NUCLEAR SPIN RELAXATION IN SOLID HD WITH H_2 IMPURITY

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Since the initial success of lanthanum magnesium nitrate single crystals as polarized proton targets in nuclear scattering experiments, physicists have begun to search for polarizable material richer in unbound protons.[1] Solid ortho-H_2, the most desirable candidate, appears to be quite unsuitable for dynamic polarization by the solid effect because of its short nuclear spin relaxation time.[2,3] Solid HD, the next best choice, is more promising as at low temperatures the HD molecules are in the rotational state $J=0$, and one expects the intrinsic coupling of the nuclear spins to the lattice to be very weak. However, as Bloom[3] has shown from measurements in solid HD containing 2.5% H_2, the proton relaxation time T_1 is governed by the ortho-H_2 impurity present and can be quite short at liquid helium temperatures. This is due to the fact that the HD protons can exchange energy with the ortho-H_2 spins by means of mutual spin flips that conserve energy so long as the spin energy levels of the ortho molecules are not appreciably perturbed by the quenching of the molecular rotation. In this Letter we present measurements of the proton T_1 as a function of ortho-H_2 concentration, temperature, and magnetic field intensity. Some incidental details pertinent to the polarization of solid HD are also included.

Figure 1 shows the dependence of T_1 on normal-hydrogen (n-J_2) concentration k for a magnetic field of 2.05 kG and $T=4.2$°K. The HD was obtained by double distillation at 20.4°K of chemically prepared HD; the purest sample was then mixed with known quantities of n-H_2. It is found empirically that for small k, a plot of $T_1^{-3/8}$ versus added n-H_2 concentration gives a straight line, and by extrapolation we have estimated the initial n-H_2 concentration of the sample to be 0.85×10^{-4}. This procedure is of doubtful validity and one should consider the concentrations given in Fig. 1 to be uncertain by some additive constant. Nevertheless, such an uncertainty in concentration does not mask the extremely strong dependence of T_1 on ortho-H_2 concentration for low k. Even more startling is the dependence of T_1 on the n-H_2 impurity concentration at lower temperatures, i.e., at 1.2°K T_1 increases faster than k^{-4}.

The variation of T_1 with temperature (Fig. 2) shows a marked dependence on impurity H_2 concentration: At $k\approx10^{-3}$ there is essentially no temperature dependence; whereas the T_1 of our purest samples increases by a factor ~16 as the temperature is changed from 4.2 to 1.2°K. The temperature dependence of two HD samples containing 0.6 and 6% neon are also shown in Fig. 2. Because of the marked increase of T_1 at 1.2°K, the addition of neon would be advantageous for HD used in a polarized target.

The magnetic field dependence of T_1 for very pure HD samples at 4.2°K is roughly described by $T_1 \propto H_0^{1/3}$. T_1 of a less pure sample ($T_1=100$ sec at 1.4°K) showed no field dependence (±10%) for H_0 between 6.0 and 11.0 kG. The field dependence of the sample with 6% neon behaved roughly as $H_0^{1/3}$ down to 200 G at 1.3°K.

As a qualifying remark to the above, we note that in general the recovery of the nuclear magnetization in HD is observed to be nonexponential. Although the most useful single quantity characterizing a distribution of relaxation times

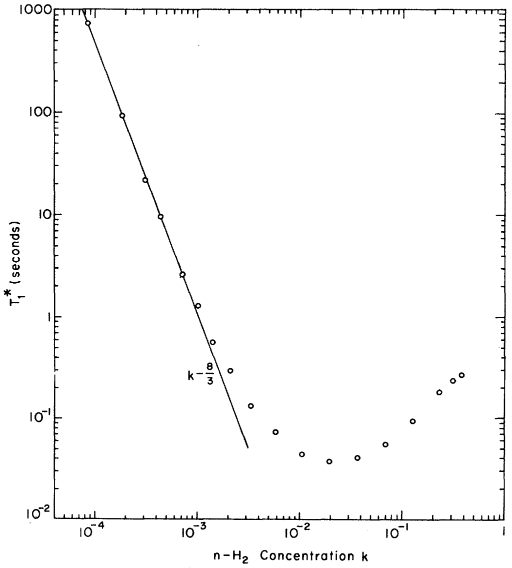

FIG. 1. Nuclear relaxation time in solid HD at $T=4.2$°K and $H_0=2.05$ kG as a function of normal H_2 concentration k.

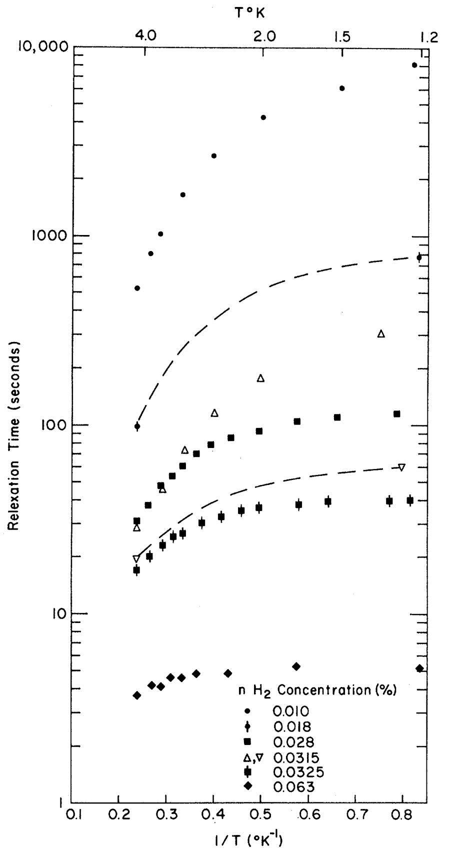

FIG. 2. Nuclear relaxation times in HD samples containing different amounts of n-H_2 as a function of inverse temperature $1/T$. The n-H_2 concentrations were inferred using the concentration dependence given in Fig. 1 neglecting effects of the unknown D_2 impurity. The triangles designate a particular HD sample before (▽) and after (△) addition of 6 % neon. (The same sample with 0.6% Ne had very nearly the same dependence as the 6% sample.)

is $\langle 1/T_1\rangle$, which is the slope of the recovery at the origin, this is not well defined experimentally in the absence of a priori information on the form of the distribution. For this reason the quantity $T_1{}^*$, defined to be the time at which the magnetization recovers to within $1/e$ of its equilibrium value, has been used. As far as could be ascertained, $T_1{}^*$ was never more than 30% larger than $\langle 1/T_1\rangle^{-1} = (T_1)_{\text{initial}}$. Even though it is expected that the nuclear relaxation time of an impurity ortho-H_2 molecule varies from site to site,[4] a simple calculation shows that spin diffusion should be fast enough to produce a single relaxation time in HD.[5] It is quite possible that $T_1{}^{H_2}$ depends on the orientation of H_0 with respect to the crystalline axis,[6] giving rise to a distribution of T_1's in our polycrystalline sample. We have tried inconclusively to demonstrate this by rotating the sample during a T_1 measurement.

For n-H_2 concentrations greater than 2×10^{-3}, the concentration dependence of T_1 in HD can be explained in terms of relaxation results obtained in solid H_2,[4] which in turn admit of a simple qualitative explanation. Assuming that the spin-diffusion process in HD is fast, one can write the relaxation time $T_1(x)$ for a solid containing HD and H_2 in terms of the relaxation time for the isolated ortho-H_2 spin system $T_1{}^{H_2}(x)$, and the ratio of the spin-system heat capacities

$$T_1(x) = \frac{c_{\mathrm{HD}} + c_{\mathrm{H_2}}}{c_{\mathrm{H_2}}} T_1{}^{H_2}(x) = \frac{\frac{1}{2}(1+\frac{4}{3}x)}{\frac{4}{3}x} T_1{}^{H_2}(x), \quad (1)$$

where x is the ortho-H_2 concentration ($x = \frac{3}{4}k$). The values of $T_1{}^{H_2}(x)$ predicted by Eq. (1) are in quite good agreement with values of T_1 in solid H_2 having the same ortho concentration. This is to be expected; for as far as molecular reorientation is concerned (and this is what determines the nuclear relaxation time of an ortho-H_2 molecule), HD is very similar to para-H_2. Down to the lowest concentrations studied (0.2% ortho), the time dependence of the orientation of an ortho molecule in solid H_2 seems to be adequately accounted for by the adiabatic process of mutual reorientation of the molecular electric quadrupole moments.[4,7] This indicates that ortho-para interactions have a very weak effect on molecular reorientation in the solid. The lack of temperature dependence of T_1 in HD for $k \approx 10^{-3}$ suggests that the splitting of the $J=1$ level of ortho-H_2 by interactions with HD neighbors is much less than 1°K in apparent contradiction with the heat-capacity results.[8]

The broad minimum in T_1 occurring as the ortho-H_2 concentration decreases from 10^{-2} to 10^{-3} is most certainly associated with the correlation times for molecular reorientation becoming equal to the nuclear Larmor period. However, the frequency spectra associated with molecular reorientation at low ortho-H_2 concentrations are probably complex and cannot be completely characterized by a single correlation time. This is a result of the short range of the quadrupole-quadrupole interaction: At low concentrations the interaction of an ortho molecule with its nearest ortho neighbor is dominant, giving rise to resolved energy levels, the widths of which are determined by the interactions with the rest of the ortho molecules. Frequencies associated with splittings of the $J=1$ level by ortho-para-type interactions will also appear in the spectra leading to a complicated distribution of frequencies and widths.

For n-H_2 concentrations below 10^{-3} the nuclear T_1 results are not well understood. The concentration and temperature dependence suggest two competing mechanisms for molecular reorientation: the previously mentioned one which becomes weaker and weaker at lower concentrations and which should be temperature independent, and the intrinsic relaxation of the molecule in its HD environment which is concentration independent but which is expected to be temperature dependent.[9] However, the results have resisted so far a quantitative analysis of this sort. The field dependence $T_1 \propto H_0^{1/3}$ should not be too surprising since the reorientation spectra are complex.

The stronger temperature dependence of T_1 in the samples containing neon can be explained as follows: The presence of a neon atom near an ortho-H_2 molecule can induce crystal field splittings of the $J=1$ rotational state. These splittings will vary from molecule to molecule and hence, the adiabatic mutual reorientation among the ortho-H_2 molecules will be quenched.[10] The observed temperature dependence will then be characteristic of the intrinsic molecular process.

The T_1 of an HD sample containing a small but unknown amount of H_2 and D_2 impurity was measured as a function of time the sample spent at 4.2°K. The relaxation time (initially 18 sec) increased exponentially by 1.2% per hour for one week and ≅0.9% per hour during the second week because of conversion of the ortho-H_2 to the para form. If one combines the initial rate with the observed concentration dependence of T_1 (Fig. 1), one obtains an estimate of 0.45% per hour for the ortho-para conversion rate of H_2 in HD. The drop in the rate of increase of T_1 during the second week is probably due to the presence of para-D_2 ($J=1$), which can affect the molecular reorientation rate of the ortho-H_2. It should be noted that the time dependence of T_1 provides an obvious but important proof that relaxation in our HD samples is controlled by ortho-H_2 (or para-D_2) rather than by other impurities.

It is interesting to note that the decomposition of HD into H_2 and D_2 is very slow at room temperature. The T_1 of our purest sample (~1 part in 10^4 H_2) did not change noticeably after 6 months storage at room temperature at a pressure of 450 mm Hg.

We have made some relaxation measurements in HD samples irradiated at 4.2°K with Co^{60} γ rays. The main effect is a lowering of the value of T_1, presumably due to the production of ortho-H_2. As an example, the T_1^* of one sample dropped from 755 to about 200 sec after an irradiation of about 4×10^6 rad, indicating an increase in ortho-H_2 concentration of less than 0.3×10^{-4}.

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[1] R. J. Wagner and R. P. Haddock, Phys. Rev. Letters 16, 1116 (1966).

[2] Solid H_2 is unsuitable for another reason: The paramagnetic impurities required for polarization by the solid effect very quickly convert neighboring ortho-H_2 molecules to the nonmagnetic para state. In one hour the radius of the surrounding sphere of para H_2 is about 3 lattice spacings, leaving the impurity magnetically isolated. See K. Motizuki and T. Nagamiya, J. Phys. Soc. Japan 11, 93 (1956); 14, 1639 (1959).

[3] M. Bloom, Physica 13, 767 (1957).

[4] W. N. Hardy and J. R. Gaines, to be published.

[5] See, for example, A. Abragam, Principles of Nuclear Magnetism (Oxford University Press, New York, 1961), pp. 138-139.

[6] This could arise for several reasons: (1) the appearance of a Pake doublet because of either depopulation of one of the $J=1$ sublevels or a slow transition rate among the sublevels; (2) the lifting of the degeneracy of the $J=1$ level so that the projection of the reorientational spectral densities onto the direction of H_0 will involve angular factors; or (3) possible existence inho-

mogeneously distributed stresses that would induce splitting of the $J=1$ level.

[7] T_1 in solid H_2 with high concentrations of ortho was first calculated by T. Moriya and K. Motizuki, Progr. Theoret. Phys. (Kyoto) 18, 183 (1957). The calculation has been repeated recently by A. B. Harris and E. Hunt, Phys. Rev. Letters 16, 845 (1966).

[8] G. Grenier and D. White, J. Chem. Phys. 40, 3451 (1964).

[9] J. Van Kranendonk and V. F. Sears, Can. J. Phys. 44, 313 (1966).

[10] A similar phenomenon is observed in solid methane when krypton is added. C. A. DeWitt, thesis, University of British Columbia, 1966 (unpublished).

OBSERVATION OF DEGENERATE STIMULATED FOUR-PHOTON INTERACTION AND FOUR-WAVE PARAMETRIC AMPLIFICATION

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We report in this Letter the observation of stimulated four-photon or light-by-light scattering for the case where the coupling is due to the molecular-orientation Kerr effect. In this process two forward-going photons in an intense beam of light scatter to produce two photons traveling at small angles $+\theta$ and $-\theta$, respectively.[1] If photons are already present in the $+\theta$ and/or $-\theta$ beams, this stimulates the process. In contrast to the stimulated Raman case, coupling of these weak waves produces gain.[2] One type of four-photon or four-wave mixing experiment was performed by Maker and Terhune involving $\chi^{(3)}(\omega+\Delta\omega, \omega-\Delta\omega, \omega, \omega)$ where the beams are all collinear and $\Delta\omega \neq 0$.[3] In our experiment, weak-wave retardation allows phase matching and hence strong exponential gain even for the degenerate case when all the waves have the same frequency and are <u>not</u> collinear.[4] Furthermore, this experiment isolates the fundamental process causing beam trapping, namely, the amplification of nonforward directed Fourier components of the beam.

A Q-switched ruby-laser beam with a power of 150-300 MW and a divergence of 6 mrad was focused by a lens of 1-m focal length into a short liquid cell. A weak beam in the $+\theta$ direction was obtained from the forward laser beam by a beam splitter and mirror arrangement (as shown in Fig. 1). Both beams were then focused and deflected by the same lens so as to cross within a nitrobenzene cell. The $+\theta$ beam is amplified in the process of stimulated light-by-light scattering and, in addition, a beam in the $-\theta$ direction is generated. The appearance of this $-\theta$ beam is the signature of this effect. For the purpose of alignment, a large-diameter He-Ne gas-laser beam was arranged to coincide with the ruby beam. This was used in conjunction with a focusing alignment telescope which assured that the two beams

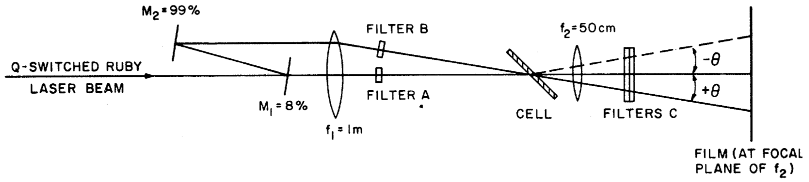

FIG. 1. The experimental arrangement. Q switching was accomplished by a combination of a rotating prism and a saturable dye cell.