gradient, it will be desirable to study[5] the relative sign of the Cd^{111} coupling constant in the metal as compared to that in an ionic crystal[1] so that the sign of Q itself will not be involved.

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Surface Structure of Electron-Hole Droplets

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We consider the surfaces of the condensed phase of excitons in semiconductors, the electron-hole liquid (EHL). By using the theory of the inhomogeneous electron gas and a variational technique we estimate the surface tension for the EHL in Ge to be 10^{-4} erg/cm^2; the carrier density in the surface region varies on a scale of ≈ 50 Å. We suggest an experiment to measure the surface tension of the EHL.

The condensation of excitons in certain semiconductors at low temperatures has been the subject of much recent interest.[1-8] The metastable condensed phase which results has become known as the electron-hole liquid (EHL). A source of particular fascination in the study of this phase is its apparently unique microscopic structure: Most current investigations[1-5,7,8] consider that the EHL consists of two interpenetrating plasmas (the electrons and holes) *both* of which have quantum dynamics, in strong contrast with an ordinary solid or liquid. The differences in microscopic structure might be expected to affect, among other things, the nature and properties of the surface of the EHL.

In an ordinary metal the surface properties can be understood by assuming the ions give rise to a fixed potential in which the electrons move. One then calculates surface energies, dipole layers, etc.[9] In the EHL the mass ratio of electrons and holes is near unity. We might anticipate unusual surface energies and surface structure; very likely both components will have slowly varying density near the surface, each density depending on the other, and we can expect the dipole layer to be much reduced. In this paper we will investigate these phenomena.

The calculation of properties such as equilibrium density and ground-state energy indicate that the details of the band structure of the host crystal play a central role in determining the properties of the EHL.[7,8] We will focus our attention on the EHL in Ge; we must adopt a model simple enough to allow us to proceed, and one which takes sufficient account of the nature of the host material. We allow for four isotropic electron sub-bands, each with the density-of-states mass $m=0.22m_e$; for the holes we use only the heavy-hole band with mass $M=0.347m_e$.[8] We use units in which the mass unit is the optical reduced mass $\mu=0.46m_e$, and $\hbar=e^2/\epsilon=1$, where ϵ is the dielectric constant. The principal simplification here is ignoring the large anisotropy of the electrons.

To investigate the surface properties of the EHL, we use the theory of the inhomogeneous electron gas,[10] in which the ground-state energy E of the system is expressed as a functional of the densities of electrons and holes. We write

$$E=\sum_j T_j[n_j]+\sum_j X_j[n_j]+\tfrac{1}{2}\sum_{jk}\int d^3r_j\, d^3r_k\, e_j e_k n_j n_k/\epsilon|r_j-r_k|+E_c[n_j]. \tag{1}$$

Here the index j runs over sub-bands occupied by electrons and holes; $e_j=\pm e$ is the charge associated with the particle, and n_j the number density. The functionals T_j, X_j, and E_c, represent the kinetic, exchange, and correlation energies, respectively.

In the following we will neglect E_c. We can write the kinetic and exchange energies as a sum of functionals each depending on the electron density in the corresponding sub-band. An explicit form of the functional can be obtained in terms of a gradient expansion of the densities of electrons and holes.[10] For each sub-band, we have

$$\int d^3r\,(yAn_j^{5/3}+Bn_j^{4/3})+\int d^3r\,|\nabla n_j|^2(yCn_j^{-1}+Dn_j^{-4/3})+\cdots, \tag{2}$$

where, defining $\eta=(3\pi^2)^{1/3}$, we have $A=3\eta^2/10$, $B=-3\eta/4\pi$, $C=\frac{1}{72}$, and $D=7/432\pi\eta$. The coefficients A, C and B, D refer to the gradient expansion of the kinetic and exchange energies, respectively. Also, $y=\mu/m$ for the electron bands, and μ/M for the holes. We terminate the gradient expansion in Eq. (2) after the terms in $|\nabla n_j|^2$.

We will at first assume that the third term in Eq. (1), the Hartree energy, is so large that the liquid is forced to be everywhere neutral. Then E can be expressed entirely in terms of the hole density n_0 which is 4 times the electron sub-band density:

$$E=\int d^3r\,[(1/4^{2/3}m+1/M)\,\mu An_0^{5/3}+(1/4^{1/3}+1)Bn_0^{4/3}]$$
$$+\int d^3r\,|\nabla n_0|^2[(1/m+1/M)\,\mu Cn_0^{-1}+(4^{1/3}+1)Dn_0^{-4/3}]. \tag{3a}$$

We can then define new coefficients A', B', C', D' and write

$$E=\int d^3r\,(A'n_0^{5/3}+B'n_0^{4/3})+|\nabla n_0|^2(C'n_0^{-1}+D'n_0^{-4/3}). \tag{3b}$$

Consider a situation in which the EHL fills half of space, $x<0$. Deep within the material the ground-state energy per pair $\tilde{\mu}$ and the hole density $\tilde{n}_0$ can be easily expressed in terms of A' and B' (the gradient terms vanish in the bulk material). From Eq. (3b), $\tilde{\mu}=-B'^2/4A'$; $\tilde{n}_0=(-B'/2A')^3$.

The surface energy is then given by $E-\tilde{\mu}N$, where E is the energy of N electron-hole pairs in the semi-infinite EHL calculated from Eq. (3b), and $\tilde{\mu}N$ is the energy these N pairs would have had in an infinite medium. This quantity is to be minimized with respect to $n_0(\vec{r})$, keeping N fixed. To minimize we choose

$$n_0(\vec{r})=\tilde{n}_0/[1+\exp(\alpha x)], \tag{4}$$

where α is a variational parameter. Then the surface tension, or surface energy per unit area, is

$$\gamma=-\,\tilde{\mu}\int_{-\infty}^{\infty}dx\,[1+(n_0/\tilde{n}_0)^{2/3}-2(n_0/\tilde{n}_0)^{1/3}]+\int_{-\infty}^{\infty}dx\,(dn_0/dx)^2 g. \tag{5}$$

Here g, the coefficient of the squared gradient, is exactly as in Eq. (3b). Using Eqs. (3b), (4), and (5) the minimization is simple and can be carried out analytically. The result is

$$\gamma = -2\tilde{\mu}\tilde{n}_0^{2/3}\xi\nu, \quad \alpha = \tilde{n}_0^{1/3}\xi/\nu; \tag{6a}$$

$$\xi^2 = (9 - 3\ln 3 - \sqrt{3}\pi)/2 \approx 0.1314; \tag{6b}$$

$$\nu^2 = C'/2A' - 9D'/5B'. \tag{6c}$$

For our model of Ge, we find

$$\begin{aligned} &\tilde{\mu} \approx -0.6 = -1.2\ \mathrm{Ry}^* \\ &\tilde{n} \approx 0.92(a^*)^{-3}\ (\text{i.e., } r_s \approx 0.64), \\ &\gamma \approx 0.04 = 0.08\ \mathrm{Ry}^*/(a^*)^2 \approx 1\times 10^{-4}\ \mathrm{erg/cm^2}, \\ &\alpha^{-1} \approx 0.29a^* \approx 50\ \text{Å}. \end{aligned} \tag{7}$$

Here a^* is the Bohr radius associated with the exciton, and Ry* the exciton binding energy.[11] We have taken Ry* = 2.65 meV and $a^* = 1077$ Å.[8]

We have checked the validity of using Eq. (4) for the functional form of the variational density by converting our minimum condition to an Euler-Lagrange equation and solving numerically. The results are essentially the same. We checked that the one-dimensional semi-infinite problem gave the same surface energy and surface thickness as a three-dimensional drop of finite radius. The results were identical for drop radii greater than around 10 Bohr radii. The assumption of local charge neutrality was checked by introducing two independent density profiles, one for electrons and the other for holes, each of the form of Eq. (4). A numerical minimization leads, again, to essentially the same results as Eq. (6) with the scale of surface thickness of both distributions close to $1/\alpha$. The calculated dipole layer is very small and does not significantly alter the surface tension.

One result of our use of the Hartree-Fock approximation is that the calculated binding energy $|\tilde{\mu}|$ is less than one would obtain by including correlation effects.[7,8] We do not feel that this invalidates our calculation of surface properties, because the correlation energy is expected to vary much more slowly as a function of density than the kinetic or exchange energies. One indication of this is that the calculated density $\tilde{n}_0$ agrees rather well with the calculation of Brinkman and Rice,[8] for example.

We cannot justify on theoretical grounds the validity of terminating the gradient expansion at second order terms. One indication of trouble is that $\alpha/k_F \approx 1$, so that the criterion of a "slowly varying density"[10] is not met. We believe, however, that the simple gradient expansion gives a reasonable approximation to the actual surface tension; this point will be the subject of further study. Such an approximation appears to work for other surface problems such as chemisorption on metal surfaces.[12]

It would be extremely interesting to measure the surface tension of the EHL to compare with Eq. (7). An indirect estimate can be given by considering the classical condition for the stability of a droplet: A droplet is stable free of a nucleation center only if its size exceeds a critical size[13]:

$$r_c = \frac{2\gamma}{\tilde{n}_0 k_B T \ln(P/P_\infty)}. \tag{8}$$

Here P is the pressure and P_∞ the vapor pressure. If the logrithmic term is of order unity in a given experiment, and $T \simeq 1$ K, we would expect droplets to be stable if $r > 10^{-5}$ cm. Electron-hole droplets are usually observed[2,14] with $r \approx 10^{-4}$–10^{-3} cm.

A direct measurement also seems possible by exploiting the existence of the shape oscillations of droplets known as capillary modes. The lowest frequency mode of this type has quadrupole symmetry; the drop oscillates between a "pancake" and a "cigar" shape. Hydrodynamic theory gives for the frequency of the oscillation[15]

$$\omega = (8\gamma/\rho R^3)^{1/2}. \tag{9}$$

Here ρ is the mass density of the fluid in the drop and R its radius. Using γ from Eq. (6) we find $\omega \approx 10^9\ \mathrm{sec}^{-1}$. In fact, it is far from clear that hydrodynamics is applicable here. Nevertheless, even if we are in the collisionless regime it is reasonable to expect that the mode still exists, though perhaps with a frequency somewhat shifted from Eq. (9). An estimate of the symmetric breathing mode of the droplet (also on a hydrodynamic model) indicates a frequency around 50 times higher than the capillary mode; consequently, the assumption of incompressible motion in the calculation of Eq. (8) should be valid. In the collisionless limit, the capillary mode can be thought of as a transverse acoustic plasmon, with restoring force provided by the surface tension. Such a mode could be Landau damped; we have not as yet obtained an estimate of the damping.

If the quadrupole mode could be excited, we might expect to observe resonances at ω, i.e., in the radio-frequency range. It is easy to show that an external uniform rf electric field should couple nonlinearly to the oscillation. The mechanism may be visualized as a modulation of depolarization factors due to changes in shape of the highly conducting droplet. The resulting term in the Hamiltonian is proportional to BE_e^2, where B is the amplitude of the oscillation and E_e is the external field. We expect to observe resonant absorption, or (in the presence of a static applied electric field in addition to the rf field) resonant second-harmonic generation, both at an applied frequency of $\omega/2$. Estimates of the amplitudes of these processes indicate that they could be observable. If so, the frequency of the resonance would provide information about γ via Eq. (8), and the width could, assuming small damping, reflect the size distribution of the electron-hole droplets.[16]

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Spin-Orbit Effect in the Si Valence Band*

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We report experimental evidence for a strong spin-orbit effect on the Si valence band. A theoretical evaluation of this effect on the hole mobility in the range of temperatures between 12 and 200°K is consistent with band-structure calculations, cyclotron-resonance measurements, and transport properties.

The small value of the spin-orbit energy in Si ($\Delta = 0.044$ eV[1]) introduces a strong nonparabolicity of the two degenerate valence bands in a region near $\frac{1}{3}\Delta$. This effect, theoretically predicted by Dresselhaus, Kip, and Kittel[2] and by Kane,[3] has not yet received full experimental evidence,[4] mainly because of the great difficulties met in investigating regions of $\vec{k}$ space away from critical points.

The aim of this paper is to present new experimental data whose theoretical interpretation, in the light of the existing theories, seems to give unambigously evidence for the nonparabolicity of the Si valence band. This evidence arises from an anomalous behavior which has been experimentally found here in the temperature dependence of the hole mobility μ between 20 and 30°K (see Figs. 1 and 2). At these temperatures, provided the crystal is so perfect that only acoustic scattering is effective in determining the low-field transport properties, theory predicts a $T^{-3/2}$ temperature dependence for μ in spherical and parabolic bands. On the contrary, we have observed a strong deviation from this slope in the above temperature range, as is shown in Fig. 2. In Fig. 2(b) we have reported the behavior of $d(\ln\mu)/d(\ln T)$ as a function of T. Its peak can be correlated in detail to a band-structure effect which is expected to occur in the Si valence band because of its small spin-orbit energy. In fact a