag{7}$$

By definition

$$\left.\begin{aligned} n(n_{\mathrm{tot}}) &= n_{\mathrm{tot}} \\ n_{\mathrm{ex}}(n_{\mathrm{tot}}) &= 0 \end{aligned}\right\} \text{ for } n_{\mathrm{tot}} > n_{\mathrm{Mott}}. \tag{8}$$

In general we may use

$$\mu(n_{\mathrm{tot}}, T) = \mu_{eh}(n(n_{\mathrm{tot}}), n_{\mathrm{ex}}(n_{\mathrm{tot}}), T) \tag{9}$$

as the chemical potential of the electron-hole system. This is the only thermodynamic function physically relevant to our problem. The decomposition into ionized and bound states only serve as an approximate method of calculation. The ionization degree will be given by

$$\alpha = n/n_{\mathrm{tot}}. \tag{10}$$

The thermodynamic potentials remain continuous where bound states disappear,[17] i.e., for $\alpha \to 1$. According to Eq. (4), unstable regions arise when

$$\left(\frac{\partial \mu(n_{\mathrm{tot}}, T)}{\partial n_{\mathrm{tot}}}\right)_T = \left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}} + \left[\left(\frac{\partial \mu_{eh}}{\partial n_{\mathrm{ex}}}\right)_{T,n} - \left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}}\right] \times \left(\frac{\partial n_{\mathrm{ex}}}{\partial n_{\mathrm{tot}}}\right)_T < 0. \tag{11}$$

The well-known instability leading to metallic drops will be shown to be due to $(\partial \mu_{eh}/\partial n)_{T, n_{\mathrm{ex}}} < 0$ in the intermediate density range. Additional instabilities might occur at lower densities in spite of $(\partial \mu_{eh}/\partial n)_{T, n_{\mathrm{ex}}} > 0$. Two cases can be considered: If

$$\left(\frac{\partial \mu_{eh}}{\partial n_{\mathrm{ex}}}\right)_{T,n} > \left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}} > 0, \tag{12}$$

condition (11) requires

$$\left(\frac{\partial n_{\mathrm{ex}}}{\partial n_{\mathrm{tot}}}\right)_T < -\left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}} \left[\left(\frac{\partial \mu_{eh}}{\partial n_{\mathrm{ex}}}\right)_{T,n} - \left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}}\right]^{-1}, \tag{13}$$

which is more restricting than

$$\left(\frac{\partial n_{\mathrm{ex}}}{\partial n}\right)_T = \left(\frac{\partial n_{\mathrm{ex}}}{\partial n_{\mathrm{tot}}}\right)_T - 1 < 0, \tag{14}$$

discussed in Ref. 17. Inequality (14) is necessary, but not sufficient for the existence of an additional instability. This explains why Haug[16] could find stability where condition (14) was satisfied.

The nature of the two coexisting phases follows from Eq. (13). The high-density phase was characterized by a high ionization degree, while the low-density phase was exciton rich. Consequently, a discontinuous metal-nonmetal transition could be expected before the proper gas-liquid transition sets in.[17,18]

Then, if (12) does not hold, a different type of instability might occur for

$$\left(\frac{\partial n_{\mathrm{ex}}}{\partial n}\right)_T > -\left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}} \times \left[\left(\frac{\partial \mu_{eh}}{\partial n_{\mathrm{ex}}}\right)_{T,n} - \left(\frac{\partial \mu_{eh}}{\partial n}\right)_{T, n_{\mathrm{ex}}}\right]^{-1} > 0. \tag{15}$$

In this case the high-density phase had the (relative) lower ionization degree, the Mott transition should then occur at densities above the equilibrium density of this "dielectric drop." Up to now there is no experimental evidence for such a collectively bound exciton state. It was argued in Ref. 6 that the attractive interaction between excitons might be too weak. A final conclusion on that will have to be based on a more careful study of the exciton-exciton interaction.[26-28]

We will now introduce simplifying assumptions, which will allow a straightforward theory for the electron-hole system. When the excitons do not influence the free-carrier system neither by a contribution to the dielectric constant, by occupying parts of the electron and hole $\vec{k}$ spaces, nor by scattering, we will have

$$\left(\frac{\partial \mu_{eh}}{\partial n_{\mathrm{ex}}}\right)_{n,T} = 0. \tag{16}$$

An additional instability could then occur only under the condition of Eq. (15), i.e.,

$$\left(\frac{\partial n_{\mathrm{ex}}}{\partial n_{\mathrm{tot}}}\right)_T > 1, \tag{17}$$

which implies $(\partial n/\partial n_{\mathrm{tot}})_T < 0$. Now, if we take repulsive exciton-exciton interactions[27] only, condition (17) cannot be satisfied. On the contrary, screening of excitons will guarantee $(\partial n/\partial n_{\mathrm{tot}})_T > 0$. So no additional instability can be expected. At the same time exciton molecules will not be formed, which is consistent with the basic idea of our two-subsystem model. On the other hand, this means—at least within this model—that the inclusion of strong excitonic contributions to the dielectric constant, to the Pauli exclusion and/or attractive exciton-exciton interactions is necessary to establish additional unstable regions.

In the following paragraphs we will approximately derive $\mu_{eh}(n, T)$ and $\mu_{\mathrm{ex}}(n_{\mathrm{ex}}, n, T)$. This will be done in several steps; we first consider the internal energy of the free-carrier system.

III. TWO-COMPONENT PLASMA

A. Internal energy

The Hamiltonian of the $2N$-particle system (N electrons and N holes in a volume V) can be written

$$H^N = H^N_{\mathrm{kin}} + H^N_x + H^N_c, \tag{18}$$

where H^N_{kin} denotes the kinetic, H^N_x the exchange, and H^N_c the correlation part. The corresponding energy E^N may conveniently be defined in terms of the mean energy per pair:

$$E_0(n,T) = E_{\mathrm{kin}} + E_x + E_c, \tag{19}$$

$$E^N = N[E_0(n,T) + E_g]. \tag{20}$$

The mean kinetic energy is obtained from

$$E_{\mathrm{kin}} = \frac{1}{N}\sum_{\vec{q},\sigma,j} E^0_j(\vec{q})n^{(j)}_{\vec{q},\sigma}. \tag{21}$$

$n^{(j)}_{\vec{q},\sigma}$ is the occupation number of the single-particle state

$$E^0_j(\vec{q}) = \hbar^2 q^2/2m_j \tag{22}$$

of momentum $\vec{q}$, spin σ, and band index j. The dispersion relation and the Fermi distribution function allow us to determine the mean kinetic energy of the particles in band j and density $n_j = N_j/V$,[25]

$$E_{\mathrm{kin}} = \frac{1}{N}\sum_j N_j E^{(j)}_{\mathrm{kin}}, \tag{23}$$

$$E^{(j)}_{\mathrm{kin}} = \frac{2^{1/2}m_j^{3/2}}{n_j\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{3/2}\,d\epsilon}{\exp[(\epsilon-\mu^0_j)/k_BT]+1}. \tag{24}$$

The parameters μ^0_j are implicitly defined by

$$n_j = [2^{1/2}(m_jk_BT)^{3/2}/\pi^2\hbar^3]J_{1/2}(\mu^0_j/k_BT), \tag{25}$$

where $J_s(x)$ denotes the Fermi integral

$$J_s(x) = \int_0^\infty \frac{z^s\,dz}{e^{z-x}+1}. \tag{26}$$

The exchange term is given by[19]

$$E_x = \frac{1}{N}\sum_j N_jE^{(j)}_x, \tag{27}$$

$$E^{(j)}_x = \frac{2\pi e^2}{N_jV\epsilon_0}\sum_{\substack{j,\vec{q},\sigma\\ \vec{k}}}\frac{1}{k^2}n^{(j)}_{\vec{q},\sigma}n^{(j)}_{\vec{q}+\vec{k},\sigma}. \tag{28}$$

E_x and E_{kin} represent the Hartree-Fock approximation.

E_c can be studied within different approaches,[6-8,15] which are largely equivalent. According to a model proposed by Overhauser[29] we describe the correlation by the coupling of a single particle to one effective plasmon mode $\omega_{\vec{k}}$:

$$H^N_c = \sum_{\vec{k}} h\,\omega_{\vec{k}}n_{\vec{k}} + \sum_{\substack{\vec{q},\sigma,j\\ \vec{k}}} M^j(\vec{k})(a^\dagger_{\vec{k}} + a_{-\vec{k}})c^{\dagger(j)}_{\vec{q}+\vec{k},\sigma}c^{(j)}_{\vec{q},\sigma}. \tag{29}$$

Here the $c^{\dagger(j)}_{\vec{q},\sigma}$ are the creation operators of the particles in state (22), $a^\dagger_{\vec{k}}$ the creation operator of an effective plasmon, and $n_{\vec{k}} = a^\dagger_{\vec{k}}a_{\vec{k}}$. The form factor $M^j(\vec{k})$ and the mode $\omega_{\vec{k}}$ itself are yet to be determined. Treating H^N_c as a perturbation, one can calculate the respective energy shift by second-order perturbation theory:

$$E^N_c = \sum_j N_jE^{(j)}_c = -\sum_j N_j(E^{(j)}_{x\,\mathrm{lr}} + W^{(j)}). \tag{30}$$

The long-range exchange energy is defined by

$$E^{(j)}_{x\,\mathrm{lr}} = -\frac{1}{N_j}\sum_{\substack{\sigma,\vec{q}\\ \vec{k}}} V_j(\vec{k},\vec{q})n^{(j)}_{\vec{q}+\sigma}n^{(j)}_{\vec{q}}, \tag{31}$$

and the Coulomb self-energy part by

$$W^{(j)} = \frac{1}{N_j}\sum_{\substack{\sigma,\vec{q}\\ \vec{k}}} V_j(\vec{k},\vec{q})n^{(j)}_{\vec{q},\sigma}, \tag{32}$$

where

$$V_j(\vec{k},\vec{q}) = \{|M^j(\vec{k})|^2/[\hbar\omega_{\vec{k}} + E^0_j(\vec{k}+\vec{q}) - E^0_j(\vec{q})]\}. \tag{33}$$

Here $\bar{n}_k = 0$ was assumed, i.e., no effective plasmons are present in the ground state.

It is known from the work of Bohm and Pines[30] that the introduction of proper plasmons freezes out the long-range part of the exchange and Coulomb self-energy. Guided by this idea one may define a cutoff wave vector $\tilde{k}^{(j)}_c$ such that

$$V_j(\vec{k},\vec{q}) = \begin{cases} 2\pi e^2/\epsilon_0Vk^2 & \text{for } k \le \tilde{k}^{(j)}_c, \\ 0 & \text{for } k > \tilde{k}^{(j)}_c. \end{cases} \tag{34}$$

Then one gets, according to Eq. (32),

$$W^{(j)} = (e^2/\pi\epsilon_0)\tilde{k}^{(j)}_c. \tag{35}$$

This can only be true if

$$\tilde{k}^{(j)}_c = \frac{\pi\epsilon_0}{e^2N_j}\sum_{\substack{\sigma,\vec{q}\\ \vec{k}}}\frac{|M^{(j)}(\vec{k})|^2n^{(j)}_{\vec{q},\sigma}}{h\omega_{\vec{k}} + E^0_j(\vec{k}+\vec{q}) - E^0_j(\vec{q})}. \tag{36}$$

Equation (31) can now easily be combined with Eq. (28) to give the short-range exchange energy per particle in band j

$$E^{(j)}_{x\,\mathrm{sr}} = E^{(j)}_x - E^{(j)}_{x\,\mathrm{lr}} = -\frac{2\pi e^2}{V\epsilon_0N_j}\sum_{\substack{\sigma,\vec{q},\vec{k}\\ k>\tilde{k}^{(j)}_c}}\frac{1}{k^2}n^{(j)}_{\vec{q}+\vec{k},\sigma}n^{(j)}_{\vec{q},\sigma}. \tag{37}$$

For $T=0$ this equation gives[19]

$$E^{(j)}_{x\,\mathrm{sr}} = -(3e^2/4\pi\epsilon_0)k^{(j)}_F(1 - \tfrac{4}{3}Y_j + \tfrac{1}{2}Y_j^2 - \tfrac{1}{48}Y_j^4), \tag{38}$$

where

$$Y_j = \tilde{k}^{(j)}_c/k^{(j)}_F < 2. \tag{39}$$

$k^{(j)}_F$ is the Fermi wave vector of the particles in band j. The energy $E^{(j)}_{x\,\mathrm{sr}}$ turns out to be negligible compared to $W^{(j)}$ for small densities (compare Fig. 1), where the finite temperature becomes important. So we may simply use this $T=0$ result for the total-density regime studied here.

The exchange-correlation energy E_{xc} can now alternatively be written

$$E^{(j)}_{xc} = E^{(j)}_{x\,\mathrm{sr}} - W^{(j)} = E^{(j)}_x + E^{(j)}_c. \tag{40}$$

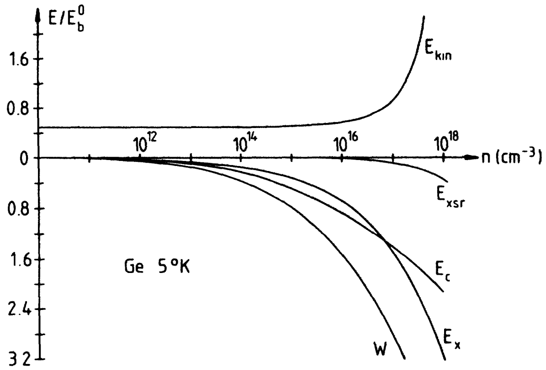

FIG. 1. Contributions to the internal energy per pair of the free-carrier system in Ge at $T = 5$ K.

This energy is determined once we know $\tilde{k}_c^{(j)}$. Also the temperature comes in only via $\tilde{k}_c^{(j)}$.

B. Determination of $\tilde{k}_c^{(j)}$

The effective plasmon mode is supposed to approximate the dielectric response of the system, characterized by

$$\epsilon(k,T) = 1 + 4\pi \sum_j \alpha_j(k,T), \tag{41}$$

where α_j is the polarizability[19]

$$\alpha_j(k,T) = \frac{e^2}{\epsilon_0 V k^2} \sum_{\vec{q},\sigma} \frac{n^{(j)}_{\vec{q}+\vec{k},\sigma} - n^{(j)}_{\vec{q},\sigma}}{E_j^0(\vec{q}) - E_j^0(\vec{q}+\vec{k}) + i\delta}. \tag{42}$$

At $T = 0$ one gets[19]

$$\alpha_j(k,0) = Q_j(k) k_c^{(j)}(0)^2 / 4\pi k^2, \tag{43}$$

with $k_c^{(j)}(0)$ being the Thomas-Fermi wave vector

$$k_{\mathrm{TF}}^{(j)2} = 6\pi n_j e^2 / \epsilon_0 E_F^j, \tag{44}$$

and $E_F^{(j)}$ the Fermi energy. The k-dependent term is given by

$$Q_j(k) = \frac{F(k/2k_F^{(j)})}{1 + S_j(k/2k_F^{(j)}) F(k/2k_F^{(j)})}, \tag{45}$$

with

$$F(x) = \tfrac{1}{2} + [(1-x^2)/4x] \ln|(1+x)/(1-x)|, \tag{46}$$

$$S_j(x) = 2x^2/(1 + 4x^2 + \beta_j). \tag{47}$$

S_j classifies different levels of approximation for the exchange-correlation corrections to the dielectric response. The Lindhard formula with $S_j = 0$ neglects these corrections completely, with $\beta_j = 0$, only exchange corrections in the Hubbard scheme are considered, whereas with $\beta_j \neq 0$ also correlation effects are included. According to Singwi[31] we adopt

$$\beta_j = k_{\mathrm{TF}}^{(j)} / k_F^{(j)}. \tag{48}$$

For $T > 0$ we have, instead of Eq. (44),[32]

$$k_c^{(j)2} = k_{\mathrm{DH}}^{(j)2} J_{-1/2}(\mu_j^0/k_B T) [J_{+1/2}(\mu_j^0/k_B T)]^{-1}, \tag{49}$$

where

$$k_{\mathrm{DH}}^{(j)} = 4\pi n^j e^2 / \epsilon_0 k_B T \tag{50}$$

is the classical Debye-Hückel screening wave vector. In the nondegenerate case, $T \gg T_0^{(j)}$,

$$T_0^{(j)} = \frac{\hbar^2 2\pi}{2^{2/3} m_j k_B} n_j^{2/3}, \tag{51}$$

$k_c^{(j)}(T)$ approaches $k_{\mathrm{DH}}^{(j)}(T)$.

The important range of k contributing to the calculation of $\tilde{k}_c^{(j)}$ is roughly given by $0 < k < k_c$. For this range we have in the highly degenerate case

$$k/2k_F \lesssim k_c(0)/2k_F \sim n^{-1/6} \rightarrow 0, \tag{52}$$

as well as for low densities at finite temperatures

$$k/2k_F \lesssim k_c(T)/2k_F \sim n^{1/6} T^{-1/2} \rightarrow 0, \tag{53}$$

i.e., in both limits the long-wavelength behavior of $\epsilon(k,T)$ dominates $\tilde{k}_c^{(j)}$. We may therefore neglect the temperature dependence of $Q(k)$ and write $\epsilon(k,T)$ in the factorized form

$$\epsilon(k,T) = 1 + k^{-2} \sum_j k_c^{(j)}(T)^2 Q_j(k). \tag{54}$$

Requiring the single mode $\omega_{\vec{k}}$ to reproduce this $\epsilon(k,T)$ leads to the condition[29]

$$\omega_k^2 = \omega_P^2 \epsilon(k,T) / [\epsilon(k,T) - 1], \tag{55}$$

where

$$\omega_P^2 = \frac{4\pi e^2}{\epsilon_0} \sum_j \frac{n_j}{m_j}. \tag{56}$$

In order to demonstrate the properties of the dispersion relation (55), one may consider a single-component plasma for small k:

$$\omega_k^2 = \omega_P^2 + C k^2 + \cdots. \tag{57}$$

In the nondegenerate case, $T \gg T_0$, it is found

$$C = k_B T / m, \tag{58}$$

as compared with $C' = 3C$ for the proper plasma mode.[30] For $T \ll T_0$,

$$C = \tfrac{1}{3} v_F^2, \tag{59}$$

where now $C' = 9/5C$. Here v_F is the Fermi velocity. The k dependence is obviously reduced.

$M^j(k)$ is determined with the help of the f sum rule

$$\sum_t E_{jt0} |(\rho_k)_{t0}|^2 = \frac{e^2 \hbar^2 k^2}{2} \sum_j \frac{N_j}{m_j}. \tag{60}$$

Here

$$\rho_{\vec{k}} = \sum_l e_l \exp(-i\vec{k} \cdot \vec{r}_l) \tag{61}$$

is the Fourier transform of the charge density, e_l the charge of particle l, and E_{t0} the energy difference between the ground state and any excited state t of the system. If the single mode $\omega_{\mathbf{k}}$ is required to fulfill this sum rule, one gets in analogy to Overhauser[29]

$$M^j(\vec{\mathrm{k}}) = -e_j(2\pi\hbar\omega_p^2/\epsilon_0 k^2 \omega_k V_q)^{1/2}[1 - S_j(k/2\pi k_F^{(j)})]. \tag{62}$$

We now can proceed to calculate $\tilde{k}_c^{(j)}$ according to Eq. (36). It turns out that the q dependence can be neglected, so that

$$\tilde{k}_c^{(j)} = \frac{\pi\epsilon_0}{e^2}\sum_{\mathbf{k}}\frac{|M^{(j)}(\vec{\mathrm{k}})|^2}{\hbar\omega_{\mathbf{k}} + \hbar^2 k^2/2m_j}, \tag{63}$$

$$\tilde{k}_c^{(j)}(T) = \int_0^\infty \frac{[\epsilon(k,T) - 1](1 - S_j)^2\, dk}{\epsilon(k,T)(1 + \hbar^2 k^2/2m_j\hbar\omega_{\mathbf{k}})}. \tag{64}$$

It is easily proved that, for $T \gg T_0^{(j)}$,

$$\tilde{k}_c^{(j)} = \tfrac{1}{2}\pi k_{\mathrm{DH}}, \tag{65}$$

so $E_{xc}^{(j)} \sim W^{(j)}$ in this case is the classical Debye-Hückel energy[25] of an interacting system of point charges:

$$W^{(j)} = +(e^2/2\epsilon_0)k_{\mathrm{DH}}. \tag{66}$$

k_{DH} is the total screening wave vector of the system. As expected, in the high-density limit $E_{xc}^{(j)}$ approaches the exchange energy as Y_j in Eq. (38) goes to zero.

C. Band structure

We consider only the lowest conduction-band minima, which consist of $g = 4$(Ge) and $g = 6$(Si) equivalent valleys, respectively, characterized by an anisotropic effective mass $\{m_t, m_l\}$. With $n_e = n/g$ the mean energy E^e of an electron in any of these valleys will be the same. Intervalley scattering is not considered. From this anisotropic mass the optical mass

$$m_{oe}^{-1} = \tfrac{1}{3}(2/m_t + 1/m_l) \tag{67}$$

can be defined, and the density-of-states mass

$$m_{de} = m_t^{2/3} m_l^{1/3}, \tag{68}$$

which enters the kinetic energy, Eq. (24), and T_0^e according to Eq. (51). The exchange energy of anisotropic bands has been studied in Ref. 7. It turns out that the ellipsoidal Fermi volume can be substituted by a sphere of radius

$$k_F^e = (3\pi^2 n_e)^{1/3}\phi(\gamma_e), \tag{69}$$

where

$$\gamma_e = m_t/m_l < 1 \tag{70}$$

and

$$\phi = \gamma_e^{1/6}\sin^{-1}(1 - \gamma_e)^{1/2}/(1 - \gamma_e)^{1/2}. \tag{71}$$

The calculation of W^e is based on the optical mass.

The valence bands to be included here are a heavy-hole band m_{hh} and a light-hole band m_{lh}; warping of the bands is neglected (compare Ref. 6). The Fermi wave vector k_F^h, i.e., the maximum momentum occupied at $T = 0$, will be given by

$$k_F^h = [3\pi^2 n/(1 + \gamma_h^{3/2})]^{1/3}, \tag{72}$$

with

$$\gamma_h = m_{\mathrm{lh}}/m_{\mathrm{hh}}, \tag{73}$$

which is a fundamental property of the Fermi liquid and independent of interactions. The temperature of degeneracy is the same in both bands and denoted by T_0^h. For the calculation of E_{xc}^h the two hole bands are substituted by two isotropic bands of mass[6]

$$m_{oh}^{-1} = \tfrac{1}{2}(1/m_{\mathrm{hh}} + 1/m_{\mathrm{lh}}). \tag{74}$$

Inter-valence-band coupling[7] is thus neglected. m_{oh} and m_{oe} are used to define the exciton Rydberg energy E_b^0.

D. Chemical potential

The free energy F^N is related to E^N by[25]

$$F^N = E^N + \left(\frac{\partial F^N}{\partial T}\right)_{V,N} T, \tag{75}$$

so the chemical potential can be obtained from

$$\mu_{eh}(T) = \left(\frac{\partial F^N}{\partial N}\right)_{T,V} = \left(\frac{\partial E^N}{\partial N}\right)_{T,V} + \left(\frac{\partial \mu_{eh}}{\partial T}\right)_{V,N} T \tag{76}$$

or

$$\mu_{eh}(T) = f(T) + T\mu_{eh}'(T), \tag{77}$$

where

$$f(T) = E_0 + n\left(\frac{\partial E_0}{\partial n}\right)_T \tag{78}$$

and E_0 is the mean energy per pair for a given density, Eq. (19). This linear differential equation can be solved numerically with the help of polynomial expansions, asymptotically correct for $T > T_0$, and $T < T_0$, respectively.

$$T_0 = (T_0^e T_0^h)^{1/2}. \tag{79}$$

These expansions are, for $T > T_0$,

$$f(T) = a_1 T + a_0 + a_{1/2}T^{-1/2} + \cdots, \tag{80}$$

which gives

$$\mu_{eh}(T) = a_0 + a_1 T\ln(T_0 T^{-1}) + \tfrac{2}{3}a_{1/2}T^{-1/2} \tag{81}$$

and, for $T < T_0$,

$$f(T) = a_0 + a_2 T^2 + a_4 T^4 + \cdots, \tag{82}$$

which leads to the solution

$$\mu_{eh}(T)=a_0-a_2T^2-\tfrac{1}{3}a_4T^4-\cdots\,. \tag{83}$$

The coefficients a_j are found by a numerical fit of the function $f(T)$ to the polynomials (80) or (82), respectively. For low temperatures the last term in Eq. (83) can be neglected. $\delta=a_2$ for the equilibrium density n_0 of the condensate has been considered by various authors.[5,9] Our result is given in Table I. This completes the discussion of the plasma subsystem.

IV. EXCITON SYSTEM

A. Renormalization

According to our approximations any influence of the exciton system on the free carriers is neglected, but not vice versa. The renormalization of the excitons is consistently described by a coupling to the effective plasmon field

$$H^{(2)}=H_0^{(2)}+\sum_{\vec{k}}\hbar\omega_{\vec{k}}n_{\vec{k}}+\sum_{\vec{k}}\left[M^e(\vec{k})a_{\vec{k}}e^{i\vec{k}\cdot\vec{r}_e}+M^h(\vec{k})a_{\vec{k}}e^{i\vec{k}\cdot\vec{r}_h}\right]+\text{c.c.}, \tag{84}$$

where

$$H_0^{(2)}=\hbar^2q_e^2/2m_{oe}+\hbar^2q_h^2/2m_{oh}-e^2/\epsilon_0 r_{eh} \tag{85}$$

is the Hamiltonian of the unperturbed single exciton, which defines the Rydberg energy E_b^0. Owing to the complicated band structure, E_b^0 deviates from the experimental value E_b. The reduced mass will therefore be fit to reproduce E_b.

Equation (84) is in complete analogy with the Hamiltonian for an exciton in a polar medium. So similar methods can be used to calculate the ground-state energy. We apply a variational method first proposed by Haken,[33] which, however, does not include exchange corrections. One gets the effective Hamiltonian

$$H_{\text{eff}}^{(2)}=H_0^{(2)}+V^e(r_{eh})+V^h(r_{eh})-W^e-W^h, \tag{86}$$

$$V^{e,h}(r_{eh})=\sum_{\vec{k}}\frac{M^{e,h}(\vec{k})^2e^{-i\vec{k}\cdot\vec{r}_{eh}}}{h\omega_{\vec{k}}+\hbar^2k^2/2m_{e,h}}. \tag{87}$$

If exchange is included, we expect $E_{xc}^{e,h}$ instead of $W^{e,h}$. For weakly bound excitons it suffices to use the dielectric function in the long-wavelength limit. Equation (87) can then be solved analytically to give

$$V^{e,h}(r_{eh})=\frac{e^2}{2\epsilon_0 r_{eh}}\left(1+\frac{k_c^2R_{e,h}^2}{1-k_c^2R_{e,h}^2}e^{-r_{eh}/R_{e,h}}-\frac{1}{1-k_c^2R_{e,h}^2}e^{-k_c r_{eh}}\right), \tag{88}$$

with

$$R_{e,h}=(\hbar^2/2m_{e,h}\hbar\omega_p)^{1/2}. \tag{89}$$

This solution is identical with the Thomas-Fermi result only for $k_c^2R_{e,h}^2\to 0$, k_c is the total wave vector according to Eq. (49). In general, (88) includes "dynamical" effects, which make the screening by light particles more effective, as they are

TABLE I. Results. E_0 is the ground-state energy per pair in the condensate; φ is the work function for $T\sim 0$; E_F is the Fermi energy in the condensate at $T\sim 0$; $\Delta_{1/2}$ is the recombination half width; n_0 is the equilibrium density of the condensate; n_c is the critical density; T_c is the critical temperature; and for δ see Eq. (83).

	Ge		Si	
	Theory	Experiment	Theory	Experiment
$E_0(n_0,0)$ (meV)	5.9	5.9 [a]	19.6	
φ (meV)	1.8	1.8 [a]	4.9	8.2 [b]
$E_F(n_0,0)$ (meV)	6.12	6.43 [c]	20.5	22.2 [b]
$\Delta_{1/2}$ (meV)	3.24	3.4 [d]	11.2	11 [e]
n_0 (cm^{-3})	2.26×10^{17}	2.38×10^{17} [f]	3.0×10^{18}	3.33×10^{18} [b]
n_c (cm^{-3})	7×10^{16}	8×10^{16} [g]	4×10^{17}	1.3×10^{17} [h]
T_c (K)	7	6.5 [f]	20	20 [i], 33± 6 [i]
δ (meV K^{-2})	16×10^{-3}	15.5×10^{-3} [a]	3.6×10^{-3}	5.9×10^{-3} [b]

[a] See Ref. 39.

[b] See Ref. 5.

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able to react instantaneously to the motion of the particles under consideration. The binding energy $E_b(n,T)$ is then calculated from Eq. (86) using a hydrogenic trial wave function. The total potential energy is

$$E^{\mathrm{ex}}_{\mathrm{pot}}(n,T) = -E_b(n,T) + E^{e}_{xc} + E^{h}_{xc}. \tag{90}$$

B. Chemical potential

The chemical potential in the nondegenerate case

$$T > T_0^{\mathrm{ex}} = (2\pi\hbar^2/M_{\mathrm{ex}}k_B)(n_{\mathrm{ex}}/g_{\mathrm{ex}})^{2/3} \tag{91}$$

will be given by[25]

$$\mu_{\mathrm{ex}}(n_{\mathrm{ex}},n,T) = \tfrac{3}{2}\ln(T_0^{\mathrm{ex}}/T) - 2^{-3/2}k_B T_0^{\mathrm{ex}}(T_0^{\mathrm{ex}}/T)^1 + E_{\mathrm{pot}}(n,T) + E_{\mathrm{ex\text{-}ex}}(n_{\mathrm{ex}}). \tag{92}$$

The second term is a quantum correction and the third term is given by Eq. (90). The last term approximately describes the exciton-exciton interaction due to exchange and Pauli repulsion[2]

$$E_{\mathrm{ex\text{-}ex}}(n_{\mathrm{ex}}) = \tfrac{1}{3}26\pi a_B^{*3} n_{\mathrm{ex}} E_b^0. \tag{93}$$

This equation is expected to hold approximately also for finite temperatures. Attractive contributions to the exciton-exciton interaction, mainly of the Van der Waals type, are not considered, as they might lead to additional instabilities. A study of these requires a more elaborate treatment of the exciton system than undertaken in this paper.

V. PHASE DIAGRAM

The calculation of the phase diagram is carried out step by step in the following way: From the input data given in Table II the mean kinetic energy per pair, $E_{\mathrm{kin}}(n,T)$ and $E_{xc}(n,T)$, according to Eq. (40) are calculated; results for Ge for $T = 5$ K are shown in Fig. 1. As already discussed, $E_{x\,\mathrm{sr}}$ is negligible for small densities, while E_x dominates E_{xc} in the high-density limit. $E_0(n,T)$ according to Eq. (19) is shown in Fig. 2 and exhibits the minimum behavior typical for all the electron-hole plasmas at low temperature, be it in Ge, Si or any other semiconductor. This minimum, due to a combined effect of attractive correlations and the Pauli repulsion, is already present in a simple Hartree-Fock calculation.[34] If stable, the equilibrium density n_0 of the condensate at $T = 0$ is just defined by $\partial E_0/\partial n = 0$. Obviously, this condensation will strongly be influenced by quantum statistics, and it may therefore be termed quantum condensation. The classical condensation (like the Van der Waals type instability) comes about via direct interparticle forces, independent of whether the constituent particles are bosons or fermions (compare Ref. 20, also Ref. 5). This Fermi condensation may therefore be discussed in connection with the Bose-Einstein condensation of interacting bosons. Originally, however, this latter condensation has been introduced with respect to ideal systems (for a recent review see Ref. 36).

TABLE II. Input data.[a]

	m_l	m_t	m_{lh}	m_{hh}	ϵ_0	E_b^0 (meV)
Ge	1.58	0.082	0.042	0.342	15.36	2.66
Si	0.916	0.1905	0.154	0.523	11.4	13.0

[a] See Ref. 6.

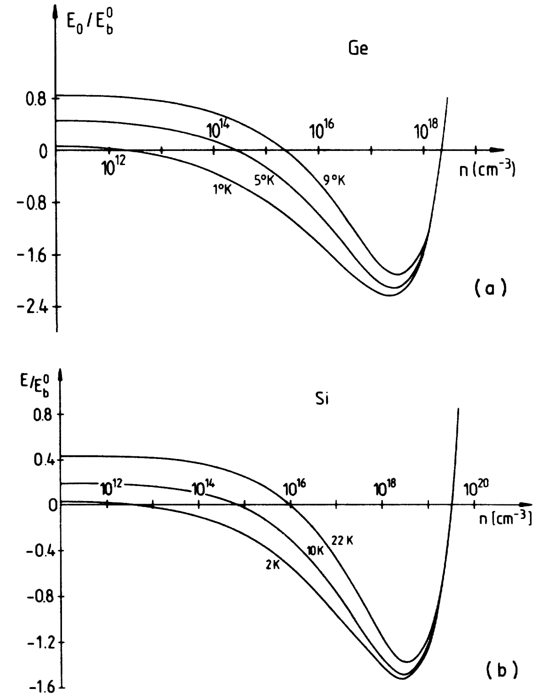

FIG. 2. Internal energy $E_0(n,T)$ of the free-carrier system as a function of density n. (a) Ge; (b) Si.

From $E_0(n,T)$ the corresponding chemical potential $\mu_{eh}(n,T)$ is found using Eq. (77). The result can be seen in Fig. 3. Below a critical temperature T_c there is a density region for which $(\partial\mu_{eh}/\partial n)_T < 0$. Also in the presence of the exciton system this fact is basic to the occurrence of the metallic drop.

$\mu_{\mathrm{ex}}(n_{\mathrm{ex}},n,T)$ can now be calculated according to Eq. (92):

$$\mu_{\mathrm{ex}}(n_{\mathrm{ex}},n,T) = \mu_{\mathrm{ex}}(n_{\mathrm{ex}},0,T) + E^{\mathrm{ex}}_{\mathrm{pot}}(n,T) + E_b(0,T). \tag{94}$$

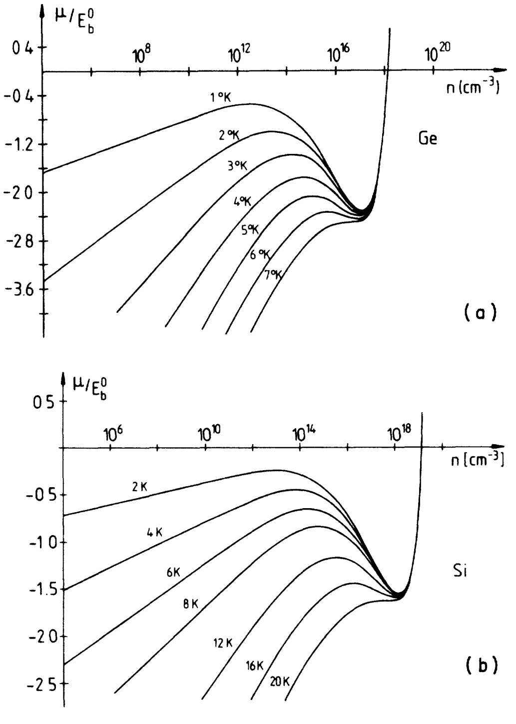

FIG. 3. Chemical potential $\mu_{ch}(n, T)$ of the free-carrier system as a function of density n. (a) Ge; (b) Si.

$E_{\mathrm{pot}}^{\mathrm{ex}}$ is shown in Fig. 4 for Ge. Contrary to $E_b(n, T)$ this potential energy is almost independent of n, in agreement with experiments on free-carrier screened excitons.[37] Finally, the chemical potential $\mu(n_{\mathrm{tot}}, T)$ is constructed according to Eq. (9). For any n and fixed T n_{ex} is derived from condition (6). As μ_{ex} is a monotonic function of n_{ex} (under the present approximations) this procedure uniquely determines $n_{\mathrm{tot}} \geq n$, corresponding to the value $\mu_{eh}(n, T)$. As indicated in Fig. 5, the influence of the excitons thus rescales the function $\mu_{eh}(n, T)$.

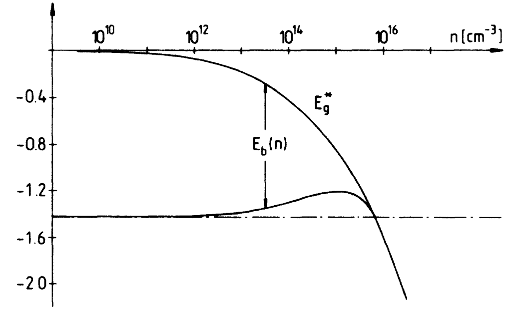

FIG. 4. Potential energy $E_{\mathrm{pot}}^{\mathrm{ex}}(n)$ for Ge at 5 K. $E_g^* = E_{xc} + E_g$.

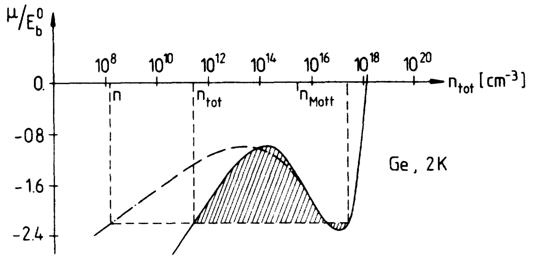

FIG. 5. Construction of $\mu(n_{\mathrm{tot}}, T)$. Explanation in text.

Of course, the regions of instability cannot be removed in that way. So the Maxwell construction is applied to this function $\mu(n_{\mathrm{tot}}, T)$

$$\oint \mu(n_{\mathrm{tot}}, T)\, dn_{\mathrm{tot}} = 0. \tag{95}$$

This construction, which enforces the vapor pressure to obey the Clausius-Clapeyron equation, is also sketched in Fig. 5. The resulting phase diagrams for Ge and Si are presented in Fig. 6. It is important to note that the inclusion of excitons leaves the properties of the liquid phase of density $n_0(T)$ practically unchanged, at least in Ge and Si. This may serve as a justification for the

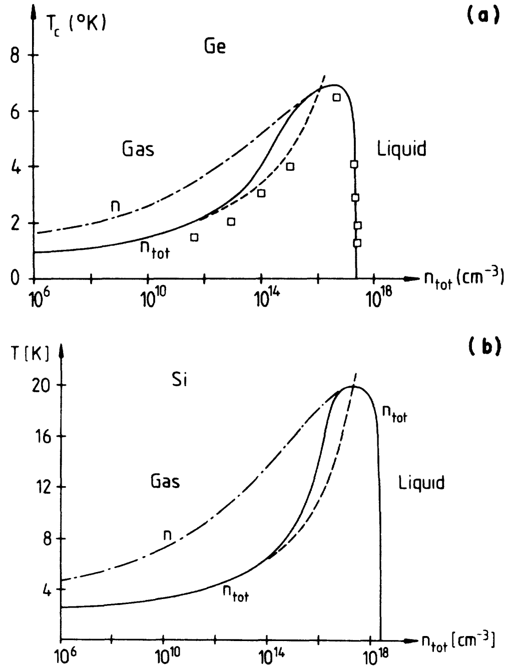

FIG. 6. Phase diagram. The dotted line is the density of the free-carrier gas in thermal equilibrium with the condensate. The broken line is the limit according to Eq. (97). (a) Ge, □ experimental points (Ref. 35, compare also Ref. 41); (b) Si.

use of simple-fluid models. In general, this is not true for other semiconductors, where drops might form in a high-pressure exciton gas only.[15]

The present result, obtained numerically, may be compared with a simple approximation valid for low densities of the gas phase. In this case, $n_{tot} \sim n$, and thermal equilibrium between gas and liquid leads to the condition

$$\mu_{ex}(n_{tot}, 0, T) = \mu_{eh}(n_0, T). \tag{96}$$

Assuming further the exciton gas to be an ideal Boltzmann gas this equation is equivalent to

$$n_{tot}(T) = g_{ex}(k_B T M_{ex}/2\pi\hbar^2)^{3/2} \exp[\varphi(T)/k_B T], \tag{97}$$

where

$$\varphi(T) = E_b(0, T) + \mu_{eh}(n_0, T) \tag{98}$$

is the work function, which in this limit and in a homogeneous theory determines the condensation curve.[2,38,39]

Unfortunately, an absolute determination of the gaseous phase boundary is very difficult. Instead, experimental data is usually interpreted on the basis of simple models like Eq. (97). However, as shown by Westervelt,[40] it tends to underestimate φ and overestimate n_{tot} due to oversaturation. Agreement between our theory and experiment[38] is considerably improved, when surface and lifetime effects are included (see Fig. 6).

The ionization degree of the gas phase in Ge is shown separately in Fig. 7. In agreement with experiment[3,41] the nature of the gas-phase changes from an exciton gas at low temperatures to an ionized plasma near T_c.

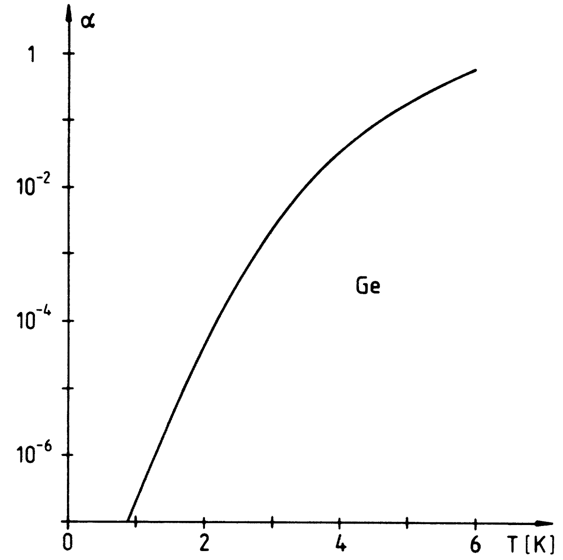

FIG. 7. Ionization degree of the gas phase as a function of temperature.

VI. SEMICONDUCTOR-METAL TRANSITION

The relation of the EHD theory to the semiconductor-metal transition has first been discussed by Brinkman and Rice.[6] Contrary to the situation discussed so far, the electrons and holes formed, when the indirect energy gap is reduced, will be in thermal equilibrium at the lattice temperature. It was argued that, in Ge and Si, a first-order transition directly to the metallic state should occur, when the gap equals the ground-state energy per particle of the metallic phase. This idea was adopted by Mott.[22] This model would confirm his original idea of a discontinuous change of the conductivity at the transition point. As we calculated the chemical potential of the electron-hole plasma, we can easily derive the free-carrier density as a function of the energy gap E_g from

$$\mu_{eh}(n, T) = -E_g. \tag{99}$$

The result for Ge is shown in Fig. 8, the corresponding phase diagram in Fig. 9. For $T > T_c$ the discontinuity in the free-carrier density disappears.

This model does not exclude the possibility of an excitonic phase[42] in general. However, it seems likely that even in semiconductors, where the metallic condensate is not the stable state of the carriers, the transition might *finally* be of this type.

VII. SUMMARY AND DISCUSSION

In this paper a first-principles calculation of the electron-hole phase diagram has been attempted. The main purpose has been to get a theoretical account of a number of characteristic parameters of the diagram as they depend on the band struc-

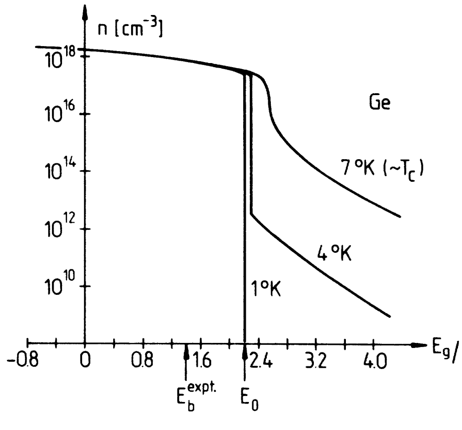

FIG. 8. Metal-semiconductor transition in Ge: the free-carrier density as a function of the indirect energy gap E_g.

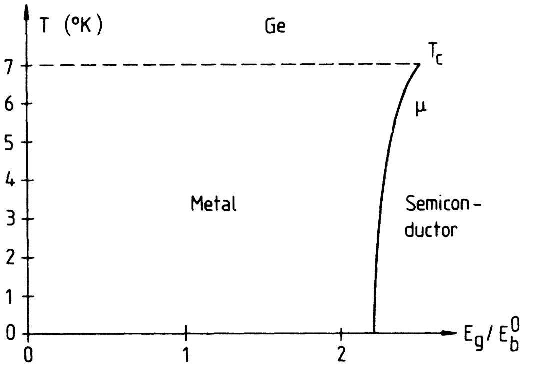

FIG. 9. Phase diagram of the metal-semiconductor transition in Ge.

ture. Improved studies in this direction will be necessary to clarify more delicate features, e.g., with respect to the Mott transition and the possible occurrence of the Bose-Einstein condensation. Here a number of approximations have been used, which limit the applicability of our method and will briefly be reviewed.

Our approach is based on a mean-field theory of the chemical potential $\mu(n_{\text{tot}}, T)$. Surface effects, which necessarily come into play with the phase separation, are neglected as well as lifetime effects. The equilibrium properties of the coexisting phases are obtained by means of a Maxwell construction.

The chemical potential is found assuming thermal equilibrium between two interacting subsystems, the ionized plasma and the exciton gas. The influence of exciton molecules as well as of excited exciton states is not taken into account. The excitons are assumed to interact via net repulsive forces due to exchange and Pauli principle. Renormalization of the excitons due to the presence of the plasma is included approximately. The results are expected to be rather insensitive to this renormalization procedure within the frame of our model, where additional instabilities are excluded. The chemical potential is derived from the respective internal energy $E_0(n, T)$ by means of an interpolation scheme between the classical and the quantum limit.

$E_0(n, T)$ has been studied within the effective plasmon approach, which allows a rather intuitive interpretation of Coulomb correlations. These depend on the dielectric constant, for which a modified Hubbard function has been used. Contributions from the exciton system are not considered. Multiple electron-hole scattering is completely neglected in the high-density limit. In the intermediate- and low-density regime this type of correlation becomes increasingly more important. In our model this effect is described by an increasing part of the pairs residing in the exciton subsystem. The instability leading to the phase transition, however, is basically due to the Fermi subsystem (Fermi condensation).

In addition to the figures some of the numerical results are comprised in Table I. We see that there is a good overall agreement between theory and experiment (the excellent results for Ge may be in part accidental), somewhat less good for Si. This latter situation was found for practically all theoretical investigations published so far[5] and might be due to inconsistent input data for Si. The resulting properties of the liquid are comparable to those found previously.[6-9] In addition we get a consistent set of data characteristic for the phase diagram.

It has thus been demonstrated that a first-principles calculation can account for the known properties of the electron-hole system in semiconductors, even quantitatively. The method, to be sure, is not suitable for a detailed investigation near the critical point, e.g., a study of critical exponents. An extension of the theory to include additional instabilities is possible and will be discussed elsewhere.

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