Solid Hydrogen in Hydrogenated Amorphous Silicon

J. E. Graebner, B. Golding, and L. C. Allen
Bell Laboratories, Murray Hill, New Jersey 07974

and

D. K. Biegelsen and M. Stutzmann
Xerox Palo Alto Research Center, Palo Alto, California 94304

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The thermal properties of hydrogenated amorphous Si at temperatures between 0.1 and 5 K are shown by calorimetry to be dominated by the presence of molecular hydrogen H_2 in microvoids. A spontaneous release of heat due to conversion of o-H_2 to p-H_2 is observed from which the concentration (0.5 at.%) and bimolecular conversion rate ($0.025\ h^{-1}$) are obtained. The specific heat is time dependent, varies roughly as T^2 between 0.1 and 3 K, and is attributed to a highly broadened orientational ordering transition of H_2 in restricted geometry.

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At low temperatures, solid H_2 exists in several crystalline phases.[1] For an o-H_2 ($J=1$) molar fraction x greater than 0.55, a first-order transition from an orientationally disordered hcp phase to an orientationally ordered fcc phase occurs at temperatures below 3 K as a result of electric quadrupole-quadrupole interactions. For x less than 0.55, a quadrupolar glass phase exists below 0.3 K. Most of the information on solid H_2 has been obtained with bulk samples. The role that restricted geometry plays in influencing the H_2 phase diagram has not been addressed so far. In the present Letter we draw attention to a new system for studying this problem—hydrogenated amorphous silicon. Although it is well known that hydrogenation of a-Si incorporates as much as 30 at.% hydrogen in the form of SiH_n, we have found[2] that suitably prepared samples also contain *molecular* hydrogen[3,4] H_2 at a concentration as high as 0.5% relative to the Si.

Calorimetric measurements on films of a-Si:H in the temperature range 0.1–5 K show a significant spontaneous evolution of heat. The decay of the heat flux with time is not exponential but can be described by a bimolecular process of o- to p-H_2 ($J=0$) conversion. The rate of conversion is close to that for bulk solid hydrogen, implying that the H_2 is clustered in the microvoids of a-Si:H. The heat capacity is large, varies roughly as T^2, and exhibits time-dependent broad structure which we attribute to a highly broadened orientational ordering transition. The absence of sharp structure in the heat capacity indicates that surface and size effects play a significant role in determining the properties of this form of solid H_2.

The a-Si:H was prepared by plasma decomposition of silane using aluminum substrates held at 230 °C. The average rf power was 2 W, and the resulting hydrogen content was 15 at.% of the Si. The films, 5 μm thick, were annealed for 15 min each at various temperatures between 200 and 550 °C. Data are presented here for a 500 °C anneal; a full report will appear later.[2] After being annealed, the samples (typically 40 mg) were removed from the substrates, broken up and mixed with 20 mg of Apiezon-N vacuum grease for thermal contact, and mounted on a low-thermal-mass calorimeter[5] in a ^{3}He-^{4}He dilution refrigerator. The active parts of the calorimeter, including the sample, an Al_2O_3 mounting disc, a Ge resistance thermometer, and a thin-film Au heater, were thermally linked to the refrigerator at temperature T_r by a thin Au wire. In the absence of a sample, the thermometer was calibrated and the conductance of the link $k(T)$ and heat capacities of the empty calorimeter and grease were measured.

With a sample of a-Si:H mounted on the calorimeter, it was observed that the calorimeter temperature T_c was always higher than T_r. The temperature difference was attributed to a heat flux $\dot{Q}$ from the sample to the refrigerator. $\dot{Q}$ was calculated according to

$$\dot{Q} = \int_{T_r}^{T_c} k(T)dT \qquad (1)$$

and monitored as a function of time after the relatively rapid (~ 2 h) cooling from 150 to 4.2 K. It decreased slowly with time but, as shown by the plot of $\dot{Q}$ versus time in Fig. 1, the decay is clearly not a simple exponential. No evolution of heat is observed in measurements of the grease or the empty calorimeter.

Our interpretation assumes that the heat evo-

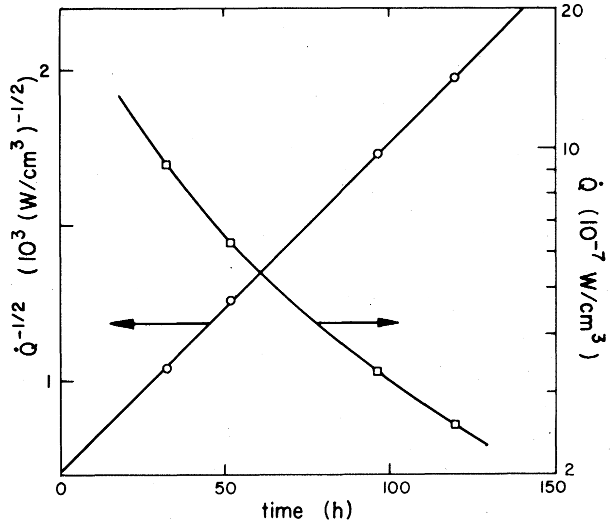

FIG. 1. Heat evolution $\dot{Q}$ from a-Si:H annealed at 500°C. The zero of time corresponds to the beginning of cooling from 150 to 4.2 K. $\dot{Q}$ is plotted in two ways: directly as $\dot{Q}$ (squares), and as $\dot{Q}^{-1/2}$ (circles). The curved line drawn through the squares illustrates the nonexponential decay of $\dot{Q}$. The straight line is indicative of a bimolecular rate equation (see text). The uncertainty in $\dot{Q}$ is comparable to the size of the symbols.

lution is given by ortho-para conversion of molecular H_2. The nonexponential decay of $\dot{Q}$ indicates[1] that the conversion is not catalyzed by magnetic impurities or spins located at dangling bonds. Ortho-para conversion of H_2 in the bulk solid is due[1] to magnetic dipolar interaction of neighboring pairs of o-H_2. The time dependence in this case is described by a bimolecular rate equation,

$$\dot{x} = -cx^2. \tag{2}$$

In these terms, $\dot{Q} = L\dot{n}_0 = L\dot{x}N$, where L is the energy per molecule released on conversion, n_0 is the number density of o-H_2, and N is the total number density of H_2. The solution to Eq. (2) can be written as

$$\dot{Q}^{-1/2} = at + b, \tag{3}$$

where $c = a/x_i b$, $N = 1/Lx_i ab$, and x_i is the initial value of x. The dependence of $\dot{Q}^{-1/2}$ on t is linear, as shown in Fig. 1, from which we deduce a conversion rate $c = 0.024$ h^{-1} and $N = 2.5 \times 10^{20}$ cm^{-3}. This value of N represents a H_2 concentration of 0.5% relative to the Si or approximately 5% of the hydrogen remaining in the sample after a 500 °C anneal. We have assumed that the room-temperature ortho concentration ($x = \frac{3}{4}$) is maintained during the rapid cooling and that L is given by its solid-hydrogen value of $k_B \times 170$ K. The conversion rate is very close to that in solid H_2 at zero pressure (0.019 h^{-1}).

The presence of molecular hydrogen in a-Si:H has been inferred from NMR relaxation measurements[3,6] in unannealed material where a rate of 0.010 h^{-1} was determined. The advantage of calorimetric measurements is the ability to measure N directly. We have found[2] that annealing a-Si:H between 400 and 550 °C increases the H_2 concentration by nearly an order of magnitude, and it is therefore associated with hydrogen released[7] at SiH and SiH_2 sites. Once formed, H_2 apparently diffuses only slowly to the surface of the material, and with the present 15-min annealing time a significant fraction of the liberated hydrogen is trapped in the voids or pores comprising the microstructure[8] of a-Si:H.

The observation of a bimolecular rate dependence is strong evidence that the H_2 is clustered in groups of two or more rather than an isolated molecules. The nuclear dipole interaction between neighboring ortho molecules which governs the bimolecular conversion rate is a sensitive function of the intermolecular separation R_0, which in solid hydrogen at zero pressure is 3.8 Å. The observation of a well defined rate indicates a farily well defined R_0. R_0 is not uniquely related to the conversion rate, however, as the latter depends also on the phonon density of states.

The heat capacity C_p was measured in the temperature range from 5 K down to the minimum temperature allowed by $\dot{Q}$ and k. C_p was determined from k and the characteristic time (in the range 3–30 sec) for thermal relaxation[9] after the heater power was turned on or off. Figure 2 shows results for a sample measured on days 1, 3, 6, and 11, after cooling from 150 K. The corresponding values of x according to Eq. (2) are 0.68, 0.35, 0.20, and 0.13, respectively. The heat capacity of the empty calorimeter and grease has been subtracted. The total heat capacity can be described as a time-independent term varying approximately as T^3 (dashed line) plus a time-dependent contribution varying, at least on the first day, approximately as T^2. The magnitude of the time-dependent contribution is roughly proportional to x but is also temperature dependent. For $x = 0.68$, the largest absolute contribution above the dashed line occurs near 3 K. For lower values of x, the bulk of the excess heat capacity moves to progressively lower tem-

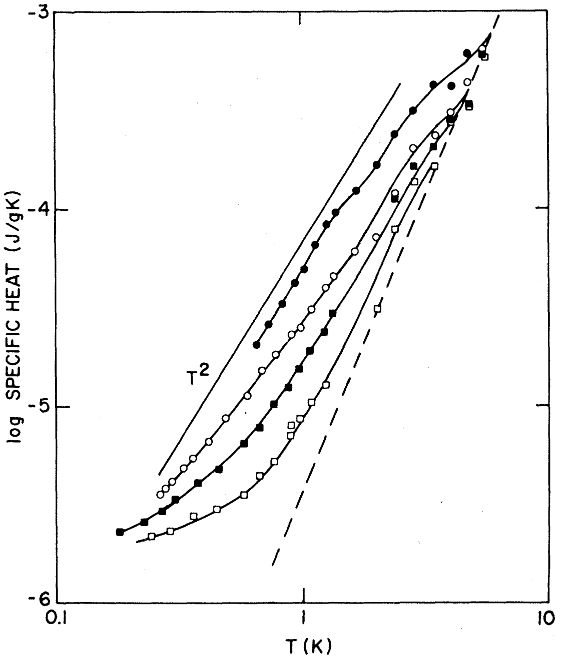

FIG. 2. Specific heat of a-Si:H. The data were taken at intervals over a period of eleven days as the spontaneous ortho-para conversion steadily diminishes the fractional concentration x of o-H_2: $x = 0.68$ (filled circles), 0.35 (open circles), 0.20 (filled squares), and 0.13 (open squares). The dashed line is an estimate of the time-independent specific heat.

peratures. At all temperatures the specific heat is much larger than the expected contribution[10] of the phonons. At low temperatures and high x, the specific heat is also large compared with either the quasilinear component of the heat capacity[11] due to tunneling systems or that observed[12] in vapor-deposited films of a-Si. The T^2 contribution is much weaker[2] in material annealed at temperatures lower than 400 °C and therefore can be quantitatively related to the higher H_2 concentration produced by annealing.

The data can be compared with the specific heat of bulk H_2 in the vicinity of the orientational order-disorder transition. The transition temperature depends[1] on the density ρ as well as on x. In particular, for $x = 0.75$ and $\rho \approx 1.3\rho_0$ where ρ_0 is the density of solid H_2 at zero pressure, the transition occurs near 3 K. The transition moves to lower temperature as x falls below 0.75. We believe that the broad contribution observed in the time-dependent component near 3 K for large x, as well as the shift to lower temperatures for smaller x, are associated with such a transition in the clustered H_2. We can picture two types of clustered H_2—either a few monolayers adsorbed on the internal surfaces of interconnected pores of diameter 5–50 Å, or pockets of H_2 trapped within closed voids of comparable diameter. In either case, one might expect surface and size effects to be important, producing an effective $\rho > \rho_0$, imperfect crystalline order, and a broadening of the transition region. There is the interesting additional possibility of a quadrupolar[13] glass of o-H_2 in a highly defective H_2 matrix.

The total entropy per mole of o-H_2, determined by integrating the time-dependent part of C_p from 0.1 to 4 K for $x = 0.68$, is $0.25R$, which may be compared with $R\ln 3 \approx 1.1R$ for freely rotating molecules. Thus a significant fraction of the o-H_2 participates in the ordering.

In conclusion, we have presented direct calorimetric evidence for molecular hydrogen in a-Si:H at the 1% level. At this concentration the specific heat is dominated by the effects of o-H_2 interactions. Orientational ordering is observed below 3 K but with differences from bulk solid hydrogen which are attributed to the effects of confined geometry and large surface area. Other measurement techniques should also be sensitive to H_2 at this concentration and should be useful in determining the phase diagram of this unique form of solid hydrogen.

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[1] For a comprehensive review of the properties of solid hydrogen, see I. F. Silvera, Rev. Mod. Phys. 52, 393 (1980); J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

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and J. P. deNeufville, Phys. Rev. Lett. 32, 538 (1974)]; A. Cruz-Uribe and J. Trefny, in *Amorphous and Liquid Semiconductors*, edited by W. E. Spear (Center for Industrial Consultancy and Liaison, Univ. of Edinburgh, Edinburgh, Scotland, 1977), p. 175. It is found that the cubic term in a-Ge is 1.7 times larger than in c-Ge. Assuming that the same ratio occurs in a-Si yields a T^3 contribution one order of magnitude smaller than the dashed line in Fig. 2. The phonon contribution of the *hydrogen*, assuming it were in bulk form, would lie lower yet by a factor of 2.

[11] *Amorphous Solids: Low-Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

[12] H. v. Löhneysen and H. J. Schink, Phys. Rev. Lett. 48, 1121 (1982). The quasilinear term was attributed to spins associated with the dangling bonds. Because of the low density N_s of spins in the present material ($N_s \approx 3 \times 10^{17}$ cm^{-3}), entropy considerations rule out dangling bonds as the source of the large C_p in Fig. 2.

[13] D. G. Haase and M. A. Klenin, Phys. Rev. B 28, 1453 (1983).