Molecular relaxation versus orientational ordering of H_2 in a-Si:H

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Recently reported experimental results on a-Si:H have led to suggestions that H_2 in the microvoids of a-Si:H undergoes a phase transition to an orientational ordered state at temperatures ranging from 3 to 20 K. The interpretation is based upon the onset of a Pake doublet in NMR experiments that is suggestive of an order parameter and also by peaks in the heat capacity of H_2 in a-Si:H. We show that orientational ordering of microvoid H_2 is extremely unlikely at any temperature and certainly not above the critical temperature of bulk single-crystal H_2. Instead we shall show that the observed Pake doublet is a manifestation of the slow molecular relaxation regime and that the heat capacity can be explained entirely by a distribution of electric field gradients. Neither phenomenon requires a phase transition driven by the electric quadrupole-quadrupole molecular interactions. However, the sharp onset of the Pake doublet reflects the size and surface conditions of the microvoids.

Recent experimental results have shown that the molecular hydrogen contained in a-Si:H exhibits some remarkable properties. For example, it is subject to effective pressures of about 2 kbar,[1] it remains at liquid densities up to temperature well above room temperature,[2,3] and the temperature at which freezing occurs is considerably higher[3] than in bulk H_2. It also has been suggested that H_2 in the microvoids undergoes a phase transition into an orientationally ordered state at temperatures ranging from 3 to 20 K. These suggestions are based upon heat-capacity measurement[4] and, more dramatically, upon the observation of a Pake doublet in NMR studies.[2]

In this paper we shall argue that orientational ordering of the H_2 in the microvoids is unlikely to occur at any temperature and certainly not above the critical temperature of single-crystal bulk normal H_2 ($n-H_2$). Here we are using the standard definition of orientational ordering below a certain critical temperature which describes a long-range ordering of the molecular quadrupole moments driven by interparticle interactions that in this case are the electric quadrupole-quadrupole (EQQ) interactions between the H_2 molecules.[5,6] Further, a spin-glass state (driven by interparticle interactions) is unlikely unless the voids are very large. Instead we shall show that the Pake doublet observed in a-Si:H arises from a slowing down of the phonon induced relaxation rate among the molecular m_j states and not from the EQQ interactions. This picture, in turn, yields some interesting insights into the elastic coupling of the H_2 molecules to the rest of the a-Si:H. Further, we show that the measured excess heat capacity arises from the electric field gradients (EFG's) acting on the H_2 molecules and again, not from the EQQ interactions.

It has been demonstrated[7,8] that H_2 near the surfaces of microvoids is responsible for the relaxation of the bonded H nuclear spin in NMR measurements. These H_2 molecules must experience EFG's that yield energy splittings large compared to those produced by the EQQ interactions. This effectively quenches the EQQ interactions[7]

and yields the observed[8] phonon-dominated molecular relaxation rate instead of the much larger and temperature-independent rate[9] that the EQQ interactions would induce. For the quenching to be effective the EFG's acting on the molecules must be large and random in direction. Thus the dominant term in determining the low-temperature angular momentum properties of the H_2 molecules is associated with the static EFG's and the smaller EQQ interactions can be treated as a perturbation. The situation is quite similar to that of a system of spins with large random magnetic fields at each site and smaller exchange interactions. This condition does not lead to orientational ordering even though each individual spin may be ordered by the magnetic field if its Zeeman energy is large compared to $k_B T$. There is no long-range order, the effect does not arise from interparticle interactions, and there is no transition temperature. This system cannot be described as a spin glass either since a spin glass exhibits short range order due to interparticle interactions. The amount of short-range order (if any) in the H_2 system is due to correlations in the magnetic field. The heat capacity of this model system will exhibit a broad maximum whose width in temperature is at least as large as the peak temperature. The heat capacity of a single H_2 molecule in an axial electric field gradient is

$$(dE/dT) = 2kx^2 e^{-x}/(2 + e^{-x})^2 ,$$
$$x = \beta E_0 ,$$

(1)

where E_0 is the energy of the $m = 0$ state with respect to the $m = \pm 1$ state. This function is plotted in Fig. 1 for $E_0 > 0$ and $E_0 < 0$. Any distribution of electric field gradients will, of course, broaden the peak. In fact this gives a reasonable picture of the data in Ref. 4 which show no evidence of a sharp ordering peak.

The molecules in the interior of the voids will experience a different environment that probably includes smaller EFG's. However, it will be much more difficult for these molecules to orientationally order than molecules in
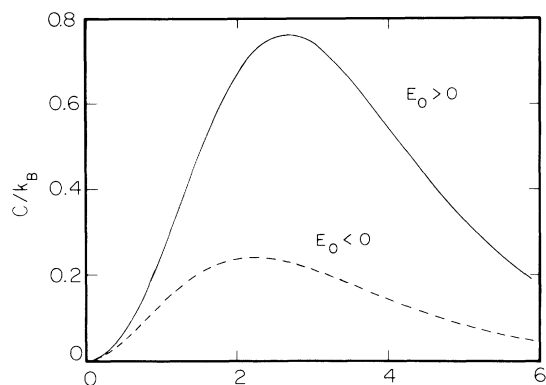

FIG. 1. Heat capacity of a single H_2 molecule as described by Eq. (1) plotted versus $y = (E_0/k_B T)$: $E_0 > 0$ (———) and $E_0 < 0$ (— — —).

bulk crystalline H_2. One reason is that there will be remnants of the random EFG's from the walls that are still very large. More important, it is unlikely that the solid H_2 in the microvoids is in a crystalline form unless the voids are very large. If it is amorphous any tendency toward orientational ordering will be suppressed in two different ways. First, each H_2 will experience a large static EFG because of crystalline anisotropy. Second, since the EQQ interactions have a strong angular dependence, the amorphous nature of the structure will lead to massive frustration. This is a much more important effect with the EQQ interactions than with the dipolar interaction that is not as angular dependent. As an example of the strength of the frustration in this problem we note that solid bulk H_2 has a critical temperature $T_c = 2.8$ K at an ortho concentration of $x = 1$. However T_c drops to 1.6 K at $x = 0.75$ (the concentration for n-H_2) and to 0 K at $x = 0.55$. For these reasons the T_c of the H_2 in the voids will be lowered far below the value $T_c = 1.6$ K of n-H_2 and it is very doubtful that the ordered phase can exist at all. Furthermore, annealing should decrease the EFG's and frustration and thus will raise T_c, not lower it as was observed.[2]

On the other hand Boyce and Stutzmann[2] did observe a Pake doublet and the amplitude of this doublet as a function of temperature is very suggestive of an order parameter in that it rises steeply as T goes below T_c and then levels off as T is lowered further. However, it should noted that in low temperature bulk H_2 it is the frequency of the Pake doublet and not the amplitude that is proportional to the order parameter.[6] The amplitude of the bulk H_2 doublet does not exhibit the characteristic temperature dependence of the order parameter.

Instead, we believe that the onset of the Pake doublet in a-Si:H is a manifestation of the slow molecular relaxation (SMR) regime. That is Γ_m, the relaxation rate between the states of different m_j for the $J = 1$ molecular states, decreases rapidly with decreasing temperature. As Γ_m passes below ω_d, the nuclear spin-molecular coupling frequency, a Pake doublet appears in the spectrum. The peak-to-peak width of this doublet is $3\omega_d$, no matter what $\langle 3J_z^2 - 2 \rangle$ is, as long as the molecular site has a symmetry

lower than axial. However, even though the width of this doublet is constant, the amplitude of the doublet is a sensitive function of Γ_m/ω_d. Since Γ_m varies as T^7 at low temperatures,[8] the ratio Γ_m/ω_d can change by an order of magnitude as T changes by only 40%. This will lead to a very sharp onset of the Pake doublet as is observed. Computed line shapes[10] as a function of Γ_m/ω_d are in Fig. 2. Finally we note that the phonon dominated Γ_m is conclusive evidence that the EQQ interactions are quenched because otherwise one should observe a T_1 that is independent of temperature.

It should be noted that the phenomena discussed in the above paragraph does not occur in bulk H_2 because in that case Γ_m is dominated by the EQQ interactions and thus remains much larger than ω_d. In this case the splitting of the Pake doublet is proportional to the order parameter or $\langle 3J_z^2 - 2 \rangle$.[5,6]

Boyce and Stutzmann observed the onset of the Pake doublet at a temperature $T_p = 10$ K for the annealed sample and $T_p = 20$ K for their unannealed sample. By assuming that

$$\Gamma_m = AT^7 , \tag{2}$$

we can obtain A and compare it to the A's of other systems. As a standard we shall use A_0, the value of A obtained by Leopold et al.[8] for surface H_2 in a-Si:H. By using the onset of the Pake doublet for a criterion we find that A / A_0 is 0.02 for the Boyce and Stutzmann annealed sample and is 0.002 for their unannealed sample. As a further comparison we note that A / A_0 for isolated H_2 in Ne is 35 and the ratio is 3.5 for isolated H_2 in Ar. In fact, as will now be argued, the increase in A due to annealing is to be expected.

There is a large acoustic impedance mismatch between Si and H_2 because of the great difference in their mass densities. Thus the amplitude of elastic waves in a-Si will be severely decreased in an H_2 cluster, only the surface H_2 layer will be well coupled to the bulk H_2, and the spectral weight at the interior H_2 sites will be made up of modes that are mostly localized within the cluster. For small
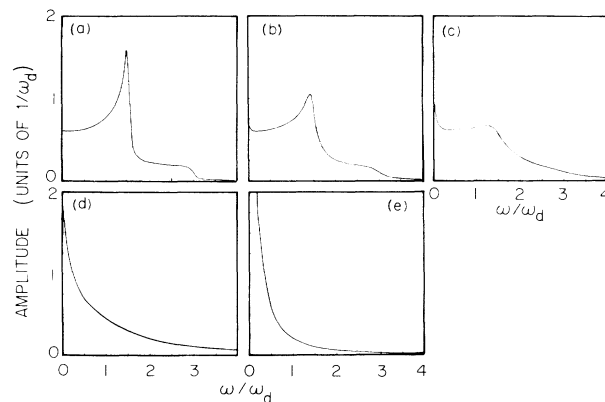

FIG. 2. Computed line shapes for an H_2 molecule in an environment of no symmetry and $\langle A_{20} \rangle = 0$. The values of Γ_m/ω_d are 0.1, 0.3, 1.0, 3.0, and 10.0 for panels (a), (b), (c), (d), and (e), respectively.

clusters the density of states will be very spikey with some broadening due to the surrounding material. As the size of the cluster increases, the local density of states will approach that of solid H_2.

The Debye temperature of bulk H_2 is 120 K which is a good measure of the range of phonon energies in the material. The energy levels for a pair of H_2 molecules at the typical interatomic spacing are split up to 10 K and this sets the scale for typical EQQ energies. If there are large EFG's, the splitting will be even larger. Thus, in small clusters, very few of the locally spikey elastic modes will have the right frequency difference to relax the H_2 molecules by the usual Raman process and thus relaxation rates Γ_m will be quite small compared to Γ_m for isolated H_2 in nonmagnetic hosts at the same temperature. As the cluster grows the spikey nature of the density of states will smooth out and the molecular relaxation rate will increase. Thus, T_p the temperature at which the Pake doublet appears will decrease.

In fact, the approximate T^7 as well as the increase of A upon annealing may well have been observed.[11] That is, at low enough temperatures so that $\Gamma_m \ll \omega_0$ (where ω_0 is the Lamor frequency) T_1 is proportional to $1/\Gamma_m$ while T_1 is proportional to Γ_m at higher temperatures where $\Gamma_m \gg \omega_0$. The substantial decrease of T_1 at low temperatures and a modest increase of T_1 at higher temperatures after annealing has been observed in the sample in Ref. 1. This can most easily be explained by an increase in A and an increase in the ratio of the number of H_2 molecules to the number of bonded H's.

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