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Neutron diffraction study of the pore surface layer of Vycor glass

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Analysis of small-angle scattering and powder diffraction data combined with macroscopic measurements have revealed the structure of a pore surface layer in Vycor glass, consisting of OH groups and chemisorbed water. Chemisorbed water exists on the pore surface in two forms: compact water clusters of ~40–60 molecules, connected to each other by hydrogen bonds, and more spaciously distributed individual molecules (or groups of several molecules). Heating to 650 °C reconstructs the pore surface: the number of OH groups is significantly decreasing due to the reaction of dehydration between Si-OH and B-OH surface groups. However, the temperature treatment does not affect the process of H_2O clusters formation, which still appear on the pore surface after the condensation. [S1063-651X(97)08002-1]

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I. INTRODUCTION

The adsorption of water on silica surfaces has been an active area of investigation for over forty years. It is well known that the adsorption of water depends on the treatment of the silica surface [1,2] and that hydroxylated silica surfaces readily adsorb water, while dehydroxylated silica surfaces (prepared by outgassing to high temperatures ~1000 °C) do not.

The effect of pore size (in the case of porous silica) on the adsorption isotherms of water has also been investigated. Kiselev [3] found a small effect of the pore diameter on the adsorption isotherms, compared to adsorption on nonporous quartz. Contrary results were found for microporous silica gels [4–6], but these results may be related to capillary condensation effects. The structural details of how water adsorbs on the surface of silica do not seem to have been investigated at the microscopic level. In this paper, we present the results of neutron scattering and differential scanning calorimetry (DSC) investigations of water adsorbed on the internal surface of porous Vycor glass. These results suggest the picture of chemisorbed layers of water associated with the OH groups on the silica surface, and also give information on the presence of hydrogen-bonded-surface ''crystalline'' clusters.

The method of treated borosilicate glass fabrication was patented more than fifty years ago [7] and Porous Vycor Glass No. 7930 (PVG-7930) [8] is widely applied for industrial and scientific purposes as special filters, semipermeable membranes, catalyst supports, thermal insulators, etc. Within the last ten years, PVG-7930 has also been used in many scientific studies as a convenient model system for the experimental study of the behavior of condensed matter in confined geometry [9–15] and of photochemical reactions. [16,17] On the other hand, it is known that the surface layer of the pores plays an important role in the water adsorption ability of PVG-7930 ''Thirsty'' glass.

PVG-7930 has been studied by methods of electron microscopy, small-angle x-ray and neutron scattering, direct energy transfer, and molecular adsorption [18–22]. According to the data obtained in these studies, Vycor could be defined as a bicontinuous structure (all pores are connected to each other) with a characteristic pore spacing 200–300 Å. The total pore volume of PVG-7930 is ~32–36% and the interfacial pore surface is 90–125 m^2/g.

The small-angle scattering pattern from dry Vycor shows departures from Porod's Law [21], and may be related to the internal surface roughness in terms of the surface fractal dimension [20] of $D=2.4$ and with the upper cutoff <20 Å, as estimated by transmission electron microscopy and molecular adsorption techniques. But the interpretation of the Vycor pore interface as surface fractals has been done within the assumption that PVG-7930 is a two-phase system containing only a chemically uniform borosilicate glass (concentration of boron ~3%) and pores. On the other hand, it has been shown in [22] that the small-angle neutron scattering experiments on Vycor, in contrast to protonated and deuterated cyclohexane, reveal local composition gradients within the glass, and this fact indicates that PVG-7930 is not a simple two-phase system. According to [8], Vycor Thirsty glass contains an adsorptive layer on the pore surface which could be activated by heating up to 180 °C. After this treatment, Vycor reaches the best water adsorption ability at room temperature, which decreases with increasing activation temperature due to destruction of adsorptive sites. It is also known that there is chemisorbed water [16,17] on the pore surface.

One can assume that the chemical composition of the PVG-7930 surface layer is different from that of the bulk

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uglass and may be considered as the third phase of this system. But it has to be pointed out that the concepts of the surface roughness and of a third surface phase do not, in principle, contradict each other if one takes into consideration the process of Vycor glass manufacture. The bicontinuous structure is obtained as a result of spinodal decomposition of the two phases: SiO_2 and $B_2O_3+Na_2O$. It is obvious that they are chemically in contact with each other and give rise to an interfacial layer during the formation process. This layer can be destroyed after leaching away the acid-soluble phase of $B_2O_3+Na_2O$, and at this stage of PVG-7930 manufacture, Si-OH and B-OH groups can be created on the pore surface and roughness also cannot be excluded.

II. SAMPLES AND INSTRUMENTS

The samples under study were prepared from PVG-7930 [cylindrical rods of 7.2 and 13 mm in diameter (lots No.742098 and No. 742096, respectively)], and produced by Corning Glass Works. The samples of 50-mm length for large-angle diffraction were cut from the thinner rod and the wafers of 1.2-mm thickness were prepared from the second one for the small-angle scattering experiments. The purification procedure, described in [17], has been used to remove possible residual products of leaching from pores: the samples were extracted in water over ten days in a soxhlet extractor and first dried at a temperature of $\sim 45\ ^\circ C$ over a period of 48 h to evaporate the bulk of water from pores. Finally, one set of samples (PVG-7930/175) was dried at $T=175\ ^\circ C$ and the other set (PVG-7930/650) at $T=650\ ^\circ C$.

The small muffle furnace FB-1315M (temperature stabilization of $\sim 2\%$) was used for further temperature treatment, and thermal analysis was done using a DSC-910 (Du Pont). The boron concentration in PVG-7930/175 and PVG-7930/650 was measured using a Varian Liberty 100 inductively coupled plasma emission spectrometer (ICP).

Neutron-diffraction studies were carried out in the High Flux Beam Reactor, at Brookhaven National Laboratory. The H4S instrument, set up as a powder diffractometer, has been used for measurements within the range of scattering vectors $0.5\ \text{Å}^{-1} \leqslant Q \leqslant 3.6\ \text{Å}^{-1}$ (where $Q=4\pi \sin\theta/\lambda, 2\theta$ is the scattering angle, and λ is the neutron wavelength). The parameters of the primary beam were wavelength 2.37 Å, and collimation in horizontal plane ~40 min of arc. The small-angle scattering machine H9B equipped with a two-dimensional position-sensitive detector was selected to cover the Q region $0.05\ \text{Å}^{-1} \leqslant Q \leqslant 0.2\ \text{Å}^{-1}$. For the latter runs, the primary-beam wavelength and the sample-to-detector distance were 7.5 Å and 1.75 m, respectively.

III. MACROSCOPIC MEASUREMENTS

Weight and dimension measurements, DSC, and ICP techniques were used to characterize the samples under study after temperature treatment. Figure 1 shows that the weight of PVG-7930, upon heating for the first time after cleaning, decreases with increasing temperature over the range $100\ ^\circ C \leqslant T \leqslant 900\ ^\circ C$ (curve D). Because this process stops at the consolidation point ($T=1150\ ^\circ C$), the weight of consolidated Vycor was taken as the reference weight W_0, and the relative weight at the chosen temperature has been defined as $[W(T)-W_0]/W_0$ (Fig. 1). The samples were held for 24 h at each temperature to reach saturation of the value $W(T)$. According to the diagram, the weight of PVG-7930 at $T=100\ ^\circ C$ exceeds the value of W_0 by $\sim 4.8\%$, and the $W(T)$ function contains two steps: at $T=175$–$200\ ^\circ C$ and at $T=300$–$350\ ^\circ C$. Since the first step $T=175$–$200\ ^\circ C$ corresponds to the end of water desorption process [21], one can assume that the decrease of the weight of PVG-7930 for the temperature range $T>200\ ^\circ C$ indicates the removal of material chemisorbed on the pore surface or chemically connected with it. This assumption can be supported by the fact that the same measurements, performed for the samples preheated at 650 °C and 700 °C and then hydrated again at room temperature (curves E, F), gave a different result from the first measurement (curve D) made right after the extraction. This feature shows that after drying at 650–700 °C the amount of material, removed from PVG-7930 within the temperature range 200–700 °C, cannot be recreated by the hydration of the pore volume, which indicates that the heat treatment has significantly modified the pore surface. The weight and geometrical dimensions of the reference sample, hydrated before and after heating up to 650 °C, make it possible to determine that the sample volume and the total internal volume of pores decrease by $\sim 3\%$ during the temperature treatment, which excludes any possible geometrical explanation (pore closing) for the observed effects (Fig. 1); the relative weight of the sample at $T=200\ ^\circ C$ decreases several times after the treatment (curves E, F).

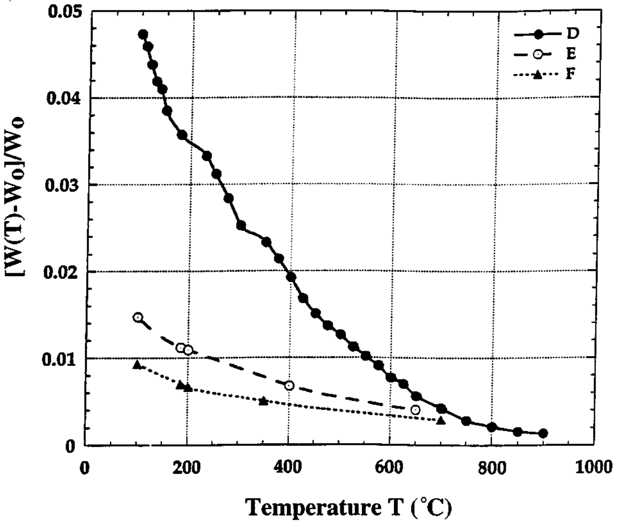

FIG. 1. Temperature dependence of PVG-7930 weight: D—the sample after extraction; E—the sample hydrated after the heating to 650 °C; F—the sample hydrated after heating to 700 °C.

The total porosity, determined by the geometrical measurements of the porous and consolidated samples, gave the value ~36%; the density of consolidated Vycor was found to be 2.15 g/cm^3.

The DSC data (Fig. 2), obtained for the sample dried at 45 °C after the extraction (dashed line), reveal the exothermal peak at $T=320\ ^\circ C$ and the endothermal peaks at 95 °C and 180 °C, corresponding to the physisorbed and chemisorbed water desorption process, respectively. But one

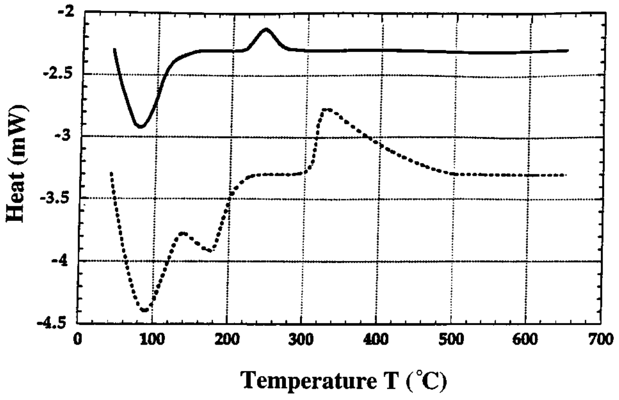

FIG. 2. Thermal analysis: dashed line—the sample after extraction and drying at 45 °C; solid line—the sample hydrated and dried at 45 °C after heating to 650 °C.

endothermal peak at 95 °C remains, and the small exothermal peak occurs at 250 °C (solid line) in the case of the sample measured after the temperature treatment at 650 °C, hydration and drying at 45 °C. One should note the correlation between the steps in curve D (Fig. 1) and the thermal peaks in the DSC data. The most important result of the thermal analysis is the presence of the exothermal peak, which usually indicates that new chemical bonds are being formed. It has also been observed that the samples of PVG-7930 change color when heating and become gray within the temperature region 350–450 °C and after that, transparent again as the temperature is raised to 650 °C.

A saturated solution of Vycor glass in HF (40% aqueous solution), diluted 100 times by water, was prepared for ICP spectroscopy to measure the concentration of boron in the samples PVG-7939/175 and PVG-7930/650. It has been found that the boron content remains the same within the accuracy ±3% of the measurement: 56 mg/1 for the sample heated to 175 °C and 60 mg/1 for PVG-7930 treated at 650 °C. These data prove that the chemical composition of the bulk of Vycor glass does not change when heating.

IV. SMALL-ANGLE NEUTRON SCATTERING

The contrast variation method (e.g., in [23]) has been used to detect the supermolecular compositional inhomogeneities [22] in PVG-7930/175 and PVG-7930/650. This method was originally designed to study the internal structure of biological macromolecules in solution [24].

It is well known that the small-angle scattering from PVG-7930 has a pronounced peak (the ''Vycor peak'') at $Q\sim 0.25$ Å^{-1} [19–22], arising from the quasiperiodicity of the bicontinuous pore structure resulting from the spinodal decomposition during the formation process of glass. If dry Vycor is a pure single-phase material of a uniform scattering length density ρ_v, filling the pore space with liquid of a certain scattering length density ρ_1 should simply change the contrast and the intensity but not the Q dependence of the small-angle scattering function $I(Q)$. At the contrast matching point, $I(Q)$ should simply be reduced to uniform (background) scattering. If, on the other hand, there is a layer on the pore surface with a different contrast than the Vycor, complete contrast matching will never be achievable. In the case where the contrasting liquid matches in bulk Vycor (interior) phase, $I(Q)$ will be proportional to the scattering from the surface layer alone. Lin *et al.* [25] have studied the scattering from Vycor in such a situation using adsorbed hydrocarbon chains of various lengths to produce the surface layer and have shown that such ''skin'' scattering corresponds to a peak shifted from the Vycor peak to $Q\sim 0.037$ Å^{-1}, and the position of the skin peak is slightly dependent on the skin thickness. It is also obvious that if the adsorbed layer is one with lower scattering length density ρ_{sk} than that of the bulk Vycor, as would be the case with a strong hydrogen-containing surface layer (since the scattering length of protons is negative), then we should observe basically the scattering from the bulk Vycor when the liquid scattering length density $\rho_1<\rho_{sk}<\rho_v$; when $\rho_1=\rho_v>\rho_{sk}$ (the contrast matching limit), we should see the shifted peak due to the skin but not the Vycor peak. If $\rho_1>\rho_v>\rho_{sk}$, we should see a combination of the Vycor peak and the (shifted) skin peak.

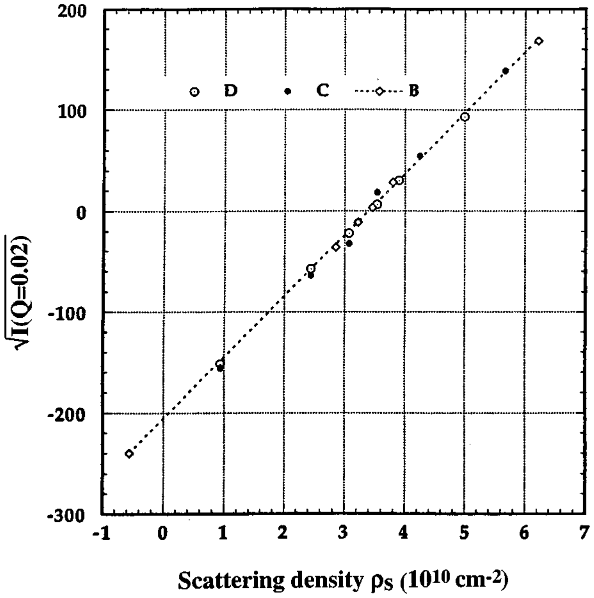

FIG. 3. Contrast variation diagram of Vycor: B—PVG-7930/175 in H/D-toluene, C—PVG-7930/650 in H/D-toluene, D—PVG-7930/650 in H_2O/D_2O.

In the particular case of PVG-7930, which contains the exchangeable hydrogen atom of the OH groups on the pore surface, deuterated and protonated toluene were chosen as contrasting liquids because the molecules of $C_6D_5CD_3$ have no exchangeable D atoms. So D-toluene cannot change the local chemical composition of the Vycor pore surface as happens when one uses D_2O. A H_2O/D_2O mixture has been used only as a reference, contrasting liquid for the samples PVG-7930/650. The range of variable scattering densities for H/D-toluene is $(0.94<\rho_t<5.67)\times 10^{10}$ cm^{-2}, and for H_2O/D_2O is $(-0.56<\rho_w<6.34)\times 10^{10}$ cm^{-2}, so both of the liquids are useful for varying the contrast against Vycor glass, the calculated scattering density of which is $\rho_v=3.4\times 10^{10}$ cm^{-2} (ρ_v of Vycor has been calculated for pure SiO_2 with the density 2.15 g/cm^3). The matching point, calculated for H/D-toluene and for H_2O/D_2O mixture, are 52% D-toluene and 52% D_2O, respectively.

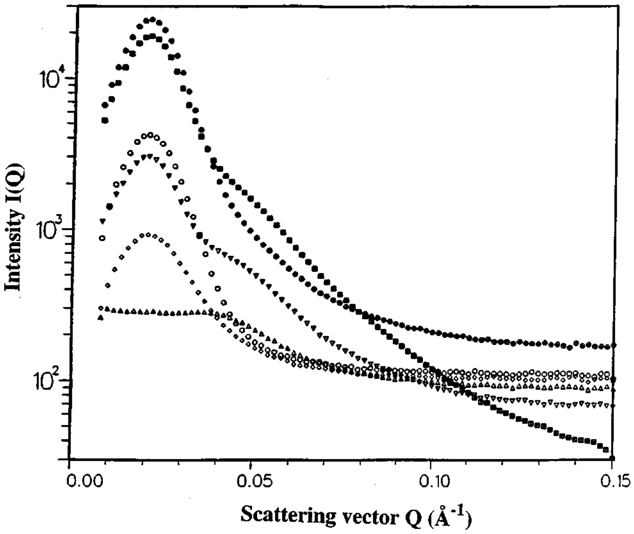

FIG. 4. Small-angle neutron diffractograms of PVG-7930/175 in H/D-toluene mixture ○—30% D-toluene, ◇—45% D-toluene, △—55% D-toluene, ▽—70% D-toluene, □—D-toluene, ⊗—H-toluene.

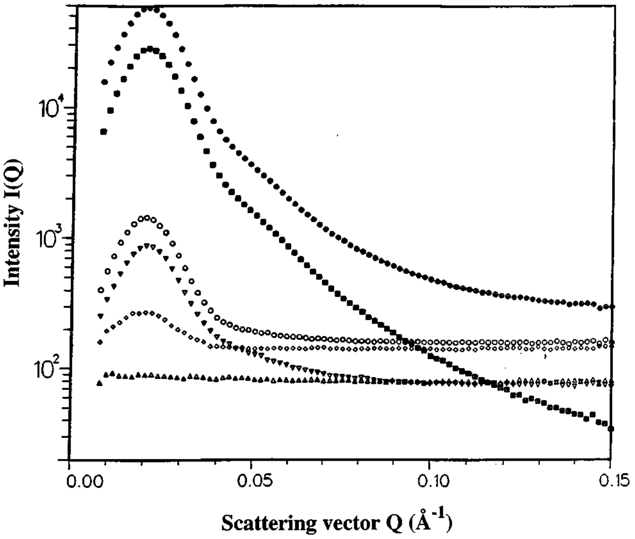

FIG. 6. Small-angle diffractograms of PVG-7930/650 in H_2O/D_2O mixture: ○—51% D_2O, ◇—55% D_2O, △—58% D_2O, ▽—65% D_2O, □—D_2O, ⊗—H_2O.

Figure 3 shows the square root of the Vycor peak intensity as a function of the scattering length density ρ_e of H_2O/D_2O and H/D-toluene mixtures for both the PVG-7930/175 and PVG-7930/650 samples showing the expected linear variation. The contrast matching point is at $\rho_v = 3.43 \times 10^{10}$ cm^{-2}, in good agreement with the calculated value of 3.4×10^{10} cm^{-2}.

The small-angle scattering curves of PVG-7930/175 and PVG-7930/650 in toluene, recorded at six different values of ρ_t for each of the samples, are presented in Figs. 4 and 5, respectively. Comparison of the data shows that, in the case of PVG-7930/175 (Fig. 4), the diffractograms, obtained for the samples with the concentration of D-toluene higher than 52% D-toluene (matching point), a second broad diffraction peak appeared at $Q = 0.045$ Å^{-1}. But this peak is completely absent when the scattering density of the contrasting liquid is smaller than ρ_v. Additional measurements have also shown that it is impossible to match PVG-7930/175 in H/D-toluene and obtain a residual scattering smaller than that which was recorded for this sample in 55% D-toluene (Fig. 4). Thus, we conclude that there is a surface layer of lower scattering length density than the bulk Vycor on the pore surface. However, temperature treatment at $T = 650$ °C significantly changes the profiles of the scattering curves for the sample PVG-7930/650, making them much more identical. This effect is displayed (Fig. 5) most strongly in the vicinity of the matching point (55% D-toluene): the intensity of the coherent scattering at $Q = 0.02$ Å^{-1} (Vycor peak) is ~5 times smaller than that for PVG-7930/175, and there is no shoulder at $Q = 0.045$ Å^{-1}.

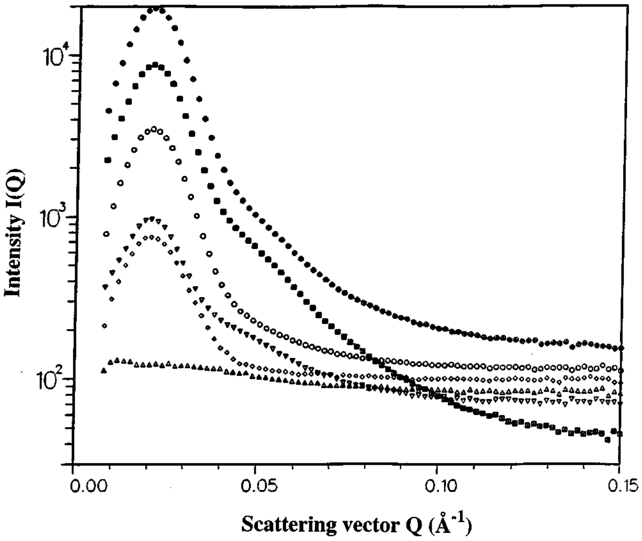

FIG. 5. Small-angle neutron diffractograms of PVG-7930/650 in H/D-toluene mixture: ○—30% D-toluene, ◇—45% D-toluene, △—55% D-toluene, ▽—64% D-toluene, □—86% D-toluene, ⊗—H-toluene.

In both samples, there is a broad shoulder in the scattering at $Q = 0.05$ Å^{-1} when $\rho_t \gg \rho_v$. Thus, there is still some surface coverage by a layer of $\rho_{sk} < \rho_v$, which now becomes visible by the greater contrast between ρ_{sk} and ρ_t. The coverage must be much less for the PVG-7930/650 sample. since this shoulder is not visible at the contrast matching point in the latter sample.

We propose that the surface layer consists of two types of hydrogen adsorbed on the silica surface: chemisorbed water associated with Si-OH and B-OH groups, which is not present in the sample heated to 650 °C, and a more weakly bound layer, whose nature we will discuss. Contrast matching with the H_2O/D_2O mixtures in the pore space should make the skin relatively invisible, owing to the exchange of the protons on the surface layer and the deuterons in the mixture. Figure 6 shows that this is indeed the case.

It is also informative to analyze the scattering curves from the dry PVG-7930/175 and PVG-7930/650 samples (Fig. 7). The Porod invariant [26],

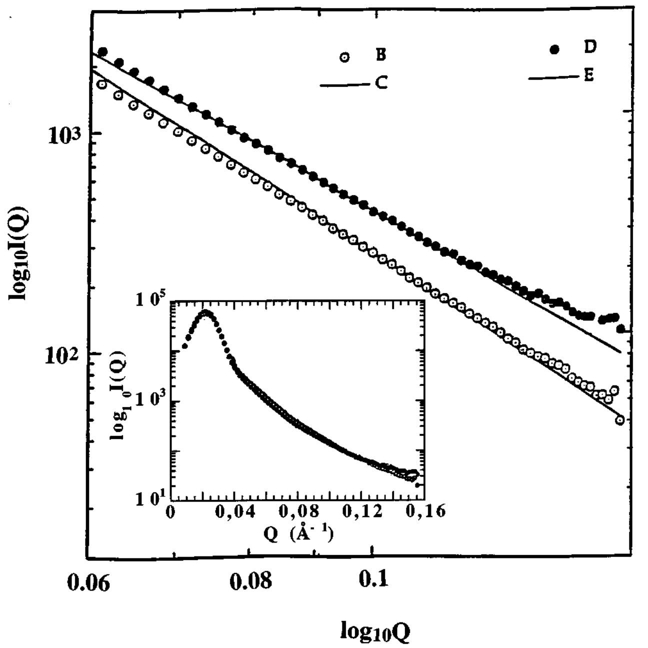

FIG. 7. Final slope of the small-angle neutron diffractograms: D—PVG-7930/175, B—PVG-7930/650. Calculated $Q^{-3.5}$ and Q^{-4} slopes are given by solid lines E and C, correspondingly.

$$P=\int Q^2 I(Q)dQ,$$

calculated for these two curves, differs by only 3%, indicating that the total scattered intensity did not change significantly after heating to 650 °C. Because the Porod invariant is proportional to $\varphi(1-\varphi)$ (φ is porosity), and because the Vycor peak position of the two curves is exactly the same, one can draw the conclusion that the scattering volumes of the samples PVG-7930/175 and PVG-7930/650 are the same, $\pm 3\%$. The same result has been also obtained independently by the microscopic measurements.

The asymptotic form of the scattering curve (the range $0.06<Q<0.15$ Å^{-1}) changes (see Fig. 7) after the temperature treatment at 650 °C from $Q^{-3.5}$ to Q^{-4}, indicating a transition from a rough to a smooth internal surface, and this fact could also be considered as independent evidence of a significant change in the pore surface structure and composition.

V. WIDE-ANGLE SCATTERING

The neutron diffraction pattern in the range $0.5<Q<3.6$ Å^{-1}, recorded for D_2O in PVG-7930/175 (curve C) and PVG-7930/650 (curve D) are represented in Fig. 8. The dry PVG-7930/650 sample was used as a reference sample in both cases to subtract the scattering from the bulk of Vycor glass. The diffraction from pure bulk D_2O (curve B) is also included in this set of data for comparison. The qualitative analysis of the data shows that an additional diffraction peak at $Q=2.65$ Å^{-1} appeared in the diffraction patterns from D_2O in the samples of Vycor (in comparison with the pattern from D_2O in bulk). Also, it should be noted that the liquid peak position is slightly shifted to the smaller Q and that the diffractogram of PVG-7930/650 contains a broad shoulder within the range $0.5<Q<1.3<$Å^{-1}.

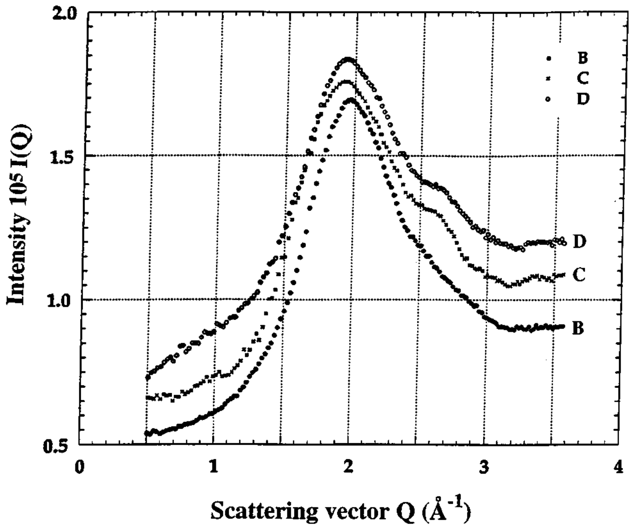

FIG. 8. Neutron diffractograms of D_2O : B—bulk of D_2O, C-D_2O in PVG-7930/650, full hydration, D—D_2O in PVG-7930/175, full hydration.

Following these measurements, another set of samples was measured, prepared in the following way: sample No. 1: PVG-7930/650 with a calibrated amount of H_2O condensed in equal to 3.5% of the weight of the consolidated sample; sample No. 2: PVG-7930, taken from the extractor, was soaked in H_2O and dried at 175 °C; Sample No. 3: the same with sample 2, but soaked in D_2O.

Thus, the prepared samples had approximately the same amount (weight) of water in the pore surface layer. the idea of the experiment was to measure the difference in the structure of the surface layer before and after the temperature treatment at 650 °C.

The result of these measurements (with the dry Vycor scattering subtracted) is represented in Fig. 9. The differences in the background levels are due to the extra incoher-

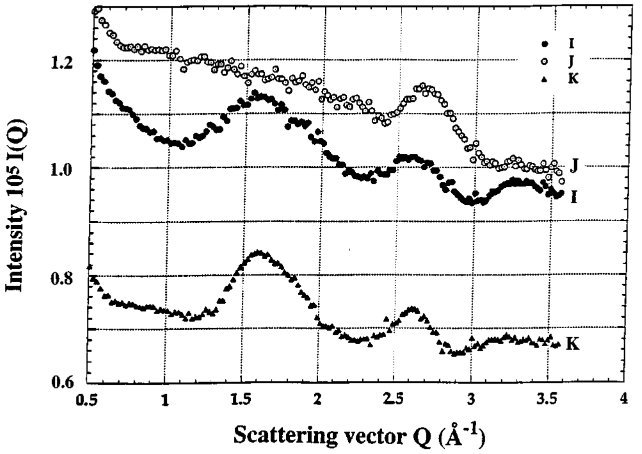

FIG. 9. Neutron diffractograms of pore surface layer : J—H_2O (3.5% of dry Vycor weight), adsorbed on PVG-7930/650, I—PVG-7930/175 dried at 175 °C after hydration by H_2O, K—PVG-7930/175 dried at 175 °C after hydration by D_2O.

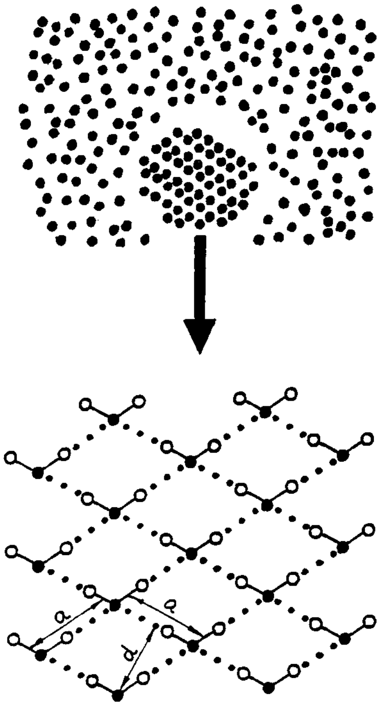

FIG. 10. Chemisorbed water molecules on Vycor pore surface and the structure of H_2O cluster: open circles—hydrogen, closed circles—oxygen.

ent scattering from H_2O relative to D_2O. It is reasonable to start the analysis of the diffractogram with the peak at $Q = 2.65 \pm 0.03$ Å^{-1}, which is present in all cases including the scattering curves from the fully hydrated samples of PVG-7930/175 and PVG-7930/650 (Fig. 8). The D spacing corresponding to this peak (which is equal to $2\pi/Q$) is 2.57 ± 0.04 Å^{-1} and the half width $\Delta Q/Q$ is 0.14 ± 0.01 Å^{-1}, which corresponds to crystallite dimensions of ∼6–8 crystallographic planes. It is reasonable to emphasize that neither the position nor the width of this diffraction peak depends significantly on the temperature treatment at 650 °C and this fact distinguishes it in the diffraction curves of Fig. 9.

We attribute this peak to strongly chemisorbed and ordered arrays of water molecule clusters on the silica surface. The second (much broader) peak at $Q = 1.6$ Å^{-1}, which is not present in the PVG-7930/650 sample, we attribute to short-range order between much more dilute OH groups on the remainder of the surface.

VI. DISCUSSION AND CONCLUSIONS

From the above diffraction and macroscopic measurements, we propose that the cleaned Vycor surface contains three types of adsorbed water on the surface: (a) a physisorbed layer which is desorbed by 90 °C, (b) a chemisorbed layer associated with individual OH groups on the surface, which comes off on heating above 190 °C, and (c) a more strongly chemisorbed layer consisting of clusters of protons bonded to each other via the oxygen atoms on the silica and forming an ordered array of water molecules (see Fig. 10). Assuming hexagonally ordered lattice of these molecules, and assuming that the lattice constant or distance between two neighboring oxygen atoms is equal to the length of a hydrogen bond, 2.76 ± 0.08 Å, the value of the largest d in the corresponding structure is 2.39 ± 0.07 Å, which corresponds closely to the peak observed $Q = 2.65$ Å^{-1}. The linear dimensions of such a cluster are ∼17/22 Å and the thickness is one molecular layer. (The characteristic asymmetric pattern of the diffraction from a two-dimensional structure is masked by the broadening of the peak due to finite size effects). Such hydrogen-bonded protons (at least in schematic form), as well as free OH groups, have been proposed by several researchers [1,2]. Evidence of these two kinds of groups also comes from infrared measurements, which reveal [2] narrow absorption lines ascribed to the free OH groups and shifted and broader lines ascribed to the hydrogen-bonded atoms. However, no structural details regarding the latter have been previously obtained. We note that the broadening of the infrared lines for the hydrogen-bonded atoms is consistent with our identification of the latter as dense, locally ordered clusters. It is also known that the free energy of adsorption of water and other molecules on the ''free'' OH groups is lower than that of water in the hydrogen-bonded sites. This is consistent with the desorption of the part of the chemisorbed water layer associated with these sites by 190 °C while the hydrogen-bonded water clusters are present even in the samples heated to 650 °C. The broad peak in Fig. 9, at $Q = 1.6$ Å^{-1} in the sample heated to 650 °C, is due to the short-range correlations between these free OH groups distributed on the surface (and their associated chemisorbed water molecules). However, on heating to 650 °C, the free OH groups are selectively removed (dehydration reaction; this reaction may be associated with the exothermic peak in the DSC at ∼300 °C) so that the peak at $Q = 1.6$ Å^{-1} is no longer present in the diffraction pattern, even after the sample is cooled back to room temperature and reexposed to water vapor. (Previous studies indicate that the rehydroxylation of the surface on exposure to water happens very slowly [3].) This is also consistent with the lack of ability to adsorb water in samples heated 650 °C, since the strongly hydrogen-bonded atoms (which are still on the surface) must be ineffective in adsorbing further water, unlike the free OH groups.

The present neutron scattering results thus confirm and shed more detailed light on microscopic details of the process of water adsorption on silica surfaces.

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