

## Multilayer Adsorption of H<sub>2</sub> on Uniform MgO Substrates

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(Received 25 July 1988)

Adsorption-isotherm and heat-capacity measurements on monolayer and multilayer H<sub>2</sub> adsorbed on MgO are reported. We observe layer by layer growth with at least six layer steps measurable at 8.88 K. A complete first layer is solid at temperatures much higher than the bulk triple point. The second layer has a phase diagram with a liquid-vapor critical point at  $10.05 \pm 0.05$  K and a solid-liquid-vapor triple point at  $7.20 \pm 0.05$  K. The third, fourth, fifth, and sixth layers show layering critical points in the vicinity of 10 K that may point to a roughening transition in bulk crystals.

PACS numbers: 68.35.Md, 67.40.Kh, 68.45.Gd, 82.65.Dp

Condensed molecular hydrogen is the thermodynamic system with the lowest-temperature vapor-liquid-solid triple point. The small molecular mass and the relatively large intermolecular attractive potential combine to produce a quantum system intermediate between the helium isotopes and the classical rare gases. It is widely believed that if the 13.9-K triple point could be suppressed to somewhere below 6.5 K (and probably below 4 K), the supercooled fluid will undergo a transition to a Bose-condensed state.<sup>1</sup> A careful analysis of the supercooling problem has been made by Maris, Seidel, and Huber<sup>2</sup> and successful attempts at depressing  $T_l$  are reported in the literature for H<sub>2</sub> filling the pores of Vycor glass capillaries,<sup>3</sup> with the lowest reported temperature at which a triple point (or melting) transition is observed being 8.5 K for a mean pore diameter of 25 Å.<sup>4</sup> Smaller-diameter capillaries show no melting transition. Experiments with H<sub>2</sub> and D<sub>2</sub> partially filling zeolite pores show a broad specific-heat anomaly in the 9 to 10 K range, perhaps due to film melting.<sup>5</sup>

Instead of starting with bulk material in a restricted and somewhat uncharacterized geometry, we have chosen to study H<sub>2</sub> films starting with a well characterized substrate, doing a thermodynamic study of the layer by layer growth towards three-dimensional (3D) H<sub>2</sub>. In recent times it has been possible to produce highly homogeneous, large-specific-area powders whose starting material is MgO smoke, obtained by burning pure Mg ribbons in air and processing a small portion of the collected samples by baking in vacuum above about 900°C,<sup>6,7</sup> and fairly homogeneous sintered pills whose starting material is a slurry of Mg(OH)<sub>2</sub> and 1% to 5% MgCl<sub>2</sub>.<sup>8</sup> The MgCl<sub>2</sub> decomposes into MgO and HCl (mostly removed during processing) and aids in the production of sintered MgO cubes of a very uniform size (about 4000-Å edges). Kr isotherms performed in both smoke and sintered samples have identical features at identical pressures, with the sintered samples being slightly more heterogeneous. We have done H<sub>2</sub> adsorption-isotherm measurements using smoke substrates, and heat-capacity measurements using a sintered-pill substrate. The ad-

sorption isotherms have been performed on two different samples and cryostats (cell A and cell B) in the temperature range between 8.56 and 27.5 K, while the heat-capacity measurements have been run between 4.5 and 11 K on cell C. Results can be summarized as follows: (a) The isotherms indicate the formation of at least six layers at 8.88 K. (b) The first layer is solid to temperatures much higher than the bulk triple point, with a solid-solid or melting transition visible near monolayer completion in our 16 to 20 K isotherms. (c) Both the isotherms and the heat capacity show that the second layer has a "conventional" phase diagram with a triple point at  $7.20 \pm 0.05$  K and a critical point at about  $10.05 \pm 0.05$  K, both temperatures being lower than classical expectations because of quantum effects. (d) The third, fourth, fifth, and sixth layers appear to have layer critical points as described by lattice-gas<sup>9</sup> and solid-on-solid models,<sup>10</sup> with critical temperatures in the vicinity of 10 K; these critical temperatures should converge to a roughening temperature also in the vicinity of 10 K.<sup>9,10</sup>

For the adsorption isotherms we used quartz cells with a quartz to Pyrex to Kovar graded seal, the Kovar finally soft soldered to a stainless-steel vacuum-jacketed fill line. The magnetism of the Kovar tube appears to greatly aid in the ortho-para conversion process when the H<sub>2</sub> dosing is changed from a room-temperature storage. MgO smoke was produced by our following the recipe of Refs. 6 and 7. The isotherms on cell A concentrated on the first, second, and third layers and were measured between 8.56 and 27.50 K. These results<sup>11</sup> were used to design cell C. The isotherms on cell B were measured between 8.88 and 14.10 K and explored the thicker films. For the thickest films, we did extensive comparisons among the temperature of cell B measured by a calibrated thermometer ( $T_{\text{MgO}}$ ), the vapor pressure of the cell, and the temperature of the Kovar tube (always  $T_{\text{tube}} > T_{\text{MgO}}$ ). The very-thick-film vapor pressure for a given  $T_{\text{MgO}}$  was that of *p*-H<sub>2</sub> for all low-temperature measurements. A sintered pill (for cell C) of about 1.5 cm height and 1 cm diameter was made by our following

a procedure described by Hamano, Nakagawa, and Watanabe<sup>12</sup> and investigated by Mikijelj and Whittemore<sup>8</sup> and Sullivan.<sup>13</sup> The pill was pressed into a stainless-steel container and connected to the adsorption line of our cryostat where it was baked and evacuated. The fill line serves as a support and cooling link for the calorimeter.

Figure 1(a) shows the 8.88-K isotherm taken with cell B together with the second-layer isotherms at 8.56 and 9.27 K taken with cell A. Only about half the points taken are plotted. The isotherms start on the second layer at these temperatures since the first-layer vapor pressure is too low to measure with our equipment. Pressures have been corrected for thermomolecular effects. The volumes adsorbed are correct for cell B; those for cell A have been multiplied by the ratio of the coverages at 77 K at the melting transition of the first monolayer of Kr for each cell [(2.62 cm<sup>3</sup>)/(1.105 cm<sup>3</sup>)] to obtain a uniform scale. The small uncertainty in final coverages by use of this procedure (about 3%) shows as the small vertical displacement of the cell-A isotherms with respect to those of cell B. Starting at the lowest coverages, one can successively observe the second-layer liquid-vapor coexistence, the second-layer melting (indicated by vertical arrows), and then "vertical" steps cor-

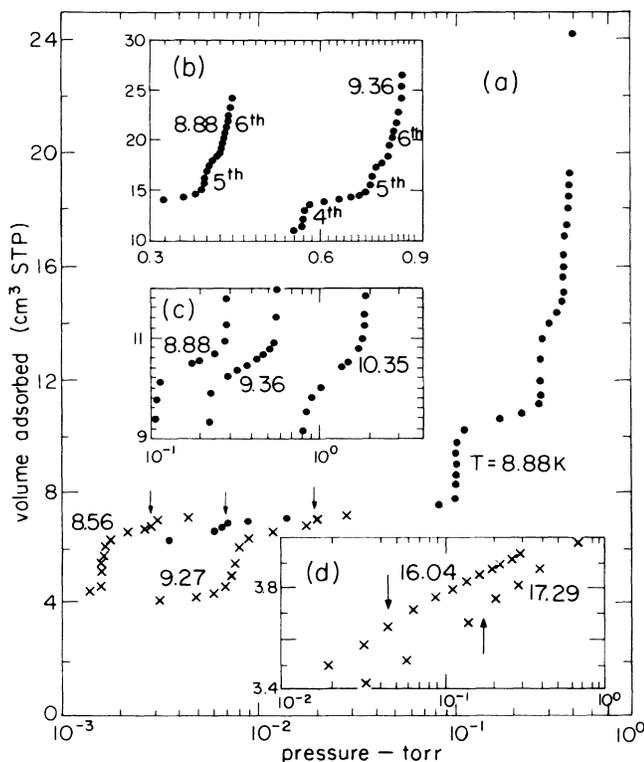


FIG. 1. Adsorption isotherms of H<sub>2</sub> on MgO smoke. ●: cell B; ×: cell A. (b)-(d) (insets) Details in the same units as (a). Ordinals refer to layer number. Numerals are temperatures in K.

responding to third-, fourth-, fifth-, and at least a partial sixth-layer formation. The insets in this figure show important details of portions of the isotherms. Figure 1(b) shows the higher steps in the 8.88- and 9.36-K isotherms on a very expanded pressure scale. At 8.88 K we measured points up to 39 cm<sup>3</sup>, well above the range shown in this inset, where the pressure was 0.4340 Torr and still, on the average, slowly increasing. Temperature stability and pressure-gauge resolution become crucial at this point so that it is difficult for us to resolve any more steps. Figure 1(c) shows on an expanded coverage scale the region between the third and fourth steps at low temperatures. There is no evidence for substeps like the ones indicated by the arrows in Fig. 1(a) for the second-layer melting. Figure 1(d) shows, with a greatly magnified coverage scale, the region between the first and second layers at higher temperatures. Here it is possible to detect an inflection point, similar to the one reported for molecular deuterium (D<sub>2</sub>) on MgO (Ref. 14) in about the same coverage and temperature range. For the D<sub>2</sub> monolayer, neutron-scattering measurements show that the substep corresponds (at lower temperatures) to a transition from a *c*(2×4) to a *c*(2×6) structure. It could be that a similar transition occurs in H<sub>2</sub>, but also it could be that at this higher temperature the substep signals the melting of the first monolayer. It is impossible to extract a first-layer substep from our highest-temperature isotherms and so we cannot follow this feature to higher temperatures.

It had been deduced in Ref. 11 by extrapolation of the data taken with cell A on the second layer that a triple point (solid-liquid-vapor coexistence) should exist at about 7.6 K and that a critical point (liquid-vapor) should also exist at about 10.5 K. The present heat-

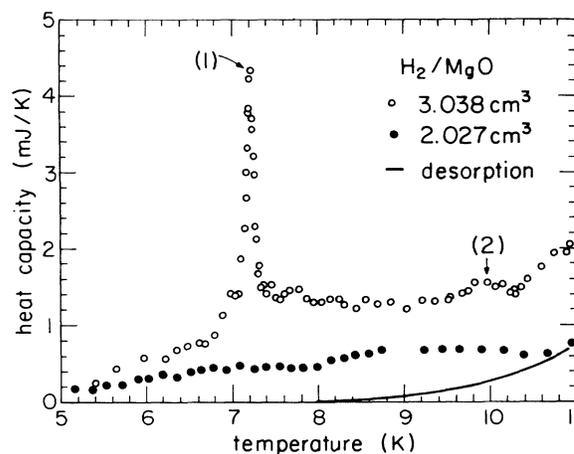


FIG. 2. Heat capacities measured with cell C of two films of H<sub>2</sub> adsorbed on sintered MgO. The adsorbed volumes indicated in the figure are the ones at the lowest temperature measured. Estimated desorption correction for the highest coverage is shown as a full line. The lowest coverage (2.027 cm<sup>3</sup>) corresponds to approximately one full monolayer.

capacity measurements explored extensively the second layer. Figure 2 shows the results for the total heat capacity (minus calorimeter background) for  $3.04 \text{ cm}^3$  of  $\text{H}_2$  adsorbed in this bilayer film, corresponding to  $5.84 \text{ cm}^3$  of gas adsorbed when translated to the coverages of cell B with a procedure similar to the one described above (Kr coverage for melting at 77 K for cell C is  $1.36 \text{ cm}^3$ ). Also shown in Fig. 2 is the heat capacity of a completed first layer in this range of temperatures ( $2.03 \text{ cm}^3$ ) and what we calculate the desorption heat capacity to be for the bilayer coverage. The desorption correction has been calculated from our own isotherms with procedures described by Dash.<sup>15</sup> A large heat-capacity peak is found at 7.20 K, corresponding to melting at the triple point, and a much smaller "bump" is observed at about 10 K corresponding to the liquid-vapor coexistence. Our measured  $T_t$  is lower than the estimate of Ref. 11; this is discussed below.<sup>16,17</sup> The maximum triple-point heat capacity corresponds to a specific-heat maximum of only  $C_2/N_2k = 10.4$ , and furthermore, the heat of fusion obtained by integration of  $C_2$  vs  $T$  is only 3.2 cal/mol, about  $\frac{1}{5}$  of the 3D heat of fusion. This may be indicative of only a small number of  $\text{H}_2$  molecules undergoing the transition, in which case our estimate of  $N_2$  could be grossly wrong, or of a high degree of order in the 2D liquid after melting. Small triple-point melting peaks have been observed previously, particularly in Ar-on-graphite monolayer melting,<sup>18</sup> where a large degree of liquid ordering has been speculated.

We have summarized the results in Figs. 3(a) and 3(b) as surface density versus temperature and chemical potential versus temperature graphs. Surface densities have been calculated with the assumption that the density of a monolayer of Kr at its melting substep is  $0.0704 \text{ \AA}^{-2}$ .<sup>19</sup> The chemical-potential difference  $\Delta\mu$  is the difference between the chemical potentials of the film and of the bulk solid parahydrogen at the same temperature as calculated from the vapor pressure by assuming that the vapor behaves like an ideal gas. The two-phase coexistence regions of Fig. 3(a) appear as solid lines in Fig. 3(b). To avoid overcrowding, relevant temperatures are indicated in the top portion while layer labeling is done in the bottom. The temperature axes of both portions have slightly different magnification. From the figures it is easy to suggest that for any multilayer experiment done on this substrate at temperatures below 13.8 K at least the first two layers will be solid. The melting line of the second layer ends at a low temperature at a triple line at  $7.20 \pm 0.05 \text{ K}$ . Thus there is a monolayer "fluid" film down to this temperature in a small window of densities, but this temperature is still too high for both ideal 3D Bose condensation or a 2D film superfluid transition. This fluid has a liquid-vapor coexistence region that ends at a critical point at  $T_c = 10.05 \pm 0.05 \text{ K}$ . Both  $T_t$  and  $T_c$  are close to expectations from the quantum theory of corresponding states applied to 2D sys-

tems<sup>11,20,21</sup> and substantially lower than the respective classical values for 2D systems. Above the second layer, the film grows in a layer by layer mode, at least up to six layers. These layers have critical points, determined by graphing  $T(d \ln P / dV_{\text{ads}})$  vs  $T$  from the isotherm steps; the differential is a quantity proportional to the inverse isothermal compressibility of the monolayer. All critical points are around 10.1–10.4 K, probably an overestimate of the true critical points due to heterogeneities and our linear extrapolation procedure used to find  $T_c$ . The lack of a "substep" between the third- and fourth-layer isotherms [Fig. 1(c)] or any of the higher-layer ones may indicate that these layers are already solid; thus these vertical steps in the coexistence regions represent a basically different phenomenon than on the second layer. In particular, we looked with our heat-capacity cell at a film in the  $0.24\text{-}\text{\AA}^{-2}$  density range down to 5 K and

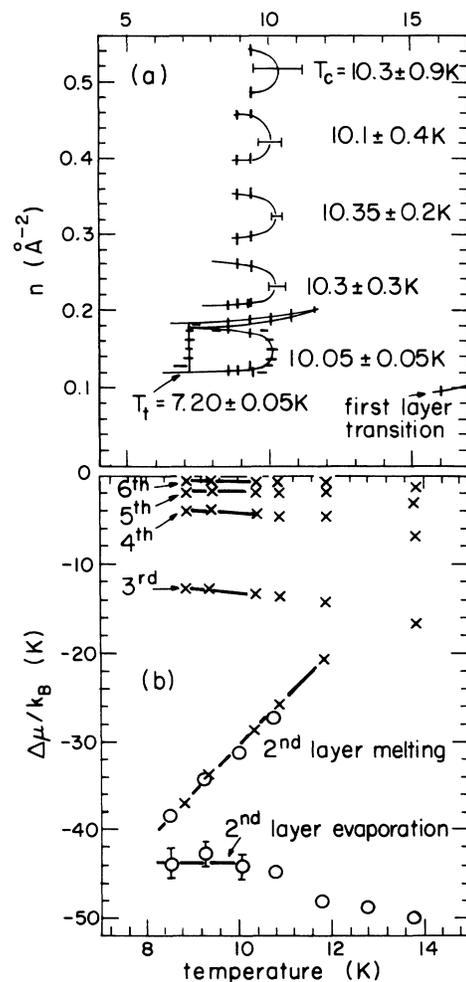


FIG. 3. Phase diagrams for  $\text{H}_2$  on  $\text{MgO}$ . (a) Surface density vs temperature. Horizontal dashes: heat capacity. Vertical dashes: isotherms (length of dash is approximate error of point). (b) Chemical-potential difference between film and solid parahydrogen vs temperature. O: cell A; X: cell B.

found no triple line. We thus believe that the third- and upper-layer steps signal the formation of solid  $H_2$  on a layer by layer mode, with layering critical points converging towards a roughening transition at bulk coexistence (technically an infinite number of layers).<sup>10</sup> If this is so, for very thick films below  $T_r \approx 10.4$  K a smooth surface should exist (or faceted crystals could be grown), while above  $T_r$  a rough surface (or rounded crystals) should be obtained. This temperature is about 75% of  $T_r(3D)$ , slightly lower than the 80% of  $T_r(3D)$  determined by Zhu and Dash on Ar and Ne monolayers adsorbed on graphite.<sup>22</sup> Since we do not know which crystallographic plane is growing on this substrate, we cannot speculate any further, but the vapor pressure of parahydrogen is relatively high at this temperature (about 3 Torr) and thus it might be possible to study faceting and roughening for a crystal grown in equilibrium with its vapor and observe the effect of quantum mechanics on the relationship between  $T_r$  and  $T_i$  for various crystal faces.<sup>23</sup>

We thank J. G. Dash, D.-M. Zhu, M. Schick, S. Lipson, and M. den Nijs for many helpful discussions. This research was supported by the National Science Foundation, Grant. No. DMR 86-11466.

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