that reported for the average over the entire sample. This may be observable as a sharp increase in the intensity of RS over a narrowed excitation-frequency range from a surface containing more nearly uniform metal features.

We wish to acknowledge useful discussions with A. Nitzan.

---

[1] M. Fleischman, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. 26, 123 (1974); D. L. Jeanmaire and R. P. VanDuyne, J. Electroanal. Chem. 84, 1 (1977).

[2] E. Burstein, C. Y. Chen, and S. Lundquist, in *Light Scattering in Solids*, edited by J. L. Birman, H. Z. Cummins, and K. K. Rebane (Plenum, New York, 1979).

[3] J. F. Evans, M. G. Albrecht, D. M. Ullevig, and R. M. Hexter, J. Electroanal. Chem. 106, 209 (1980).

[4] J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, Phys. Rev. Lett. 44, 1770 (1980).

[5] A. Z. Genack, D. A. Weitz, and T. J. Gramila, to be published.

[6] J. A. Creighton, C. G. Blatchford, and M. G. Albrecht, J. Chem. Soc. Faraday Trans. II 75, 790 (1979).

[7] R. W. Rendell, D. J. Scalapino, and B. Mühlschlegel, Phys. Rev. Lett. 41, 1746 (1978).

[8] J. C. Tsang, J. R. Kirtley, and J. A. Bradley, Phys. Rev. Lett. 43, 772 (1979).

[9] M. Moscovits, J. Chem. Phys. 69, 4159 (1978), and Solid State Commun. 32, 59 (1979).

[10] J. I. Gersten and A. Nitzan, to be published.

[11] J. I. Gersten, D. A. Weitz, T. J. Gramila, and A. Z. Genack, to be published.

[12] G. Ritchie, C. Y. Chen, and E. Burstein, Bull. Am. Phys. Soc. 25, 259 (1980).

Hydrogen-Associated Disorder Modes in Amorphous Si:H Films

W. E. Carlos and P. C. Taylor
Naval Research Laboratory, Washington, D. C. 20375

(Received 17 March 1980)

NMR spin-lattice relaxation rates T_1^{-1} of ^{1}H in a-Si:H films exhibit a maximum near 40 K. Both the magnitude, the temperature, and frequency dependences of T_1 are well described by a model which assumes a coupling to disorder modes which are associated with some hydrogen atoms. Results suggest that some hydrogen sites may contribute to the electronic states within the gap.

PACS numbers: 63.50.+x, 61.40.Df, 72.80.Ng, 76.60.Es

The existence in many amorphous solids of atoms or groups of atoms which at low temperatures can exist in two positions of local equilibrium is well documented.[1] Such disorder modes are a common feature of oxide and chalcogenide glasses, but they have yet to be observed[2] in amorphous Ge, Si, or Si:H.

In this Letter we report pulsed ^{1}H NMR experiments which indicate the presence of disorder modes associated with hydrogen in a-Si:H. We propose a model which explains both the magnitude and the temperature and frequency dependences of the spin-lattice relaxation time T_1 for the hydrogen atoms. Because the disorder modes may also influence the electronic properties of an amorphous solid,[3] the present results suggest some interesting new considerations for both the defects and electronic densities of states in a-Si:H.

Samples were obtained from several different sources and contained between 7 and 15 at.% H. All samples were deposited on heated substrates (250–330 °C) at relatively slow rates (~ 300 Å/min) by use of pure silane gas. Sample thicknesses ranged from 1 to 10 μm. All samples were found by ESR measurements to be free of detectable paramagnetic impurities except for the usual "intrinsic" signal whose magnitude varied between ~ 10^{14} and 10^{16} spins per cubic centimeter. Other common impurities, oxygen and nitrogen, varied between about 2 and 0.2 at.% and between 0.1 and 0.01 at.%, respectively. Voids were seen in some samples by use of small-angle x-ray scattering[4] but no microstructure was seen by electron microscopy.[1]

The ^{1}H pulsed NMR data were taken with a standard setup. Frequencies were varied from ~ 10 to ~ 42 MHz and temperatures from ~ 4 to ~ 475 K. Spin-lattice relaxation time (T_1) measurements were taken on the free-induction-decay (FID) signal with a repetition-rate technique.[5] All decay curves were exponential within experimental error.

NMR samples were made by dissolving away the aluminum foil or glass substrates in dilute hydrochloric or hydroflouric acids, respectively. Also, some samples on glass substrates were scraped off. There were no differences in either T_1 measurements or NMR line shapes which could be attributed to the method used to prepare the NMR samples. Typical samples contained between 10 and 50 mg of a-Si:H.

Some subtle differences were observed in both the NMR spectra and the spin-lattice relaxation rates T_1^{-1} among the samples studied, but in this Letter we shall focus primarily on those features which are common to all films. For simplicity we restrict the data to those measurements performed on one representative sample which was obtained from RCA.

Figure 1 illustrates the FID signal observed in the RCA sample at 4.2 K. The transformed line shape in frequency space is indicated in the inset. There are two components to the line shape shown in Fig. 1, a broad Gaussian line (curved portion at short times) superimposed on a narrow Lorentzian line (exponential decay at long times). The intensities of the broad and narrow lines correspond to ~ 9 and ~ 3 at.% H, respectively, and the full linewidths at half maximum are $\sigma = 25.7$ and 3.8 kHz, respectively. These results are very similar to those reported previously by Reimer, Vaughan, and Knights,[6] who observed two overlapping, but distinct, hydrogen lines. In all our samples the broad line is Gaussian and the narrow line has a Lorentzian shape, whereas in the earlier measurements[6] both lines were observed to be Gaussian.[7] "Solid echo" experiments[8] indicate that there is little spectral diffusion between the two hydrogen sites and that the linewidths are dominated by homonuclear dipolar interactions as previously reported by Reimer, Vaughan, and Knights.[6] The magnitudes of the two linewidths indicate that the hydrogen atoms on both types of sites are clustered.

The temperature dependence of the ^{1}H spin-lattice relaxation times T_1 is displayed in Fig. 2 for two operating frequencies, $v_0 = 42.3$ and 12.3 MHz. While there exist two distinct hydrogen NMR sites in a-Si:H, both sites exhibit spin-lattice relaxation rates which are identical within experimental error (± 10%). The chief features

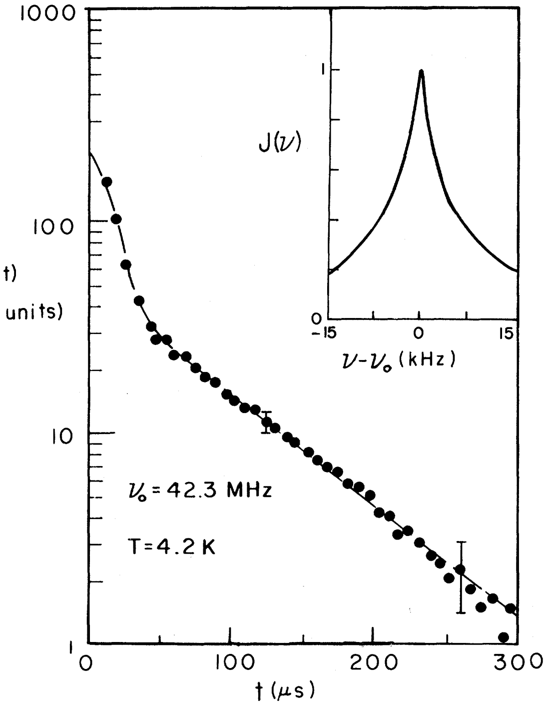

FIG. 1. ^{1}H NMR free induction decay in a-Si:H at 4.2 K (semilogarithmic scale). Circles represent experimental data. Inset: transformed frequency spectrum (linear scale).

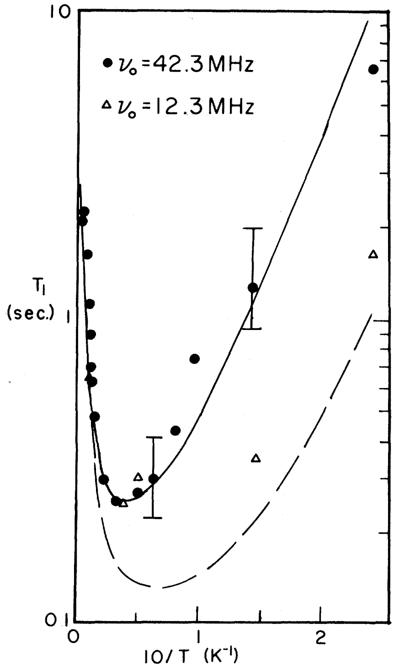

FIG. 2. Temperature dependence of ^{1}H spin-lattice relaxation time T_1 in a-Si:H at two frequencies. Curves represent fits to the data with the model described in the text.

seen in Figs. 2 and 3 are (1) an asymmetric minimum in T_1 at a temperature T_M near 40 K which is relatively insensitive to v_0, and (2) a strong dependence of T_1 on v_0 for $T < T_M$ which is suppressed for $T > T_M$.

In solids three physical processes are known to produce a minimum in T_1 as a function of T—physical diffusion of nuclei, Raman-like processes involving disorder modes and phonons,[9] and rapidly relaxing paramagnetic impurities. The first process can be eliminated for a-Si:H because there is no significant narrowing of the line shapes at temperatures above the temperature of the T_1 minimum, T_M. The second process, which involves a modulation of the chemical-shift term of the Hamiltonian by the disorder modes, predicts[9,10] that T_1 is essentially independent of v_0 contrary to our results. The third process requires ~ 10^{19} cm^{-3} randomly distributed paramagnetic impurities whose relaxation rates near 40 K are ~ 10^{-8} sec to produce a minimum in T_1 near 40 K of ~ 0.3 sec. The only paramagnetic impurities likely to exhibit relaxation rates in this range are non-s-state transition metals. However, our low-temperature ESR results, as well as other diagnostic techniques such as secondary-ion mass spectroscopy,[11] place an upper bound of 10^{17} cm^{-3} of paramagnetic impurities.

To explain the data of Figs. 2 and 3 we propose a new mechanism in which we postulate the existence of disorder modes associated with a small fraction of the hydrogen atoms (perhaps 10^{16}–10^{18} cm^{-3}) and suggest that hopping over the potential barrier which separates the two equilibrium positions of the disorder modes provides both a relaxation to the lattice and a modulation of the dipolar interaction. This modulation directly relaxes those nuclei closest to the disorder mode. The relaxation then proceeds via proton-proton spin diffusion to the bulk of the ^{1}H sites. This process is similar to ordinary relaxation via paramagnetic impurities[12] except for the following significant differences: (1) For paramagnetic impurities the direct relaxation rate is much faster than the spin diffusion process for nuclei close to the impurity while for the case of hydrogen-associated disorder modes the two rates can be comparable for nuclei adjacent to the disorder mode; (2) for paramagnetic impurities the direct process is driven by electron spin relaxation of the impurity to the lattice while for hydrogen-associated disorder modes the process is driven by relaxation of the two-level (pseudospin) disorder mode which rapidly relaxes the hydrogen associated with the disorder mode and modulates the dipolar interaction with surrounding hydrogen nuclei.

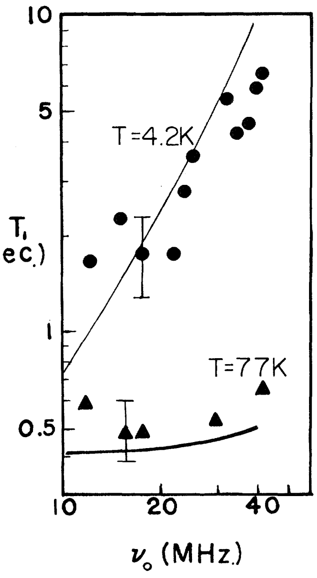

FIG. 3. Frequency dependence of ^{1}H spin-lattice relaxation time T_1 in a-Si:H at two temperatures. Curves represent fits to the data with the model described in the text.

The direct relaxation rate for nuclei next to a disorder mode is easily calculable and is of the form

$$1/T_1^D = R \cong \gamma^2 h_0^2 \tau/(1+\omega_0^2\tau^2), \qquad (1)$$

where h_0 is the fluctuating magnetic field due to the hydrogen on the tunneling mode, γ is the nuclear gyromagnetic ratio for ^{1}H, $\omega_0/2\pi$ is the NMR operating frequency, and τ is the disorder-mode relaxation time. At the temperatures of interest (4–300 K) we assume that τ is due to hopping over barriers of height ΔE; i.e.,

$$\tau = \tau_0 e^{\Delta E/kT}. \qquad (2)$$

We note that the parameter ΔE, which is a barrier height, is not the parameter most important to the tunneling phenomena attributed to disorder modes at low temperatures ($T \lesssim 1$ K) in glasses,[13] and it is not evident that the hydrogen-associated disorder modes probed by the ^{1}H NMR in a-Si:H will yield the normal low-temperature properties observed in glasses.

To determine the average relaxation rate T_1^{-1} one solves the standard diffusion equation[12] with the appropriate boundary conditions. We assume for simplicity a constant distribution of barrier heights from E_{min} to E_{max}. This assumption is not necessary but it does allow for an analytic solution to the problem. The average rate becomes

$$T_1^{-1} \cong \alpha[-1 - S + (1 + 6S + S^2)^{1/2}], \qquad (3)$$

where

$$\alpha = 2\pi a D/d^3, \quad S = \langle R\rangle/2\alpha,$$

with

$$\langle R\rangle = (\gamma^2 h_0^2/\omega_0)\{\tan^{-1}[\omega_0\tau_0 \exp(E_{\mathrm{max}}/kT)] - \tan^{-1}[\omega_0\tau_0 \exp(E_{\mathrm{min}}/kT)]\}.$$

The parameter $D \cong 2\times10^{-12}$ cm^2/sec is the nuclear diffusion constant for ^{1}H in a-Si:H; $a \cong 3$ Å is the average H-H separation at a disorder mode; and d is the average spacing between disorder modes. The quantity α is essentially the rate of nuclear spin diffusion, so that the parameter S of Eq. (3) describes the relative importance of the direct and the diffusion processes. Near the minimum in T_1 the two processes are of comparable importance ($S \sim 1$) while away from the minimum the direct process limits the rate ($S \ll 1$). The present model provides a natural explanation for the observation that T_1 is identical for the two different hydrogen environments because the rate $\langle R\rangle$ of Eq. (3) depends only on the parameters of the disorder modes (a, h_0, d) and the nuclear diffusion constant (D) which are insensitive to the degree of hydrogen clustering. The most striking feature of disorder modes, which are a common occurrence in most amorphous solids, is the insensitivity of these modes to details of the local bonding arrangements. Also, it can be shown that the dependence of D on the linewidth σ is at best rather weak and not experimentally detectable within current experimental error.

The fit of Eq. (3) to the data at 42.3 MHz is indicated by the solid line in Fig. 2. The asymptotic slopes at high and low temperature determine $E_{\mathrm{max}} = 80$ K and $E_{\mathrm{min}} = 25$ K, respectively. The position of the minimum determines $\tau_0 \cong 10^{-9}$ sec although the fit is very insensitive to the choice of this parameter. The final parameters, $h_0 \cong 2$ G and $d \approx 40$ Å are estimated from the magnitude of T_1 near 40 K. This choice of h_0 is quite reasonable because the magnetic dipolar field of ^{1}H at a distance of ~ 1 Å is ~ 5 G. Because there must be at least one disorder mode per hydrogen cluster, we estimate a *minimum* cluster diameter of ~ 40 Å from the fit to the data. With this fit at 42.3 MHz, we obtain both the fit at 12.3 MHz in Fig. 2 and the frequency dependences at 4.2 and 77 K in Fig. 3.

It has been suggested[3] that disorder modes can mediate an interaction which localizes electrons both singly and in pairs. The present observation of disorder modes associated with ^{1}H indicates that perhaps the addition of hydrogen to a-Si not only sweeps electronic states from the gap but may actually contribute a small density of residual electronic states localized at disorder modes. The importance of these hydrogen-associated states for the interpretation of photoluminescence, ESR, and other experimental probes[14] of electronic gap states should be considered.

The authors gratefully acknowledge D. E. Carlson and J. Dresner (RCA), H. Fritzsche and C. C. Tsai (University of Chicago), R. W. Griffith (Brookhaven National Laboratory), and P. Reid (U. S. Naval Research Laboratory) for supplying well-characterized films of a-Si:H. The experimental support of U. Strom during the early stages of this work is greatly appreciated. This work was supported by the U. S. Department of Energy under Contract No. DE-AI01-79ET23078. One of us (W. E. C.) is a National Research Council-Naval Research Laboratory Postdoctoral Research Associate.

---

[1] See, for example, S. Hunklinger and W. Arnold, *Physical Acoustics* (Academic, New York, 1976), Vol. 12, p. 155; J. E. Graebner and B. Golding, Phys. Rev. B <u>15</u>, 964 (1979).

[2] C. N. King, W. A. Phillips, and J. P. de Neufville, Phys. Rev. Lett. <u>32</u>, 538 (1974).

[3] E. N. Economou, K. L. Ngai, and T. L. Reinecke, in *Linear and Nonlinear Electron Transport in Solids*, edited by J. T. Devreese and V. E. van Doren (Plenum, New York, 1976), p. 595.

[4] P. D'Antonio and J. H. Konnert, Phys. Rev. Lett. <u>43</u>, 1161 (1979).

[5] S. Alexander and A. Tzalmona, Phys. Rev. <u>138</u>, A845 (1965).

[6] J. A. Reimer, R. W. Vaughan, and J. C. Knights, Phys. Rev. Lett. <u>44</u>, 193 (1980).

[7] Lorentzian lines have been observed by the authors of Ref. 6 in annealed samples (J. A. Reimer, private communication).

[8] J. G. Powles and P. Mansfield, Phys. Lett. <u>2</u>, 58 (1962); P. S. Allen, W. Harding, and P. Mansfield, J.

Phys. C 5, L89 (1972).

[9] T. L. Reinecke and K. L. Ngai, Phys. Rev. B 12, 3476 (1975).

[10] J. Szeftel and H. Alloul, Phys. Rev. Lett. 34, 657 (1975), and J. Non-Cryst. Solids 29, 253 (1978).

[11] D. E. Carlson, private communication.

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[13] W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972); P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 8, 1 (1972).

[14] See, for example, J. Non-Cryst. Solids 35/36 (1980).

Dissipation of Flow in Superfluid ^{3}He-A

M. A. Paalanen and D. D. Osheroff
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 21 April 1980)

The first direct measurements of the dissipation due to flow are performed and the effects of that flow on the NMR properties of ^{3}He-A are studied. A temperature-independent critical velocity $v_c = 0.52$ mm/s is observed, above which a pressure difference proportional to $v_s - v_c$ develops across our flow orifice. Simultaneously, the NMR frequency in ^{3}He-A is lowered by an amount also proportional to $v_s - v_c$, in contrast to current theoretical predictions.

PACS numbers: 67.50.Fi

^{3}He-A is a highly anisotropic superfluid and hence can dissipate the kinetic energy of mass flow far more easily than either ^{3}He-B or ^{4}He II. Previous measurements of hydrodynamic heat flow[1] and superfluid mass flow between two connected compressional cooling devices[2] have shown the critical velocity in ^{3}He-A to be between 0.1 and 0.8 mm/s while the critical velocity in ^{3}He-B is found to be perhaps an order of magnitude higher.[3] The A-phase critical velocity measured in oscillatory superflow[4] seems to be higher, 2.0 mm/s at $0.9T_c$, decreasing slightly towards T_c, but it is again less than the B-phase critical velocity measured under the same conditions. However, none of the previous experiments have determined the mechanism which causes the dissipation of flow in ^{3}He-A. Possible sources of dissipation which have been treated theoretically include the creation and subsequent motion of 4π vortices as discussed by Anderson and Toulouse,[5] the creation of a soliton lattice as suggested by Vollhardt and Maki,[6] and the general precession of singular $\hat{l}$ textures as described by Hook and Hall.[7] Our results suggest that none of these theories describe the behavior of bulk ^{3}He-A near its critical velocity.

In our experiment liquid ^{3}He was driven at constant velocity through a flow channel of rectangular cross section 0.5×0.05 cm^2, while the pressure head across the channel and the NMR spectra of the ^{3}He within the channel were monitored. The epoxy channel was about 1 cm long, and its cross section flared out gradually at the ends to about 0.8×0.2 cm^2. A piece of Millipore filter paper with ~8-μm channels was glued across the bottom end of the channel. The purpose of the filter paper was to increase the flow impedance of the channel to prevent the normal fluid component from slipping. We estimate the fluid velocity in the filter was only about 20% of the velocity at the center of the channel.

The flow channel was mounted on a 2.54-cm-diam silver bellows, which divided the ^{3}He cell into two parts (Fig. 1). The flow channel could be raised or lowered by altering the ^{4}He pressure in two smaller-diameter bellows, one above and one below the flow channel. The position of the flow channel was monitored with a concentric cylinder displacement capacitor. The volume flow rate through the channel, $\dot{V}$, was then the velocity of the channel times the cross-sectional area of the larger bellows. The superfluid velocity, v_s, was $(\dot{V}/A)(\rho/\rho_s)$, where A is the cross sectional area of the flow channel and ρ_s/ρ is the relative superfluid density. Because the static magnetic field which was necessary for thermometry and NMR studies was parallel to the flow and greater than 20 Oe, the $\hat{l}$ vector was at least initially perpendicular to the flow; consequently it is the perpendicular superfluid density $\rho_{s\perp} = \frac{6}{5}(\rho_s)_{\mathrm{av}}$ that relates mass flow to velocity. The $(\rho_s/\rho)_{\mathrm{av}}$ values were taken from the measurement of Archie *et al.*[8]

The pressure head across the flow channel was