Hall Mobility of Electrons Injected into Fluid Neopentane (Dimethyl Propane) along the Liquid-Vapor Coexistence Line between the Triple and the Critical Points

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Measurements of the Hall and the time-of-flight mobilities of electrons injected into neopentane along the liquid-vapor coexistence curve between the triple and the critical points are reported. The ratio of the Hall mobility to time-of-flight mobility always exceeds unity; it decreases linearly from 1.8 at low temperatures to 1.4 near 410 K and increases thereafter to nearly 5.8 in the vicinity of the critical point. This is suggestive of localized states associated with density fluctuations. These density fluctuations are probably the dominant scattering mechanism that determines the Hall mobility.

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The purpose of the present communication is to report the first measurement of the Hall mobility (μ_H) of electrons injected into an insulating liquid in equilibrium with its vapor, from a few degrees above the triple point to the critical point. The most interesting result that we report is that the Hall mobility, which is only determined by scattering events, differs significantly from the time-of-flight mobility (μ_{TOF}), which is also sensitive to trapping.

We have chosen to study neopentane [$C(CH_3)_4$], a tetrahedral molecule that forms a liquid whose triple point is 256.6 K and whose critical point is 433.75 K.[1] The molecules are bound to each other by van der Waals forces. Molecules similar to $C(CH_3)_4$, such as CH_4, Ar, Kr, and Xe, form insulating liquids in which the mobilities of injected electrons[2] are comparable to those found in crystalline semiconductors. No detailed understanding of the mechanisms responsible for these high mobilities exists.

Care in the sample purification made it possible to have the lifetime of the injected electrons longer than 200 μsec. The Hall mobility was measured by adaptation of the Redfield technique, which was successfully used in insulating solids, to the present case. Electrons were injected into the sample by illuminating it with x rays produced by a 4-MeV linear electron accelerator.[3]

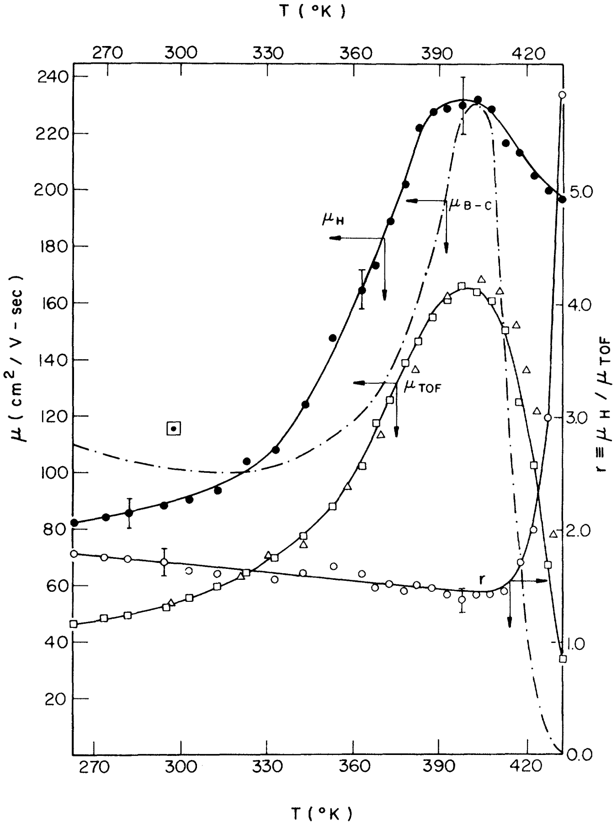

FIG. 1. Temperature dependence of the Hall mobility (solid circles) and time-of-flight mobility (squares) of electrons injected into neopentane. The triangles represent the data from Ref. 7 divided by 1.15 so as to coincide with our room-temperature results and those from Refs. 4 and 6. The broken line is the mobility that is calculated from the theory of Basak and Cohen (Ref. 9, also see text) and the point indicated by the dot inside the square is what is calculated from Ref. 9 with use of the measured room-temperature compressibility (Ref. 10). The points indicated by open circles represent the ratio of μ_H and μ_{TOF}.

The dependence of μ_H and μ_{TOF} on temperature is shown in Fig. 1. Our measurements of the latter are in good agreement with those of others,[4-8] which at room temperature range between 50 and 70 cm^2/V sec. To ascertain that our measurement of μ_H was not affected by spurious signals, we checked that the Hall voltage had a linear dependence on both the magnetic field ($0.15\ T \leq B \leq 0.87\ T$) and on the longitudinal electric field ($45\ V/cm \leq E_L \leq 250\ V/cm$) but did not depend on the carrier density ($10^7\ \mathrm{cm}^{-3} \leq n_e \leq 3\times 10^8\ \mathrm{cm}^{-3}$). Furthermore, a measurement of μ_{H} in CdS at 300 K gave a value of 268 $\mathrm{cm}^2/\mathrm{V\ sec}$, in good agreement with the results of others.[11,12] Possible reasons for the discrepancy between the values of μ_{H} and μ_{TOF} are discussed below.

When an electron undergoes only a single type of scattering (acoustic phonon, optical phonon, charged impurities, dipoles, or disorder) that depends on the electron energy ϵ as ϵ^{-s}, the ratio, r, of the Hall to the drift mobility ($r = \mu_{\mathrm{H}}/\mu_D$) is calculated from Boltzmann's equation. Its value is independent of temperature and larger than $3\pi/8$ only in the case of charged impurity scattering.[13] In order to obtain $r \sim 1.5$ another mechanism must be combined with ionized impurity scattering; furthermore the concentration of charged scattering centers must be $\sim 10^{15}$ to $\sim 10^{16}\ \mathrm{cm}^{-3}$. If such a concentration of ions were present, the resistivity of the liquid would be $\sim 10^5\ \Omega\ \mathrm{cm}$ ($\mu_{\mathrm{ion}} > 10^{-5}\ \mathrm{cm}^2/\mathrm{V\ sec}$) instead of the observed value which is larger than $10^{12}\ \Omega\ \mathrm{cm}$.

Another conceivable origin for the values of $r > 1.4$ is if two or more different carriers occupying different bands were present in the liquid.[13] Either or both of their relative concentrations (n_1/n_2) and their relative mobilities (μ_1/μ_2) should depend on temperature. Neither TOF nor photoemission measurements can detect the existence of several carriers if they alternate repeatedly between the different bands in a time short compared with the measurement time; such a combination of "fast" and "slow" electrons has not been observed in liquids.

A final possible source of discrepancy between μ_{H} and μ_{TOF} is traps. If we consider a concentration of traps N_t that have a single temperature-independent bound state E_t below the conduction-band minimum, we expect[14]

$$r = \mu_{\mathrm{H}}/\mu_{\mathrm{TOF}}$$
$$\sim \mu_D/\mu_{\mathrm{TOF}} = 1 + (N_t/N_c)\exp(E_t/kT).$$

Here $N_c = 2(2\pi m^* kT/h^2)^{3/2}$. For simplicity, we consider $\mu_{\mathrm{H}}/\mu_D = 1$. After correcting for the fact that N_t should depend on temperature in the same way as the density of the liquid, we find that a plot of $\ln(r-1)N_c/N_t$ vs $1/T$ gives $E_t < 0$. Thus extrinsic traps of constant binding energy are inconsistent with the temperature dependence of r.

Intrinsic traps should originate from density fluctuations (Δn). These fluctuations are also the source of the scattering potential considered in the theories of mobility developed by both Basak and Cohen[9] (BC) and Berlin, Nykos, and Schiller[15]; both assume that the energy of the bottom of the conduction band has a local value $[V_0(n)]$ that depends on the local density (n) of the fluid. Neither theory considers the possibility that density fluctuations could give rise to a potential well (ΔV_0) sufficiently deep and whose radius, a, is sufficiently large to yield a bound state ($\Delta V_0 > \pi^2\hbar^2/8ma^2$ in the case of a square well). The value of a is of the order of the correlation length, which diverges at the critical point. The maximum of r should therefore occur near T_c. On the other hand, within the framework of BC ideas, density fluctuations cannot give rise to a bound state when V_0 is a minimum.[16] In these conditions trapping should be absent. Thus the density (or temperature) at which r is a minimum should coincide with the density (or temperature, ~410 K) where V_0 is a minimum (Fig. 2). Both predictions are corroborated by our results, thus underlining the importance of density fluctuations.

We can now compare the temperature (or density) dependence of μ_{H} with the results of the BC calculation. At room temperature all the parame-

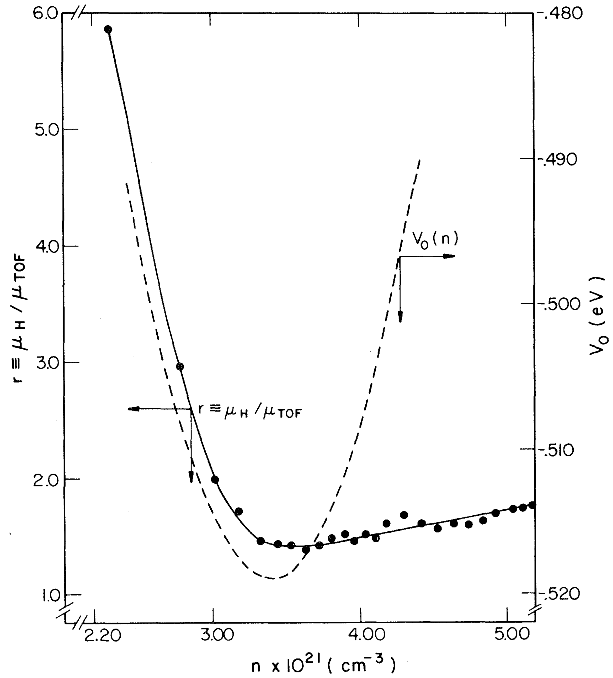

FIG. 2. Dependence of $r = \mu_{\mathrm{H}}/\mu_{\mathrm{TOF}}$ (solid circles) and of V_0 on the density (n) of the fluid. The curve for $V_0(n)$ was calculated by fitting a parabola to the data of Ref. 16.

ters are known: the isothermal compressibility[10] (χ_T) and $V_0(n)$. The derivatives of the latter are calculated after a parabola is fitted to the experimental data.[16] If we assume $m^* = m_0$ the mobility calculated at room temperature (116 cm^2/V sec) is 30% larger than the experimental value of μ_H. Only the term of the BC Hamiltonian proportional to Δn is considered for this comparison; as will be seen below, inclusion of other terms will decrease this calculated mobility by less than 10%.

Except at room temperature, χ_T is unknown. We estimated it by using the law of corresponding states, i.e., we assumed that the equation of state of neopentane as a function of the reduced variables (T/T_c, P/P_c, n/n_c) is the same as that of Ar.[17] Along the liquid-vapor coexistence curve, this assumption is in fair agreement with experiment. The calculated room-temperature value of χ_T is 13% above the experimental value.

When one includes other terms beyond that proportional to Δn in the BC Hamiltonian, a calculation of the mobility requires the introduction of a cutoff wave number q_c that is a measure of the smallest possible dimension of a density fluctuation. We used it as a parameter to adjust the magnitude of the maximum of the calculated mobility so that it would coincide with the experimental value of μ_H. The required value of q_c is $0.21\pi/r_0$, where r_0 is determined from the density of the liquid: $n^{-1} = 4\pi r_0^3/3$. An increase of q_c decreases the calculated maximum of the mobility. The terms of the Hamiltonian involving powers of Δn beyond the first give a contribution to the calculated value of μ that is smaller than 10% of that of the leading term for $T < 370$ K; they are instead dominant near the mobility maximum. The calculated mobility is shown by the broken line in Fig. 1.

The principal conclusion to be drawn from these measurements is that, at least in neopentane, if we neglect the possibility of two or more types of carriers, $\mu_{\rm TOF}$ is not the microscopic mobility. The most likely source of the discrepancy is localized states produced by density fluctuations where the electron can be temporarily trapped. This conclusion is based on the coincidence of the minimum of V_0 with the minimum of $\mu_H/\mu_{\rm TOF}$ and the large increase of the latter towards the critical point. The fact that even at its minimum $\mu_H/\mu_{\rm TOF}$ is not equal to what is expected from the BC theory ($r = 3\pi/8$) suggests the existence of some other contribution that determines the residual value of r. These could be intrinsic traps that cannot be described in BC's deformation-potential approximation, extrinsic traps, or carriers moving in separate bands.

Agreement between the BC theory and experiment is encouraging at temperatures below that corresponding to the mobility maximum. Part of the discrepancy may arise either on account of our estimate of χ_T or from changes of m^* with temperature (or density) that were not considered in the theory. Above the temperature corresponding to the mobility maximum, the discrepancy may depend largely on the fact that when density fluctuations give rise to localized states that can trap an electron, resonant scattering due to potential wells and potential barriers may also be important. This would decrease the scattering cross section in a way reminiscent of the Ramsauer effect.

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