wise the electronic structure of the (211) surface resembles the bulk band structure of copper. This suggests that the enhanced reactivity of the stepped surface—observed in this case for O_2—may well arise more from steric effects due to step-adsorbate geometry than from any particular electronic-structural property of these steps.

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Phase Separation of the Electron-Hole Drop in ⟨111⟩-Stressed Ge

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We present a theoretical study of the electron-hole drop containing both "hot" and "cold" carriers in ⟨111⟩-stressed Ge at $T=0$. We predict that for certain values of the stress this system phase separates into two degenerate Fermi liquids, one containing "cold" and the other containing both "hot" and "cold" electrons. It should be possible to verify this prediction experimentally.

When a ⟨111⟩ uniaxial stress is applied to Ge the fourfold degeneracy of the conduction-band minimum is lifted, three conduction valleys rising in energy while the fourth one is lowered. Recent experiments.[1,2] have indicated that in an electron-hole drop (EHD) in this system it is possible for a substantial fraction of the electrons to be present in the three upper valleys in quasiequilibrium with the electrons in the lower valley and with the holes. The relaxation time for the so-called "hot" electrons associated with the three upper valleys to decay into the lower valley (the "cold" valley) was measured[1,2] to be microseconds at moderate stresses. This value is in agreement with a theoretical estimate of the electron intervalley scattering time,[1] and comparable with, although smaller than, the total lifetime of an EHD electron in the conduction band. An independent observation of "hot" electrons in the EHD in Ge in high magnetic fields has also been reported.[3] Thus, there is substantial evidence for the existence of both "hot" and "cold" electrons in the same EHD system.

In this Letter we present our theoretical prediction that in Ge at $T=0$ and at suitable (experimentally attainable) values of $\langle 111\rangle$ uniaxial stress, the EHD system containing "hot" and "cold" electrons can exist in two forms. There exists a critical value x_{crit} of the ratio $x=N_h/N_c$ of the numbers of hot and cold electrons such that for $x>x_{\mathrm{crit}}$, the EHD is homogeneous (i.e., contains both the hot and the cold electrons) while for $x<x_{\mathrm{crit}}$ a separation into two coexisting electron-hole liquid phases is predicted. One phase consists entirely of cold electrons (and holes) while the other contains both hot and cold electrons. If verified experimentally, this would constitute a unique case of a phase separation of two degenerate Fermi liquids.

In this calculation we shall be treating the hot and cold electrons as two separate species in quasiequilibrium with each other. For this to be valid it is necessary that the intervalley relaxation time be much longer than the intravalley relaxation time for establishing thermal equilibrium. Further, the electrons are assumed to be in quasiequilibrium with the holes. This latter assumption has been widely used in EHD calculations when no hot electrons are present.[4-7] For hot electrons the quasiequilibrium assumption is still justified because the intervalley relaxation time is comparable with the total conduction-electron lifetime which is much longer than the intravalley relaxation time. Let N_h, N_c, N_H, and E be the numbers of hot and cold electrons and of holes and the energy of the system, respectively, and n_h, n_c, n_H, and ϵ the corresponding densities. Then at $T=0$, at equilibrium

$$\left(\frac{\partial E}{\partial V}\right)_{N_h,N_c,N_H}=0, \tag{1}$$

where V is the EHD volume. For a homogeneous system, (1) becomes

$$\epsilon-n_h\left(\frac{\partial\epsilon}{\partial n_h}\right)_{n_c}-n_c\left(\frac{\partial\epsilon}{\partial n_c}\right)_{n_h}=0, \tag{2}$$

where the derivatives are taken keeping $n_H=n_h+n_c$. Now define the electron-hole pair chemical potentials

$$\mu_h=\left(\frac{\partial E}{\partial N_h}\right)_{V,N_c,N_c+N_h=N_H}=\left(\frac{\partial\epsilon}{\partial n_h}\right)_{n_c}, \tag{3}$$

$$\mu_c=\left(\frac{\partial E}{\partial N_c}\right)_{V,N_h,N_c+N_h=N_H}=\left(\frac{\partial\epsilon}{\partial n_c}\right)_{n_h}, \tag{4}$$

using the same convention as in (2). Differentiation of (2) yields

$$0=d\left[\epsilon-n_h\left(\frac{\partial\epsilon}{\partial n_h}\right)_{n_c}-n_c\left(\frac{\partial\epsilon}{\partial n_c}\right)_{n_h}\right]$$

$$=-n_h d\mu_h-n_c d\mu_c, \tag{5}$$

or

$$x\,d\mu_h=-d\mu_c, \tag{6}$$

where $x=n_h/n_c$. The differentials in (6) are taken between quasiequilibrium states which satisfy (1).[8]

By integrating (6) one finds that a Maxwell construction in μ_h-x space can be used to take care of the chemical potential condition for phase equilibrium. If one plots the values of μ_h obtained for the equilibrium states against x, several cases occur as shown in Fig. 1. In case (a) a phase separation occurs if $x_c'<x<x_c''$. In case (b) a phase separation occurs if $x<x_c$ where x_c is given by the equal-area construction. Here one phase corresponds to $x=0$ and the other to $x=x_c$. Since the $x=0$ phase contains no hot electrons, the chemical potential condition for phase equilibrium is that $\mu_h(x=0)\geqslant\mu_h(x_c)$ and $\mu_c(x=0)=\mu_c(x_c)$. In case (c), and for $x>x_c$ in case (b), there is no phase separation.

The energy density ϵ was calculated as follows: The electron kinetic energy was calculated assuming that N_c electrons occupy one ellipsoidal valley and that N_h electrons are equally distributed among the other three valleys. The hole kinetic energy was calculated numerically taking account of the stress splitting of the valence band and the associated nonparabolicity and warping within the $\vec{k}\cdot\vec{p}$ formalism of Pikus and Bir.[9] The

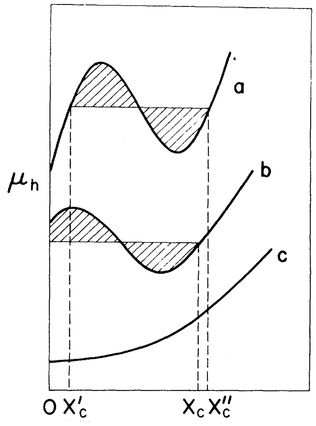

FIG. 1. Schematic diagram of possible forms for the hot-pair chemical potential vs $x=N_h/N_c$.

valence band parameters were taken from Hensel and Suzuki.[10]

In calculating the exchange-correlation energy (ϵ_{xc}) of the EHD we use the fact that this quantity is insensitive to the *details* of the band structure of the system (or to how many conduction valleys contain electrons) and depends only on the total density of electrons or holes, provided that exactly the *same* band-structure features are included in calculating both the exchange and the correlation energy. From Table I we notice that while the exchange and correlation energies separately vary considerably from one band structure to another, their consistently calculated sum does not. The near independence on band structure parameters (including the number of valleys) of the exchange-correlation energy is remarkably good, but we do not know whether it is the result of any general theorem. Note that in Table I all entries relating to Ge have been written in the same units.[6,7]

Thus our numerical procedure was to choose a particular model band structure (for example, that labeled "Ge⟨111⟩, FSC anisotropic" in Table I) and use the consistent ϵ_{xc} for that model computed as a function of density to represent the ϵ_{xc} for our system of hot and cold electrons at the same density, irrespective of how the electrons are distributed among the hot and cold valleys. Using this ϵ_{xc} and the kinetic energy described above, we numerically located the hole density at which the total energy of the system is minimized for a fixed x. At the density we evaluated μ_h and μ_c. This was repeated for various values of stress and of x. The results of the calculation for the consistent ϵ_{xc} corresponding to the model case "Ge⟨111⟩, FSC anisotropic" are given in Fig. 2. μ_h is found to possess a minimum which is most pronounced for intermediate values of stress. The curves shown are of the class (b) of Fig. 1, so that a phase separation in the EHD is predicted for $x < x_{\text{crit}}$ which is arrowed. At very small and very large stresses the minimum in the μ_h curve becomes extremely shallow or disappears completely resulting in a curve of class (c) of Fig. 1, and no phase separation is expected. At large stress the minimum disappears at $S \sim 12$ meV (S denotes the value of the stress-induced splitting of the valence band at $\vec{k}=0$). For very small x it is found numerically that $\mu_h(x) - \mu_h(0) \propto x^{2/3}$ as expected.

The calculation was repeated for a variety of consistent ϵ_{xc}'s corresponding to other band structures and the above qualitative results were reproduced in *all* cases.

The interesting case is when x is small. Then the low value of the hot-electron kinetic energy, which results from the hot electrons being distributed among three valleys, favors condensation of the hot electrons into a smaller volume

TABLE I. The consistently calculated exchange-correlation energies (per pair) in exciton Rydbergs. The exchange and then the correlation contributions follow separately in parentheses. For Ge, 1 Ry = 2.65 meV.

r_s	Ge⟨111⟩[a] FSC[c] Isotropic	 FSC Anisotropic	Si⟨100⟩[a] FSC Anisotropic	Ge (unstressed)[b] SPH[c] Model I
1.7	−3.451	−3.390	−3.340	−3.260
	(−2.618)	(−2.371)	(−2.293)	(−1.864)
	(−0.833)	(−1.019)	(−1.047)	(−1.396)
1.0	−2.582	−2.552	−2.531	−2.500
	(−1.833)	(−1.659)	(−1.605)	(−1.305)
	(−0.749)	(−0.893)	(−0.926)	(−1.195)
1.3	−2.105	−2.089	−2.088	−2.085
	(−1.410)	(−1.276)	(−1.235)	(−1.003)
	(−0.695)	(−0.813)	(−0.853)	(−1.082)

[a] Ref. 6.

[b] Ref. 7.

[c] For a detailed explanation of the abbreviations FSC and SPH we refer the reader to Refs. 6 and 7. Ge⟨111⟩, Si⟨100⟩, and Ge (unstressed) refer, respectively, to systems in which one, two, and four conduction valleys are populated with electrons.

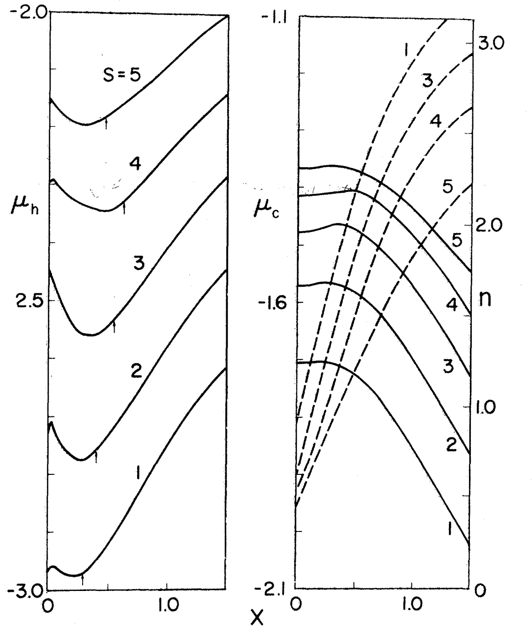

FIG. 2. Chemical potentials (solid lines) in exciton Ry and hole densities in units of $10^{17}/\text{cm}^3$ (dashed) for the consistent model exchange-correlation energy "Ge ⟨111⟩, FSC anisotropic," vs $x = N_h/N_c$. The curves are labeled according to the value of S, the valence-band splitting at $\vec{k}=0$, in MeV. Arrows show x_{crit}. The hot and cold chemical potentials are given relative to respective band minima.

than that occupied by the cold electrons. But at very large and very small stresses the extra hole kinetic energy which would be gained by this prevents such a condensation from taking place. However, at intermediate stresses where the hole Fermi energy is comparable with the valence-band splitting, the hole density of states near to the Fermi level is greatly enhanced by the stress-induced valence-band nonparabolicity and by the presence of the deeper stress-split valence band. This effect (which is absent at very large and very small stress) reduces the hole kinetic energy cost of condensation making phase separation possible. The strong effect of the valence-band nonparabolicity on the EHD properties in the absence of hot electrons has been demonstrated by Liu.[11]

In order to test further the model independence of our prediction, we repeated our calculations for a number of ϵ_{xc}'s where the exchange and correlation were *not* calculated consistently in the sense explained previously. A similar phase separation to that described above was again found in *all* cases.

Several experimental tests of our prediction are possible. It would be desirable to carry out spectroscopic studies similar to those already reported[1,2] but using time-resolved luminescence line-shape analysis to test for the predicted phase separation. In such time-resolved experiments the system would begin at a large value of x and then decay to lower values of x at which the phase separation is predicted to take place. Regarding the time scale for the phase separation we can at this stage only suggest that it would be comparable with the normal EHD nucleation time. In Ref. 1 no phase separation was reported. However, the luminescence line shapes were analyzed on the basis of a one-phase model only. Work is now in progress to check the present predictions.[12]

At small stresses ($S \approx 1$) it is possible to populate all four conduction valleys irrespective of the length of the intervalley scattering time. Although this situation is very much simpler experimentally, the probability of observing effects related to the phase separation is smaller because the minimum in the curve for μ_h (Fig. 2) is very shallow.

Another possible experiment would be to study the plasma-frequency resonances in the absorption spectrum of the EHD noting the large difference in total electron density between the two predicted phases (a factor of approximately 3 for $S = 3$ meV in Fig. 2).

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Electronic Structure of Intercalated Graphite Determined by Magnetothermal Oscillations

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We report the first observation of magnetothermal quantum oscillations in $C_{12n}(SbCl_5)$ for $n=2$ and $n=4$. We interpret these results assuming that the compound is composed of two phases: pure graphite and intercalated sandwiches which behave like two-dimensional metals. This model explains simultaneously the metallic reflectivity and conductivity and the immeasurably small Hall coefficient observed in these compounds.

The graphite intercalation compounds consist of an alternating sequence of intercalate layers separated by n graphite layers. These compounds are interesting for two applications: conductors of electricity and catalyists in electrolytic cells. The electrical conductivity is especially high, even higher than that of copper for certain compounds.[1] This metallic conductivity is still not yet well understood, even though many experimental results have been published.[2] The electronic structure is still unknown. One of the major parameters is the fractional free-carrier generation rate per intercalated atom or molecule, f. Estimations of f ranging from 0.01 to 1 have been reported.[3]

Quantum oscillatory effects are known as one of the best tools to determine the Fermi surface (FS) of metals. Oscillations in the magnetoresistance (Shubnikov–de Haas effect) have been reported by Bender and Young[4] in graphite bromine residual compounds, with a very low concentrations of bromine ranging (from 1 to 2)$\times 10^{-2}$ at.%. Dresselhaus, Dresselhaus, and Fischer[5] proposed a rigid-band model valid for very dilute compounds. In their model, the size of the FS increases continuously with donor or acceptor density. This can be directly tested by measuring the size of the FS for various intercalation stages n.

We report the first experiments on magnetothermal oscillations for the compounds $C_{12n}(SbCl_5)$ with $n=2$ and $n=4$. Contrarily to the residual compounds, these compounds are well-defined both chemically and structurally.

We have studied the magnetothermal oscillations (MTO) of the de Haas–van Alphen (dHvA) type. As is well known,[6] a thermally isolated degenerate electron gas at low temperature in a high magnetic field presents oscillations in its temperature versus magnetic field B. These oscillations, the so-called MTO, arising from the Landau level quantization, are observed by the temperature variation produced in the coupled crystal lattice. The frequency of the MTO is proportional to the extremal section of the FS perpendicular to $\vec{B}$.

Among the quantum effects the MTO are particularly well adapted for the study of the FS of the lamellar compounds, because they do not need electrical contacts and can be measured on very small samples ($\leq 10^{-3}$ g). We have used for these experiments the low-frequency field-modulation technique[7] in an 80-kOe superconducting coil, at 4.2°K. The samples of $C_{12n}(SbCl_5)$, small disks of