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Dense H_2 and proton NMR in *a*-Si:H

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A model is proposed which resolves an apparent paradox in the results and interpretation of various experiments detecting H and H_2 in *a*-Si:H. A number of measurements indicate that the H_2 in *a*-Si microvoids is at densities of the order of the density of solid H_2. However, at these densities, the electric quadrupole-quadrupole (EQQ) interactions between molecules in bulk fluid or solid H_2 dominate the nuclear spin relaxation $T_1(H_2)$ and its temperature dependence in such a way that it cannot be used to explain the proton NMR $T_1(H)$ relaxation results for Si-bonded H. In order to fit the *a*-Si:H relaxation data it is necessary that the effective EQQ interaction varies widely among H_2 in *a*-Si:H. The $T_1(H)$ relaxation in *a*-Si:H arises from interaction with that part of the adsorbed H_2 fraction which has a small effective EQQ.

There is an apparent paradox associated with the molecular hydrogen trapped in microvoids in hydrogenated amorphous silicon. The dense fluid and solid $H_2(D_2)$ which has been detected in *a*-Si:H(D) in recent calorimetric,[1-3] infrared,[4,5] and NMR[6-9] measurements cannot, for the most part, be the molecular hydrogen responsible for the observed nuclear spin-lattice relaxation $T_1(H)$ of silicon-bounded atomic hydrogen.[10-12] The temperature dependence, magnetic-field dependence, and magnitude of the relaxation all disagree with those which would follow from relaxation via dense fluid and solid H_2.

The original reason for proposing that H_2 exists in *a*-Si:H was that the temperature dependence and magnetic-field dependence of the proton $T_1(H)$ closely resembled those for the phonon-dominated and much faster proton $T_1(H_2)$ of isolated H_2 molecules in nonmagnetic hosts.[13,14] $T_1(H_2)$ in the normal solid or dense fluid phases of H_2 is very different from that for dilute H_2 because of the EQQ interactions between *o*-H_2 molecules in the dense material. The *a*-Si:H NMR $T_1(H)$ results require relaxation via effectively isolated *o*-H_2 molecules with no significant EQQ interactions between them, while the ortho-to-para conversion results, infrared results, and NMR spin counts, indicate H_2 at roughly solid densities. Our proposed resolution to this paradox is that the relaxation-center *o*-H_2 molecules are a part of those dominated by contact with the silicon surfaces, have their intermolecular EQQ interactions quenched, and thus are effectively dilute insofar as nuclear relaxation is concerned.

It now is generally accepted that for most samples of plasma-deposited *a*-Si:H, ≤ 0.1 at.% H_2 located in microvoids act as the dominant nuclear spin-lattice relaxation centers[9-11] (between 3–300 K) for protons bonded into the *a*-Si structure. The proton magnetization diffuses to rapidly relaxing effectively dilute *o*-H_2 molecules, where it then relaxes to the lattice. If this dipolar spin diffusion is fast enough, the temperature variation of $T_1(H)$ is proportional to that which would have been anticipated[10,13] for $T_1(H_2)$ of the uncoupled *o*-H_2 relaxation centers. The resulting observed $T_1(H)$ characteristically shows a phonon-related power-law minimum located between 25–55 K. The $T_1(H)$ minimum is deeper[9,12] for samples known to have microstructure and hence more absorbed H_2.

The open symbols in the upper part of Fig. 1 show such $T_1(H)$ results reported by Boyce and co-workers[15,16] for lattice-bound protons in a high-quality unannealed *a*-Si:H sample deposited from 100% SiH_4 at low-power density (0.025 W/cm^2) onto an Al substrate heated to 230 °C. This is the same unannealed sample in which Boyce and Stutzmann[8] have observed the Pake-doublet spectrum for oriented *o*-H_2 molecules in solid H_2 in the voids below 20 K. The open triangles show $T_1(H)$ for 92.5 MHz and the open circles show $T_1(H)$ for 46 MHz. The 92.5-MHz data in fact extend[16] to 2 K at which temperature $T_1(H)$ has in-

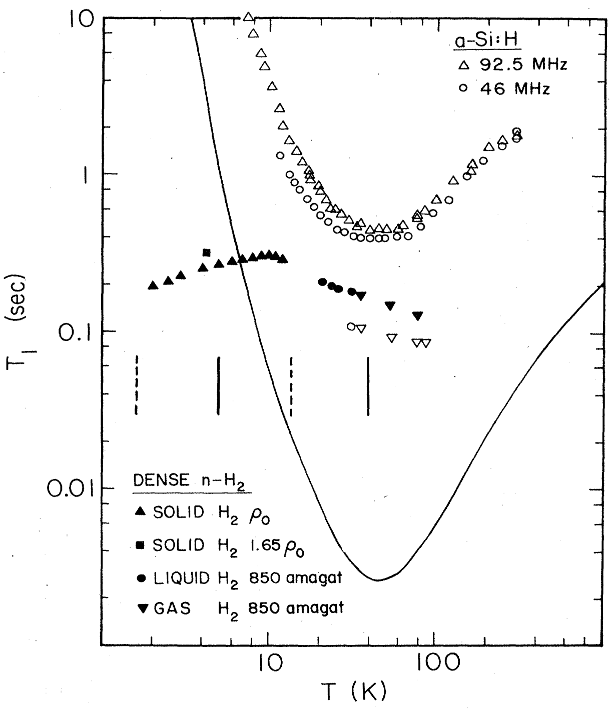

FIG. 1. Proton-relaxation times observed for bonded H in a plasma-deposited sample of *a*-Si:H are compared with those reported for isochoric solid H_2 and dense fluid H_2. The curved line indicates $T_1(H_2)$ calculated for effectively isolated *o*-H_2 at 92.5 MHz and under conditions described in the text. The dashed vertical lines indicate the spin-ordering transition for *o*-H_2 and the melting temperature for bulk H_2 at zero pressure. The solid vertical lines indicate corresponding transitions in the *a*-Si:H sample.

creased to 600 sec. Analysis of the temperature dependence of $T_1(\mathrm{H})$ above 150 K in this sample has led to the conclusion[17,18] that the relaxation-center o-H_2 molecules in this case are located in sites with large static electric-field gradients (EFG) of low symmetry. The curved solid line shows the relaxation time $T_1(\mathrm{H}_2)$ calculated[13] for effectively dilute o-H_2 at 92.5 MHz and with a T_1 minimum at 48 K. The calculation has assumed large static electric-field gradients of no symmetry with parameters[14] $r=0$ and $\Theta_c=40$ K. The deviation from a T^2 temperature variation of $T_1(\mathrm{H}_2)$ above 150 K is that characteristic[17,18] for EFG of no symmetry. The minimum value of $T_1(\mathrm{H}_2)$, here determined only by ω_0 and the EFG symmetry, is 2.6 msec.

The solid symbols in Fig. 1 show, for comparison, EQQ-dominated spin-lattice relaxation times $T_1(\mathrm{H}_2)$ observed in bulk solid n-H_2 and in dense fluid n-H_2 at 850 amagat. The solid triangles indicate the frequency-independent 6.8- and 12.8-MHz results of Amstutz, Meyer, Myers, and Mills[19] for solid n-H_2 at the usual solid density $\rho_0=790$ amagat. The solid square indicates the 4.2 K $T_1(\mathrm{H}_2)$ for solid H_2 with $x=0.67$ compressed[20] to $1.65\rho_0$ (at some 7 kbar). The solid circles and inverted triangles indicate the Lipsicas and Hartland[21,22] 30-MHz $T_1(\mathrm{H}_2)$ observed for liquid and gas n-H_2 compressed to 850 amagat. The lower open circles and inverted triangles indicate corresponding $T_1(\mathrm{H}_2)$ results for fluid n-H_2 at 650 amagat. The dashed vertical lines indicate for saturated vapor pressure (SVP) bulk n-H_2 the usual $T_c=1.6$ K temperature of o-H_2 orientational ordering and the usual melting point, $T_m=13.6$ K. Below 1.6 K the relaxation time $T_1(\mathrm{H}_2)$ increases[23,24] by a factor of 10^3 in an 0.8 K interval as the o-H_2 molecules freeze out into the $m_J=0$ state. The solid vertical lines indicate the much-increased corresponding approximate transition temperatures observed[8] for H_2 in the unannealed a-Si:H sample of Fig. 1. T_c for much of the H_2 increases to $\simeq 10$ K and melting occurs over an interval from about 20 K up to the 40 K indicated. Even with the bulk H_2 data shifted and averaged in temperature, it is apparent that there is no similarity between the temperature variations of the proton-relaxation times $T_1(\mathrm{H})$ for the a-Si:H and those of $T_1(\mathrm{H}_2)$ for the isochoric solid and dense fluid n-H_2 at densities near those proposed for H_2 in a-Si:H. The bulk H_2 results exhibit no $T_1(\mathrm{H}_2)$ minimum and are independent of Larmor frequency. Proton spin systems in thermal equilibrium with each other relax as a single entity with a common relaxation rate $\Gamma=T_1^{-1}$ given by

$$\Gamma=\frac{\Sigma_l C_l\Gamma_l}{\Sigma_l C_l} , \tag{1}$$

where the C_l are the spin-heat capacities of the various proton systems (H or H_2) with relaxation rates Γ_l. Clearly, bulk dense H_2 in the voids cannot provide the necessary relaxation centers responsible for the observed $T_1(\mathrm{H})$ of the bonded H in amorphous silicon.

The numerical discrepancies associated with the disagreement are significant. More importantly, there are major qualitative discrepancies evident in Fig. 1 for the dependence of relaxation on magnetic field and temperature. The nuclear $T_1(\mathrm{H}_2)$ of isolated H_2 molecules in a host lattice is a function of Γ_m, the molecular relaxation rate. The temperature dependence of the nuclear spin relaxation arises from the tempeature dependence of Γ_m and the nuclear T_1 depends on the magnetic field when the frequency ω_0 of the NMR experiment is larger than Γ_m. For isolated H_2 molecules in a nonmagnetic host, Γ_m is dominated by the (molecular) spin-phonon interaction. However, with an appreciable density of o-H_2 molecules the intermolecular EQQ interactions dominate. Ebner and Myles[25] have performed extensive calculations for nuclear spin-lattice relaxation in solid H_2. Their results can be approximated by the expression

$$T_1(\mathrm{H}_2)=0.5(\rho/\rho_0)^{5/3}\ \mathrm{sec} , \tag{2}$$

where ρ is the density of o-H_2 and ρ_0 is the 790-amagat density of solid H_2. For n-H_2 at ρ_0, Eq. (2) yields $T_1(\mathrm{H}_2)\simeq 0.3$ sec in reasonable agreement with the solid and liquid $T_1(\mathrm{H}_2)$ data in Fig. 1. Using the methods of Ref. 13, Eq. (2) yields an EQQ-induced temperature-independent molecular relaxation rate $\Gamma_m=\Gamma_Q$

$$\Gamma_Q=2.6\times10^{12}(\rho/\rho_0)^{5/3}\ \mathrm{sec}^{-1} . \tag{3}$$

At densities near that of the solid, $\Gamma_Q >> \omega_0$ and $T_1(\mathrm{H}_2)$ is nearly independent of magnetic field and temperature at any frequency employed in a reported NMR experiment. The small temperature dependence of the solid and liquid H_2 $T_1(\mathrm{H}_2)$ data in Fig. 1 principally arises from motional narrowing of the Γ_Q EQQ contribution to Γ_m. At 36 K and 850 amagat the coefficient of self-diffusion[21] in fluid H_2 is 2.1×10^{-4} cm^2/sec. This corresponds to a molecular-diffusion motional-correlation frequency near 10^{12} sec^{-1}, of the order of the rigid lattice EQQ rate and more than 10^3 times larger than ω_0. In addition, the observed $T_1(\mathrm{H})$ in typical a-Si:H samples requires the presence of o-H_2 relaxation centers at concentrations significantly smaller than the 0.5–5 at.% deduced[1-9] for bulk H_2 in the voids. For the sample shown in Fig. 1 Boyce and Stutzmann[8] have reported 0.1 at.% H_2 from an analysis of $T_1(\mathrm{H})$, but 0.25 at.% H_2 from the Pake-doublet oriented-H_2 signal intensity. In an annealed sample they found 0.2 and 1.0 at.% H_2, respectively.

The nuclear relaxation paradox is resolved if the wide distribution of characteristics for H_2 in a-Si:H voids includes a wide distribution of EQQ interactions, with small EQQ more probable for the H_2 fraction in contact[5] with the Si void surfaces. For some of these molecules large surface-related static EFG much greater than EQQ can vary appreciably between nearby o-H_2. This effectively quenches the EQQ interaction and results in a small rate $\Gamma_Q << \omega_0$. For such o-H_2 the phonon-induced temperature-dependent molecular rate $\Gamma_m(T)$ can vary through ω_0 and produce a $T_1(\mathrm{H}_2)$ minimum with a power-law temperature dependence similar to that characteristic[10-14] of isolated o-H_2 molecules in a solid nonmagnetic host. These surface-relaxation-center H_2 usually are present at concentrations[9,12] $\leqslant 0.1$ at.%. Although the effective EQQ is small (because of the large surface EFG), these surface o-H_2 have significant numbers of near neighbors so that ortho-to-para conversion takes place via the bimolecular process at the rate observed[26] from proton NMR. In fact large EFG's have been observed for H_2 on zeolite surfaces,[27] in contrast with the much smaller EFG's inferred[28] for H_2 on grafoil surfaces. If an appreciable fraction of the H_2 is adsorbed on internal Si surfaces, then the pressure needed to hold it at large density is greatly reduced. The ortho-to-para conversion-rate constant observed[26] for the relaxation-center o-H_2 in one a-Si:H sample was 0.010 h^{-1}. This is in reasonable agreement with the 0.017 h^{-1} determined[5] (in another sample) for infrared components associated with H_2 in contact with the Si surfaces of voids and in contrast with the 0.07 h^{-1} characteristic[5] of H_2 not in contact with the void surfaces.

A second H_2 species from the point of view of proton relaxation, includes those surface H_2 for which the EFG do not vary appreciably between H_2 sites and the H_2 in the volumes of larger voids for which the same thing is true. In these cases EQQ remains large; there is a large corresponding molecular rate $\Gamma_Q >> \omega_0$; there can be no $T_1(H_2)$ minimum, and the intrinsic $T_1(H_2)$ given by Eq. (2) remains long (~ 0.3 sec) compared with that for the relaxation-center o-H_2 at all temperatures between a few and 300 K.

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

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

[3] J. E. Graebner, L. C. Allen, and B. Golding, Phys. Rev. B **31**, 904 (1985).

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

[5] Y. J. Chabal and C. K. N Patel, Phys. Rev. Lett. **53**, 1771 (1984).

[6] B. Lamotte, Phys. Rev. Lett. **53**, 576 (1984).

[7] C. G. Fry, T. M. Apple, and B. C. Gerstein (unpublished).

[8] J. B. Boyce and M. Stutzmann, Phys. Rev. Lett **54**, 562 (1985).

[9] D. J. Leopold, B. S. Coughlan, P. A. Fedders, R. E. Norberg, J. B. Boyce, and J. C. Knights, J. Non-Cryst. Solids **66**, 121 (1984).

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

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

[12] D. J. Leopold, P. A. Fedders, R. E. Norberg, J. B. Boyce, and J. C. Knights, Phys. Rev. B (to be published).

[13] P. A. Fedders, Phys. Rev. B **20**, 2588 (1979).

[14] M. S. Conradi, K. Luszczynski, and R. E. Norberg, Phys. Rev. B **20**, 2594 (1979).

[15] J. B. Boyce and M. J. Thompson, J. Non-Cryst. Solids **66**, 127 (1984).

[16] J. B. Boyce, M. Stutzmann, P. A. Fedders, and R. E. Norberg (unpublished).

[17] R. E. Norberg, Phys. Rev. B (to be published).

[18] P. A. Fedders, Phys. Rev. B **30**, 3603 (1984).

[19] L. I. Amstutz, H. Meyer, S. M. Meyers, and R. L. Mills J. Phys. Chem. Solids **30**, 2693 (1969).

[20] P. L. Pedroni, R. Schweizer, and H. Meyer, Phys. Rev. B **14**, 896 (1976).

[21] M. Lipsicas and A. Hartland, Phys. Rev. **131**, 1187 (1963).

[22] M. Lipsicas and A. Hartland, J. Chem. Phys. **44**, 2839 (1966).

[23] S. Washburn, M. Calkins, H. Meyer, and A. B. Harris, J. Low Temp. Phys. **53**, 585 (1983).

[24] A. B. Harris, Phys. Rev. B **2**, 3495 (1970).

[25] C. Ebner and C. W. Myles, Phys. Rev. B **12**, 1638 (1975).

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

[27] P. Monod, J. A. Cowen, and W. N. Hardy, J. Phys. Chem. Solids **27**, 727 (1966).

[28] P. R. Kubik and W. N. Hardy, Phys. Rev. Lett. **41**, 257 (1978).