It is interesting to note that on the basis of the proposed model the exciton state is either not degenerate or has much lower degeneracy than is usually the case, e.g., in the alkali halides.[10] This is due to the low symmetry of the $Ga_2O_3$ lattice. Thus, the $O_I$-to-$Ga_I$ transition involves only one pair of ions at the same distance, the $O_{II}$ to $Ga_I$ only two. This could lead to interesting consequences, e.g., in calculations of the polarization energies.

The relationship of the photoconductivity to the absorption edge is not clear from the data presently available. The long-wavelength response is presumably due to impurities. The short-wavelength cutoff is a surface-sensitive property typical of ionic photoconductors.

---

[10] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963), p. 64.

A study of the photoresponse as a function of temperature, applied voltage, illumination history, etc., of crystals prepared under a variety of conditions may be required before a complete understanding is obtained.

Although the good agreement between the observed position of the $Ga_2O_3$ absorption edge and the crude calculations based on the model presented here may be somewhat fortuitous, it is believed that this model forms a convenient basis for further work, both theoretical and experimental.

## ACKNOWLEDGMENTS

---

# Nuclear Magnetic Resonance of Solidified H₂-D₂ Mixtures. I. Steady-State Experiments*

J. R. GAINES,† E. M. DE CASTRO,‡ AND J. G. DAUNT

*Department of Physics, The Ohio State University, Columbus, Ohio*

(Received 9 April 1965)

Steady-state NMR measurements using a marginal oscillator technique at 10 Mc/sec have been made on solid mixtures of $n$-$H_2$–$n$-$D_2$ of $n$-$H_2$ concentration from 100% to 1% in the temperature range 1.1°K to about 12°K. Striking differences in the line shape were observed, particularly in the $n$-$D_2$-rich sample, with change in temperature, the line shape at the lowest temperatures revealing a composite structure. The question whether this line shape transition is due to isotopic phase separation is discussed, and this interpretation is considered unlikely. It is concluded that the transition is probably associated with a hindering of the rotation of the ortho-$H_2$ molecule. Narrowing of the resonance lines with increasing rf power was observed. It is shown that no satisfactory explanation of this effect is possible using the Bloch equations. This narrowing is in excellent agreement with a recent calculation by Provotorov, however, and his theory is used to obtain a value of the exchange interaction in solid $H_2$ of approximately $10^{-7}$ °K. The progressive-saturation technique is used to obtain values of the product $T_1T_2$ for several of the mixtures. The data showed that $T_1T_2$ has a value at 4.2°K of about $2\times10^{-6}$ sec² for concentrations of $n$-$H_2$ from 10% to 100%.

## I. INTRODUCTION

SOLID $H_2$ is a mixture of ortho ($J=1$) and para ($J=0$) molecules which might in a first approximation be considered a random array near the melting point (approximately 14°K). Because of the relatively large gyromagnetic ratio of the proton and the slow conversion rate from the ortho species to the ground-state para species, solid $H_2$ is a favorable solid to study in detail from the standpoint of NMR and has been the subject of several extensive investigations.[1–3] The

investigations revealed two linewidth transitions, one associated with a translational motional narrowing at about 10°K and the other, the so-called $\lambda$ transition, at about 1.5°K due to lifting of the rotational degeneracy of the orthomolecule in the solid. On the other hand, $D_2$ has a relatively weak nuclear magnetic moment and this solid has not been so extensively studied. However, the same linewidth transitions as in solid $H_2$ have been observed in solid $D_2$.[4,5] No experiments have been done upon mixtures of $H_2$ and $D_2$

---

[1] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) A199, 222 (1949).

[2] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).

[3] T. Sugawara, Y. Masuda, T. Kanda, and E. Kanda, Sci. Rept. Res. Inst., Tohoku Univ. A7, 67 (1955).

[4] B. V. Rollin and E. Watson, *Proceedings of the Conference on Low Temperature Physics, Paris, 1955* (Centre Nationale de la Recherche Scientifique and UNESCO, Paris, 1956), Paper 63.

[5] J. R. Gaines, E. M. de Castro, and D. White, Phys. Rev. Letters 13, 425a (1964).
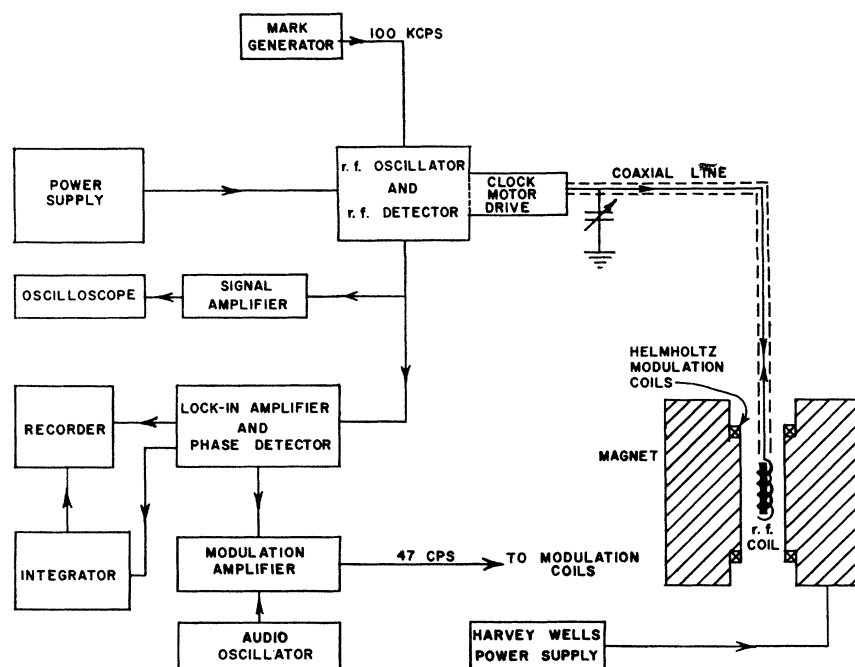
FIG. 1. Block diagram of the steady-state spectrometer.

prior to those reported herewith, although brief preliminary accounts of some aspects of this work have been previously reported.[6-8]

The original purpose of this investigation was to observe NMR in solid mixtures of $H_2$ and $D_2$ over the entire range of concentrations at temperatures between solidification and 1°K, to investigate linewidth transitions, and in particular to search for possible isotopic phase separation. The latter was stimulated in part by the reported observation of a solid isotopic phase separation in such mixtures.[9] Due to the sensitivity of NMR techniques to changes in local field conditions, such a separation would result in a predictable change in line shape and it seemed that such studies would be very revealing regarding the dynamics of such a transition. In addition, these experiments were viewed as preliminary experiments to similar studies of $He^3-He^4$ mixtures where the phase separation in both liquid and solid had been observed. Due to the lower temperatures needed and the additional complication created by the rather high pressures necessary to solidify helium, the work on hydrogen isotopes was given priority.

In addition to the supposed phase separation in the solid mixtures, several problems concerned with normal $H_2$ (75% ortho) were of interest, namely the question

of a phase separation between the ortho and para molecules, and the anomalous saturation behavior of the resonance line in $H_2$, suggested in a footnote by Reif and Purcell[2] to be due to a clumping of orthomolecules and by Sugawara[10] to be due a distribution of spin-lattice relaxation times $T_1$ in the solid.

In any attempt to observe a phase separation, the question of diffusion rates is of critical importance. Bloom[11] has measured the diffusion rate in solid $H_2$ and HD near the melting point. His data indicated that no phase separation could be observed in any reasonable time in the solid hydrogens below about 10°K *if* the diffusion process remained thermally activated or unless something peculiar happened in the solids, such as the diffusion rate becoming independent of $T$ as it seemingly does[12] in solid $He^3$.

## II. APPARATUS

### A. Nuclear Resonance Equipment

The spectrometer used for these studies is shown in block diagram form in Fig. 1. Since this spectrometer is of very conventional design, only a few remarks seem pertinent. The oscillator unit was a modified Pound-Watkins[13] oscillator with a linear frequency sweep derived by means of suitable capacitor plate design and a very smooth clock motor drive. The electromagnet (manufactured by Newport Instruments) was

[6] J. R. Gaines, E. M. de Castro, and J. G. Daunt, Phys. Letters 8, 167 (1964).

[7] J. G. Daunt, E. M. de Castro, and J. R. Gaines, Bull. Am. Phys. Soc. 9, 572 (1964).

[8] E. M. de Castro, D. Husa, J. R. Gaines, and J. G. Daunt, *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum Press, Inc., New York, 1965, in press).

[9] V. S. Kogan, B. G. Lazarev, and R. F. Bulatova, Zh. Eksperim. i Teor. Fiz. 34, 238 (1958) [English transl: Soviet Phys.—JETP 7, 165 (1958)].

[10] T. Sugawara, Sci. Rept. Res. Inst., Tohoku Univ. A8, 95 (1956).

[11] M. Bloom, Physica 23, 767 (1957).

[12] H. A. Reich, *Proceedings of the Second Symposium on Liquid and Solid He³*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 63; Phys. Rev. 199, 630 (1963).

energized by a Harvey Wells power supply (Model HS-1365). At the field used for these measurements (approximately 2.5 kg) the magnet inhomogeneity as determined by pulsed-magnetic-resonance experiments was about 100 mG over a cylinder of length 1 cm and diam 1 cm. The detected signal was fed to P.A.R. Model (JB-4) lock-in amplifier and phase sensitive detector and then to a Mosely X-Y recorder if the derivative of the absorption signal was desired or into a dc amplifier (Solartron Type AA 1023) with a very long constant (and then to the recorder) if the absorption itself was desired.

The amplitude of the radio frequency field was determined in two ways: first the emf across the coil was measured and the value of the magnetic field determined from the known geometrical factors such as coil area and number of turns and the frequency; secondly the voltage across the coil was measured under conditions when the coil was filled with glycerin and a spin echo was observable. From the measured values of the time necessary to produce 90° and 180° pulses, one can determine H$_1$ as a function of the driving rf voltage.



FIG. 3. Block diagram of the mixing system and associated vacuum systems.

Although the magnitudes of the H$_1$'s in the two cases were roughly in the ratio of one to one thousand, the ratio of the driving rf voltage to the field produced (H$_1$) was constant to within 2%.

## B. The Probe

The probe design was quite simple, the transmission line and the sample cell (with associated fill tube) being the two main components. The details of the assembly are shown in Fig. 2. The sample cell, made of Teflon, was sealed to the threaded brass bushing, $J$, by a thin coat of vacuum grease at room temperature and the differential thermal contraction on cooling to lower temperatures ensured a satisfactory joint. The transmission line was electrically similar to RG11/U coaxial cable. The coil plus transmission line had a $Q$ of about 50 at 10.0 Mc/sec at liquid-helium temperatures.

## C. The Mixing System

The mixing of the isotopes was done at room temperature in the gaseous state. The system used in these experiments is shown in Fig. 3. The gases were allowed to mix for a few minutes in the one-liter mixing chamber, and the resulting mixture liquified and eventually solidified. The concentrations were determined from measurements of the gas partial pressures. The nuclear resonance signal was monitored on the oscilloscope during the process of cool-down to liquid-helium temperatures by increasing the modulation amplitude to
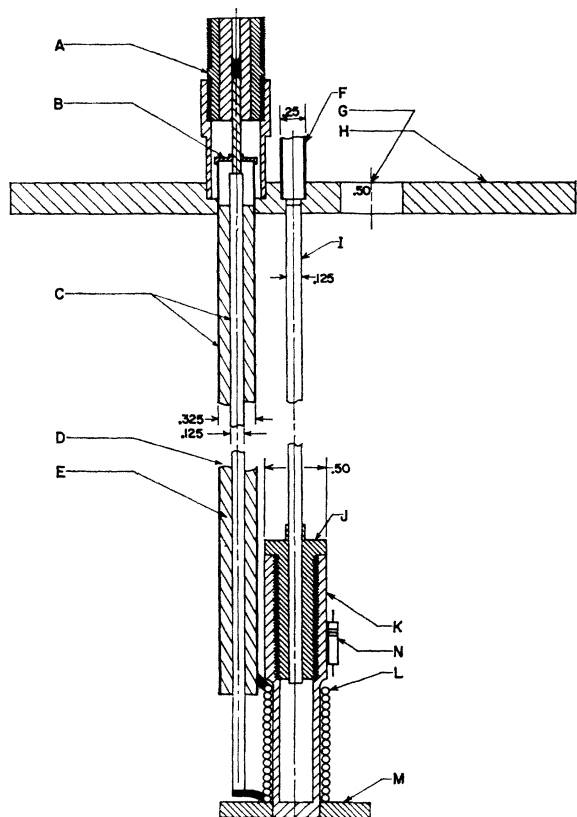


FIG. 2. The transmission line and sample container. (Dimensions are in inches.) A, Amphenol connector. B, Kovar seal. C, cupronickel (30%) tubes. D, coaxial transmission line. E, Teflon insulator. F, fill tube. (G), helium-transfer port. H, top flange (4.5″×0.25″). I, sample tubing (cupronickel, 30%). J, brass bushing (threaded). K, Teflon container. L, rf coil. M, Teflon spacer disk. N, resistance thermometer.
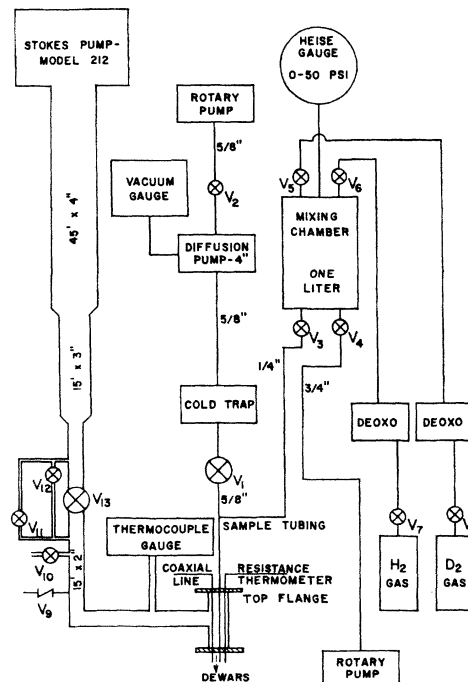
CONCENTRATION

$\left(\dfrac{H_2}{H_2 + D_2}\right)$ %        T(°K)

| | |
|---|---|
| ● – 4.9 % | – 9.6 |
| ○ – 40 % | – 10.9 |
| ▼ – 60 % | – 9.2 |
| ▽ – 90 % | – 9.6 |

r f = 8.5 mgauss
Mod: 350 mgauss
   at 47 CPS

ΔH(gauss)

Fig. 4. The derivative of the resonance line near
10°K for several concentrations.

## III. RESULTS

The steady-state data on the mixtures of $H_2$ and $D_2$ consisted of one set of curves in which the derivative of the absorption $(d\chi''/dH)$ was obtained and a second set containing the absorption signal $(\chi'')$. These two sets of curves were recorded at various temperatures $T$ for various concentrations $\chi$ (selected to cover the entire range of solid solutions from 1 to 100% $n$-$H_2$) as a function of the radio-frequency power (proportional to $H_1^2$) used. Since it is not possible to present all these data conveniently, only typical curves showing the significant results are presented here. Moreover, data on the observed line-narrowing transitions above 10°K and on the line splitting near 1°K, obtained with pulsed NMR techniques, are left to a subsequent publication. Derivative curves obtained at low rf power levels are presented in Figs. 4, 5, and 6 for various concentrations at $T \approx 9.6°K$, $T \approx 4.2°K$, and $T \approx 1.1°K$, respectively.[14] For intercomparison, derivative curves for a 40% $H_2$ concentration at various temperatures are shown in Fig. 7.
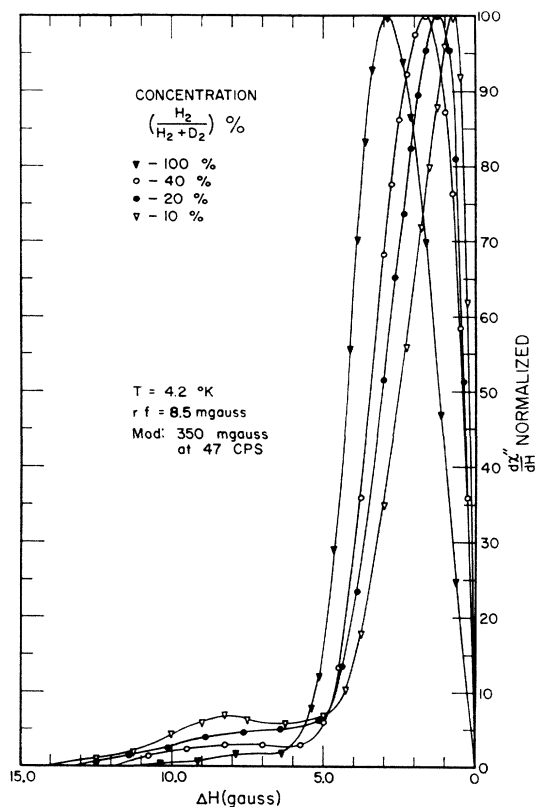
a few G. The mixtures could be held as liquid indefinitely by transferring the liquid helium into the main Dewar very slowly. When it was desired to solidify the mixtures, liquid helium was transferred faster so that it collected in the Dewar. Although this technique is admittedly crude, it was extremely successful in that the sample tube did not block during the fill process. Due to the success of this technique, the design of the probe could be made very simple.

### D. Temperature Control

The fundamental components of the temperature-control system are shown in Fig. 3. Temperatures down to 1.10°K could be obtained by pumping directly on the helium bath. Conventional carbon resistance thermometry was used, the value of resistance $N$ (see Fig. 2) being determined by measuring the voltage across it and the voltage across a standard resistor in series with it. Temperatures down to 10°K were obtained by pumping a bath of equilibrium $H_2$. The range between 4.2 and 10°K was covered by pumping off helium vapor adsorbed on charcoal. A plastic cylinder was fixed around the rf coil containing 37 g of activated charcoal of 6–14 mesh for these experiments.



CONCENTRATION

$\left(\dfrac{H_2}{H_2 + D_2}\right)$ %

| |
|---|
| ▼ – 100 % |
| ○ – 40 % |
| ● – 20 % |
| ▽ – 10 % |

T = 4.2 °K
r f = 8.5 mgauss
Mod: 350 mgauss
   at 47 CPS

ΔH(gauss)

Fig. 5. The derivative of the resonance line at
4.2°K for several concentrations.

[13] R. V. Pound, Progr. Nucl. Phys. 2, 21 (1952).
[14] In Fig. 6, pure solid $H_2$ at 1.1°K shows no splitting of the line because it had a low orthoconcentration due to the fact that it was recorded many hours after condensation.
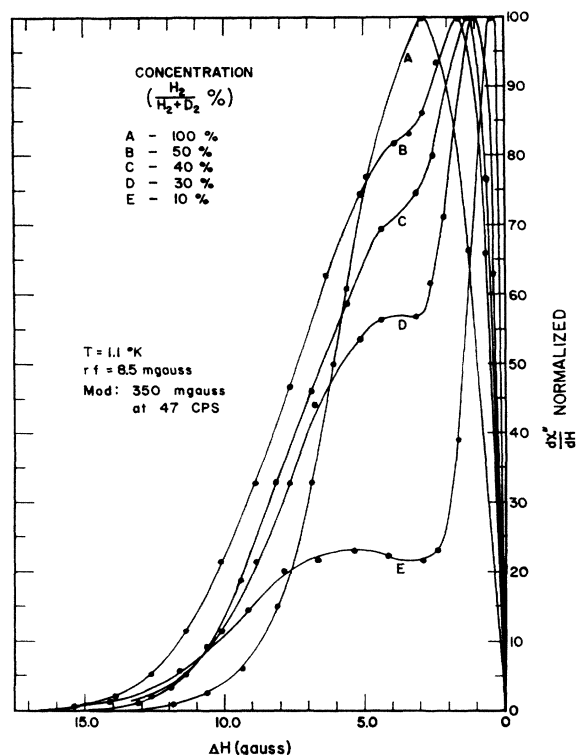
Fig. 6. The derivative of the resonance line at
1.1°K for several concentrations.

None of the resonance lines observed could be de-
scribed by either a pure Gaussian or a pure Lorentz
curve. This, however, seems to be the rule rather than
the exception in solids. For pure $n$-H₂ at 4.2°K, the
line shape became more Lorentz-like at high rf power
levels. As is evident in Figs. 4 and 5 the lines showed
small but definite "tails" at the higher temperatures. At
1.1°K, on the other hand, the tails become very marked,
especially for the deuterium-rich mixtures, and give
the line the appearance of a composite structure. For
very small concentrations of H₂ the resonance line is
almost resolved into a broad line of width about 12 G
peak to peak and a very narrow line at the center. The
linewidth of the broad part, moreover, is not very sensi-
tive to change in the H₂ concentration. The results
appear to indicate a transition of some kind within the
temperature range studied, but a determination of the
temperature of the transition is difficult because it
was found that the change in shape of the line does not
occur abruptly at any temperature. It is to be noted
that the composite line was observed always immediately
on cooling to the lowest temperature, the time taken
in going from 4.2 to 1.1°K being about 2 min. More-
over, it was found that prolonged maintenance of the
temperature at 1.1°K for several hours did not result
in any observable change in the line structure. A dis-
cussion of the possible interpretation of this line-shape
transition is given subsequently, but it should be noted

that the low-temperature line structure in these solid
mixtures is quite similar to that observed by Sugawara
and co-workers[3] in pure solid H₂ with orthoconcentra-
tion below 34%.

The linewidth was observed to be quite dependent
on the rf level used. The linewidth $\Delta H$, measured from
peak to peak of the narrow part of the derivative line,
is shown in Fig. 8 as a function of concentration at 4.2°K
for both the lowest and the highest rf level obtainable.
It will be observed that the line narrows appreciably
with increasing rf power, the ratio of the "unsaturated
width" to the "saturated width" being roughly a
factor of 2 for solutions rich in H₂. The curve labeled
"second moment calculation" is obtained from the
following arguments:

(i) The linewidth $\Delta H$ is proportional to the square
root of the second moment of the resonance line, the
value of the constant of proportionality being sensitive
to the assumed line shape.

$$\Delta H = k M_2^{1/2}. \tag{1}$$

It should be noted that $\Delta H$, defined as the magnetic
field or frequency interval between the maximum and
minimum of the derivative curve, is equal to $2M_2^{1/2}$ if
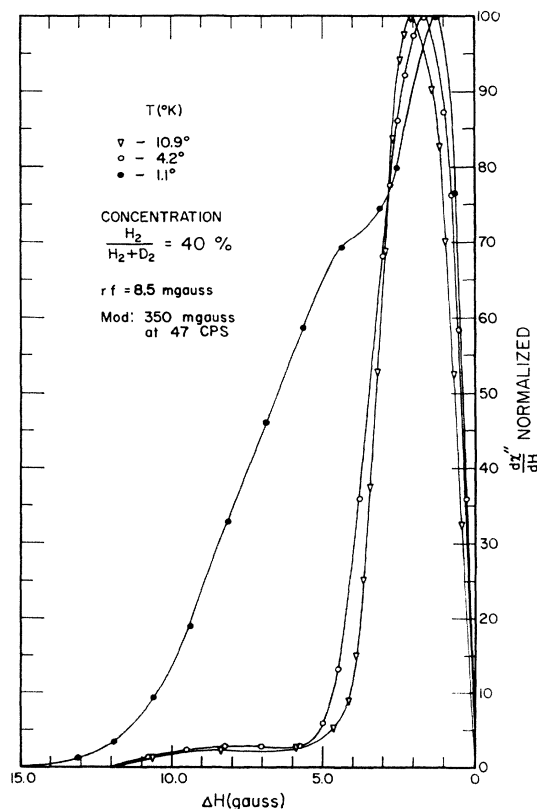one assumes a Gaussian line shape function.



Fig. 7. The derivative of the 40% line at selected
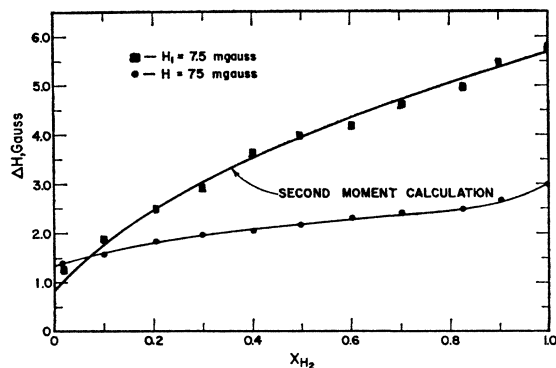temperatures showing the line shape change.

FIG. 8. The width $\Delta H$ of the resonance line as obtained from a derivative curve plotted as a function of the $n$-$H_2$ concentration for two rf levels at 4.2°K.

(ii) The second moment of a mixture of two magnetic ingredients is related to the second moment of one of the components (pure $n$-$H_2$ in this case) by the following relationship[6]:

$$M_2^{1/2}(x) = M_2^{1/2}(x=1)\{x+\bar{\eta}(1-x)\}^{1/2}, \qquad (2)$$

where

$$\bar{\eta} = \frac{4}{9}\left(\frac{\gamma_{D_2}}{\gamma_{H_2}}\right)^2 \frac{I_{D_2}(I_{D_2}+1)}{I_{H_2}(I_{H_2}+1)}.$$

The value of $\bar{\eta}$ obtained by averaging $x$ over all possible $D_2$ spin states is $\bar{\eta}=0.021$. One extremely important assumption is made in the derivation of Eq. (2), namely that the replacement of a $H_2$ molecule by a $D_2$ molecule does not alter the intermolecular separations or produce a change in crystal structure. The value of $kM_2^{1/2}$ (pure) is obtained by a least-squares fit of the experimental points from Fig. 7.

In Fig. 9 the width $\Delta H$ obtained from the maximum and minimum of the derivative curve is compared to the full width at half-maximum amplitude $W$ measured directly from $\chi''$ as a function of rf power at 4.2°K. Both parameters indicate a narrowing of the resonance line with increasing rf power. The data used in constructing Fig. 9 yield further information. For example, it is possible to obtain an estimate of the spin-lattice relaxation time $T_1$ from the steady state data providing one can measure $H_1$ with some accuracy and obtain a value for $T_2$, the spin-spin relaxation time. If one plots the reciprocal of the observed amplitude of the line

TABLE I. Values of the product of spin-spin and spin-lattice relaxation times for various hydrogen concentration.

| $x_{H_2}$ | $T_1T_2(\text{sec}^2)\times10^{-6}$ (at 4.2°K) |
|---|---|
| 1.00 | 2.06 |
| 0.70 | 1.93 |
| 0.60 | 2.07 |
| 0.40 | 2.23 |
| 0.20 | 2.23 |
| 0.10 | 2.34 |

"on resonance" (i.e., $\omega-\omega_0=0$) as a function of $H_1^2$, then the product $T_1T_2$ can be obtained from the slope and intercept of a straight line fitted to the points. The slope of this line should be $\gamma^2 T_1T_2/A$ and the intercept $1/A$ since

$$g(\omega=\omega_0)^{-1} = (1+\gamma^2H_1^2T_1T_2)/A,$$

where $g(\omega)$ is the line shape function. It is important to emphasize that the theoretical computations of Bloembergen, Purcell, and Pound, (BPP)[15] Redfield,[16] and more recently Provotorov[17] all lead to the same expression for $g(\omega)$ at exact resonance. Thus $T_1T_2$ as determined by the above procedure is compatible with all existing theories of saturation. The product $T_1T_2$ at 4.2°K is tabulated in Table I for several of the concentrations studied. The slope and intercept of the line were determined by means of a least-squares calculation. The product $T_1T_2$ so obtained is accurate to at best 10%.
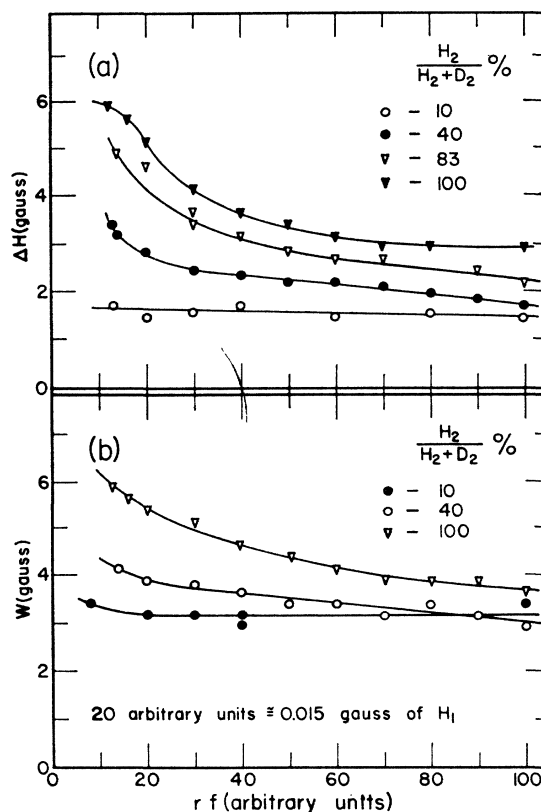


FIG. 9. The width $\Delta H$ as obtained from the derivative peaks and $w$, the full width at half-maximum, obtained from the absorption curve are plotted as a function of rf power for several concentrations at 4.2°K.

[15] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
[16] A. Redfield, Phys. Rev. 98, 1787 (1955).
[17] N. B. Provotorov, Zh. Eksperim. i Teor. Fiz. 41, 1582 (1961) [English transl.: Soviet Phys.—JETP 14, 1126 (1962)].

## IV. DISCUSSION OF THE LINE-SHAPE TRANSITION

Isotopic phase separation in solid mixtures has been shown to be thermodynamically favorable by a number of authors and theoretical estimates have been made of such possible phase-separation temperatures $T_c$, for example, by Prigogine, Bingen, and Bellemans[18] and by Simon and Bellemans,[19] $T_c$ for a 50% $n$-$H_2$ solid mixture being estimated to be between 1.5 and 3°K. Moreover, isotopic phase separation has been shown experimentally to occur in solid $He^3-He^4$ mixtures by Edwards, McWilliams, and Daunt[20] at temperatures below 0.37°K by observation of the specific heats. If solid $H_2-D_2$ mixtures separated into $H_2$-rich and $H_2$-poor regions, then the $H_2$ NMR line would appear as a superposition of two lines, one characteristic of homogeneous solid regions rich in $H_2$ giving rise to a broad line [see Eq. (2) above] and the second characteristic of the solid regions rich in $D_2$ giving rise to a narrow line. The shape of such composite lines can readily be calculated, as has been shown by the authors previously,[6] and they appear qualitatively similar to those observed by us (see Fig. 6) at the lowest temperatures of observation. It is important, therefore, to speculate on the mechanism responsible for these observations.

Some time ago, Kogan, Lazarev, and Bulatova[9] reported phase separation in the $H_2-D_2$ system at approximately 16.4°K. Their phase diagram shows a peritectic at this temperature corresponding to the co-existence of a liquid solution in equilibrium with two solid solutions of different composition. Our NMR results, including those using a pulsed technique,[6] do not agree with this phase diagram. Moreover, recent observations by White and Gaines[21] of the specific heats of solid $H_2+D_2$ mixtures between 8 and 16°K and of the liquid-solid phase boundaries show no evidence for the isotopic phase separation above 8°K reported previously by Kogan et al. It is considered, furthermore, that such a phase separation is theoretically unlikely at such high temperatures—first from a knowledge of the value of the excess Gibbs function and secondly because at temperatures above the line narrowing transition the translational freedom would preclude its stability.

At the lower temperatures around 1°K where, on the other hand, an isotopic phase separation is thermodynamically favorable,[18,19] the only experimental evidence to date is that presented here and this can be interpreted also in terms of the hindering of the rotation of the ortho-$H_2$ molecule. Some significant arguments against phase separation are:

(a) The fact, noted above, that there is no delay in establishing the observed composite line on cooling nor is there further change with time of the line shape thereafter. For phase separation one might expect time to be a factor in the growth of the separated clusters. On the other hand, no experiments have been done on $H_2-D_2$ mixtures solidified in volumes of widely different sizes.

(b) The diffusion coefficient for $H_2$ molecules in solid $H_2$, as measured by Bloom[11] down to about 10°K is $D = 1.4 \times 10^{-3} \exp(-190/T)$, which extrapolated to 2°K becomes negligible. If, therefore, isotopic phase separation were dependent on thermally activated diffusion at 2°K, it could not be observed.

(c) The specific heat of a phase-separating mixture should show a large anomaly at $T_c$, as found in solid $He^3-He^4$ mixtures by Edwards, McWilliams, and Daunt.[20] Preliminary[8] observations of the specific heat of a solid mixture of 20% $p$-$H_2$ and 80% $n$-$D_2$ between 1.5 and 4°K have failed to reveal such an anomaly. However, more data on this would be of value.

(d) The composite lines we observed are similar to those observed also at about 1°K by Sugawara et al.[3] in pure solid $H_2$ with orthoconcentration below 34%. If one were to attribute our results to isotopic phase separation, then one must assume that ortho- and para-$H_2$ molecules separate in phase in pure $H_2$ of sufficiently small $n$-$H_2$ concentration at or about 1°K.

The line-shape transition could, however, be explained without encountering the above-mentioned difficulties of interpretation by supposing that it is due to a hindering of the rotation of the ortho-$H_2$ molecule. The effect of rotational changes in the ortho-$H_2$ molecule on NMR behavior can be pronounced. Gutowsky and Pake[22] have carried out extensive investigations on the shape and temperature dependence of the proton line in hindered rotators for which there is no question of isotopic phase separation. Their results for the linewidth are very similar to ours in that the linewidth (as measured from $\chi''$) is narrow at high temperatures, becomes broader as the rotation is perturbed, and eventually reaches a constant value at lower temperatures. The increasing width of the line is accompanied by the appearance of a composite structure on the derivative, characteristic of the transition from a state of free rotation to a state of hindered rotation.

## V. DISCUSSION OF THE SATURATION BEHAVIOR

### A. Bloch Equation Predictions

The theory of Redfield[16] gives the same result for the absorption component of the complex susceptibility as the earlier theories of BPP[15] and the predictions of the Bloch equations regarding saturation. These predictions

[18] I. Prigogine, R. Bingen, and A. Bellemans, Physica **20**, 633 (1954). See also I. Prigogine, *Molecular Theory of Solutions* (North-Holland Publishing Company, Amsterdam, 1957).
[19] M. Simon and A. Bellemans, Physica **26**, 191 (1960).
[20] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Letters **1**, 218 (1962); Phys. Rev. Letters **9**, 195 (1962).
[21] D. White and J. R. Gaines, *Proceedings of the Ninth International Conference on Low Temperature Physics*, Columbus, Ohio (Plenum Press, Inc., New York, 1965, in press).

[22] H. S. Gutowsky and G. E. Pake, New York, J. Chem. Phys. **18**, 162 (1950).

will now be examined for several assumed models of hydrogen mixtures.

### Homogeneous solid

For a homogeneous solid, the NMR line will broaden with increased rf power. The shape of the line will be of the Lorentz type.

### Inhomogeneous solid

Imagine a solid in which there are considerable departures (locally) from the average concentration. To be specific consider the solid to be composed of domains with compositions $X_1$ and $X_2$. Due to the differing numbers of magnetically inert neighbors (for all practical purposes, the $D_2$ molecules can be considered to be magnetically inert in a single resonance experiment on the $H_2$ spins alone), one anticipates different relaxation times and linewidths arising from these constituents. For a simple substance (within the framework of assumptions of BPP, Bloch and Redfield) one can write

$$\chi'' = \frac{M_0 H_0}{2T_1 H_1^2 \omega (1 + T_2^2 \Delta^2 \omega)}, \quad \text{where } \gamma^2 H_1^2 T_1 T_2 \gg 1, \quad (3)$$

where $T_2$ is defined by the equation

$$1/T_2^2 = \gamma^2 [H_1^2 + 2(\delta H)^2], \quad (4)$$

the quantity $\delta H$ being a measure of the local field strength. For solid $H_2$ where exchange interactions are negligible, one has

$$(\delta H)^2 = \tfrac{1}{3}\langle \Delta H^2 \rangle,$$

where $\langle \Delta H^2 \rangle$ is the second moment of the unsaturated resonance line. Thus, in order to influence the linewidth (or $T_2$) by means of rf power, one must have $H_1 \approx H_{\text{local}}$. Since $H_{\text{local}} \approx 2$ G in solid $H_2$, no change in linewidth should be observed until $H_1 \sim \tfrac{1}{2}$ G, at which point one should observe a broadening.

For a composite (inhomogeneous) solid one has

$$\chi'' = \frac{A_1 M_0 H_0}{2T_{11} H_1^2 \omega [1 + T_{21}^2 \Delta^2 \omega]}$$
$$+ \frac{A_2 M_0 H_0}{2T_{12} H_1^2 \omega [1 + T_{22}^2 \Delta^2 \omega]}, \quad (5)$$

where $A_1$ is the amount of substance 1 present, $A_2$ the amount of substance 2 present, $T_{11}$ the spin-lattice relaxation time of substance 1, $T_{21}$ the spin-spin relaxation time of substance 1, $T_{12}$ the spin-lattice relaxation of substance 2, and $T_{22}$ the spin-spin relaxation time of substance 2. One can replace $\omega$ by $\omega_0$ since $\chi''$ differs from zero appreciably only near $\omega_0$ to obtain

$$\left(\frac{2H_1^2 \omega_0}{M_0 H_0}\right)\chi'' = \frac{A_1}{T_{11}[1 + T_{21}^2 \Delta^2 \omega]} + \frac{A_2}{T_{12}[1 + T_{22}^2 \Delta^2 \omega]}. \quad (6)$$

Since $(T_1)_a$ is sensibly independent of $H_1$, it is seen that one can assign a $T_2$ to the composite $\chi''$ that is intermediate between $T_{21}$ and $T_{22}$ and independent of rf power until $H_1$ becomes of the order of $H_{\text{local}}$. Thus as $H_1$ is increased, the principal effect will be a reduction in magnitude of $\chi''$ with no perceptible change in width or shape until $H_1$ becomes of order of the smallest local field represented.

If we assume that this model is applicable to the case of isotopic phase separation, or a separation between the ortho- and para-$H_2$ molecules, then the effective $T_2$ for any given composition $\chi$ would be

$$\frac{1}{T_2^2} = \tfrac{2}{3}\gamma^2 \langle \Delta H^2 \rangle_x \left(1 + \frac{H_1^2}{\tfrac{2}{3}\langle \Delta H^2 \rangle_x}\right). \quad (7)$$

In terms of the concentration $(x)$ of the magnetically active species, one has

$$\langle \Delta H^2 \rangle_x \approx \langle \Delta H^2 \rangle_{\text{pure}} \times x.$$

It has been demonstrated empirically by Dickson and Meyer[23] that

$$\Delta H = 3.00 \langle \Delta H^2 \rangle^{1/2}$$

holds for solid $n$-$H_2$ in the vicinity of 4.2°K where $\Delta H$ is the width measured peak to peak from $d\chi''/dH$. Making the indicated substitutions into Eq. (7) and solving for the concentration $x^*$ that makes the second term equal to unity, one has

$$x_{H_2}^* = \frac{81}{8}\left(\frac{H_1}{\Delta H}\right)^2.$$

The maximum value of $H_1$ used was 75 mG, whereas $\Delta H$ is approximately equal to 6.0 G. This leads to $x_{H_2}^* \approx 0.0016$. Thus, one can see that for $x = 0.1$ the second term in Eq. (7) is only about 2% of the first term. An effect of this magnitude is completely inadequate to explain the observed saturation behavior in $H_2$. In addition, of course, the above model would predict that the narrower line (long $T_2$) would be broadened (the other line remaining essentially unchanged) and thus shift the "effective" $T_2$ toward lower values [since $(T_2)_{\text{long}} > (T_2)_{\text{eff}} > (T_2)_{\text{short}}$]. Thus the phase separation model of solid $H_2$ coupled with an expression for $\chi''$ given by Eq. (3) gives erroneous predictions regarding the saturation behavior.

It is of some interest to note that an assumption such as that the observed saturation behavior is the result of a hindering of the rotation of the ortho molecules is no more successful. Suppose we write the resultant line as a superposition of lines, with various degrees of hindered rotation, denoted by the variable $\xi$—ranging

[23] S. A. Dickson and H. Meyer, *Proceedings of the Ninth International Conference on Low Temperature Physics*, Columbus, Ohio (Plenum Press, Inc., New York, 1965, in press).

FIG. 10. A block diagram of the energy reservoirs for the Provotorov calculation showing the various couplings.
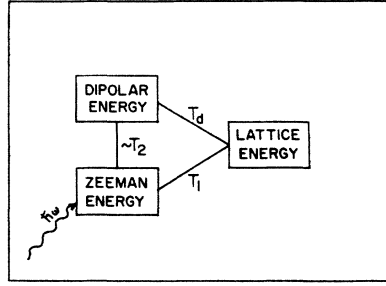
from free rotation to a completely rigid dumbbell:

$$\left(\frac{2H_1^2\omega_0}{M_0H_0}\right)\chi'' = \int d\xi \frac{A(\xi)}{T_1(\xi)[1+\Delta^2\omega T_2^2(\xi)]}.$$

This same argument applies in this case as in the previous case, namely let $T_2$ represent the narrowest line in the ensemble (free rotation); then no effect will be found until $H_1$ becomes nearly equal to $H_{\text{local}}$, clearly not a condition realized in the experiments herein reported. Thus, neither the assumption of a phase separation nor of a hindered rotation coupled with the Bloch equations can predict successfully the saturation behavior in H₂.

## B. The Provotorov Theory of Saturation

### Homogeneous Solid

Following the lead of Redfield, Provotorov[17] considers the following system shown schematically in Fig. 10. There is one important distinction between the Redfield calculation and Provotorov's, namely that Provotorov includes effects arising from the absorption of quanta in the Zeeman system when $\Delta\omega\neq0$. For such processes, one changes the dipolar energy $\langle\mathcal{3C}_d\rangle$ from its equilibrium value $\langle\mathcal{3C}_d\rangle_0$. This system will then tend to relax back to its equilibrium state by exchanging energy with the lattice at a rate characterized by time constant $T_d$. By a simple argument (due to Redfield) one can ascertain the order of magnitude of $T_d$. The Zeeman Hamiltonian is linear in the spin operators $\mathbf{I}_j$ and relaxes toward the lattice bath with a rate $R_Z\equiv1/T_1$. The dipolar Hamiltonian is quadratic in the spin operators and hence should relax toward the lattice bath at a rate twice as fast as the Zeeman system if the spins flip *independently* (since a flip of *either* spin is sufficient to produce relaxation in the dipolar system, $R_D=1/T_d$) so $R_D=2R_Z$ giving $T_d=\frac{1}{2}T_1$. Anderson and Redfield[24] have made a careful study of the situation in which spin flips are not independent but correlated. They find $1/T_d=\delta/T_1$ where

$$\delta = 2+\sum K_{jk}r_{jk}^{-6}/\sum r_{jk}^{-6},$$

with

$$K_{jk} = \langle\mathbf{h}_j(t)\cdot\mathbf{h}_k(t)\rangle/\langle|\mathbf{h}_j^2(t)|\rangle$$

[24] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

being the correlation function for the time-fluctuating magnetic fields $\mathbf{h}(t)$ seen at sites $j$ and $k$. For complete statistical independence $K_{jk}=0$ for all $j$ and $k$ giving $\delta=2$ as above, whereas for complete correlation $K_{jk}=1$ so that $\delta=3$. Thus the limits are $2\leq\delta\leq3$.

The expression obtained by Provotorov for the absorption component of the complex susceptibility $\chi''$ is

$$\chi'' = \frac{\mu^2 I_{0z}}{2\hbar}\frac{\pi g(\Delta\omega)}{1+\gamma^2 H_1^2 T_1\pi g(\Delta\omega)[1+\hbar^2\Delta^2\omega T_d/\langle H_0^2\rangle_{\text{av}}T_1]},$$

$$\langle H_0^2\rangle_{\text{av}} = \frac{\text{Tr}(H_0)^2}{\text{Tr}I_z^2}, \tag{8}$$

where $H_0$ is the secular portion of the dipolar interaction. Clearly when $\gamma^2 H_1^2 T_1\pi g(\Delta)\gg1$ the above expression reduces to

$$\chi'' = (\mu^2 I_{0z}/2\hbar)(\gamma^2 H_1^2 T_1)^{-1}(1+\Delta^2\omega\tau^2)^{-1}, \tag{9}$$

where $\tau^2$ has been set equal to $(\hbar^2 T_d/\langle H_0^2\rangle_{\text{av}}T_1)$. Thus $\chi''$ which was a replica of $g(\Delta\omega)$ before saturation now contains no information about the lineshape function but is instead a Lorentz curve with $T_2=\tau$. In the previous saturation theories one needed to increase $H_1$ until it became of the order of the local fields (not a difficult requirement in liquids); but in the Provotorov expression, one only needs to achieve saturation (i.e., $S^2=\gamma^2 H_1^2 T_1 T_2\gg1$) to observe a change in linewidth. Quite obviously these two conditions are identical in the case of a liquid where one usually takes $T_1\approx T_2 \approx(\gamma(\Delta H))^{-1}$ but quite different for solids in which $T_2\ll T_1$. The linewidth that would be obtained from Eq. (9) is related to $\tau$ by the expression

$$\gamma(\Delta H)_{\text{sat}} = (2/\sqrt{3})\tau^{-1}, \tag{10}$$

since $\chi''$ is a Lorentz curve in the saturation region. Thus from the definition of $\tau$ one has

$$\frac{T_d}{T_1} = \frac{4}{3}\frac{\langle H_0^2\rangle_{\text{av}}}{\hbar^2\gamma^2(\Delta H)_{\text{sat}}^2}. \tag{11}$$

A simple calculation (see Appendix I) shows that

$$\langle H_0^2\rangle_{\text{av}} = \frac{1}{3}\gamma^2\hbar^2\langle\Delta H^2\rangle,$$

where $\langle\Delta H^2\rangle$ is the rigid-lattice second moment for the unsaturated line.

Substituting the value of $M_2$ from Eq. (1) yields

$$\left(\frac{\Delta H_{\text{sat}}}{\Delta H_{\text{unsat}}}\right)^2 = \frac{4}{9}\frac{1}{k^2}\left(\frac{T_1}{T_d}\right) = \frac{4\delta}{9k^2}. \tag{12}$$

Since $2\leq\delta\leq3$ one has the general result that for an assumed Gaussian lineshape function ($k=2$), the observed linewidth will *decrease* with increasing rf power. Applying this argument to the observed behavior in solid $n$-H₂, one can estimate $\delta$ from the ratio of the saturated width to the unsaturated width (see Fig. 4) and knowledge of $k$. If one picks $k=2$, then $\delta=2.25$ but

if $k=3$ (corresponding to the Dickson-Meyer result) is chosen, one obtains $\delta \approx 5$. The value of $k \approx 3$ has been confirmed independently by us and will be discussed in a subsequent paper on pulsed nuclear magnetic resonance experiments in $n$-$H_2$.

Such a large value of $\delta$ can be explained in the following manner: An exchange interaction in solid $H_2$ also contributes to the spin energy and must be included in the evaluation of $\langle H_0^2 \rangle_{av}$. This addition contribution to $\langle H_0^2 \rangle_{av}$ will reduce the value of $\delta$ for $k=3$. The evaluation of $\langle H_0^2 \rangle_{av}$ for an appreciable exchange interaction is given in Appendix II [see Eq. (A8)]. The modification of Eq. (12) due to the exchange interaction $A$ is given by

$$\frac{T_d}{T_1} = \frac{4}{3}\left\{ \frac{1}{3}\frac{\langle \Delta H^2 \rangle}{(\Delta H^2)_{sat}} + \frac{z}{6}\frac{I(I+1)A^2}{\hbar^2\gamma^2(\Delta H^2)_{sat}} \right\} = \frac{1}{8}. \quad (13)$$

By making use of the condition $2 \leq \delta \leq 3$, one can now arrive at an estimate of the magnitude of the exchange interaction. Choosing $k=3$, we obtain

$$(A/\kappa)_{\delta=2} = 1.6 \times 10^{-7} \ {}^\circ K,$$

$$(A/\kappa)_{\delta=3} = 1 \times 10^{-7} \ {}^\circ K,$$

where $\kappa$ is the Boltzmann constant. Thus the magnitude of $A$ is not extremely sensitive to the value of $\delta$ chosen. These two values of $A$ represent upper limits only since Eq. (13) would normally contain terms linear in $A$ if the summations of the type

$$\sum_{j>k}\sum A_{jk}A_{jk}{}^{(0)} \quad \text{and} \quad \sum_{j>k}\sum A_{jk}B_{jk}$$

do not vanish. Indeed this is the case in $n$-$H_2$ solid since not all the nearest-neighbor sites are occupied by magnetically active molecules (ortho).

It should be noted that the Provotorov theory provides a very adequate description of the gross features of the saturation behavior in solid $H_2$. A more acceptable approach, however, would also have to take into account the crystalline Stark energy (proportional to $I_z^2$) and incorporate this into the Zeeman energy. The effect of this new term would be that the splitting between the $(m_I=0, \ m_I=+1)$ levels would not be the same as the splitting between the $(m_I=0, \ m_I=-1)$ levels. Furthermore, the addition of a crystalline Stark energy to the Zeeman energy would modify the relaxation rate of the new reservoir consisting of Stark energy $(I_z^2)$ and Zeeman energy $(I_z^1)$ toward the lattice. In addition, the exchange interaction should be incorporated into the dipolar energy reservoir (see Fig. 10).

It should be emphasized that the saturation parameter $(s^2)$ is of order 10 for $H_1 \approx 0.1$ G (at a Larmor frequency of 10 Mc/sec). Hence the effect anticipated by Provotorov occurs at much lower values of $H_1$ (and is in the proper direction) than the saturation effects predicted by the Bloch equations (which also predict a broadening rather than a narrowing).

*Inhomogeneous Solid*

For a composite structure, one anticipates that the two resonance lines will saturate at about the same rate (since $T_1T_2$ is not strongly concentration-dependent), that the ratio of heights of the composite peaks in the derivative curve will be constant, and that each peak will be shifted toward zero (corresponding to a narrowed line) by the same ratio since $(\Delta H)_{sat}/(\Delta H)_{unsat}$ is approximately independent of concentration (unless a line shape change occurs that alters the values of $k$ and $\delta$). These effects have not been observed. As in the case of phase separation, the line shape from a superposition of lines with various degrees of hindered rotation will be rather complicated and tend to narrow with increased rf power. However, no simple statement can be made about the ratio of derivative peaks or their respective shift since no information concerning $s^2(\xi) = \gamma^2 H_1^2 T_1(\xi)T_2(\xi)$ is currently available. One would anticipate, however, that hindering the rotation will increase $T_1$ and decrease $T_2$, but whether their product is a constant cannot be determined intuitively. Thus, no clear-cut distinction between phase separation and hindering of the rotation is available from the saturation data.

### C. Conclusions

The saturation behavior of the resonance lines seems to be adequately accounted for by the Provotorov theory applied to a homogeneous solid. Indeed by making suitable modifications in his expressions for the dipolar energy to include exchange effects we are able to estimate the magnitude of the interaction. Clearly solid $n$-$H_2$ is a more complicated solid than the Provotorov theory was intended for. The extension of Provotorov's method to a solid (such as $n$-$H_2$) with appreciable Stark crystalline energy arising from the lattice influence on the rotational motion of the ortho molecules and also exchange energy should be reasonably straightforward but possibly quite cumbersome.

The saturation data permit one to determine the product $T_1T_2$ as we have done in Table I, but no accurate separation of these two relaxation times can be made from our data due to the rather complicated lineshape function $g(\omega)$ and hence $T_2$ since

$$T_2 = \pi g(0), \quad (14)$$

where $g(\omega)$ is normalized to unity. Values of $T_1$ will be reported in a subsequent paper where the determination of $T_2$ is made in detail. Let it suffice to say that if the concentration dependence of $T_1$ were given by the relationship[25]

$$T_1 = k\sqrt{x} \quad (15)$$

and $T_2 \approx (\gamma\Delta H)^{-1} \approx [\gamma(\Delta H)_{x=1}\sqrt{x}]^{-1}$ from Eq. (2), then the product $T_1T_2$ should be independent of concentra-

---

[25] T. Moriya and K. Motizuki, Progr. Theor. Phys. (Kyoto) **18**, 183 (1957).

tion. The absolute values of $T_1$ obtained from these data are not reliable since no attempt was made to purify the samples with regard to any oxygen impurity. If one selects $T_2 \approx 20$ $\mu$sec for $n$-$H_2$ at 4.2°K then $T_1 \approx 100$ msec, a value about one-half of that obtained in our pulse experiments on purified samples.

## APPENDIX I

### Evaluation of $\langle H_0{}^2 \rangle_{\text{av}}$ (No Exchange)

$$H_0 = \sum_{j>k} \sum (A_{jk}+B_{jk}) I_{jz} I_{kz}$$
$$+ \sum_{j>k} \sum A_{jk}(I_{j+}I_{k-}+I_{j-}I_{k+}), \quad (A1)$$

with

$$A_{jk} = A_{jk} + (\gamma^2 \hbar^2/r_{jk}{}^3)(\tfrac{3}{2}\cos^2\theta_{jk}-\tfrac{1}{2}) = A_{jk}+A_{jk}{}^{(0)}, \quad (A2)$$

and

$$B_{jk} = (3\gamma^2\hbar^2/r_{jk}{}^3)(\tfrac{3}{2}\cos^2\theta_{jk}-\tfrac{1}{2}).$$

Thus to evaluate the "trace" of $H_0{}^2$ one must find the diagonal matrix elements for products of spin operators of the type:

$$I_{j\nu}I_{k\mu}I_{m\xi}I_{l\eta}.$$

This result has been worked out[4] and yields

$$\text{Tr} I_{j\nu}I_{k\mu}I_{m\xi}I_{l\eta} = \tfrac{1}{9}I^2(I+1)^2(2I+1)^N \delta_{jk}\delta_{ml}\delta_{\xi\eta}\delta_{\nu\mu}. \quad (A3)$$

Combining this result with Eq. (A1) yields

$$\text{Tr} H_0{}^2 = \tfrac{1}{9}I^2(I+1)^2(2I+1)^N$$
$$\times \sum_{j>k}\sum (3A_{jk}{}^2+2A_{jk}B_{jk}+B_{jk}{}^2). \quad (A4)$$

If one ignores the exchange interaction contained in the term $A_{jk}$, then since $\text{Tr} I_z{}^2 = \tfrac{1}{3}I(I+1)N(2I+1)^N$, one

obtains

$$\langle H_0{}^2 \rangle_{\text{av}} = \frac{\text{Tr} H_0{}^2}{\text{Tr} I_z{}^2} = \tfrac{1}{2}I(I+1)\frac{(\gamma^2\hbar^2)^2}{N}$$
$$\times \sum_{j>k}\sum (1-3\cos^2\theta_{jk})^2 r_{jk}{}^{-6}. \quad (A5)$$

The expression for the second moment $\langle \Delta H^2 \rangle$ is

$$\langle \Delta H^2 \rangle = \tfrac{3}{2}\gamma^2\hbar^2(I(I+1)/N)\sum_{j>k}\sum (1-3\cos^2\theta_{jk})^2 r_{jk}{}^{-6}. \quad (A6)$$

This leads to the result

$$\langle H_0{}^2 \rangle_{\text{zv}} = \tfrac{1}{3}\hbar^2\langle\Delta\omega\rangle = \tfrac{1}{3}\gamma^2\hbar^2\langle\Delta H^2\rangle. \quad (A7)$$

## APPENDIX II

### Evaluation of $\langle H_0{}^2 \rangle_{\text{av}}$ (Exchange Energy Included)

If the exchange interaction is included, we must add to Eq. (A4) the following terms:

$$\tfrac{1}{9}I^2(I+1)^2(2I+1)^N \sum_{j>k}\sum (3A_{jk}{}^2+6A_{jk}{}^{(0)}+2A_{jk}B_{jk}).$$

Consider the first of these terms and pick out site $j$ as a typical site in the crystal:

$$\sum_{j>k}\sum A_{jk}{}^2 = \tfrac{1}{2}N\sum_{\substack{k \\ k\neq j}} A_{jk}{}^2.$$

Since the exchange interaction is a short-range interaction depending primarily upon a significant overlap of wave functions, we may neglect all terms in the summation over the index $k$ except those terms corresponding to the $z$ nearest neighbors. The exchange interaction between typical nearest neighbors will be denoted by $A$. Thus

$$\sum_{j>k}\sum A^2{}_{jk} \approx \tfrac{1}{2}NzA^2.$$

The remaining two terms can be considered in the following manner:

$$\sum_{j>k}\sum A_{jk}A_{jk}{}^{(0)} = \tfrac{1}{2}\sum_{\substack{j \ k \\ j\neq k}}\sum A_{jk}A_{jk}{}^{(0)} \approx \tfrac{1}{2}NAz\sum_{\substack{\text{nearest} \\ \text{neighbors}}} A_{jk}{}^{(0)}$$

with an equivalent expression for the $A_{jk}B_{jk}$ term. The summation of the angular factors appearing in $A_{jk}{}^{(0)}$ and $B_{jk}{}^{(0)}$ [i.e., $(1-3\cos^2\theta_{jk})r_{jk}{}^{-3}$] is identically zero for lattices with cubic symmetry and even the hexagonal close-packed lattice providing the summation is taken over only nearest-neighbor sites. Thus one has for the complete expression:

$$\langle H_0{}^2 \rangle_{\text{av}} = z/6(I+1)IA^2+\tfrac{1}{3}\gamma^2\hbar^2\langle\Delta H^2\rangle. \quad (A8)$$