

# Non Diffusive Mobility of Solid Hydrogen Films

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*We have used a "hole-burning" technique to study the mobility of thin solid films of  $H_2$  and  $D_2$  for temperatures between 1.6 K and 5 K. Even at low temperatures where transport through the vapor is negligible, the solid films remain mobile. The transport is thermally activated with an activation energy of 19 K for  $H_2$  and 38 K for  $D_2$ . The time dependence of the regrowth shows that surface transport is not due to simple diffusion.*

## 1. INTRODUCTION

Bulk self diffusion in solids occurs because a vacancy and a molecule in the lattice exchange places. In conventional solids, the activation energy for diffusion consists of the energy of formation of a vacancy  $E_{\text{vac}}$  and the energy required to overcome the potential barrier for vacancy/molecule exchange,  $E_{\text{ex}}$ . Since these energies are typically of the order of the cohesive energy of the solid, diffusion slows down rapidly as the temperature is lowered, and ceases altogether at  $T=0$ . In quantum solids such as solid He and  $H_2$ , the vacancy concentration is also determined by the temperature, but at sufficiently low temperatures, the vacancy/molecule exchange is governed by quantum tunneling rates.<sup>1,2</sup> Since these rates are independent of temperature, diffusion in quantum solids at low temperature has an activation energy equal to the free energy of formation of a vacancy  $E_{\text{vac}}$ . The thermal concentration of vacancies becomes very small at low temperatures, so bulk diffusion rates in quantum solids go to zero at  $T=0$  just as in a conventional solid.

The low temperature behavior of quantum diffusion on a surface can be distinctly different. For low coverages, motion of an adatom does not require the formation of a vacancy, so at low temperature, the tunneling diffusion rate is independent of temperature. This type of temperature independent diffusion has been observed for  $H_2$  and  $D_2$  on stepped tungsten surface.<sup>3</sup> At higher coverage, motion of an adatom may involve surface

vacancies or other surface defects, but the activation energy of these surface defects is expected to be small compared to the activation energy for bulk vacancies. For these reasons, the surfaces of quantum solids may be quite mobile even at very low temperatures. Since helium does not solidify at zero pressure, solid hydrogen presents the most promising opportunity to study the mobility of the free surface of a quantum solid. Several recent experiments have investigated the kinetics of dewetting and bulk crystallite growth in thick quench condensed films of  $H_2$  and  $D_2$ <sup>4, 5, 6, 7</sup> and in equilibrium films of HD.<sup>8</sup> These experiments have indeed shown that the surfaces of quantum solids are remarkably mobile even at temperatures at which bulk diffusion is negligible. The experiments reported here extend these results by showing that similar mass transport mechanisms exist in thin equilibrium films at temperatures as low as 1.5 K. Our experiments also clearly show the transition between bulk vapor transport and surface transport, and provide information about the time dependence of the relaxation process. Simple diffusive transport models fail to explain the time dependence of the mass transport observed in the experiments.

## 2. EXPERIMENTAL MODELS

We have studied surface mobility in equilibrium films of  $H_2$  and  $D_2$  using a hole burning technique which gives a direct measurement of mass transport in thin solid hydrogen films. A hole is created in the film by desorbing hydrogen molecules with a heat pulse applied to a heater on the substrate beneath the film (refer to inset Fig. 1). The desorbed molecules are detected by a superconducting transition edge bolometer. After a delay time which can range from fractions of a second to hundreds of hours, a subsequent pulse desorbs the hydrogen which has been transported back onto the heater. The resulting bolometer signal is proportional to the number of molecules which have accumulated on the heater during the delay. These measurements determine the rate of mass transport in the hydrogen film as a function of time; repeating these measurements at different temperatures yields the activation energy for surface transport.

Our experiments were performed inside a double walled isothermal cell suspended in vacuum and thermally coupled to a continuously filling  $^4\text{He}$  refrigerator. The cell could be thermally regulated between 1.6 K and 30 K. A heated fill line connected the cell to a room temperature source of pure hydrogen gas. Normal  $H_2$  (75% ortho, 25% para) and normal  $D_2$  (66% para, 33% ortho) were used for the experiments. The heated fill line was used to introduce the gas into the cell at saturated vapor pressure conditions. The gas was introduced with the temperature of the cell slightly above the triple point of hydrogen (deuterium), after which the cell was

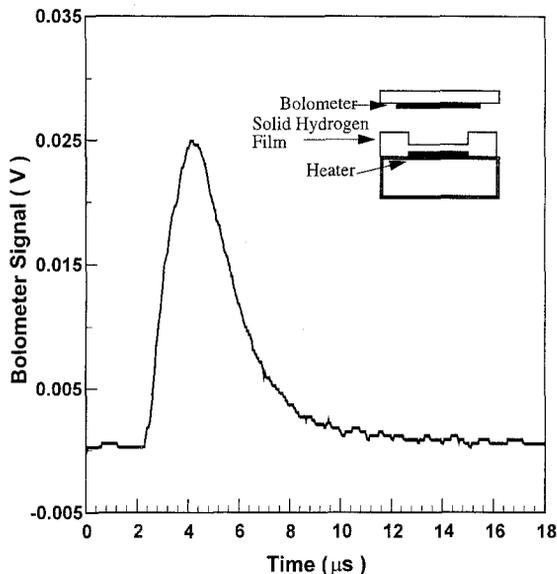


Fig. 1. Single Shot Bolometer Signal vs. Time. The integral of the bolometer signal is defined as the Signal Amplitude. Inset: The Heater-Bolometer arrangement.

slowly cooled back down to the desired temperature. During the experiments, the cell was isolated from the fill line by a low temperature valve.

Although enough gas is introduced into the cell to form several cubic millimeters of solid, most of the surface area is coated with a film only a few monolayers thick while the remainder of the material forms a bulk crystallite at a favorable nucleation site on the bottom of the cell. The equilibrium thickness of the film is determined by the condition that the free energy is minimized at that value.<sup>9</sup> The substrate is said to be wet if the minimum occurs at infinite thickness. Solid hydrogen is known not to wet most substrates,<sup>10</sup> which means that it has a finite thickness at equilibrium. We determined the equilibrium thickness in our apparatus using a quartz microbalance which was mounted at the same height (3 cm) above the bottom of the cell as the heater film and bolometer. The equilibrium thickness on the gold surfaces of the microbalance was approximately 4 layers, and we assume that a similar film existed in equilibrium on the heater surface.

The heater consists of a thin Nichrome film (1 mm by 0.3 mm) evaporated onto a sapphire substrate ( $1.5 \times 1 \times 1$  cm). The heater resistance is  $1.5 \text{ k}\Omega$  (for  $\text{H}_2$ ) and  $150 \Omega$  (for  $\text{D}_2$ ). A pulse generator was used to provide 20 V rectangular pulses of duration  $1 \mu\text{s}$  and  $0.1 \mu\text{s}$  for  $\text{H}_2$  and  $\text{D}_2$  respectively. The power density going into the heater indicates that the temperature of the heater is locally raised to  $\sim 8.8 \text{ K}$  for  $\text{H}_2$  and  $\sim 15.6 \text{ K}$

for  $D_2$ .<sup>11</sup> The resistances of the heater and the duration of the pulses were chosen so that these heat pulses would not desorb the most strongly bound layers of the solid hydrogen (deuterium) film above the heater. At a fixed temperature, the desorption rate is a strong function of the binding energy, which in turn is a strong function of the hydrogen coverage. The binding energy of the first two layers of  $H_2$  are approximately 340 K and 170 K, respectively, for a wide variety of substrate materials,<sup>12</sup> while the binding energy of subsequent layers rapidly approaches the bulk latent heat of 95 K. For our experimental conditions, kinetic theory<sup>13</sup> shows that the heat pulse completely desorbs the third and higher layers and leaves the first two layers intact. This ensures that the bolometer detects only the reaccumulated film with every pulse of the heater. Since mass transport always takes place on top of the two strongly bound layers of hydrogen, we expect that our results are independent of the details of the composition of the heater or substrate.

The bolometer is evaporated on a separate sapphire substrate and placed a short distance ( $\sim 1$  mm) above the heater (see inset Fig. 1). The bolometer is biased at its sharp superconducting transition point at each temperature by means of a magnetic field. The bolometer signal as a function of time due to molecules desorbed from the heater is shown in Fig. 1. The shape of the signal reflects the thermal distribution of molecular velocities, which is determined by the isotopic mass and the heater temperature. The area under the curve is proportional to the number of hydrogen(deuterium) molecules desorbed and therefore to the amount of film that reaccumulated in the hole since the previous pulse. The integral of the bolometer signal, which we denote as the signal amplitude, is a useful measure of the amount of adsorbate on the heater.

Unless special precautions were taken, the low temperature bolometer signal for  $H_2$  did not look like that shown in Fig. 1, but rather had two peaks with distinct arrival times. The smaller peak which arrived later was particularly visible for short delay times when the signal due to hydrogen was still small. The ratio of the arrival times of the two peaks was approximately  $\sqrt{2}$ . The  $\sqrt{1/m}$  dependence of the thermal velocity indicates that the slow signal is due to an impurity of mass 4. The fact that this component of the signal had a very rapid relaxation time even at our lowest temperatures strongly suggests that the surfaces were contaminated with helium. We verified that the source of the helium was not a leak to the bath, but rather came directly from the research grade gas bottle supplied by the manufacturer with a specified purity of six nines. The residual pressure of helium in the low temperature cell could be estimated from the characteristic recovery time for the mass 4 signal. Our estimates of the helium pressure are compatible with the stated gas purity, but the

bolometer signal is extremely sensitive to helium contamination since it is concentrated in the gas and forms an adsorbed film on top of the hydrogen. The amount of helium in the cell could be reduced by several orders of magnitude by vacuum distillation at  $T \sim 9$  K. Variation of the helium concentration over this range did not significantly affect the relaxation times of the hydrogen film. Our experience with nominally high purity hydrogen suggests that previous experiments on hydrogen surfaces may also have been covered with thin films of helium.

We have also attempted to do measurements with HD, which is commercially available with only 99.9% purity. Using our low temperature, time-of-flight mass spectroscopy, we could observe peaks corresponding to mass 2, 3, and 4 amu. The impurities are such a large effect in HD that reliable measurements using the hole burning technique would not be possible without elaborate purification, which we did not pursue.

### 3. DISCUSSION

The kinetics of regrowth of the adsorbed film can be determined from the primary bolometer data by plotting the signal amplitude as a function of the time delay between subsequent pulses, as shown in Fig. 2 for  $H_2$  at  $T = 2.8$  K. The main characteristics are a nearly linear region at short times and then saturation at long times when the film completely recovers to its equilibrium thickness between heat pulses. The rate of the regrowth process can be characterized by the time,  $\tau$ , required for the film to regrow to half its equilibrium value, as illustrated in Fig. 2. A plot of these characteristic times as a function of  $1/T$  for both  $H_2$  and  $D_2$  is shown in Fig. 3. The plot clearly shows that the mass transport rate has two different behaviors at high and low temperatures, each of which is characterized by an activation energy. At high temperatures, the vapor pressure of the bulk solid is sufficiently high that regrowth of the film is dominated by transport through the gas phase. Since the equilibrium vapor pressure is proportional to  $e^{-L/t}$ , where  $L$  is the latent heat of sublimation, the activation energy expected for vapor transport is  $L$ . The dashed lines in Fig. 3 have slopes corresponding to 95 K and 140 K, which are the latent heats of  $H_2$  and  $D_2$ , respectively.<sup>14</sup>

Below approximately 3 K, the expected regrowth time due to vapor mass transport is of the order of years, while the observed relaxation times are of the order of hours. The 112 K<sup>15</sup> energy of formation of vacancies needed for bulk diffusion eliminates this process as well at low temperatures. Thus, the fast relaxation at low temperatures is apparently due to surface transport, which becomes dominant for  $T < 3$  K for  $H_2$  and  $T < 3.6$  K in  $D_2$ . A least squares fit to the low temperature data in Fig. 3

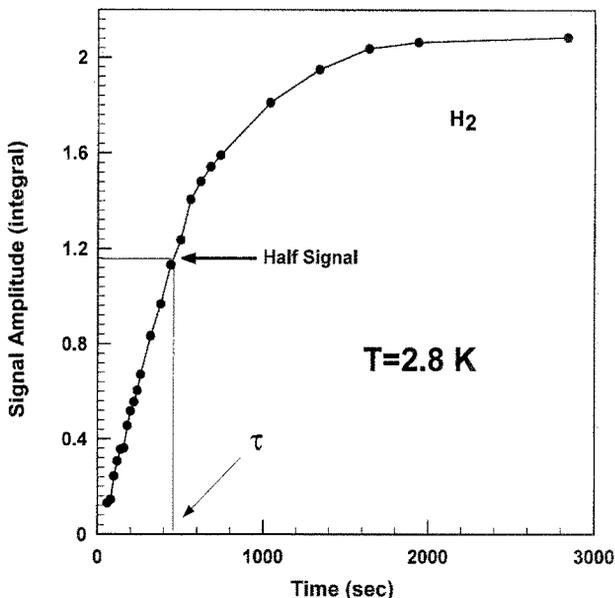


Fig. 2. Signal Amplitude vs. the time-delay between successive pulses for  $\text{H}_2$  at  $T=2.8$  K.  $\tau$  is the characteristic regrowth time, defined as the time-delay required for the film to reach half of its maximum (asymptotic) thickness.

yields values for the activation energy of  $19 \pm 1.5$  K for  $\text{H}_2$  and  $38 \pm 4$  K for  $\text{D}_2$ . The activation energies did not change over the three month duration of the experimental run, which suggests that the ortho-para concentrations of the gas do not play an important role.

An important advantage of our experimental technique is that the time dependence of the mass transport can be measured over a wide range. Hole burning experiments on a variety of conventional adsorbates at coverages less than a monolayer typically show that the coverage relaxes at a rate proportional to  $\sqrt{t}$ , which is the signature of diffusive transport.<sup>16,17</sup> This type of data can be analyzed to determine the surface diffusion coefficient  $D$ . We have attempted to perform such an analysis of our experimental results by assuming that the surface mass flux  $J$  is proportional to the gradient of the film thickness  $h$ ,  $J = -D \nabla h$ . This form of the mass flux leads to a diffusion equation for the film thickness. If the heater is regarded as an infinite strip of width  $2a$ , the solution of this equation for the initial condition  $h(x, 0) = 0$  for  $|x| < a$  and  $h(x, 0) = h_0$  otherwise, is

$$h(x, t) = \frac{h_0}{2} \left( \operatorname{erfc} \left( \frac{a-x}{2\sqrt{Dt}} \right) + \operatorname{erfc} \left( \frac{a+x}{2\sqrt{Dt}} \right) \right) \quad (1)$$

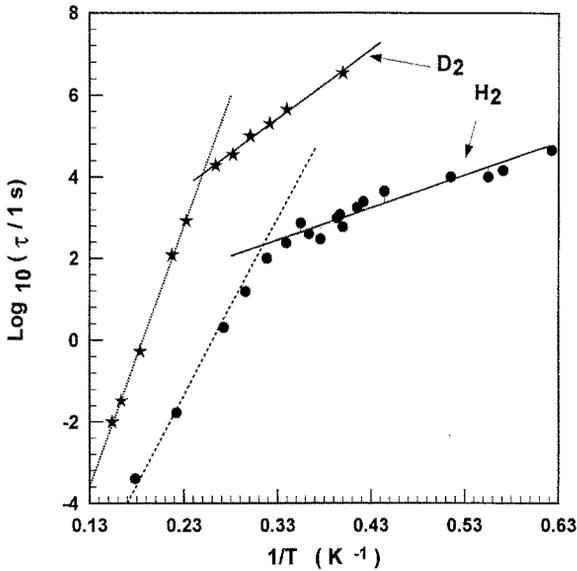


Fig. 3. Plot of  $\text{Log}(\tau)$  vs.  $1/\text{Temperature}$ . The dashed lines indicate the vapor dominated regions and the solid lines indicate the surface dominated regions. The activation energies of  $\text{H}_2$  and  $\text{D}_2$  for the surface motion are 19 K and 38 K. Solid circles represent the data for  $\text{H}_2$  and Stars represent the data for  $\text{D}_2$ .

We have used this diffusive transport model to compute the expected signal amplitude  $S(t)$ , which is proportional to the total amount of material which has diffused back onto the heater surface after a time  $t$ , with  $S(t) = A \int_{-a}^a h(x, t) dx$ , where  $A$  is a constant that measures the sensitivity of the bolometer. The product  $Ah_0$  determines the signal amplitude at large times. Least squares fits to the data using  $Ah_0$  and  $D$  as adjustable parameters are shown as dotted curves in Figs. 4 and 5. The figures show that the model does not describe the data very well, and is particularly poor for the  $\text{H}_2$  data of Fig. 4. The main discrepancy between the model and the data comes from the behavior at short times. Diffusive transport models have a  $\sqrt{t}$  behavior at short times, while the  $\text{H}_2$  data shown in both Figs. 2 and 4 show linear growth until the coverage reaches approximately  $2/3$  of its asymptotic value. The fit to the  $\text{D}_2$  data shown in Fig. 5 is quantitatively better than the  $\text{H}_2$  fit, but the fit is achieved by balancing errors in the short and long time behavior, neither of which is accurately represented by the model. We conclude from this analysis that diffusion driven by gradients in the film thickness  $h$  is not the only surface mass transport mechanism in quantum solids, and that an alternative mass transport mechanism which is linear in time is particularly important in  $\text{H}_2$ .

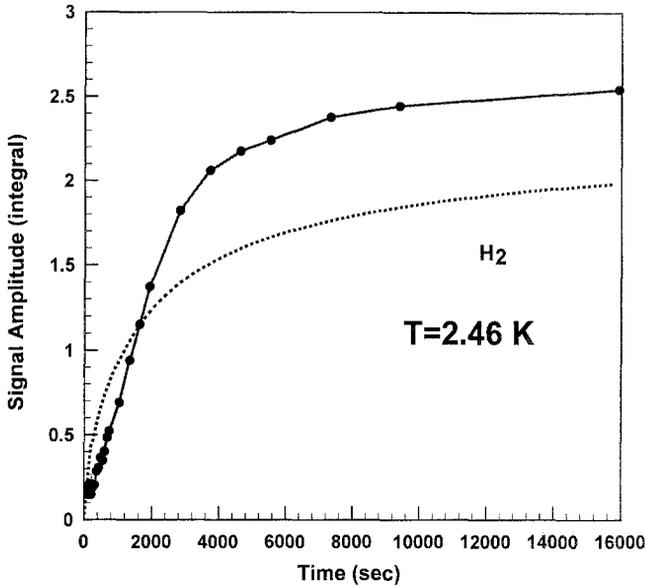


Fig. 4. Regrowth of H<sub>2</sub> film at  $T = 2.46$  K with a least squares fit (dotted curve) to the data using the diffusive transport model (Eq. 1).

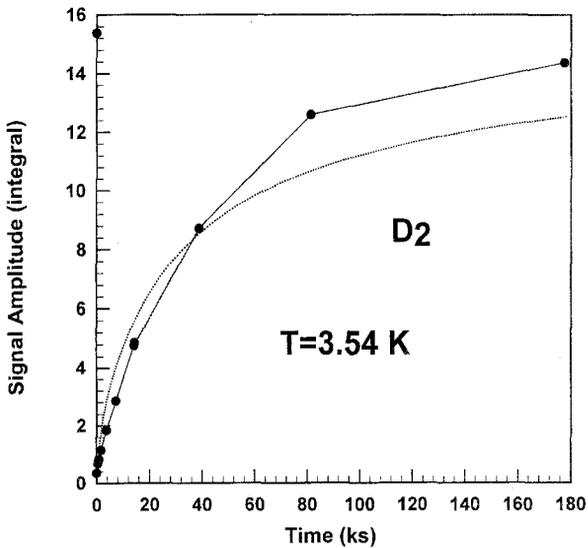


Fig. 5. Regrowth of D<sub>2</sub> film at  $T = 3.54$  K with a least squares fit (dotted curve) to the data using the diffusive transport model (Eq. 1).

We have considered two simple candidate models to explain the linear rate of mass transport observed in the  $H_2$  experiments. The first is ballistic transport of a 2D surface gas. This model is motivated by the behavior at high temperature where the hole is filled in by ballistic transport from the 3D gas. In this regime, the filling rate is linear because the sticking coefficient on the thin region is large but the reevaporation rate is very small, so the filling rate is determined by the rate of incident gas molecules. As the coverage approaches the equilibrium value, the reevaporation rate approaches the deposition rate, as dictated by the principle of detailed balance.

The 2D analog of this type of process requires a gas of adatoms whose concentration  $n$  is determined by the equality of the chemical potentials of the 2D and 3D gases. In the 2D gas,

$$\mu = T \ln \left( \frac{n}{\lambda^2} \right) - E_b \quad (2)$$

where  $\lambda^2 = (MkT/2\pi h^2)$ , and  $E_b$  is the binding energy of the adatom to the surface. The chemical potential is approximately  $-L$  in the low temperature regime considered here. The adatom concentration is therefore

$$n = \lambda^2 e^{(E_b - L)/T} \quad (3)$$

The flux of ballistic transport is proportional to the product of the concentration and the characteristic thermal velocity  $\sqrt{(kT)/M}$ , which is approximately  $10^4$  cm/sec for  $H_2$  at  $T=2$  K. The dominant temperature dependence of the flux is due to factor  $e^{(E_b - L)/T}$  in the concentration, and the activation energy determined in the experiment is  $E_b - L$  within the context of this model. This implies that  $E_b$  is approximately  $95 \text{ K} - 19 \text{ K} = 76 \text{ K}$  for  $H_2$ . When this value of  $E_b$  is used to compute the surface concentration, the derived mass flux is nearly five orders of magnitude higher than observed. The mass flux can be reduced by introducing a mean free path, but then the transport becomes diffusive and scales as  $t^{1/2}$  rather than  $t$ .

Another possible model for mass transport in a film is viscous flow at a constant velocity which results from a balance of a driving force and viscous dissipation. The driving force is the large difference in surface free energy  $\Delta\Omega$  between the thin region of the film and the regions with equilibrium thickness. The film will flow in response to this energy gradient with a characteristic velocity determined by dimensional considerations to be of order  $(\Delta\Omega)/\eta$ , where  $\eta$  is the viscosity of the material. This type of hydrodynamic analysis which leads to a fluid front moving at nearly constant velocity, is commonly used to describe spreading of viscous liquids on

a surface, and is known as Darcy's law.<sup>18</sup> If this model is applicable to flow of solid hydrogen films, the activation energy we observe must be interpreted as the energy which characterizes the Arrhenius behavior of the viscosity  $\eta \sim e^{E_a/T}$ . The viscosity can be related to the diffusion coefficient  $D$  through the Einstein relation,<sup>19</sup> which gives  $D \sim kT/(\eta a)$ , where  $a$  is a molecular length.

#### 4. COMPARISON WITH PREVIOUS WORK AND CONCLUSION

Several recent experiments have investigated the behavior of quench condensed films of solid hydrogen formed by condensing gas on to a substrate held at 1.5 K. The thickness of these films is determined by the deposition process and is typically much larger than the equilibrium thickness. As the temperature is raised above 1.5 K, the films coarsen and become rough as the film phase separates into regions with the equilibrium thickness and regions with bulk crystallites. The temperature dependence of the roughening process has been monitored using plasmon,<sup>5,7</sup> the mobility of surface electrons<sup>6</sup> and surface acoustic wave scattering.<sup>4</sup> Classen *et al.*<sup>4</sup> have obtained activation energies of 23 K and 47 K for H<sub>2</sub> and D<sub>2</sub> respectively. In those experiments, the film approaches equilibrium from a state that is too thick, while in our experiments, equilibrium was approached from an initial state that was too thin. It is noteworthy that the activation energy for both types of processes are similar.

The surface mobility of solid HD of equilibrium thickness adsorbed on MgO(100) powder has been investigated using quasi-elastic neutron scattering<sup>8</sup> for temperatures between 7 and 15 K. These temperatures are far too high to use our hole-burning technique, since the transport is completely dominated by gas phase processes. The width of the neutron scattering line is a measure of the surface mobility, which was found to be thermally activated with an activation energy of 16.1 K. The high value of the surface mobility was explained in terms of a quasi-liquid layer (QLL) at the surface of the solid film. This type of surface melted layer is known to exist in a variety of materials near the triple point temperature  $T_3$ . In most non-quantum systems, the quasi-liquid surface layer is expected to vanish below  $0.7T_3$ .<sup>20</sup> In HD, the activated behavior persisted down to at least  $0.5T_3$  (8 K), but Maruyama *et al.*<sup>8</sup> suggest that the large zero-point energy of a quantum solid may tend to stabilize the QLL down to anomalously low temperature. If the QLL is responsible for activated surface mobility, our observations would imply the existence of the QLL at temperatures as low as  $0.1T_3$ .

The results of previous experiments have been interpreted in terms of enhanced surface diffusion at low temperature. The most surprising result

of our work is that simple models of surface diffusion do not explain the time dependence of the surface mass transport. Our results suggest that the surface of solid hydrogen behaves in some ways like a highly viscous liquid. The high surface mobility of solid hydrogen places constraints on attempts to dope solid hydrogen with atomic impurities, which is of interest for applications as a high energy density material.

### ACKNOWLEDGMENTS

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