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# Pulsed-NMR study of the long-range order in solid $H_2$ and $D_2$

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Quadrature Fourier transform NMR detection has been employed to study the disorder-order transition in high $J=1$ concentration solid hydrogen and deuterium. In solid $H_2$, where the ortho-para conversion is rapid, quick measurements were made possible by computer batch files containing pulse programs. Newly obtained order parameters were compared with those from the so-called quadrupole glass phase. In addition, peculiar emission of power was detected and regarded as characteristic of the long-range order which distinguishes it from the local order in the quadrupole glass phase.

## I. INTRODUCTION

NMR has proven to be a very useful probe of short-range interactions in all phases of matter. The quantities usually measured, namely, $T_1$, the spin-lattice relaxation time, $T_2$, the spin-spin relaxation time, and line shape are (with some exceptions) predominantly determined by interactions with the nearest neighbors. It is therefore interesting to examine in some detail usage of NMR techniques to probe long-range order in systems.

At low temperatures, the homonuclear hydrogen molecules $H_2$, $D_2$, and $T_2$ form a solid consisting of ground-state $J=0$ and $J=1$ metastable species. At $J=1$ concentrations over 56%, the electric quadrupole-quadrupole (EQQ) interaction between the $J=1$ molecules leads to a transition to an orientationally (long-range) ordered phase.

For a quadrupolar system ($J=1$), two normalized local order parameters can be defined:[1]

$$\sigma=-\tfrac{1}{2}\langle 3J_z^2-2\rangle_T \tag{1}$$

and

$$\eta_i=\langle J_{xi}^2-J_{yi}^2\rangle_T \ . \tag{2}$$

The temperature dependence of the order parameter was first measured in $D_2$ by using NMR.[2] The "splitting" $\Delta\nu$ between the flattened peaks in the absorption spectrum was shown to be

$$\Delta\nu=3d\langle 1-\tfrac{3}{2}J_z^2\rangle_T=(15d/4)\sigma \ , \tag{3}$$

where $d$ is the intramolecular splitting constant.

Although NMR order parameters have been measured and reported in these phases in the $D_2$ solids, which have a slow $J=1$ to $J=0$ conversion rate,[2,3] no comprehensive data have been available in the $H_2$ solids in which a very fast ortho-to-para conversion rate (1.9%/h) makes such measurements difficult. A high signal-to-noise ratio, coupled with the use of automated computer batch files, enabled us to obtain excellent data in the normal $H_2$ (n-$H_2$) ($x_J=0.75$) solids. The order parameters were also measured using n-$H_2$ impurities (1%) in the high $J=1$ concentration $D_2$ lattice ($x_J=0.90$). The detection of an emission of power is also reported and discussed.

The existence of a new phase, the quadrupole glass, was proposed in the intermediate range ($x_J<0.55$).[4,5] Subsequently, an experiment was done in $D_2$ in that same concentration range and cusplike behavior in the $T_1$ was reported.[3] A line shape resembling a Pake doublet was also obtained, which is characteristic of an ordered state with a well-defined order parameter. In this paper, the order in this phase is compared with that in the higher-concentration long-range-ordered phase.

## II. EXPERIMENT

A pulsed quadrature detection spectrometer was used for the experiments in the temperature range 1.1–4.2 K. A 90° pulse of length 1 $\mu$s for proton NMR at 30 MHz and 4 $\mu$s for the $D_2$ NMR at 6 MHz was used. The dead time in the FID (free-induction decay) signals, typically 7 $\mu$s, was replaced by a Gaussian fit. To obtain the line shape, the FID files were Fourier transformed. In addition, where appropriate, the line shape was differentiated to obtain the order parameter $\Delta\nu$.

The high $J=1$ concentration $D_2$ sample was made by an apparatus set up in our laboratory. It makes use of the preferential adsorption of the $J=1$ molecules on the surface of aluminum oxide at the temperature of liquid hydrogen (20 K).[6] The concentration is determined by a thermal conductivity cell.[7] The calibration is done using samples of known concentrations.

## III. RESULTS AND DISCUSSION

Following previous workers, we have defined two order parameters $\Delta\nu$ and $Q$. First, $\Delta\nu$ is the splitting of the Pake doublet characteristic of the ordered phase, as defined by Eq. (3).[2] $Q$ is defined as the ratio of the average frequency in the absorption spectrum to that in an ideal Pake doublet;[3]

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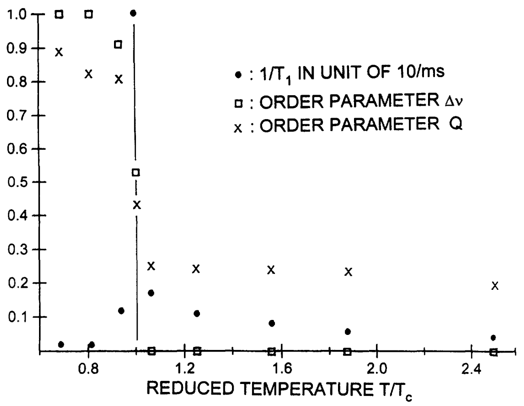

FIG. 1. n-$H_2$ order parameters $\Delta\nu$ and $Q$ and $1/T_1$ vs $T/T_c$, where $T_c$ is the transition temperature, 1.6 K.

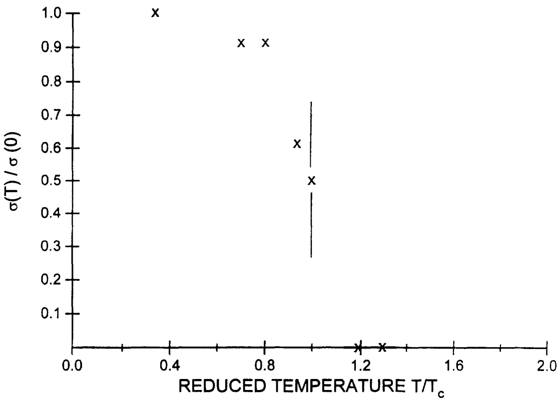

FIG. 2. Order parameter $\Delta\nu$ vs $T/T_c$ by proton NMR in the 90% p-$D_2$ sample, where the transition temperature $T_c = 3.1$ K.

$$Q = \frac{\int_0^\infty \omega I(\omega) d\omega}{\int_0^\infty \omega I_{\rm PD}(\omega) d\omega} , \tag{4}$$

where $I_{\rm PD}(\omega)$ is the line shape of the ideal Pake doublet. This quantity should be more sensitive to changes in the line shape than the splitting. The $Q$ can be thought of as the first term in an expansion of the line shape, while the splitting is the zeroth-order term. The order parameters for n-$H_2$ are shown in Fig. 1 as a function of temperature.

The phase transition in the hydrogen isotopes is sharp, drastically changing the line shape over a temperature range of less than 3% in the reduced temperatures $T/T_c$. For this phase transition, the conventional order parameter $\Delta\nu$, which is a measure of the line splitting, appears to be a good order parameter for the long-range order that accompanies the transition. On the other hand, the quantity $Q$ better characterizes short-range (or local) order. In other words, while $\Delta\nu$ vanishes above the transition, $Q$ is nonzero above $T_c$ although it does change at $T_c$, reflecting local order in clusters and possibly also long-range order. The phase transition is marked by an abrupt change in all of the quantities $T_1$, $\Delta\nu$, and $Q$.

In order to investigate the quadrupole glass phase, Sokol put 1% n-$H_2$ in 52% para- ($J=1$) deuterium (p-$D_2$) for proton NMR in the p-$D_2$ lattice.[3] This has advantage over direct deuteron NMR with much shorter $T_1$ and much higher Larmor frequency. Deuteron NMR also gives an unwanted signal from the $J=0$, $I=2$ ortho molecules. The ortho-$H_2$ (o-$H_2$) molecules share many properties with the para-$D_2$ molecules (both have $I=1$, $J=1$), like the same quadrupole moment which is nearly independent of their mass difference. Thus the $H_2$ molecules act as mass defects in the p-$D_2$ lattice and they should show the properties of the $D_2$ lattice. In this work, we also put 1% n-$H_2$ impurities in the 90% p-$D_2$ to compare the order parameters from this high $J=1$ concentration system with those from the 52% p-$D_2$ quadrupole glass phase.

Figure 2 shows the temperature dependence of the order parameter $\Delta\nu$ as obtained from proton NMR in 90% p-$D_2$. It is verified from Fig. 2 that o-$H_2$ molecules undergo a phase transition at the same temperature, 3.1 K, as the p-$D_2$ lattice, as determined by direct deuteron NMR, which was performed to verify the use of the n-$H_2$ impurities as a probe of the $D_2$ lattice.[8]

In the experiment on 1% n-$H_2$ in $D_2$, we have shown that n-$H_2$ in $D_2$ is an acceptable probe of the orientational ordering transition in $D_2$. In other words, a NMR experiment on n-$H_2$ in $D_2$ reflects the properties of $D_2$. The change in the line shape (e.g., line splitting) and the order parameters $\Delta\nu$ and $Q$ as well as in the relaxation rate occur at $T_c$ for $D_2$.

For comparison, the order parameter $Q$ of n-$H_2$ is shown in Fig. 3 together with those from the 90% p-$D_2$ and the 52% p-$D_2$ samples, as obtained from the proton NMR. The 75% $J=1$ n-$H_2$ and the 90% p-$D_2$ samples show a sharp change through the phase transition. On the other hand, it is seen that Sokol's 52% p-$D_2$ quadrupole glass phase sample shows a much milder change in the order parameter $Q$ with respect to the reduced temperature around the $T_c$ determined from the cusp in $T_1$. It is possible that, in the intermediate concentrations, the order shown in $1/T_1$ and the line shape is short-range (or local) order rather than the long-range order seen for the

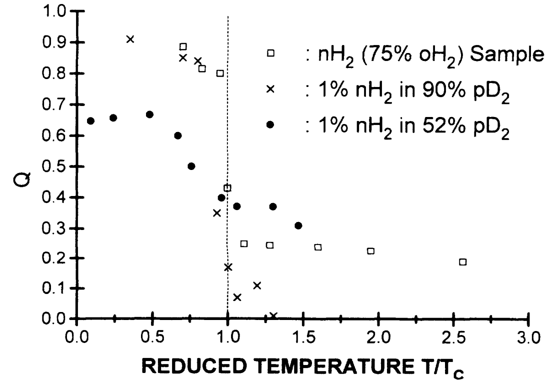

FIG. 3. Order parameter $Q$ vs $T/T_c$ in n-$H_2$ and in 90% and 52% p-$D_2$ measured by 1% n-$H_2$ impurities.

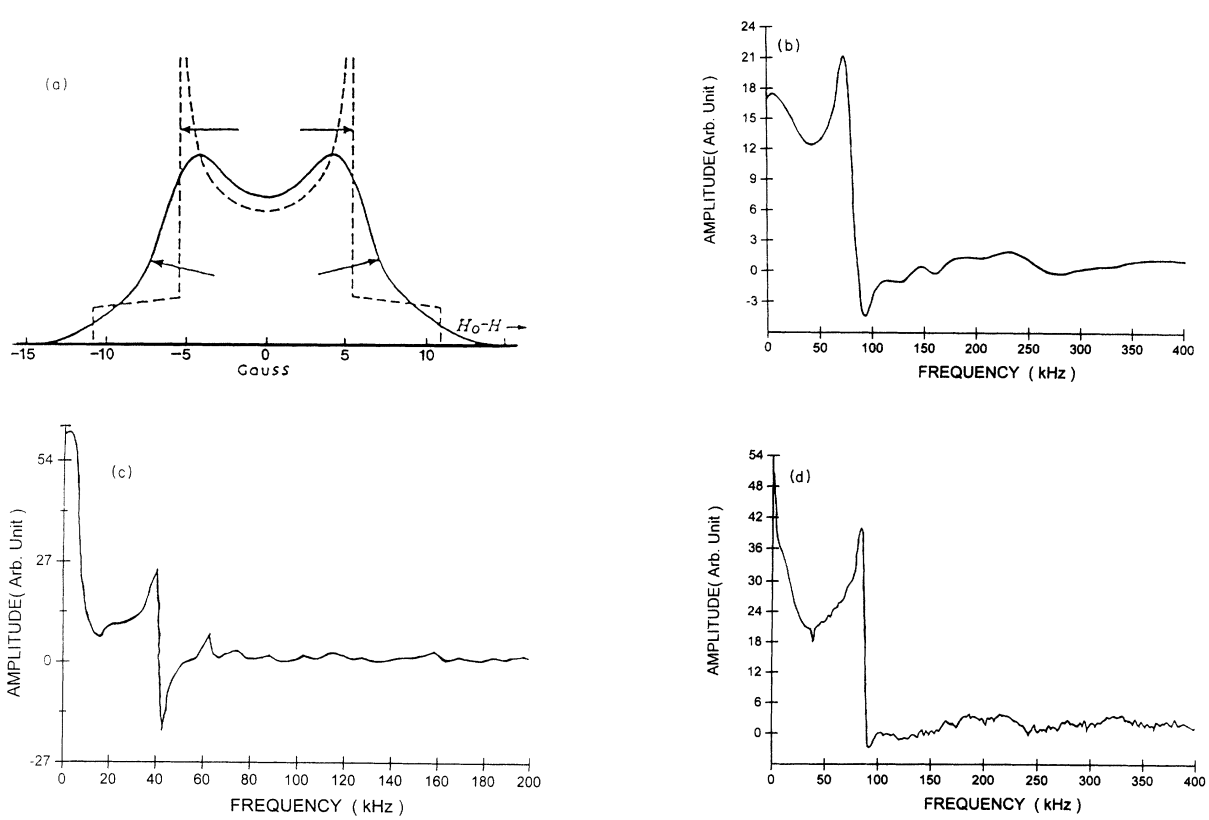

FIG. 4. (a) Pake doublet: dashed line, unbroadened; solid line, dipolar broadened. Line shapes showing an emission of power in (b) n-$H_2$ and (c) 90% p-$D_2$ by deuteron NMR and (d) 90% p-$D_2$ by proton NMR.

higher $J=1$ concentrations.

In this paper, we report in Fig. 4 the first observation, as far as we know, of an emission of power, i.e., a negative part in the absorption spectrum, by pulsed NMR in the long-range-ordered state of $H_2$ and $D_2$. This emission of power has been reported previously by continuous-wave (cw) NMR in the high-concentration long-range-ordered state.[9] The emission of power was interpreted as due to a balance between the ortho-para pumping mechanism and the normal spin-lattice relaxation processes, because in the ordered phase conversion takes place from only one of the $J=1$ substrates ($J_z=0$).[10] In contrast, Sokol's quadrupole glass phase line shape showed no negative part, nor any structure on the tail part,[3] although it may have to be repeated with quadrature detection to make this absolutely sure.

By means of proton NMR in n-$H_2$ and high concentration $J=1$ $D_2$, we have observed a special feature of NMR in the ordered state, namely, power emission resulting from selective $J=1$ to $J=0$ conversion that depends on the particular $m_J$ state. This emission had only been observed in $H_2$ before this study. While Hardy and Berlinsky theoretically predicted and also reported an observation of power emission in the ordered state of $H_2$, the observation in $D_2$ reported in this paper is the first one to our knowledge.

Power emission in $D_2$, which comes from the conversion of $J=1$ molecules, is of special interest because the conversion rate in $D_2$ (0.06% per hour) is much smaller than in $H_2$ (1.9% per hour). In our line shapes, the emission part in $D_2$ was as visible as in $H_2$ in spite of the much smaller conversion rate. This would seem to require some additional theoretical exploration or some improved physical insight.

The observed power emission in $D_2$ also casts light onto the characterization of the quadrupole glass (where a cusp in $1/T_1$ was also observed) range of concentrations. It suggests a set of experiments to probe that range because the observation of the power-emission effect seems to be a characteristic of the long-range-ordered state. In the intermediate $J=1$ concentrations for the quadrupole glass with the same experimental setup as in this work, by testing for power emission in those concentrations, we can test if the so-called quadrupole glass is the same long-range-ordered phase as the high-concentration phase studied here.

To conclude this paper, a systematic NMR study has been done on the high-concentration $J=1$ range in $H_2$ and $D_2$ using quadrature detection.

## ACKNOWLEDGMENTS

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