Electron-hole plasma in direct-gap semiconductors with low polar coupling: GaAs, InP, and GaSb

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The ground-state energy of the electron-hole plasma in GaAs, InP, and GaSb is determined using several spectroscopic techniques. Comparison with calculated values shows that the data can be understood within the many-body theory for a high-density plasma in semiconductors; however, the experimental values for the ground-state energy are lower than predicted from the theory. Although these results imply that binding of the electron-hole plasma should be possible, the existence of a liquid in GaAs could not be proven. The experimental data can be explained assuming that at least for temperatures higher than 7 K the density of the plasma is determined by the Mott density rather than by the equilibrium liquid density.

I. INTRODUCTION

Renormalization of the band-gap energy due to many-body interactions in highly excited direct-gap semiconductors, e.g., GaAs, has been observed and discussed by several authors.[1-3] Although the theoretical scheme to describe this effect has been developed in these early papers, the understanding of the properties of highly excited semiconductors advanced considerably after the discovery of electron-hole drops (EHD) in indirect-gap materials like Ge and Si.[4,5] It turned out that applying theoretical schemes that describe the many-body interactions of electrons in metals[6] to the two- or more-component plasma in semiconductors yields fundamental understanding of the observed phenomena.[7-10] In spite of the rather complex band structure of the indirect-gap materials the theoretical description of the ground-state energy E_G and the kinetics of the EHD is satisfactory.[4,5,11]

Although the situation in direct-gap semiconductors seems to be less complicated because of the simpler band structure, at present the situation is more controversial than in the indirect materials. For semiconductors with large polar coupling, an extended theory taking into account polaron effects[12-14] yields good agreement with the experimental data for CdS,[15-18] CdSe,[18,19] and ZnO.[20] The study of the electron-hole plasma (EHP) in direct-gap semiconductors with low polar coupling, like GaAs, InP, GaSb, etc., where polaron effects on E_G are expected to be small, should yield a more direct access to exchange and correlation effects. Up to now only little work has been reported for GaAs,[21-24] leading to different results on the ground-state energy E_G and its agreement with theory.

In this paper we report new experimental results on the EHP in GaAs. Furthermore, E_G for InP and GaSb has been determined for the first time and is compared with calculated values. The theory, as available for GaAs[7,10,25] is applied to InP and GaSb and the effects of finite temperature ($T>0$) are included. This will be reported in Sec. II of the paper. Section III will describe the experimental techniques. In Sec. IV we will then compare the experimental results with the theoretical values. This will show that for all three materials the ground-state energy E_G is lower than expected theoretically. The possibility of electron-hole-liquid (EHL) formation in GaAs finally will be discussed in Sec. V.

II. THEORETICAL CONCEPT

There have been different approaches to compute E_G for GaAs.[7,10,25] Essentially, these calculations differ in the approximations used to calculate the correlation energy E_c and in taking into account the valence band structure. Yet, the results of these various calculations differ only slightly. Therefore, to get an analytic expression for E_G, we have approximated E_c in the following way: besides the electrons, only the heavy holes have been taken into account. Then the values for E_c as given in Ref. 7 have been interpolated by a second-order polynomial. Since the kinetic and exchange energy can be expressed analytically anyhow, an analytic form for E_G is obtained (see below). A comparison of these results (broken line in Fig. 1) with, e.g., those of Mahler and Birman[10] (dotted line in Fig. 1) justifies our "polynome approximation." For InP and GaSb, no cal-

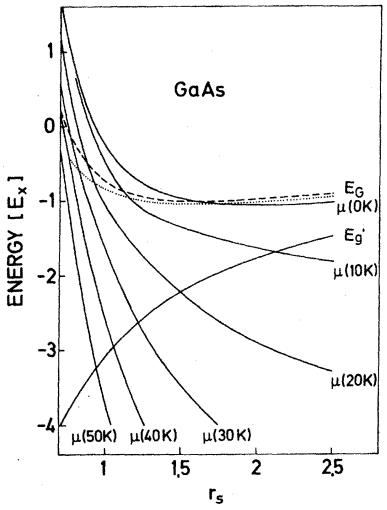

FIG. 1. Calculated values for the ground-state energy E_G, the reduced band-gap energy E_g', and the chemical potential μ, and its temperature dependence for the EHP in GaAs vs density parameter r_s. The energy scale is in units of the exciton Rydberg E_x. The broken and dotted line correspond to different approximations made to calculate E_G as it is described in the text.

culations for E_G have been available up to now. Therefore we have computed E_G for these materials following the scheme as described in detail in Ref. 10 (dotted line in Figs. 2 and 3). Again, this yields only slightly lower values than the "polynomial approximation" (broken line in Figs. 2 and 3).

For comparison with the experimental results the effect of finite temperatures has to be considered. (The temperature T that enters in the theoretical expressions is the effective carrier temperature T_{eff}.) In this case, the free energy and the chemical potential μ of the EHP decrease with increasing temperature because of the entropy contribution. In detail, the following assumptions are made. (i) Only the kinetic energy depends on the carrier temperature; this is valid as long as the thermal energy kT is small compared to the Fermi energy E_F as well as to the plasmon energy ($\hbar\omega_{pl}$).[26] (ii) Thermal expansion[5] is neglected in the calculation of the temperature dependence of E_F, because the existence of an EHL or EHD has not been proven in the materials discussed here (cf. Sec. IV). Then the Fermi energies for the electrons (E_F^e) and holes (E_F^h) are implicitly determined by

$$n = p = (m_d^{e,h} kT/2\pi\hbar^2)^{3/2} f_{1/2}^{e,h}(E_F^{e,h}/kT), \tag{1}$$

where $f_{1/2}^{e,h}(E_F^{e,h}/kT)$ is given by

$$f_{1/2}^{e,h}\left(\frac{E_F^{e,h}}{kT}\right) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}\, dx}{\exp(x - E_F^{e,h}/kT) + 1}. \tag{2}$$

The chemical potential at any temperature is

$$\mu(n, T) = E_g' + E_F^e + E_F^h. \tag{3}$$

The parameters used for the calculations are listed in Table I. All energies are normalized to the respective exciton Rydberg $E_x = \mu/m\epsilon^2$ Ry; the density is characterized by the density parameter $r_s = (n_0/n)^{1/3}$, where $n_0 = (\frac{4}{3}\pi r_0^3)^{-1}$ and r_0 is the exciton Bohr radius. All the analytic expressions are based on the "polynome approximation" as described above which is valid for $0.5 < r_s < 2.5$.

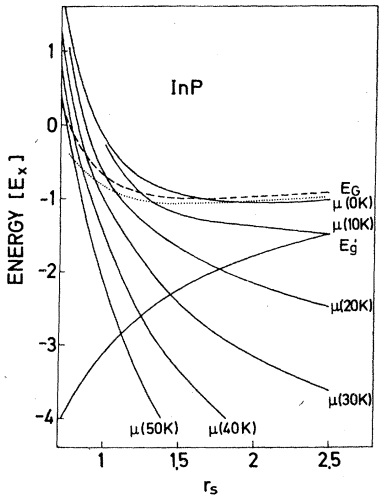

FIG. 2. Same plot as Fig. 1 for the case of InP.

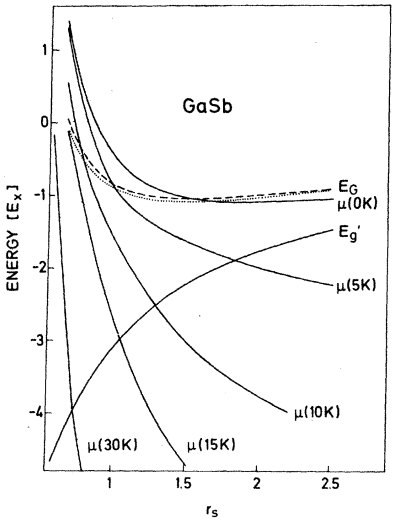

FIG. 3. Same plot as Fig. 1 for the case of GaSb.

TABLE I. Parameters used for the calculations.

	m_e (m_0)	m_{lh} (m_0)	m_{hh} (m_0)	ϵ_∞	ϵ_0	E_g (eV)	$E_{x,\mathrm{exp}}$ (meV)	$E_{x,\mathrm{theor}}$ (meV)
GaAs	0.0665 [a]	0.082 [b]	0.50 [c,d]	10.91 [a]	12.91 [a]	1.5192 [e]	4.2 [e]	3.69
InP	0.0803 [f]	0.115 [c]	0.65 [c]	9.55 [a]	12.38 [a]	1.4237 [g]	5.01 [g]	5.13
GaSb	0.0405 [a]	0.045 [c]	0.35 [c]	14.44 [a]	15.69 [a]	0.8113 [h]	1.4 [h]	1.48

[a] D. L. Rode, in *Semiconductors and Semimetals*, Vol. 10, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1975).
[b] A. L. Mears and R. A. Stradling, J. Phys. C 4, L22 (1971).
[c] J. D. Wiley, in Ref. a.
[d] These are the hole masses as obtained from transport data. The masses as obtained from the experimentally determined parameters Γ_1, Γ_2, Γ_3 differ slightly; however, the average value is close to the value we use. It should be noted that small changes in the valence band masses do not affect E_G appreciably (cf. Sec. IV).
[e] D. D. Sell, Phys. Rev. B 6, 3750 (1972).
[f] D. Bimberg, K. Hess, N. O. Lipari, J. U. Fischbach, and M. Altarelli, Physica (Utr.) 89B, 139 (1977).
[g] K. Lösch, PhD. thesis, (University of Stuttgart, 1977)(unpublished) and unpublished.
[h] See Ref. 46.

The ground-state energy E_G of the EHP then can be written

$$E_G(r_s, T=0) = (B_G/r_s^2) - (C_G/r_s) - D_G. \tag{4}$$

At $T=0$ the chemical potential μ is defined as

$$\mu(r_s, T=0) = -\frac{r_s}{3}\frac{\partial E_G}{\partial r_s} + E_G \ ,$$

which yields

$$\mu(r_s, T=0) = \frac{B_\mu}{r_s^2} - \frac{C_\mu}{r_s} - D_\mu \ . \tag{5}$$

For temperatures $T>0$, $\mu(r_s, T)$ is calculated via Eq. (3), where the reduced band gap energy E_g' is given by

$$E_g'(r_s) = (B_g'/r_s^2) - (C_g'/r_s) - D_g'. \tag{6}$$

The Fermi energies for the electrons, E_F^e, and holes, E_F^h, are calculated from Eq. (1), which in terms of r_s can be rewritten

$$r_s\sqrt{kT} = A^{e,h}\left[f_{1/2}^{e,h}\left(\frac{E_F^{e,h}}{kT}\right)\right]^{-1/3} \tag{7}$$

The constants, which appear in Eqs. (4)–(7) are computed on the base of the parameters listed in Table I and are summarized in Table II.

The curves corresponding to Eqs. (4)–(6) for GaAs, InP, and GaSb are plotted in Figs. (1)–(3), respectively. Concerning the ground-state energy E_G, the results are very similar: as it has been known for GaAs,[7,10,25] no or only very weak binding is expected also for InP and GaSb. According to the "exact" calculations (dotted lines) the minimum values for E_G, $E_{G,\mathrm{min}}$, and the corresponding value for r_s, $r_{s,\mathrm{min}}$, are as follows: GaAs: $E_{G,\mathrm{min}} = -1.1E_x$, $r_{s,\mathrm{min}} = 1.57$; InP: $E_{G,\mathrm{min}} = -1.1E_x$, $r_{s,\mathrm{min}} = 1.55$; GaSb: $E_{G,\mathrm{min}} = -1.09E_x$, $r_{s,\mathrm{min}} = 1.37$. The effect of the increasing temperature on $\mu(r_s, T)$ (see Ref. 27) is strongest for GaSb due to the relatively small electron mass. From this point of view liquid formation is expected to be very unlikely in GaSb. It has been the aim of our experiments to verify the results of Figs. (1)–(3).

III. EXPERIMENTAL TECHNIQUES

Besides analyzing luminescence spectra, three additional experimental techniques have been applied to determine the properties of the EHP, namely: gain measurements, transmission ex-

TABLE II. Numerical values for the constants in Eq. (1)–(7).

	n_0 (10^{16} cm^{-3})	B_G	C_G	$D_G = D_\mu = D_g'$	B_μ	B_g'	$C_\mu = C_g'$	A^e	A^h
GaAs	6.87	1.90	2.39	0.261	3.166	0.352	3.187	1.438	0.514
InP	15.6	1.96	2.388	0.266	3.26	0.349	3.184	1.469	0.505
GaSb	0.81	1.83	2.38	0.272	3.048	0.339	3.175	1.42	0.476

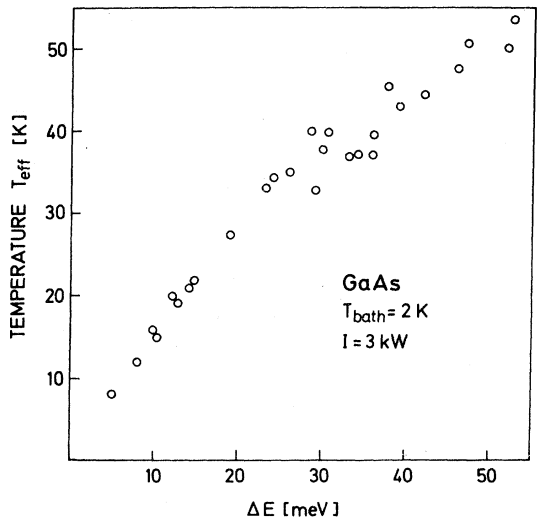

FIG. 4. Effective carrier temperature T_{eff} of the EHP as determined from the high-energy tail of the EHP emission vs the mean excess energy of the laser created carriers, $\Delta E = h\nu_L - E_G$, at a pump intensity of 3 kW.

periments, and excitation spectroscopy. The most important tool in these experiments was a N_2-laser pumped pulsed dye laser system.[28] Maximum pulse power of this dye laser was about 5 kW over the entire visible spectrum and the near infrared up to 1 μm. In addition, for the investigations on GaSb a Q-switched Nd-YAlG laser has been employed.

The use of a tunable dye laser for the creation of the EHP in GaAs and InP is extremely important, because this enables us to vary the effective carrier temperature T_{eff} of the EHP by varying the photon energy of the excitation laser, $h\nu_L$.[29] The variation of T_{eff} versus excess energy ΔE of the carriers created by the laser with photon energy $h\nu_L$ ($\Delta E = h\nu_L - E_G$) is shown in Fig. 4. It can be seen that T_{eff} decreases to values close to the bath temperature as $h\nu_L$ approaches the case of resonant excitation ($\Delta E = 0$). It is important to note that in direct gap materials with low polar coupling this is the only way to achieve very low temperatures T_{eff} under the condition of strong optical excitation.

Gain measurements[30] and *transmission spectroscopy*[16,17,21] as described in the literature allow us to determine the position of the chemical potential $\mu(r_s, T)$, the band gap energy E_g', and the Fermi energy E_F. By varying the laser photon energy $h\nu_L$, these data can be taken for different temperatures T_{eff}, and the result can be compared with the calculations. Measuring additionally the *excitation spectrum* of the EHP, i.e., the dependence of the integrated EHP emission intensity on $h\nu_L$, allows a direct determination of $E_{G,\min}$ at temperatures $T_{eff} \approx T_{bath}$. This is because of the following two reasons. (i) For exact resonant excitation no additional heating of the EHP should occur, because no excess energy is available.[31] Therefore, the mean energy per particle in the EHP must be equal to $h\nu_L$ (or smaller). (ii) To obtain stationary absorption, $h\nu_L$ must be larger than the chemical potential $\mu(r_s, T)$. From these two conditions it follows directly that the excitation spectrum of the EHP will show a low-energy cutoff at an energy where the chemical potential $\mu(r_s, T)$ intersects the mean energy per particle. For $T = 0$ (mean energy per particle $= E_G$) this defines $E_{G,\min}$. Since the bath temperature in our case is about 2 K, the value for the low-energy cutoff of the excitation spectrum is close to $E_{G,\min}$.

A combination of all four different techniques—luminescence, gain measurements, transmission, and excitation spectroscopy—allows an accurate determination of the energetic situation of the EHP. In the case of GaAs, all techniques have been employed. For InP, luminescence spectra, gain experiments, and excitation spectra will be reported. Because of the lack of tunable lasers in the energy region corresponding to the band-gap energy of GaSb, in this case only luminescence and gain spectra could be measured.

The samples used in the experiments were not initially doped and were grown by liquid phase epitaxy. Typical values for the room temperature carrier concentration $|N_D - N_A|$, amount to 1×10^{14} cm^{-3} for GaAs (p-type), 5×10^{14} cm^{-3} for InP (n-type), and 5×10^{15} cm^{-3} for GaSb (p-type). In the case of GaAs, the samples were etched as described in Ref. 21 to a residual thickness of the epitaxial layer of about 10 μm.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Our experimental results on the EHP in GaAs, InP, and GaSb will be presented in this section. These data will be compared with the theoretical values. It will be shown that the theory as discussed in Sec. II is the proper description of the EHP. However, quantitatively the experimental values for E_G are lower than predicted from theory by somewhat more than $1E_x$.

A. GaAs

The material we have studied most extensively was GaAs. The existence of an EHP has been proven by several authors.[21-24] However, different values for the ground state energy E_G have been obtained. An experimental determination of E_G in direct gap semiconductors like GaAs is more complicated than, e.g., in Ge or Si, because of

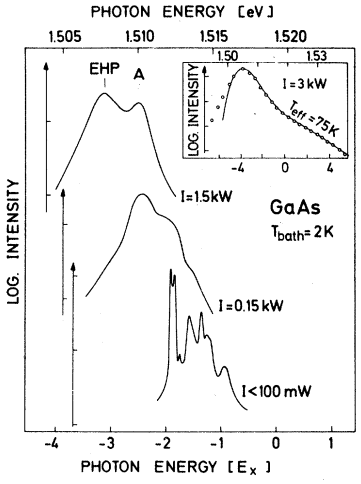

FIG. 5. Luminescence spectra of a pure epitaxial GaAs sample at different pump intensities. The intensity is drawn on a logarithmic scale vs the emission photon energy (in units of the exciton Rydberg E_x). The bottom curve corresponds to very weak excitation and shows the well-known excitonic structure. The upper curves are obtained at high excitation levels: at a pump intensity of $I = 0.15$ kW emission due to excitonic scattering processes (line A—not discussed in this paper) is observed. At still higher intensities ($I = 1.5$ kW) the EHP emission begins to dominate. The insert shows an emission spectrum as obtained in a gain arrangement (cf. text). The solid line represents a fit on the base of Eq. (8).

stimulated emission and saturation effects. The latter effect especially can cause a considerable spectral shift of the EHP emission depending on the light intensity.[32] Consequently, from luminescence measurements accurate data for E_G can only be obtained, if stimulated emission is taken into account when fitting the data. Beyond this, T_{eff} must be determined experimentally, because —as already mentioned—the carrier temperature in the materials with low optical-phonon coupling can be appreciably higher than the bath temperature.[29]

Figure 5 depicts the luminescence spectra of a pure GaAs epitaxial layer for different pump intensities. The bottom curve shows the well-known near-band-edge emission at low excitation intensity with the characteristic excitonic structure.[33] The upper curves are obtained when exciting at high intensities. These spectra have been discussed in previous papers[22,23,34,35]: line A is due to excitonic scattering processes,[34,35] line EHP—which is observed only at higher pump intensities—is caused by free-carrier recombination within the plasma. It is obvious that it will be hard to obtain values for, e.g., the chemical potential from these luminescence measurements only. The insert shows a luminescence spectrum as obtained in a 90° arrangement (gain experiments) at still higher pump levels (circles). Because of the high gain[32,34,37] the EHP emission dominates in this particular experimental arrangement. From the slope of the high-energy tail T_{eff} can be determined ($T_{eff} = 75$ K in this case). As long as saturation can be neglected, the line shape in the presence of stimulated emission can be fitted by[30,31]:

$$I(\hbar\omega) \propto [r_{spon}(\hbar\omega)/r_{stim}(\hbar\omega)]\,(e^{g(\hbar\omega)L} - 1). \qquad (8)$$

r_{spon} and r_{stim} are the spontaneous and stimulated emission rates, $g(\hbar\omega)$ is the net optical gain, which is proportional to $r_{stim}(\hbar\omega)$ [$g(\hbar\omega)$ can be positive or negative]. L is an effective length over which amplification of the spontaneous emission takes place. The emission rates $r_{spon}(\hbar\omega)$ and $r_{stim}(\hbar\omega)$ have been calculated assuming that the band-to-band transition in the EHP takes place without k-selection rule.[36,37] However, although this assumption yields good agreement with the experimental data, one ought to realize that the line shape should rather be calculated in a many particle model.[38,39] As shown by Brinkman and Lee,[38] many particle effects like self-induced tail states and variation of the enhancement factor with energy already yield line shapes which differ appreciably from the single particle line shape *with* k-selection rule. However, the details of the line-shape function do not affect the determination of T_{eff}, $E_g'(r_s)$, $\mu(r_s, T)$, and E_G appreciably.

1. Gain spectra

Gain spectra of pure GaAs at a bath temperature, $T_{bath} = 2$ K, for two different pump levels are shown in Fig. 6. The position of the chemical potential

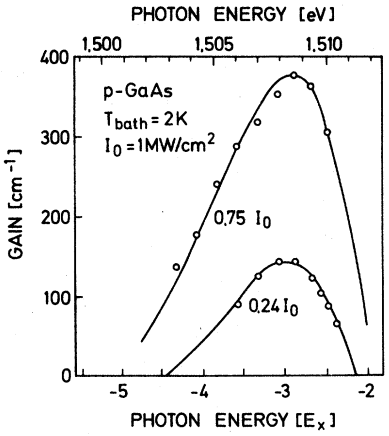

FIG. 6. Gain spectra of GaAs at two different pump intensities. The solid lines are calculated as described in the text.

$\mu(r_s, T)$ is at 1.511 eV, nearly independent of pump level. Referring to Fig. 1, this could be the case if the density and the temperature stay constant when the pump intensity is changed. However, in this case the width of the gain curves should also be constant. On the other hand, there could be a balance between the effects of increasing density and a corresponding increase in temperature. As long as both the density and the temperature T_{eff} are used as fitting parameters, agreement of the experimental data with Fig. 1 can always be obtained. For instance, the gain curve at a pump level of $0.75I_0$ can be fitted assuming $T_{\text{eff}} = 100$ K and $r_s = 0.5$. These parameters yield $E_F = 2.89E_x$ (=11 meV) and $\mu = -2.15E_x$ ($\simeq 1.511$ eV), which nearly agrees with the theory (cf. Fig. 1). However, since the experimentally determined T_{eff} is appreciably lower ($T_{\text{eff}} = 60$ K), the data cannot be brought into agreement with Fig. 1: the experimentally observed chemical potential μ is lower than the expected value by roughly $1E_x$. This result will be confirmed by the transmission experiments.

2. *Transmission experiments*

Transmission experiments as first reported by Hildebrand *et al.*[21] are the most direct access to the EHP data. Figure 7 shows the transmission spectrum of the EHP for an excitation photon energy $h\nu_L$ of 1.518 eV ($\Delta E = 7.2$ meV) and a pump intensity of 1 MW/cm^2. Under these conditions the experimentally determined carrier temperature was 15 K (cf. Fig. 4). Since all the important parameters—$T_{\text{eff}} = 15$ K, $\mu = -1.8E_x$, $E_g' = -4.6E_x$, and $E_F = 2.8E_x$—are determined experimentally, the results can now be compared with the calculated values of Fig. 1. This shows that the experimental values again are lower than the theoretical ones: For $T_{\text{eff}} = 15$ K and $\mu = -1.8E_x$ the corresponding E_F should be $0.4E_x$, which is too small compared to the experimental value of $2.8E_x$. By tuning $h\nu_L$ we can change T_{eff} and thus obtain experimental data at different points in the energy diagram of Fig. 1. It turns out that for all temperatures T_{eff}, the experimental values do not agree with Fig. 1. However, if we postulate that all the theoretical curves are too high by about $1.5E_x$ agreement with the experimental data is quite good.[40] This is summarized in Fig. 8, where the data of five transmission spectra at different temperatures ($T_{\text{eff},a} = 40$ K, $T_{\text{eff},b} = 30$ K, $T_{\text{eff},c} = 15$ K, $T_{\text{eff},d} = 10$ K, $T_{\text{eff},e} \sim 3$ K) are drawn into the energy diagram. For each transmission spectrum the amount, by which the experimental values are lower than the theoretical ones, is depicted in Fig. 9 versus the corresponding r_s value. The average value of this shift is $1.5E_x$, which corresponds to 9.2 meV. This value is definitely above the experimental error. Consequently we would expect E_G to be lower by the same amount and this can be proven by excitation spectroscopy.

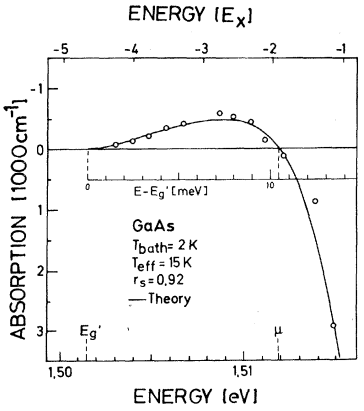

FIG. 7. Transmission spectrum of the EHP in GaAs. The absorption coefficient (negative absorption corresponds to optical gain) is shown as a function of photon energy. The transmission has been probed with a second, low-intensity dye laser while the EHP was created with a high power laser with photon energy, $h\nu_L = 1.518$ eV. The solid line is a fit to the experimental points. T_{eff} is determined experimentally and from the fit $r_s = 0.92$ is obtained.

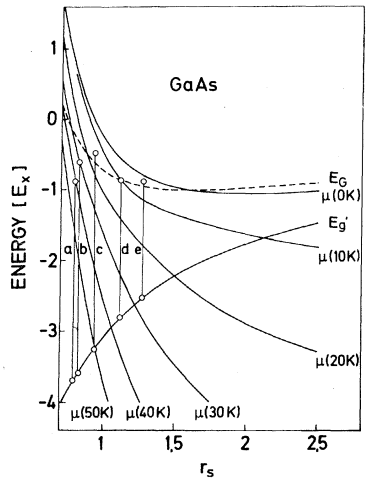

FIG. 8. Summary of the transmission data. The vertical lines correspond to five different experiments at different temperatures T_{eff}: (a) = 40 K; (b) = 30 K; (c) = 15 K; (d) = 10 K; (e) ~ 3 K. The length of each of these lines corresponds to E_F. Originally the data do not agree with the theoretical values (Fig. 1), because the experimental values for μ and E_g' are too low (cf. Fig. 7). Agreement can only be obtained if we shift the theoretical curves by an amount as shown in Fig. 9.

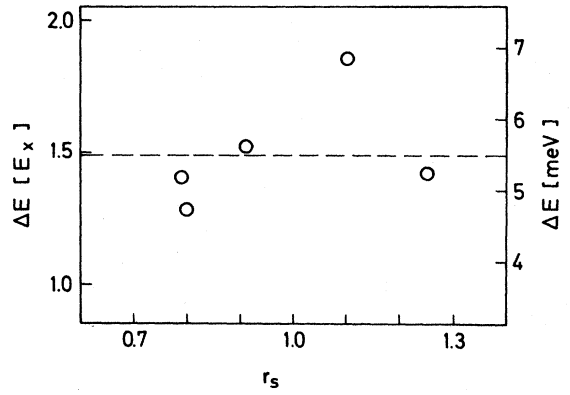

FIG. 9. Energy shift ΔE of the theoretical curves to obtain agreement with the experimental data. Each point corresponds to one of the transmission data of Fig. 8. The broken line gives the average value for ΔE ($\Delta E_{\text{average}} = -1.5 E_x$).

3. *Excitation spectroscopy*

Figure 10 depicts the excitation spectra of the EHP emission in GaAs at three different pump levels. These spectra show a sharp low-energy cutoff, from which E_G can be derived. As discussed in Sec. III in the case of the EHP this cutoff has to be independent of pump power and this in fact has been observed. The value obtained for E_G is at $-2.1E_x$ which is consistent with the transmission and gain data.

The shape of the excitation spectrum can be explained qualitatively as follows: with decreasing photon energy, $h\nu_L$, of the excitation laser the excess energy ΔE decreases and therefore—referring to Fig. 4—T_{eff} also decreases. As long as the density stays approximately constant, this leads to higher gain values,[36] thus causing higher intensities as can be seen from Eq. (8). With $h\nu_L$ coming closer to the corresponding chemical potential of the EHP, the density begins to decrease until $h\nu_L = E_G = \mu$ is reached. (Exact resonant excitation ($h\nu_L = E_{G,\min}$) and excitation at still lower energies ($h\nu_L < E_{G,\min}$) is not possible because of lack of absorption.) The solid line in Fig. 10 has been calculated according to Eq. (8) under the conditions just discussed. The values for T_{eff} as a function of ΔE as presented in Fig. 4 have been used. In summary, the data obtained from gain spectra as well as from transmission and excitation spectroscopy consistently show for GaAs that E_G is lower than the theoretical prediction by $(1.1\text{–}1.5)E_x$.

B. InP

InP and GaAs have very similar band structures. In this section we will compare the properties of the EHP in InP with those of the EHP in GaAs. The main result will be that again E_G is lower than theoretically predicted by approximately $1E_x$.

Luminescence spectra of InP at low[41] and high excitation levels are shown in Fig. 11. In principle, the spectra look very similar to those of GaAs, yet, the critical pump level for the creation of an EHP is higher for InP than for GaAs. This fact could be connected to the smaller exciton Bohr radius in InP (Ref. 42): If the plasma is formed via a Mott transition, a higher pump level

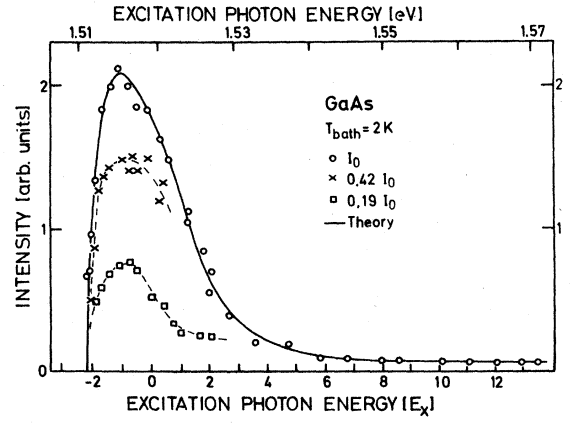

FIG. 10. Integrated emission intensity of the EHP in GaAs as a function of the excitation laser photon energy $h\nu_L$, for three different pump intensities ($I_0 \simeq 3$ kW). The low-energy cutoff yields the minimum value of E_G. The solid line has been calculated as sketched in the text.

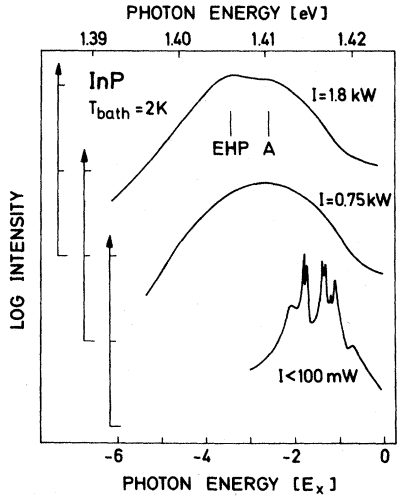

FIG. 11. Luminescence spectra of a pure InP epitaxial sample at low (bottom curve) and high excitation levels. At the high pump levels excitonic scattering processes (line A) and the EHP emission are observed.

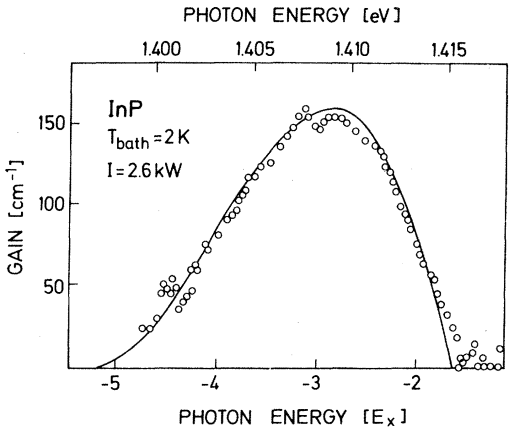

FIG. 12. Gain spectrum of InP at a pump intensity of $I = 2.6$ kW. The calculated gain spectrum for the EHP emission is shown by the solid line. The Fermi energy has been used as a fitting parameter (this is equivalent to taking r_s as a fitting parameter).

would indeed be required.

The EHP emission is again accompanied by the occurrence of optical gain. In Fig. 12 a gain spectrum at an excitation level of 2.6 kW is shown. The position of μ is at 1.4153 eV, corresponding to $-1.64E_x$. The Fermi energy E_F amounts to $3.5E_x$. Maximum gain values are in the order of 150–200 cm^{-1}, which is lower than in GaAs at comparable excitation conditions. The temperature T_{eff} has been determined experimentally to be 50 K. As seen in the theoretical plot for InP (Fig. 2), for $T_{eff} = 50$ K and $\mu = -1.64E_x$ the Fermi energy should be $1.7E_x$, which is smaller than the experimental value of $3.5E_x$. The experimental results can be made to agree with the theoretical ones, if the curves are shifted to lower energies by $1.3E_x$. The same observation has already been made in the case of GaAs.

We have also performed excitation spectroscopy measurements on InP. The results are shown in Fig. 13. The shape of the excitation spectra is very similar to GaAs. The low-energy cutoff is at 1.412 eV, corresponding to $-2.28E_x$, and again is independent of pump intensity. As discussed, this low energy cut off corresponds to the minimum ground-state energy $E_{G,\min}$. Therefore we conclude that $E_{G,\min}$ is lower than expected by about $1.2E_x$.

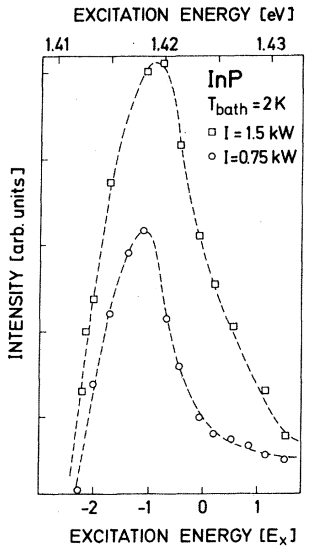

FIG. 13. Excitation spectra of the EHP emission in InP for two different pump levels. In order to obtain the integrated emission intensity, the luminescence spectrum has been defolded for the A-line emission. However, since the excitation spectrum of the A line does not show any energy dependence up to an energy of $h\nu_L = -2E_x$ [O. Hildebrand, Diploma thesis (University of Stuttgart, 1974) (unpublished)] even the integrated emission of the EHP and A-line emission yields a similar excitation spectrum.

C. GaSb

Because of its special band structure, GaSb is an interesting candidate for studies of the EHP state: GaSb is a direct gap semiconductor with the indirect minimum (at the L point) being only 80 meV higher than the Γ-conduction-band minimum.[43] Therefore by applying hydrostatic pressure,[44] the band structure can be changed from a direct gap material to an indirect semiconductor with a band structure very similar to Ge.[45] The study of the properties of the EHP in a semiconductor where the gap can change from a direct to an indirect one certainly will be an exciting experiment. Here we report for the first time the observation of the EHP in GaSb at zero pressure in order to compare the results with GaAs and InP. Since no suitable tunable lasers were available in the energy range of the band-gap energy of GaSb, only luminescence and gain spectra could be measured.

Figure 14 shows the luminescence spectra of GaSb at low excitation levels[46] (lower curve) and at high pump intensities. At the highest intensities the typical broad emission of the EHP is observed and excitonic structure is absent. As characteristic for the EHP emission, the maximum is below the band-gap energy and the high-energy side of the spectrum shows an exponential tail characterized by the temperature of the EHP. The critical pump power for the creation of the EHP is lower than in GaAs and InP, which is connected with the large Bohr radius in GaSb. The EHP in

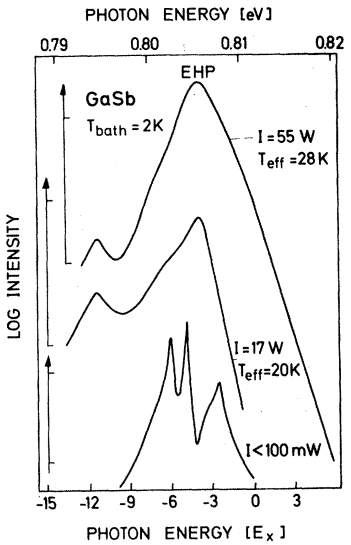

FIG. 14. Luminescence spectra of GaSb at low (bottom curve) and high excitation levels. Whereas at low pump intensities excitonic emission is observed, at high excitation levels the broad EHP emission dominates. Because of the small exciton binding energy in GaSb the emission due to excitonic scattering processes and the EHP emission could not be resolved spectrally.

GaSb could even be observed when pumping with a 500-mW cw-Nd-YAlG laser; in this case, however, the carrier temperature was appreciably higher (T_{eff} = 75 K) than in Fig. 14.

A gain spectrum of the EHP in GaSb is shown in Fig. 15 for a pump power of 55 W. The chemical potential, μ, is at 0.8064 eV, corresponding to $-3.3E_x$. The Fermi energy is $2.7E_x$ and T_{eff} as determined experimentally amounts to 30 K. Agreement with these experimental values can be

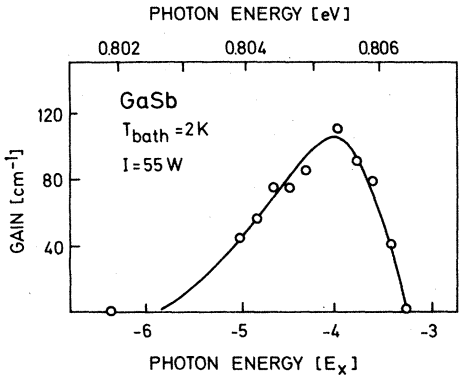

FIG. 15. Gain spectrum of GaSb at a pump intensity of I = 55 W. The circles represent the experimental points and the solid curve has been calculated with E_F as a fitting parameter.

reached if the theoretical curves (Fig. 3) for E_G and μ again are shifted to lower energies by approximately $1.6E_x$.

D. Comparison of results

Summarizing all the results of the materials we have discussed, we find that the experimental data can be qualitatively explained by a many-body theory. Quantitatively, however, the observed values for the ground state energy in all three materials—GaAs, InP, and GaSb—are lower than expected. In the following we will discuss some of the possible origins for this deviation, but, as will be seen, they cannot account for the observed discrepancy.

Taking the theory as it is, only the calculation of the correlation energy is somewhat uncertain. There are different approaches for computing E_c based on different theoretical schemes and slightly different approximations for the actual valence band structure. However, all the calculations of E_G based on different approaches for E_c differ only within $\pm 10\%$ (GaAs). The values for $E_{G,\min}$ are as follows: Brinkman and Rice,[7] -3.62 meV; Vashista *et al.*,[25] -4.08 meV; Mahler and Birman,[10] -3.9 meV; Beni,[47] -4.48 meV. The experimental value for $E_{G,\min}$ is between −7.3 and −9.2 meV, which is beyond the "uncertainty range" of the theoretically determined correlation energy.

Phonon interaction also could lower E_G, however, in the materials discussed here, phonon coupling is small compared to, e.g., II-VI-compounds[48] and the effect on E_G is expected to be small. For GaAs Keldysh and Silin[12] have calculated that polar coupling of the carriers would lower E_G by only 5%.

Within the approximations available at present, neither the uncertainty in E_c nor polar coupling can obviously account for the large value of E_G which we observe experimentally. There might be some uncertainty in the evaluation of the experimental data caused by changes of the density of states (tail states[38,49]) and the matrix element (enhancement factor[38,39]) at high excitation levels. However, calculations of the gain and transmission spectra line shapes with phenomenologically included tails show that this would affect only E_g' and E_F slightly, but, e.g., does not influence the low-energy cutoff in the excitation spectra.[50]

In summary, although there are effects which can lower E_G, they do not explain the systematic deviation we have observed experimentally: the experimental values for E_G are lower than the theoretical ones by $(1.1-1.5)E_x$ for GaAs, $(1.2-1.3)E_x$ for InP, and $1.6E_x$ for GaSb, respectively. On the other hand, there is no doubt that the many-body theory as it has been developed for semiconductors qualitatively describes the situation in

GaAs, InP, and GaSb. From our experimental data we expect a pronounced minimum for E_G, because for large values of r_s, E_G has to converge to $-1E_x$.

V. POSSIBILITY OF EHL FORMATION IN GaAs

The existence of a liquid state in direct gap materials has been proven so far only for materials with large polar coupling such as CdS,[15-17] CdSe,[19] and ZnO.[20] On the basis of the experimentally observed minimum for E_G, formation of an EHL would be quite likely for GaAs. However, we found instead that the plasma density in GaAs is not determined by the minimum in the free energy $F(r_s, T)$, but rather seems to be correlated to the Mott density.[51]

In order to investigate if EHL formation does occur in GaAs we have measured the Fermi energy E_F as a function of excitation intensity for different temperatures T_{eff}. For an EHL state, E_F is expected to be independent of pump intensity and to decrease slightly with increasing temperature.[5,14,52] Several typical results for GaAs are shown in Fig. 16, where on the left-hand side the position of E_g' and μ is depicted versus r_s^*. r_s^* is a measure for the pump intensity, and is defined in analogy to r_s: $r_s^* = (I_0/I)^{1/3}$, where $I_0 \approx 5\times10^4$–10^5 W/cm^2. The values for E_g' and μ were obtained from gain experiments. As can be seen from the right-hand side of Fig. 16, the Fermi energy, $E_F = \mu - E_g'$, stays nearly constant over a considerable range of pump intensity as it would be expected for an EHL. (The increase of E_F at the highest pump intensities at low temperatures could be connected to the fact that the EHP under these conditions does not completely relax to its final density—see below.) However, the temperature dependence of E_F is in contrast to the expected EHL behavior. As shown in Fig. 17, the Fermi energy increases at low temperatures, whereas in the case of an EHL E_F is expected to decrease. It is also interesting to note that on the low density side (large r_s^*) the gain disappears abruptly at a critical pump power.

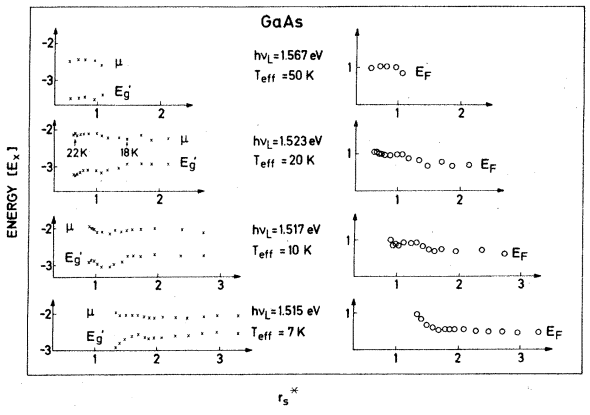

FIG. 16. Dependence of the chemical potential μ and the reduced band gap E_g' (left-hand side) and the Fermi energy, $E_F = \mu - E_g'$ (right-hand side) on the pump intensity I, for four different laser photon energies, corresponding to four different temperatures, T_{eff}. r_s^* is defined in analogy to r_s and is proportional to $I^{-1/3}$.

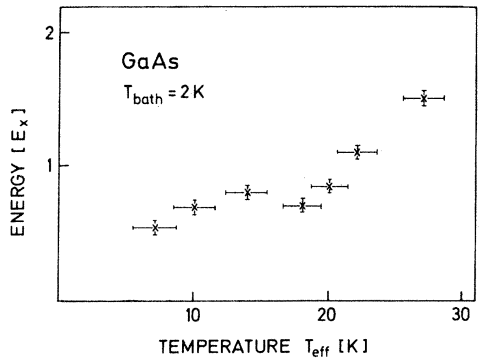

FIG. 17. Fermi energy E_F as a function of carrier temperature T_{eff}, as obtained from the data of Fig. 16 for temperatures up to 30 K. The error bars represent the statistical error mainly due to the uncertainty in the determination of T_{eff} and E_g'.

In Fig. 18 we have plotted T_{eff} as a function of the corresponding plasma density n. The density has been determined with the values for E_F from Eqs. (1) and (2). The circles represent gain data and the squares stand for data from transmission experiments (cf. Fig. 8). These two independent measurements basically show the same temperature dependence and the values for the carrier concentration agree within a factor of 3. Contrary to the case of an EHL the density, n, increases linearly with temperature T_{eff} (note the semilogarithmic plot which has been chosen in analogy to the usual plots of the phase diagram). This linear relation and the fact that the gain disappears abruptly at a critical pump power (cf. Fig. 17) indicates that the EHP density is related to the Mott density: for static screening the Mott density is given by: $n_M = kT\,(16E_x r_0^3)^{-1}$ (classical case).[51,53] However, in the case of the EHP, dynamical screening should be considered.[54] For dynamical screening n_M is expected to be higher than in the static case.[55] To explain our experimental data in terms of a Mott transition we have to postulate that the Mott density for dynamic screening is higher by a factor of 15–20 than for static screening. The corresponding curve is shown as a broken line in Fig. 18.

The conclusion of the experimental results is that in GaAs for temperatures $T_{eff} > 7$ K no EHL is

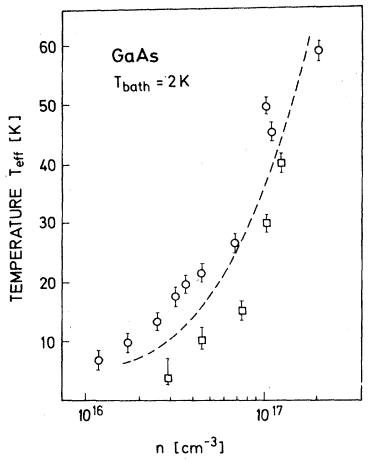

FIG. 18. Temperature of the EHP in GaAs vs corresponding carrier concentration. The carrier concentration—which is nearly independent of the pump intensity (cf. Fig. 16)—has been determined from the experimental values for E_F. The density is drawn in a logarithmic scale in analogy to the plots of the EHD phase diagrams of Ge and Si. The circles stand for the gain data and the squares correspond to the transmission data (cf. Fig. 8). The solid line is calculated on the basis of the Mott criterion as discussed in the text.

formed. Assuming that the results of Fig. 18 can be explained by the Mott criterion, indeed no EHL formation is possible, even if the critical temperature for EHL formation would be higher than 7 K: at $T_{eff}=7$ K (lowest temperature in Fig. 16) the Mott density $[n_M(7\text{K}) = 2.1\times 10^{16}\ \text{cm}^{-3}]$ already exceeds the density corresponding to $r_{s,\min}$ at $T=0$ K $[n_{\min}(0\ \text{K}) = 1.8\times 10^{16}\ \text{cm}^{-3}]$. This means that the EHL state cannot be reached, because the system undergoes a Mott transition before the EHL is formed. On the other hand, to explain that the plasma density is independent of excitation power, we have to assume that an initially overdense plasma—i.e., a plasma with a density higher than n_M—expands to n_M within the lifetime. A crude estimate of the times involved in the expansion of the EHP from Euler's equation[56] yields that the time to expand by, e.g., 10% are in the order of 0.1–1 nsec depending on the size and density of the EHP, which is in agreement with the above assumption (for contraction of the EHP the times are larger: 5–10 nsec). This tentative model which is strongly supported by our experimental data could be further confirmed by measuring the time behavior of the EHP and exciton luminescence in a similar way as recently reported for CdS.[57] At very low temperatures, EHL formation could be possible, however, because of experimental reasons (resonant excitation), it is difficult to measure the excitation intensity dependence of the properties of the EHP for temperatures, $T_{eff} \leq 5$ K.

VI. SUMMARY

The EHP in direct gap semiconductors with low polar coupling can be described by a many-body theory taking into account interaction amongst the carriers. This theory, as developed by several authors, allows fundamental understanding of the observed high excitation phenomena like band-gap reduction, etc. However, quantitatively the ground-state energy of the electron-hole plasma in GaAs, InP, and GaSb is lower than expected from the theory.

In spite of the large experimental value for the binding energy of the electron-hole plasma (more than $1E_x$) the existence of an electron-hole liquid in GaAs could not be proven. Though the density of the plasma is independent of excitation intensity—as it would be expected for an electron-hole liquid—its temperature dependence is in contradiction with the assumption of electron-hole-liquid formation. The experimental data indicate that for plasma temperatures $T_{eff} > 7$ K the Mott density is higher than the density corresponding to the minimum of the free energy $F(r_s, T)$. Thus, in GaAs formation of an electron-hole liquid is not possible, even if the critical temperature for EHL formation would be higher than 7 K.

ACKNOWLEDGMENTS

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