PHYSICAL REVIEW B VOLUME 53, NUMBER 17 1 MAY 1996-I

Hydrogen in porous Vycor glass

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(Received 28 November 1995; revised manuscript received 12 January 1996)

Hydrogen in porous Vycor glass (pore radius $R_p=3.0$ nm) has been investigated with a torsional oscillator technique at 7.5 K $\leqslant T \leqslant$ 22 K. H_2 molecules which are adsorbed in Vycor at $T>T_3$ (T_3, triple point of bulk H_2) leave the Vycor when decreasing the temperature to below a characteristic value $T_c \leqslant T_3$; T_c depends on the amount of H_2 in the Vycor. This interpretation of the data is supported by simultaneous measurements of the H_2 vapor pressure. A similar phenomenon is observed with a capacitor filled with Vycor into which H_2 is condensed. We conclude that the free energy of solid H_2 in the Vycor is larger than that of bulk solid H_2. Information on the free energy of H_2 confined in the Vycor is important to understand the depression of its freezing temperature in restricted geometries. We also discuss the properties of solids and the depression of their freezing temperature in restricted geometries.

I. INTRODUCTION

Liquid hydrogen below its bulk triple point $T_3=13.8$ K has attracted a lot of attention experimentally and theoretically, because of the hope of realization of a new superfluid.[1–6] The superfluid transition temperature of H_2 should be of the order of 1 or a few kelvin considering the analogy of H_2 to ^{4}He.[2] The superfluid transition temperature (2.18 K) of ^{4}He is comparable to $T_{BC}=3.13$ K (Bose-Einstein condensation temperature). T_{BC} is obtained by treating the system as an ideal Bose gas, which gives $T_{BC}=6.6$ K for para-hydrogen (p-H_2).[1] However, bulk p-H_2 freezes at 13.8 K; therefore one must achieve a substantial depression of the freezing temperature to obtain a superfluid transition. The most widely employed technique to realize H_2 in the liquid state at $T<T_3$ is confining it into a small space, such as micropores of porous glasses[3–7] or zeolites.[8] Although this technique is very common, the mechanism of the freezing temperature depression is not yet clear.[7,8] For example, the free energies of a solid and liquid in restricted geometries are not well known and usually simply assumed to be the same as those of the bulk phases. In order to obtain information on the free energies of solid and liquid H_2 confined in a restricted geometry, we have used a torsional oscillator technique[9] to measure the H_2 mass inside of porous Vycor glass[10] as a function of temperature and of an initial H_2 filling; the latter is determined by the chemical potential outside of the Vycor at $T>T_3$. Our experimental system is analogous to the setup which has been employed to study wetting transitions of various combinations of adsorbates and substrates, and which has provided information on the free energies of adsorbed layers.[11] We selected Vycor as a restricted geometry because a large amount of data has been accumulated for hydrogen and helium in Vycor. Torii *et al.*[4] reported a ''phase'' diagram of H_2 in Vycor glass which is quite similar to that of ^{4}He in Vycor glass.[12] In the case of ^{4}He, it contains a superfluid phase. Brewer *et al.*[5] have measured the heat capacity of H_2 in porous Vycor glass (typical $R_p \approx 3$ nm) at 4 K $<T<$ 15 K. They observed an anomalous behavior and interpreted it as a possible indication of a superfluid transition of H_2 at around 9.6 K. We have already presented some of the results discussed in this paper in a short communication: It focused on the search for a possible superfluid transition of H_2 in Vycor glass.[6] Here we concentrate on the free energies of solid and liquid H_2 in porous Vycor glass.

This paper is organized as follows. Section II describes the experimental details. In Sec. III the data are presented and analyzed for different H_2 fillings. In Sec. IV the properties of solids and the mechanism of the depression of their freezing in restricted geometries are discussed. Section V summarizes the results of this work.

II. EXPERIMENTAL DETAILS

A. Vycor

Porous glass, for example Vycor 7930,[10] is produced from a melt of 75% SiO_2, 20% B_2O_3, and 5% Na_2O. Heat treatment leads to a separation in a silicon-rich phase and a boron-rich one. After removing the boron-rich phase, there remains an interconnected solid skeleton of nearly pure SiO_2 with a rather homogeneous distribution of mass and pores.[13] The microscopical structure of the surface is rough, which leads to a wide variation of the attractive potential from the wall.[14]

Our Vycor sample for the torsional oscillator experiments is a cylinder of 6 mm height and diameter, cut from a plate of Vycor (Corning 7930) with a diamond cutter. The sample for the capacitive measurements is a disk of 8 mm diameter, which was cut from the same plate of Vycor, and polished to 0.5 mm thickness. Both Vycor samples were separately rinsed for 5 h in a 30% H_2O_2 solution at 100 °C, and then for 1 h in boiling distilled water to remove H_2O_2. Drying the Vycor samples was done in two steps. First a slow process in a desiccator filled with silica gel (to avoid damages of pores). After 2 days of gentle drying, we heated the Vycor samples to 200 °C and pumped away adsorbed H_2O molecules with a turbomolecular pump for 1 day. After the drying process, the Vycor samples were immediately installed into the cells, which were then sealed.

To determine the characteristics of the Vycor, we measured the N_2-adsorption isotherm at 77 K with the torsional

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oscillator cell (the mass of the Vycor is 0.2356 g). Using the Brunauer-Emmett-Teller (BET) equation for monolayer adsorption[15] and assuming a cylindrical shape of the pores with an uniform radius R_p, we calculated $R_p = 3.0$ nm which is in good agreement with the reported pore size for this type of Vycor.[13] At T_3, $n_0 = 1.85 \pm 0.05$ mM of H_2 is necessary to fill the Vycor (see Sec. III A 1). With a molar volume of bulk liquid H_2 of 26 cm^3/mol at T_3, we obtained the open volume of the pores, $V = 0.048$ cm^3, and a porosity of 0.28.[16] The somewhat smaller value of the porosity compared to the reported value of 0.30±0.03 (Ref. 13) may be caused by blocking of some pores by Stycast 2850FT which was used to fix the Vycor in the torsional oscillator cell.

B. Torsional oscillator

The torsional oscillator was machined from a single piece of BeCu. It consists of a cylindrical cell (6 mm height and diameter), a torsion tube (5 mm long, 1.4 mm o.d. with a 0.7 mm hole to admit hydrogen), and a cylindrical platform (24 mm diameter and 20 mm height with a 2 mm hole for filling).[9] It was ultrasonically cleaned and annealed for 3 hours at 320 °C to improve the mechanical properties.[17] Another torsion tube (12 mm long, 2.5 mm o.d., and 1.4 mm i.d.) with ~100 Hz resonance frequency is connected to the large mass of the BeCu platform and works as a mechanical low pass filter to decouple the oscillator from the rest. The Vycor cylinder was fitted closely into the cell and fixed with a small amount of Stycast 2850FT to the wall. We saw the Stycast penetrating slightly into the pores, which may lead to a decrease of the open volume of the Vycor as mentioned in Sec. II A. The cell with the Vycor glass was sealed with a BeCu piece containing a central electrode using Stycast 2850FT. To excite and detect the oscillation, we use two brass electrodes of about 0.1 mm distance on each side of the central electrode.

The oscillator is working in self-resonance mode.[9] The signal from the pickup electrode is amplified, phase shifted, and fed back to a drive electrode. The oscillator is always in resonance and its frequency is measured with a frequency counter connected to a computer. The stability of the frequency with 1 min averaging time is about 0.1 mHz at a resonance frequency of $f_0 = 2706$ Hz for the cell without H_2 (empty cell) at low temperature. The frequency f_0 is a function of temperature through the temperature dependence of the rigidity modulus D of the torsion tube according to $f_0 = (2\pi)^{-1}\sqrt{D/J_0}$, where J_0 is the moment of inertia of the cell without H_2. The quality factor Q of the oscillator is determined by measuring the exponential decay of the oscillation after stopping the drive. Q is a function of temperature and pressure of H_2 in the cell: Q is 45 000 at room temperature and increases to 1.8×10^6 at 7.5 K for the empty cell in vacuum. f_0 is a smooth function of temperature without any anomalies.

The oscillator is hanging inside and screwed to the top flange of a Cu radiation shield on which a heater (metal resistor) and a calibrated Ge resistance thermometer are mounted. The whole setup is mounted on the top flange of a vacuum can with an intervening Teflon part. The radiation shield is weakly coupled via a Cu strip to the ^{4}He bath. The lowest temperature of the radiation shield and oscillator is 7.5 K. In order to reduce mechanical noise from the floor, the cryostat is sitting on a large mechanical low pass filter which consists of a sand box as a heavy mass and a Styrofoam cushion as a weak and lossy spring.

A variation of heating power causes an immediate change in temperature and in resonance frequency; hence there is a good thermal contact between radiation shield, heater, thermometer, and torsional oscillator. After changing the temperature, the empty oscillator reaches within 5 min a new equilibrium in frequency and amplitude.

To fill the cell with H_2, we use a stainless steel capillary (1.5 mm o.d., 0.78 mm i.d., 2 m length) from the gas handling system at room temperature to the torsional oscillator at low temperature. It sits inside an evacuated tube to avoid any contact to the ^{4}He bath. The used gas handling system is composed of a standard volume V_S, a pressure gauge (0.1 mbar resolution), a cold trap at liquid nitrogen temperature to remove impurities, and a storage vessel of 99.999% pure H_2. The amount of H_2 admitted into the cell including the room temperature dead volume of pressure gauge and filling capillary, we referred to as n hereafter, is determined with a standard volumetric method. The thermomolecular correction for the pressure measurement is of the order of 0.1 mbar and can be neglected for pressures higher than 10 mbar.

The viscous penetration depth δ is given by $\delta = \sqrt{2\ \eta/\rho\omega}$, where η, ρ, and ω are the viscosity and density of H_2, as well as the angular frequency of the torsional oscillator. For liquid H_2 at a frequency $f = 2.7$ kHz, $\delta = 5\,\mu$m is much larger than R_p. Therefore, normal liquid (as well as solid) H_2 is totally clamped to the Vycor glass in the oscillator. Adsorption of H_2 in the Vycor increases the moment of inertia to $J = J_0 + \Delta J$ and decreases the resonance frequency f according to $f = (2\pi)^{-1}\sqrt{D/J}$. Since $\Delta J/J_0$ is very small, $\Delta f = f_0 - f$ is in good approximation proportional to ΔJ due to adsorbed H_2.

C. Capacitor

Using a capacitive technique, we performed additional experiments with H_2 in Vycor. The design of this second cryostat is shown in Fig. 1.

A disk of Vycor glass (0.5 mm thickness and 8 mm diameter) is fixed, after cleaning and drying, with a tiny amount of GE varnish at its perimeter inside an oxygen-free

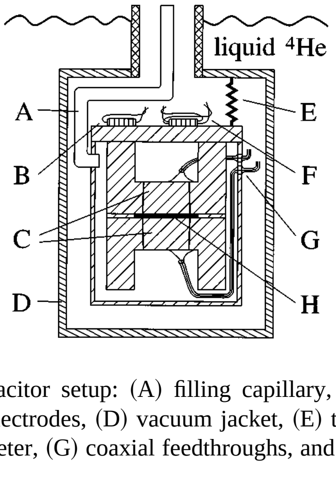

FIG. 1. Capacitor setup: (A) filling capillary, (B) heater, (C) OFHC copper electrodes, (D) vacuum jacket, (E) thermal link, (F) carbon thermometer, (G) coaxial feedthroughs, and (H) disk of Vycor glass.

high-conductivity (OFHC) copper ring of the same thickness. This setup is tightly screwed between two OFHC copper electrodes (6 mm diameter) which are insulated with sheets of thin paper from the outer shielding ring electrodes. They are made of OFHC copper to avoid any temperature gradients within the capacitor. The whole capacitor unit is screwed to the top flange of the sample cell to enable good thermal contact between the Vycor and the thermometer which is glued outside on the top flange of the sample cell.

The temperature is controlled by a combination of a metal-film resistor for heating and an Allen-Bradley carbon resistor for measuring. The thermometer is calibrated in each run by measuring the saturated vapor pressure of H_2 in the sample cell. Readings of the temperature and of the capacitance of the empty cell (without H_2) reach a new stable value within a few minutes after changing the heating power. The temperature dependence of the empty cell capacitance shows the typical behavior of silica.[18]

The H_2 vapor pressure is measured at the room temperature end of the filling capillary. To avoid any errors due to the thermomolecular effect or blocking of the filling line, we use a capillary with a rather large inner diameter (1.8 mm). The filling capillary sits inside of an evacuated tube and is equipped with a heating wire to ensure that no H_2 condenses in it.

The capacitance C is measured with a commercial capacitance bridge,[19] using the three-terminal method, a test voltage of 15 V, and a measurement frequency of 1 kHz. The accuracy is about 10^{-6} pF at $C = 1.4$ pF.

III. RESULTS AND ANALYSIS

A. Torsional oscillator data

1. Condensation of H_2 into the cell

Hydrogen is admitted to the cell at a pressure p smaller than its saturated vapor pressure at a given temperature to avoid condensation of bulk H_2 in the torsion tube and filling capillary. It is possible to condense H_2 at $T > T_3$ with pressures lower than the saturated vapor pressure because of the attractive potential of the Vycor walls and of the capillary action.

During filling the cell with H_2 in small steps at constant temperature $T > T_3$, Δf increases. It takes always several hours for the system to reach a new equilibrium, presumably because of the small pores of the Vycor and relatively large volume V_S at room temperature. Δf as a function of the amount n_T of H_2 condensed into the torsional oscillator, determined with a standard volumetric method, is shown in Fig. 2. Note that $n_T \neq n$ (the total amount of H_2 in the system) when the vapor pressure of H_2 is not negligible. For $n_T < n_0 = 1.85$ mmole, $\Delta f \propto n_T$. For $n_T \geqslant n_0$, Δf is no longer proportional to n_T, because H_2 starts to condense outside of the Vycor. We determine the open volume of the Vycor from the maximum amount n_0 of adsorbed H_2 in the Vycor. Close inspection of the data for $n_T < 0.2$ mmole reveals a nonnegligible offset as shown in the inset of Fig. 2. This offset is beyond our measurement error and indicates a nonhomogeneous distribution of H_2 in the Vycor. We assume that for these smallest fillings the H_2 molecules occupy first the region near the perimeter of the Vycor cylinder, and thus they produce a higher moment of inertia than for a homogeneous distribution. Such a nonhomogeneous distribution may be caused by the wide variation of the attractive potential of the Vycor wall.[14]

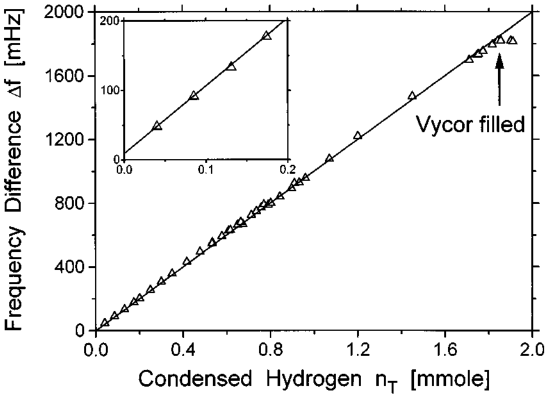

FIG. 2. Frequency difference Δf as a function of the amount n_T of H_2 in the oscillator. n_T is calculated with a volumetric method by taking into account the dead volume. At $n_T = 1.85$ mmole, Δf starts to saturate: The Vycor is completely filled. The magnified part shows that there is an offset, from which we conclude that there is an inhomogeneous distribution of H_2 in the Vycor for small n_T's. The data are taken at different temperatures above T_3 and from different runs.

After filling H_2 at constant temperature, the oscillator is connected only to the pressure gauge and not to the standard volume V_S, the cold trap, or the storage vessel anymore. The oscillator is then cooled down step by step while monitoring its frequency and amplitude as well as the H_2 pressure. After each step of temperature change, typically from 1.0 to 0.1 K, the pressure decreases exponentially and reaches a new stable value after 1 h at 20 K and 2 h at T_3 in the case of a half-filled cell. These time constants slightly increase for higher H_2 fillings. The frequency follows the behavior of the empty cell within the first 5 min, and then it decreases exponentially simultaneously to the pressure because of the condensation of H_2 from the dead volume into the Vycor. At $T < T_3$, the amount of H_2 in the dead volume is small and condensation of H_2 into the Vycor is negligible. After admitting H_2 we usually spend 50 to 200 h before reaching T_3. Assuming the ortho-para conversion rate of bulk H_2, the para concentration should be more than 80%, possibly even 100%, if the ortho-para conversion rate is enhanced in the Vycor.

2. Less than 0.66 mmole H_2

The temperature dependence of the frequency of the oscillator for $n = 0.2$, 0.35, 0.6, and 0.66 mmole H_2 in the setup is in principle the same as that of the empty cell except for offsets depending on n. $\Delta f(T)$ is shown in Fig. 3(a). The 0.6 and 0.66 mmole measurements show a small increase of Δf with decreasing T for $T > T_3$ due to the condensation of H_2 from the dead volume into the Vycor.

The measured vapor pressure is much smaller than the saturated vapor pressure of H_2 in the whole temperature range. Figure 3(b) shows this pressure normalized to the saturated vapor pressure $p_{\mathrm{SVP}}(\mathrm{liq})$ of liquid p-H_2 (Ref. 20)

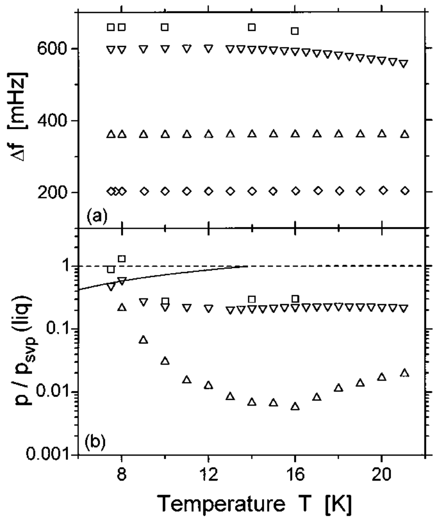

FIG. 3. Data for $n=0.2$ (◇), 0.35 (△), 0.6 (▽), and 0.66 (□) mmole H_2 in Vycor. (a) Frequency difference Δf as a function of temperature. The slight increase of the frequency difference Δf of the 0.6 and 0.66 mmole data between 21 K and T_3 is caused by condensation of H_2 from the dead volume ($n_T<n$ for these fillings at temperatures above T_3). At low temperatures Δf is constant. (b) H_2 vapor pressure normalized by the bulk liquid p-H_2 vapor pressure p/p_{SVP}(liq) as a function of temperature. The solid and dashed lines represent the vapor pressure of bulk solid and liquid p-H_2, respectively. At the lowest temperatures the measured pressure is of the order of the resolution of the manometer and thus not reliable.

on a logarithmic scale, which is a measure of the chemical potential. For $n\leqslant 0.2$ mmole, the pressure is lower than the manometer resolution. No indication of a liquid-solid phase transition of H_2 in the Vycor can be seen.

3. Between 0.7 and 1.2 mmole H_2

For larger fillings, $\Delta f(T)$ is shown in Fig. 4(a). Below a characteristic temperature $T_c<T_3$, which depends on n, Δf sharply decreases. This implies that below T_c some of the H_2 does not participate in the oscillation anymore. The amount of H_2 which does not take part reaches up to 1/3 of n (see $n=1.1$ mmole data). At $T<T_c$, $\Delta f(T)$ follows a universal curve, which means that the amount of H_2 that takes part in the oscillation at $T<T_c$ is independent of the original filling n. The normalized vapor pressure p/p_{SVP}(liq) first slightly increases when decreasing the temperature because of condensation of H_2 into the Vycor from the dead volume as shown in Fig. 4(b). At a certain temperature, p reaches the vapor pressure of bulk solid H_2 [solid line in Fig. 4(b)]. This temperature corresponds very well to T_c determined by Δf. At $T<T_c$, the abrupt change of measured pressure follows the bulk solid-vapor pressure (except for the lowest temperatures presumably because of errors in the pressure measurement). From these vapor pressure data we conclude that bulk solid H_2 must have been formed at T_c somewhere in the setup. We interpret this information, together with the torsional oscillator data, as that H_2 escapes from the Vycor and forms bulk solid at $T<T_c$ outside of the Vycor in the filling capillary. This implies that the chemical potential of H_2 in Vycor is higher than that of bulk H_2.

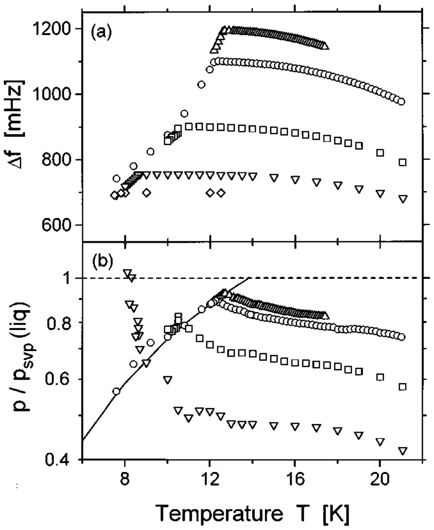

FIG. 4. Data for $n=0.7$ (◇), 0.75 (▽), 0.9 (□), 1.1 (○),and 1.2 (△) mmole H_2 in Vycor. (a) Frequency difference Δf as a function of temperature. At a certain temperature T_c depending on n, Δf starts to decrease: There is less H_2 which contributes to the moment of inertia of the torsional oscillator at $T<T_c$ than originally condensed into the Vycor. (b) H_2 vapor pressure normalized by the bulk liquid p-H_2 vapor pressure p/p_{SVP}(liq) as a function of temperature. The solid and dashed lines represent the vapor pressures of bulk solid and liquid p-H_2, respectively. Below T_c, the pressure follows the vapor pressure of bulk solid H_2.

For $n=1.1$ mmole, Δf as a function of temperature, both in cooling and warming, is plotted in Fig. 5. No hysteresis is observed even close to T_c.

There is a marked difference in the oscillator response after changing the temperature above and below T_c. At $T_c<T<T_3$, the oscillator reaches a new equilibrium condition within 5 min after changing the temperature like the empty cell. Below T_c, the frequency changes in two steps: a fast response (within 5 min as above T_c according to the behavior of f_0) followed by a very slow one. The responses of pressure and frequency above and below T_c after changing the temperature are shown in Fig. 6 for $n=1.2$ mmole. The frequency behavior starting 5 min after the temperature

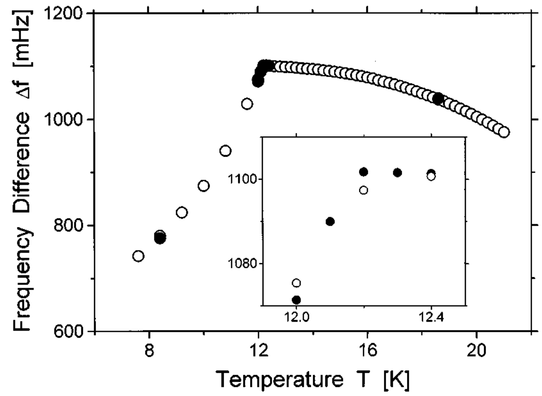

FIG. 5. Frequency difference $\Delta f(T)$ in cooling (○) and warming (●) for $n=1.1$ mmole H_2. The inset shows the data near $T_c=12.2$ K. No hysteresis can be seen.

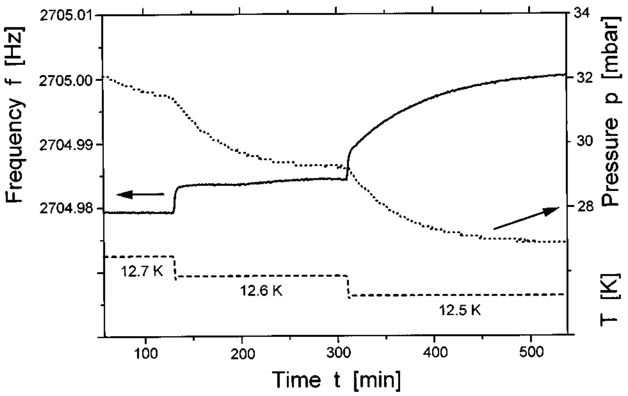

FIG. 6. Response of the oscillator and vapor pressure to temperature changes. The frequency (solid line), the pressure (dotted line), and the temperature (dashed line) above and below $T_c = 12.6$ K for $n = 1.2$ mmole H_2 are shown. The pressure always changes exponentially, whereas the frequency response changes at T_c from an empty cell-like behavior to a response in two steps: an empty cell-like behavior followed by a slow exponential response with a time constant of about 50 min. During the time at $T = 12.6$ K, we see already a very slight increase in frequency starting at $t \approx 200$ min. This indicates that the temperature is already very close to T_c.

change is an exponential decay. Its time constant increases from 100 min at 11 K to 500 min at 8 K.

4. Between 1.5 and 1.92 mmole H_2

For these larger fillings, we also see the effect that H_2 leaves the Vycor below T_c. The frequency behavior, however, is more complicated, as shown in Fig. 7: No universal behavior below T_c is observed. For $n = 1.5$ mmole H_2, the same behavior in frequency and pressure as already discussed in the above section can be seen. Δf, however, does not follow the universal curve of the data shown in Fig. 4(a) at $T < T_c$. For $n = 1.80$ mmole, we first see a small decrease of Δf at $T < T_3$, which is probably caused by the influence of solid H_2 in the torsion rod (note that from Δf there should be only 1.75 mmole H_2 in the Vycor). At $T_c = 12$ K, Δf sharply decreases and the slow frequency response starts: H_2 begins to leave the Vycor. For $n = 1.92$ mmole ($n > n_0$), we also see the influence of solid H_2 in the torsion rod, indicated by a small decrease of Δf below T_3. In addition, the measured pressure for this filling is identical to the vapor pressure of bulk liquid (solid) p-H_2 above (below) T_3. At $T_c = 12.5$ K, H_2 starts again to leave the Vycor which leads to a strong decrease of Δf. The time constants to reach a new equilibrium state after each cooling down at $T < T_c$ are the same as for smaller n at the same temperatures.

5. Mass flow rate and T_c as a function of n

The speed of escaping of H_2 as a function of temperature is shown in Fig. 8, where the time derivative of f just after the slow response started, normalized by the temperature change ΔT, $(\delta f/\delta t)\Delta T^{-1}$, is plotted. There is no dependence on n within our experimental accuracy. $(\delta f/\delta t)\Delta T^{-1}$, which is proportional to the mass flow rate, varies exponentially with temperature, which suggests a thermally activated type of motion of H_2 molecules.

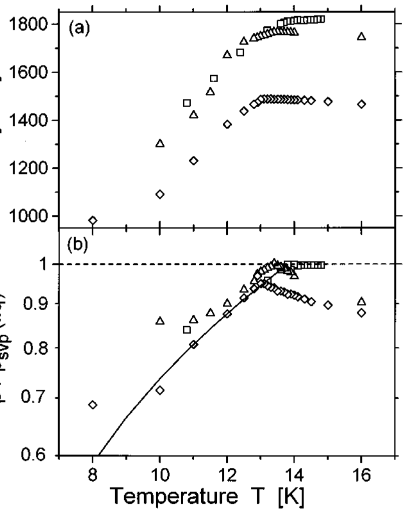

FIG. 7. Data for $n = 1.5$ (◇), 1.75 (△), and 1.92 (□) mmole H_2 in Vycor. (a) Frequency difference Δf as a function of temperature. For the highest n, the influence of solid H_2 in the torsion rod causes a small decrease of Δf below T_3. (b) H_2 vapor pressure normalized by the bulk liquid p-H_2 vapor pressure p/p_{SVP}(liq) as a function of temperature. The solid and dashed lines represent the vapor pressure of bulk solid and liquid p-H_2, respectively. The pressure data also indicate the presence of a bulk phase for the highest n. See text for more details.

The values of T_c, the temperature where H_2 starts to leave the Vycor, as a function of n are presented in Fig. 9. T_c is determined by the balance between the chemical potential of H_2 in the Vycor and the chemical potential of bulk solid H_2 outside of the Vycor. The more H_2 is admitted, the higher is the chemical potential of H_2 in the Vycor, which is in equilibrium condition to the H_2 vapor outside of the Vycor. The chemical potential of H_2 in the Vycor is still smaller than that of the bulk liquid, since it is reduced by the van der Waals potential from the Vycor wall and is a function of distance. Consequently, T_c increases when increasing n: T_c is related to the adsorption isotherms of H_2 molecules in the

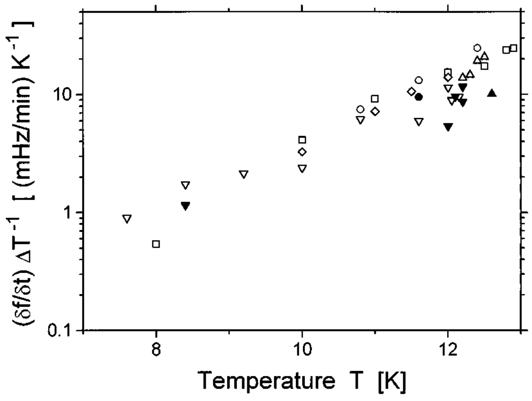

FIG. 8. Slope $(\delta f/\delta t)\Delta T^{-1}$ (the time derivative of f just after the slow response started, normalized by the temperature change ΔT) as a function of temperature for all fillings between 1.1 and 1.92 mmole H_2 in cooling (open symbols) and warming (solid symbols).

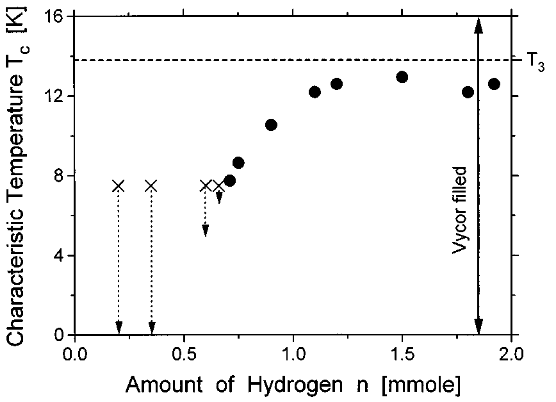

FIG. 9. Characteristic temperature T_c (●) as a function of n. ×'s represent the measured fillings $n \leqslant 0.66$ mmole to which no escaping of H_2 has been observed down to the minimum temperature of 7.5 K. The arrows are indicating the possible developement of T_c(n) down to $T = 0$ K. It seems that about 0.4 mmole of H_2 is ''inert'' or does not escape from the Vycor even at 0 K.

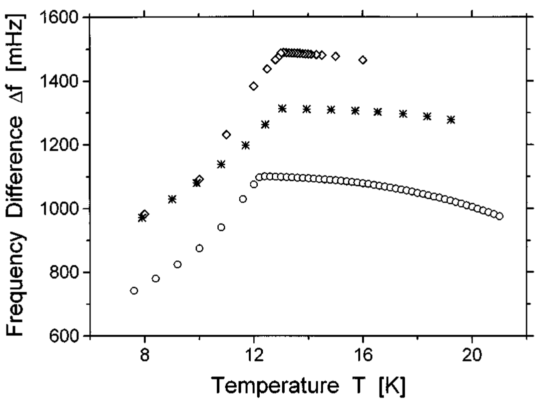

FIG. 10. Frequency difference $\Delta f(T)$ for $n = 0.9$ (*) mmole HD in Vycor. For comparison, $\Delta f(T)$ is also shown for $n = 1.5$ (◇) and 1.1 (○) mmole H_2 in Vycor. The larger Δf for HD for the same n as for H_2 is due to its larger mass. We see that HD shows the same behavior in Δf like H_2 with a higher T_c compared to an equivalent filling of H_2.

Vycor. When the Vycor is almost filled with H_2, capillary condensation occurs and makes $\Delta f(T)$ and the temperature dependence of the pressure as complicated as discussed in Sec. III A 4. Therefore, in this case the determination of T_c is less accurate than for fillings with $n \leqslant 1.5$ mmole. Some H_2 (about 20% of $n_0 = 1.85$ mmole, the total amount of H_2 to fill the cell) seems to stay in the Vycor even at $T = 0$ K. This amount of H_2 may correspond to the strongly bound H_2 layer(s) observed in Raman scattering experiments.[21]

Our measurements indicate that the chemical potential of solid H_2 in Vycor is larger than that of bulk solid H_2. Otherwise, H_2 would solidify and stay in Vycor when lowering the temperature.

6. 0.9 mmole HD

In order to investigate the influence of different hydrogen isotopes, we repeated the experiment with HD. For a filling $n = 0.9$ mmole HD, we find essentially the same features as for H_2 described in Sec. III A 3. with a slightly higher $T_c = 13$ K as shown in Fig. 10, which is caused by the higher triple-point temperature of HD: $T_3^{\mathrm{HD}} = 16.6$ K. The characteristic relaxation time for the oscillator to reach a new equilibrium frequency after changing the temperature below T_c is about 350 min at 11 K which is larger than that of H_2, presumably because of the larger mass of the HD molecule.

The same frequency behavior of the HD measurement as observed for H_2 also excludes the possibility of a superfluid transition (Bose-Einstein condensation) as an interpretation of our observations in the case of H_2, since the HD molecule is a fermion.

7. 3.1 mmole H_2

Most of the former liquid-solid phase transition experiments were performed when there was bulk solid outside of the Vycor.[5,7,22–24] We also studied this case for $n = 3.1$ mmole ($n \approx 1.7 n_0$). The pressure after filling is higher than that of bulk H_2 at the temperature of the cell. It corresponds to a temperature that is about 0.4 K higher than the temperature of the cell. We conclude that bulk H_2 has formed in part of the filling capillary closely above the cell.

The frequency behavior is completely different from all the others discussed in Secs. III A 2–III A 6. When cooling from 14.3 K to 13.4 K, we see a linear increase of Δf (see Fig. 11), which can be caused by the H_2 in the torsion rod in combination with a mass flow of H_2 into the Vycor due to the density increase of liquid H_2 in the Vycor when decreasing the temperature. At 12.4 K $< T <$ 13.4 K, Δf shows only a small increase. The time constants to reach a new equilibrium state after changing the temperature at $T > 12.4$ K are the same as for the empty cell. At $T = 12.2$ K, Δf starts to increase sharply and reaches a new stable value below 10 K. We identify this effect as solidification of H_2 in the Vycor in this run with $n = 3.1$ mmole. H_2 has to solidify in the Vycor because escaping is impossible due to bulk solid outside of

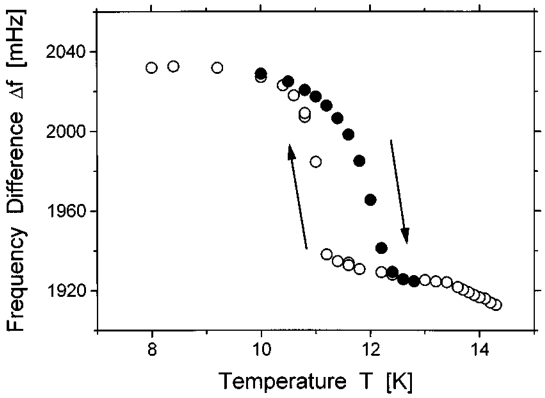

FIG. 11. Frequency difference $\Delta f(T)$ in cooling (○) and warming (●) for $n = 3.1$ mmole H_2 in the setup. For this ''overfilling,'' some H_2 solidifies in the torsion tube and blocks it. As a result, H_2 cannot leave the Vycor at T_c and has eventually to solidify in the pores. The change in Δf is caused by a mass flow into the Vycor at the solidification of H_2 in the pores. For details see text. Note that there is a hysteresis in solidification and melting.

the Vycor blocking the torsion rod. The time response of the frequency after changing the temperature in this temperature range also indicates a mass flow into the Vycor, with values of the time constant of the same order as for the case when H_2 leaves the Vycor.

Even if we assume that only 80% of the H_2 in the Vycor transforms from liquid to solid according to the Raman scattering experiment[21] as well as to our observation, the observed frequency change of 0.10 Hz (or increase of the amount of H_2 in the Vycor of 0.1 mmole) at solidification is smaller than expected for solidification of the same amount of bulk liquid H_2, which should be 0.15 mmole. We conclude therefore that the molar volume change at the solidification of H_2 in the Vycor is smaller than that of bulk H_2. A similar observation was reported for ^4He in Vycor.[7]

When warming up from the lowest temperature, a hysteresis can be seen in this run. The freezing (melting) temperature $T_f \simeq 11.2$ K ($T_m \simeq 12.2$ K) is in good agreement to values in the literature.[4,5,25]

A discussion on the solidification process of H_2 in Vycor can be found in Sec. IV.

B. Capacitor data

Independently, we have confirmed with a capacitor filled with Vycor that H_2 molecules once adsorbed in Vycor leave it when decreasing the temperature.

The capacitance of the cell shown in Fig. 1 without H_2 does not exhibit any anomalies at $6 \text{ K} < T < 20$ K but shows a linear temperature dependence[18] as can be seen in Fig. 12 (□).

First, we measured the adsorption isotherms at $T > T_3$(14.0 K and 18.5 K); see Fig. 13. Unlike in usual adsorption isotherm measurements, the amount of adsorbed H_2 is determined from $\Delta C = C_{\text{Vycor+H}_2} - C_{\text{Vycor}}$. The obtained isotherms are quite similar to those reported in Ref. 14: it seems that ΔC is almost proportional to the amount of H_2 between the electrodes.[26] The difference between the two measurements at different temperatures becomes smaller when the data are plotted as a function of the difference in the chemical potential between the adsorbed state and the bulk instead of the normalized vapor pressure.[14] We, however, prefer the reduced pressure representation since it shows clearly two steps of capillary condensation: into the Vycor pores at $p/p_{\text{SVP}}(\text{liq}) \simeq 0.8$ and into the gap between the Vycor and the electrodes at $p/p_{\text{SVP}}(\text{liq}) \simeq 1$. The capacitance change ΔC associated with H_2, which is needed to fill the Vycor, is about 0.073 pF.

At the saturated vapor pressure of bulk H_2, $C(T)$ shows at $T > T_3$ the same temperature dependence as the empty cell, as shown in Fig. 12 (○). (H_2 is filled at 18.5 K and the filling process is shown in Fig. 13.) This is expected because the temperature dependence of the dielectric constant of bulk H_2 is small at $T < 20$ K.[27] At $T \leqslant T_3$, however, $C(T)$ shows a complicated behavior because of triple-point wetting.[11,28] The H_2 capillary condensed into the gap between the Vycor and the electrodes dewets at $T < T_3$. An example of this dewetting can be seen in the inset of Fig. 12. It shows hysteresis, and its temperature is not reproducible and depends on the temperature sweep time.

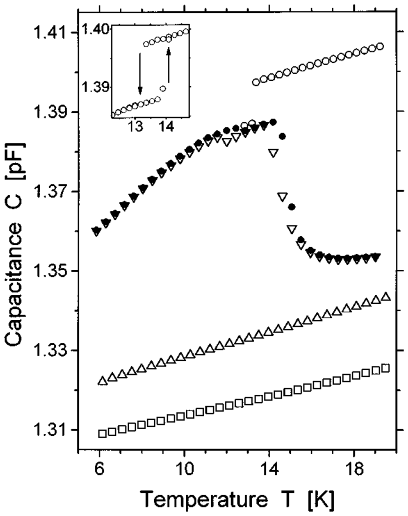

FIG. 12. Temperature dependence of the capacitance $C(T)$ for the empty cell and with different H_2 fillings in it. The empty cell behavior C_{Vycor} (□) and one measurement with the pores being full up to a temperature of 20 K (bulk H_2 coexists in the cell outside of the Vycor) $C_{\text{Vycor+H}_2}$ (○) are shown. The inset shows the complication at $T \approx T_3$ for the full pore measurement (○) because of triple-point wetting in the gap between the Vycor and the electrodes. $C_{\text{Vycor+H}_2}(T)$ is hysteric and not reproducible in this temperature region. ▽'s (cooling) and ●'s (warming) show the data when the capillary condensation into the gap between the Vycor and the electrodes is avoided by reducing the amount of H_2 in the cell. △'s show the data when only 13% of the volume of the Vycor pores is filled with H_2. See text for more details.

In order to avoid the complication due to triple-point wetting outside of the Vycor, we conduct the experiment as follows: (1) The Vycor is filled with H_2 at $T = 14.0$ K. The filling process is shown in Fig. 13. (2) We wait for 2 weeks. (3) H_2 is removed until $p/p_{\text{SVP}}(\text{liq}) = 0.62$ at $T = 14.6$ K is obtained. (4) The temperature sweep is started. The total cooling and warming time together is 11 h. The results are

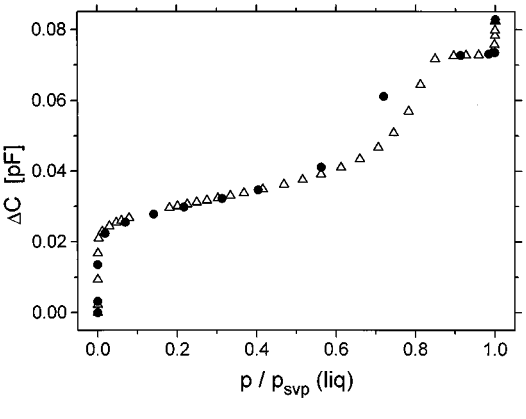

FIG. 13. Adsorption isotherm of H_2 in Vycor measured by the capacitor shown in Fig. 1: $\Delta C = C_{\text{Vycor+H}_2} - C_{\text{Vycor}}$ as a function of the normalized vapor pressure $p/p_{\text{SVP}}(\text{liq})$ at $T = 14.0$ K (●) and at $T = 18.5$ K (△). Two steps of capillary condensation into the Vycor pores [at $p/p_{\text{SVP}}(\text{liq}) \simeq 0.8$] and into the space between the Vycor and the electrodes [at $p/p_{\text{SVP}}(\text{liq}) \simeq 1$] can be seen.

shown in Fig. 12 (▽ for cooling and ● for warming). Since the pressure in the cell is the saturated vapor pressure only below 13.2 K, the capillary condensation into the gap between the Vycor and the electrodes can be avoided because of the triple-point wetting phenomena. At $T\approx 11$ K the capacitance starts to decrease with a slope larger than that of the empty cell. This indicates that H_2 starts to leave the Vycor at this temperature, which is in good agreement with the torsional oscillator experiment.

At $T>T_3$ the capacitance for this filling decreases very rapidly because $p/p_{\mathrm{SVP}}(\mathrm{liq})$ becomes much smaller than 1 due to the increase of the saturated vapor pressure and thus H_2 leaves the Vycor. The fact that the capacitance is still larger than the empty cell value at $T>17$ K can be explained with the strongly bound H_2 layers on the Vycor surface as discussed in Sec. III A 5. This interpretation is supported by a measurement with only about 13% of the total volume of the pores filled with H_2: The data are almost parallel to those of the empty cell as shown in Fig. 12 (△). It implies that below 20 K the first H_2 layer(s) adsorbed on the Vycor surface stays in the pores regardless of temperature. This again agrees well with the results from the torsional oscillator experiment (Sec. III A 2).

Note that all our capacitive measurements were done after more than 1 week waiting time in order to make sure that most of the ortho-H_2 is converted to p-H_2.

IV. DISCUSSION

In this section, we will discuss more details about solidification in restricted geometries, which have not yet been discussed extensively and might be partly speculative.

A. Excess free energy of solid hydrogen in Vycor

We concluded in Sec. III that the free energy of solid hydrogen in Vycor glass is larger than that of bulk solid H_2. In this section we will discuss the origin of this excess free energy.

Dash has proposed a mechanism to increase the free energy of solids in restricted geometries compared to the bulk solid.[22] According to his argument, a solid which grows from a rough surface must be a polycrystal with many grain boundaries which increase its energy. The grain boundary energy per unit area is $\overline{E}\approx 0.05\mu a$, where μ and a are the shear modulus and the lattice constant, respectively. After Dash (also Ref. 8), the free energy difference between liquid and solid with grain boundaries in pores is

$$\delta F_{LS}=A_{\mathrm{GB}}\overline{E}-Vn_S(f_L-f_S), \tag{4.1}$$

where A_{GB}, V, n_S, f_L, and f_S are the total area of the grain boundaries, the pore volume, the number density of bulk solid, and the chemical potential of bulk liquid and of bulk solid, respectively. He assumed that the thermodynamical properties of a liquid and solid in restricted geometries are the same as those of the bulk phases. In addition, he introduced a parameter α which represents the surface roughness to obtain $A_{\mathrm{GB}}\simeq\alpha A$, where A is the total surface area of the pores. The required overpressure to solidify ^{4}He in packed alumina powder of 50 nm average particle size was found to be about 2.5 bars which gives $\alpha\simeq 40$ for $V/A\simeq 50$ nm.[22] In the case of ^{4}He in Vycor glass, the required overpressure, by assuming $\alpha\simeq 40$ as in the case of alumina powder, would be about 20 bars which is in good agreement with experimental observations.[22] However, his argument seems to be not very physical. In order to define grain boundaries in the pore, there must be at least one layer of molecules on both sides of them and the volume of those layers, $A_{\mathrm{GB}}2a$, must be much less than V. In the case of alumina powder, $A_{\mathrm{GB}}2a/V\simeq\alpha 2aA/V\sim 0.5$, which seems to be too large. In the case of Vycor, it gives the nonphysical value of 4.

Another possible mechanism to increase the free energy of a solid in restricted geometries is an elastic energy of the solid on the substrate which is extensively discussed in the context of wetting transitions.[29] The solid which grows on a substrate is strongly strained if the lattice constants or the symmetry of the solid and the substrate do not match each other. A solid on an atomically rough surface like the surface of Vycor pores must be strongly strained, too. The possible size of the elastic energy is estimated in the following way. The molar volumes of solid H_2 are 23.15 and 22 cm^3/mol at 0 and 112 bars, respectively. If the deformation is elastic from 23.15 to 22 cm^3/mol, the elastic energy should be of the order of $\Delta V\cdot\Delta p\sim 13$ J/mol which corresponds to $1.5k_B$ per molecule. Note that $f_L-f_S\approx 1k_B$ at $T_3-T=1$ K,[2] which should be compared to some other energies, for example to the above-mentioned elastic energy, in order to discuss H_2 in the liquid state below T_3. Since this volume change requires only a 1.7% change of the lattice constant, such a deformation may be possible under the influence of the substrate.

B. Amorphous layers on rough surfaces in restricted geometries

There is accumulating evidence that amorphous solid layers generally grow on rough surfaces of restricted geometries, such as Vycor[14] and metallic sinters.

First we consider the case when the restricted geometry is filled with a liquid. Broad vibrational and rotational Raman scattering spectra of H_2 in Vycor glass were reported in Ref. 21, which were attributed to strongly bound layers on the Vycor wall. Golov and Pobell pointed out that amorphous helium layers grow on surfaces of Vycor as shown by their heat capacity data.[30] They also recognized a similar component in the heat capacity of ^{3}He adsorbed on sintered silver.[31] Spin-lattice relaxation times T_1 of liquid ^{3}He confined in spaces between fluorocarbon spheres[32] or porous glass[33] (similar to Vycor glass) were found to be proportional to the Larmor frequency, which indicates the wide range of distribution of exchange interactions among ^{3}He atoms. All these observations can be explained by the hypothesis of amorphous solid layers on the substrates. The amorphous layers which coexist with a liquid in the center of the pores are at most two atom (or molecule) diameters thick since they are caused by the attractive potential of the substrate.

Now we consider the case where the restricted geometries are filled with a solid. According to Raman scattering experiments,[21] the amorphous layers which coexist with a liquid and which are responsible for the broad, temperature-independent background in the spectra do not change their property when the H_2 in the Vycor solidifies at low temperatures. In the center of the pores, a ''crystalline'' solid exists at low enough temperatures as shown by neutron scattering experiments,[34,35] although its crystal structure is not known yet. There must be a transition region between the ''inert'' amorphous, strongly bound layer near the substrate and the ''crystalline'' solid in the center of the pores. Because of the temperature independence of the properties of the amorphous layer on the substrate and because of the bulklike behavior of the central part, it must be this transition region which is responsible for the observed ''anomalies'' of hydrogen and helium in restricted geometries. These ''anomalies'' are the following. Sokol *et al.* found broad neutron scattering spectra of D_2 confined in Vycor.[34] Adams *et al.* reported that the molar volume change at the liquid-solid phase transition of ^{4}He in Vycor is smaller than that of bulk ^{4}He.[7] We also recognize this fact for H_2 in Vycor; see Sec. III A 7.

The thickness of the transition region is estimated to be of the order of 1 nm from the broad neutron scattering spectra observed for D_2 in Vycor (typical size of 3 nm),[34] while the existence of this transition region in silver sinter (typical size of 70 nm) has not been recognized until very recently.[36] This estimated thickness of the transition region is also consistent with the size of the dislocation core,[37] which is also a measure of the elastic healing length of solid hydrogen from a strong disturbance. We note that 1 nm for the elastic healing length is quite large and is caused by the small shear modulus of a quantum solid such as hydrogen or helium. In the case of classical crystals, the thickness of the transition region is expected to be smaller because of their strong shear modulus. This is demonstrated by the sharp neutron scattering spectra of the classical solid O_2 in Vycor in Ref. 34.

We believe that the transition region introduced in this section is strained and increases the free energy of a solid in restricted geometry, as discussed in Sec. IV A. It is then responsible for the escaping of H_2 out of the Vycor at $T<T_c$, as discussed in Secs. III A 3 and III A 4. The part of H_2 remaining in the Vycor at $T=0$ K corresponds in this model to the amorphous layers immediately adjacent to the rough Vycor surface.

C. Depression of freezing temperature in restricted geometries

We consider the case when the restricted geometries containing liquid are closed by a bulk solid. A widely accepted explanation of the depression of the freezing temperature in restricted geometries is as follows.[7,8] The free energy difference $\delta F(R)$ between a liquid and solid depends on the radius R of a nucleating solid droplet,

$$\delta F(R)=4\pi R^2\sigma_{LS}-(4/3)\pi R^3 n_S(f_L-f_S), \tag{4.2}$$

where σ_{LS} is the surface energy between a liquid and solid. $\delta F(R)$ has a maximum at $R_0=2\sigma_{LS}/[n_S(f_L-f_S)]$. Once a thermal fluctuation forms a solid nucleus larger than R_0, the solid grows without limit. However, a restricted geometry with characteristic size L_c limits the size of a solid nucleus to $R<L_c/2$. Therefore, $\delta F(L_c/2)<0$ is necessary for solidification, and thus a freezing temperature depression by

$$\delta T_D \approx \frac{3\sigma_{LS}T_m}{n_S\,\ell_{LS}L_c/2} \tag{4.3}$$

can be expected, taking $f_L-f_S\approx\delta T_D\,\ell_{LS}/T_m$, where ℓ_{LS} and T_m are the latent heat per molecule and the melting temperature, respectively.

Another explanation of the depression of the freezing temperature in restricted geometries is as follows. A free energy balance between liquid and solid phases is considered including their surface energies with the substrate,

$$\delta F_{LS}=(A\sigma_S+Vn_Sf_S)-[A\sigma_L+Vn_Lf_L+V(n_S-n_L)f_S], \tag{4.4}$$

where σ_S, σ_L, and n_L are the sum of the energies of the amorphous and transition regions which were introduced in Sec. IV B, the energy of the amorphous layer, and the number density of the liquid, respectively (see also Ref. 4). $(A\sigma_S+Vn_Sf_S)$ is the free energy of solid after the phase transition, while $[A\sigma_L+Vn_Lf_L+V(n_S-n_L)f_S]$ is the free energy before. $V(n_S-n_L)f_S$ is included in order to take into account mass transport from outside to inside the restricted geometries at the solidification, according to our observation in Sec. III A 7. Note that these surface energies include the energy associated with the attractive potential from the surface. The volumes of the amorphous layer and the transition region are ignored here. Assuming $\delta F_{LS}=0$ at solidification and $f_L-f_S\approx\delta T_D\,\ell_{LS}/T_m$, one can get the freezing temperature depression δT_D,

$$\delta T_D \approx \frac{A}{V}\,\frac{(\sigma_S-\sigma_L)T_m}{n_L\,\ell_{LS}}. \tag{4.5}$$

If we assume that a ''pore'' is a slab of height L_c, Eq. (4.5) differs by about factor of 3 from Eq. (4.3) (assuming $n_L\simeq n_S$ and $\sigma_S-\sigma_L\simeq\sigma_{LS}$), which comes from the difference in the shape of the solid. If the mass in the restricted geometry is conserved at solidification, $V(n_S-n_L)f_S$ is not necessary in Eq. (4.4), and thus Eq. (4.5) should be modified slightly.

The proportionality $\delta T_D\propto A/V$ was confirmed for the depression of the freezing point of alcohols in a well-defined single pore.[38] In this experiment, the single ''pore'' was a slab formed by two mica surfaces whose separation was controlled to a precision of 0.1 nm with a surface force apparatus. This proportionality alone does not exclude the widely accepted model [Eq. (4.3)]. However, the obtained surface tension between a liquid and solid suggests that this model is not relevant. The surface tension between liquid and solid t-BuOH calculated from Eq. (4.5) is about 14 mN/m which is reasonable when compared to that between a liquid and vapor of 19.6 mN/m.[38] If we take Eq. (4.3), we obtain about 4 mN/m, which seems to be too small.

A model, which may be considered as a modified invasion model, was introduced to explain the freezing process observed by heat capacity measurements of H_2 in Vycor.[4] In this model, the pores are divided into three classes: (1) Nucleation pores where a solid can form by overcoming the energy barrier between liquid and solid phases. (2) Propagator pores where the solid phase is thermodynamically stable but an energy barrier prevents solidification. In Vycor the number of the propagator pores is expected to be much greater than that of the nucleation pores. (3) Stable pores where the liquid phase is thermodynamically stable. These types of pores are distributed randomly in the Vycor. When the temperature decreases, the number of the nucleation and of the propagator pores will increase. At some temperature, the propagator and nucleation pores are dense enough to percolate and solidification suddenly occurs in a large number of pores. At lower temperatures, a further increase of the numbers of propagator and nucleation pores gives a more gradual spread of the solid in the Vycor. In this model, the depression of the freezing temperature is determined by Eq. (4.5) not by Eq. (4.3).

In the case of helium or hydrogen in Vycor or other porous glass systems, the proportionality $\delta T_D \propto A/V$was also confirmed for large pores although there is some ambiguity because of the distribution of pore sizes in each sample.[7,23] However, there are clear deviations from this proportionality for pore sizes less than about 5 nm radius.[7,8] This deviation can naturally be understood when the thicknesses of the amorphous layer and of the transition region are taken into account. In this case, V in Eqs. (4.4) and (4.5) should be replaced with $V - At$ where t is the total thickness of the amorphous layer and transition region.

In the case that V/A is less than the thickness of the transition region (of the order of 1 nm), all solids in the pores at low temperatures must be highly disordered. Then, we expect a glass-freezing-like solidification process instead of a sharp liquid-solid phase transition. The lack of a sharp phase transition for H_2 in Vycor samples of typical size of 1 nm in Ref. 4 may be understood as a glass transition. According to our understanding described here, it is mysterious that rather sharp liquid-solid phase transitions were observed for H_2 in zeolite in Ref. 8.

V. SUMMARY

We have investigated hydrogen in porous Vycor glass with a torsional oscillator as well as a capacitive technique. We find that below a characteristic temperature which depends on the H_2 filling, H_2 starts to leave the Vycor instead of solidifying in the Vycor pores. Therefore, we conclude that the chemical potential of a solid H_2 in Vycor is larger than that of bulk solid H_2. A small fraction of about 20% of the total amount of H_2, which is necessary to totally fill the Vycor, seems to build a strongly bound amorphous layer on the substrate. We expect this layer to stay in the Vycor at temperatures even down to 0 K. Under different experimental conditions we forced the H_2 to solidify in the pores, which took place at a temperature which is lower than the bulk freezing temperature. This observed depression of the freezing temperature is in good agreement with former experiments by other groups. We find that the properties of solid hydrogen in Vycor glass are quite different from those of bulk hydrogen. According to this knowledge, we discuss general features of freezing in restricted geometries.

ACKNOWLEDGMENTS

We wish to thank M. Chan, A. Golov, N. Masuhara, P. Leiderer, J. Reppy, and K. Shirahama for discussions. This work is supported by the Deutsche Forschungsgemeinschaft through Graduiertenkolleg Po 88/13, by the German-Israeli Foundation for Scientific Research and Development through Grant No. I-295-0.90.07/93, and by the European Community through project No. ERBCHGECT920002.

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