ELECTRON MOBILITY VARIATION IN DENSE HYDROGEN GAS *

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We present electron mobility measurements in H_2 gas for $5 \times 10^{19} < \rho < 5 \times 10^{21}$ cm^{-3} and $26 < T < 32$°K. The data consist of coexisting high and low mobility branches. The high mobility branch is due to electrons; the low mobility, probably due to ions. The electron branch shows strong evidence of bubble formation, in accordance with theoretical predictions.

Electrons form microscopic bubbles ($R \approx 10$ Å) in certain fluids, this fact being reflected in mobilities some orders of magnitude lower than one would predict for free electrons. A theory [1] has been developed for the stability of such bubbles in non-polar fluids and it predicts that under certain conditions they will form in He, H_2, D_2 and perhaps Ne. Such bubbles were first observed and explained in liquid He [2], and subsequently the systematics of their formation in gaseous He have been studied [3–6]. Limited measurements in the liquid and solid have so far not shown their existence in Ne [7]. The only published results for H_2 at reasonably high densities are those of Grünberg [8] at 293°K and Halpern and Gomer [9] in the liquid. Grünberg's data show an anomalously varying cross section, whilst in [9] a mobility of approximately 0.02 cm^2 V^{-1} sec^{-1} was found. Both of these results are compatible with bubble formation. The data we present in this letter are a first attempt to study bubble formation in gaseous H_2 by observing the associated mobility collapse. Our results are not entirely conclusive because of some unexpected experimental limitations.

We used a heavily gold-plated tritium source and a single gate velocity spectrometer to measure the mobility as a function of ρ and T. The gas number density was obtained from pressure and temperature measurements and empirical equations of state [10]. Details of the experimental arrangement may be found in [5]. We presume we had normal rather than equilibrium H_2, but this should not make any significant difference to our results. In fig. 1a we present smoothed values of our measurements, which have an absolute accuracy of ±10%, and each curve has an internal accuracy of ±5%. Also included in fig. 1a are the 293°K data of [8], the dashed part being an extrapolation based on a cross section which increases linearly with density, since such a cross section used in conjunction with the standard expressions reproduces the data very well. We might note that the theory of Legler [11] with a cross section, σ, of 9.1×10^{-16} cm^2 also fits this curve well. As is apparent, we observe coexisting high and low mobility branches; (the data for the 30.0°K isotherm lying virtually on top of that for 31.7°K isotherm for the low mobility branch). There is no difficulty in discerning the two mobilities experimentally since they are so well separated.

The limitations on these curves are the following:
(i) our cell is limited in the pressure it can withstand;
(ii) the values of ρ, T that can be obtained are restricted by the coexistence curve of H_2; in fact, from our ^{4}He measurements [4,5] we know that the values of ρ, T that would be most favorable for bubble formation are inaccessible; and
(iii) the maximum current obtainable from our source decreased as ρ increased, and further the relative signal

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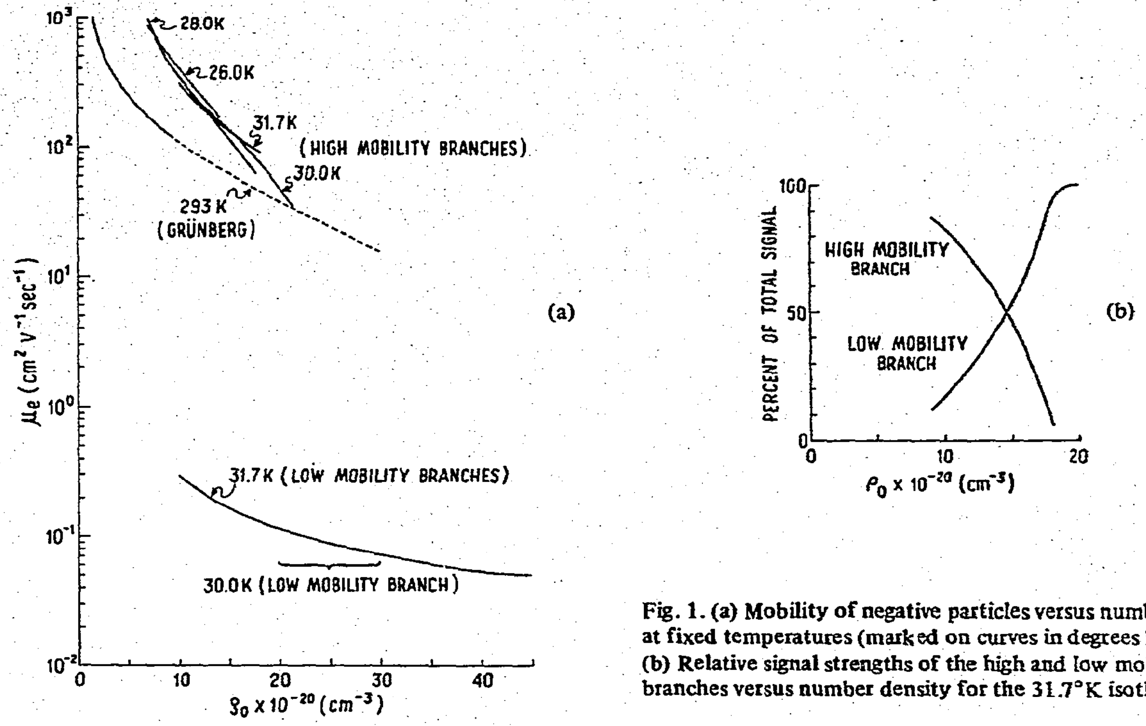

Fig. 1. (a) Mobility of negative particles versus number density at fixed temperatures (marked on curves in degrees kelvin). (b) Relative signal strengths of the high and low mobility branches versus number density for the 31.7°K isotherm.

strengths of the two carriers changes markedly with density, as illustrated in fig. 1b. These factors combined to prevent us from obtaining data at higher ρ and/or lower T.

We shall discuss first the high mobility branch in terms of the expected behavior. Semi-classically, the mobility is given by [3]

$$\mu = \tfrac{3}{4} e(1+B_1\rho)/\rho\sigma(2\pi mkT)^{1/2}, \quad (1)$$

where m is the electronic mass and B_1 is the second virial coefficient. At the lower densities, this equation describes the data quite well, but μ decreases well below the value given by (1) as the density increases. In particular, note that the 30.0°K isotherm has a definite downward trend and seems to cross the 293°K isotherm. This is precisely the behavior observed in He [5]. How close we are to a mobility collapse is hard to say by direct examination of these curves. The coexistence curve prevents us from going to higher densities on the 30.0°K isotherm. For this and higher temperatures the signal strength due to electrons becomes too small to detect at the highest densities. One can however plot the data in a more revealing manner. The underlying cause for bubble formation is that the zero point energy of the electron becomes greater than kT, so that the electron prefers to dig a hole in the gas which lowers the energy of the whole electron–gas system [1]. The zero point energy at the densities in question is given well enough by the optical potential,

$$V_0 = (\hbar^2/2m)4\pi\rho a, \quad (2)$$

where a is the electron–atom scattering length. The quantity V_0/kT then is a measure of the probability of bubble formation. Legler made use of this fact in his theory [11]. Fig. 2 shows Legler's theory as the solid line. The dashed line in fig. 2 is our data for ^{4}He, where the ratio of measured to calculated free electron mobility is plotted against V_0/kT. This dashed curve is obtained from about one hundred data points and covers the range of mobility collapse in He where one is certain bubbles are being formed. The data plotted as squares are from [8] and our data from fig. 1a are plotted as circles. As can be seen our H_2 data depart significantly from unity, the value we expect using (1), and follows the He data very closely. We take this to be strong evidence for electron bubble formation in H_2. We might remark that the crossing of the mobility curves for the various isotherms is not experimental

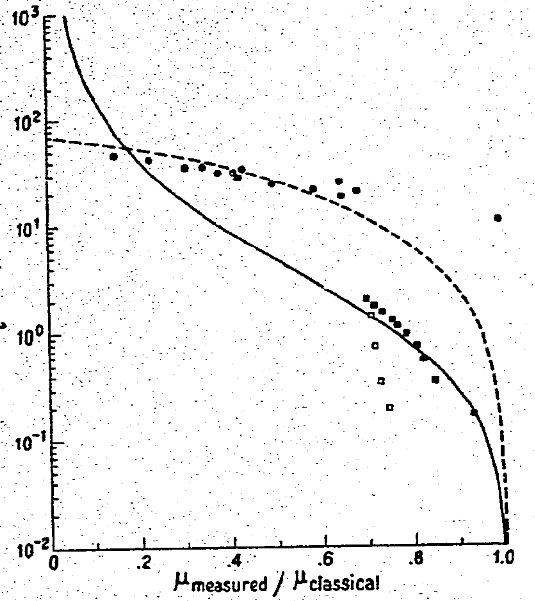

Fig. 2. Solid curve, Legler's theory; dashed curve based on our data in ^{4}He. Open and solid squares, Grünberg's data for ^{4}He and H_2, respectively; solid circles, our data for H_2.

uncertainty but a real effect due to bubble formation. This is because at low density $\mu \propto T^{-1/2}$ and at high density $\mu \propto \exp[-\Delta(\rho)/kT]$, thus at fixed ρ, μ is a decreasing function of T at low density and an increasing function of T at high density.

The low mobility branch is due either to electron bubbles or ions. We were able to rule out impurities by a series of checks during the course of the experiments – notably that the results were unaffected by using H_2 gas of different impurity levels. We first evaluated the radius, R, of the low mobility object by using an interpolation formula [3] for μ,

$$\mu = (e/6\pi\eta R)\ [1+9\pi\eta/4\rho R(2\pi MkT)^{1/2}]\ , \tag{3}$$

where η is the gas viscosity and M is a molecular reduced mass. (3) yielded values of R which varied as shown by the solid line in fig. 3a. It can be seen that the object is quite large as we expect a bubble to be. Using the theory of electron bubbles [1,5] we calculated the expected size and obtained the curves shown in fig. 3a, which seem to suggest that the low mobility branch may be due to bubbles. If this is the case it is hard to see why electrons and bubbles should coexist since this implies long relaxation times for both the

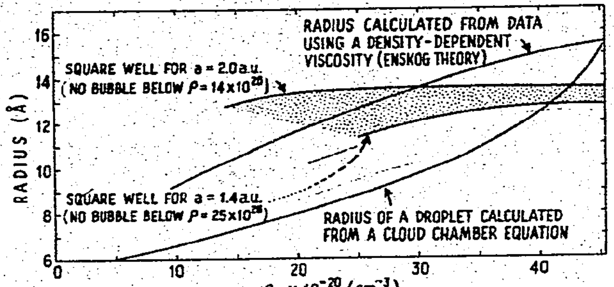

Fig. 3a. Radius of the low mobility object versus number density for the 31.7°K isotherm; values extracted from the data and various predictions.

electron and the bubble. If we are seeing a stable bubble, then, there must be a very large barrier against it relaxing back into an electron, because at the densities in question the binding energy of the bubble is barely larger than kT. In fact, if we take the view that H_2 parallels He quite closely the bubble lifetime should be considerably shorter than its transit time through our apparatus. Thus we feel it unlikely that the low mobility branch is due to bubbles. However, as the details of bubble formation, as opposed to bubble stability, are unknown we cannot completely eliminate this possibility.

Since we are using a radioactive source with a mean β^- energy of ≈2 keV we must consider negative ion creation. The two possibilities are H_2^- and H^-. On the basis of cloud chamber theory [12] we calculated the expected size of cluster ions with the result shown in fig. 3a. This too appears compatible with experiment. The calculation is approximate in that we used an ideal gas equation of state. Assuming that the low mobility branch is due to ions we can use data like those of fig. 1b to obtain the ratio of electron-to-ion densities. Inserting this result in a mass action equation allows us to find the dependence of the activation energy, Δ, on density. Because V_0 depends on ρ we expect Δ to depend on ρ, which we indeed find to be true. Since we are dealing with a cluster ion, however, we must take its formation into account in the mass action formula. The result is that the following equation should be satisfied,

$$\ln\{[^{n+1}H_2^-]/[e^-][H_2]\} - (4\pi/3)R^3\rho_{\text{liq}} \ln[H_2] = (\Delta_2 - \Delta_1 + V_0)/kT + C, \tag{4}$$

where [. . .] means concentration of the quantity concerned, $^{n+1}H_2^-$ is the cluster ion containing the bare ion plus n H_2 molecules, R is the radius obtained from (3), Δ_2, Δ_1 are activation energies involved in forming the cluster and bare ion respectively, and Δ_2 depends very slowly on ρ, V_0 is as given by (2) and occurs because we expect Δ_1 to shift by the electron's zero-point energy, and C is a constant which comes from the mass action equations. The expression on the left-hand side of (4) can be obtained from our data, noting that $[^{n+1}H_2^-]/[e^-] = (I_-/\mu_-)(\mu_e/I_e)$, where I is the current as shown in fig. 1b. If then we plot the l.h.s. of (4), which is an experimental quantity, against $\rho = \rho_{gas}$ we should get a straight line of slope $(\hbar^2/2m)(4\pi a/kT) = 1.49 \times 10^{-20}$ cm^{+3} for a=0.85 Å. This plot is shown in fig. 3b. The slope of the straight line shown there is $(2.0 \pm 0.2) \times 10^{-20}$ cm^{+3} which is in very good agreement with the predicted value.

In conclusion, we have presented evidence that electrons do form bubbles in H_2 gas. Calculations based on [1] predict that we should see the bubble formation process occurring where we do, i.e., $\rho \gtrsim 1.5 \times 10^{21}$ cm^{-3} for $T \approx 30$°K. The low mobility object we see appears to be a cluster ion formed in the source region, though we cannot rule out the possibility that it is a stable bubble. In order to provide incontrovertible evidence for bubble creation, that is, to follow the mobility collapse in its entirety, it is necessary to perform experiments at $T > T_{crit}$, $P > 25$ atm, using a low energy electron source so that the probability of formation of cluster ions is severely reduced, and to use more sophisticated measurement schemes in order to detect the very low signals to be expected in these circumstances. To perform similar measurements in Ne, even higher pressures would be necessary because of the small value of the scattering length for that gas.

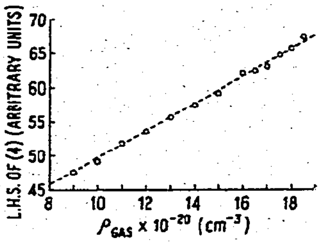

Fig. 3b. L.H.S. of eq. (4) versus gas number density, from the data at 31.7°K.

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