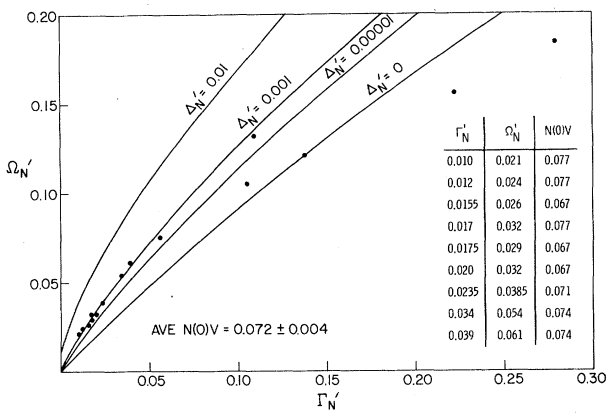

Γ_N'	Ω_N'	N(0)V
0.010	0.021	0.077
0.012	0.024	0.077
0.0155	0.026	0.067
0.017	0.032	0.077
0.0175	0.029	0.067
0.020	0.032	0.067
0.0235	0.0385	0.071
0.034	0.054	0.074
0.039	0.061	0.074

FIG. 3. Measured values of Ω_N' plotted against Γ_N', with theoretical curves generated from Eq. (2) shown for comparison. Inset table gives data for $\Gamma_N' < 0.05$ with the calculated values of $N(0)V$.

the usual BCS relation

$$\Delta_N = 2\omega_c \exp[-1/N(0)V].$$

We find $N(0)V$ for an 1800-Å gold film to be 0.72 ± 0.004.

Recent measurements[6] of $N(0)V$ for copper and silver indicate similar results, and we plan further measurements on these metals. It would also be of interest to study the thickness dependence and extrapolate $N(0)V$ to the bulk metal.

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Metallic State of the Electron-Hole Liquid, Particularly in Germanium

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We have calculated the ground-state energy of an electron-hole liquid. The kinetic and exchange energies are included exactly, and the correlation energy is estimated using Hubbard's modification of the random-phase approximation. In an isotropic electron-hole liquid, the metallic state is not bound relative to free excitons. In Ge the anisotropic band structure leads to a substantial binding of the metallic state. Application of a large ⟨111⟩ strain to Ge reduces the situation to one resembling the isotropic case.

Recently there has been much interest in the properties of Ge in which a high concentration of excitons have been optically excited.[1] Since the lowest exciton states in Ge are indirect, they are relatively long-lived and many experiments can be performed under equilibrium conditions. Keldysh[2] has proposed that the striking changes that occur with increasing exciton density in the recombination radiation, far infrared absorption, and the electrical conductivity, are due to the formation of metallic droplets of the electron-hole liquid. In this Letter we wish to report microscopic calculations of the ground-state energy of a metallic electron-hole liquid. We consider three cases: (a) an ideal electron-hole liquid of equal-mass particles, (b) Ge (unstrained), and (c) Ge with a large ⟨111⟩ strain.

In the weak-binding limit in which the exciton binding energy $E_B \ll E_d$, the lowest direct energy gap, and the total number of excited carriers is very small compared to the number of atoms, we may write the Hamiltonian as

$$H = \sum_{\vec{k},\sigma,i=1}^{I} \epsilon_i^a(\vec{k}) a_{\vec{k},i,\sigma}^{\dagger} a_{\vec{k},i,\sigma} + \sum_{\vec{k},\sigma,j=1}^{J} \epsilon_j^b(\vec{k}) b_{\vec{k},j,\sigma}^{\dagger} b_{\vec{k},j,\sigma} + \sum_{\vec{q}} \frac{4\pi e^2}{\kappa q^2} \rho(\vec{q})\rho(-\vec{q}), \tag{1}$$

where $a_{\vec{k},i,\sigma}^{\dagger}$ and $b_{\vec{k},j,\sigma}^{\dagger}$ are creation operators for electrons and holes with spin σ in I and J sub-bands, respectively, and the wave vector $\vec{k}$ is measured from the extremum of each sub-band. The Coulomb

interaction is reduced by the dielectric constant κ, and the density operator $\rho(\vec{q})$ is given by

$$\rho(\vec{q}) = \sum_{\vec{k}\sigma ii'} M_{ii'}(\vec{k}, \vec{k}+\vec{q}) a_{\vec{k}+\vec{q},i,\sigma}^{\dagger} a_{\vec{k},i',\sigma} - \sum_{\vec{k}\sigma jj'} M_{jj'}(\vec{k}, \vec{k}+\vec{q}) b_{\vec{k},j,\sigma}^{\dagger} b_{\vec{k}+\vec{q},j',\sigma}. \quad (2)$$

In an isotropic electron-hole liquid we consider only one isotropic sub-band for each carrier, $M_{11} \equiv 1$, and write $\epsilon_1^a(\vec{k}) = \epsilon_1^b(\vec{k}) = k^2/2m$. It is convenient to express the energy in units of the exciton Rydberg ($E_B = \mu e^4/2\kappa^2$, where $\mu = m/2$), and to introduce the interelectron separation r_s measured in units of the Bohr radius $a_B = \kappa/\mu e^2$. The ground-state energy E_g per electron-hole pair can be written as

$$E_g = \frac{2.21}{r_s^2} - \frac{1.832}{r_s} + \epsilon_{\mathrm{corr}}, \quad (3)$$

where the first and second terms are the usual kinetic and exchange energies. The correlation energy has been calculated by generalizing an approximation introduced for the electron gas by Hubbard.[3] In his approach one modifies the random-phase approximation (RPA) to include approximately the second-order exchange diagrams between particles in the same sub-band. In the present case we generalize Hubbard's expression for the total polarizability ($A' + i\Sigma'$) to include the contribution from each sub-band,

$$A' + i\Sigma' = \sum_{i=1}^{I} f_i(\vec{k}) \Pi_i^{\mathrm{RPA}}(\vec{k}, \omega) + \sum_{j=1}^{J} f_j(\vec{k}) \Pi_j^{\mathrm{RPA}}(\vec{k}, \omega), \quad (4)$$

where Π_i^{RPA} is the usual RPA polarizability for the i sub-band and

$$f_i(k) = \{k_{\mathrm{F},i}^2 + [1 - \tfrac{1}{2}(I+J)^{-1}] k^2\}/(k_{\mathrm{F},i}^2 + k^2),$$

with k_F the Fermi wave vector. In Fig. 1, curve a, we plot the resulting ground-state energy versus r_s. We obtain a minimum value of $E_g^0 = 0.86$ at $r_s = 2.0$. This value is considerably lower than the value ≈ -0.35 found by Hanamura[4] who used the high-density expansion to estimate ϵ_{corr}. As in the electron gas there are substantial corrections to the high-density expansion for $r_s \gtrsim 1$. However, $E_g^0 > -1$ indicates that the metallic state is not bound relative to free excitons. In our approximate calculation, while we may hope to have included electron-electron and hole-hole correlations reasonably well, it is not clear that we have adequately treated electron-hole correlations. We have included electron-hole scattering to second order but it is the repeated scattering of the electron and hole which is responsible for the exciton bound state as $r_s \to \infty$. An approximate criterion for the occurrence of such a bound state was given by Mott,[5] i.e., $k_{FT} a_B = 1$, where k_{FT} ($= 1.63 r_s^{1/2} k_F$) is the Fermi-Thomas screening wave vector. This leads to a critical value $r_s^{\mathrm{Mott}} \approx 10$ which is 4 times larger than that in a single-carrier model because of the increased screening and reduced mass in the presence of two carriers. In fact, the ideal electron-hole gas, because of perfect nesting of the electron and hole Fermi spheres, is always unstable at zero temperature. We find, however, that the binding energy of the electron-hole paired state is extremely small for $r_s < 8$. Thus the omission of the electron-hole multiple scattering in the region of interest, $r_s \lesssim 2$, may not be crucial. A second argument can be found by examining the Wigner-Huntington[6] calculation for the metallic

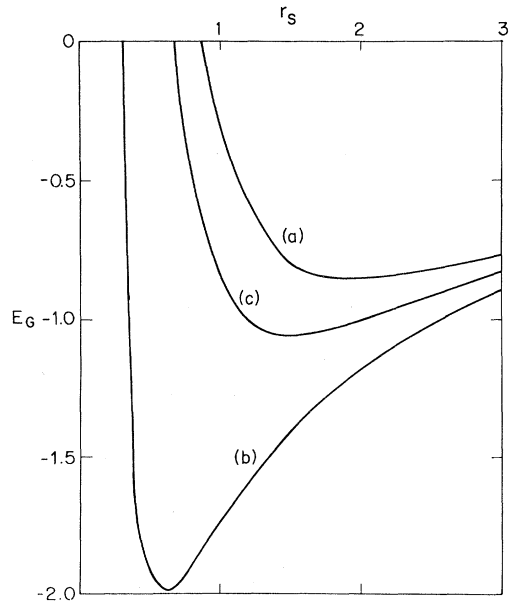

FIG. 1. The ground-state energy E_g of the electron-hole metallic liquid as a function of the interelectron spacing r_s. Curve a, an ideal isotopic band structure, with equal masses; curve b, Ge (unstrained); and curve c, Ge in presence of large $\langle 111 \rangle$ strain. The units are exciton Rydbergs and the exciton Bohr radius. For Ge we choose $\mu = 0.046m$ and $\kappa = 15.4$ (see text).

phase of hydrogen. Since the hole (proton) is assumed localized, the electron-hole interaction is accurately treated and they find for mass ratio $m_h/m_e \gg 1$

$$E_g^0(m_e/m_h) = -1.05 + 0.8(m_e/m_h)^{1/2} . \quad (5)$$

Thus for a mass ratio $m_h/m_e < 256$ the metallic phase is unbound. Thus we may expect that $E_g^0(m_e/m_h = 1) \gtrsim -1$.

In the low-density limit, there is a weak Van der Waals attraction between excitons. Theoretical studies[7] have shown that two excitons will bind into an exciton molecule even for equal masses. Therefore, for large r_s, $E_g(r_s) < -1$. However, estimates of De Boer's[8] quantum parameter Λ^* indicate that in this density regime the exciton gas is in the quantum limit. The form of $E_g(r_s)$ for an ideal electron-hole gas is a difficult theoretical problem and it is not clear whether there are, in fact, two separate minima for $E_g(r_s)$ as our calculations indicate.

In Ge it is important to include explicitly the band structure. The electrons are in four ellipsoids of revolution at the L point of the Brillouin zone with transverse and longitudinal masses $m_t = 0.082$ and $m_l = 1.58$.[9] There are two degenerate valence bands at Γ with an energy spectrum

$$\epsilon(\vec{k}) = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2} ,$$

where $A = 13.38$, $B = 8.48$, and $C = 13.15$ in units of $\hbar^2/2m$.[10] In this case the average masses entering into the exciton binding energy and into the kinetic energy of the metallic state are very different. In the former case, because of the s-like symmetry of the exciton wave function, a reduced mass μ, defined by

$$\mu^{-1} = \tfrac{1}{3}(2m_t^{-1} + m_l^{-1}) + A^{-1} \quad (\mu = 0.046), \quad (6)$$

gives a value of 2.65 meV for the exciton binding energy, in fair agreement with the experimental values of 3.6 and 2.8 meV.[11,12] The kinetic energy of the metallic state depends on the density-of-states mass which, for the electrons, is given by $m_d = (m_t^2 m_l)^{1/3} = 0.22$. For the holes the heavy band gives a mass $m_{hh} = 0.347$ and the light band, $m_{lh} = 0.042$. Thus the density-of-states masses are much larger than the masses entering the exciton and lead to a much reduced kinetic energy in the metallic phase. For the electrons, taking $M_{ii'} = \delta_{ii'}$, the exchange energy between electrons in each ellipsoid can be evaluated numerically. The exchange energy does not depend on the mass but does depend weakly on the shape of the Fermi surface. For the holes, the matrix elements $M_{jj}(\vec{k}, \vec{k}+\vec{q})$ are complicated functions of the angle[9] and the exact evaluation of the exchange energy can only be carried out numerically. We find that the ground-state energy per electron including the kinetic and exchange energies exactly has the form

$$E_g = 0.468/r_s^2 - 1.136/r_s + \epsilon_{corr} , \quad (7)$$

where the energy and r_s are in exciton units with $\mu = 0.046$ and $\kappa = 15.4$. In evaluating the correlation energy in the Hubbard approximation, the band structure is replaced by four spherical electron sub-bands and two spherical hole sub-bands with $M_{ii'} = \delta_{ii'}$ with the masses that enter into Eq. (6). The results are shown in Fig. 1, curve b. While our treatment of the correlation is surely conservative[13] we find that the metallic state is strongly bound relative to free excitons, in contrast to the ideal case discussed above. The equilibrium value of $r_s = 0.63$ corresponds to a density of electrons (or holes) of 1.8×10^{17} cm^{-3}, in good agreement with the experimental value of 2×10^{17} cm^{-3}.[1] We find the binding energy ϵ_B relative to the experimental exciton energy to be 1.7 meV. Pokrovskii and Svistunova,[14] by measuring the shape of the coexistence curve at low densities, found a value $\epsilon_B = 2.7$ meV.

In the presence of a $\langle 111 \rangle$ stress larger than 500 kg/cm^2, the band structure of Ge simplifies considerably. The degeneracies between the four electron ellipsoids and between the valence bands at Γ are lifted and there is just one electron and one hole ellipsoid. The former masses are as quoted above and the latter have values $m_t^{-1} = A - \frac{1}{2}(B^2 + \frac{1}{3}C^2)^{1/2}$; $m_l^{-1} = A + (B^2 + \frac{1}{3}C^2)^{1/2}$. The kinetic and exchange energies can be calculated straightforwardly, and we find

$$E_g = 1.616/r_s^2 - 1.631/r_s + \epsilon_{corr} , \quad (8)$$

where the units are the same as in unstrained Ge. Because of the simple band structure it is possible to carry through exactly the modified RPA calculation as described previously and the results are shown in Fig. 1, curve c. The metallic state minimum is shifted to lower densities and in our calculations has a value $E_g^0 = 1.06$. Undoubtedly, improvements will move E_g^0 lower, but it is not clear if the metallic state is lowest in energy. It should be pointed out that if one estimates the correlation energy using the masses appropriate for calculation of the exciton binding energy, one obtains a value smaller by 0.1 Ry for ϵ_{corr}. Experiments on the coexistence curve for strained Ge have not been carried out to our knowledge

and would be of great interest since the density difference between the two phases should be considerably reduced. Recombination radiation studies have been reported by Bageev, Galkina, and Gogolin,[1] which indicate a large reduction in metallic state binding. Benoit à la Guillaume, Salvan, and Voos[15] have measured a density of 2×10^{16} cm^{-3} in the metallic phase which is somewhat larger than the value of 1.2×10^{16} cm^{-3} that we find.

In conclusion we find that the large binding energy of the metallic state of the electron-hole liquid in Ge is due mainly to its special band structure. For simple band structure, such as in strained Ge, the binding is much weaker if indeed the metallic phase is bound. A detailed account of the calculations reported here will be published elsewhere.

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Normal Modes of Vibrations in CuI

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Phonon dispersion curves for CuI have been measured at room temperature for the [100], [110], and [111] symmetry directions by using inelastic neutron scattering. The results are interpreted in terms of a rigid-ion model. Estimations are given for elastic constants.

Continuing the study of the lattice dynamics of cuprous-halide crystals with zinc-blende structure, we report in this paper the results of coherent inelastic neutron scattering from CuI.

Our interest in these compounds dates from some years ago, since the unfruitful attempt to fit zero-wave-vector phonons of CuCl with an oversimplified rigid-ion-lattice dynamical model.[1] Mar-