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Solid Hydrogen in Amorphous Silicon: Phase Transition

Y. J. Chabal and C. K. N. Patel
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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We report the first measurement of the gas-to-solid phase transition of hydrogen occluded in amorphous silicon. The transition is very broad and occurs around 30 K confirming the nonuniform and highly compressed nature of hydrogen. The infrared-absorption spectra of the solid phase show that the H_2 structure is strained with considerable interaction between the H_2 and the Si walls of the microvoids.

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A number of recent studies have confirmed[1-5] the assumed incorporation of H_2 in hydrogenated amorphous silicon[6] up to a volumetric ratio of about 4%. These studies include monitoring of o-H_2 to p-H_2 conversion at $T \leq 5$ K and the observation of H_2 vibrational spectra around $T \geq 80$ K. The latter studies have shown that at room temperature H_2 is incorporated into microvoids in *a*-Si at densities as high as 800 amagats corresponding to a pressure of 2 kbar. In this Letter we report the gas-to-solid phase transition of H_2 around $T = 30$ K which is accompanied by a volume change. This observation helps to shed light on the earlier observation of the very highly strained nature of hydrogenated *a*-Si films[7] and lends additional confirmation to the interpretation of optical spectra which required the H_2 to be incorporated at high densities in *a*-Si. At atmospheric pressure the gas-to-liquid phase transition would occur at 19 K, and solidification would take place at 14 K for unconfined geometries. The observed transition around 30 K further requires that the phase change involves a direct "gas"-to-"solid" transition of the trapped H_2.[8] Additionally, we find that within the microvoids, under solidification, there is a considerable amount of interaction between the H_2 molecules and the Si walls of the cavity as seen by the strong Si-phonon sidebands superimposed upon the relatively weak zero-phonon[9] H_2 transitions. The width of the "gas"-to-"solid" phase transition and the strength and time dependence of the Si-phonon sidebands lead us to conclude that the microvoids in *a*-Si are small, containing less than 100 H_2 molecules. The time dependence of the zero-phonon transition $S_1(0)$ indicates that the solid H_2 at ≈ 10 K has a density corresponding to a volumetric contraction[10] of $\approx 25\%$.

The experimental apparatus used for carrying out the infrared spectroscopy has been described earlier[5] and will not be detailed here. The heavily hydrogenated *a*-Si samples were prepared by rf decomposition of silane[11] on both sides of a crystalline Si plate with beveled edges shown in the inset in Fig. 1. The samples were cooled down to a temperature of 9 K by mounting the *c*-Si prism on the cold finger of a closed-cycle refrigerator which maintained the sample temperature (monitored with a Si diode) at 9 K for periods as long as 200 h.[12] A good thermal contact between holder and sample was achieved by acid etching and subsequently wetting with molten Ga the mating faces of the Si sample and the Cu holder before tightly clamping them together. Infrared spectra covering the region from 1500 to 6000 cm^{-1} were obtained by means of a Nicolet Fourier-transform spectrometer. Each one of the spectra had an apodized resolution of 8 cm^{-1} and was obtained in a time of 20 min by collecting and averaging 4096 scans.

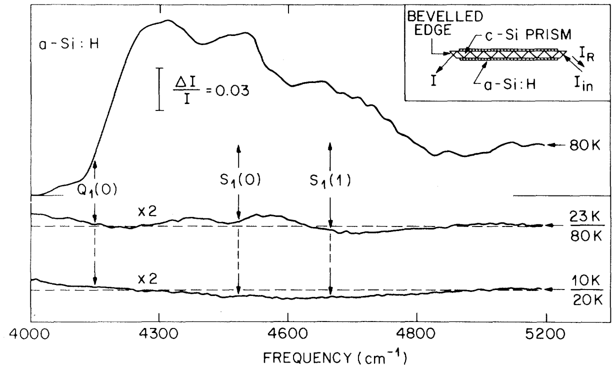

FIG. 1. Inset: Cross section of the part of the silicon prism coated with *a*-Si:H film. The ir radiation is totally reflected 100 times at the silicon-vacuum interface (incidence angle ~ 37°) before exiting through the beveled edge. Half of the prism remains uncoated so that a reference spectrum, $I_0(\nu)$, can be measured by translating the sample with respect to the ir beam. Main figure: (top) Absolute absorption, $I(\nu) - I_0(\nu)$, associated with normal H_2 gas occluded in *a*-Si:H (Ref. 5). (bottom) Difference spectra, $I_{T_1}(\nu) - I_{T_2}(\nu)$, for $T_1/T_2 = (23\text{ K})/(80\text{ K})$ and (10 K)/(20 K), all taken within $\frac{1}{2}$ h of initial cooling.

There can be no infrared absorption on the vibrational-rotational transitions of H_2 in the electric dipole approximation because H_2 is a homonuclear diatomic molecule. Electric quadrupole transitions are allowed and show up as weak, sharp, absorption features. In gaseous H_2 at high densities, collisions induce electric dipole moments in the colliding pair of H_2 molecules, which makes single and double transitions possible.[13] In solid phase, the role of collisions is provided by the fact that because of its very light mass the zero-point motion of hydrogen atoms in a H_2 molecule is a significant fraction of the intermolecular spacing in solid hydrogen. The overlap and quadrupolar induction have been indentified[9] as the important mechanism for the induced dipole moment.

Figure 1 shows the temperature dependence of infrared-absorption spectra of the multiple-reflection–geometry sample starting from 80 K. The spectra between 80 and 300 K have been well studied[5] and hence we shall focus our attention only on the spectra at lower temperatures. Unlike in the absorption spectrum of unconstrained H_2 which develops sharp zero-phonon molecular lines in going from gas phase to solid phase,[14] we do not observe such a drastic change in the infrared-absorption spectra of H_2 trapped in *a*-Si on cooling. This observation is indicative of the highly strained nature of H_2 in the microvoids and consistent with a distribution of densities among the microvoids embedded in *a*-Si:H. Further, in our spectra the absence of sharp long-range quadrupolar $Q_1(0)$, etc., lines indicates that there is little long-range orientational ordering in this low-temperature phase.

The indication that a phase change actually takes place below 30 K is not given by a clear sharpening of the spectral lines but instead by the observation of a small volume change within the microvoids ($\Delta V/V \sim 2\%$). Such an observation requires monitoring the transmitted intensity I (Fig. 1, inset) as a function of temperature for small temperature changes (~ 1 K) over a wide range of frequencies (1500–6000 cm^{-1}). While no changes were observed in the difference spectra in the range 80 to 30 K (Fig. 2, curve *a*), except for small spectral changes in the 4200–5000-cm^{-1} region, clear oscillatory features were observed over the *whole* frequency range in the difference spectra taken in the 22- to 29-K region (Fig. 2, curve *b*) with maximum amplitude of $\Delta I/I \sim 10^{-2}$ and a period of 500 cm^{-1}. Below 22 K such an oscillation is not observed (Fig. 2, curve *c*). The appearance of weak oscillations in the difference spectra can only be explained by a relative change in the *a*-Si film thickness[15] of 2×10^{-4}. Since a noticeable effect is observed over a temperature change of 2 K in a region where both *c*-Si and *a*-Si show negligible thermal contraction, the volume change is assigned to a phase change of the occluded solid H_2 in the premelting region[16] resulting in a 2% microvoid volume change. The small volume change indicates that there is little difference between the high-temperature "gas" phase and the low-temperature "solid" phase. The breadth of the observed transition, ~ 5 K, suggests that there is a distribution both of densities within the microvoids and of sizes

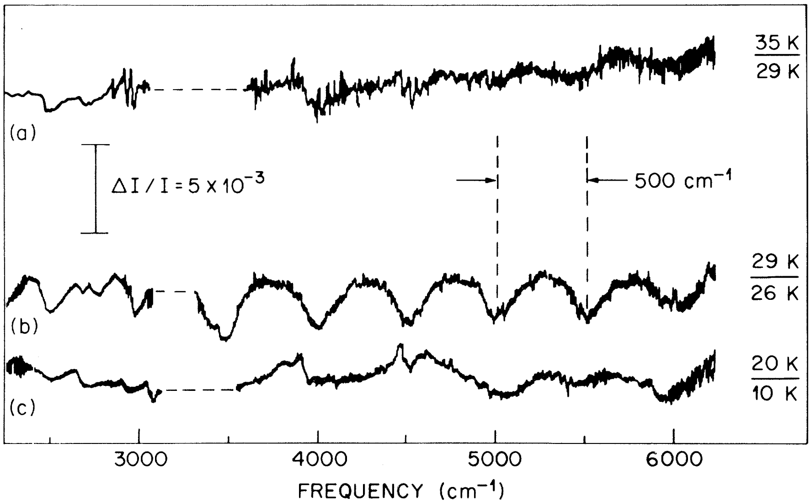

FIG. 2. Representative difference spectra, $I_{T_1}(\nu) - I_{T_2}(\nu)$, for $T_1/T_2 = (35\text{ K})/(29\text{ K})$, $(29\text{ K})/(26\text{ K})$, and $(20\text{ K})/(10\text{ K})$ taken 120 h after initial cooling. The dashed lines represent an uncertain range of data as a result of water adsorption from one run to the next.

of microvoids.

A further confirmation that the infrared absorption in the 4000–5000-cm^{-1} region arises from solid hydrogen is shown in Fig. 3 where double transitions and associated phonon sidebands are seen to predominate over the single transitions —an observation that is consistent with the differences seen between the fundamental absorption spectrum of unconstrained H_2 gas and that of unconstrained solid hydrogen.[17] The observation of double transitions, e.g., $S_1(0)+S_0(0)$, provides a definitive proof that the H_2 embedded in *a*-Si is in microvoids which contain more than one H_2 molecule, as suggested by Graebner *et al.*[4]

Figure 3 summarizes the changes in the infrared-absorption spectra as a function of time, which show distinct features developing as the sample is maintained at the low temperatures. These features, labeled $Q_R(0)$, $S_1(0)$, $S_R(0)$, and $S_R(0)+S_0(0)$, can be identified with the conversion of o-H_2 to p-H_2. The ortho/para ratio at room temperature is 3:1 as dictated by statistical weights. As the sample remains at low temperatures, the features arising from the fundamental absorption due to o-H_2, e.g., $S_1(1)$, $Q_1(1)$, etc., weaken in intensity with a corresponding increase[18] in the absorption intensity arising from p-H_2, e.g., $S_1(0)$, $Q_R(0)$, etc. The phonon sidebands, $Q_R(0)$ and $S_R(0)$, reflect a higher phonon frequency (100 cm^{-1} instead of 60 cm^{-1}) than that of zero-pressure solid hydrogen,[14] which requires that the "solid" H_2 in the microvoids have a density equivalent to at least 1-kbar pressure.[19] The frequency of the zero-phonon line, $S_1(0)$, is 4475 cm^{-1} (10 cm^{-1} lower than that of zero-pressure solid hydrogen[14]) and can be accounted for by the increase of intermolecular forces in the compressed solid.[20] Finally, the ortho-para bimolecular conversion rate measured from the intensity variations of $Q_R(0)$, $S_1(0)$, and $S_R(0)$ is $(7\pm3)\times10^{-2}\ \text{h}^{-1}$ (much faster than that for unconstrained solid), and can be attributed to solid hydrogen at a density equivalent to a pressure between 1 and 4 kbar.[21]

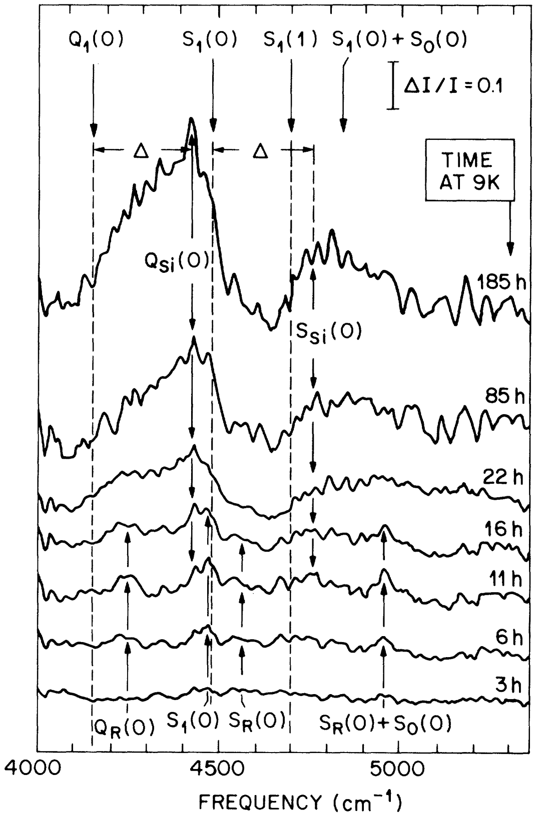

FIG. 3. Time dependence of the transmission spectrum, $I(\nu)$, for a sample held at 9 K. The time origin is taken at $\frac{1}{2}$ h after $T=9$ K is reached. Note that the signal-to-noise ratio degrades with time because of the system instabilities which develop over a period of a week and appear as spurious, sharp oscillatory features. The dashed lines labeled $Q_1(0)$, $S_1(0)$, $S_1(1)$, and $S_1(0)+S_0(0)$ mark the positions of the zero-phonon lines in unconstrained solid H_2.

A second question that is now resolved by the spectra shown in Fig. 3 is the nature of solid H_2 in microvoids. In particular, the earlier data[3,4] on the heat released during the ortho-to-para conversion of H_2 in *a*-Si:H provided no information regarding what happens at the Si walls of the microvoids which contain the solid H_2; e.g., is the solid H_2 free to rattle around freely as a ball inside a hollow cavity or are there surface adsorption processes which coat the inside wall of the microvoids with H_2 and the solid H_2 is then attached everywhere to the Si wall? Figure 3 shows relatively sharp features, e.g., $Q_{\text{Si}}(0)$ and $S_{\text{Si}}(0)$, developing and growing slowly at ≈ 4030 and $\approx 4765\ \text{cm}^{-1}$. These features cannot be associated with pure H_2 vibrational-rotational frequencies. On the other hand, the identification of these features as arising from the combined excitation of H_2 zero-phonon molecular transitions and a single-phonon excitation of the Si-Si vibration[22] at $\Delta \approx 280\ \text{cm}^{-1}$ appears reasonable. In addition, the measured bimolecular conversion rate is $(1.75\pm0.1)\times10^{-2}\ \text{h}^{-1}$, much slower than what would be expected[21] for pure solid H_2 at similar pressures but infinitely removed from the Si walls of the microvoids. A slower rate is expected for "surface" molecules because of the decrease in the number of H_2 nearest neighbors and a reduction of the phonon density of states. Therefore, we assign the two above-mentioned features to a Si-phonon sideband of the $Q_1(0)$ and $S_1(0)$ H_2 zero-phonon lines, respectively, associated with H_2 molecules in contact with the Si walls. Thus, our data show that the number of "surface" molecules is comparable to that of "volume" molecules,[23] indicating that large bubbles with more than 10^2 H_2 molecules cannot account for more than a few percent of the occluded hydrogen. Further data on the uniformity and shape of the microvoids are needed to draw a more detailed picture of the voids. However, if the hydrogen is confined in very small voids as suggested from our data, then a melting temperature lower than that for the free molecular solid is expected.[24] Since the gas-solid transition for unconstrained H_2 at 1 kbar occurs at ~ 34 K, our observation of a lower transition temperature (25–30 K) is consistent with the highly confined geometry of H_2 in *a*-Si:H. Although no qualitative differences were observed in the absorption spectra of different samples above 80 K,[5] there may be variations of the low-temperature properties from sample to sample. We note, however, that the conversion rate measured by Graebner *et al.*[4] on samples prepared differently (0.024 h^{-1}) falls within our two measured rates. Further, our data show that for the highly constrained "solid" H_2 in the microvoids in *a*-Si:H the vibrational and rotational quantum numbers remain good quantum numbers just as in unconstrained solid hydrogen.[9] Finally, we note that H_2 bubbles have also been found in Cu,[25] and overpressurized bubbles of rare gases have been produced in Al.[26]

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[1] W. E. Carlos and P. C. Taylor, Phys. Rev. B **25**, 1435 (1982).

[2] D. J. Leopold, J. B. Joyce, P. A. Fedders, and R. E. Norberg, Phys. Rev. B **26**, 6053 (1982).

[3] H. v. Löhneysen, H. J. Schink, and W. Beyer, Phys. Rev. Lett. **52**, 549 (1984).

[4] J. E. Graebner, B. Golding, L. C. Allen, D. K. Biegelsen, and M. Stutzmann, Phys. Rev. Lett. **52**, 553 (1984).

[5] Y. J. Chabal and C. K. N. Patel, Phys. Rev. Lett. **53**, 210 (1984).

[6] M. S. Conradi and R. E. Norberg, Phys. Rev. B **24**, 2285 (1981).

[7] J. P. Harbison, A. J. Williams, and D. V. Lang, J. Appl. Phys. **55**, 946 (1984).

[8] R. D. McCarty, in *Hydrogen: Its Technology and Implications: Hydrogen Properties,* edited by K. E. Cox and K. D. Williamson (CRC Press, Boca Raton, 1975), Vol. 3, p. 59.

[9] J. van Kranendonk, *Solid Hydrogen* (Plenum, New

[10] W. England, R. Etters, R. Raich, and R. Danilowicz, Phys. Rev. Lett. **32**, 758 (1974), and references cited herein.

[11] Growth conditions: 30% SiH_4, 70% Ar, at a pressure of 0.36 Torr, a power of 5 W, a substrate temperature of 523 K, and a rate of 1 μm per hour.

[12] The low-temperature data presented here were obtained on one sample only. Data were taken at and above 80 K on several different samples and did not show any qualitative difference.

[13] See, for example, A. R. W. McKellar and H. L. Welsh, Proc. Roy. Soc. London, Ser. A **322**, 421 (1971).

[14] H. P. Gush, W. F. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. **38**, 176 (1960).

[15] Y. J. Chabal and C. K. N. Patel, to be published.

[16] I. F. Silvera, A. Driessen, and J. A. de Waal, Phys. Lett. **68A**, 207 (1978).

[17] A. Watanabe and H. L. Welsh, Can J. Phys. **45**, 2859 (1967).

[18] W. H. Hare, E. J. Allen, and H. L. Welsh, Phys. Rev. **99**, 1887 (1955).

[19] R. Jochemsen, V. V. Goldman, and I. F. Silvera, J. Low Temp. Phys. **36**, 243 (1979).

[20] J. van Kranendonk and G. Karl, Rev. Mod. Phys. **40**, 531 (1968).

[21] P. Pedroni, F. Weinhaus, and H. Meyer, Solid State Commun. **14**, 279 (1974).

[22] R. R. Lucchese and J. C. Tully, Surf. Sci. **137**, 570 (1983).

[23] Because the relative magnitude of the dipole moment induced by the Si-H_2 interaction to that of pure H_2-H_2 collisions is not known, we can only conclude that the number of surface molecules is of the same order of magnitude as that of volume molecules.

[24] E. A. Adams, K. Uhlig, Y.-H. Tang, and G. E. Haas, Phys. Rev. Lett. **52**, 2249 (1984).

[25] M. Schwark, F. Pobell, W. P. Halperin, Ch. Buchal, J. Hanssen, M. Kubota, and R. M. Mueller, J. Low Temp. Phys. **53**, 685 (1983).

[26] A. vom Felde, J. Fink, Th. Müller-Heinzerling, J. Pflüger, B. Scheerer, G. Linker, and D. Kaletta, Phys. Rev. Lett. **53**, 922 (1984).