in a very broad peak, $\sim 400 \text{ cm}^{-1}$, making it difficult to observe experimentally.

In conclusion, we have demonstrated the use of Raman scattering in determining the wave-vector dependence of the coupling between LO phonons and plasmons, and have clarified the relative roles played by the skin depth and the accumulation layer in determining the wave vectors of the modes participating in Raman scattering at the E_1 gap of *n*-InAs.

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Thermodynamics of the Electron-Hole Liquid in Ge, Si, and GaAs†

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Thermodynamic properties of the electron-hole liquid are calculated for five systems: Ge, Si, and Ge under large (111) uniaxial stress, Si under large (100) uniaxial stress, and GaAs. Important effects of multiple scatterings and anisotropy are included in the correlation energy. For Ge, the ground-state energy, enhancement factor, compressibility, critical temperature, critical density, temperature dependence of Fermi energy, chemical potential, and equilibrium density are in good agreement with experiments.

In germanium and silicon at liquid helium temperatures the condensation of free excitons (FE) into "liquid" electron-hole drops (EHD) has been observed.¹ For Ge the values of the binding energy, φ , of EHD relative to FE, and the equilibrium density n(0) at T=0 K are reasonably well established.¹⁻⁵ Recently Thomas *et al.*,³ McGroddy, Voos, and Christensen,⁴ and Lo, Feldman, and Jeffries⁵ have experimentally studied the thermodynamics of EHD in Ge and determined the ground-state energy, ϵ_s , enhancement factor, ρ , compressibility, $\chi(0)$, temperature depen-

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dence of the Fermi energy, $E_F(T)$, chemical potential, $\mu_F(T)$, equilibrium density, n(T), critical temperature, T_c , and critical density, $n(T_c)$. A less complete investigation has been done for Si.⁶

Ground-state energy calculations of EHD have been reported by Brinkman *et al.*⁷ and Brinkman and Rice (BR),⁷ and independently by Combescot and Nozières (CN).⁸ The basic theoretical approaches of these two groups of authors are equivalent in principle, although they differ in details, such as the consideration of anisotropy and degeneracy of hole bands in the calculation of the correlation energy, ϵ_c .

We present in this paper results of microscopic calculations of several thermodynamic quantities of EHD in five systems: (i) Ge, (ii) Si, (iii) Ge under large $\langle 111 \rangle$ uniaxial stress, Ge[111], (iv) Si under large $\langle 100 \rangle$ uniaxial stress, Si[100], and (v) GaAs which is a direct gap semiconductor. Our calculations include the effect of (e, e), (h, h), and (e, h) multiple scatterings, and the anisotropy of bands on the correlation energy.⁹ On the basis of the calculated φ and T_c we believe that EHD should be observable in Ge[111] and Si[100] which are effectively two- and three-band systems, respectively. Our values of the thermodynamic quantities agree very well with the experiment for Ge. Predictions are made for other systems.

We express energy and temperature in units of excitonic rydberg, $E_{ex} = \mu e^4/2 \kappa^2 \hbar^2$, and density, $n^{-1} = \frac{4}{3} \pi r_s^{-3} (\kappa \hbar^2 / \mu e^2)^3$, in terms of r_s . The groundstate energy, ϵ_0 , per *e*-*h* pair, at T = 0 K can be written as a sum of kinetic, exchange, and correlation energies, where the former two include the effect of band structure.^{7,8} ϵ_c can be written as

$$\epsilon_{c} = \left[\frac{1 \cdot 2217}{r_{s}^{2} q_{\mathrm{F}}} \int_{0}^{r_{s}} \sum_{ij} \xi_{i} \xi_{j} \left(\frac{n_{i}}{n}\right) \left(\frac{n_{i}}{n}\right) \int_{0}^{\infty} dq \int_{0}^{1} d\mu \gamma_{ij}(q,\mu;r_{s}') dr_{s}' - \epsilon_{x}\right],\tag{1}$$

where $\xi_i = \frac{+1(h)}{-1(e)}$, ϵ_x is the exchange energy, and $\gamma_{ij}(\vec{q})$ is the structure factor. In our case $\gamma_{ij}(\vec{q})$ is obtained by solving a set of coupled-nonlinear integral equations [fully self-consistent (FSC) approximation]. Because of limitations on the computing time, the effect of anisotropy is estimated in the Hubbard approximation (HA). Numerical accuracy of our ϵ_c is better than $\frac{1}{4}\%$. ϵ_0 for Ge and Si in HA and FSC approximation is shown in Fig. 1. It is clear from the figure that multiple scatterings and anisotropy contribute significantly in lowering ϵ_0 .

To calculate the temperature dependence of $E_F(T)$, n(T), and $\mu_F(T)$ we expand the free energy per *e*-*h* pair at low temperature as

$$F = \epsilon_0(n) - \frac{1}{2}\gamma(n)(E_{ex}T)^2, \qquad (2)$$

where $\gamma(n) = (\pi/3)^{2/3} (m_e^* + m_h^*)/\hbar^2 n^{2/3}$. In our calculations we take $m^* = m$. Equation (2) leads to a T^2 correction to the Fermi energy, $E_F(T) = E_F(0) \times (1 - \delta_B T^2)$, equilibrium density, $n(T) = n(0)(1 - \delta_n T^2)$, and chemical potential, $\mu_F(T) = \mu_F(0) - \delta_\mu E_F(0)T^2$, where

$$\delta_{E} = \frac{\pi^{2}}{12} \frac{E_{ex}^{2}}{E_{F}^{e}(0)E_{F}^{h}(0)} - \frac{1}{3} \frac{E_{ex}^{2} \gamma'(0)}{n(0)\epsilon_{0}''(0)}, \qquad (3a)$$

$$\delta_n = -\frac{\gamma'(0)E_{ex}^2}{2n(0)\epsilon_0''(0)} , \qquad (3b)$$

$$\delta_{\mu} = \frac{1}{2} [\gamma(0) / E_{\rm F}(0)] E_{\rm ex}^{2}; \qquad (3c)$$



FIG. 1. Ground-state energy per e-h pair, ϵ_0 , versus r_s for Ge and Si. HA, FSC, ISO, and ANISO stand for Hubbard approximation, fully self-consistent approximation, with isotropic conduction bands, and with anisotropic conduction bands, respectively. HA(ISO) is same as Brinkman and Rice (BR) approximation.

TABLE I. Theoretical results calculated in a fully self-consistent (FSC) approximation which takes into account the multiple scatterings between all components of the plasma. The anisotropy of conduction and valence bands for Ge[111] (two component) and Si[100] (three component) and anisotropy of conduction bands for Ge and Si are also taken into account.

	Ge [111]	Si[100]	Ge	Si	GaAs
$-\varepsilon_{g}(meV)$	3.08	14.73	5.89	21.97	4.08
$n_{c}(0) (cm^{-3})$	1.11 x 10 ¹⁶	4.47 x 10^{17}	2.20×10^{17}	3.20×10^{18}	1.59×10^{16}
$\rho \equiv g_{eh}(r=0)$	6.8	7.4	2.33	3,46	6.93
$E_{F}^{e}(0)$ (meV)	0.82	4.18	2.40	7.46	3.44
$E_F^h(0)$ (meV)	2.06	9.06	3.72	13,72	0.36
$E_{F}^{(0)}(meV)$	2.88	13.24	6.12	21.18	3.80
$\varepsilon''_{g}(0)(\text{meVcm}^{6})$	3.37×10^{-33}	1.17×10^{-35}	1.88×10^{-35}	3.17×10^{-37}	2.42×10^{-33}
$\delta_n (meV^{-2})$	6.72	0.246	1.245	0.10	8.19
$\delta_{\rm E}^{\rm (meV^{-2})}$	4.96	0.185	0.922	0.078	6.12
δμ(meV-2)	1.45	0.065	0.276	0.024	1.98
$T_{c}(K)$	2.6	14.3	5.9	20.8	2.3
n $(T_c)(cm^{-3})$	0.42×10^{16}	1.7×10^{17}	0.93×10^{17}	1.2×10^{18}	0.64×10^{16}

the primes denote the derivative with respect to the density.

At very low *T* the gas is composed essentially of excitons. The insulating phase transforms into a conducting gas of *e* and *h* as *T* increases, so that near the critical temperature, the critical potential of the gas can be reasonably represented by using a plasma model. T_c and critical density $n(T_c)$ are given by the inflection point in $\mu_F(n, T)$ and we calculate them numerically using the expansion up to T^2 of $\mu_F(n, T)$. The results are given in Table I.

We shall briefly compare our results for Ge with those of BR and CN and with the experiments. Our value of $\epsilon_g = 5.89$ meV is higher than 5.3 meV (BR)⁷ and 5.6 (CN).⁸ The difference between BR and our value, 0.59 meV, is the contribution of multiple scatterings and anisotropy of conduction bands. One needs an accurate value of E_{ex} to obtain φ ; however, because of experimental uncertainty in the value of E_{ex} (3.6, 3.8, 4, 4.15 meV),¹⁰ it is difficult to make definite conclusions. E_{ex} is presumably larger than 3.6 meV and may lie in the vicinity of 3.9 meV (the average of the four values) which with our $\epsilon_g = 5.89$ meV leads to $\varphi = 1.99$ meV; and 1.4 and 1.7 meV, respectively,

for BR and CN.¹¹ Although the value of φ from thermodynamic measurements is lower than the value from luminescence data, it is reasonably well established that $1.55 < \varphi < 1.98$ meV ($18 < \varphi < 23$ K).²⁻⁵ More definite comparisons with the experiments can be made for n(0), ρ , $\epsilon_g''(0)$, δ_E , δ_n , δ_u , T_c , and $n(T_c)$.

Our value of $n(0) = 2.2 \times 10^{17}$ cm⁻³ is larger than 1.8×10^{17} cm⁻³ (BR) and 2.0×10^{17} cm⁻³ (CN) and is in good agreement with recent experimental value of 2.4×10^{17} cm⁻³.^{3,5} The effect of multiple scatterings is most pronounced on the enhancement factor ρ . Recent experiments by Westervelt *et al.*⁵ determine for Ge ρ = 3.4, which agrees well with our value of 2.33. Thomas $et \ al.^3$ determine $\epsilon_{g}''(0) = [\chi(0)n(0)^3]^{-1} = (1.96 \pm 0.45) \times 10^{-35}$ meV cm⁶ which is in good agreement with our result 1.88×10^{-35} meV cm⁶. Our value of $E_F(0)$ = 6.12 meV also agrees favorably with the value from Thomas et al., 6.43 ± 0.04 meV, whereas the corresponding BR value is 5.3 meV. Our values of δ_E , δ_n , and δ_μ are 0.922, 1.245, and 0.276 meV^{-2} , whereas the experimental values are $0.71 \pm 0.14, ^3$ 1.35 \pm 0.14, 5 and 0.33 \pm 0.14 $meV^{-2}, ^3$ respectively. BR values are $\delta E = 0.98 \text{ meV}^{-2}$ and $\delta_u = 0.37 \text{ meV}^{-2}$.

Recent values of T_c and $n(T_c)$ from an experimental study of the density-temperature phase diagram of EHD in Ge are 8.3 K, 0.7×10^{17} cm^{-3,5} and 6.5 ± 0.1 K,³ $(0.8 \pm 0.2) \times 10^{17}$ cm^{-3,3} respectively. Our $T_c = 5.9$ K and $n(T_c) = 0.93 \times 10^{17}$ cm⁻³ are in excellent agreement with the more accurate measurements of Thomas *et al.*³ Combescot has calculated $T_c = 8$ K and $n(T_c) = 0.7 \times 10^{17}$ cm^{-3.8}

For Si our values φ (meV) = 21.97 - 14.7 = 7.27, $n(0) (10^{18} \text{ cm}^{-3}) = 3.2$, and T_c (K) = 20.8 agree well with experimental values of 6.8, 3.7, and 20,⁶ respectively. BR and CN values, $\varphi = 5.7$ (BR), 6.3 (CN), n(0) = 3.4 (BR), 3.1 (CN), and $T_c = 28$ (Combescot) also compare well with experiment.

Under large $\langle 111 \rangle$ and $\langle 100 \rangle$ uniaxial stress the band structure of Ge and Si simplifies considerably.⁹ For Ge[111] and Si[100] we find $\varphi = 4.9$ and 21.8 K, and T_c for the two systems are, respectively, 2.6 and 14.3 K. It is thus quite feasible to perform an experiment at low temperatures and verify the existence of EHD in Ge[111] and Si[100].

For GaAs our $\epsilon_g = 4.08$ meV is larger than the BR value 3.7 meV, whereas the experimentally determined value of $E_{\rm ex}$ is $= 4.2 \pm 0.2$ meV¹² and hence the value of the binding energy φ is going to be small (if any).¹³

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