PHYSICAL REVIEW B VOLUME 24, NUMBER 4 15 AUGUST 1981

Molecular H_2: Nuclear-spin-relaxation centers for protons in *a*-Si:H

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(Received 27 April 1981)

It is proposed that dilute H_2 molecules are the source of proton spin-lattice relaxation in those *a*-Si:H samples which show a T_1 minimum. Two-phonon Raman processes relax the H_2 molecular rotational states, modulating the intramolecular dipolar interactions and relaxing the protons of the H_2. The majority of protons in the sample then relax to the H_2 by spin diffusion. The model explains the reported temperature and frequency variations of T_1 as well as the change in T_1 upon dilution of H with D.

Proton NMR observations in *a*-Si:H have many puzzling aspects. Some samples exhibit a T_1 minimum below 30 K; others do not. In those that do show a minimum, the T_1 variation is not accompanied by any motional narrowing of the two-component NMR line.[1] Such behavior would not be unusual for proton relaxation by paramagnetic centers. However, there is no apparent connection in good-quality *a*-Si:H material between the proton T_1 and the electron-spin density determined by ESR.[2] Carlos and Taylor[1] have suggested that local disorder modes serve as relaxation centers for the protons. Motion in such disorder modes is assumed to modulate dipolar fields, relaxing nearby protons and producing a sharply asymmetric T_1 minimum, on a T^{-1} scale. However, Moghavar and Schweitzer[3] have pointed out that the depth of the observed T_1 minima would require that an unreasonably large fraction (10%) of the protons participate in disorder modes. Reimer, Vaughan, and Knights[2] have reported that dilution of the protons by replacement with deuterons increases the proton T_1, suggesting that spin diffusion limits the relaxation. However, such a spin-diffusion limited rate ought to be temperature independent, contrary to experiment. Two more aspects of the observed proton relaxation which must be explained are the frequency independence[1,4] of the minimum T_1 and the lack of a single apparent energy of activation.[1]

Figure 1 shows the 42.3- and 12.3-MHz proton T_1 data reported for a typical sample by Carlos and Taylor[1] replotted as $\ln T_1$ vs $\ln T$. It is apparent that the 42.3-MHz data approach a T^2 temperature dependence (indicated by the dashed lines at high temperatures) above the temperature of the minimum and below 200 K. The temperature variation of the 42.3-MHz T_1 at temperatures below the T_1 minimum is more rapid than T^{-2}. The overall temperature dependence below 200 K is suggestive of two-phonon Raman relaxation.[5] We propose that the proton relaxation of Fig. 1 reflects the presence of a dilute system of fast-relaxing H_2 molecules which serve as relaxation centers. The protons of an ortho-H_2

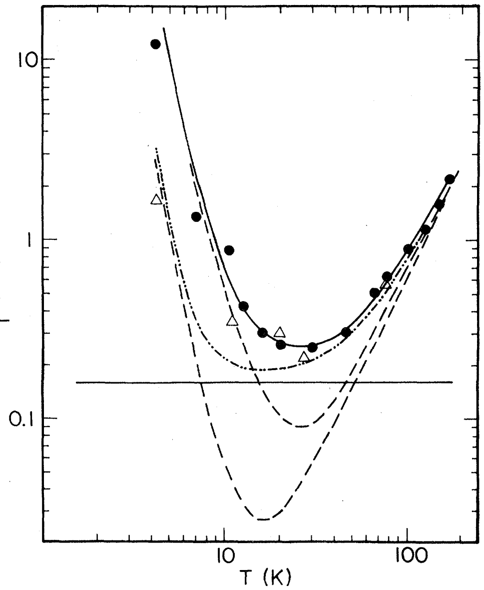

FIG. 1. Proton relaxation times below 200 K reported by Carlos and Taylor (Ref. 1) for *a*-Si:H at 42.3 MHz (solid dots) and at 12.3 MHz (triangles). The solid and dot-dashed lines are fits of a proposed relaxation model to the data. The horizontal line indicates a spin-diffusion bottleneck $T_1 = 0.16$ sec and the dashed lines indicate the quantity $T_1^\dagger$ calculated for the two frequencies and the case of rapid spin diffusion.

molecule (para-H_2 has zero nuclear spin) are relaxed rapidly by modulation of their dipole-dipole interaction by the rotational motion of the molecule. The remaining great majority of protons relax by spin diffusion to these o-H_2 molecules. The temperature dependence of the observed T_1 thus is determined by the temperature dependence of the o-$H_2 T_1$. However, when T_1 of the o-H_2 becomes very short, as it does near the observed T_1 minimum (and especially at the lower NMR frequency 12.3 MHz), the spin-diffusion process becomes a significant temperature-independent bottleneck. Hence, T_1 near the minimum is nearly independent of temperature and frequency. The proposed relaxation model is similar to one previously applied[6,7] to the proton relaxation of solid HD in the presence of dilute o-H_2 impurities.

The temperature dependence of T_1 of dilute H_2 in the solid hosts Ne, Ar, Kr, and para-H_2 has been found[8] to exhibit the power law temperature dependence characteristic of two-phonon Raman processes. Phonons induce transitions between the molecular rotation quantum sublevels at a rate τ^{-1}. The rotational transition rate τ^{-1} is expected on very general grounds to vary as T^2 for temperatures above or near the Debye temperature.[9] The transition rate will be a stronger function of temperature for lower temperatures, eventually going as T^7 for low temperatures.[9] The rate τ^{-1} is proportional to $E(T^*)T^{*2}$, where $E(T^*)$ is given as a tabulated function by Van Kranendonk.[10] T^* is T/Θ_c, where Θ_c is a characteristic temperature for the local phonon dynamics as they enter the Raman process. The rotational transitions modulate the intramolecular dipolar interaction, leading to a relaxation rate[11]:

$$\frac{1}{T_1(H_2)} = \frac{A\tau}{1+\omega_0^2\tau^2} + \frac{B\tau}{1+4\omega_0^2\tau^2} \quad . \tag{1}$$

The spin-rotation coupling for H_2 does not appear above because crystalline fields are expected to quench the individual components of the rotational angular momentum.

The proposed relaxation model is a three-bath model (covalently bonded hydrogen, dilute molecular H_2, and phonons) with no direct link between the phonons and the covalent H. Hence, if one assumes spin diffusion to be rapid, the observed $T_1^\dagger$ will be longer than $T_1(H_2)$ by a ratio of spin heat capacities:

$$T_1^\dagger = T_1(H_2)\frac{n(H)I(I+1)}{\frac{3}{4}n(H_2)S(S+1)} \quad . \tag{2}$$

Here $n(H)$ and $n(H_2)$ are the number densities of total hydrogen in the sample and of total H_2 molecules, respectively. The $\frac{3}{4}$ factor is the fraction of H_2 molecules which are o-H_2 and assumes that the room-temperature ortho-para ratio is frozen in, as is common. The value of I above is the proton spin, $\frac{1}{2}$, and $S=1$ is the nuclear spin of o-H_2. The only temperature-dependent quantity in Eq. (2) is $T_1(H_2)$; so $T_1^\dagger$ is expected to follow $T_1(H_2)$ as long as spin diffusion is sufficiently rapid.

The solid line in Fig. 1 is a fit of the proposed model to the 42.3-MHz T_1 data (solid dots). The fit has employed a spin-diffusion bottleneck T_1 (SD) of 0.16 sec, indicated by the horizontal line. The crystal fields for H_2 in a-Si:H are expected to be of low symmetry and the o-H_2 relaxation rate has been calculated using Fedders's no-symmetry, $r=0$ case[11] with the T_1 minimum taken to occur at 26 K and a characteristic temperature $\Theta_c = 40$ K (the same value as was found appropriate[8] for dilute o-H_2 in rare-gas solids). The calculated minimum $T_1(H_2)$ is 1.19 msec at 42.3 MHz. The upper dashed curve in Fig. 1 is $T_1^\dagger = 76T_1(H_2)$. The solid curve is the sum of the upper dashed curve and the spin-diffusion bottleneck: $76T_1(H_2)+0.16$ sec. Thus the heat-capacity ratio in Eq. (2) is determined to be 76 and Eq. (2) yields $n(H_2) = 3.3\times10^{19}$ cm^{-3}, assuming $n(H) = 5\times10^{21}$ cm^{-3} (for 10 at.%).

Using the $n(H_2)$ and $T_1(SD)$ determined from the 42.3 data, the dot-dashed line shows T_1 predicted for 12.3 MHz. The lower dashed curve indicates $T_1^\dagger = 76T_1(H_2)$ calculated for 12.3 MHz. The calculated $T_1(H_2)$ minimum here occurs near 16.5 K and Θ_c again has been taken to be 40 K. The dot-dashed line represents $76T_1(H_2)+0.16$ sec for 12.3 MHz. It is a reasonable fit to the limited data (triangles) and shows a substantial limitation by the spin-diffusion bottleneck.

An independent estimate of $n(H_2)$ can be determined from the spin-diffusion limited T_1 given by[12]

$$T_{1(SD)}^{-1} = 4\pi D\frac{3}{4}n(H_2)b \quad . \tag{3}$$

The parameter b is the mean spacing between H_2 and its nearest H neighbors and is expected to be about 4 Å. The spin-diffusion coefficient D is approximately given by[13]

$$D = \frac{d^2}{30\langle T_2\rangle} \quad , \tag{4}$$

where d = the mean proton spacing (about 4 Å) and $\langle T_2\rangle$ is an average T_2 of the multicomponent NMR line, taken as 50 μsec. Both the broad and narrow components of the NMR line show considerable clustering of H. The spin-diffusion coefficient we compute is an average over the various regions of H in the sample. It should be noted that samples with different total H content have similar NMR line shapes and hence similar spin-diffusion coefficients. With the above numbers Eq. (4) yields $D = 1\times10^{-12}$

cm^2/sec in reasonable agreement with the value 2×10^{-12} cm^2/sec previously estimated[1] for this *a*-Si:H sample. Equation (3) and $T_1(SD) = 0.16$ sec then yield $n(H_2) = 1.7 \times 10^{19}$ cm^{-3}, a result within a factor of 2 of the $n(H_2) = 3.3 \times 10^{19}$ cm^{-3} obtained above from $T_1(H_2)$ and Eq. (2). Thus Eqs. (2) and (3) fit the T_1 and $T_1(SD)$ data with about the same value of $n(H_2) \simeq 2.5 \times 10^{19}$ cm^{-3} (an atomic fraction of 5×10^{-4}). The simultaneous fit to $T_1^\dagger$ and $T_1(SD)$ will not occur for proton-containing entities with a different proton-proton interaction than *o*-H_2. Because H_2 has such a small bond length, H_2 is unique in being able to fit the data. The NMR signal of the dilute H_2 should not be easily distinguishable, nor should any significant motional narrowing be associated with the T_1 minimum.

As indicated in Fig. 1 the temperature dependence of T_1 in *a*-Si:H is very similar to that of H_2 in Ne and Ar and the temperature of the minimum in *a*-Si:H (26 and 16.5 K at 42.3 and 12.3 MHz) is similar to those in Ar (13 K at 20 MHz and 17 K extrapolated to 42 MHz). It should be remarked that the power-law behavior of $T_1(T)$ is expected only for systems that can make transitions between states without surmounting an energy barrier. Such behavior is found for H_2 rotational levels (because of their quantum-mechanical nature arising from the small moment of inertia) and also for electron spins.

The observed T_1 is independent[1] of ω_0 on the hot side of the minimum, as expected from Eq. (1). This equation also predicts $T_1 \propto \omega_0^2$ on the cold side of the minimum, provided one is well away from the spin-diffusion bottleneck. The limited data in this range[1] agree with this prediction.

The proposed model also is consistent with reported proton T_1 results on samples diluted with deuterium. Reimer, Vaughan, and Knights[2] have studied the T_1 of two samples of *a*-Si:H,D, comparing them with otherwise similar (same total hydrogenic content and preparation conditions) samples of *a*-Si:H. Taking C to be the relative concentration of H in the partly deuterated sample compared with that in the undeuterated sample, these workers found that T_1^{-1} was proportional to C. That is, one deuterated sample which contained only 40% as many protons as the otherwise identical nondeuterated sample had a proton relaxation rate 40% of the nondeuterated sample's rate. These experiments were carried out near room temperature, and T_1 was found to have some temperature dependence, verifying that spin diffusion was not the rate-determining process in the data. The partly deuterated samples were prepared by glow discharge of SiH_4-D_2 mixtures. If one reasonably assumes that the dilute H_2, HD, and D_2 molecules in *a*-Si:H,D are formed from atomic H and D, then statistically $n(H_2)$ should vary as C^2 while $n(H)$ varies as C. Hence Eq. (2) predicts that T_1 will vary as C^{-1} away from the spin-diffusion limit, in agreement with the experimental observations.[2]

It should be remarked that any nonexponential relaxation (which often occurs in the presence of spin diffusion to relaxation centers) will involve an exceedingly small fraction of the H in the *a*-Si sample. This is true because the relaxation centers have such a small effective radius (~4 Å) compared with the mean spacing between them (~60 Å). Even in the diffusion-limited regime, the observed decays would appear exponential, unless exceptional signal-to-noise ratios were attained. Indeed, the reported recoveries are exponential; furthermore, spin diffusion causes the entire line to relax at the same rate, as observed.[1,4]

Carlos and Taylor[1] have reported that similar T_1 minima are observed (with some variation in the magnitude of T_1) in a number of glow-discharge samples of good quality from various laboratories. One sample that was sputtered in a fairly high pressure (4 mTorr) of H_2 also showed[14] such a minimum. However, two samples sputtered with less H_2 (0.4 mTorr) showed quite different results, longer T_1 and the absence of a deep T_1 minimum. This suggests that the latter samples may have contained much less H_2. Results reported[15] from the Ames group on sputtered material also fail to show the T_1 minimum.

Presumably, *a*-Si:H is permeable to H_2. Hence we assume that the small amount of H_2 is present in atomic size "cages," regions where the H_2 is trapped by geometrical considerations. Reimer, Vaughan, and Knights have observed[16] motional narrowing of a small fraction of the protons at room temperature in *a*-C:H, *a*-Si·C:H, and *a*-Si·N:H. The corresponding resonance lines are narrow, so that these protons are accomplishing a good average of dipolar interactions. Such a good average probably is more typical of small symmetric molecules (H_2 or CH_4) than local disorder modes. Hence we feel Reimer *et al.* may have observed trapped small molecules in these amorphous semiconductors.

One test of the proposed relaxation model is to measure the H_2 content of *a*-Si:H. Different samples should contain different amounts of H_2 and the minimum T_1 of these samples should differ. Measurements of T_1 at frequencies higher than 42.3 MHz should show a minimum increasing with ω_0 as spin-diffusion bottlenecking becomes less significant. Also, an *a*-Si:H sample which shows a proton T_1 minimum should have that minimum destroyed and T_1 increased upon proton decoupling by magic-angle spinning. The most conclusive test, however, involves ortho-para conversion of the H_2. The H_2 should convert at reasonable rates because of the presence of electron spins. A striking confirmation of the model would be provided if the minimum T_1 were greatly increased by a prolonged waiting time at or below 20 K (where almost all of the H_2 will convert to para-H_2). Subsequent reheating to room temperature for an appropriate interval should then restore the 3:1 ortho-to-para ratio and the T_1 minimum upon recooling to ~20 K.

We wish to thank W. Carlos and P. C. Taylor for helpful discussions and for kindly providing us with their data. We also thank J. A. Reimer for lengthy discussions and for communicating his data prior to publication. Conversations with P. A. Fedders and R. Fisch also have been helpful. R.E.N. was supported by the NSF Grant No. DMR 80-10818 and M.S.C. was supported by a Joseph H. DeFrees Grant of the Research Corporation and ACS-PRF Grant No. 12334-G6.

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