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Nuclear Longitudinal Relaxation in hcp D_2[†]

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We present a systematic study of longitudinal nuclear relaxation times T_1 in hcp D_2 between 0.4 °K and the triple point, about 18.7 °K, at a frequency of 4.7 MHz. The concentration range of the para molecules (i.e., those with a rotational angular momentum $J = 1$) was between $C = 0.02$ and $C = 0.91$. Following saturation, the recovery of the longitudinal magnetization was observed to be exponential as a function of time for all concentrations, and hence the relaxation time T_1 was always well defined. In the region below 11 °K, where thermally activated diffusion is "frozen out," the main relaxation mechanisms are by means of the modulation of the intramolecular dipolar fields by the intermolecular electric quadrupole-quadrupole interaction, and by cross relaxation between the nuclei of molecules with $J = 0$ (ortho D_2) and $J = 1$ (para D_2). The agreement between the limiting high-temperature value $T_{1\infty}$ and that calculated from theory is good at high concentrations of (J=1) molecules, but only fair at low concentrations. For the latter region, systematic discrepancies between experiment and theory are discussed. The strong temperature dependence of T_1 below 4 °K is not well understood. In the region above about 12 °K, where diffusion narrows the linewidth, and for concentrations C above about 0.3, the relaxation time T_1 is hardly affected by diffusion and shows only a small increase with T. However, T_1 for low ($J = 1$) concentrations shows a strong increase with T and a maximum near 17 °K. This behavior can be understood in terms of a theory by Bloom, which was applied to the similar case of solid HD with H_2 impurities. At temperatures above 13 °K, T_1 becomes influenced by diffusion, and the data could be quantitatively fitted to Bloom's theory using two parameters with values close to those estimated theoretically.

I. INTRODUCTION

The longitudinal relaxation mechanisms in solid H_2, HD, and D_2 have long been the subject of a number of theoretical studies. The experimental literature on solid H_2 and HD is, however, more abundant by far than that on solid D_2, where only very recently have systematic investigations been started. Because the rotational motions and intermolecular interactions are very similar in solid H_2 and D_2, a number of theories developed for H_2 readily apply to D_2. Hence it will be convenient to review briefly the findings in the former before starting with the subject of the present paper, solid hcp D_2.

In H_2, only the molecules with a rotational angular momentum ($J = 1$), i.e., ortho H_2, have a nuclear magnetic moment, and thus have an associated relaxation time T_1. In the solid phase, one may, roughly speaking, consider three regions where different relaxation mechanisms are operative.

In the first region, between the triple point, $T = 13.7$ and 10 °K, the nuclei relax by means of the intramolecular dipolar interaction as modulated by the intermolecular electric quadrupole-quadrupole interaction (EQQ)[1-3] characterized by an interaction parameter Γ,[4] and by thermally activated diffusion.[1] In the second region, below about 8 °K, the diffusion mechanism is inoperative and the relaxation is entirely by means of the electric quadrupolar coupling mechanism. The third region is the orientationally ordered cubic phase,[4] which is formed at low temperatures for ($J = 1$) concentrations above about 0.55.[5] The relaxation mechanism believed to be dominant here is that due to scattering of the librational waves by the nuclear moments.[3,6]

In the first region, investigated experimentally by Bloom[7] and more recently by Hass *et al.*,[8] a quantitative interpretation of the T_1 results has still to be made. A complication is that the two relaxation mechanisms mentioned above possibly do not operate independently.

In the second region, there has been almost quantitative agreement between theory[3,9] and experiment[10] for high concentrations ($C > 0.50$) at temperatures where comparison is possible, namely, above about 6 °K. Recently Harris[3] has made a detailed calculation using the Gaussian approximation for the spectral density functions $J(\omega)$, first employed by Moryia and Motizuki.[1] There he calculates the first term in $1/T$ which shows the departure of $T_1(J = 1)$ from the high-temperature limit $T_{1\infty}(J = 1)$. Still more recently, Hama and Nakamura[9] have calculated T_1 by taking into account the departure from the Gaussian approximation, as indicated by the 2nd and 4th moments of $J(\omega)$. For a given electric quadrupolar coupling parameter, they find $T_{1\infty}(J = 1)$ to be shorter by about 10% than that obtained using the Gaussian approximation.[1,3] This more recent theory[9] shows the best agreement with the experiments.[10] For ($J = 1$) concentrations below about 0.4, Sung[11] has predicted a $C^{5/3}$ dependence for T_1, using a statistical model. The data taken at 4.2 °K,[12] however, only qualitatively verify his theory. For a correction of Sung's results see Ref. 3.

In the third region, only some scattered data, mainly unpublished, have been taken[13,14] and the experimental situation is an unsatisfactory one at the present time. The difficulties in the experiment are partly associated with the high ortho-para conversion rates and the long relaxation times.

The situation in solid D_2 is complicated by the fact that in addition to the $(J=1)$ molecules with $I=1$, $\frac{5}{6}$ of the molecules with $J=0$ (ortho D_2) have a nuclear magnetic moment. Hence one has to consider the relaxation mechanism of the combined $(J=0)$ and $(J=1)$ systems. However, a number of recent papers[3,6,9] on the theory of relaxation in solid H_2 can still be applied to the D_2 problem. For convenience to the reader, we present in Fig. 1 a diagram of the various energy systems and the relaxation times connected with the energy transfers between these systems in D_2.

In this paper we present a study of T_1 in hcp D_2 between 0.4 °K and the triple point and over a large range of concentrations of $(J=1)$ molecules. Experiments in the cubic phase along with data in the hcp phase have been reported by other authors[15,16] and the relaxation theory and the experiments in the cubic phase will not be discussed here. In Sec. II, we present a short review of the nuclear relaxation mechanisms considered relevant for hcp D_2. In Sec. III, the experimental techniques are discussed and reference is made to the methods of measuring the concentration of $(J=1)$ molecules. Finally, in Sec. IV, we present and discuss the results. Where possible, comparisons with previous experiments[15-17] are made.

II. THEORETICAL REVIEW

We shall treat separately two temperature regions in the hcp phase, as distinguished by the early NMR-linewidth work of Rollin and Watson.[18] In the first region, below about 11 °K, where the observed linewidth is that of the "rigid lattice," the electric quadrupole-quadrupole interaction constitutes the dominant mechanism for longitudinal nuclear relaxation. In the second one, above about 13 °K, where the linewidth has narrowed to about $\frac{1}{5}$ of the value at 11 °K, classical diffusion becomes influential in the relaxation process at concentrations of $(J=1)$ molecules below about 0.3.

A. T_1 in the Nondiffusion Region

Moryia and Motizuki[1] were the first to correctly estimate the relaxation rates in this region. They estimated that the spin-spin relaxation time between the two nuclear species (which we shall henceforth call the cross relaxation time T_x), was much shorter than the direct spin-lattice relaxation time of the $(J=1)$ molecules $T_1(J=1)$, which in turn was much shorter than the spin-lattice relaxation time of the $(J=0)$ molecules $T_1(J=0)$. Hence the nuclei of the $(J=0)$ molecules were predicted to exchange energy with the lattice mainly by means of the $(J=1)$ molecules. Taking into account the heat capacities of the Zeeman systems of the para and ortho molecules between which energy is exchanged, Moryia and Motizuki[1] calculated the observable relaxation time to be

$$\frac{1}{T_1}=\left(\frac{5(1-C)}{T_1(J=0)}+\frac{2C}{T_1(J=1)}\right)\frac{1}{5-3C}\,, \tag{1}$$

where C is the concentration of $(J=1)$ molecules. Assuming $T_1(J=0) \gg T_1(J=1)$, one then has

$$T_1=T_1(J=1)\,[(5-3C)/2C]\ . \tag{2}$$

Using the Gaussian approximation for the spectral density function, expected to be valid for $C \gtrsim 0.5$, and the appropriate nuclear interaction parameters for D_2, they then calculated the relaxation time in the high-temperature limit $T_{1\infty}(J=1)$, and thus $T_{1\infty}$ for an hcp single crystal in the direction of the c axis. Their result for $T_{1\infty}(J=1)$ due to the EQQ processes, which we denote by $T_{1\infty}^{Q}(J=1)$, was

$$T_{1\infty}^{Q}(J=1)=3.62\,C^{1/2}(\Gamma/k_B)\ \text{sec}, \tag{3}$$

using nearest-neighbor interaction only. Here we have factored out the explicit dependence on Γ/k_B, taking into account that these authors chose an incorrect value for this parameter in their Eq. (62).

More recently, Harris[3] has derived an expression containing the first temperature-dependent term, using also the Gaussian approximation and some improved assumptions. For a single crystal, his calculations indicate an anisotropy in $T_1^{Q}(J=1)$ less than 1%. His expression for a powder, the

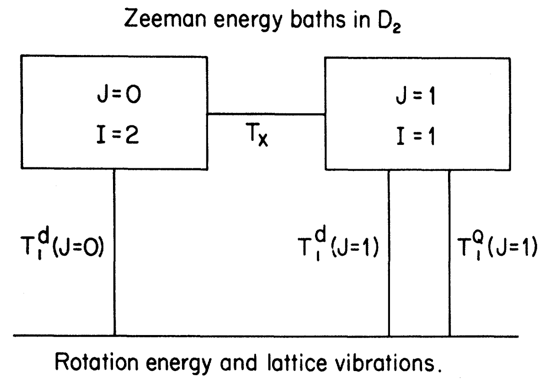

FIG. 1. Various energy systems in solid D_2 and the relaxation times that govern the energy flow between them. Lattice and rotational system for the $(J=1)$ molecules are assumed to be very strongly coupled.

more relevant one to this work, is

$$T_1^Q(J=1) = T_{1\infty}^Q(J=1)\,[1 - \tfrac{9}{14}\,(\Gamma/k_BT) - \tfrac{1857}{1792}\,C(\Gamma/k_BT)]^{1/2}, \tag{4}$$

with

$$T_{1\infty}^Q(J=1) = 3.56\,(\Gamma/k_B)C^{1/2}\text{ sec}, \tag{5}$$

using nearest-neighbor interaction only. This is in good agreement with the earlier work.[1] The more refined calculations of Hama and Nakamura[9] on solid H_2 can also be applied to solid hcp D_2. Inserting the relevant nuclear interaction parameters for D_2, quoted in Ref. 1, and using nearest-neighbor EQQ interaction only, we find

$$T_{1\infty}^Q(J=1) = 3.17(\Gamma/k_B)[C^{1/2}/(1+0.021\,C^{-1})]\text{ sec}. \tag{6}$$

If contributions from the second and further neighbors are included and dielectric screening neglected, the numerical coefficient in Eq. (6) is 3.21. The expression of Hama and Nakamura[9] for the temperature dependence of $T_1^Q(J=1)$ is identical to that obtained by Harris[3] [Eq. (4)].

At low $(J=1)$ concentrations, where the $(J=1)$ molecules interact with only a small number of the $(J=1)$ neighbors, the statistical model of Sung[11] appears appropriate. Using this model and in addition modifying some averaging processes in the calculation, Harris has obtained[3]

$$T_1^Q(J=1) = 13.0(\Gamma/k_B)C^{5/3}\text{ sec}. \tag{7}$$

Still more recently, Nakamura and Hama[19] have been engaged in calculating the concentration dependence of $T_1^Q(J=1)$ by considering the effect of the various configurations of $(J=1)$ molecules on the spectral density functions. Their theory, which is not complete at the present time, will be compared with the experimental results elsewhere.[19]

B. T_1 in the Diffusion Region

A general theory of the relaxation times which result from the interactions of the nuclei with fluctuating local magnetic fields, in particular, when influenced by self-diffusion, has been given in several papers[20] and textbooks.[21] We first consider the relaxation for a system of nuclear spins I in an fcc lattice.[21,22] As can be seen from the T_2 results for D_2 quoted below, the diffusion is slow enough that it is reasonable to consider the situation where $\omega\tau \gg 1$. Here $\omega/2\pi$ is the Larmor frequency and τ is the correlation time characterizing self-diffusion. One obtains, using a random-walk calculation for the fcc lattice,[21]

$$1/T_1^d = 84\,[\gamma^4\hbar^2 I(I+1)n]\,(D/\omega^2a^5), \tag{8}$$

where T_1^d indicates that diffusion is the source of relaxation. Here γ is the gyromagnetic ratio, n the number of nuclei per cm^3, a is the distance of closest approach, which we take to be the average distance between nearest neighbors, and D is the diffusion constant expressed as

$$D = D_0 e^{-E/k_BT}, \tag{9}$$

where E is the activation energy.

Likewise, one calculates[20] for the linewidth

$$(T_2^d)^{-1} = 4\gamma^4\hbar^2 I(I+1)n/5Da. \tag{10}$$

At this point, it is interesting to compare the relaxation times for $(J=1)$ molecules, $T_1^Q(J=1)$ and $T_1^d(J=1)$. The former can be estimated for any concentration of $(J=1)$ molecules from Eqs. (4) and (7) by taking a value of $\Gamma/k_B = 1.1$ °K.[4,23] The latter can be estimated using Eqs. (8) and (10) and recent unpublished[24] T_2 data on D_2 in the diffusion region, where[25]

$$T_2^d \approx T_2 = 3.31\times10^6 e^{-288/T}\text{ sec} \tag{11}$$

in the range $13 < T < 17.5$ °K, independent of C. It turns out that for any concentration of $(J=1)$ molecules and at all temperatures right up to the triple point, $T_1^Q(J=1) \ll T_1^d(J=1)$. Hence, for D_2, it is predicted that diffusion will have very little influence on the relaxation of the $(J=1)$ molecules, even at high concentrations. This is different from the situation in solid H_2 in the diffusion region, where T_1 at high $(J=1)$ concentrations decreases as T increases.

For the $(J=0)$ molecules in the solid mixture, the longitudinal relaxation rate will be via diffusive motion and via cross relaxation with the $(J=1)$ molecules. Rather than developing expressions for an arbitrary concentration of $(J=1)$ molecules, we shall only consider the situation where $C \ll 1$. These conditions are very similar to those of solid HD with impurities of H_2, studied by Bloom.[7] The similarity is based on the observation that solid ortho D_2, like HD and para H_2, has an angular momentum $J=0$; and para D_2, like ortho H_2, has $J=1$. Furthermore, the nuclear spins in the ortho $D_2(I=2)$-para $D_2(I=1)$ resonating system have the same gyromagnetic ratio, which is the same situation that we find for the HD-H_2 system. We therefore can use the relation obtained by Bloom for small concentrations, where one essentially observes the signal (and hence the effective relaxation rate) of the $(I=2)$ spin system. By making some reasonable assumptions on the relevant spectral densities, and on the comparative magnitude of the relaxation times involved, Bloom[7] has obtained

$$1/T_1 = 1/[T_1^d(J=0)] + f/[T_x + T_1(J=1)], \tag{12}$$

where $f = 2C/[5(1-C)]$ for D_2 for low $(J=1)$ concentrations, and for $T_x \ll T_1(J=1)$ this expression reduces to Eq. (2). Here T_x is the cross relaxation time which in the diffusion region is given by

$$1/T_x = 4\pi\gamma^4\hbar^2 nI(I+1)/45a[D(J=0)+D(J=1)], \quad (13)$$

where $I=2$, n is the number of molecules per cm^3 with spin $I=2$, and $D(J=0)$ and $D(J=1)$ are, respectively, the diffusion constants for the $(J=0)$ and $(J=1)$ molecules. Making the crude assumption that these two quantities are equal, we obtain by combining Eqs. (10) and (13)

$$T_x = BT_2^d \quad \text{with } B\approx 6. \quad (14)$$

By combining Eqs. (8) and (10), we also obtain

$$T_1^d(J=0) = (AT_2^d)^{-1} \quad \text{with } A\approx 10^{-1}\ \text{sec}^{-2}. \quad (15)$$

Here we have used $C=0.05$, $\gamma=4.11\times 10^3$, $a=3.6\times 10^{-8}$ cm,[26] $\omega/2\pi = 4.7\times 10^6$ Hz and we have taken into account the fact that $\frac{5}{6}$ of the molecules with $J=0$ have $I=2$. Hence we expect that the observed relaxation rate T_1^{-1} can be expressed by the relation

$$1/T_1 = AT_2^d + [2C/5(1-C)]\{1/[BT_2^d + T_1^Q(J=1)]\}. \quad (16)$$

It is apparent from Eq. (4) that the temperature variation of $T_1^Q(J=1)$ at low $(J=1)$ concentration will be small above about 8 °K, and hence for all practical purposes the measured $T_1(J=1)$ value at this temperature can be taken as the limiting $T_1^Q(J=1)$. Therefore for $C \ll 1$ the T_1 data, together with the T_2^d and the $T_1^Q(J=1)$ data, can be fitted to Eq. (16) using as unknown parameters A and B. The values obtained in this manner can then be compared with those estimated above.

In summary, the numerical estimations made of various quantities occurring in the relaxation processes permit the prediction that, at high concentrations of $(J=1)$ molecules, the influence on T_1 by the diffusive motion will be small. As the concentration decreases, the observed NMR signal will be coming more and more from $(J=0)$ molecules that relax by means of diffusion and cross relaxation. Hence the longitudinal relaxation at low $(J=1)$ concentrations will show a competition between these two mechanisms. At the low-temperature end of the diffusion region, the cross-relaxation mechanism is the faster one, while the direct relaxation by diffusion becomes the dominant one at high temperatures. A maximum in T_1 can then be expected at low $(J=1)$ concentrations.

III. EXPERIMENTAL

The relaxation times were measured using a phase coherent pulse system described elsewhere.[27] For this system, a 90° pulse required a width of approximately 70 μsec. The detection system then required another 50 μsec to recover following this pulse. An electronic counter was used to monitor the oscillator whose frequency, 4.7 MHz, was kept within about 100 Hz of the center of the absorption lineshape.

Measurements of T_1 were carried out using a 90°-t-90° pulse sequence. The amplitude of the free induction decay $M(t)$ was measured 200 μsec after the leading edge of the second 90° pulse. Semilogarithmic plots of $M(t=\infty) - M(t)$ vs t were linear within the scatter, for all concentration C, and the relaxation time T_1 in the hcp phase could be determined within 3% from the plots, regardless of temperature. The reproducibility from sample to sample of the same concentration was of the order of 3%, except in the diffusion region where some irreproducibilities of the order of 8% were observed. These seem to be associated with different crystallizations of the sample into a powder. There was no indication of two relaxation times as one finds in the liquid (see below) and in the cubic phase.[15,16] Note that for H_2, $M(t=\infty) - M(t)$ does not vary exponentially with t for the concentration of $(J=1)$ molecules smaller than about 0.3.[13,14] This is due to the existence of isolated clusters of $J=1$ molecules which, in the absence of cross relaxation, exchange energy with the lattice at different rates. Such a situation does not occur in D_2, because of the rapid cross relaxation between $(J=0)$ molecules with $I=2$ and $(J=1)$ molecules. A common spin temperature is thus maintained in hcp D_2 for all nuclei, so that one obtains a unique T_1.

The cryostat used for the measurements was the same as that used in a previous research[28] and covered a continuous temperature range between 0.4 and 25 °K. The sample was contained in a Kel-F cylinder of about 8-mm i.d. and 25-mm length, screwed onto a copper fitting. Thermal contact with the metal was by means of thin copper wires inside the container. The samples with $C > 0.33$ were prepared by mixing highly enriched p-D_2 gas with "normal" D_2 (33% p-D_2). The enriched p-D_2 gas had been prepared by preferential adsorption on cold alumina and was kindly provided by Mills of Los Alamos Scientific Laboratories. The enrichment process improves the purity of the D_2 to probably better than 99.99%, the remainder being primarily HD. The "normal" D_2 was C. P. grade from the Matheson Co. and contained 0.39% HD, 20 ppm H_2, 180 ppm N_2, and less than 4 ppm O_2. Since HD, the only appreciable impurity contribution, has a spherically symmetric wave function (hence $J=0$), we have assumed that the impurities were of no consequence in T_1 measurements.

The para concentration C of the samples was determined both before and after the experiments by measuring the thermal conductivity of the gas. For experiments which took an appreciable amount of time, interpolation of the measurements was used to obtain C at a given time during an experiment. Here, the conversion rate $dC/dt = -KC$ was used,[29] with K determined from the concentration at the beginning and at the end. An additional measurement of C was made possible by the observation that, in the liquid phase, the NMR signal after a 90°-t-90° sequence consisted of two components with longitudinal relaxation times differing by about 2–5 orders of magnitude, depending on the concentration. The component with the short relaxation time, 60 msec $< T_1 < 2.1$ sec for $0.02 < C < 0.94$ and $T = 19.9$ °K, was attributed to the ($J = 1$) molecules. The other component with 3200 sec $> T_1 > 770$ sec for $0.02 < C < 0.94$ at $T = 19.9$ °K was then the signal of the $J = 0$ molecules. The component amplitudes, extrapolated to $t = 0$ from semilogarithmic plots of $M(t = \infty) - M(t)$ vs t, were then taken to be in the ratio $\frac{2}{5}\, C/(1 - C)$. The numerical factor $\frac{2}{5}$ takes into account the relative signal strengths per molecule for the two species. These measurements usually confirmed the concentration from the thermal-conductivity method to within about 0.5% in C. An account of the T_1 data in the liquid phase and their interpretation will be given elsewhere.[30] We want to stress, however, the sharpness of the transition from the solid to the liquid as measured by T_1. This is shown in Figs. 2 and 3, where the decoupling between the $I = 2$ and $I = 1$ nuclear systems becomes very evident in the liquid, since they show relaxation times differing by several orders of magnitude.

IV. RESULTS AND DISCUSSIONS

The concentrations used in our experiments are listed in Table I along with their respective uncertainties. The indicated values are the averages of the concentration between the beginning and the end of the actual T_1 measurements. The largest variation ΔC is about 0.03 at 0.913. In Table I, we present a tabulation of the smoothed values of the data at regular temperature intervals. A representative plot of the data at several concentrations C is shown in Figs. 2 and 3. For convenience we shall discuss the results separately for the two temperature regions mentioned before.

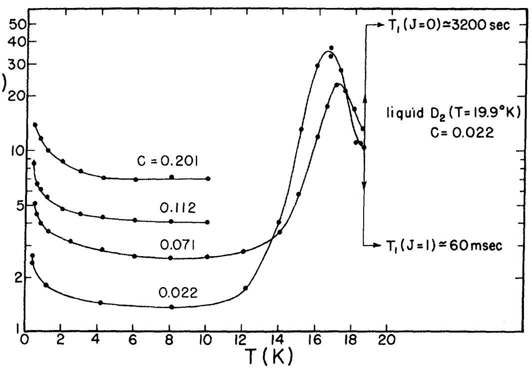

FIG. 2. Relaxation times as a function of T in hcp D_2 for several low ($J = 1$) concentrations.

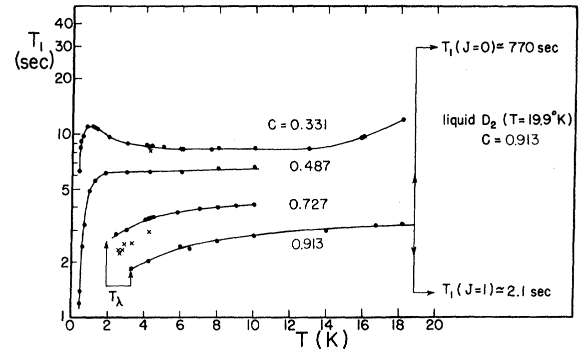

FIG. 3. Relaxation times for hcp D_2 at high ($J = 1$) concentrations as a function of T. Circles, present work. Crosses, results of Smith (Ref. 13) for concentrations $C = 0.33$ and 0.72, respectively. The symbol T_1 indicates the transition temperature to the ordered phase.

A. T_1 in the Nondiffusion Region

As mentioned before, the thermally activated diffusion becomes "frozen out" at about 11 °K.[18] Below this temperature, an analysis of the data in terms of the EQQ interaction mechanism can in principle be carried out. Unfortunately, the theory does not yet cover a large temperature range, and we shall first deal with the data at the high-temperature end, where an expansion series of T_1 in powers of $1/T$ [Eq. (4)] is available. The convergence of this series is slow, however, at temperatures below say 10 °K. In order to obtain the experimental high-temperature limit $T_{1\infty}^{Q}$, we have plotted the T_1 data vs $1/T$ between 4 and 11 °K for all concentrations except those below $C = 0.3$. Then $T_{1\infty} = T_{1\infty}^{Q}$ was obtained graphically by extrapolation to $1/T = 0$. The $T_{1\infty}^{Q}$ for concentrations below $C = 0.3$ were taken at the minimum value of T_1 near 8 °K. All the values of $T_{1\infty}$ calculated in this manner are listed in Table I. Then by using Eq. (2), we have obtained $T_{1\infty}(J = 1)$, and these results are plotted on a logarithmic scale versus C in Fig. 4. The solid lines have the predicted slopes of $\frac{1}{2}$ and $\frac{5}{3}$ from Eqs. (5) and (6). We also show the errors attached to the various data.

At this point, some remarks concerning the uncertainty in $T_1(J = 1)$ are appropriate. First, there is a possible systematic error due to the extrapolation technique of T_1 to $T_{1\infty}$. This is due to the nonnegligible temperature dependence of T_1 above 4 °K for certain regions of ($J = 1$) concentration. As expected from Eq. (4), the slope $dT_1/d(T^{-1})$ decreases with C. Hence one might expect the least uncertainty at low ($J = 1$) concentrations. This is not strictly true, because for this concentration range there is an unexpected increase of T_1 with temperature already by 9 °K, but still in a temperature region where effects from diffusion should be negligible. Hence, provisorily, the most reasonable value of $T_{1\infty}$ for $C < 0.3$ appears to be that taken at 8 °K.

Second, a systematic error may be made in the calculation of $T_1^Q(J=1)$ [Eq. (1)] by assuming it to be much larger than T_x. The cross-relaxation time T_x is of the order of T_2 (rigid lattice), which below the diffusion region can be obtained roughly from the free induction decay of the signal. Using experimental results for this decay, we estimate $T_2 \approx 400$ μsec. At $C = 0.022$, using Eq. (2), we calculate $T_{1\infty}^Q(J=1) = 0.013$ sec. Hence the assumptions made in Eq. (1) may only be approximately valid at low concentrations.

The third uncertainty is in concentration. We estimate that the NMR pulse analysis in the liquid phase, combined with Pirani gas-conductivity analysis, and the para-ortho conversion give an uncertainty of $\delta C = \pm 1.6\%$ at the highest concentrations, diminishing to $\delta C = \pm 0.2\%$ near $C = 0.02$. This means, however, that the relative error $\delta C/C$ increases as C decreases. Hence this uncertainty by itself attaches to $T_{1\infty}(J=1)$ an uncertainty of about ±10% near $C = 0.02$. Nevertheless the data as presented in Fig. 4 are smooth to well within the combined uncertainties.

A fit of our results then gives for the high-concentration region

$$T_{1\infty}(J=1) = (2.80 \pm 0.08)C^{1/2}\ \text{sec}.$$

By identification with the theoretical expressions, we have obtained, respectively, $\Gamma/k_B = 0.78$ °K (Gaussian approximation) and $\Gamma/k_B = 0.87$ °K (Hama and Nakamura). This compares with the value of $\Gamma/k_B \simeq 1.1$ °K derived from an analysis[23] of optical data[31] and from $(\partial P/\partial T)_v$ measurements.[5] As expected, the agreement is best with the more refined theory of Hama and Nakamura,[9] but the discrepancy is still outside the experimental uncertainty.

TABLE I. Smoothed values of T_1 for hcp D_2 at the various concentrations C of $(J=1)$ molecules as a function of temperature. The values $T_{1\infty}$ at $T=\infty$ are the extrapolated ones from the region where diffusion has no influence, and have been obtained as explained in the text. They are interpreted in terms of the EQQ interaction relaxation mechanism and hence $T_{1\infty} = T_{1\infty}^Q$. The values in parentheses are extrapolations. Except those at $C = 0.112$ and 0.487, where the uncertainty is, respectively, ±5% and ±10%, these extrapolations have an uncertainty of ±3%.

T(°K)	0.022 ±0.002	0.035 ±0.002	0.056 ±0.005	0.071 ±0.005	0.112 ±0.005	0.157 ±0.005	0.201 ±0.006	0.331 ±0.005	0.487 ±0.011	0.596 ±0.007	0.727 ±0.008	0.913 ±0.016
0.4	2.58							7.75				
0.45	2.34			(5.30)	(9.00)	(11.0)	(13.8)	8.60	(1.00)			
0.5	2.27			4.95	7.10	10.5	13.4	9.40	1.50			
0.6	2.08			4.45	6.50	9.80	12.7	10.1	2.45			
0.7	2.03			4.20	6.25	9.25	12.2	10.6	3.20			
0.8	2.00			4.00	6.05	8.90	11.5	10.8	4.00			
0.9	1.95			3.88	5.85	8.55	11.1	11.1	4.60			
1.0	1.90			3.78	5.70	8.25	10.7	11.1	5.00			
1.2	1.82			3.62	5.45	7.70	10.1	10.8	5.50			
1.6	1.72			3.45	5.10	7.00	9.30	10.3	6.00			
2.0	1.63	1.90		3.30	4.85	6.55	8.65	9.75	6.15		(2.63)	
3.0	1.52	1.79		3.02	4.50	5.90	7.70	8.95	6.20		3.02	(1.77)
4.0	1.42	1.70	(2.23)	2.84	4.30	5.75	7.25	8.75	6.25		3.38	1.99
5.0	1.42	1.63	2.13	2.72	4.20	5.60	7.10	8.50	6.30		3.60	2.19
6.0	1.39	1.57	2.07	2.63	4.10	5.55	7.05	8.35	6.35	4.95	3.78	2.37
7.0	1.38	1.54	2.02	2.59	4.08	5.50	7.00	8.35	6.40	5.05	3.90	2.52
8.0	1.37	1.52	2.00	2.57	4.05	5.50	7.00	8.35	6.45	5.15	4.00	2.63
9.0	1.38	1.54	2.00	2.58	4.02	5.50	7.00	8.35	6.45	5.25	4.08	2.73
10.0	1.42	1.61	2.04	2.61	4.00	5.55	7.00	8.35	6.50	5.35	4.15	2.82
11.0	1.48	1.72	2.12	2.65		5.60		8.35		5.45		2.89
12.0	1.66	1.88	2.26	2.77		5.65		8.35		5.50		2.96
13.0	2.41	2.22		3.02		5.70		8.35				3.00
14.0	4.15	3.45		3.55		5.90		8.55				3.05
15.0	11.5			5.75		6.50		9.00				3.10
16.0	30.0			11.8		8.50		9.70				3.12
16.5	36.0			17.6		10.5		10.2				3.15
17.0	32.0			23.2		14.5		10.7				3.18
17.5	22.4			21.5		17.3		11.2				3.19
18.0	13.6			17.3		16.7		11.8				3.20
18.5	10.3			13.3		(13.5)						
∞	1.37	1.52	1.98	2.57	4.05	5.50	7.00	8.35	6.95	5.80	4.60	3.30

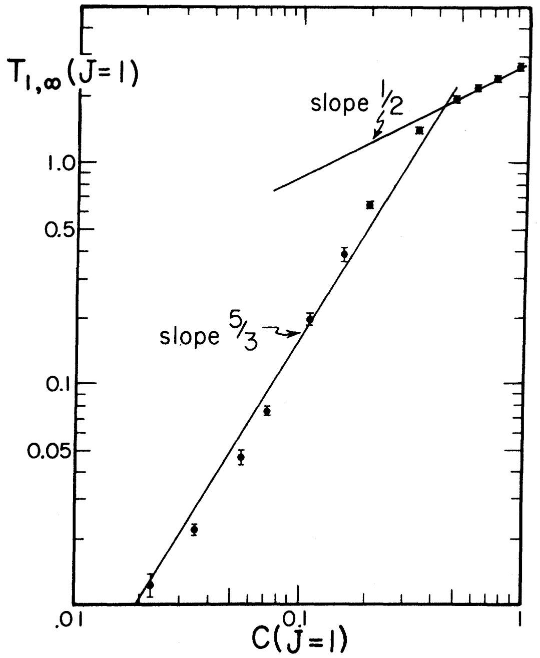

FIG. 4. Logarithmic plot of $T_{1\infty}(J=1)$ in hcp D_2 vs concentration. The solid lines with slopes of $\frac{1}{2}$ and $\frac{5}{3}$ are discussed in the text.

For concentrations C below about 0.3, where the $C^{5/3}$ dependence is expected to hold, one notices from Fig. 4 that there is some systematic departure from this behavior. Nevertheless if one fits the data to a power of $\frac{5}{3}$, one obtains roughly

$$T_{1\infty}(J=1) \simeq 9C^{5/3} \text{ sec.}$$

Identifying with the theoretical prediction [Eq. (7)] one obtains $\Gamma/k_B = 0.7$ °K. The disagreement with the value $\Gamma/k_B = 1.1$ °K is of the same order as for the case of H_2.[3]

Only the data for $C = 0.913$ that extend to the triple point are thought to be suitable for comparison with Eq. (4), since they are probably not affected by diffusion, as discussed in Sec. II. This comparison is shown in Fig. 5, after normalizing the theoretical curve to the experimental value of T_1 at the triple point. As can be seen, the slope of the experimental curve is steeper than that of the theoretical one. Nevertheless, the predicted temperature dependence is qualitatively correct.

We shall now compare the $T_1^Q(J=1)$ results briefly to those in H_2 in the temperature region below 11 °K. For concentrations of $(J=1)$ molecules above about 0.4, the results are similar. In both solids, rotational ordering within the hcp phase is apparently accompanied by a faster relaxation rate. In particular, the fast decrease of T_1 below 2 °K at $C = 0.49$ is also observed in H_2 for a similar concentration.[14] At lower concentrations, the comparison becomes more difficult, since below 4 °K the recovery of the longitudinal magnetization from saturation in H_2 is not exponential with time and a unique value of T_1 is not obtained. Also data for the temperature variation of T_1 in H_2 below $C = 0.4$ are scattered and therefore unsuitable for comparison with D_2.

At the present time, we are not able to understand quantitatively the temperature variation for T_1 at concentrations below about $C = 0.4$, where an increase of T_1 is observed when the temperature is decreased below 4 °K (Fig. 2). Qualitatively we propose the following explanation, based on two factors. First, as the temperature becomes lower, the linewidth attributed to $(J=1, I=1)$ molecules increases[3] because of the gradual rotational ordering, while that of the $(J=0, I=2)$ molecules does so to a much smaller extent. Hence a simultaneous flip of $I=1$ and $I=2$ spins is less likely to be degenerate in energy. This would result in an increase in T_x. Second, $T_1^Q(J=1)$ decreases rapidly with decreasing C and may become comparable with T_x at low concentrations. Therefore an increase in T_x with decreasing temperature might lengthen the measured T_1.

Finally, we compare in Fig. 3 the data of Smith for $C = 0.33$ and 0.72 with the present results. The older data are found to be generally lower than those in the present paper. Although Smith used a resonant frequency of 9.7 MHz, it should be noted that below the diffusion region, no frequency de-

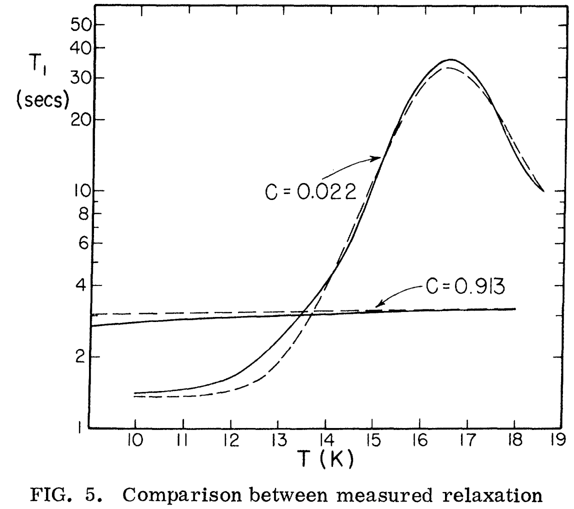

FIG. 5. Comparison between measured relaxation times (solid curves) and theory (dashed curves). For the concentration of $J=1$ molecules $C = 0.022$, the relaxation mechanism is influenced by diffusion and Eq. (16) was used to fit the data. Dashed curve was calculated from $A = 0.16$ sec^{-2} and $B = 6.5$ and constitutes the best fit over the temperature range $14 < T < 18.5$ °K. For $C = 0.913$, the relaxation is not influenced by diffusion and Eq. (4) was used to fit the data. This equation had been normalized to the 18 °K data point and is also represented by a dashed curve.

pendency of T_1^Q is expected.

Although we are not in possession of the original data of Wang and White,[17] we gather from the results quoted by Harris[3] [Eq. (6.37)] that they are in substantial agreement with those in the present work.

B. T_1 in the Diffusion Region

As predicted from Eq. (16), T_1 for small concentrations of $(J=1)$ molecules shows a drastic variation with temperature. We have performed a least-squares fit for the data at $C=0.022$ and 0.071 between 14 and 18.5 °K, using the values of T_2 given before[24] and the respective $T_{1\infty}^Q(J=1)$ data. Below this temperature range, it is believed that the rigid lattice T_2 is not negligible compared with T_2^d. This can be gathered from the departures of the data from the fit [Eq. (16)] as seen in Fig. 5. For $C=0.022$, the least-squares fit gave $A=0.16$ and $B=6.5$. Considering the approximations made in the estimation of these constants in Sec. II, the agreement between experiment and prediction is remarkable. The quality of the fit is shown in Fig. 5, where also the calculated curve is extended to $T=10$ °K. As can be seen, there is a systematic discrepancy below 14.0 °K, which is probably caused by the assumptions leading to Eq. (16), in particular in the calculation of T_x. There the approximation was made that $T_x = BT_2^d = BT_2$. As a first-order approximation, the strong increase of T_1 with temperature can hence be explained by an averaging out of the cross-relaxation mechanism due to diffusion. Above 17 °K, the direct relaxation of the $(J=0)$ molecules to the lattice by means of the diffusion mechanism would again decrease T_1. As noted before, the effect of diffusion on T_1 diminishes with the increase of the concentration of $(J=1)$ molecules.

A similar fit was carried out for $C=0.071$, and the values determined from the least-squares analysis were $A=0.12\ \text{sec}^{-2}$ and $B=6.7$. The quality of the fit was even better than that for the lower concentration. It should be noted that the theoretical estimation of A [Eqs. (8) and (10)] shows this quantity to be proportional to $(1-C)^{-2}\omega^{-2}$. Hence the observed decrease in A when C is increased is consistent with expectations. The frequency dependence of A leads to the prediction that the observed T_1 will increase with increasing frequency. For instance, we calculate, using our data for $C=0.022$ and Eq. (16), that for a resonant frequency of 8 MHz, the experimental T_1 should be, respectively, 12.1, 53.5, and 28.7 sec at the temperatures of 15.0, 17.0, and 18.5 °K. Measurements of T_1 at higher frequencies would therefore provide a test of the analysis presented above.

V. CONCLUSION

The measurements of the longitudinal relaxation time T_1 of hcp D_2 at 4.7 MHz can be satisfactorily analyzed using the electric quadrupole-quadrupole interaction and the thermally activated diffusion as relaxation mechanisms which operate in different temperature regions. For the region where the EQQ interaction relaxation mechanism dominates, we have verified that $T_{1\infty}(J=1)$ is proportional to $C^{1/2}$ for $C \gtrsim 0.5$. However, below about $C=0.3$, we find some departures from the $\frac{5}{3}$ law expected to hold in this region. Also the EQQ interaction parameter Γ, obtained from an analysis of the T_1 data is smaller than that from other experiments. Part of the difficulty may lie in the assumptions made in deriving Eq. (2). Here the cross relaxation, which is of the order of T_2 (rigid lattice), is taken to be very small as compared with $T_{1\infty}^Q(J=1)$. However, at the lowest concentrations used, this may not be true.

The behavior of T_1 below 4 °K, which should also be understood in terms of the EQQ interaction, is rather complex and needs more study, both experimentally and theoretically.

In the diffusion region, the measured T_1 increases faster for $10 < T < 14$ °K than anticipated by the simple theory presented for low $(J=1)$ concentrations. Possibly a more careful theoretical study of the cross-relaxation mechanism will eliminate this discrepancy. However, above 14 °K the relaxation theory based on the diffusion effects can be fitted very well to the experiment with parameters that are consistent with those estimated from theory. On the basis of the relaxation equation for D_2 used to describe the system of coupled $(J=0,\ I=2)$ and $(J=1,\ I=1)$ molecules, one anticipates that, as the concentration of $(J=1)$ molecules increases, T_1 will gradually become less dependent on the diffusion mechanism in the diffusion region. This is indeed observed, the low concentrations showing a drastic variation of T_1 with T due to diffusion, while at high concentrations the EQQ interaction relaxation mechanism can account for the mild temperature variation of T_1 up to the triple point. Thus, generally speaking, the behavior of T_1 in the diffusion region appears qualitatively understood.

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