RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 9 1 NOVEMBER 1985

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Two-level systems in hydrogenated amorphous silicon: NMR studies

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(Received 29 July 1985)

A low-temperature deviation from the spin-lattice relaxation of bonded hydrogen by molecular hydrogen is observed in a-Si:H. Two likely causes for this deviation, namely, relaxation by paramagnetic electronic spins and by two-level systems (TLS), are both shown to be negligible. In ruling out TLS's or tunneling modes, a second NMR experiment is performed that allows a low limit to be placed on the number or excursion of H atoms involved in a tunneling mode. These results indicate that the H-atom motion is not involved to any significant degree in the atomic motion associated with a TLS.

Tunneling modes or two-level systems (TLS's) are recognized as being responsible for many of the anomalous low-temperature properties of glasses and amorphous materials. They give rise to additional contributions to the specific heat, thermal resistivity, and ultrasonic attenuation in amorphous solids over those for their crystalline counterparts, leading also to a different temperature variation for these qualities.[1] Likewise, the spin-lattice relaxation rate $1/T_1$ of electrons[2] and nuclei[3] is found, in many cases, to be significantly larger in the amorphous materials than in the crystalline ones. This additional contribution to $1/T_1$ is attributed to TLS's and is proportional to $n_T T^{\alpha}$, where n_T is the total density of two-level systems, T is the temperature, and the exponent α is between one and two for nuclear spins and approximately two for electronic spins. In the specific case of hydrogenated amorphous silicon, a-Si:H, the relaxation rate of the dangling-bond electrons,[4] $1/T_1(\mathrm{DB})$ is about 10 sec^{-1} at 4.2 K and varies as $T^{2+\epsilon}$. This is to be compared with the relaxation rate of donor electrons in lightly P-doped samples of crystalline Si, where $1/T_1$ is more than two orders of magnitude smaller and has a T^7 variation.[5] The substantial difference is attributed to the additional relaxation process due to TLS's in a-Si:H.

For the nuclear spin-lattice relaxation of the H spins in a-Si:H, a U-shaped variation of T_1 vs T with a minimum near 50 K is observed (see Fig. 1). This temperature variation was initially interpreted as due to TLS's,[6] but the magnitude of T_1 required 10% of the H atoms to be involved in these tunneling modes.[7] Since the concentration of H is about 10 at.%, this meant that $n_T \geqslant 5\times 10^{20}$ cm^3. Estimates of the density of states of the TLS's from specific-heat measurements[1] yield $n(E)=10^{21}$ $\mathrm{eV}^{-1}\mathrm{cm}^{-3}$. For a constant density of states[1] and a bandwidth of order 100 K, this $n(E)$ gives $n_T \sim 10^{19}$ cm^3, considerably smaller than that required to explain T_1. It was later proposed that T_1 was not due to TLS's, but rather due to molecular H_2 trapped in voids in the film.[8] This model has been confirmed experimentally.[9,10] So the T_1 of the H nuclei is dominated by molecular-H_2-relaxation centers rather than by TLS's containing H atoms. Nonetheless, low-temperature deviations from the predictions of the H_2-relaxation model do exist.[11,12] The magnitude of T_1 and its variation with Larmor frequency for temperatures below the T_1 minimum do not accurately fit the molecular-H_2 model. The explanation

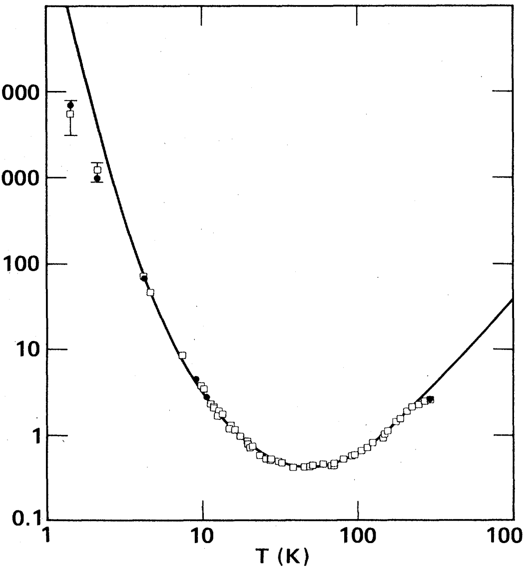

FIG. 1. Hydrogen nuclear-spin-lattice relaxation time vs temperature for a-Si:H. The open squares are for the as-deposited sample and the solid line is a fit to these data using the relaxation-by-molecular-H_2 model, Eqs. (1) and (2). Significant deviations occur below 4 K. The solid dots are for the same sample after it had been illuminated with white light at 90 ° C for an extended period. These data agree with those on the as-deposited sample despite the fact that this treatment leads to order-of-magnitude changes in the electronic T_1.

often given is that there is a distribution of correlation times (relaxation times of the molecular angular momentum) rather than a single correlation time. This would qualitatively account for the discrepancies. But the question arises as to whether the low-temperature deviations are due to TLS's and, if so, whether additional information on the nature of the TLS's can be obtained.

We have measured T_1 of the H nuclei in an a-Si:H film of good electronic quality down to 1.43 K, well below the temperature of the T_1 minimum (≈ 50 K). The a-Si:H sample was prepared from the plasma decomposition of pure SiH_4 gas. An Al substrate was heated to 230 °C and a low power density of 0.025 W/cm^2 was used. The Al was etched away with hydrochloric acid and the resulting a-Si:H sample was dried and weighed. The NMR measurements were performed at a Larmor frequency of 92.5 MHz using a standard pulsed NMR apparatus. The NMR spectrum was obtained from a Fourier transform of the free-induction decay and yielded the following: the H content $n(\mathrm{H})$ is 9.3 at.% with 3.8 at.% in a narrow Lorentzian line with a full width at half maximum (FWHM) of 3.0 kHz and 5.5 at.% in a broad Gaussian line with FWHM = 22 kHz. These results are typical of a number of so-called "good" samples.[13]

The NMR spin-lattice relaxation time T_1 of the H from 1.43 to 300 K is shown in Fig. 1. These data again are representative of good plasma-deposited a-Si:H samples.[9–12,14,15] The characteristic minimum in the vicinity of 50 K is due to the presence of a small number of H_2 molecules trapped in the a-Si host. The H atoms in the molecule relax quickly due to interactions between the rotational angular momentum of the ortho-H_2 and the phonons of the host. The H_2 molecules thereby serve as relaxation centers for the H atoms bonded to the Si (the predominant type of H in the sample), relaxing them by spin diffusion. The resulting T_1 for the bonded H due to the H_2 molecules is[8,16]

$$T_{1,\mathrm{H}_2} = A T_1(\mathrm{H}_2) + T_{1,\mathrm{SD}} , \tag{1}$$

where $A = \frac{1}{2} n(\mathrm{H})/n(\mathrm{H}_2)$ is the ratio of the spin heat capacity of H to that of ortho-H_2, and $T_{1,\mathrm{SD}}$ accounts for the bottleneck in the spin-diffusion process. $1/T_1(\mathrm{H}_2)$ is the molecular-H_2-relaxation rate, given by

$$1/T_1(\mathrm{H}_2) \approx (\tfrac{6}{5})\omega_d^2 \tau/(1+\omega_0^2\tau^2) , \tag{2}$$

where ω_d is the dipolar coupling constant for the H_2 molecule (3.6×10^5 sec^{-1}). ω_0 is the Larmor frequency and τ is the relaxation time of the molecular angular momentum. For a Raman process, $1/\tau \sim T^2$ for $T > \Theta$ and $1/\tau \sim T^7$ for $T << \Theta$, where Θ is a characteristic temperature for the local phonon dynamics ($\Theta \approx 30$ K). This leads to a short $T_1(\mathrm{H}_2)$ of about 2 msec at the minimum ($T \approx 50$ K). This model has been quite successful in explaining the hydrogen T_1 data in a-Si:H, as is also the case here. The fit of these expressions to the data over the temperature range 4–200 K is shown as the solid line in Fig. 1. The best-fit parameters are $A = 75$, corresponding to $n(\mathrm{H}_2) = 620$ ppm, and $T_{1,\mathrm{SD}} = 0.22$ sec. If the low-temperature data (< 4 K) are included in the fit, the quality of the fit parameter, the R value, decreases by a factor of 3 and significant deviations between theory and experiment are introduced between 4 and 20 K as well as in the vicinity of the minimum. Clearly then, the data below 4 K are not fit well by the molecular-H_2 model and the deviations in this temperature region are real. The case is similar, although the deviations are smaller, for the data in the high-temperature region above 200 K.

The fit of this molecular-H_2 model to the data is quite good except for the deviations in the high (> 200 K) and low (< 4 K) temperature regions. The high-temperature deviations are readily explained in terms of the extra relaxation contributions from ortho-H_2 with $J > 1$.[17] The occupation of these higher-J states is negligible at low temperature, where only the $J = 1$ state contributes and Eqs. (1) and (2) apply, but becomes significant near room temperature. Corrections to Eqs. (1) and (2) have to be made in this high-temperature regime, leading to a shorter T_1 qualitatively consistent with the deviation in Fig. 1. The discrepancy at low temperatures is not so readily explained and is the major point of this discussion.

The extra relaxation rate at low temperatures, $1/T_{1,x}$ is given in terms of the measured rate, $1/T_{1,\mathrm{expt}}$, by

$$1/T_{1,x} = 1/T_{1,\mathrm{expt}} - 1/T_{1,\mathrm{H}_2} . \tag{3}$$

This expression assumes that the extra rate is independent of the relaxation rate due to the H_2 molecules. The various rates are tabulated in Table I, where it is seen that, despite the large discrepancy between $T_{1,\mathrm{expt}}$ and T_{1,H_2}, the extra relaxation rate needed to account for the deviation is quite small ($\sim 10^{-4}$ sec^{-1}), but is still large compared with $1/T_{1,\mathrm{H}_2} \approx 2\times10^{-5}$ at 1.43 K. Since $T_{1,\mathrm{expt}}$ and T_{1,H_2} are so large, a small $1/T_{1,x}$ can cause a significant deviation in the T_1's. In other words, the data are sensitive to any additional relaxation mechanism, even one that is quite weak. Several mechanisms exist that could be responsible for this extra relaxation rate: (1) paramagnetic spins, (2) tunneling modes, or (3) deviations from Eqs. (1) and (2) for T_{1,H_2} due, for example, to a distribution in τ, the relaxation time of the molecular angular momentum.

The first mechanism, relaxation by paramagnetic impurities or dangling bonds, can readily be ruled out. The relaxation rate due to paramagnetic electronic spins in the rapid-diffusion case, the one appropriate here, is[18]

$$1/T_{1,p} = (4\pi/3)NC/b_0^3 , \tag{4}$$

with

$$C \sim \gamma_e^2\gamma_H^2\tau_e/(1+\omega_H^2\tau_e^2) . \tag{5}$$

N is the density of electronic spins and b_0 is the spin-diffusion barrier distance, i.e., the distance from the elec-

TABLE I. The experimentally observed hydrogen T_1 and the calculated value for relaxation due to H_2 molecules at low temperatures. The difference between these two relaxation rates, $1/T_{1,x}$, is due to some additional relaxation process that becomes significant at low temperatures.

T (K)	$T_{1,\mathrm{expt}}$ (sec)	T_{1,H_2} (sec)	$1/T_{1,x}$ (sec^{-1})
4.2	71 ± 4	75	$(10 \pm 10)\times10^{-4}$
2.14	1200 ± 200	4200	$(6 \pm 2)\times10^{-4}$
1.43	5500 ± 2000	68 000	$(2 \pm 1)\times10^{-4}$

tronic spin, where the dipolar field of the electron is about equal to the local nuclear field. γ_e and $\gamma_{\rm H}$ are the electronic and hydrogen nuclear gyromagnetic ratios, respectively, $\omega_{\rm H}$ is the H Larmor frequency, and τ_e is the electronic spin-lattice relaxation time. For the lowest temperature studied ($T = 1.43$ K), $b_0 \sim 10$ Å and $\omega_{\rm H}\tau_e >> 1$, so that $1/T_{1,p} \sim 10^{-27} N/\tau_e$. ESR measurements on this sample indicate that only dangling bonds are present with $N \approx 10^{16}$ cm^{-3} and $\tau_e(4.2\ {\rm K}) \simeq 0.1$ sec. Extrapolating to 1.43 K using $\tau_e \sim 1/T^2$ gives $\tau_e(1.43\ {\rm K}) \sim 1$ sec, so that $1/T_{1,p} \sim 10^{-11}$ sec^{-1}. This is negligible compared with the extra relaxation rate from Table I of $1/T_{1,x} = 2 \times 10^{-4}$ sec^{-1}. The relaxation due to the paramagnetic electrons is negligible because of their very low density and small relaxation rate. This is true in general for a-Si:H over the entire temperature range. For example, at 300 K, $1/T_{1,p} \sim 10^{-5}$ sec^{-1}, much smaller than the observed nuclear relaxation rate of 0.4 sec^{-1}.

The second possible mechanism, that of two-level systems, is a likely candidate, since it is responsible for the relaxation of the dangling-bond electronic spins.[4] This mechanism is similar to the one discussed above, except that now the relaxation center is a hydrogen atom in a tunneling mode. In the rapid-diffusion case,[6,7]

$$1/T_{1,{\rm TLS}} = x\gamma_{\rm H}^2 h_0^2 \tau/(1+\omega_{\rm H}^2\tau^2) \ , \tag{6}$$

where h_0 is the mean fluctuating field caused by the modulation of the dipolar interaction due to the motion of the H atom in a tunneling mode and $1/\tau$ is the tunneling rate. x is the ratio of the nuclear-spin heat capacity of the H nuclei participating in the tunneling modes to that of all the H nuclei, i.e., the fraction of the H atoms that are in a TLS. x is, therefore, proportional to n_T and is equal to $n_T/n({\rm H})$ for a random distribution of H atoms. Equation (6) is only appropriate for a single local relaxation time τ, whereas, in fact, there is a distribution of τ's due to a distribution of tunneling barrier heights. If one assumes that $\tau = \tau_0 e^{U/kT}$, with U the barrier height and $1/\tau_0$ the attempt frequency of order 10^{12} sec^{-1}, and that the density distribution of barriers is constant from $U_{\rm min}$ to $U_{\rm max}$, then Eq. (6) becomes[6,7,19]

$$1/T_{1,{\rm TLS}} \approx x(\gamma_{\rm H}^2 h_0^2/\omega_{\rm H})[k_B T/(U_{\rm max} - U_{\rm min})]\{\tan^{-1}[\omega_{\rm H}\tau_0 \exp(U_{\rm max}/k_B T)] - \tan^{-1}[\omega_{\rm H}\tau_0 \exp(U_{\rm min}/k_B T)]\} \ . \tag{7}$$

There is certainly a set of reasonable parameters in Eq. (7) that could yield $1/T_{1,{\rm TLS}} \approx 1/T_{1,x}$. But due to the large uncertainty in these quantities, this agreement could merely be fortuitous and would not be conclusive proof for relaxation by TLS.

To narrow the number of possibilities, a second experiment was performed in which we changed the effective density of the TLS. The sample was illuminated with white light for an extended period at 90 °C. These are the conditions for a maximal change in the dangling bond T_1, which increases by an order of magnitude at 20 K.[20] This change implies a decrease in the density of TLS by an order of magnitude since $1/T_1({\rm DB}) \sim n_T T^\alpha$, with α near 2.[4,20] The elimination of a factor of 10 of the TLS by illumination at 90 ° C is reversible, since a subsequent anneal in the dark at 165 ° C for one hour restores the as-deposited value of T_1(DB); i.e., n_T has increased by an order of magnitude to its original value.

If the extra H nuclear T_1 at low temperatures were due to TLS's, then a decrease in n_T by a factor of 10 would cause a decrease in $1/T_{1,x}$ by this factor; i.e., the measured T_1 should approach $T_{1,{\rm H}_2}$. This assumes that the illumination affects all the tunneling modes so that $n(E)$ is reduced uniformly rather than having a hole burned in it. The ESR results only follow T_1(DB), and thereby $n(E)$, down to 20 K, in observing the order of magnitude reduction in $n(E)$.[20] It is possible that the TLS with lower energies (< 20 K) could remain unaffected. On the other hand, strain interactions between the TLS tend to homogenize $n(E)$.[21] Such a homogenization is consistent with the fact that a single value of T_1(DB) is observed. As a result, one expects the illumination to lower $n(E)$ more or less uniformly for all E. Thus the nuclear relaxation rate due to TLS should be reduced by approximately the same factor as for $1/T_1$(DB). The experimental results on the illuminated sample are shown in Fig. 1. It is seen that no significant change in T_1 has occurred. This implies that the extra low-temperature relaxation is not due to TLS.

With this result that the TLS have a negligible effect on T_1, we can arrive at some specific information on the nature of the TLS by using the model for T_1 represented by Eq. (7) and using reasonable estimates for some of the unknown parameters. Typical estimates are $U_{\rm max}/k \sim 100$ K and $U_{\rm min}/k < 4$ K.[1,20] For our lowest temperature, $T = 1.43$ K, for $\omega_{\rm H}/2\pi = 92.5$ MHz and for $1/\tau_0 \sim 10^{12}$ sec^{-1}, the first inverse tangent in the curly brackets of Eq. (7) is within 10% of $\pi/2$ for $U_{\rm max}/k \geqslant 14$ K. Likewise, the second inverse tangent is $\leqslant \frac{1}{10}\pi/2$ for $U_{\rm min}/k \leqslant 8$ K. These limits are well within the estimated endpoints of the barrier distribution, so that, in Eq. (7), $\{\ \} \approx \pi/2$. Taking the bandwidth as 100 K, Eq. (7) becomes

$$1/T_{1,{\rm TLS}}(1.43\ {\rm K}) \sim 0.03 x h_0^2 \ , \tag{8}$$

with h_0 in Gauss. Since changing n_T (or equivalently x) by an order of magnitude with illumination has no significant effect on T_1, we have that $1/T_{1,{\rm TLS}} << 1/T_{1,x}$. Applying this to Eq. (8) yields $xh_0^2 << 7 \times 10^{-3}$. So either x or h_0 is small, or both. An estimate of h_0 caused by an H atom moving a distance of a bond length (2.3 Å) in a tunneling mode is 2 G so that $x << 2 \times 10^{-3}$. The value of x expected if the H atoms are randomly distributed throughout the sample on all sites, whether tunneling modes or not, is $x_{\rm random} \approx n_T/n({\rm H})$. Using $n_T \sim 10^{19}$ cm^3 and $n({\rm H}) = 9.3$ at. % $= 5 \times 10^{21}$ cm^{-3} gives $x_{\rm random} \sim 2 \times 10^{-3}$. So the above inequality implies $x << x_{\rm random}$. The conclusion then from the fact that the TLS have a negligible effect on T_1 plus some rough estimates of the parameters that enter Eq. (7) is that $x << x_{\rm random}$; i.e., there is a negligible number of H atoms involved in the tunneling mode. A second possibility is that an H atom is involved in a tunneling mode but its motion is small (< 1 Å), so that h_0 is << 1 G. In either case, H-atom motion is not involved to any significant degree in the TLS. This conclusion is also consistent with the fact that the TLS density from ESR measurements[4] is independent of whether the sample is Si:H or Si:D.

Returning to the cause of $1/T_{1,x}$, the remaining and most likely candidate is the third possibility, namely, a distribution of H$_2$ molecular-relaxation times, τ in Eq. (2). Such a distribution is not unreasonable, given the inherent fluctuations in the structure of *a*-Si:H. Also, there is some evidence that a distribution does exist, since the Larmor frequency dependence is often observed not to be $1/\omega_H^2$ on the low-temperature side of the T_1 minimum, as Eq. (2) would predict. A frequency dependence of $1/\omega_H^n$, with $n < 2$, is often the indicator of the existence of a distribution of correlation times rather than a single correlation time. The data are not adequate to yield any detailed information on this distribution. The effect of the orientational ordering of the H_2 relaxation centers below 20 K may also have to be considered.[22]

In conclusion, a low-temperature deviation from the spin-lattice relaxation of H by molecular H_2 is observed in *a*-Si:H. The most likely candidate is a distribution of molecular-relaxation times rather than a single such time which is used to analyze the data. The contribution from paramagnetic electronic spins and two-level systems are shown to be negligible. In ruling out TLS, a low limit can be placed on the number or the excursion of the H atoms involved in a tunneling mode. In other words, H-atom motion is not involved to any significant degree in the motion associated with a TLS.

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