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Solid H_2 in *a*-Si:H at low temperatures

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Molecular hydrogen in *a*-Si:H has been detected by the heat released during ortho-para conversion. Calorimetric measurements in the temperature range 0.05—5 K indicate as much as 0.5 mol % H_2 trapped in microvoids at least 10 Å in diameter. The specific heat is dominated by a broad peak near 3.5 K due to short-range orientational order of the ortho-H_2 within each cluster. No sharp order-disorder transition occurs, which would signal the onset of long-range order as in bulk solid H_2. The absence of long-range orientational order is attributed to the small size of the clusters and to positional disorder within each cluster. The concentration of H_2 can be maximized by a short anneal at 500 °C, during which Si—H bonds are broken and H diffuses to the microvoids.

I. INTRODUCTION

At temperatures below 300 K and pressures below 10 kbar, molecular hydrogen[1,2] consists of a mixture of molecules in the two lowest-angular-momentum states, para-H_2 ($J=0$) and ortho-H_2 ($J=1$). The phase diagram of the crystalline solid below a few kelvins is strongly influenced by electric quadrupole interactions among neighboring ortho molecules. The ground state of the solid for more than 55% ortho-H_2 is an array of ortho molecules with long-range orientational order on an fcc lattice, while for less than 55% ortho-H_2, long-range orientational ordering does not occur. It has been proposed that a quadrupolar glass phase occurs instead, but this phase is currently the subject of considerable controversy. The properties of solid hydrogen have previously been studied only in the bulk. In the present work,[3] small clusters of molecular hydrogen have been found in the microvoids of hydrogenated amorphous silicon, *a*-Si:H, permitting the study of solid H_2 under conditions of restricted geometry. The *a*-Si:H thus serves as a convenient container for an unusual form of solid hydrogen.

The pure, elemental amorphous semiconductors[4] *a*-Ge and *a*-Si are not homogeneous materials; they do not form a continuous random network. Rather, they display a preparation-dependent microstructure consisting of microvoids interspersed in an amorphous matrix with nearly crystalline density. Dangling bonds at atoms with lower than fourfold coordination give rise to spin densities as high as 10^{20} cm^{-3}. These dangling bonds also trap carriers and have a strong influence on transport and optical properties. A number of investigations of the properties of pure *a*-Si and *a*-Ge below a few kelvins have recently appeared.[5–9] As in other disordered solids,[10] evidence for two-level atomic tunneling systems has been found at these temperatures, with a tunneling-system density of states which depends, in the case of *a*-Ge films,[8] on the average mass density of the samples. These tunneling systems appear to be intrinsic to *a*-Ge and *a*-Si in that they are associated primarily with structural defects in the network rather than with impurities.

The purpose of hydrogenating *a*-Si:H is to satisfy the dangling bonds and therefore eliminate electron traps. As much as 50 at. % hydrogen can be incorporated in *a*-Si:H, bonded for the most part as silicon hydride or dihydride, depending on preparation conditions. For preparation by plasma decomposition of silane, growth conditions have been found[11] which produce high-quality films, i.e., low spin density and minimal microstructure. It was assumed until recently that all the hydrogen in *a*-Si:H was bonded atomically to silicon. A few years ago, however, NMR data were interpreted[12,13] by assuming the presence of a small number of hydrogen *molecules* which could serve as relaxation centers for the resonant H atoms. Molecular hydrogen was not observed directly in NMR, although the long-term behavior of the atomic-hydrogen relaxation times[14] was consistent with expectations based on ortho-para conversion of H_2.

In the present work, molecular hydrogen in *a*-Si:H has been directly and quantitatively detected by low-temperature calorimetric measurements. The heat released by ortho-para conversion after cooling from room temperature follows a bimolecular decay, as expected for solid hydrogen. The characteristics of the decay imply clustered H_2 with a *minimum* of 10—15 molecules per cluster. The heat capacity of *a*-Si:H is dominated by the clustered H_2, showing a broad peak near 3 K which we attribute to short-range orientational ordering of the electric quadrupoles of ortho molecules. The long-range orientational order which is known to occur in bulk solid H_2 is inhibited in the clusters. By studying samples of *a*-Si:H annealed at temperatures up to 550 °C, we have also used the H_2 to elucidate the movement of hydrogen in *a*-Si:H at elevated temperatures.

II. EXPERIMENTAL DETAILS

High-quality *a*-Si:H was prepared by plasma decomposition of silane on aluminum substrates (2.5×10^{-3} cm thick) held at 230 °C, resulting in a concentration of 15 at. % hydrogen. Identical samples were given different anneals for 15 min in vacuum at temperatures T_A between 200 °C and 550 °C. The 5-μm-thick films of *a*-Si:H were removed from the Al substrate by dissolving the latter in HCl, followed by a thorough rinse in water and acetone. Each sample, typically 35—40 mg, was broken into a powder and mixed with 18 ± 0.2 mg of Apiezon N vacuum grease. The mass of grease was kept constant from sample to sample to minimize errors in the subtraction of the grease heat capacity.[15] One sample was left on the aluminum substrate to test for any effect of the removal procedure. The sample annealed at 550 °C was unusual in that several small regions were visibly reacted with the Al substrate. These regions were cut away before removal from the substrate.

A thick sample (~ 1 mm) of *a*-Si:H, taken from the wall of the plasma chamber after many runs, was also measured. The sample was prepared in the substrate temperature range of 120—180 °C and has been described previously.[16] This sample offered the convenience of solid material, but was not as well characterized.

The thermal measurements were performed with a low-mass thermal-relaxation calorimeter[17] mounted in a dilution refrigerator. The sample-grease mixture, or the bulk sample with a small amount of grease on one face, was placed on the 1-cm-diam×0.025-cm sapphire calorimeter plate, to which were attached a thin-film Au electrical heater and a 1.3-mg Ge-resistance thermometer. The plate was supported by three 0.005-cm-diam NbTi wires which also served as electrical leads for the heater. The thermometer leads were 0.0015-cm-diam NbTi for thermal isolation and low thermal mass. The thermal link to the bath consisted of a 5-cm length of 0.0025-cm-diam Au wire ultrasonically bonded to a Au pad on the Al_2O_3 plate.

Because the equilibrium ortho-para ratio and the rate of ortho-para conversion are both temperature dependent, the thermal history of the sample was an important variable. In order to reliably calculate the ortho-para ratio, our standard procedure was to cool the sample in 2 h from 150 to 5 K. Data were taken on cooling further to 0.5 K while the dilution refrigerator was started. On the second day, data were taken beginning at the lowest temperature, $T_0^{\min}$, allowed by $\dot{Q}$ with the refrigerator at $T_r = 20$ mK, and continuing up to $T_r \approx 0.5$ K. For several samples, this procedure was repeated on later days (without warming above 5 K), as $\dot{Q}$, and therefore $T_0^{\min}$, slowly decreased.

III. DATA ANALYSIS

As noted above, the present samples were distinguished by a release of heat $\dot{Q}$ which extended over a period of many days after cooling from room temperature.[18] The flow of heat was detected by a temperature difference $T_0 - T_r$ across the thermal link, where T_r was the temperature of the refrigerator and T_0 was that of the sample in the absence of *electrical* heating. $\dot{Q}$ was measured quantitatively by integrating the thermal conductance of the link:

$$\dot{Q} = \int_{T_r}^{T_0} k(T')dT' \,. \tag{1}$$

The heat capacity C of the sample plus addenda was measured by analyzing[17] the temperature transient following the application or removal of electric power $\dot{q}$.

In general, it is possible to show[19] that the method is independent of the presence of $\dot{Q}$. By conservation of energy, with T representing the sample temperature, we may write

$$\dot{Q} - C\frac{dT}{dt} = \int_{T_r}^{T} k(T')dT' = \int_{T_r}^{T_0} k(T')dT' + \int_{T_0}^{T} k(T')dT' \,, \tag{2}$$

or, making use of Eq. (1) to eliminate $\dot{Q}$,

$$\frac{dT}{dt} = -\frac{1}{C}\int_{T_0}^{T} k(T')dT' \,. \tag{3}$$

Equation (3) has the same form as Eq. (2) in the absence of a heat flow $\dot{Q}$, and the usual analysis follows readily. That is, if the equilibrium temperature excursion $T_1 - T_0$ generated by $\dot{q}$ is small compared to T_0, k may be removed from the integral and replaced by its average value k_{01} over the temperature interval T_0 to T_1:

$$k_{01} \equiv (T_1 - T_0)^{-1}\int_{T_0}^{T_1} k(T')dT' \,. \tag{4}$$

Then,

$$\frac{dT}{dt} = -\frac{k_{01}}{C}(T - T_0) \,, \tag{5}$$

which leads to the usual exponential rise and fall of temperature based at T_0 as $\dot{q}$ is turned on or off, with a time constant $\tau = C/k_{01}$. It is important to note that the measurable ratio $\dot{q}/(T_1 - T_0)$ is also equal to k_{01}, as can be seen by replacing $\dot{Q}$ by $\dot{Q} + \dot{q}$ in Eq. (2) and setting $dT/dt = 0$. Thus *both* the measurement of the appropriate conductance and the determination of C are independent of the presence of $\dot{Q}$. This result is useful not only for the present case of $\dot{Q}$ generated within the sample, but, more generally, for a parasitic heat leak as well. Vibrational heating, for example, which usually causes a temperature difference across the thermal link at the lowest temperature, does not invalidate the straightforward procedure for measuring k_{01} and C.

In practice, $\Delta T = T_1 - T_0$ was kept less than 5% of T_0 for $T < 1$ K, and less than 10% of T_0 for higher temperatures. The heater power was repeatedly turned on and off at equal time intervals $\Delta t \approx 5\tau$ under the control of a microcomputer, which also read the thermometer resistance and performed signal averaging. A nonlinear least-squares fit to the exponentially rising and falling signals was used to determine τ and ΔT, from which $C(\overline{T}) = \tau k_{01} = \tau\dot{q}/\Delta T$ was calculated for the average sample temperature $\overline{T} = (T_0 + T_1)/2$. The heat capacities of the empty calorimeter and the grease were determined separately and subtracted from the total heat capacity.

IV. RESULTS

We first discuss the analysis of $\dot{Q}$, which, by Eq. (1), required only two temperatures, T_r and T_0, and the previously measured $k(T)$. Figure 1(a) shows the results for a

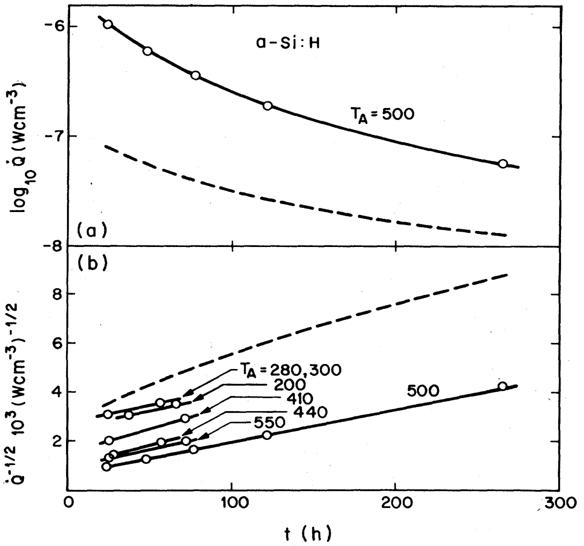

FIG. 1. The flow of heat $\dot{Q}$ from a-Si:H to a heat sink maintained at 0.1 K. The samples were cooled from room temperature at time $t=0$. T_A is the temperature at which each sample was annealed. The dependence of $\dot{Q}$ on time is not a simple exponential, as shown in (a). (b) The plot of $\dot{Q}^{-1/2}$ vs time is a test for a bimolecular process (see text). The solid lines denote data from films, the dashed, from bulk a-Si:H.

series of measurements on both a film sample and the bulk[16] a-Si:H. Uncertainties in the values of $\dot{Q}$ were approximately equal to the size of the symbols. At times longer than 300 h, they became rapidly worse as $T_0 - T_r$ became smaller than a few millikelvins. The largest source of error was thought to be in the measurement of T_0 because of small stress-induced changes in the characteristics of the Ge thermometer glued to the calorimeter plate. To minimize systematic errors, all the data in Fig. 1(a) were obtained with the refrigerator held at an intermediate temperature, $T_r = 101$ mK. The largest and smallest heat currents represented in the figure are 2×10^{-8} and 4×10^{-10} W, corresponding to $\Delta T = 210$ and 10 mK, respectively.

Heat-capacity data for samples of a-Si:H annealed at various temperatures are shown in Fig. 2. The data were taken during the first 2 d of each of the experimental runs represented in Fig. 1. This is important because C was found to be *time* dependent, as discussed below. The measurement errors were typically ±5% for $T < 2$ K, increasing to 20–30% at the highest temperatures, primarily because the calorimeter was optimized for operation at temperatures below 1K. Another source of error at the highest temperatures was the subtraction of the heat capacity of the grease, which in the worst case ($T_A = 25\,^\circ$C, $T = 5$ K) became 20 times larger than that of the sample.

For $T_A < 400\,^\circ$C the data were roughly independent of T_A, while for higher values of T_A the heat capacity was larger at all measuring temperatures. The largest heat capacity was observed for $T_A = 500\,^\circ$C and 550 °C, with a broad maximum centered at $T \approx 3.5$ K. (The data for $T_A = 500\,^\circ$C and 550 °C shown in Fig. 2 do not extend

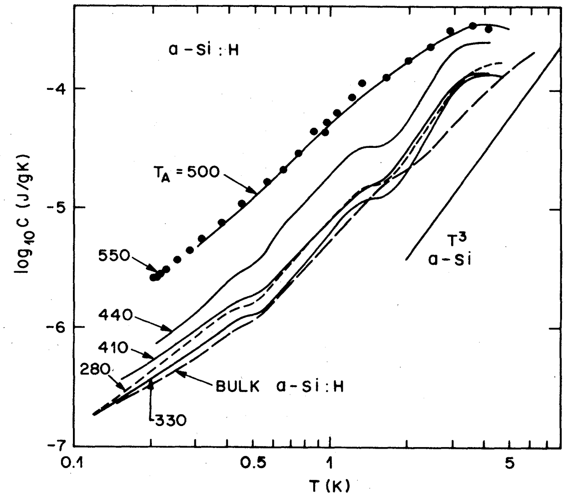

FIG. 2. Heat capacity of plasma-deposited a-Si:H annealed for 15 min at various temperatures T_A and measured on the first 2 d after cooling from room temperature to liquid-helium temperatures. For clarity, data points are shown only for $T_A = 550\,^\circ$C. Also included is the T^3 contribution of pure a-Si (Ref. 20).

down past $T = 0.3$ K because of the large value of $\dot{Q}$ during the first few days.) The broad anomaly at 3.5 K for $T_A = 500\,^\circ$C and 550 °C decreased in size for lower values of T_A, with observable structure developing at $T = 1.2$ and 0.4 K. For comparison, in Fig. 2 we include results for the unannealed bulk a-Si:H sample. The bulk data for days 1 and 2 after cooling from room temperature have been reported previously.[16] The heat capacity of a sample ($T_A = 500\,^\circ$C) *not* immersed in HCl was, after subtraction of the heat capacity of the aluminum substrate, and within larger error limits, qualitatively similar to that shown in Fig. 2. $\dot{Q}$ was certainly unchanged. Thus the use of acid for removal of the substrate had no large effect. The straight line in Fig. 2 represents the T^3 variation[20] of the heat capacity of *unhydrogenated* a-Si prepared by sputtering.

The dependence of the heat capacity on time was demonstrated most clearly for the sample annealed at 500 °C, Fig. 3. The data on successive days extended to lower and lower temperatures as $\dot{Q}$ slowly decreased (Fig. 1). The broad anomaly at $T \approx 3.5$ K observed immediately after cooling from high temperatures (day 1) decreased in magnitude with time and developed structure consisting of peaks at $T = 3.5$, 1.2, and 0.4 K. Measurements to temperatures below 0.1 K after 18 d revealed what appears to be the high-temperature side of another peak located below ~60 mK.

V. DISCUSSION

A. Ortho-para conversion

Neither set of data in Fig. 1(a) can be described by a simple relaxation process with an exponential decay in time. If the heat is the result of ortho-para conversion of H_2, one might expect a bimolecular process similar to that which occurs[1,2] in solid hydrogen as the result of a nu-

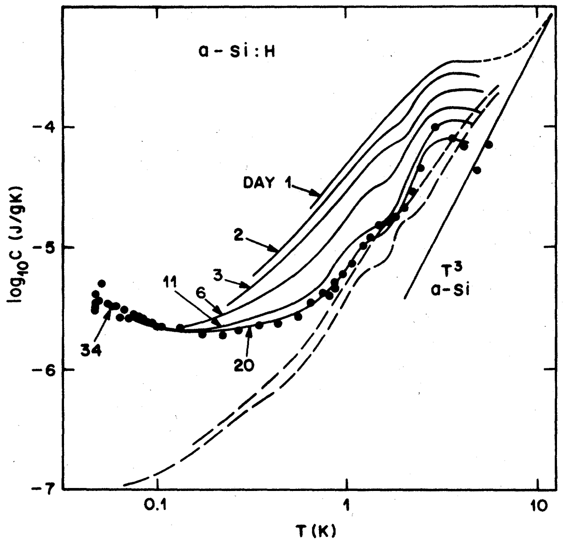

FIG. 3. Heat capacity of a film of *a*-Si:H annealed at 500 °C and measured periodically over a time span of 34 d as the ortho fraction x decayed from ~ 0.7 to 0.05, according to the analysis of $\dot{Q}$ using Eq. (6). For clarity, data points are shown only for day 34. Also shown, for comparison, are data for a sample with much less molecular hydrogen (bulk *a*-Si:H) on days 1 and 20 (upper and lower dashed lines, respectively). The straight line at high temperatures represents the heat capacity of pure *a*-Si (Ref. 20).

clear dipolar interaction between nearest-neighbor ortho molecules. If x is the fraction of H_2 molecules that are in the ortho state, then

$$\dot{x} = -\alpha x^2 \tag{6}$$

describes the bimolecular decay process. In terms of $\dot{x}$, $\dot{Q} = -L\dot{n}_0 = L\dot{x}N$, where L is the heat of conversion per molecule, n_0 is the number density of ortho-H_2, and N is the total number density of H_2. The solution to Eq. (6) is

$$x = (x_i^{-1} + \alpha t)^{-1} , \tag{7}$$

or

$$\dot{Q}^{-1/2} = at + b , \tag{8}$$

where $\alpha = a/x_i b$, $N = 1/Lx_i ab$, and x_i is the initial value of x. The data of Fig. 1(a) are replotted as $\dot{Q}^{-1/2}$ vs t in Fig. 1(b), along with data from shorter runs for film samples annealed at other temperatures. The film annealed at 500 °C displays a very-well-defined bimolecular decay over a period of at least 12 d. This result may be compared with the data of Löhneysen *et al.*,[18] who were unable to distinguish between bimolecular and exponential decay on the basis of their heat-flow data. It is also independent of any assumptions for the initial x or the value of L. Values of N and α can be calculated by assuming that the room-temperature value of $x = 0.75$ is maintained during the rapid cooling to 5 K and that L is equal to its solid-hydrogen value of $k_B \times (170\ \mathrm{K})$. If the other annealed samples are assumed to obey a similar bimolecular decay, the values of N and α are those which appear in Fig. 4 and Table I. The decay constant α for low annealing temperatures ($T_A < 400\,^\circ\mathrm{C}$) is very similar to the rate inferred from NMR measurements[14] (on an unannealed sample) which extended over a period of 90 d. The decay of $\dot{Q}$ from the *bulk* sample is not a simple bimolecular process; the two values for N and α in Table I are obtained from the short and long-time behavior of $\dot{Q}^{-1/2}$ in Fig. 1(b). Annealing the films at temperatures below $T \approx 400\,^\circ\mathrm{C}$ had little effect on either α or N. A sharp rise in both quantities occurred, however, for $T_A > 400\,^\circ\mathrm{C}$, with a maximum at $T_A \approx 500\,^\circ\mathrm{C}$. The dependence of α on N is given in the inset of Fig. 4.

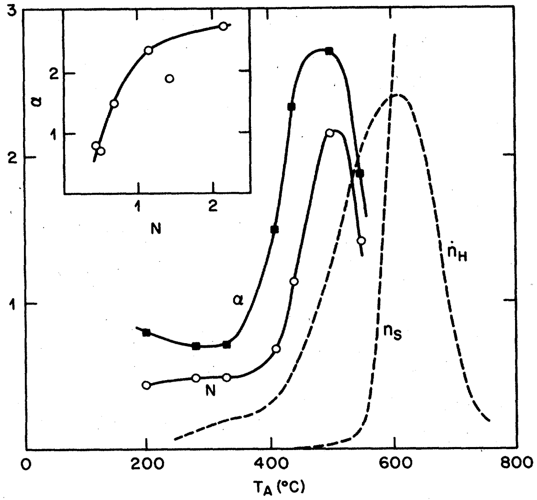

FIG. 4. Bimolecular decay constant α and average number density N of H_2 molecules for samples annealed for 15 min at temperature T_A. The explicit dependence of α on N is shown in the inset, where the point lying off the smooth curve is for $T_A = 550\,^\circ\mathrm{C}$. The rate of evolution of hydrogen from similar films upon heating, as well as the spin density, are shown (Ref. 11) for comparison. Units are the following: α (% h^{-1}), N ($10^{20}\ \mathrm{cm}^{-3}$), $\dot{n}_H$ (arbitrary), and n_s ($10^{17}\ \mathrm{cm}^{-3}$).

A more detailed picture of H_2 in *a*-Si:H can be deduced by comparing α, N, and C with the corresponding quantities for bulk, solid, molecular hydrogen. The bimolecular conversion rate constant for one-phonon conversion via the nuclear dipole interaction has the following dependence:

$$\alpha \propto n_{\mathrm{ph}}(L)\eta / r^8 , \tag{9}$$

where $n_{\mathrm{ph}}(L)$ is the density of states of phonons with $\hbar\omega = L$ ($=170$ K for bulk H_2 at zero pressure), η is the number of nearest H_2 neighbors, and r is the intermolecular separation. For pressures $0 \le p < 2$ kbar, corresponding to $3.5 < r < 3.8$ Å, α lies in the range 1—3 % h^{-1}. The similarity of this range of α and the range of values in Fig. 4 is strong evidence that the same ortho-para conversion mechanism is dominant in *a*-Si:H. If the H_2 in *a*-Si:H was *uniformly* distributed, however, the average molecular separation would be $N^{-1/3} \approx 20$ Å, which, according to Eq. (9), is far too large to give rates similar to solid hydrogen. We conclude, therefore, that the H_2 in *a*-Si:H is clustered, with an intermolecular separation in the range 3—4 Å. The size of these clusters can be given a

TABLE I. Conversion rate constant α and spatially averaged density N of H_2 molecules for samples of a-Si:H annealed at various temperatures T_A.

T_A (°C)	α (h^{-1})	N (10^{20} cm^{-3})
200	0.008	0.44
280	0.007	0.48
330	0.007	0.49
410	0.015	0.68
440	0.023	1.14
500	0.027	2.15
550	0.019	1.41
25 (bulk, early)	0.015	0.23
25 (bulk, late)	0.005	0.28
25 (Ref. 14)	0.010	

lower bound by considering the duration of the bimolecular decay. For $T_A = 500$ °C, Fig. 1 shows a bimolecular decay for at least 12 d after cooling from room temperature, to an orthohydrogen concentration as small as $x = 0.10$. A cluster size of, for example, three molecules could not produce such a low value of x, as the bimolecular decay would stop at $x = 0.33$, when only one ortho-H_2 molecule would remain. Bimolecular decay to $x \leq 0.10$ therefore implies a bare minimum of 10 molecules per cluster. We suggest that a more realistic lower bound, taking into account surface effects and the statistics of small clusters, might be closer to 20 molecules per cluster. Packed at the density of zero-pressure solid hydrogen, a spherical cluster of 20 molecules would have a diameter of 10 Å. One could, in principle, calculate the decay rate in small clusters by taking into account statistical distributions in both the cluster size and the initial ortho concentration.

The agreement of the data with a bimolecular conversion also implies the absence of quantum rotational diffusion, a phenomenon well known[1,2] in solid hydrogen at temperatures below 1 K and x below 0.3. In this process a nearest-neighbor pair of molecules consisting of one ortho-H_2 and one para-H_2 exchange not their positions but their angular-momentum states. This allows a clustering of $J = 1$ molecules and, consequently, a faster-than-bimolecular conversion which is readily observable[21] for $x < 0.3$. Rotational diffusion in crystalline solid H_2 is inhibited by local strains.[22] It is easy to imagine that small clusters might be highly strained, thus accounting for the absence of rotational diffusion.

A model for cluster formation at high temperatures can be deduced by comparing $N(T_A)$ and $\alpha(T_A)$ with measurements[11] of hydrogen evolution from similar films, Fig. 4. The evolution of hydrogen from the material upon slow heating in vacuum has been correlated,[11] on the basis of infrared-absorption measurements, with the breaking of Si—H bonds above ~400 °C. (In high-quality material such as the films used here, the predominant bonding configuration is known to be Si—H.) The hydrogen diffuses slowly out of the sample and leaves a large number of dangling Si bonds. It is at $T_A = 400$ °C that the average density N of nearest-neighbor (NN) H_2 molecules begins to rise sharply, Fig. 4, followed by a maximum at $T_A = 500$ °C. We interpret these data as follows: For $200 \lesssim T_A \lesssim 400$ °C, hydrogen atoms diffuse through the material, perhaps via a mechanism of reconstructing Si—H bonds,[23] and eventually are trapped in microvoids where they combine to form H_2. At higher T_A, this process is enhanced and results in a larger N. At sufficiently high T_A ($\gtrsim 500$ °C), however, even the molecular hydrogen can escape from the sample, and N decreases. We note that the as-grown material has an average H_2 density N which is as much as $\frac{1}{3}$ of the maximum value, and we suggest that a similar process of diffusion and trapping at microvoids occurs already *during growth*. This picture would also explain the recently observed high-pressure H_2 gas in the microvoids at room temperature.[24]

For the tetrahedral amorphous semiconductors, there is ample evidence of microstructure[4] on a scale smaller than ~500 Å. However, high-quality films such as those used in the present work have been shown by small-angle neutron scattering[25] to be free of observable microstructure larger than ~10 Å. We propose our observation of ≥10-Å-diam clusters of H_2 as independent evidence for voids of this size in film samples annealed at 500 °C, with enough voids (as many as $\sim 10^{19}$ cm^{-3}) to occupy ~0.5% of the sample volume.

The sharp rise in α above $T_A = 400$ °C suggests a qualitative change within each cluster as N increases, rather than a proliferation of the same type of cluster. In an attempt to understand this behavior, we consider each of the three factors in Eq. (9) which determine α. It is difficult to estimate the effective phonon density of states for such small clusters, and for simplicity we assume that it is given by the density of states of the a-Si matrix, which should not change significantly over our range of T_A. Then the factor-of-3 change in α would be due to a change in η/r^8. The average number η of nearest neighbors could easily change by a factor of 2 or 3 if a cluster in the as-grown material is only a monomolecular layer covering part of the internal surface ($\eta \approx 3$—6), enlarging with annealing to a three-dimensional cluster for which η approaches 12. An interesting variation of this model would have the H_2 located in nonspherical, perhaps threadlike, voids,[26] which, upon annealing and under the effect of high-pressure H_2, reform and join together to form larger and more spherically shaped microvoids which allow a higher average number of nearest-neighbor H_2 molecules. (Another plausible explanation is that the change in α results from a 20% decrease in r as more H_2 is clustered in each void, resulting in a higher pressure for higher T_A.) The absolute value of α is more difficult to interpret. We note that the values range from $\frac{1}{3}$ of the rate for zero-pressure solid H_2 to the rate for solid H_2 at ~1 kbar pressure. The variation of α in solid H_2, however, is dominated by the variation in the phonon density of states and a transition from two-phonon to one-phonon conversion. Such complication should be unimportant if the phonon density of states is given at least approximately by that of the surrounding a-Si.

B. Orientational ordering

The properties of the clustered H_2 are further revealed by the specific heat. The dependence of the specific heat on both time and T_A shown in Figs. 2 and 3 suggests that

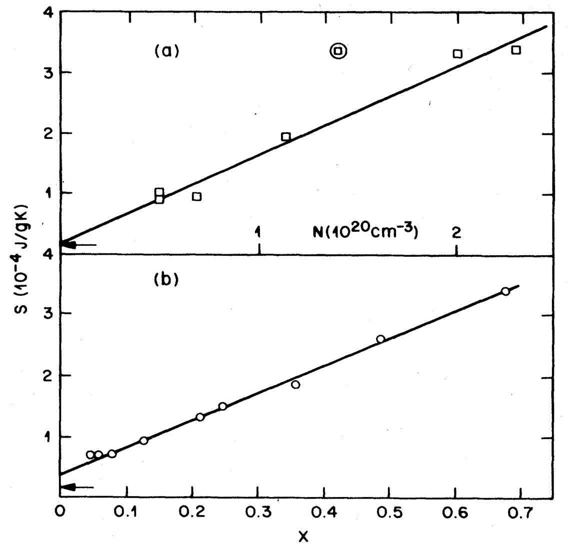

FIG. 5. Entropy per gram of *a*-Si:H calculated from the specific heat of (a) the various samples in Fig. 2 and (b) the sample annealed at 500 °C, Fig. 3. The circled point in (a) is for $T_A = 550\,^{\circ}\mathrm{C}$. The horizontal arrows indicate the entropy of the T^3-phonon contribution of *a*-Si (Ref. 20).

the large, excess heat capacity is associated with the ortho-hydrogen in the sample. To test this hypothesis, we compute the entropy $S(T)$ represented by the data in Figs. 2 and 3. The maximum contribution to the integral of $S = C/T$ between 0.1 and 5 K occurs above 1 K. Therefore the straight-line extrapolation to 0.1 K, where necessary, introduces negligible error. We use $N(T_A)$ from Fig. 4 and $C(T_A)$ from Fig. 2 to plot S vs N in Fig. 5(a) for samples annealed at various temperatures but measured at roughly constant x ($\approx$0.6—0.7). Similarly, $C(t, T_A = 500\,^{\circ}\mathrm{C})$ from Fig. 3 and $x(t)$ from Eq. (7) yield S vs x in Fig. 5(b). A linear dependence of S on both x and N is observed.

The heat capacity of the sample annealed at 500 °C is shown in Fig. 6(a) after subtracting the T^3-phonon contribution of *a*-Si. The broad peak in Fig. 6(a) dominates S in Fig. 5 and is seen to move slightly downward in temperature as x decreases. We interpret the peak in terms of the orientational ordering that occurs in the heat capacity of solid hydrogen,[27–31] Fig. 6(b). In that case, a phase transition at T_c is driven by the electric-quadrupole—quadrupole (EQQ) interaction of neighboring ortho-H_2 molecules. [For an isolated pair of ortho-H_2 molecules at zero pressure, the characteristic EQQ interaction energy is scaled by $\Gamma = 0.9$ K, with $\Gamma(r) \sim r^{-5}$.] The dependence of T_c on x at zero pressure is shown in the inset of Fig. 6(b). The orientational order-disorder transformation is accompanied by a lattice transformation, but has been shown to be first order even without it.[1] The long-range order (LRO) of the ordered state with $x = 1$ consists of a four-sublattice array with the molecular axes aligned along body diagonals of the fcc lattice. The considerable specific heat above T_c is associated[1,2,32] with a highly frustrated short-range order (SRO) favoring a local but very stable T-pair configuration, which, however, cannot be accommodated on the four-sublattice array. T_c drops rapidly with decreasing x as LRO is made less favorable by the random conversion of ortho-H_2 to para-H_2, which has no electric-quadrupole moment. T_c goes to zero at $x = 0.55$.

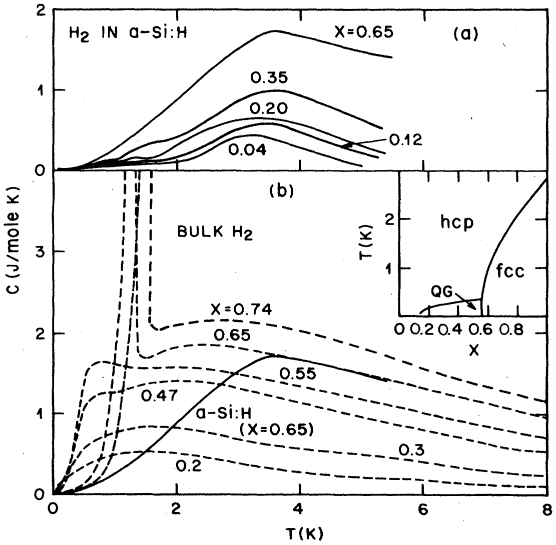

FIG. 6. (a) The heat capacity of an *a*-Si:H film annealed at 500 °C (Fig. 4) with a T^3-phonon contribution subtracted. C is expressed in J/K per mole of H_2. (b) Heat capacity of bulk solid H_2 at zero pressure (dashed lines) compiled from the literature (Refs. 27—31). The phase diagram for bulk solid H_2 is shown in the inset, including the controversial quadrupolar-glass phase below 0.3 K and $x < 0.55$. The present data (solid line) for clusters of H_2 in *a*-Si:H with $x = 0.65$ are reproduced from (a) for comparison.

On the basis of NMR data on bulk solid H_2, it has been proposed[33,34] that there is a gradual transformation to an orientationally ordered quadrupolar-glass (QG) state at yet lower temperatures [Fig. 6(b)]. As expected for such a state, no anomaly associated with the transformation is seen in the specific heat.[31,35,36]

If the peak in C of *a*-Si:H is due to the EQQ interaction between ortho-H_2 molecules, the r^{-5} dependence of Γ guarantees that the ordering occurs *within* isolated clusters. The average intercluster separation, which is 50 Å for 10-Å-diam clusters and average $N = 2\times10^{20}$ H_2 molecules/cm^3, is much larger than the typical intermolecular separation of 3—4 Å.)

The most obvious interpretation of the peak in C at 3.5 K is a broadened first-order transition at a pressure of $1.2\rho_0$, where ρ_0 is the density of bulk H_2 at zero pressure.[1] The difficulty with this interpretation is that the peak in *a*-Si:H does not shift rapidly to lower temperatures with decreasing x as required by the bulk phase diagram for pressurized H_2. In fact, the peak in *a*-Si:H is still visible above 2.5 K for as little as 5% orthohydrogen.

An alternate interpretation is that the excess heat capacity at our highest temperatures (4—5 K) is due to the excitations (short-wavelength librons) associated with SRO, just as in bulk H_2, but that LRO is suppressed in the small clusters. The heat capacity in the temperature range 0—2 K is then drastically reduced from that of the

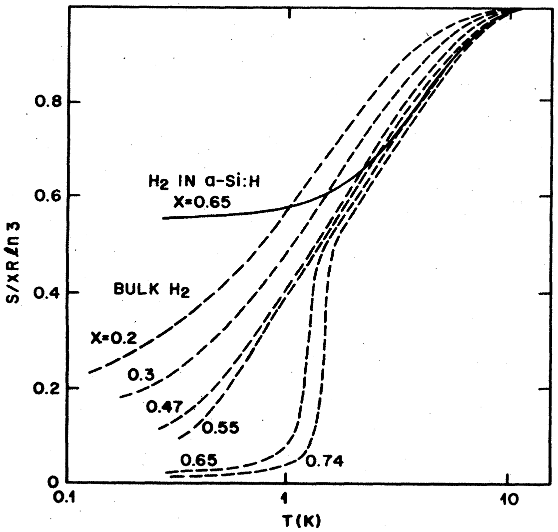

FIG. 7. Excess entropy per mole of H_2 calculated from temperature T up to $T \approx 12$ K, where it is assumed that the full rotational entropy of $R\ln 3$ is attained at 12 K. The entropy is calculated from the curves in Fig. 6.

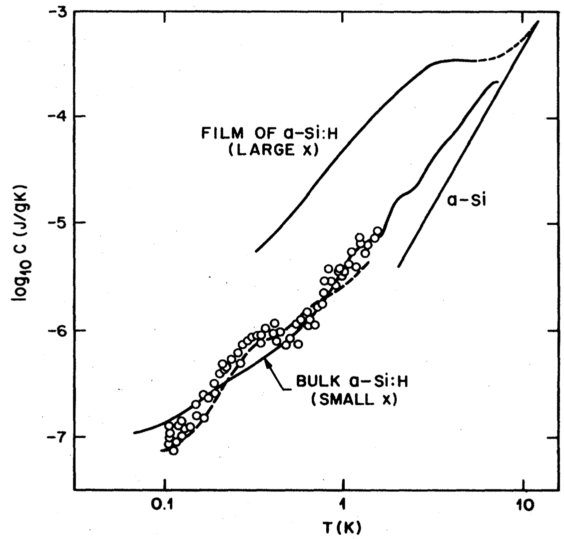

FIG. 8. The heat capacity of various materials related to a-Si:H. The present results fall between the data for a-Si:H at large and small x, indicated by solid curves. The heat capacity of a-Si:H prepared under less than ideal conditions is shown by the circles (Ref. 9). The heat capacity of pure a-Si is indicated by a straight line above 1.5 K (Ref. 20) and a dashed curve below 1.5 K (Ref. 9).

bulk, i.e., a first-order transformation to LRO does not occur. The suppression of long-range order can be ascribed to the small size of the clusters and/or positional disorder of the molecules within the (undoubtedly highly strained) clusters.

It is useful to compare the entropy of bulk and clustered H_2 (Fig. 7). The maximum rotational entropy of bulk H_2 is $R\ln 3$ per mole of ortho-H_2. The SRO above 2 K accounts for as much as 30—40% of $R\ln 3$ for both bulk and clusters, while the order-disorder transformation in the bulk accounts for only 40% at $x=0.75$ and progressively less for smaller x. In the absence of LRO for $x<0.55$, bulk H_2 loses[31] all but $\sim 10\%$ of $R\ln 3$ as T approaches zero. The small clusters, on the other hand, show very little change in entropy for $T<1$ K. This is consistent with the above arguments for the presence of only SRO in the clusters, and demonstrates that a large fraction of the high-temperature rotational disorder is frozen in below 2 K. The residual orientational entropy at $T\approx 0$ is comparable to the positional entropy of typical glasses,[37] so that the frozen array of quadrupoles within a cluster may reasonably be termed a QG at least on a very local level. It has been suggested[38] that the current controversy over the existence or nonexistence of a quadrupolar-glass state in bulk H_2 may hinge on the fact that the sharpest transitions are seen in samples which are probably strained, being grown around fine wires to assure good thermal contact. The present results are consistent with local strains favoring the formation of an orientational glassy state. In this regard it would be interesting to extend the present measurement to include samples which are annealed at, say 12—13 K prior to measurement.

At low values of x, separate peaks are discernible in the heat capacity (Fig. 4). By comparison with bulk[29,39] H_2 for $x<0.04$, we identify the peak at 1.2 K as a Schottky anomaly due to NN pairs and triplets of ortho-H_2, and the peak below 80 mK with a Schottky anomaly due to isolated ortho-H_2 with its degeneracy lifted by the local crystal field. The weak peaks at 0.4 and perhaps 0.15 K may be due to other small groups such as next-nearest-neighbor pairs, triplets, etc.

Samples annealed at temperatures below 400 °C, Fig. 2, exhibit sharper structure even on the first day after cooling from room temperature, as well as a relatively weaker contribution at 3—4 K. We take this as evidence that the as-prepared samples contain a relatively higher proportion of very small clusters (perhaps 2—5 H_4 molecules in each cluster), and these are not changed much by annealing below 400 °C. It is only above $T_A = 400\,^{\circ}\mathrm{C}$ that the clusters grow significantly. This picture is also consistent with the lower decay rate α (Fig. 4) for $T_A < 400\,^{\circ}\mathrm{C}$, as the lower average coordination number of very small clusters would decrease α according to Eq. (9).

C. Comparison with related materials

The present results are plotted in Fig. 8 with earlier heat-capacity measurements on related material. Data for the a-Si:H samples with the largest ($T_A = 500\,^{\circ}\mathrm{C}$, days 1 and 2) and smallest (bulk a-Si:H, day 20) time-dependent contributions are included to span the heat-capacity range of the present study. Also shown are data for pure[9,20] a-Si, and a-Si:H prepared[9] on a room-temperature substrate which presumably resulted in a very large amount of microstructure and relatively high hydrogen content. It is remarkable that all samples (except for $T_A = 500\,^{\circ}\mathrm{C}$) have the same C within a factor of 2 over the range 0.1—1 K, despite wide variations in hydrogen content and spin density. Furthermore, C for these samples is approximately a linear function of temperature in this range, reminiscent of the linear heat capacity observed in many insulating glasses.[10] The data are, in fact, very close to the contribution from two-level tunneling systems in bulk *a*-SiO_2 in this range of temperature. The origin of this quasilinear C in Fig. 8 is not known. The similarity of the data for various samples suggests a common origin which is neither hydrogen nor spins. We suggest that this contribution arises from two-level tunneling systems as have been found[8] in *a*-Ge, where they were correlated with the amount of microstructure. von Löhneysen and Schink,[5] on the other hand, have speculated that the reduction in C of *a*-Ge upon annealing is indicative of a magnetic origin[40] for the quasilinear component of C. We point out that while annealing decreases the spin density, it may also modify other properties such as the microstructure. Thus the decrease of C with annealing cannot be unambiguously ascribed to a magnetic origin.

The release of heat observed here bears a superficial similarity to the heat released[41,42] upon rapid cooling of disordered materials in the liquid-helium-temperature range, which has been attributed to relaxation of two-level tunneling systems. The present $\dot{Q}$, however, is reactivated only by heating the sample to ~100 K. Furthermore, the long-time behavior of $\dot{Q}$ observed here is t^{-2} rather than t^{-1}, and the magnitude of $\dot{Q}$ as well as the time scale over which $\dot{Q}$ is observable are 2—3 orders of magnitude larger than in the measurements on more traditional glasses. Finally, the similarity of the bimolecular decay constant deduced in our analysis and that of bulk hydrogen lend strong support to an interpretation in terms of ortho-para conversion of H_2.

VI. CONCLUSIONS

Low-temperature calorimetry measurements of high-quality films of *a*-Si:H have revealed a slow release of heat which has been ascribed to ortho-para conversion of clustered molecular hydrogen within the sample. Annealing studies suggest the following model: For samples deposited at substrate temperatures of $\sim 250\,^{\circ}\mathrm{C}$, ~ 0.1 mol % of H_2 is accumulated in microvoids of the material. This may occur, for example, through diffusion of atomic hydrogen within the bulk of the film *during* deposition, resulting in a collection of the H in microvoids where it combines to form H_2. Annealing at temperatures above 400 °C allows atomic hydrogen in the bulk of the material to diffuse even more readily at these higher temperatures and to be similarly trapped in microvoids, forming even larger clusters of at *least* 10—20 molecules each, as deduced from the duration of the bimolecular conversion. These clusters may fill microvoids of ≥ 10 Å in diameter, with an average concentration of 0.5 mol % relative to the Si. At yet higher annealing temperatures, $T_A > 500\,^{\circ}\mathrm{C}$, the amount of H_2 trapped in microvoids is reduced, presumably by diffusion out of the sample.

The specific heat of *a*-Si:H contains a large, time-dependent contribution which is proportional to the number of ortho-H_2 molecules present. A broad peak above ~2 K is indicative of the short-range order of the ortho-H_2 within each cluster due to electric-quadrupole—quadrupole interactions, as in bulk solid hydrogen. The rapid decrease of C below 2 K is in marked contrast to solid hydrogen, which for large ortho concentration displays a sharp peak associated with a first-order transition to a state of long-range rotational order. The lack of long-range rotational order in the clusters is due to their small size and the probable positional disorder of the molecules. The residual entropy of the ortho-H_2 remaining in the clusters at 0.1 K is more than half of the total rotational entropy at high temperatures, even for large ortho concentrations. Thus we have strong evidence that a quadrupolar-glass state is present locally in the clusters at temperatures below ~2 K for all ortho concentrations.

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