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Nuclear magnetic resonance wide-line study of hydrogen
in the yttrium-yttrium dihydride system

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M.S. Thesis submitted to Iowa State University

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in the yttrium-yttrium dihydride system

by

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ABSTRACT

The ^1H nuclear magnetic resonance was studied in the yttrium-hydrogen system YH_x in the composition range $0.20 \leq x \leq 1.98$ and temperature range $77\text{K} \leq T \leq 490\text{K}$. Both α and β -phases of YH_x were investigated in polycrystalline (powdered) specimens.

Rigid lattice proton resonance second moments were obtained for both α and β -phase samples. Analysis of the second moment for $\alpha\text{-YH}_x$ (α -phase) indicates that the hydrogen resides in both the tetrahedral and octahedral interstitial sites of the hcp Y lattice. Second moment values for $\beta\text{-YH}_x$ (β -phase) indicate that a sizeable fraction of the octahedral interstitial sites in the fcc yttrium metal lattice are occupied by hydrogen, while a nonnegligible fraction of the tetrahedral interstitial sites are vacant. For example, in $\text{YH}_{1.98}$, 28% of the octahedral sites are occupied, while 15% of the tetrahedral sites are vacant. The results for $\beta\text{-YH}_x$ also indicate that as the H concentration increases, the probability of H occupation of octahedral sites increases.

The room temperature phase boundaries of the two-phase region (i.e., $\alpha+\beta$) were estimated on the basis of measurements of the NMR intensities of the α and β -lines of $\text{YH}_{0.44}$

and $\text{YH}_{0.88}$. The results were: $\text{H/Y} = 0.15$ for the upper limiting composition of the solid solution (α -phase), and $\text{H/Y} = 1.69$ for the lower limiting composition of the dihydride (β -phase).

The line-narrowing behavior of the proton resonance in samples of α and $\beta\text{-YH}_x$ was measured and analyzed to obtain the activation energy for hydrogen diffusion for these samples. Typical values of 0.42 ± 0.02 eV were obtained for the activation energy in both the α and β -phases.

The saturation behavior of the absorption mode resonance signal in $\text{YH}_{1.92}$ and $\text{YH}_{1.98}$ was studied in the rigid lattice region. Saturation narrowing of the linewidth occurred for both samples at 160K, while saturation broadening occurred at 200K. The Provotorov theory of resonance saturation was judged to be the most adequate in explaining the experimental results. In addition, as a further test of the Provotorov theory, the proton spin-lattice relaxation time T_1 was measured by a progressive saturation method utilizing the dispersion mode derivative signal amplitude in $\text{YH}_{1.92}$. T_1 values of 2.42 and 1.04 seconds were obtained at 160K and 200K, respectively, in reasonable agreement with pulsed NMR results.

I. INTRODUCTION

The magnetic moment $\vec{\mu}$ of a nucleus having nonzero intrinsic spin $\vec{I}$ is given by

$$\vec{\mu} = \gamma \hbar \vec{I} \quad (1)$$

where $\hbar$ is Planck's constant divided by 2π and γ is the gyromagnetic ratio of the nucleus. When placed in a magnetic field $\vec{H}$ the Zeeman interaction energy of the nucleus is given by

$$\mathcal{H} = -\vec{\mu} \cdot \vec{H} = -\gamma \hbar \vec{I} \cdot \vec{H} . \quad (2)$$

Letting $\vec{H} = H_0 \hat{z}$ we find that the eigenvalues of the above Hamiltonian are

$$E_m = -\gamma \hbar m H_0 \quad m = I, I-1, \dots, -I+1, -I \quad (3)$$

and the difference in energy between two adjacent energy levels is given by

$$\Delta E = E_{m-1} - E_m = \gamma \hbar H_0 . \quad (4)$$

The application of a radio frequency (rf) magnetic field at right angles to the magnetic field $H_0 \hat{z}$, with frequency ω_0 such that its energy quantum is

$$\hbar \omega_0 = \Delta E = \gamma \hbar H_0 , \quad (5)$$

will induce transitions between adjacent Zeeman energy levels at the frequency

$$\omega_0 = \gamma H_0, \quad (6)$$

which is the resonance condition. In a nuclear magnetic resonance (NMR) continuous wave (cw) experiment one detects the transitions induced by the rf field and records them as a function of magnetic field H .

The above discussion is a great simplification of the actual situation in a solid, however, as Equation (2) considered only the interaction of an isolated nuclear moment with an external magnetic field and ignored many other interactions of importance in solids. In a solid we must take into account such things as the electric quadrupole interaction, the contact hyperfine interaction (interaction between nuclear moments and the field produced by the conduction electrons), and the nuclear dipole-dipole interaction. Since the nucleus (proton) under investigation in this study has $I = 1/2$, there is no quadrupole interaction; and therefore the most important interaction we must consider is the dipolar interaction between the nuclear moments. This interaction has the effect of broadening the resonance absorption line so that instead of its being a delta function spike, it has a finite width and approximates either a Gaussian or Lorentzian curve. The width, shape, and intensity of the resonance line yield valuable information about microscopic internal fields and also the location and motion of the nuclei themselves. We will discuss the dipolar interaction in greater

detail in Section III.A.1.

In this investigation we have studied the metal-hydrogen (M-H) system YH_x (yttrium hydride) using cw NMR. Many other M-H systems have been studied using NMR, as recently reviewed by Cotts (1). Metal-hydrogen systems have been the focus of considerable attention within the last decade because they possess a number of unique features as well as possible technological applications. One possible application is to use a metal hydride to store hydrogen, which, when discharged from the metal, can be used as a source of energy to power vehicles. This has led to the search for an optimum hydride for on-board vehicular storage of hydrogen. One of the most promising hydrides found to date for such purposes is $\text{Mg-MgNi}_2\text{-Y}$ (2). One of the unique features of M-H systems is the relative simplicity of the hydrogen atom in comparison with other interstitials, which makes the M-H system more readily understandable than other more complicated metal-interstitial systems. Calculations which could not possibly be attempted for more complicated systems can be done on M-H systems. For example, band structure calculations have been successfully carried out on a number of M-H systems (3) including YH_2 (4).

We have studied YH_x over the composition range $0.20 \leq x \leq 1.98$ and temperature range $77\text{K} \leq T \leq 500\text{K}$. In this temperature and composition range our samples of YH_x contained

the following hydride phases. For $0.20 \leq x \leq 1.72$, YH_x is a two-phase system composed of both α and β -phases, while only the β -phase occurred in the range $1.90 \leq x \leq 1.98$. (We did not have any samples in the region $1.73 \leq x \leq 1.89$ so we just report the phases present in our samples.) Figure 1.1 (reprinted from Reference (5)) shows a partial phase diagram of the Y-H system where $\text{H/Y} = x$, αY denotes α -phase (i.e., the solid solution phase), and YH_{2-x} denotes β -phase (also called the dihydride). The phase boundary between the solid solution and the two phase region has since been worked out at somewhat lower temperatures (including room temperature) by Beaudry and Spedding (6) and will be discussed further later in this thesis. For notational convenience we will refer to α -phase YH_x as $\alpha\text{-YH}_x$ and β -phase YH_x as $\beta\text{-YH}_x$ in the following pages.

In $\beta\text{-YH}_x$, the hydrogen resides in the interstitial tetrahedral (T) and octahedral (O) sites of the fcc Y-lattice. Figure 1.2 shows the location of the T-sites which are analogous to the location of F' in CaF_2 . The O-sites are easier to visualize as these sites make up another fcc lattice offset by half a lattice constant (i.e., by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$) from the Y-lattice. In $\alpha\text{-YH}_x$, yttrium has its normal hcp structure and the hydrogen again reside in interstitial T and O-sites. Details of the location of these sites in $\alpha\text{-YH}_x$ will be considered in Section III.A.2.

Figure 1.1. Phase diagram of the yttrium-hydrogen system (after Mueller et al. (5))

Figure 1.2. Location of the tetrahedral sites in the fcc yttrium lattice. The small light spheres are yttrium and the larger dark spheres are hydrogen. The hydrogen is located at the center of a tetrahedron formed by its four nearest yttrium neighbors. The octahedral sites (not shown) are located midway between every pair of yttrium atoms

In this investigation we have done the following: 1. We attempted to ascertain the location of the hydrogen in both α and β -YH_x. That is, from the NMR measurements we have estimated how many of the T-sites are occupied and how many O-sites are occupied. Previous studies made on similar M-H systems suggest that most of the T-sites are occupied, but that very few if any O-sites are occupied in the β -phase. We have tested this tentative conclusion by analysis of the proton resonance rigid lattice second moments in our samples.

2. We have also estimated the locations of the phase boundaries (at room temperature) of the two-phase region from measurements of the NMR intensities of the α and β -lines.

3. The line-narrowing behavior of both α and β -YH_x has been measured and used to obtain the activation energy of hydrogen diffusion in both α and β -phase samples.

4. Although we did not set out initially to study it, saturation narrowing and broadening of the resonance line was observed to occur at very low rf levels. This behavior was studied and the spin-lattice relaxation time T_1 was measured by a progressive saturation experiment as a test of the Provotorov theory of saturation.

II. EXPERIMENTAL DETAILS

A. Sample Preparation

Ames Laboratory Y metal was used in the preparation of the yttrium hydride samples. It was prepared by B. J. Beaudry of the Ames Laboratory. Table 2.1 lists the impurity concentrations, in ppm by weight, found in the yttrium. Only those elements with an impurity concentration of 10 ppm or greater are listed in the table. The complete analytical report, Code No. Y-5972, is available from Dr. D. T. Peterson. All other elements had an impurity concentration of less than 10 ppm, most of them being much less than 10 ppm.

Table 2.1. Impurity concentrations, in ppm by weight, of elements found in Ames Laboratory Y metal

Impurity	Concentration (ppm)
C	38
N	10
O	90
Fe	20
Ta	10
W	10

* The yttrium hydride samples were prepared by A. Johnson and S. O. Nelson of the Metallurgy Division of The Ames Laboratory, Ames, Iowa, by first mechanically cutting thin slices from an arc melted finger of Y metal using a diamond

saw. After mechanical and electro-polishing, the yttrium was degassed at 900°C for approximately twenty minutes in a Sieverts type apparatus. It was then charged at 800°C with hydrogen gas which was obtained from the decomposition of uranium hydride (UH_3). Following charging, the sample was homogenized for approximately ten hours at 800°C. This allowed the hydrogen to diffuse throughout the sample. After cooling, the samples were analyzed for hydrogen content by hot vacuum extraction, in which a small portion of the sample is heated to a very high temperature in a vacuum. The hydrogen boiled off is collected and measured, and the global composition determined.

B. Apparatus

1. NMR equipment

All NMR measurements were made using the conventional nuclear induction method (crossed-coil) of Bloch, Hansen and Packard (7). A Torgeson spectrometer (8) and Varian Associates Model V4320B crossed-coil probe were used at operating frequencies of 16 and 32 MHz along with a Varian 6" magnet which could achieve fields up to 10 kOe. Signal averaging (9) was used to improve the signal-to-noise ratio. A simplified block diagram of the apparatus is shown in Figure 2.1.

In all the experiments the frequency was held constant

Figure 2.1. Block diagram of the NMR spectrometer used in this study

while the magnetic field was scanned. The rf (radio frequency) signal was generated by a crystal oscillator stable to within a few parts in 10^7 . The frequency was monitored by a Monsanto Model 110A Programmable Counter-Timer. Peak-to-peak rf fields ($2H_1$) of 0 to 270 mOe (milli Oersted) were attained at the sample position in the probe.

To improve the signal-to-noise ratio of the spectra, the technique of signal averaging over a number of passes was employed. This was done by using the channel address voltage of the RIDL 24-2 400 channel analyzer to drive the magnet power supply which established a one-to-one correspondence between the magnetic field and analyzer memory channel. This resulted in the adding of the signal from one pass to the combined total of all previous passes, with the signal-to-noise ratio increasing as the square root of the number of passes.

Conventional audio frequency modulation of the magnetic field and phase sensitive detection by means of a lock-in amplifier were used. We will commonly refer to spectra so obtained as "lock-in" spectra. The magnetic field was modulated at frequencies of 80 and 200 Hz via a set of Helmholtz coils in the probe. The modulation amplitude was controlled by a Varian V4250A sweep unit. The lock-in amplifier (Varian Output Control Unit Model V4270A) amplifies the detected audio signal from the receiver, demodulates the

signal by means of a chopper-type phase detector, and amplifies the resulting d.c. signal, which is proportional to the derivative of the resonance signal. The d.c. signal is converted to a sine wave with a frequency proportional to the magnitude of the input signal by a voltage-to-frequency converter. This frequency is counted by the RIDL analyzer and stored in the appropriate channel. The resultant spectra were recorded on chart paper by an XY plotter.

To avoid distortion of the resonance shape due to modulation saturation, the amplitude of the modulation field, $2H_m$, was usually taken to be less than one-fifth of the linewidth ΔH , or $2H_m < \Delta H/5$.

2. High and low temperature equipment

A nitrogen gas flow cryostat system which could attain temperatures between 100 and 500K was used to study the temperature dependence of the spectra for various samples of the hydride. One of the main components was a dewar insert which fit through the sample chamber of the probe. It allowed the sample to be heated or cooled while keeping the probe at room temperature. The dewar insert and nitrogen gas flow apparatus can be seen in Figure 2.2. In this investigation it was necessary to keep the sample tube sealed, so the monitoring thermocouples were placed outside the sample tube: one directly next to the sample (measurement thermocouple); the other slightly beneath the sample (control thermo-

Figure 2.2. Construction of the variable temperature gas-flow apparatus used in this study. In the experiments described in the text the sample tube is sealed, and the thermocouples are located directly next to and slightly beneath the sample

couple). The control thermocouple was used as a reference for the temperature control unit while the measurement thermocouple monitored the temperature of the sample.

Temperatures above room temperature were obtained by passing heated nitrogen gas across the sample. The gas is heated by a 13 Ω main heater and then by a 13 Ω reheater situated just beneath the sample. The reheater is connected directly to the temperature control unit which allowed fine adjustments to the temperature to be made.

To achieve temperatures below room temperature, cold nitrogen gas was passed across the sample. The cold gas was obtained by a controlled boiling of liquid nitrogen with two 66 Ω 150W heaters in a 25 liter dewar. The temperature was controlled by regulating the gas flow rate, larger flow rates producing lower sample temperatures. Again, fine adjustments to the temperature could be made with the reheater.

The temperature of the sample was monitored at all times by the measurement thermocouple which was placed directly next to the sample. This thermocouple was connected to a Leeds and Northrup 7554 Type K-4 Potentiometer. The temperature control system's setting was based upon the temperature measured by the measurement thermocouple and not the control thermocouple as this thermocouple gave a more accurate indication of the temperature. By monitoring the

temperature in this manner, one could be reasonably certain of the sample temperature for a specific spectrum.

III. RESULTS AND DISCUSSION

A. Rigid Lattice Second Moments and Site Occupancies

1. $\beta\text{-YH}_x$

a. Experimental results The experimental rigid lattice proton second moments (M_2) for $\beta\text{-YH}_x$ were determined for samples with $x = 1.63, 1.72, 1.90, 1.92,$ and 1.98 . They were obtained by direct numerical integration of the derivative line trace. Each spectrum was taken at a temperature low enough to assure that the rigid lattice condition applied. Modulation broadening, which was only on the order of 0.10 Oe^2 , was corrected for using Andrew's formula (10). It should also be mentioned here that the M_2 spectra were taken at extremely low rf (radio frequency) fields in order to avoid saturation narrowing. An H_1 on the order of only 2-3.5 mOe (milli Oersted) was used for all but the $\text{YH}_{1.63}$ and $\text{YH}_{1.72}$ samples; for which H_1 was 9.44 mOe. Saturation narrowing will be discussed in greater detail in Section III.C.

The results for the proton second moment values are summarized in Table 3.1. Also included in the table is the linewidth ΔH , the exponent n of the Harper-Barnes line-shape function (11), the lock-in time constant (TC) and sweep rate of the magnetic field through the resonance used for that

Table 3.1. Linewidth ΔH , second moment M_2 , and exponent n of the Harper Barnes line shape function for β -YH_x (the time constant (TC) and sweep rate (Oe/sec) are also included)

Sample	ΔH (Oe)	M_2 (Oe ²)	n
YH _{1.63} 3 sec TC 0.10 Oe/sec	8.49	11.07	2.5
YH _{1.72} 3 sec TC 0.08 Oe/sec	8.53	10.49	2.6
YH _{1.90} 10 sec TC 0.08 Oe/sec	8.81	12.23	2.5
3 sec TC 0.08 Oe/sec	8.19	11.40	2.4
YH _{1.92} 10 sec TC 0.05 Oe/sec	8.61	11.58	2.4
10 sec TC 0.08 Oe/sec	8.71	12.21	2.4
3 sec TC 0.08 Oe/sec	8.41	10.79	2.5
YH _{1.98} 10 sec TC 0.05 Oe/sec	8.76	13.01	2.4
3 sec TC 0.10 Oe/sec	8.67	12.83	2.4
$M_2(1.80) = 10.78 \text{ Oe}^2 \pm 0.30$ $M_2(1.91) = 11.64 \text{ Oe}^2 \pm 0.80$ $M_2(1.98) = 12.92 \text{ Oe}^2 \pm 0.10$			

particular spectrum. The linewidth was defined in the usual manner as the separation distance between the maximum and minimum points on the derivative trace. The three M_2 values listed at the bottom of Table 3.1 were obtained as follows. M_2 (1.98) is the average second moment value of $YH_{1.98}$. The second moments for $YH_{1.63}$ and $YH_{1.72}$ were averaged and the new value called M_2 (1.80). The same was done for all five second moments of $YH_{1.90}$ and $YH_{1.92}$ and the average value called M_2 (1.91). A justification for this type of manipulation for the latter case is that the uncertainty in x for $\beta\text{-}YH_x$ is ± 0.02 to 0.04 . Thus for $YH_{1.90}$ and $YH_{1.92}$, this uncertainty makes these samples essentially indistinguishable. Hence, we refer to the average M_2 value for both samples as the average of their compositions, $M_2(1.91)$. For the two samples in the two phase region, $YH_{1.63}$ and $YH_{1.72}$, it is very difficult to ascertain the exact concentration of H in the dihydride phase since there is some H present in the α -phase ($\alpha\text{-}YH_x$). The x values, 1.63 and 1.72, are really the global compositions of the samples as it refers to the total H content and not to the amount of H present in the dihydride phase ($\beta\text{-}YH_x$). Thus, we have assigned these samples an x value of 1.80, a value which we assume to be the lower limiting composition of the dihydride phase. Although this value is somewhat arbitrary, present evidence suggests that it is somewhere in the vicinity of 1.80 (5). One obtains then, the

values for $M_2(1.80)$ and $M_2(1.91)$ along with $M_2(1.98)$ given at the bottom of Table 3.1. It is now apparent that M_2 increases with increasing hydrogen content. This same phenomenon was found by Stalinski, Coogan, and Gutowsky (12) (hereafter SCG) in their study of titanium hydride. However, titanium hydride has different properties than yttrium hydride in that the maximum value of H/Ti is 2.00. We shall therefore interpret our data differently than did SCG.

Various lock-in time constants and sweep rates were used while taking the rigid lattice spectra. For some as yet unknown reason, this did seem to have an effect upon M_2 . For example, M_2 for $YH_{1.90}$ was 12.23 Oe^2 when a 10 sec TC was used, while it decreased to 11.40 Oe^2 when a 3 sec TC was used. (The sweep rate was the same in both cases.) A similar phenomenon occurred for $YH_{1.92}$, and also for $YH_{1.98}$, but to a much lesser extent. (Also for $YH_{1.98}$, the sweep rates were very different for the two spectra, which could possibly account for the smaller difference between M_2 values.) Thus, it seems that lowering the lock-in time constant has the effect of decreasing the second moment.

As was mentioned previously, the third column of Table 3.1 lists the exponent n of the Harper-Barnes line shape function. The analytic form of this function is

$$g(x) = A \exp(-b|x|^n) \quad (7)$$

where $x = H - H_0$ (or $\nu - \nu_0$) and the exponent n is allowed to vary between 1.5 and 4.0. The derivative of this function, which was compared with the experimental traces, can be written as

$$g'(x) = e^R |x|^{n-1} \exp(-R|x|^n) \quad (8)$$

where $R = (n-1)/n$. The relation between second moment M_2 , linewidth Δx , and n is given by

$$\frac{M_2}{(\Delta x)^2} = \left(\frac{n}{n-1}\right)^{2/n} \frac{\Gamma(3/n)}{4\Gamma(1/n)} \quad (9)$$

where $\Gamma(z)$ is the gamma function of z . Table 3.2 gives values of $M_2/(\Delta x)^2$ as a function of n , while Appendix A lists $g'(x)$ for various n values.

With this information, n can be determined from the experimental linewidth and second moment values. The shape function with this n value was usually a fairly good fit to the experimental trace. However, in some cases, an n that differed by only ± 0.1 would be a better fit. For example, for the $\text{YH}_{1.92}$ spectrum that had an M_2 of 11.58 Oe^2 , one finds that $M_2/(\Delta x)^2 = 0.1562$ which gives an n of 2.5. It turns out however, that $n = 2.4$ fits the experimental trace better than does $n = 2.5$. Consequently, an n of 2.4 is listed in Table 3.1 for that particular spectrum. Figure 3.1 displays the actual experimental derivative trace for this

Table 3.2. Values of $M_2/(\Delta x)^2$ calculated from Equation (9) for various values of n

n	$M_2/(\Delta x)^2$
1.5	0.7211
1.6	0.5714
1.7	0.4324
1.8	0.3473
1.9	0.2922
2.0	0.2500
2.1	0.2207
2.2	0.1979
2.3	0.1807
2.4	0.1669
2.5	0.1559
2.6	0.1446
2.7	0.1389
2.8	0.1326
2.9	0.1269
3.0	0.1222
3.5	0.1063
4.0	0.0976

Figure 3.1. Experimental derivative trace of the proton resonance in $\text{YH}_{1.92}$ for which $M_2 = 11.58 \text{ Oe}^2$. Also shown are the derivatives of the Harper-Barnes ($n=2.4$) and Gaussian curves which are fit to the experimental curve

spectrum along with the derivatives of the Harper-Barnes lineshape function for $n = 2.4$ and Gaussian curves ($n = 2.0$). One can see immediately from the figure how much more accurately the Harper-Barnes line shape fits the experimental trace as compared to the Gaussian curve.

After one has determined the n value which gives the best fit to the experimental spectra, one can turn the above method around and determine M_2 from n and Δx , and then compare this value with the M_2 obtained by numerical integration. This allows one to make an additional check upon the experimental second moment. For example, with $n = 2.4$ and $\Delta x = 8.61$ Oe, one obtains an M_2 of 12.36 Oe^2 for the trace shown in Figure 3.1. This compares quite favorably with the experimental M_2 of 11.58 Oe^2 , as the percent difference between the two is only 6.5%. This procedure substitutes an overall goodness-of-fit for the usual difficulty of determining the wings of the resonance line. One then can obtain information which will support the experimentally obtained M_2 .

b. Theory and discussion Let us now turn our attention to the problem of the location of the hydrogen in the fcc yttrium lattice. In order to do this we need to obtain a theoretical expression for M_2 which allows for random occupation of tetrahedral (T) and octahedral (O) sites by the

hydrogen. But before doing this, a few comments should first be made regarding the magnetic dipolar interaction and its relation to the linewidth and the second moment.

The magnetic dipole-dipole interaction is the interaction common to all nuclear spins in a solid. Nuclear dipolar fields, which we shall refer to as H_{loc} , are on the order of a few Oersteds. One can see this by the following rough calculation. The magnetic field produced by neighboring nuclei a distance r apart and having magnetic moment μ is roughly

$$H_{loc} = \frac{\mu}{r^3}.$$

If we assume that $r \approx 2\text{\AA}$ and $\mu \approx 10^{-23}$ erg/Oe (10^{-3} of a Bohr magneton), we find that $H_{loc} \approx 1$ Oe. Since this field may either aid or oppose the static field H_0 , a spread in the resonance condition ($\omega_0 = \gamma H_0$) results, with significant absorption occurring over the range of H_{loc} (~ 1 Oe).

Cotts (1), in his review of M-H systems, points out that the principal source of the resonance linewidth is the magnetic dipole-dipole interaction. Without this interaction, the resonance line would merely be a delta function spike, since then we would have a system of noninteracting spins and energy could be absorbed only at the resonance condition. However, since we have a system of interacting spins, the resonance line is broadened by the dipolar fields

as energy can now be absorbed over a range of values centered on the resonance.

The form of the dipolar interaction between two spins having spin operators $\vec{I}_1$ and $\vec{I}_2$ is

$$\mathcal{H}_{12} = \hbar^2 \gamma_1 \gamma_2 \left[\frac{\vec{I}_1 \cdot \vec{I}_2}{r_{12}^3} - \frac{3(\vec{I}_1 \cdot \vec{r}_{12})(\vec{I}_2 \cdot \vec{r}_{12})}{r_{12}^5} \right] \quad (10)$$

where γ_1 and γ_2 are the gyromagnetic ratios of the nuclei, and $\vec{r}_{12}$ is the displacement from spin 1 to spin 2. For N interacting spins, Slichter writes the form of the dipolar contribution to the Hamiltonian as (13)

$$\mathcal{H}_d = \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \left[\frac{\vec{\mu}_j \cdot \vec{\mu}_k}{r_{jk}^3} - \frac{3(\vec{\mu}_j \cdot \vec{r}_{jk})(\vec{\mu}_k \cdot \vec{r}_{jk})}{r_{jk}^5} \right] \quad (11)$$

where r_{jk} is the distance between spins j and k and $\vec{\mu}_j = \gamma_j \hbar \vec{I}_j$. (With this quantum mechanical substitution we see that Equation (11) is just the generalization of Equation (10) for N spins.)

In a M-H system such as our case, $\mathcal{H}_d$ will contain three basic terms: (1) the interaction between H spins; (2) the interaction between H and M spins; and (3) the interaction between M spins. Letting I denote the H spin system and S the host M spin system Cotts writes the full nuclear Hamiltonian for such a two spin system as

$$\mathcal{H} = -\hbar\gamma_I H_O \sum_j I_z^j - \hbar\gamma_S H_O \sum_k S_z^k + (\mathcal{H}_d^{II} + \mathcal{H}_d^{IS} + \mathcal{H}_d^{SS}) \quad (12)$$

where the first two terms are the Zeeman energies of the respective spin systems, and $\mathcal{H}_d^{II}$, $\mathcal{H}_d^{IS}$, and $\mathcal{H}_d^{SS}$ are (1), (2) and (3) above, respectively. In principle the exact shape of the resonance line is dictated by Equation (12), however due to the complexity of Equation (12) it is not practical to solve it explicitly for its eigenfunctions and eigenvalues. Instead we go to the method of moments, which is a clever technique due to Van Vleck (14) whereby one can compute properties of the resonance line without solving Equation (12) explicitly. We turn now to the calculation of the theoretical second moment for $\beta\text{-YH}_x$.

The general expression for the second moment of a polycrystalline (powder) sample containing two nuclear spin species is (14)

$$M_2 = \frac{3}{5} I(I+1) (\gamma\hbar)^2 \sum_j r_{ij}^{-6} + \frac{4}{15} I'(I'+1) (\gamma'\hbar)^2 \sum_k r_{ik}^{-6} \quad (13)$$

where I and γ are the spin and gyromagnetic ratio of like spins, I' and γ' refer to unlike spins, and r_{ij} is the distance between spins i and j .

Following the procedure developed by SCG (12) for random occupancy of T and O-sites, we define the probability of an O-site being occupied as α and of a T-site β . Since there are two T-sites for each O-site, we find for the

fraction of H-atoms in O and T-sites, f_o and f_t , respectively (hereafter referred to as simply fractional occupancy), the following expressions

$$f_o = \frac{\alpha}{2\beta + \alpha}, \quad f_t = \frac{2\beta}{2\beta + \alpha} \quad (14)$$

The second moment may then be written as

$$M_2 = f_o M_2^o + f_t M_2^t \quad (15)$$

where M_2^o and M_2^t are the H second moments of the O and T-sites respectively. Letting

$$C = \frac{3}{5} I(I+1) (\gamma \hbar)^2 \quad \text{and} \quad C' = \frac{4}{15} I'(I'+1) (\gamma' \hbar)^2 \quad (16)$$

we have

$$M_2^o = C(\alpha \sum_o r_{oo}^{-6} + \beta \sum_t r_{ot}^{-6}) + C' \sum_m r_{om}^{-6} \quad (17)$$

and

$$M_2^t = C(\alpha \sum_o r_{to}^{-6} + \beta \sum_t r_{tt}^{-6}) + C' \sum_m r_{tm}^{-6} \quad (18)$$

where the indices o, t, and m designate octahedral, tetrahedral, and host metal sites, respectively, surrounding the nucleus at the origin of the summation. (For example, $\sum_t r_{ot}^{-6}$ is a sum on all T-sites with an O-site at the origin of the summation, and $\sum_o r_{to}^{-6}$ is a sum on all O-sites with a T-site at the origin.) The above lattice sums have been calculated in terms of the lattice constant a_o , by Gutowsky and McCarvey (15). Using these values and the fact that $C' = 0.001075C$, we obtain finally

$$M_2 = \frac{a_o^{-6}}{2\beta + \alpha} [115.6\alpha^2 + 2643\alpha\beta + 1075.4\beta^2 + 1.42\beta + 0.46\alpha] \quad (19)$$

where a_o is the cube edge of the fcc Y-lattice and whose value is 5.205 Å (16).

For notational convenience, the second moment calculated from Equation (19) will be referred to as M_2^{th} , denoting theoretical second moment, while the experimentally measured second moment will be referred to as M_2^{exp} .

Equation (19) will now permit us to calculate the occupation probabilities and fractional occupancies of the O and T-sites. The procedure is to find the appropriate values of α and β which when inserted into Equation (19) will yield a theoretical second moment which is as near as possible to the experimental second moment. We must remember though that choosing α determines β since they are related by the expression $x = 2\beta + \alpha$, x being the H concentration in the dihydride. For reasons previously discussed, x was given the value of 1.80 for the two samples in the two phase region ($YH_{1.63}$ and $YH_{1.72}$) in calculating M_2^{th} .

In Table 3.3 various values of α ranging from 0 to 0.30 have been used to calculate M_2^{th} . Table 3.4, on the other hand, lists the most likely occupation probabilities and fractional occupancies for each composition. In both tables, the second moments for 1.90, 1.92, and 1.98 have been averaged to give a single M_2^{exp} . It is interesting to note

Table 3.3. Comparison of experimental second moment (M_2^{exp}) with theoretical second moment (M_2^{th}) for various values of α , the occupation probability of an O-site

Global composition x	M_2^{exp} (Oe ²)	M_2^{th} (Oe ²)			
		$\alpha=0, \beta=x/2$	$\alpha=0.10$	$\alpha=0.20$	$\alpha=0.30$
1.63	11.07	8.72	10.04	11.17	-
1.72	10.49	8.72	10.04	11.17	-
1.90	11.82	9.21	10.53	11.67	12.64
1.92	11.53	9.30	10.63	11.77	-
1.98	12.92	9.59	10.92	12.08	13.06

Table 3.4. Values of α , β , f_o , and f_t for each sample based upon comparison of M_2^{th} with M_2^{exp} (f_o and f_t are given in percent)

Global composition x	M_2^{exp} (Oe ²)	M_2^{th} (Oe ²)	α	β	f_o (%)	f_t (%)
1.63	11.07	11.06	0.19	0.805	10.6	89.4
1.72	10.49	10.51	0.14	0.83	7.8	92.2
1.90	11.82	11.88	0.22	0.84	11.6	88.4
1.92	11.53	11.56	0.18	0.87	9.4	90.6
1.98	12.92	12.88	0.28	0.85	14.1	85.9

that all the M_2^{exp} values are larger than M_2^{th} for the case $\alpha=0$, $\beta=\frac{x}{2}$ in Table 3.3. This M_2^{th} assumes that the O-sites are inaccessible and therefore that the hydrogen can reside only in T-sites. The experimental results though, suggest that this is not the case; that some of the O-sites are occupied as we can see from the values of α in Table 3.4. This result differs from another NMR study done in $\beta\text{-YH}_x$ (17) and also from NMR studies done on other M-H systems (12, 18) in which the authors conclude that very few if any O-sites are occupied but that most of the T-sites are occupied in this same composition range. This point will be discussed in more detail further on.

We can obtain a clearer picture of which sites the hydrogen occupies as a function of composition if we analyze our data, as we did before, by averaging M_2^{exp} for the compositions 1.63 and 1.72 and likewise for 1.90 and 1.92. The corresponding occupation probabilities and fractional occupancies are summarized in Table 3.5 where the quantity H/Y refers to the ratio of hydrogen (H) to yttrium (Y). One can see now that as H concentration increases, the probability of H occupation of O-sites also increases. The key point being that even for the compositions $x = 1.80$ and 1.91 , a sizable percentage of the O-sites are occupied, while a nonnegligible percentage of the T-sites are unoccupied. We find that 16% of the O-sites are occupied (we are referring

Table 3.5. Occupation site probabilities (α and β) and fractional occupancies (f_o and f_t given in percent) for the most likely hydrogen concentrations (values were based upon comparison of M_2^{th} with M_2^{exp})

Best estimate (H/Y) x	M_2^{exp} (Oe ²)	M_2^{th} (Oe ²)	α	β	f_o (%)	f_t (%)
1.80 ^a	10.78	10.73	0.16	0.82	8.9	91.1
1.91	11.64	11.62	0.19	0.86	9.9	90.1
1.98	12.92	12.88	0.28	0.85	14.1	85.9

^aAssumed lower limiting composition of the dihydride phase.

to α) for $x = 1.80$, 19% for $x = 1.91$, and 28% for $x = 1.98$, a rather large increase over the previous two values. On the other hand, the percentage of T-sites occupied (referring to β) is 82% for $x = 1.80$, 86% for $x = 1.91$, and 85% for $x = 1.98$.

As was earlier remarked, these results differ from previous NMR studies on β -YH $_x$ and other M-H systems. Stalinski, Zogal, and Drulis (17) in their study of YH $_{1.91}$ and YH $_{2.00}$ concluded from their analysis of the second moment values that hydrogen occupied mainly T-sites. No experimental second moment values were listed in their paper so we were not able to make any comparison between M_2 values. Schreiber and Cotts (18), in their study of the lanthanum-hydrogen system LaH $_x$, suggest that for $x < 1.95$, the T-sites are effectively full with the other 0.05 sites inaccessible due to impurities or lattice defects. Thus, the O-sites are empty for $x < 1.95$, and only begin to fill after $x > 1.95$. SCG (12) find that at most only 1.25% (referring to f_o) of the O-sites are occupied in the titanium-hydrogen system TiH $_x$, in the composition range $1.6 < x < 2.0$. However, our results do agree qualitatively with a very recent (1979) study done by Venturini and Richards (19) using electron spin resonance (ESR) of dilute Er ions in YH $_x$. Their results suggest that 8% (referring to α) of the O-sites are occupied for YH $_{2.00}$, which although substantially

smaller than our value of 28% for $\text{YH}_{1.98}$, does indicate that yttrium dihydride may differ significantly from other dihydrides.

We should mention here briefly that Khodosov and Andrievskii (20) found a rigid lattice second moment of approximately 28 Oe^2 for $\text{YH}_{1.96}$ in their study of zirconium and yttrium hydrides. They also saw a narrow line superimposed on the wide line which the authors attributed to H in the O-sites. We, however, only saw this narrow line for $x \leq 1.72$ and did not see it in any of our spectra for $x \geq 1.90$. We attribute this narrow line to H in the α -phase of YH_x .¹ Their large value of M_2 and the observance of the narrow line is possibly due to the presence of large amounts of impurities (one possibly being Fe) which have distorted their spectra. They did not attempt to determine the location of the hydrogen on the basis of their rigid lattice second moment value.

It would be instructive at this time to take into account the uncertainty in H concentration of the samples, and to ascertain what effect, if any, this has upon our results. We will also shift slightly our assumed value for the lower limiting composition of the dihydride and see if

¹We discuss the α -phase of YH_x in Sections III.A.2, III.A.3, and III.B.2.

this also has any effect. The uncertainty in x , Δx , was taken to be ± 0.04 for $x = 1.91$; ± 0.02 for $x = 1.98$; and ± 0.04 for $x = 1.80$. The results are tabulated in Table 3.6. Inspection of the table indicates that the uncertainty in H concentration does not alter significantly our results for α , β , f_o , and f_t for either $x = 1.91$ or 1.98 . The results for $x = 1.80$ show that even if the phase boundary were at either $x = 1.76$ or 1.84 , a considerable fraction of the O-sites would still be occupied. We conclude, therefore, that the uncertainty in H concentration, and the lower limiting composition of the dihydride, have no significant effect upon our results for O and T-site occupancy.

We conclude that our results and analysis of the experimentally obtained proton second moments of $\beta\text{-YH}_x$ in the composition range $1.80 \leq x \leq 1.98$ suggest that a sizable percentage of the O-sites are occupied by H, and also that a nonnegligible percentage of the T-sites are unoccupied. We also found that as H concentration increases, O-site occupation also increases. Qualitative corroboration of our results has been given by Venturini who estimates on the basis of ESR measurements that 8% of the O-sites are occupied.

We should like to add though, that the effect of the lock-in time constant and magnetic field sweep rate upon the second moment values of YH_x should be investigated further.

Table 3.6. Effect of the uncertainty of H concentration upon occupation site probabilities (α and β) and fractional occupancies (f_o and f_t are given in percent)

Composition x	M_2^{exp} (Oe ²)	M_2^{th} (Oe ²)	α	β	f_o (%)	f_t (%)
(a) Calculation for $\text{YH}_{1.98}$ using $\Delta x = \pm 0.02$						
1.96		12.96	0.30	0.83	15.3	84.7
1.98	12.92	12.88	0.28	0.85	14.1	85.9
2.00		12.88	0.27	0.865	13.5	86.5
(b) Calculation for $\text{YH}_{1.91}$ using $\Delta x = \pm 0.04$						
1.87		11.63	0.21	0.83	11.2	88.8
1.91	11.64	11.62	0.19	0.86	9.9	90.1
1.95		11.60	0.17	0.89	8.7	91.3
(c) Calculation for $\text{YH}_{1.80}$ using $\Delta x = \pm 0.04$						
1.76		10.75	0.18	0.79	10.2	89.8
1.80	10.78	10.73	0.16	0.82	8.9	91.1
1.84		10.79	0.15	0.845	8.2	91.8

Second moment values taken at the same sweep rates but using smaller time constants, suggest that increasing the time constant increases the value of M_2 . Since larger values of M_2 give greater occupation of octahedral sites, we could possibly be overestimating the number of octahedral sites occupied by hydrogen due to inflated M_2 values.

The saturation behavior of the ^1H resonance in YH_x brings up the interesting speculation that other metal hydrides might also exhibit a similar type of behavior. If this is so, and if M_2 values were obtained while saturating the resonance, then M_2^{exp} values reported in the literature could be too small. If M_2^{exp} were actually larger, this would increase the number of octahedral sites occupied by the hydrogen.

2. $\alpha\text{-YH}_x$

a. Experimental results In the composition range $0.20 \leq x \leq 1.72$ our samples of YH_x were a two-phase system composed of both α and β -phases of the hydride. The intensity of the α -line decreased, while the intensity of the β -line increased as the global composition (H/Y) increased from 0.20 to 1.72. This behavior can be seen in Figure 3.2 which shows a series of absorption spectra for various values of x . Note the faint appearance of the β -line in $\text{YH}_{0.20}$.

In order to ascertain the location of the hydrogen in solid solution in yttrium, the experimental rigid lattice proton second moment was determined for the α -line of $\text{YH}_{0.20}$. It was obtained by direct numerical integration of the derivative line trace. And as in the previous section for $\beta\text{-YH}_x$, the spectrum was taken at a temperature low enough to assure that the rigid lattice condition applied, modulation broadening was corrected for, and an extremely low rf

Figure 3.2. Experimental derivative traces of the proton resonance in YH_x in the two-phase composition range $0.20 < x < 1.72$, showing the relative intensities of the β -phase (wide line) and α -phase (narrow line) resonances. The spectra of $\text{YH}_{0.44}$ and $\text{YH}_{0.88}$ were taken at room temperature, while the spectra of $\text{YH}_{0.20}$ and $\text{YH}_{1.72}$ were taken at 160K and 420K, respectively

level (3.45 mOe) was used to prevent saturation narrowing.

Figure 3.3 shows the spectrum from which M_2 was obtained, along with derivatives of Gaussian, Lorentzian, and Harper-Barnes ($n = 1.7$) curves which are fit to the experimental trace. The experimental trace is slightly asymmetric as $n = 1.8$ fits the right hand side better than $n = 1.7$. Comparison of this trace with the trace for $YH_{1.92}$ (Figure 3.1) reveals the Lorentzian character of the α -line of $YH_{0.20}$. It is also interesting to compare Figures 3.2 and 3.3 for the presence of a β -line in the spectra. Although rather weak, the β -line appears rather clearly in Figure 3.2, while there appears to be only a slight suggestion (on the left wing of the resonance line) of a β -line in Figure 3.3. Since it is questionable whether there even is a β -line present in the recording used to obtain M_2 (Figure 3.3), no attempt was made to correct for its possible contribution to the second moment.

The result for the experimental proton second moment of α - $YH_{0.20}$ was 0.69 Oe^2 . The linewidth was measured to be 1.28 Oe and the value of the exponent n of the Harper-Barnes line-shape function which best fit the line was 1.7. On the basis of these parameters, an M_2 value of 0.71 Oe^2 was obtained. A 3 sec TC and sweep rate of 0.022 Oe/sec were used to obtain the spectrum.

Figure 3.3. Experimental derivative spectrum of the α -line proton resonance in YH_{0.20}. An M_2 of 0.69 Oe^2 was obtained from this spectrum. Also shown are the derivatives of Gaussian, Lorentzian, and Harper-Barnes ($n=1.7$) curves which are fit to the experimental trace (note the Lorentzian character of the line)

b. Location of the hydrogen In $\alpha\text{-YH}_x$, yttrium has its normal hcp structure and the hydrogen occupies interstitial T and O-sites which are analogous to the T and O-sites of the CaF_2 structure. For the primitive cell of the hcp Y-lattice the atomic sites are given by $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$. There are two pairs of T-sites at

$$(\frac{2}{3}, \frac{1}{3}, \frac{1}{8}); (\frac{2}{3}, \frac{1}{3}, \frac{3}{8}) \quad \text{pair } T_1$$

and

$$(\frac{1}{3}, \frac{2}{3}, -\frac{1}{8}); (\frac{1}{3}, \frac{2}{3}, -\frac{3}{8}) \quad \text{pair } T_2$$

and one pair of O-sites at

$$(0,0,0); (0,0,\frac{1}{2}).$$

The experimental lattice constants for hcp Y are $a_0 = 3.648 \text{ \AA}$ and $c_0 = 5.732$ which gives a c_0/a_0 ratio of 1.571. Using these lattice parameters, we find that only $1.433 \text{ \AA}$ separates the two sites at T_1 and T_2 . Because of this close spacing, it is highly unlikely that hydrogen would occupy both sites in T_1 or T_2 at the same time. As a simplification, we took the midpoint of both T_1 $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and T_2 $(\frac{1}{3}, \frac{2}{3}, -\frac{1}{4})$ to be the two possible T-sites. Hence, in this case, we have an equal number of T and O-sites (two) per primitive cell.

We proceed now as we did in the previous section for $\beta\text{-YH}_x$ and calculate the theoretical second moment of $\alpha\text{-YH}_x$

which allows for random occupation of the T and O-sites by the hydrogen. In this analysis, though, we will ignore the contribution of the Y-spins to M_2 as it is negligible compared to the contribution of the H-spins. We have then from Equation (13) that the general expression for the second moment of a polycrystalline (powder) sample containing one nuclear spin species is

$$M_2 = \frac{3}{5} I(I+1) (\gamma\hbar)^2 \sum_j r_{ij}^{-6} \quad (20)$$

where I and γ are the spin and gyromagnetic ratio of the H-spins. Since now there are an equal number of T and O-sites, we have that

$$f_o = \frac{\alpha}{\alpha+\beta}, \quad f_t = \frac{\beta}{\alpha+\beta} \quad (21)$$

where α and β have their previous meanings. Using the same definitions of M_2^o and M_2^t as before the second moment may again be written (Equation (15))

$$M_2 = f_o M_2^o + f_t M_2^t$$

where

$$M_2^o = C [\alpha \sum_o r_{oo}^{-6} + \beta \sum_t r_{ot}^{-6}] \quad (22)$$

and

$$M_2^t = C [\alpha \sum_o r_{to}^{-6} + \beta \sum_t r_{tt}^{-6}] \quad (23)$$

where the indices t and o designate octahedral and tetrahedral sites, respectively, surrounding the nucleus at the

origin of the summation. The lattice sums and number of nearest neighbors (n.n.) used in each calculation are:

$$\sum_{\text{o}} r_{\text{oo}}^{-6} = 18.097 a_{\text{o}}^{-6} \quad 48 \text{ n.n.}$$

$$\sum_{\text{t}} r_{\text{tt}}^{-6} = 13.123 a_{\text{o}}^{-6} \quad 14 \text{ n.n.}$$

$$\sum_{\text{t}} r_{\text{ot}}^{-6} = \sum_{\text{o}} r_{\text{to}}^{-6} = 53.613 a_{\text{o}}^{-6} \quad 42 \text{ n.n.}$$

Only 14 n.n. were used to calculate $\sum_{\text{t}} r_{\text{tt}}^{-6}$ as the sum converges very rapidly and this gave the major contribution to the sum. Using these values for the lattice sums and substituting Equations (22) and (23) into Equation (15) we obtain for the second moment

$$M_2 = \frac{C a_{\text{o}}^{-6}}{\alpha + \beta} [18.097 \alpha^2 + 107.23 \alpha \beta + 13.123 \beta^2] \quad (24)$$

Again, we will refer to the second moment calculated from Equation (24) as M_2^{th} , and the experimentally measured second moment (0.69 Oe^2) will be referred to as M_2^{exp} .

Remembering that $x = 0.20 = \alpha + \beta$, we find that $M_2^{\text{th}} = 0.40 \text{ Oe}^2$ assuming exclusive T-site occupation (i.e., $\alpha=0$, $\beta=0.20$) by the hydrogen. For exclusive O-site occupation (i.e., $\beta=0$, $\alpha=0.20$) we find that $M_2^{\text{th}} = 0.55 \text{ Oe}^2$. Both values are less than M_2^{exp} indicating that the hydrogen is distributed between both types of sites. Also, since the values are approximately equal, we will not be able to determine definite

values for α and β (as we did for $\beta\text{-YH}_x$) based upon comparison of M_2^{th} with M_2^{exp} . Instead, we will calculate α and β for two cases: (1) assuming predominantly T-site occupation; and (2) assuming predominantly O-site occupation. Table 3.7 summarizes the results of the calculation where all quantities are given in percent. The results of the calculation suggest that hydrogen occupies mainly the predominant site while only a small fraction of the other site is occupied.

Studies on other M-H systems report differing results for the location of the hydrogen in the solid solution phase of the hydride. Narang et al. (21) studied a solid solution sample of zirconium hydride ($\text{ZrH}_{0.033}$) using neutron diffraction methods. The authors concluded that hydrogen occupies the T-sites in $\alpha\text{-ZrH}_x$. Weaver (22), on the other hand, studying the scandium hydrogen solid solution $\text{ScH}_{0.37}$, using NMR, found from analysis of the second moment that hydrogen resides in both the O and T-sites. However, ScH_x is quite different from YH_x , in that the contribution of the Sc spins to M_2 is quite large.

Our results suggest that the hydrogen in solid solution in hcp yttrium occupies both T and O-sites. However, our analysis is unable to ascertain quantitatively the fractions of occupied sites. Future neutron diffraction work, which is planned on $\text{YH}_{0.20}$, can hopefully reveal the occupation probabilities of hydrogen in $\alpha\text{-YH}_x$.

Table 3.7. Values of α , β , f_o , and f_t for $YH_{0.20}$ assuming either predominantly T or O-site occupation by the hydrogen

M_2^{exp} (Oe ²)	M_2^{th} (Oe ²)	α (%)	β (%)	f_o (%)	f_t (%)
0.69	0.70 ^a	18.5	1.5	92.5	7.5
0.69	0.70 ^b	2.8	17.2	14.0	86.0

^aPredominantly O-site occupation assumed.

^bPredominantly T-site occupation assumed.

3. Determination of phase boundaries

In this section we estimate the locations of the phase boundaries (at room temperature) of the two phase region (this refers to $\alpha\text{-YH}_x + \beta\text{-YH}_x$) from measurements of the NMR intensities of the α and β -lines. We make this estimation since previous studies made on the phase boundaries of the two phase region have usually been carried out at high temperatures and very few data exist for the low and intermediate temperatures where most of the NMR work in this investigation occurred. For example, Lundin and Blackledge (23) determined the phase boundaries of the two phase region in the temperature range 900-1350°C, while Yannopoulos et al. (24) did the same in the temperature range 650-950°C. (The results of both studies are shown in Figure 1.1.) Only Beaudry and Spedding (6) have obtained data at temperatures lower than these as their study covered the temperature range 25-850°C. However, as we can see from Figure 3.4, a large gap occurs in their data between approximately 25 and 250°C. In addition, they did not determine the limiting composition at the high concentration end of the two-phase region. Their result for the room temperature phase boundary at the upper limiting composition of the solid solution phase is $x = \text{H/Y} = 0.23$. (They report AT.% (atomic percent), whereas we use $x = \text{H/Y} = \text{atom ratio}$. To convert from atomic percent to atom ratio, use either $\text{AT.\%} = x/(x+1)$ or $x = \text{AT.\%}/(1-\text{AT.\%})$.)

Figure 3.4. Solubility of H in Y. This figure supplements the phase diagram of Figure 1.1 (reprinted from Reference (6))

To determine the room temperature phase boundaries we proceed as follows. We let A be the upper limiting composition (i.e., atom ratio x) of the solid solution and B the lower limiting composition of the dihydride. Since n_α molecules of YH_A contain $n_\alpha A$ H-atoms, and n_β molecules of YH_B contain $n_\beta B$ H-atoms, the intensity ratio R of the α to the β -line is given by

$$R = \frac{\text{no. of H-atoms in } \alpha\text{-phase}}{\text{no. of H-atoms in } \beta\text{-phase}} = \frac{An_\alpha}{Bn_\beta} . \quad (25)$$

The lever rule for a two-phase region gives for a sample having composition C (i.e., YH_C , where C lies between A and B)

$$(C-A)n_\alpha = (B-C)n_\beta \quad (26)$$

or

$$\frac{B-C}{C-A} = \frac{n_\alpha}{n_\beta} = \frac{B}{A} R . \quad (27)$$

Equation (27) now enables us to obtain A and B. However, since we have two unknowns we must have two compositions so that we will have two equations. Letting C_1 and C_2 be the compositions and R_1 and R_2 the NMR intensity ratios for these compositions, we have

$$\frac{B-C_1}{C_1-A} = \frac{B}{A} R_1; \quad \frac{B-C_2}{C_2-A} = \frac{B}{A} R_2 . \quad (28)$$

Solving the above equations for B and A, we have finally

$$B = \frac{C_1 C_2 (R_2 - R_1)}{R_2 C_2 (1 + R_1) - R_1 C_1 (1 + R_2)} \quad (29)$$

and

$$A = \frac{B R_1 C_1}{B(1 + R_1) - C_1} \quad (30)$$

Table 3.8 lists the values of the intensity ratios found for the various samples. The intensities of the α and β -lines were obtained by integrating twice the derivative line trace.

Table 3.8. Intensity ratio R of the α to the β -line for various compositions in the two phase region

Composition x	Intensity ratio R
0.44	0.3631
0.88	0.0943
1.15	0.1079
1.72	0.0472

Using the first two compositions in the table to find A and B, we have $C_1 = 0.88$ and $C_2 = 0.44$ and $R_1 = 0.0943$ and $R_2 = 0.3631$. Putting these values into Equations (29) and (30) we obtain for the phase boundaries, $A = 0.15$ and $B = 1.69$. All other combinations in Table 3.8 give results that are clearly unphysical, e.g., $B > 3.00$ or $A, B < 0$. This probably results from the fact that it was much more difficult to obtain reliable values of the α -line intensity when this line

was rather weak (as it was in $x = 1.15$ and 1.72).

The value we obtain for B (1.69) appears to be somewhat low as the α -line was detected for $x = 1.72$. The value we obtain for A (0.15) however, compares favorably with Beaudry and Spedding's value of 0.23 . Our value of A could be too small, since there is possibly a relative overabundance of β -YH_x as compared to α -YH_x in our samples. This is due to the fact that β -YH_x is more brittle than α -YH_x, so that when the sample is crushed into a fine powder, particles of α -YH_x will be (on the average) larger than particles of β -YH_x. Since the smaller particles are retained after sifting, and constitute the NMR sample, the net effect would be to enrich the sample in β -YH_x. This, in turn, has the effect of making A too small.

It would be interesting at this point to take into account the uncertainty in the composition of the samples (just for YH_{0.44} and YH_{0.88}) and see how large an effect this has on our results for A and B. An uncertainty of ± 0.02 was assumed for x in both samples. Table 3.9 lists the results. As we can see from the table, small variations in x have a considerable effect upon the value of B. For example, if the composition of YH_{0.88} was in fact YH_{0.90}, we would have $A = 0.14$ and $B = 1.80$, and the presence of an α -line in YH_{1.72} would be expected instead of anomalous. We conclude, therefore, that the uncertainty in the compositions does have a

Table 3.9. Effect of the uncertainty in the hydride compositions upon the room temperature phase boundaries A and B determined from NMR intensity ratios

C_1 ($R_1=0.3631$)	C_2 ($R_2=0.0943$)	A	B
0.42	0.86	0.14	1.72
0.42	0.88	0.13	1.85
0.42	0.90	0.13	1.98
0.44	0.86	0.15	1.58
0.44	0.88	0.15	1.69
0.44	0.90	0.14	1.80
0.46	0.86	0.16	1.47
0.46	0.88	0.15	1.62
0.46	0.90	0.15	1.66

significant effect upon the final results.

The fact that some of the recordings suggest the occurrence of a very weak β -line in $YH_{0.20}$ ¹ probably reflects the uncertainty in the composition of this sample. Beaudry and Spedding's value of A (0.23) would appear to rule out the appearance of a β -phase resonance in a sample having global composition $x = 0.20$. Since some uncertainty in the compositions occurs, especially when the hydrogen content is so small, small discrepancies between the results of the two studies, as

¹Contrast Figures 3.2 and 3.3 of Section III.A.2.

well as within ours, probably result in part from the difficulties inherent in accurately determining the compositions.

B. Diffusion and Line-narrowing

1. $\beta\text{-YH}_x$

The line-narrowing behavior of the proton resonance in $\beta\text{-YH}_x$ was studied for the samples $x = 1.90, 1.92,$ and 1.98 at an operating frequency, ν_{op} , of 16 MHz, and temperature range of 77-460K. Figure 3.5 shows the linewidth as a function of temperature for $\text{YH}_{1.92}$. The other two samples have very similar linewidth data. It can be seen from the figure that the linewidth is essentially constant at low temperatures but begins to narrow around 280K. It continues to narrow up to approximately 460K, at which point we reach the high temperature residual linewidth of 0.30 Oe.

It should be mentioned here that spectra were also taken at an operating frequency of 32 MHz to discover if the linewidth was field dependent and hence if any inhomogeneous broadening was occurring. It was found that there was a slight but very small effect upon the linewidth, indicating that possibly part of the high temperature residual linewidth was due to the bulk paramagnetism of the samples (25). The fact that there was such a slight effect upon the linewidth could be due to the fact that we did not go to sufficiently high field strengths. The remaining portion of the

Figure 3.5. The line-narrowing behavior of the proton resonance in YH_{1.92}

linewidth was due to the magnet inhomogeneity which was measured to be 0.13 Oe by observing the width of the proton resonance in water.

The linewidth of the two phase sample, $\text{YH}_{1.63}$, began to narrow at 490K, the high temperature limit of the equipment, so that complete line-narrowing behavior was not observable. However, based on the onset temperature of motional narrowing (490K), we estimate that $E_a \approx 1.05$ eV in this sample. The activation energy for hydrogen diffusion in $\text{YH}_{1.63}$ has also been determined from spin-lattice relaxation time measurements (26).

To analyze the line narrowing behavior, we employ a formalism developed by Hendrickson and Bray (27) (HB) in their studies of narrowing behavior in alkali-metal glasses. The linewidth ΔH is related to the activation-energy E_a and temperature T by the expression

$$\ln\left(\frac{1}{\Delta H} - \frac{1}{\Delta H_0}\right) = -\frac{E_a}{kT} + \ln\left(\frac{1}{B} - \frac{1}{\Delta H_0}\right) \quad (31)$$

where ΔH_0 is the rigid lattice linewidth and B is an assumed temperature independent linewidth related to the spin-spin relaxation time of the excited species. The magnetic inhomogeneous broadening, which varied for each of the samples, was subtracted from ΔH and ΔH_0 before applying Equation (31). A semilog plot of $(1/\Delta H - 1/\Delta H_0)$ vs. $1/T$ then yields a straight

line whose slope is E_a/k . Such a plot for one of the samples is shown in Figure 3.6. The slope was determined by using a least-squares fit to the data points. The resulting activation energies are listed in Table 3.10.

Table 3.10. Values of the activation energy (E_a) for H diffusion determined from the two methods of analyzing the linewidth-vs.-temperature data (the pulsed NMR values are from Reference (26))

Concentration x	E_a (eV)		
	HB analysis	BPP analysis	Pulsed NMR results
1.63	$\sim 1.05^a$	$\sim 1.05^a$	1.10
1.90	0.54 ± 0.02	0.40 ± 0.02	-
1.92	0.56	0.43	0.438
1.98	0.56	0.42	0.417

^aEstimated from the onset temperature of motional narrowing.

Since the narrowing of the line is likely due to thermally activated self-diffusion, as in other hydrides, the usual Bloembergen-Purcell-Pound (28) (BPP) or Kubo-Tomita (29) analysis may also be employed to obtain an activation energy. In their analysis, the dipolar correlation time τ_c^1 is given in terms of the measured linewidth ΔH

τ_c^1 is the average length of time an atom spends on a given site.

Figure 3.6. Semilogarithmic dependence of the reciprocal of the proton linewidth in YH_x on reciprocal temperature

and rigid lattice linewidth ΔH_0 by

$$\tau_c = \frac{4 \ln 2}{\gamma \pi} \frac{1}{\Delta H} \tan\left[\frac{\pi}{2} \left(\frac{\Delta H}{\Delta H_0}\right)^2\right] \quad (32)$$

where γ is the gyromagnetic ratio of the proton. Once again, the high temperature residual linewidth has been subtracted from both ΔH and ΔH_0 before applying Equation (32). If one assumes that

$$\tau_c = \tau_{oc} \exp(E_a/kT) \quad (33)$$

then E_a values can be determined from a plot of $\log \tau_c$ vs. $1/T$. Such a plot is shown in Figure 3.7. The activation energies determined in this way are also listed in Table 3.10 along with E_a values obtained from spin-lattice relaxation times (26). We note that the value of E_a for $YH_{1.63}$ is considerably larger than E_a values for the other samples.

The values for E_a are very similar to other values found in other studies of β - YH_x . Khodosov and Andrievskii (20) found an E_a of 0.425 eV for $YH_{1.96}$, while Stalinski, Zogal, and Drulis (17) found E_a values of 0.35 and 0.43 eV for $YH_{1.91}$ and $YH_{2.00}$, respectively. They are also very similar to E_a values found for other M-H systems. Schreiber and Cotts (18) found E_a values (in eV) for β - LaH_x of 0.43, 0.41, and 0.46 for $x = 1.96, 2.00$, and 2.03 , respectively. SCG (12) in their study of β - TiH_x found activation energies for their samples in the neighborhood of 0.43 eV. It is interesting to note

Figure 3.7. Semilogarithmic dependence of the correlation time τ_c , as determined from BPP theory, on reciprocal temperature

that Schreiber and Cotts also found an unusually high value for E_a of 1.10 eV for $\text{LaH}_{1.41}$ and $\text{LaH}_{1.92}$. As with our high value for $\text{YH}_{1.63}$ (1.10 eV), this phenomenon is puzzling to most observers, and at present no adequate explanation exists.

One notices from the table the excellent agreement between the BPP results and the T_1 results for E_a . The HB analysis, however, yields values of E_a that are substantially larger than either of these methods. The fact that the BPP results and the T_1 results are so similar though, should not be surprising since the BPP theory is also used to analyze the pulse measurements. On the other hand, the HB (27) analysis of motional-narrowing data is based on the predicated existence of an excited ionic state in which the moving ion exists for an appreciable period of time and in which the NMR linewidth has its fully narrowed value. In this view, line-narrowing represents a gradual transition of all ions from the nonexcited to the excited state with increasing temperature. Activation energies derived by this analysis are typically greater than those based on the BPP analysis.

One must draw the conclusion that the narrowing of the linewidth can only be the result of thermally activated self-diffusion of the hydrogen which averages out the magnetic dipole interaction. As was mentioned previously, the principal source of the resonance linewidth is the magnetic dipole-dipole

interaction between protons. When the hydrogen is in rapid relative motion, the local field, H_{loc} , seen by each proton, will fluctuate very rapidly. But only its average value taken over a time long compared with the duration of a fluctuation will be observed. Since this average is much smaller than the instantaneous value of the local field, the line narrows.

The self-diffusion of hydrogen then, is the result of the hydrogen absorbing sufficient thermal energy to surmount the potential barrier presented by its neighbors and to jump from one interstitial site to another with a jump frequency ν_c . The height of the barrier is just E_a , the activation energy. The jump frequency ν_c is the inverse of the dipolar correlation time τ_c , whence $\nu_c = 1/\tau_c$. Thus we have

$$\nu_c = \nu_{oc} \exp(-E_a/kT) \quad (34)$$

where ν_{oc} is the attempt frequency. The jump frequencies were found to increase with temperature, as expected.

At this point, one might naturally inquire as to the diffusion jump paths of the hydrogen. Although no attempt was made to answer this question in this investigation, other authors have attempted to do so in other M-H systems (30; 31). The method usually employed is based on a simple electrostatic model using screened Coulombic potentials. One calculates the energy associated with both T and O-sites and then uses this information to determine possible diffusion

paths. In the dihydride phase it was generally believed that hydrogen would diffuse from a T-site to an O-site and then back to a T-site, thereby retaining the original configuration. This might then be considered a possible diffusion path in the dihydride phase of YH_x . However, this conclusion is by no means definitive, due to the very simple physical model employed. At this time, there does not appear to be solid evidence to substantiate the above mentioned diffusion path. However, other investigators are presently working on other more sophisticated techniques that hopefully will be able to resolve this question (1).

2. $\alpha\text{-YH}_x$

The line narrowing behavior of hydrogen in the α -phase of $\text{YH}_{0.44}$ was studied at an operating frequency of 16 MHz and temperature range of 160-400K. The α -line of this sample was sufficiently intense that it could be selectively observed, thereby yielding representative spectra for this phase. Figure 3.8 shows a plot of the linewidth-vs.-temperature for the α -line in this sample. The linewidth at room temperature was only 1.38 Oe while the rigid lattice linewidth was 1.54 Oe. Saturation narrowing of the α -line was observed for this sample at temperatures below 240K. Consequently, spectra were taken at extremely low rf levels to avoid this complication.

The activation energy of the α -line was calculated using

Figure 3.8. Temperature dependence of the proton resonance linewidth for the α -line of YH_{0.44}

the same two methods of the previous section. The results were an E_a of 0.49 ± 0.02 eV from the HB analysis and an E_a of 0.42 ± 0.02 eV from the BPP analysis. The BPP value is very similar to the values obtained for E_a for $\beta\text{-YH}_x$. However, the HB value is now much closer to the BPP value than was the case for $\beta\text{-YH}_x$. Both values are fairly close, though, to E_a values obtained in the α -phase of Scandium-Hydrogen by Weaver (22). Weaver found an activation energy of 0.44 eV for $\text{ScH}_{0.37}$ from T_1 measurements, while he obtained an E_a of 0.54 eV from the BPP analysis of the line narrowing behavior.

As was the case for $\beta\text{-YH}_x$, we also conclude that the narrowing of the α -line of $\text{YH}_{0.44}$ is the result of thermally activated self-diffusion of the hydrogen which averages out the magnetic dipole interaction. The amount of energy needed to surmount the potential barrier (of height E_a) presented by its neighbors and jump from one interstitial site to another is approximately the same for $\alpha\text{-YH}_x$ as for $\beta\text{-YH}_x$. Both require approximately 0.42 eV to do this.

C. Saturation Narrowing and Broadening in $\beta\text{-YH}_x$

1. Experimental results

During the course of measuring the linewidth as a function of temperature for $\text{YH}_{1.98}$, it was observed that at a temperature of approximately 190K the line began to narrow with decreasing temperature. It continued to narrow down to a temperature of 124K at which point the decision was made to

ascertain whether or not this was a "saturation" effect. This was accomplished by holding the temperature constant while varying H_1 so as to obtain values of the linewidth ΔH as a function of rf level H_1 . These measurements were made over the temperature range 140-200K. While doing this, though, it became evident that the line did not just narrow, but that in the interval $180K \lesssim T \lesssim 300K$, the line had actually broadened. Thus, we have two distinct and quite different phenomena occurring: for $180K \lesssim T \lesssim 300K$, the line broadens; while for $T \lesssim 180K$, the line narrows. The rf level, then, had to be such that it would prevent the linewidth from broadening above 180K while also preventing its narrowing below this temperature. Based on the extensive linewidth data obtained in this temperature region, it was decided to use the smallest possible rf fields that would still allow spectra to be taken in a reasonable period of time. For $T \lesssim 300K$, H_1 was chosen to be either 2.2 or 3.5 mOe, while for $T \gtrsim 300K$, H_1 could be as high as 9.5 mOe without causing saturation effects (H_1 could be larger for $T \gtrsim 300K$ because of the rapid diffusion of the hydrogen). We should mention here that H_1 was measured by the voltage induced in a single-turn coil placed in the sample chamber of the probe. The rf output meter is calibrated in μA (microamperes) so Appendix B lists the conversion of H_1 from μA to mOe for the Varian Model V4320B probe used in this investigation.

Figure 3.9 shows a plot of ΔH vs. T for $H_1 = 9.44$ mOe, the rf level used when narrowing was first discovered, and $H_1 = 2.18$ mOe, the rf level used to prevent saturation narrowing and broadening for $YH_{1.98}$. One can see very clearly how ΔH broadens above 180K while narrowing below this temperature. For temperatures above 300K, where motional narrowing occurs, there was no significant difference in ΔH obtained with these two values of H_1 .

To investigate this phenomenon further, data on the linewidth as a function of rf level were obtained at temperatures where saturation narrowing (160K) and broadening (200K) occurred. Figures 3.10 and 3.11 show plots of ΔH vs. H_1 at these two temperatures for $YH_{1.92}$ and $YH_{1.98}$, respectively. The arrows in Figure 3.10 mark the value of H_1 , at each temperature, for which the saturation factor at the center of resonance (to be explained shortly) is unity. One can see from the figures that at the saturation narrowing temperature the linewidths of both samples exhibit the same type of behavior. As H_1 increases, the line narrows to some minimum value, after which it broadens. However, at the saturation broadening temperature, the lines for each sample exhibit quite different behavior. For $YH_{1.92}$, as H_1 increases, the line broadens, but only by a very small amount ($\sim 8\%$); then it narrows to a value less than that of the unsaturated line. While for $YH_{1.98}$, as H_1 increases, the line also broadens, but

Figure 3.9. Dependence of the linewidth on temperature and rf field amplitude H_1 . For $H_1 = 9.44 \text{ mOe}$, saturation narrowing occurs when $T \lesssim 180\text{K}$, while saturation broadening occurs above this temperature. The rf field, $H_1 = 2.18 \text{ mOe}$, was small enough to prevent these saturation effects

Figure 3.10. Saturation behavior of the proton resonance linewidth in YH_{1.92} at 160K and 200K. Saturation broadening occurs at 200K whereas saturation narrowing occurs at 160K. The arrows mark the value of H_1 , at each temperature, for which the saturation factor at the center of resonance (Equation (36)) is unity

Figure 3.11. Saturation behavior of the proton resonance linewidth in YH_{1.98} at 160K and 200K. Saturation broadening occurs at 200K whereas saturation narrowing occurs at 160K

now to a greater extent ($\sim 26\%$); then it narrows, but now the narrowing is not as marked as it was for the other sample. The linewidth of ^7Li as reported by Holcomb (32) exhibits qualitatively this same type of behavior. We will comment upon this curious behavior in the discussion of the experimental results.

As mentioned previously, the arrows in Figure 3.10 denote the value of H_1 for which the saturation factor, at the resonance center is unity. The saturation factor or parameter is given by

$$S(\Delta) = \gamma^2 H_1^2 \pi g(\Delta) T_1 \quad (35)$$

where $\Delta = \omega_0 - \omega$. Its value at the resonance center is

$$S(0) = \gamma^2 H_1^2 \pi g(0) T_1 = 1 \quad (36)$$

when $u_1(0)$, the dispersion mode lock-in signal, as calculated by Goldman (33, 34) using Provotorov's saturation theory (35), passes through its maximum value.¹ The saturation factor indicates the degree of saturation: $S(\Delta) \ll 1$ indicates negligible saturation, whereas $S(\Delta) \gg 1$ indicates considerable saturation. Another important quantity

¹Values for $u_1(0)$ as a function of H_1 were only taken for $\text{YH}_{1.92}$ and are reported in Section III.D.¹ See this section for further details on $u_1(\Delta)$ as calculated by Goldman. The values of H_1 where $S(0) = 1$ are based upon this assumption.

is $\Delta H_{\text{sat}}/\Delta H_{\text{unsat}}$, the ratio of the saturated to the unsaturated linewidth. It is referred to as either the narrowing or broadening ratio. Table 3.11 summarizes the absorption narrowing and broadening data for both samples for selected values of H_1 . The quantity H_{Lr} , referred to in the table, is the value of the local field in the rotating frame. Its value is $(M_2/3)^{1/2}$, where M_2 is calculated from the unsaturated line.

It is interesting to note that the shapes of the resonance lines change as they become progressively narrowed. We can see this from Figure 3.12 which shows absorption mode lock-in spectra for $\text{YH}_{1.92}$ obtained at various H_1 levels. The spectra at $H_1 = 3.45$ mOe (unsaturated line) and 44.5 mOe (saturated line) also show Gaussian, Lorentzian, and Harper-Barnes shape function curves. M_2 values of 11.58 Oe^2 and 13.75 Oe^2 were obtained respectively for these spectra. The first impression one obtains from this series is that, of course, the lines are narrowing, but also that they are becoming increasingly Lorentzian in shape. Comparison of the spectra at $H_1 = 3.45$ and 44.5 mOe makes this very evident along with the fact that M_2 has increased. We also note that the spectrum at $H_1 = 3.45$ mOe is only negligibly saturated since the saturation parameter at the center of resonance $S(0)$ is 0.20, while the spectrum at $H_1 = 44.5$ mOe is considerably saturated as $S(0) = 34.1$. The spectrum at $H_1 = 89.8$ mOe,

Table 3.1. Summary of saturation narrowing and broadening linewidth data for selected values of H_1

Sample and temperature	H_{Lr} (Oe)	H_1 (mOe)	ΔH (Oe)	$\frac{\Delta H_{sat}}{\Delta H_{unsat}}$	$S(0)^a$
YH _{1.92} T = 160K	1.96	3.45	8.67	1.00	0.20
		7.62	-	-	1.00
		9.44	7.35	0.85	1.53
		17.4	5.89	0.68	5.21
		36.3	5.13	0.59	22.7
		44.5	5.17	0.60	34.1
		89.8	6.08	0.70	139.0
YH _{1.92} T = 200K	1.96	3.45	8.95	1.00	0.09
		11.3	-	-	1.00
		17.4	9.49	1.06	2.37
		36.3	9.70	1.08	10.3
		72.6	8.43	0.94	41.3
		134.3	7.42	0.83	141.0
YH _{1.98} T = 160K	2.08	2.18	8.79	1.00	-
		9.44	7.80	0.89	-
		17.4	6.48	0.74	-
		36.3	6.03	0.69	-
		44.5	5.70	0.65	-
		72.6	6.01	0.68	-
YH _{1.98} T = 200K	2.08	2.18	8.82	1.00	-
		9.44	9.48	1.07	-
		36.3	11.11	1.26	-
		72.6	10.94	1.24	-
		89.8	10.43	1.18	-

^aThe value of H_1 where $S(0) = 1$ is based upon the Goldman-Provotorov theory. The other $S(0)$ values were based upon this H_1 value using $S(0) = \pi g(0) \gamma^2 H_1^2 T_1 = (H_1/H_1^*)^2$ where H_1^* is the H_1 for which $S(0) = 1$.

Figure 3.12. Absorption mode derivative lock-in spectra of $\text{YH}_{1.92}$ obtained at various rf levels, H_1 , given in mOe. Harper-Barnes, Lorentzian, and Gaussian curves are included in the spectra at $H_1=3.45$ mOe and 44.5 mOe. The spectra show the change in shape that the resonance line undergoes as it becomes progressively saturated

with $S(0) = 139$, shows the eventual broadening that occurs when $H_1 \gtrsim 36.3$ mOe, i.e., when $S(0) \gtrsim 22.7$. This is indeed a region of very high saturation, and it is interesting that in this region, the lines begin to broaden rather than continuing to narrow.

2. Theory and discussion

Saturation narrowing in a solid was first reported by Abell and Knight (36) in 1954 in their study of metallic copper. This contradicted the early NMR saturation theory of BPP (28) which predicted that the resonance should broaden as the intensity of the rf field was increased. One year after Abell and Knight's discovery, Redfield (37) verified their results on copper and also found saturation narrowing in aluminum. He then developed his own theory of saturation in solids which however is only applicable at rf field intensities that are well above the saturation level. Since then, saturation narrowing has been reported by Solomon and Ezzraty (38) in 1962, by Gaines et al. (39) in 1965, and by other investigators (32, 40-43).

Saturation broadening, on the other hand, seems not to have aroused as much interest among investigators as has saturation narrowing. There appears to be far fewer references to it in the literature than to saturation narrowing. It has been reported, though, by such researchers as Haupt and Van Steenwinkel (44) in solid benzene, by Holcomb

(32) in metallic lithium at 215K as previously mentioned, and by Alexander et al. (45) in crystalline carboranes.

In order to better understand saturation narrowing and broadening and especially how it can occur for the same material but at different temperatures, we would first briefly review the older saturation theories of BPP (28) and Redfield (37) and show how they are deficient in explaining this phenomenon. Then we discuss Provotorov's (35) saturation theory, a theory we think does the most adequate job of explaining our experimental results. Finally we use Goldman's result (33, 34), based upon Provotorov's theory, for the lock-in absorption mode signal to obtain theoretical line-width curves and a parameter which predicts whether the line-width will narrow or broaden upon saturation. The following discussion will be sketched along the lines of Janzen (40) and Alexander et al. (45).

Bloembergen, Purcell, and Pound (28) proposed the first NMR saturation theory applicable to solids. They used first-order perturbation theory for a system of spins $\vec{I}$ placed in a strong constant magnetic field $\vec{H}$ and subjected to a rf field of amplitude H_1 perpendicular to $\vec{H}$ and rotating with an angular frequency ω close to the Larmor frequency $\omega_0 = \gamma H_0$. They assumed that thermal processes (spin-lattice relaxation) would relax the spins to their equilibrium state with a time constant T_1 ; that the spins interact strongly with one another

so that any energy absorbed from the rf field at one point in the lattice is quickly transferred to all the spins; and that the complex rf magnetic susceptibility $\chi = \chi' - i\chi''$ is proportional to the population difference of the spin levels (energy levels) and is in no other way affected by the rf field. These assumptions result in an absorption component of the complex susceptibility of the form (46)

$$\chi'' = \frac{\gamma M_0 T_2 / 2}{1 + \Delta^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (37)$$

where T_2 is the spin-spin relaxation time, $\Delta = \omega_0 - \omega$, $M_0 = \chi_0 H_0$ is the equilibrium magnetization, and χ_0 is the static magnetic susceptibility. But since the line-shape function $g(\Delta)$ is related to T_2 by

$$\pi g(\Delta) = \frac{T_2}{1 + \Delta^2 T_2^2} \quad (38)$$

we can express Equation (37) as

$$\chi'' = \frac{\gamma M_0 \pi g(\Delta) / 2}{1 + \gamma^2 H_1^2 \pi g(\Delta) T_1} \quad (39)$$

where we note that the denominator of χ'' is just $[1 + S(\Delta)]$. We shall now discuss whether these equations - (37) and (39) - provide a correct description of our experimental results.

In the region of weak saturation, i.e., when the saturation factor $S(\Delta)$ is much less than 1, they do provide a correct description of experimental results.

However, when the saturation is strong, i.e., $S(\Delta) \gg 1$, they indicate that the absorption line should broaden, which is just the opposite of what occurs in the low temperature saturation narrowing region. The linewidth decreases in the region of strong saturation, and the lineshape becomes increasingly Lorentzian. In the line-broadening temperature region, there is no way that the BPP equation (Equation (39)) can explain the eventual narrowing of the line at very high saturation levels. Thus the BPP theory of saturation is deficient in explaining our experimental results and is incapable even of predicting any narrowing of the line as H_1 increases.

In order to explain the narrowing behavior observed in aluminum and copper, Redfield (37) developed a saturation theory applicable only to solids at rf fields well above the saturation level. He characterizes the spin system by a Hamiltonian in a coordinate system rotating about $\vec{H}$ with the frequency of the rf field. He made the following assumptions: (1) the time-dependent part of the rotating frame Hamiltonian is small compared to the time-independent part and can be ignored; (2) the spin system is in its most probable macrostate; and (3) the spin-lattice interaction is small compared to that with the rf field so that each spin is relaxed independently to its thermal equilibrium state by the lattice with a time constant T_1 . With these assumptions,

Redfield calculated the absorption component to be

$$\chi'' = \frac{M_O/2\gamma H_1^2 T_1}{1 + \Delta^2/\gamma^2 [H_1^2 + 2H_{Lr}^2]} \quad (40)$$

where H_{Lr} is the local field in the rotating frame.

To see if Redfield's theory predicts saturation narrowing and broadening, we assume the unsaturated absorption line to be a Gaussian curve¹ given by

$$g(h) = C \exp(-h^2/6H_{Lr}^2) \quad (41)$$

where h is the distance from exact resonance in Oersteds.

The linewidth for a Gaussian curve is

$$\Delta H_g = 2\sqrt{M_2} = 2\sqrt{3} H_{Lr}, \quad (42)$$

while the linewidth in Oe for Redfield's curve is

$$\Delta H_r = (2/\sqrt{3}) (H_1^2 + 2H_{Lr}^2)^{1/2}, \quad (43)$$

and the ratio of the two is

$$\Delta H_r/\Delta H_g = (H_1^2 + 2H_{Lr}^2)^{1/2}/3H_{Lr}. \quad (44)$$

Since the line will narrow if $\Delta H_r/\Delta H_g < 1$ and broaden if $\Delta H_r/\Delta H_g > 1$, we find that the linewidth will narrow for $H_1 < \sqrt{7}H_{Lr}$, but conversely should also broaden for $H_1 > \sqrt{7}H_{Lr}$.

¹Although we know that the unsaturated absorption lines are not exactly Gaussian, we will see that this makes very little difference in the following analysis.

Since H_{Lr} for $YH_{1.92}$ at both 160 and 200K is 1.96 Oe (M_2 is the same at both temperatures as we are in the rigid lattice region), we have as the condition for narrowing that $H_1 < 5.19$ Oe, and for broadening that $H_1 > 5.19$ Oe (at either temperature). However, both broadening and narrowing take place for $H_1 < 5.19$ Oe, so although Redfield's theory correctly predicts the narrowing, it does not predict the broadening, and has no possible explanation for the eventual narrowing of the broadened line. In fact for the rf region which brings on saturation for our samples, $\Delta H_r / \Delta H_g$ is always less than 1, indicating that only narrowing can take place. We can see this since $H_1^2 \ll 2H_{Lr}^2$ so that $\Delta H_r = 2\sqrt{2/3} H_{Lr}$ and hence $\Delta H_r / \Delta H_g = \sqrt{2/3} = 0.47$. Thus, we see that both saturation narrowing and broadening occur at rf levels considerably less than $\sqrt{7}H_{Lr}$, as $\sqrt{7}H_{Lr}$ (5.19 Oe) is a tremendous magnetic field compared to the rf fields which caused saturation (~ 0.04 Oe). However, this fact does not mean we can not use Redfield's theory in this rf region since all his theory requires is that we be well above the saturation level. And as we know from the data in Table 3.11, we indeed are well above the saturation level ($S(0) \gg 1$) for many of the rf fields that caused saturation narrowing and broadening. We conclude, therefore, that Redfield's saturation theory is also unable to adequately explain the experimental results.

As a brief remark, we should mention that had we used our actual experimental curve for the unsaturated line instead of the Gaussian function, then we would have found that $\Delta H_r / \Delta H_{\text{unsat}}$ was always less than unity as $\Delta H_r / \Delta H_{\text{unsat}}$ ranged from 0.36 to 0.39. Thus, our use of the Gaussian curve to approximate the unsaturated line did not make any difference in the interpretation of Redfield's theory.

Following the lead of Redfield's rotating frame transformation, Provotorov (35) made a major contribution to the NMR theory of saturation in solids by developing a theory which covers the weak and intermediate saturation region provided that $H_1 \ll H_{Lr}$ and $1/T_1 \ll \gamma H_{Lr}$. The latter two conditions are usually true for protons in most solids due to their long relaxation times.

Provotorov considered a spin system in a solid placed in a strong constant magnetic field to be in effect two distinct systems: a "Zeeman" system and a "dipole-dipole" system, the systems are coupled only rather weakly to each other, but are coupled rather strongly to the lattice. Consequently, each system can be characterized by a distinct energy and effective temperature. The effect of the rf field is to cause the two systems to become more strongly coupled. In Redfield's case, the mixing rate is rapid ($\sim \gamma H_{Lr}$) and a single spin temperature very quickly results. In Provotorov's case,

the mixing rate is relatively slow so that one may still ascribe separate temperatures and energies to both systems. The rates at which the dipolar and Zeeman spin temperatures relax toward the lattice temperature are designated $1/T_D$ and $1/T_1$, respectively. Figure 3.13 shows a schematic representation of the spin system as considered by Provotorov.

Provotorov's result for the absorption component is

$$\chi'' = \frac{\gamma M_O \pi g(\Delta)/2}{1 + W(\Delta) T_1 (1 + \Delta^2 T_D / T_1 D^2)} \quad (45)$$

where $D = \gamma H_{Lr}$ and $W(\Delta) = \gamma^2 H_1^2 \pi g(\Delta) = \gamma^2 H_1^2 T_2 / (1 + \Delta^2 T_2^2)$ is the mixing rate between the dipolar and Zeeman systems. It is interesting to note that for $\Delta=0$ and strong saturation ($S(0) = W(0) T_1 \gg 1$), the Provotorov, Redfield, and BPP equations for χ'' all agree. The reason for the difference when $\Delta \neq 0$ (i.e., off-resonance) is that Provotorov includes effects arising from the absorption of rf energy in the Zeeman system when $\Delta \neq 0$ while BPP and Redfield do not. Provotorov argued that since the difference in energy levels in the Zeeman system is $h\omega_O$, when one photon of rf energy $h\omega$ is absorbed (ω close to ω_O) by the Zeeman system, the balance of energy $h\Delta$ goes into the dipolar system. This latter system will then exchange energy with the lattice and relax back to the lattice temperature with a time constant T_D .

In the region of strong saturation, Provotorov's result for χ'' is

Figure 3.13. Block diagram of the spin system considered by Provotorov showing the energy reservoirs and couplings between them (adopted from Gaines et al. (39))

$$\chi'' = \frac{M_0/2\gamma H_1^2 T_1}{1 + \Delta^2 T_D/T_1 D^2} \quad (46)$$

which agrees with Redfield's result (Equation (40)) provided that $H_1^2 \ll 2H_{Lr}^2$ and $\delta = T_1/T_D = 2$, the value of δ that Redfield originally predicted. However, δ does not always have this value, as has been reported by Alexander et al. (45) and also by Haupt and Von Steenwinkel (44), so that assigning it this value may be ill-advised.

We will not discuss Equation (46) any further since it is more appropriate now to consider the work of Alexander et al. (45) who use the actual lock-in absorption mode signal, as calculated by Goldman (33, 34) using Provotorov's theory (35), to find the conditions which cause saturation narrowing and broadening.

Goldman, using the Provotorov theory of saturation, has analyzed the signals observed in a cw experiment which employs lock-in detection.¹ He considers a modulation field parallel to the main field $\vec{H}$, of amplitude H_m and angular frequency Ω . To prevent modulation saturation and to insure the validity of the Provotorov theory, the following conditions are imposed upon the modulation: (1) The modulation amplitude is much less than the linewidth. (2) The modulation frequency is much less than the linewidth expressed in angular frequency

¹Lock-in detection was used to obtain all of the spectra of this study. See Section II.B.2 on NMR equipment.

units. (3) $\Omega T_1, \Omega T_D \gg 1$; i.e., the modulation period is much shorter than either the Zeeman or dipolar relaxation times. (4) $W(0) \ll \Omega$: the mixing rate between the Zeeman and dipolar systems is much less than the modulation frequency. All the above conditions were met in this experiment since $\Omega/2\pi = 80$ Hz.

Goldman's result for the lock-in absorption mode signal, $v_1(\Delta)$, is (33, 34)

$$v_1(\Delta) = \frac{K[dg/d\Delta - \pi\omega_1^2 g^2(\Delta) T_D(\Delta/D^2)]}{1 + \pi\omega_1^2 g(\Delta) [T_1 + T_D(\Delta^2/D^2)]} \quad (47)$$

where $\omega_1 = \gamma H_1$ is the angular frequency of spin precession in the rf field, and K is a factor involving the amplitude of the modulation, the equilibrium magnetization and ω_1 .

Using Equation (47) and assuming a Gaussian curve for the unsaturated line, Alexander, et al. (45) obtained an equation for the linewidth by simply finding the Δ which satisfies $dv_1/d\Delta = 0$. Their result (Equation (3) of Reference (45)) is

$$\begin{aligned} (x^2 - 3) + (\pi\omega_1^2 g) (9T_D x^2 - 9T_D - 3T_1) \\ + (\pi\omega_1^2 g)^2 (3T_1 T_D x^2 + 3T_D^2 x^4 - 9T_1 T_D + 9T_D^2 x^2) = 0 \end{aligned} \quad (48)$$

where $x = \Delta/D$. Noting that $x^2 = 3$ for the unsaturated line (assumed Gaussian), they expressed deviations y from the unsaturated width by defining $y \equiv x^2 - 3$. Substituting this expression into Equation (48) and requiring $y > 0$ (line

broadening), they concluded that a necessary condition for saturation broadening of a Gaussian line is $\delta = T_1/T_D > 6$. Conversely however, this implies that the line should narrow if $\delta < 6$. Thus, we have a parameter δ , which will allow us to predict, from two experimental quantities, T_1 and T_D , whether a line will narrow or broaden upon saturation.

Alexander et al. have used Equation (48) to calculate theoretical linewidths as a function of H_1 for various values of δ , where δ is treated as a parameter. They based their calculations upon Holcomb's data (32) for the ^{19}F resonance in CaF_2 with the main magnetic field oriented parallel to the [110] direction in the single crystal sample. They used $T_1 = 50$ sec and an unsaturated peak-to-peak linewidth of 6.50 Oe. Figure 3.14 reproduces their figure (Figure 1 of Reference (45)) and shows the calculated relative linewidth, that is, the lock-in linewidth (obtained by solving Equation (48)) divided by the unsaturated linewidth (6.50 Oe), plotted as a function of H_1 . The arrow in Figure 3.14 denotes the value of H_1 where the saturation factor at the center of resonance, $S(0)$, equals 1. Alexander et al. have also used Equation (48) to calculate theoretical linewidth curves for the ^7Li resonance in lithium metal based upon the experimental values of δ at 77 and 215K, where saturation narrowing and broadening occur, respectively. Once again, they obtain their experimental data from Holcomb (32). Figure 3.15 is a reproduction

Figure 3.14. Theoretical saturation behavior of the relative peak-to-peak lock-in absorption node linewidth. The arrow denotes the value of H_1 where $S(0)=1$. Values of $\delta=T_1/T_D$ used in Equation (48) to calculate the curves appear with each of the curves. The values of other parameters used in the calculation are given in the text (after Alexander et al. (45))

Figure 3.15. Saturation behavior of the absorption mode lock-in linewidth in lithium metal at 77K and 215K. The circles are the experimental data of Holcomb (32), while the lines are theoretical linewidth curves calculated by Alexander et al. (45) based upon experimental data. The arrows mark the values of H_1 , at each temperature, where $S(0)=1$

of their figure (Figure 3 in Reference (45)) and shows the theoretical and experimental variation of the linewidth with rf level at 215K where $\delta = 30$, and 77K where $\delta = 2$. The arrows show where $S(0) = 1$.

Figure 3.14 illustrates rather nicely that the Provotorov theory, with different values of δ , can generate either saturation narrowed or broadened lines, and that the broadened lines eventually narrow, as do ours, in the region of high saturation. As mentioned previously, Figure 3.15 shows the similarity between the linewidth data for lithium and our own. Saturation broadening occurs at the higher temperature, while saturation narrowing occurs at the lower temperature. When saturation narrowing occurs, the linewidth also begins to increase slightly at larger H_1 , as do ours. However, the lithium data are taken in the low and moderate saturation region (as the maximum of $S(0)$ is ~ 1) whereas our linewidth data extend into the high saturation region ($S(0) \gg 1$). The saturation broadened linewidth for lithium does not eventually decrease either, but this is probably due to the fact that H_1 never reaches the region of very high saturation, which seems necessary to bring on the eventual narrowing. Nonetheless, we note that the theoretical curve does accurately describe the broadening at 215K, and does qualitatively reproduce features of the narrowing behavior at 77K, although

it does not seem to fit the experimental points all that well. In the case of our results, the eventual increase in ΔH following the initial narrowing behavior of the linewidth at the low temperature does not appear to be reproduced by the theoretical curves in Figure 3.14 either. The inability of the theoretical saturation narrowing curves to reproduce this feature could be due to the fact that Alexander et al. assumed that the shapes of the lines, both saturated and unsaturated, always remained Gaussian. We know that the unsaturated line is not Gaussian¹ and also that the shape of the line changes as saturation narrowing progresses, becoming more Lorentzian and hence less Gaussian. Not taking this into consideration may be the source of the discrepancy.² However, this would be a very difficult problem to resolve, as the shape of the line must be changed at each stage of saturation and also at each temperature. Because of the complexity of such a task and because we would not learn that much about yttrium hydride by accomplishing it, we decided not to pursue this course of investigation any further for our samples.

¹We know this is true for our samples (see Figure 3.1), and Alexander et al. point out that the lithium line at 77K is not Gaussian.

²Another possibility for the ^7Li data is that Holcomb's values of H_1 could be in error by as much as 50% due to the problem of using metallic particles whose dimensions are on the order of the skin depth.

What we can say, however, based upon our results and assuming the validity of the Provotorov theory, is that the value of δ changes between 160 and 200K. It changes from a value less than a certain critical number (160K), to a value greater than this critical number (200K). This means that T_D must be decreasing in magnitude rather rapidly as the temperature increases from 160 to 200K, since T_1 is basically constant over this temperature range. We therefore have T_D at 160K greater than T_D at 200K. Since T_D is indicative of very slow motion of the spins (47, 48), we see that the hydrogen moves at different rates at these two temperatures. Even though we are in the rigid lattice region, slow motion of the hydrogen still occurs, sufficient to affect the values of T_D .

D. Measurement of T_1 and Test of Provotorov Theory

1. Theory

In the previous section, we made use of Goldman's calculation of the absorption mode lock-in signal $v_1(\Delta)$, based on Provotorov's theory. In this section we make use of Goldman's calculation of the dispersion mode lock-in signal $u_1(\Delta)$, again using Provotorov's theory, to measure T_1 by a progressive saturation experiment and thereby test Provotorov's theory by comparing our results for T_1 with the pulsed NMR results (26).

We also discuss briefly the different saturation behavior of the absorption and dispersion mode lock-in signals. The following discussion will again be sketched along the lines of Janzen (40).

Goldman's result for the dispersion mode lock-in signal can be written (33)

$$u_1(\Delta) = \frac{\pi\gamma^2 H_m H_1 M_O [dg'/d\Delta - \Delta g'(\Delta)W(\Delta)T_D/D^2]}{1+W(\Delta)T_1(1+T_D\Delta^2/T_1D^2)} \quad (49)$$

where $g'(\Delta)$ is the dispersion mode shape function related to $g(\Delta)$ by the Kramers-Kranig transformation. At the center of resonance $\Delta=0$ and $g'(\Delta)=0$ so that Equation (49) becomes

$$u_1(0) = \frac{\pi\gamma^2 H_m H_1 M_O}{1+\gamma^2 H_1^2 \pi g(0) T_1} \left[\frac{dg'}{d\Delta} \right]_{\Delta=0} \quad (50)$$

For negligible saturation, i.e., $S(0) \ll 1$, we have

$$\frac{u_1(0)}{H_1} = \pi\gamma^2 H_m M_O \left[\frac{dg'}{d\Delta} \right]_{\Delta=0} = U_O \quad (51)$$

where we let this value of $u_1(0)/H_1$ be called U_O . Using Equations (50) and (51), we now have three methods available to find T_1 . (1) Since $u_1(0)$ passes through a maximum when $S(0)=1$ (this can be seen by solving $du_1(0)/dH = 0$), we have

$$T_1 = [\gamma^2 H_1^2 \pi g(0)]^{-1} \quad (52)$$

(2) Making use of Equation (51), $u_1(0)/H_1$ can be expressed in general as

$$\frac{u_1(0)}{H_1} = \frac{U_0}{1 + \gamma^2 H_1^2 \pi g(0) T_1} \quad (53)$$

When $S(0)=1$, $u_1(0)/H_1 = U_0/2$. Therefore, the value of H_1 at which $u_1(0)/H_1 = U_0/2$ also satisfies $S(0)=1$ and T_1 can be determined from Equation (52) using this value of H_1 . (3)
The quantity $H_1/u_1(0)$ can be written as

$$\frac{H_1}{u_1(0)} = \frac{1 + \gamma^2 H_1^2 \pi g(0) T_1}{U_0} \quad (54)$$

A plot of $H_1/u_1(0)$ vs. H_1^2 should be straight line of slope $\gamma^2 \pi g(0) T_1 / U_0$ and ordinate intercept $1/U_0$, so that $T_1 = (\text{slope}) U_0 / \gamma^2 \pi g(0)$. (In this method, we find U_0 from the ordinate intercept of $H_1/u_1(0)$ vs. H_1^2 .)

The value of $g(0)$ was obtained by using the Harper-Barnes lineshape function to analyze the unsaturated absorption mode lock-in signal. An average value of 3.93×10^{-6} sec was obtained from two unsaturated spectra of $\text{YH}_{1.92}$. The details of the calculation are given in Appendix C.

2. Experimental results and discussion

Lock-in dispersion mode proton spectra were obtained on $\text{YH}_{1.92}$ at 160 and 200K at various rf levels using 200 Hz modulation. The conditions mentioned in the previous section

to prevent modulation saturation and to ensure the validity of the Provotorov equations were once again well-satisfied in the rf region studied using this modulation frequency.

Figure 3.16 shows a plot of $u_1(0)$ vs. H_1 at 160K, while Figures 3.17 and 3.18 show the peak-to-peak absorption signals $v_1(\text{max})$ along with plots of $u_1(0)$ vs. H_1 at 160 and 200K, respectively. (Numerical values of the plots of $u_1(0)$ vs. H_1 at 200 and 160K are given in Tables 3.12 and 3.13, respectively.) One is immediately struck by the very different saturation behavior of the two signals. The absorption signals are of much greater magnitude than the dispersion signals and also reach their maximum values at much larger H_1 . In fact, $v_1(\text{max})$ has still not reached a maximum at either temperature although both cases seem to be just approaching this condition at the highest rf level. This type of behavior should come as no surprise, however, as Goldman (p. 111 of Reference (34)) has predicted that the absorption mode lock-in signal should reach a maximum when $W(0) \sim \Omega$. Since $\Omega \sim 500 \text{ sec}^{-1}$ (as $f_m = 80 \text{ Hz}$ for the absorption lock-in data) and $W(0) \sim 84 \text{ sec}^{-1}$ (at 160K) at the highest rf level, we see that $W(0)$ is still not comparable to Ω and that $v_1(\text{max})$ should not yet reach its maximum value. (The same is true at 200K). For another

¹We calculate $W(0)$ from $W(0) = S(0)/T_1$.

Figure 3.16. Amplitude of the dispersion mode lock-in signal $u_1(0)$ as a function of rf level in YH_{1.92} at 160K

Figure 3.17. Saturation behavior of the lock-in signals in YH_{1.92} at 160K. Although the amplitudes are in arbitrary units, the relative amplitudes between the dispersion $u_1(0)$ and peak-to-peak absorption $v_1(\text{max})$ are to scale

Figure 3.18. Saturation behavior of the lock-in signals in YH_{1.92} at 200K. The relative amplitudes between the dispersion $u_1(0)$ and peak-to-peak absorption $v_1(\max)$ are to scale

example of the different saturation behavior of the absorption and dispersion lock-in signals we refer the reader to Goldman (p. 113 of Reference (34)) who reports on similar behavior for metallic sodium.

We turn now to the experimentally obtained T_1 values using the three methods outlined previously. We will compare our results with the T_1 's obtained from pulsed NMR measurements (26). These are 1.40 sec at 200K, and 1.66 sec at 160K for $\text{YH}_{1.92}$. We treat our measurements at 200K first.

The numerical values of the data in the figures referred to in the following paragraphs can be found in Table 3.12 (all data at 200K) and Table 3.13 (all data at 160K).

From Table 3.12 we see that $u_1(0)$ passes through a maximum when $H_1 = 11.3$ mOe. This yields a T_1 of 0.89 sec. Figure 3.19 shows a plot of $u_1(0)/H_1$ vs. H_1 for both temperatures. (At 200K, the value of U_0 (2.10 Oe) was obtained by extrapolating the curve back to $H_1=0$.) At 200K, $u_1(0)/H_1$ equals $U_0/2$ for $H_1 = 11.35$ mOe, yielding a T_1 of 0.88 sec. Figure 3.20 shows a plot of $H_1/u_1(0)$ vs. H_1^2 at 200K. We obtain the slope ($4.82 \times 10^{-3} \text{ (Oe)}^{-1}$) and ordinate intercept (0.457 Oe) by a least-squares fit to the data points which gives a T_1 of 1.19 sec. Giving double weight to the last value of T_1 (as this method is the best since we use all of the data) we obtain an average T_1 of 1.04 sec.

At 160K, $u_1(0)$ passes through a maximum when $H_1 = 7.62$

Figure 3.19. The quantity $u_1(0)/H_1$ is shown as a function of H_1 for YH_{1.92} at T=160K and 200K. The value of U_0 at T=160K was determined from the ordinate intercept of Figure 3.21

Figure 3.20. The quantity $H_1/u_1(0)$ is shown as a function of H_1^2 for YH_{1.92} at 200K

Table 3.12. Dispersion mode lock-in data for $\text{YH}_{1.92}$ at 200K giving values of $u_1(0)$, $u_1(0)/H_1$, $H_1/u_1(0)$, and H_1^2

H_1 ($\times 10^{-3}$ Oe)	H_1^2 ($\times 10^{-4}$ Oe ²)	$u_1(0)$ A.U. ^a	$u_1(0)/H_1$ A.U.	$H_1/u_1(0)$ A.U.
3.45	.119	6.80	1.97	0.51
4.54	.206	8.53	1.88	0.53
5.62	.316	10.30	1.83	0.55
6.72	.452	11.58	1.72	0.58
7.62	.581	12.03	1.58	0.63
9.44	.891	13.33	1.41	0.71
11.3	1.277	13.41	1.19	0.84
13.4	1.796	9.03	0.67	1.48
17.4	3.028	8.13	0.47	2.14
25.8	6.656	6.40	0.25	4.03
36.3	13.177	5.20	0.14	6.98
54.5	29.703	3.75	0.069	14.53
72.6	52.701	2.80	0.039	25.93

^aArbitrary units.

mOe, which yields a T_1 of 1.95 sec. Figure 3.21 shows a plot of $H_1/u_1(0)$ vs. H_1^2 at 160K (the last data point has been omitted). If we use all the data points, we obtain a negative ordinate intercept which gives a negative value of U_0 . This is clearly an unphysical result, as U_0 must always be greater than zero. The reason for the discrepancy

Figure 3.21. The quantity $H_1/u_1(0)$ is shown as a function of H_1^2 for YH_{1.92} at 160K

is that the last four data points deviate considerably from a line drawn through the first eight points. Hence, we will use only the first eight data points in our analysis.

(Those for which $H_1 \leq 13.4$ mOe in Table 3.13.) We obtain then the slope ($5.8 \times 10^{-3} \text{ (Oe)}^{-1}$) and ordinate intercept (0.253 Oe) by a least-squares fit to these data points, giving a T_1 of 2.60 sec. A reliable value of U_0 could not be determined from a plot of $u_1(0)/H_1$ vs. H_1 (Figure 3.19) as the data points did not lead to an unambiguous extrapolation back to $H_1=0$. Hence U_0 was determined from the ordinate intercept of Figure 3.21. (This is the value of U_0 shown in Figure 3.19.) We then find that $u_1(0)/H_1$ equals $U_0/2$ for $H_1 = 6.65$ mOe, yielding a T_1 of 2.56 sec. Once again giving double weight to the value of T_1 obtained from the plot of $H_1/u_1(0)$ vs. H_1^2 we obtain an average T_1 of 2.43 sec.

Considering the experimental uncertainties in obtaining T_1 from a progressive saturation experiment, our values of T_1 are in fair agreement with the pulse T_1 values. We obtained 2.43 and 1.04 sec at 160 and 200K, respectively, while the pulse results are 1.66 and 1.40 sec at 160 and 200K, respectively. There does appear to be considerable experimental uncertainty however, in this method. For example, from Table 3.12, we see that for $H_1 = 9.44$ mOe, $u_1(0) = 13.33$ A.U.¹, while for $H_1 = 11.3$ mOe, $u_1(0) = 13.41$ A.U. Hence, only

¹Arbitrary units.

Table 3.13. Dispersion mode lock-in data for $\text{YH}_{1.92}$ at 160K giving values of $u_1(0)$, $u_1(0)/H_1$, $H_1/u_1(0)$, and H_1^2

H_1 ($\times 10^{-3}$ Oe)	H_1^2 ($\times 10^{-6}$ Oe ²)	$u_1(0)$ A.U. ^a	$u_1(0)/H_1$ A.U.	$H_1/u_1(0)$ A.U.
2.18	1.64	7.98	3.66	0.27
3.45	11.9	9.97	2.89	0.35
4.54	20.6	11.40	2.51	0.40
5.62	31.6	12.90	2.30	0.44
7.62	58.1	14.20	1.86	0.54
9.44	89.1	12.60	1.33	0.75
11.3	127.7	12.10	1.07	0.93
13.4	179.6	9.87	0.74	1.36
17.4	302.8	6.86	0.39	2.54
21.8	475.2	4.27	0.20	5.11
25.8	665.6	3.60	0.14	7.17
36.3	1317.7	2.75	0.076	13.20

^aArbitrary units.

0.08 A.U. separates the maximum of $u_1(0)$ from the next closest point, an amount which is certainly less than the experimental uncertainty in $u_1(0)$. In this case, if the maximum in $u_1(0)$ were at $H_1 = 9.44$ mOe instead of $H_1 = 11.3$ mOe, we would get a T_1 of 1.27 sec compared to 0.89 sec using $H_1 = 11.3$ mOe. This is a 43% increase in T_1 and puts it much closer to the pulse value.

The fact that inclusion of the data points for which $H_1 \geq 17.4$ mOe in the plot of $H_1/u_1(0)$ vs. H_1^2 (at 160K) give results which are clearly unphysical ($U_0 < 0$), is puzzling. A possible explanation is that in this range of H_1 values modulation saturation is occurring. However, the peak-to-peak modulation amplitude $2H_m$, was always kept less than one-fifth the linewidth, or $2H_m < \Delta H/5$, which is normally adequate to avoid modulation saturation. Furthermore, Goldman predicts (p. 110 of Reference (34)) that modulation saturation is most likely to occur for $W(0) \sim \Omega$ but that it is minimal for $W(0) \ll \Omega$ and $W(0) \gg \Omega$. Since $\Omega = 1257 \text{ sec}^{-1}$ (as $f_m = 200 \text{ Hz}$), we see from the values of $S(0)$ in Table 3.11 ($W(0) = S(0)/T_1$) that we always have $W(0) \ll \Omega$. According to Goldman then, we should be in no danger of modulation saturation. The fact that this effect did not occur at 200K, where we went to even higher rf field amplitudes, makes its occurrence at 160K that much more difficult to understand. As for the discrepancy between our results and the pulse results, several possibilities come to mind regarding our experimental method. (1) The H_1 values indicated by the rf meter may not be the same H_1 seen by the spin system because yttrium is metallic and the dimensions of the powder particles (~ 100 microns for YH_x) are on the order of the skin depth. One can see this by assuming that the conductivity of the hydride is the same as that of the

metal. One then obtains a skin depth of approximately 100 microns. (2) There was some lack of consistency in $u_1(0)$ values obtained from spectra taken at different times. For example, the magnitude of $u_1(0)$ would change or the maximum of $u_1(0)$ would shift slightly (~ 2 mOe). Because of this, the dispersion mode spectra were completely retaken, and from these new spectra were obtained the $u_1(0)$ values used in this section. (3) The value of $g(0)$ obtained from the Harper-Barnes lineshape function could have been in error. A more accurate value could possibly have been obtained by direct integration of the unsaturated lock-in absorption curve rather than by calculating its value implicitly from a theoretical lineshape function.

Taking into account the experimental uncertainty in obtaining T_1 from a progressive saturation experiment, and our lack of satisfaction with certain experimental aspects of the data - namely (1), (2), and (3) above - we can still conclude at this time that the Provotorov saturation theory correctly predicts that the lock-in dispersion signal $u_1(0)$ saturates according to the normal saturation factor $Z(0) = [1 + \pi \gamma^2 H_1^2 g(0) T_1]^{-1}$. However, a stronger indicator of the validity of the Goldman-Protorov theory comes from our data of the previous section on the linewidth as a function of H_1 and from Figures 3.17 and 3.18. These data show that the saturation behavior of $u_1(0)$ is a much better indicator of

saturation than is $v_1(\text{max})$. The Goldman-Provotorov theory correctly predicts this fact. For even though $v_1(\text{max})$ has still not reached its maximum value at either temperature, the linewidth has either narrowed or broadened considerably, and the resonance has also changed its shape. In the former case an erroneous temperature dependence of the linewidth may be recorded which is especially likely if T_D is a strong function of temperature (see Figure 3.9). In the latter case, considerable error in second moment measurements could result. The only safe procedure is to keep the rf level low enough so that the saturation factor never exceeds 0.1 or 0.2.

IV. CONCLUSIONS

A. Octahedral and Tetrahedral Site
Occupancy Estimates

Based upon analysis of the rigid lattice proton second moments, it was found that in the dihydride phase (β -YH_x) a sizable percentage of the O-sites are occupied by hydrogen, while a nonnegligible percentage of the T-sites are unoccupied. Specifically, we found that 16% of the O-sites are occupied (we are referring to α) for $x = 1.80$ ¹, 19% for $x = 1.91$, and 28% for $x = 1.98$. The percentage of T-sites occupied (referring to β) was 82% for $x = 1.80$, 86% for $x = 1.91$, and 85% for $x = 1.98$. The above results indicate that as the H concentration increases, the probability of H occupation of O-sites also increases.

Further work should be done though to investigate the effect of the lock-in time constant and magnetic field sweep rate upon the second moment values of YH_x. Second moment values suggest that increasing the time constant increases the value of M_2 , which would have the effect of increasing the inferred occupation of octahedral sites. We could thus be possibly overestimating the number of octahedral sites occupied by hydrogen due to inflated M_2 values.

¹Assumed lower limiting composition of the dihydride phase and x refers to the best estimate of H/Y.

In the solid solution phase (α -YH_x), we studied the sample YH_{0.20}. Based upon analysis of the proton second moment, we concluded that the hydrogen resides in both the T and O-sites in YH_{0.20}. We base this conclusion upon the fact that the M_2^{th} values obtained by assuming either exclusive O-site (0.55 Oe^2) or exclusive T-site (0.40 Oe^2) occupation were both less than M_2^{exp} (0.69 Oe^2) and also of approximately the same magnitude. Hence, we were unable to obtain definite quantitative results for the site occupation probabilities. We did however obtain quantitative values of α , β , f_o , and f_t for two limiting cases: (1) predominantly O-site occupation; and (2) predominantly T-site occupation. The results for (1) were: $\alpha = 18.5\%$ and $\beta = 1.5\%$; while the results for (2) were $\alpha = 2.8\%$ and $\beta = 17.2\%$.

B. Phase Boundaries at Room Temperature

From measurements of the NMR intensities of the α and β -lines (of YH_{0.44} and YH_{0.88}) we determined the room temperature phase boundaries of the two-phase region to be: $x = 0.15$ for the upper limiting composition of the solid solution, and $x = 1.69$ for the lower limiting composition of the dihydride. Although the latter value appears to be somewhat low,¹ its value is extremely sensitive to slight

¹The α -line was detected in $x = 1.72$.

variations (within the experimental uncertainty) in the global composition of the samples. Thus, this discrepancy could be due in part to the problem of accurately determining the compositions.

C. Activation Energy

From the line-narrowing behavior of the proton resonance in both α and β -YH_x, the activation energy for hydrogen diffusion was calculated for various samples using the formalisms of Hendrickson and Bray (HB) and Bloembergen, Purcell, and Pound (BPP). For β -YH_x, the HB analysis yielded E_a values of 0.54 ± 0.02 eV for $x = 1.90$, 0.56 eV for $x = 1.92$, and 0.56 eV for $x = 1.98$. The BPP analysis, on the other hand, gave E_a values (again for β -YH_x) of 0.40 ± 0.02 eV for $x = 1.90$, 0.43 eV for $x = 1.92$, and 0.42 eV for $x = 1.98$. For α -YH_x, we studied the α -line in YH_{0.44} and found an E_a of 0.49 ± 0.02 eV from the HB analysis and an E_a of 0.42 ± 0.02 eV from the BPP analysis. The BPP results for β -YH_x give E_a values which are in much better agreement with the pulsed NMR results for E_a than are the HB results.

For both α and β -YH_x, the narrowing of the linewidth can only be the result of thermally activated self-diffusion of the hydrogen which averages out the magnetic dipole interaction. The self-diffusion of the hydrogen results from the hydrogen absorbing sufficient thermal energy to surmount the

potential barrier (of height E_a) presented by its neighbors and jump from one interstitial site to another.

D. Saturation Effects and Measurement of T_1

The saturation behavior of the absorption line in $YH_{1.92}$ and $YH_{1.98}$ was studied at 160 and 200K. Saturation narrowing of the linewidth was observed to occur for both samples at 160K, whereas saturation broadening was observed to occur at 200K. Various saturation theories were examined to explain this phenomenon, and it was concluded that the Provotorov (35) theory was the most adequate in explaining our experimental results.

To test the Provotorov saturation theory, we used Goldman's (33) result for the dispersion mode lock-in signal $u_1(\Delta)$, based upon the Provotorov theory, to measure T_1 by a progressive saturation experiment. For $YH_{1.92}$, we obtained T_1 values of 2.43 and 1.04 sec at 160 and 200K, respectively, compared to pulse T_1 values of 1.66 and 1.40 sec at 160 and 200K, respectively. Allowing for the difficulties involved in measuring some of the experimental parameters, we verified that the lock-in dispersion signal $u_1(0)$ saturates according to the normal saturation factor $Z(0) = [1 + \pi \gamma^2 H_1^2 g(0) T_1]^{-1}$ as predicted by the Provotorov theory of resonance saturation. However, a stronger indicator of the

validity of the Goldman-Provotorov theory is its correct prediction (based upon our data) that the saturation behavior of $u_1(0)$ furnishes a more reliable indicator of saturation than does the peak-to-peak amplitude of the absorption mode lock-in signal $v_1(\text{max})$.

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VII. APPENDIX

A. Derivative of Harper-Barnes
Lineshape Function

Numerical values of the derivative

$$g'(x) = e^R |x|^{n-1} \exp(-R|x|^n)$$

of the Harper-Barnes lineshape function, where $R = (n-1)/n$, are listed in the following table for selected x -values and various useful values of the parameter n . The function $g'(x)$ is scaled such that the maximum and minimum occur at $(1,1)$ and $(-1,-1)$, respectively. To compare with an experimental derivative trace, one need only multiply the tabulated values by a scale factor determined from the coordinates of the extrema of the experimental derivative trace.

B. Conversion of H_1 from
 μA to mOe

A single turn circular coil of wire, which had an area of 1.37 cm^2 , was inserted into the sample chamber of the probe. This coil was then positioned in the probe to give the maximum (induced) voltage deflection, as measured by a Tektronix 475 oscilloscope. (The precision of the oscilloscope is 3%). The measurement was made at an operating frequency of 16 MHz. Using Faraday's law ($V = -d\phi/dt$), and taking for the linearly polarized oscillating

Table 7.1. Values of $g'(x) = e^{R|x|^{n-1}} e^{-R|x|^n}$ where $R = (n-1)/n$ for various values of n

x	n=1.7	n=1.8	n=2.0	n=2.1	n=2.2	n=2.3	n=2.4	n=2.5	n=2.6	n=2.7	n=2.8	n=2.9	n=3.0
0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.2	0.4764	0.4199	0.3232	0.2824	0.2462	0.2192	0.1860	0.1612	0.1396	0.1207	0.1042	0.0899	0.0775
0.4	0.7288	0.6880	0.6088	0.5709	0.5343	0.4992	0.4657	0.4338	0.4035	0.3749	0.3479	0.3224	0.2986
0.6	0.8882	0.8681	0.8263	0.8097	0.7828	0.7608	0.7386	0.7164	0.6942	0.6721	0.6502	0.6286	0.6071
0.8	0.9741	0.9690	0.9578	0.9517	0.9454	0.9388	0.9319	0.9248	0.9175	0.9099	0.9022	0.8942	0.8861
1.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.2	0.9782	0.9736	0.9630	0.9571	0.9509	0.9442	0.9372	0.9296	0.9217	0.9135	0.9048	0.8957	0.8863
1.4	0.9210	0.9041	0.8663	0.8455	0.8234	0.8002	0.7760	0.7507	0.7245	0.6975	0.6698	0.6416	0.6128
1.6	0.8397	0.8063	0.7335	0.6944	0.6541	0.6127	0.5707	0.5284	0.4862	0.4443	0.4033	0.3634	0.3250
1.8	0.7444	0.6938	0.5873	0.5329	0.4786	0.4252	0.3735	0.3242	0.2777	0.2347	0.1955	0.1603	0.1293
2.0	0.6435	0.5777	0.4463	0.3831	0.3234	0.2679	0.2176	0.1730	0.1344	0.1019	0.0753	0.0540	0.0376
2.2	0.5436	0.4667	0.3225	0.2587	0.2020	0.1533	0.1127	0.0800	0.0548	0.0361	0.0227	0.0136	0.0078
2.4	0.4496	0.3664	0.2221	0.1643	0.1168	0.0796	0.0518	0.0320	0.0187	0.0103	0.0053	0.0025	0.0011
2.6	0.3645	0.2800	0.1460	0.0982	0.0626	0.0376	0.0211	0.0110	0.0053	0.0023	0.0009	0.0003	
2.8	0.2900	0.2085	0.0916	0.0553	0.0310	0.0161	0.0076	0.0033	0.0012	0.0004			
3.0	0.2266	0.1514	0.0549	0.0293	0.0142	0.0062	0.0024						
3.2	0.1740	0.1074	0.0315	0.0147									
3.4	0.1315	0.0744	0.0173										
3.6	0.0977	0.0503											
3.8	0.0715	0.0333											
4.0	0.0516	0.0216											
4.2		0.0137											

field

$$H_x = 2H_1 \cos \omega t \quad (A1)$$

we find that the induced voltage in the coil is

$$V = -\frac{d}{dt}(AH_x) = 2A\omega H_1 \sin \omega t \quad (A2)$$

where A is the area of the coil. Since the quantity referred to in the text as the "rf field H_1 " refers to the amplitude of the rotating field, we see from Equation (A1) that this is just H_1 in Equation (A2).¹ Letting V_{pp} be the peak-to-peak voltage measured on the oscilloscope screen we see that $V_{pp} = 4A\omega H_1$ or that

$$H_1 = \frac{V_{pp}}{4A\omega} . \quad (A3)$$

The following table lists the conversion from μA , as indicated by the rf level meter on the spectrometer, to actual magnetic field amplitude H_1 in mOe for the Varian Model V4320B probe (frequency range 8-16 MHz, serial No. 652).

¹A linearly polarized oscillating field can be regarded as the superposition of two circularly polarized fields rotating in opposite senses, each with amplitude one-half the amplitude of the linear field.

Table 7.2. Conversion of H_1 from μA to mOe for Varian Model V4320B probe, serial No. 652

μA	mOe	μA	mOe
5	2.18	200	44.5
10	3.45	220	49.0
15	4.54	240	54.5
20	5.62	280	62.6
25	6.72	320	72.6
30	7.62	360	79.9
35	8.53	400	89.8
40	9.44	420	92.6
45	10.5	440	98.0
50	11.3	480	105.3
55	12.3	500	112.5
60	13.4	540	119.8
65	14.5	600	130.7
70	15.6	620	134.3
80	17.4		
100	21.8		
120	25.8		
160	36.3		
180	39.9		

C. Calculation of $g(0)$ from Harper-Barnes Lineshape Function

The shape function is given by

$$g(x) = Ae^{-b|x|^n} \quad (A4)$$

where $g(0) = A$. The normalized intensity of the line is

$$1 = 2 \int_0^{\infty} Ae^{-b|x|^n} = 2A \frac{\Gamma(1/n)}{nb^{1/n}} \quad (A5)$$

To find b we first find the linewidth Δx by setting $g''(x) = 0$. We obtain then for b

$$b = \frac{2^n R}{(\Delta x)^n} \quad (A6)$$

where $R = (n-1)/n$. Combining Equations (A5) and (A6) we get for $g(0)$ the expression

$$g(0) = \frac{nR^{1/n}}{\Gamma(1/n) \Delta x} \quad (A7)$$

To express $g(0)$ in $(\text{ang freq})^{-1}$ units we multiple Δx by γ , obtaining finally

$$g(0) = \frac{nR^{1/n}}{\Gamma(1/n) \gamma \Delta x} \quad (A8)$$

To obtain $g(0)$ for the unsaturated resonance, one measures Δx and finds the n value which yields the best fit of $g'(x)$ to the derivative lineshape. With these values of Δx and n , Equation (A8) yields $g(0)$.