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TEMPERATURE AND FREQUENCY DEPENDENCES OF NMR SPIN-LATTICE RELAXATION TIME T_1 IN a-Si:H

K.L. Ngai

Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

Abstract.- Carlos and Taylor have recently reported pulsed ^1H NMR measurements on the spin-lattice relaxation time T_1 for the hydrogen atoms in glow discharge prepared a-Si:H. They have measured both the magnitude and the temperature and frequency dependences of T_1 and observed a number of interesting features. Among these are the presence of an asymmetric minimum in T_1 at a temperature $T_{\min}$ near 40K which is relatively insensitive to frequency ν and a strong dependence of T_1 on ν for $T < T_{\min}$ which is suppressed for $T > T_{\min}$. These features are consistent with a unified and universal model of low frequency fluctuation, dissipation and relaxation properties of condensed matter.

Introduction.- Nuclear magnetic resonance and nuclear spin-relaxation have recently been employed (1-3) successfully to characterize both sputtered and glow discharge deposited a-Si:H. Thus Carlos and Taylor were able to establish the existence of two separate hydrogen environments in a-Si:H, and discovered the spin-relaxation time, T_1 , show a minimum at about 40K for glow discharge samples and a sputtered sample prepared with a high partial pressure of hydrogen. Several observed properties of T_1 help to narrow down the possibilities in the search for a model. For example the T_1 variation is not accompanied by any motional narrowing of the NMR line; and the magnitude of T_1 cannot be related to paramagnetic centers (including dangling bonds) whose number as determined by ESR is too few. Carlos and Taylor have attempted to explain the T_1 behavior using a model based on "disorder modes" which are associated with a small fraction of the hydrogen atoms ($\sim 10^{17} \text{ cm}^{-3}$). At these disorder modes the hydrogen atoms can hop over a potential barrier ΔE which separates two positions of local equilibrium. This motion of the hydrogen of the disorder mode makes it a proton relaxation center by modulating the dipolar field felt by nearby hydrogen atoms. Atoms further away are relaxed by spin diffusion. Movaghar et al. has pointed out that the method of solution of Carlos and Taylor is not valid unless the local relaxation rate T_R^{-1} is much faster than the spin-diffusion rate, T_D^{-1} , but due to the smaller nuclear moment of the hydrogen this is not expected to be the case. However, Movaghar et al. (4) in their master equation approach, have given, at the time of this writing, the solution to local mode relaxation-spin diffusion model of Carlos and Taylor only in the limits of $T_R^{-1} \ll T_D^{-1}$ and $T_R^{-1} \gg T_D^{-1}$. In the former limit, they found that the magnitude of the T_1 minimum would require at least 10% of the hydrogens have to be involved in the local mode relaxation, contrary to the assumption of $\sim 10^{17} \text{ cm}^{-3}$ by Carlos and Taylor. It remains to be seen what predictions the master equation approach will make for the case of when T_R^{-1} and T_D^{-1} are comparable, a situation probably realized in the a-Si:H. Further each local mode may involve the participation of more than one hydrogen, thereby increasing the amplitude of the fluctuating magnetic field and hence obviate the difficulty with numbers. In the absence of a general solution of the master equation and an unambiguous identification of the local mode, Carlos and Taylor's model is worth further consideration and development.

Model of Spin-relaxation.- There is considerable ambiguity in the identity of the local mode associated with some hydrogens at this moment. In view of this, our approach to NMR spin-relaxation will remain general enough to accommodate any

specific local relaxation mode that may eventually be proposed for a-Si:H; but for concreteness it is based on the ideas due to Carlos and Taylor as much as possible. We assume along with them the existence of local mode that may involve one hydrogen atom or a group of atoms hopping over a potential energy barrier ΔE which separates two positions of local equilibrium. Carlos and Taylor assume a distribution of barrier heights. With this assumption both the anomalous frequency dependence of T_1 and the strongly asymmetric T_1 minimum can be explained, although the problem of a rather low value of 10 sec^{-1} for the attempt-to-hop frequency remains. Whether a distribution of barrier heights of the extent as assumed does exist or not will remain as a question to be resolved. However, there is an underlying mechanism that will contribute to T_1 and its anomalies especially in amorphous condensed matter such as a-Si:H. Amorphous condensed matter are richly endowed with two-level systems (TLS). A subset of these TLS's can be directly probed by specific heat, thermal conductivity and ultrasonic attenuation measurements in a limited energy range of the TLS. For example, specific heat experiment is limited to the energy range of 10 mK to a few degrees Kelvin, and the linear T specific heat is often explained by the assumption of a constant density of excitation energy E of TLS. Very low temperature (30-500 mK) measurements (5) of suprasil W indicate that the specific heat varies as $T^{1.3}$ or $N(E)$ decreases as E decreases below 1K. A natural question that arises is how does $N(E)$ decrease? I have adapted Wigner's statistical theory of energy levels to condensed matter (6) and was led to propose that $N(E) \propto E$ for $E < E_c$. Here E_c can be considered as a transition energy such that for a finite range of E above E_c , $N(E)$ tends to be constant.

The local mode suggested by Carlos and Taylor is coupled to the amorphous Si:H lattice structure and hence to the TLS's. Relaxation of the local mode is accompanied by both excitation and deexcitation of the TLS's. The matrix element V between the two states of the TLS's of the perturbation caused by the local mode relaxation is uncorrelated with E for small E. This follows from the argument that the number of atomic, electronic, bonding and configurational coordinates that are involved to specify the two states of the TLS must rapidly increase as E decreases. The perturbation caused by the local mode is localized to a fraction of these coordinates and hence the magnitude of its matrix element for transition between the two states of the TLS bears no correlation with E. The sum of the transition matrix elements over all TLS's with the same energy E will again be independent of E. Hence the $|V|^2 N(E)$ depends on E through $N(E)$ only and which we have from Wigner's result is linear in E. Thus, for $E < E_c$, $|V|^2 N(E) = nE$ which is the condition for infrared divergent excitation and deexcitation of the TLS in response to the local mode relaxation. The relaxation rate of the local mode is modified from τ_1^{-1} to $\tau_1^{-1} \exp(-ny)$ ($E_c t$) where $y = 0.577$. The infrared divergence exponent n ranges from zero to one, and gives a measure of the involvement of the TLS's in the relaxation of the local mode. The correlation function is accordingly modified from $\exp(-t/\tau)$ to $\phi_n(t) \equiv \exp[-\exp(-ny) t^{1-n}/(1-n)\tau_1^n]$. From this we have calculated the spin relaxation rate of protons next to a local mode for a yet to be determined value of n by Fourier transformation of $\phi_n(t)$. Details can be found in Ref. 6.

We adopt Movaghar et al's solution (4) to spin-diffusion when the local mode relaxation is the rate limiting process. The predicted frequency dependence of T_1 is ω^{2-n} for $T \ll T_{\min}$ and independent of ω for $T > T_{\min}$. The T_1 vs. ω data at 4.2K (Fig. 1) are found to have a least square fit to the ω^{2-n} dependence with $n=0.875$. While the data at $T=77K$ are indeed roughly independent of ω . We assume along with Carlos et al. that $\tau = \tau_0 \exp[\Delta E/kT]$, then the model predicts T_1 varies with T as $\exp(\Delta E/kt)$ for $T < T_{\min}$ and as $\exp(\Delta E/(1-n)kT)$ for $T > T_{\min}$. With $n=0.875$ as determined and $\Delta E=40K$, the model prediction (solid line in Fig. 2) is in good agreement with the 42.3 MHz data. The lack of good agreement with the 12.3 MHz data is also found by Carlos and Taylor in their model calculation. It is quite possible that, in a-Si:H, T_R and T_D are comparable. Solution to the Carlos-Taylor model in this regime when available is expected to remove this discrepancy. The anomalously low prefactor of $1/\tau_0 = 10 \text{ sec}^{-1}$ determined by the condition $\omega_0 \exp(-\Delta E/kT_{\min})$ as found by Carlos et al. for $\Delta E=40K$ can be naturally explained in our model (6). We have predicted that a physically reasonable τ_0 is modified to $\tau^* = [(1-n)\exp(ny)E_c^n \tau_0]^{1/(1-n)}$. If $(E_c \tau_0) \gg 1$, then we can have $\tau^* \ll \tau_0$.

In summary, we have pointed out that the anomalous temperature and frequency dependences of T_1 is consistent with the infrared divergent excitation and deexcitation of low energy levels by the local relaxation mode. These processes should be considered on top of the effect of a distribution of barrier heights if present. Since the solution to the local mode relaxation-spin diffusion model for $T_R \sim T_D$ is not yet available, the parameters determined in this work must be considered as tentative.

Fig. 1. Frequency dependence of ^1H spin-lattice relaxation time T_1 in a-Si:H at two temperatures. Solid curves are predictions of the model described in the text.

Fig. 2. Temperature dependence of ^1H spin-lattice relaxation time T_1 in a-Si:H at two frequencies. Solid curves are predictions of the model described in the text.

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