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NMR spin-lattice relaxation in the deuterium quadrupolar glass

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We present measurements of nuclear spin-lattice relaxation in solid D_2 for para concentrations $0.24 < X < 0.31$ and temperatures $40 < T < 700$ mK. No evidence is seen for a well-defined transition into the quadrupolar glass state. A model of para-ortho cross relaxation is presented which allows our D_2 data to be compared with previous H_2 relaxation data.

The study of solid hydrogen and deuterium at low temperatures can provide a very direct experimental test for theories of randomly diluted quantum spin systems. This is because the molecular angular momentum J is a good quantum number in these solids, due to the small moment of inertia of the molecules. The $J=1$ molecules (ortho-H_2, para-D_2) form a system with effective spin one, with intermolecular electric quadrupole-quadrupole (EQQ) interactions. The $J=0$ molecules (para-H_2, ortho-D_2) dilute the spin-one system but do not otherwise enter the Hamiltonian.

The fraction X of molecules in $J=1$ states may be varied by preparation or aging. For $X > 0.55$ there is a phase transition at a few degrees Kelvin into the 4-sublattice Pa_3 structure. The Pa_3 phase has been the subject of extensive theoretical studies and is relatively well understood (see Ref. 1 for references). On the other hand, data from various laboratories have led to different interpretations of the region of the phase diagram with $X < 0.55$ and $T \lesssim 300$ mK. Sullivan *et al.* have maintained that there is a fairly sharp transition into a state closely analogous to a spin-glass, on the basis of their NMR line shape and spin-lattice relaxation measurements.[2,3] Likewise, Cochran *et al.* interpreted relaxation data for H_2 impurities in D_2 in terms of a phase transition.[4] We will follow Ref. 2 in calling the low-temperature state of hydrogen for $X < 0.55$ a "quadrupolar glass" (QG), bearing in mind that no strict analogy with spin-glasses has been established.

Washburn *et al.* also measured hydrogen NMR line shapes and relaxation times in this region of the phase diagram, and they found no evidence for a sharp transition into the more ordered state.[5,6] Previous experiments in our laboratory indicated a similar gradual dependence of NMR line shape on temperature.[7,8] Thermodynamic measurements by Haase and Saleh[9] have shown that the orientational specific heat is a smooth function of temperature.

An NMR study by Sullivan *et al.*[10] has shown that D_2 also exhibits QG ordering for $X < 0.55$. The principal evidence for a *sharp* transition of D_2 into the QG state has been the nuclear spin-lattice relaxation measurements of Sullivan and Devoret for $X = 0.33$, at a Larmor frequency of 25 MHz.[11] In deuterium, the $J=1$ molecules have total nuclear spin $I=1$, and because of the *nuclear* quadrupole interaction, they contribute a wide component to the NMR line which is difficult to observe using cw NMR methods at low X. The $J=0$ molecules, on the other hand, have a mixture of $I=0$ and 2, and contribute an easily observed narrow component to the NMR line. Sullivan and Devoret found that the relaxation of this narrow component showed clear evidence of two distinct time constants, both of which had discontinuities in their derivatives with respect to temperature at 170 mK. They interpret this as evidence that solid D_2 changes state within a small temperature interval.

We have measured the nuclear spin-lattice relaxation of the $J=0$ molecules in solid deuterium for $0.24 < X < 0.33$ and $40 < T < 700$ mK at a Larmor frequency of 46 MHz, with results significantly different from those of Ref. 11. We find no evidence of two distinct relaxation times, and the single time constant t_{1N} we measure has a very broad, rounded minimum as a function of temperature (we use the subscript "N" to refer to the narrow NMR line from the $J=0$ molecules and the subscript "W" to refer to the wide NMR line from the $J=1$ molecules). There is no discontinuity in the derivative of t_{1N} with respect to temperature, nor any other indication of a

sharp transition at 170 mK. Two earlier studies of t_1 in solid D_2, by Constable and Gaines[12] and by Weinhaus *et al.*,[13] were limited to temperatures higher than those employed in Ref. 11 and in the present work. However, the measurements of Ref. 12 did extend down to 150 mK at $X=0.33$. Consistent with our results, no evidence of a transition was seen.

Deuterium gas was condensed into a sample chamber[14] and frozen at the triple point over the course of about 15 min. The area of the NMR line was used for thermometry. We observed the recovery of the absorption line after saturation using magnetic modulation and phase-sensitive detection. By saturating the NMR line by 50% or more, we could clearly distinguish the nuclear relaxation from the thermal relaxation of the sample chamber after a saturating pulse. The data were fitted to three different functional forms, using a least-squares procedure: (1) a single exponential, (2) the sum of two exponentials, and (3) the sum of two exponentials with the shorter exponential time constant fixed at the time constant of the filter at the output of our phase-sensitive amplifier. This filter time constant was set to about $\frac{1}{10}$ the apparent nuclear relaxation time for each temperature.

An examination of trends in the fitted time constants for a large number of measured relaxation curves led us to the following conclusions: (1) While the relaxation does show departures from a single exponential for temperatures below 120 mK, there is no evidence for two distinct time constants. (2) Some of these departures were due to the low-pass filter in our electronics. These conclusions are illustrated by Fig. 1, which shows the results of fitting data with $X=0.31$ to the three different functional forms. The time constant for the smaller-amplitude component of the double exponential shows no consistent trend, and thus may be considered spurious. On the other hand, the inclusion of the low-pass filter term reduces the scatter in the nuclear relaxation time t_{1N}.

The $J=0$ relaxation times obtained in this way for $X=0.30$ and 0.24 are shown in Fig. 2. The data show no sign of a sharp transition into the QG state at 170 (Ref. 11) or 130 mK.[4] It is suggested in Ref. 4 that there is a sharp transition, but that the tem-

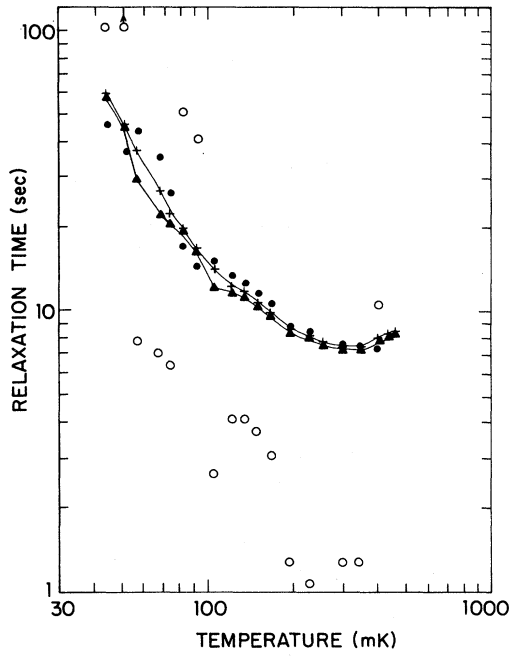

FIG. 1. Nuclear spin-lattice relaxation times of $J=0$ molecules in solid D_2 for $X=0.31$, obtained by fitting data to a single exponential (triangles), to the sum of two exponentials (open and closed circles), and to a single exponential plus a term for the low-pass filter in our apparatus (crosses). For the double exponential fit, the closed circles show the time constant for the larger-amplitude component of the relaxation, while the open circles show the time constant for the smaller component.

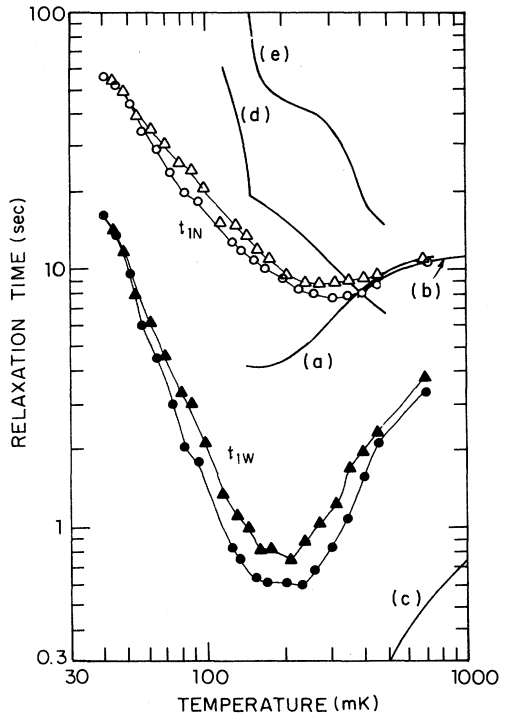

FIG. 2. Measured nuclear spin-lattice relaxation times t_{1N} for the $J=0$ line, and inferred relaxation times t_{1W} for the $J=1$ line at a Larmor frequency $\nu_l=46$ MHz (circles, $X=0.30$; triangles, $X=0.24$). Solid lines show previously reported measurements, as follows: (a) Ref. 12, t_{1N} ($X=0.29$, $\nu_l=3$ MHz); (b) and (c) Ref. 13, t_{1N} and t_{1W}, respectively ($X=0.33$, $\nu_l=5.5$ MHz); (d) and (e) Ref. 11, showing the short and long components of t_{1N} ($X=0.33$, $\nu_l=25$ MHz).

perature T_c at which it occurs falls to zero for X somewhat below 0.30. This possibility is not strictly excluded by our measurements, but it appears unlikely that the relaxation behavior is so highly dependent upon X (see Fig. 2).

The nuclear spin relaxation we measure for the $J=0$ molecules is dominated by cross relaxation with the unobserved, wide $J=1$ NMR line. In H_2, on the other hand, the nuclear spin relaxation of the $J=1$ molecules is measured directly. In order to compare our D_2 data with the H_2 data we have adapted a model of the cross relaxation developed by Weinhaus *et al.*[13] In Ref. 13, the wings of the wide $J=1$ line were approximated by a single heat bath. Because we are interested in the low-temperature regime, where the $J=1$ line is so broad that only its central section participates in the relaxation of the $J=0$ line, a different approximation is appropriate. The nuclear magnetic heat capacity associated with the part of the $J=1$ line which relaxes the $J=0$ line is much smaller than the magnetic heat capacity associated with the $J=0$ line itself (the *total* $J=1$ heat capacity is only $\frac{1}{5}$ that associated with the $J=0$ line, for $X=0.33$). This allows us to calculate the behavior of the combined $J=0,1$ system by first assuming that the $J=0$ spin temperature is fixed and computing the relatively rapid relaxation of the $J=1$ line into its nonequilibrium steady state. Then the much slower relaxation of the $J=0$ line is computed using the magnetization flow computed for the $J=1$ line steady state.

We use the following model for the combined spin system: The intrinsic relaxation in $J=0$ molecules is ignored, so all of the observed relaxation is assumed to be the result of cross relaxation with the $J=1$ molecules. The narrow $J=0$ line is characterized by a nuclear magnetization M_N, while the wide $J=1$ line is characterized by a magnetization per unit frequency $m_W(\nu)$, where ν specifies the position within the NMR line. We approximate the shape function $g(\nu)$ for the $J=1$ line [satisfying $\int g(\nu)\,d\nu=1$] by a constant $g_0=g(\nu_0)$, where ν_0 is the center frequency of the line. This is permissible because only the central part of the $J=1$ line is relevant to the relaxation of the $J=0$ line. In the same manner the spin-lattice relaxation of the $J=1$ line is described by a constant $w_1=(t_{1W})^{-1}$. A differential equation of the diffusion type may then be written for the $J=1$ line:

$$\frac{\partial m_W(\nu)}{\partial t}=-w_1[m_W(\nu)-m_{W0}]+d_m\frac{\partial^2 m_W(\nu)}{\partial \nu^2}\ , \tag{1}$$

where m_{W0} is the value of $m_W(\nu)$ when the wide line is in equilibrium with the lattice, and d_m is a spin diffusion constant. We estimate $d_m=g_0/t_2^4$, using the arguments of Bloembergen *et al.*[15] Here

$$1/(t_2)^2=(3-5X)5.41\times10^5(\text{rad/sec})^2$$

is the second moment due to intermolecular interactions.[16]

The center of the $J=1$ line is in good thermal contact with the $J=0$ line. When we take the relative heat capacities of the $J=0$ and $J=1$ lines into account, this may be expressed as

$$m_W(\nu_0)-m_{W0}=(M_N-M_{N0})[2Xg_0/5(1-X)]\ ,$$

where M_{N0} is the equilibrium value of the magnetization M_N in the $J=0$ line. Far from the center of the line, the $J=1$ spins are always in better contact with the lattice than with the narrow $J=0$ line. The steady-state solution to Eq. (1) with these boundary conditions is

$$m_W(\nu)-m_{W0}=(M_N-M_{N0})\frac{2Xg_0}{5(1-X)}\exp[-(w_1/d_m)^{1/2}|\nu-\nu_0|]\ .$$

The time scale over which this steady state is achieved is computed by solving the differential equation for the difference between $m_W(\nu)$ and its steady state. It is found that each Fourier component of the difference decays with its own exponential time constant, but that these time constants are bounded above by the $J=1$ relaxation time $t_{1W}=(w_1)^{-1}$. Thus, as might be expected, the steady state is achieved in a time on the order of t_{1W}. From the magnetization flow implied by this steady state, and our estimate of d_m, we calculate the $J=0$ relaxation rate

$$(t_{1N})^{-1}=4Xg_0^{3/2}w_1^{1/2}/[5(1-X)t_2^2]\ . \tag{2}$$

We have arrived at the following picture for the relaxation behavior of the $J=0$ line: First, there is a nonexponential transient with characteristic time t_{1W}, during which the wide $J=1$ line achieves its steady state. Then, there is an exponential relaxation with the much longer time constant given by Eq. (2). The initial nonexponential transient is not expected to be observable in the $J=0$ relaxation, because its magnitude would be at most $\frac{1}{5}$ the magnitude of the longer exponential relaxation, even if the saturating pulse were short compared to t_{1W} and the entire $J=1$ line participated in the relaxation. In fact, only a small fraction of the $J=1$ line participates, and the length of the saturating pulses we use is comparable to $t_{1N}>>t_{1W}$. This picture is consistent with our observations and with those of Ref. 13, but not with those of Ref. 11.

In order to compute the relaxation time t_{1W} for the

unobserved $J=1$ line, we have obtained estimates of the $J=1$ line density g_0 by scaling H_2 line-shape data from our previous research. The t_{1W} inferred in this way from our t_{1N} data are shown in Fig. 2. These relaxation times for the $J=1$ D_2 line may be compared with relaxation times measured in the H_2 quadrupolar glass, by scaling the temperature by 0.81 (the ratio of the EQQ coupling constants for D_2 and H_2), and scaling the relaxation time by $d_H^2/d_D^2=5.2$, where d specifies the strength of the intramolecular coupling which gives rise to the relaxation.[16] It is clear from Fig. 2 that our data do not suggest any kind of rapid change of state in the neighborhood of the supposed QG transition. The temperature dependence of the inferred $J=1$ relaxation times are in good agreement with the H_2 measurements of Washburn and coworkers[5,6] but the actual values of t_{1W} are about five times greater than the scaling relation suggests. A comparison with the higher-temperature D_2 relaxation measurements of Ref. 13 yields the same conclusion: There is excellent agreement with the present measurements if our t_{1W} are decreased by a factor of 5. This results from the roughness of our estimate of the spin diffusion constant and the t_2^{-4} dependence of t_{1W} which is implied by Eq. (2). (Sullivan *et al.*[3] have recently presented t_1 measurements for H_2 showing a sharp minimum near 400 mK for $X=0.38$, in apparent disagreement with Ref. 6 and the present work.)

Our relaxation data suggest that D_2 and H_2 really are in analogous states in the QG region of the phase diagram. One may therefore hope that future theoretical work on randomly diluted spin systems will be directly applicable to the solid hydrogens.

ACKNOWLEDGMENTS

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